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The metallurgy of copper in Italian Prehistory. New archaeometric data from Sardinia

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Abstract: When looking at the earliest metallurgy in Italy, data from Sardinia indicates a beginning during the first half of the 4th millennium cal. BC, which was followed by very gradual development that intensified during the 3rd millennium. Here we present results of XRF analysis, combined with Monte Carlo simulations, undertaken on copper artefacts recovered from the renowned sanctuary of Monte d'Accoddi (northern Sardinia), chiefly belonging to a period between the 4th and the early 2nd millennium cal. BC. Some finds were of particular interest in that they contained a high or anomalous concentration of silver.

Key Words: XRF Analysis, Monte Carlo simulations, Archaeometallurgy, Prehistoric Sardinia, Monte d'Accoddi

1. INTRODUCTION

Based on evidence of mining activity, as well as finds of metal artefacts, crucibles and slag deposits, it appears that the earliest phase of metallurgy in Italy occurred between the last centuries of the 5th and the first half of the 4th millennium cal. BC (Pearce 2015, *ivi* bibliography).

In Sardinia the most ancient metal artefacts, made from copper and silver, are datable to the first half of the 4th millennium cal. BC, whereas more direct evidence of metallurgical activity (crucibles) have been dated to the second half of the 4th millennium cal. BC (Melis 2009 and 2014): the available data suggests a limited development of metallurgy, that intensifies gradually during the second half of the 4th and the 3rd millennia cal. BC). The scarcity of finds and the restricted number of archaeometric analyses so-far completed (Lo Schiavo *et al.* 2005; Skeates *et al.* 2013; Brunetti *et al.* 2015) can only offer us a fragmentary view of the most ancient metallurgical practices and the ways in which related knowledge was transmitted.

Presented here are the results of the XRF analyses carried out on copper finds from excavations at the shrine at Monte d'Accoddi, run by Ercole Contu between 1952 and 1959 (Contu 2001; Melis 2011). The structure is a terraced monument situated in north-western Sardinia (Figure 1), surrounded by a village that was occupied in diverse periods of Prehistory. Architecturally it is unique in the Mediterranean panorama, although it has often been compared to the ziggurats of the Near East (as debated by Tinè and Traverso 1992), both for the presence of an entrance ramp and for its truncated-pyramid shape. Currently, however, the chronological data and the vague architectural similarities, but above all, the different social contexts, the absence of any documented contact with the Near East and its obvious connection to local Neolithic tradition, with which it shares the material culture and the construction technique of Monte d'Accoddi, means that the genetic hypothesis of eastern origin is impossible to confirm. The Sardinian monument therefore appears to be an original feature, although its inspiration may perhaps be related to western megalithism, which arrived in Sardinia during the second half of the 5th millennium cal BC (Guilaine 1996; Melis *et al.* 2007). The network of intense relationships surrounding the circulation of obsidian may have favoured the indirect contacts and the circulation of architectural ideas from more distant western territories that did not belong to the obsidian trade

Figure 1. Monte d'Accoddi. Plan (1), localisation (2) and aerial photo (3) (1, by Contu 2001; 2, graphics C. Caradonna; 3, photo Oben s.r.l.).

routes, places where monumental buildings and tumuli of great size, some of them stepped, are known to have existed, such as the structure at Barnenez in Brittany for example (Giot 1987).

The results of the archaeological excavations run by Ercole Contu are currently being studied by Maria Grazia Melis (author of the first and fourth paragraphs), while the XRF analyses on the metal artefacts are being followed by Antonio Brunetti (author of the second and third paragraphs).

The metal finds (Figure 2) included awls, axes, a dagger, a hook and a razor. Morphological analyses and chronological and cultural identification of the objects were in some cases compromised by their poor state of conservation; in fact, many of the pieces had significant parts missing. Nevertheless, integrating this data, together with the little available information regarding the contexts in which they were found, made it possible to speculate about their association with several of the diverse phases of use of the shrine, between the 4th millennium cal. BC and the beginning of the second.

The aims of the current research are several; increase the available archaeometric data in the context of Sardinia, provide new interpretative tools for studying the origins of metallurgy and to make a contribution to research on the dynamics of the use of one of the most important Prehistoric monuments of the Mediterranean.

The methodological choices made in relation to the diagnostic research were

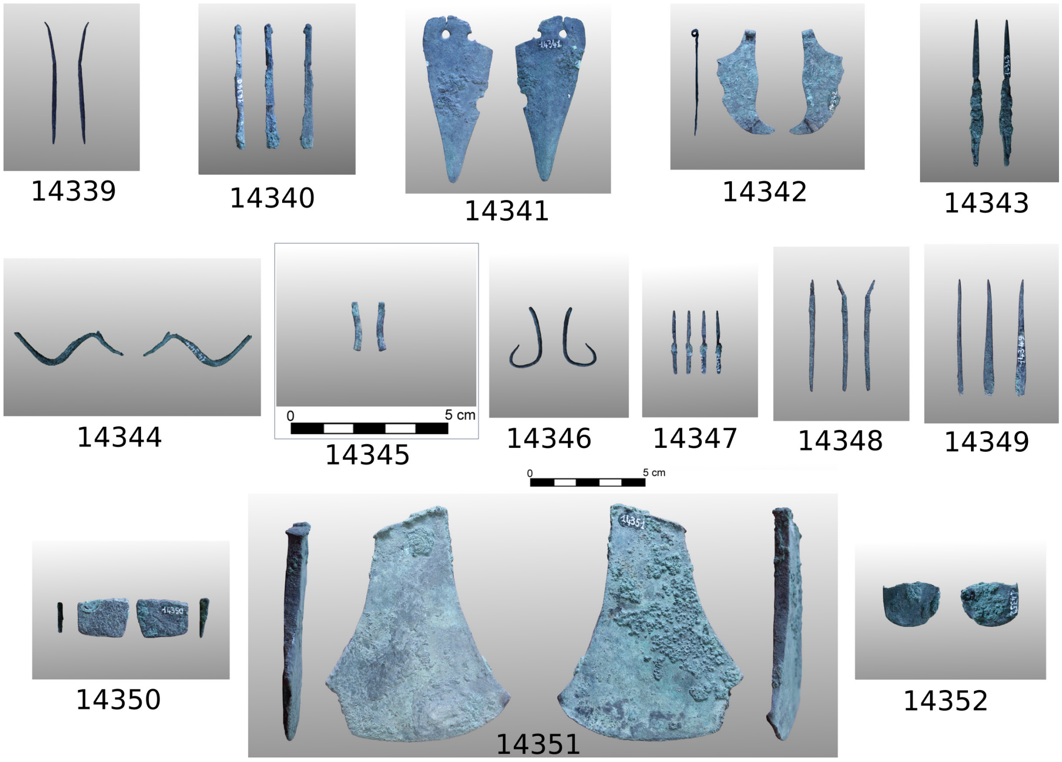

Figure 2. Copper artefacts from Monte d'Accoddi (photos M. G. Melis; graphics C. Caradonna).

influenced by the unwillingness on the part of the *Soprintendenza Archeologica* to allow destructive analytical procedures. The decision, therefore, was to initially make an XRF analysis, the results of which are presented in the present work.

2. METHODS

Determination of the structure and composition of Cultural Heritage artifacts with XRF has been widely discussed in published literature (Cesareo *et al.* 2004; Milazzo 2004; Manso *et al.* 2008; Cesareo *et al.* 2010; Guilherme *et al.* 2013; Cesareo *et al.* 2013; Brunetti *et al.* 2015; Brunetti *et al.* 2016a; Schiavon *et al.* 2016). In the case of monolayer samples with smooth surfaces any quantitative methods can be usefully adopted. The same holds for regular multilayered structures. Usually these methods require the extraction of the background, leaving only the peaks part of the spectrum which is used for the quantification step. Usually an iterative guess and try approach is applied and an estimative of the composition is obtained (Sherman 1965; Shiraiwa, Fujino 1966; Mantler 1986; De Boer 1990). Beside these methods the Fundamental Parameters Method is probably the most performing. The most critical step of these methods is connected to the extraction of the background which, especially in the case of small area peaks, can introduce large errors. In order to overcome this problem peak fit and background extraction are performed simultaneously in some implementation of this methods. In the case of multilayered structures some empirical and faster methods have been also described (Bustamante *et al.* 2013; Cesareo *et al.* 2008; Cesareo *et al.* 2009; Cesareo, Brunetti 2008). They are based on the determination of the influence (in terms of attenuation) of the outer layer on the fluorescence signal emitted by the inner layer. In order to simplify the estimative of the layer compositions and thicknesses, these methods require the use of a monochromatic or quasi monochromatic X-ray beam. However, although in the measurements described in the literature this approach has produced good results (Bustamante *et al*. 2013; Cesareo *et al*. 2008; Cesareo *et al*. 2009; Cesareo & Brunetti 2008), it strongly depends on the sample composition, on the X-ray spectrum emitted by the source and, more in general, on the experimental setup, making its generalization to other experimental situations not straightforward. However, the quantitative estimation of multilayer structures is of great importance in Cultural Heritage analysis because the samples, especially the metallic ones, are often formed by at least two layers: the so called patina, i.e. corrosion products and incrustations due to the interaction with the sediment in which the sample was buried. Moreover the presence of patina or incrustation introduces new difficulties for its quantitative characterization: a non smooth surface. The interaction of the X-ray photons strongly depends on the surface roughness (Brunetti & Golosio 2014). As a result, the presence of a rough surface can alter the area of the fluorescence peaks detected in a no easily predictable way, so making the quantitative estimation unreliable. It is possible to reduce the influence of irregular surfaces adopting some strategies in the experimental setup (Trojek *et al*. 2010; Trojek 2011; Bonizzoni *et al*. 2006; Trojek 2012). However, a better approach should be to consider the real surface in the quantitative algorithm utilized. So, to resume, two main problems can be indentified for a quantitative characterization of Cultural Heritage samples: low intensities peaks connected to low chemical concentration and irregular surfaces. In order to solve both these problems we have developed and applied a different approach based on XRF measurements and Monte Carlo simulations (Brunetti *et al*. 2016a; Brunetti *et al*. 2016b; Bottaini *et al*. 2015). This method is not new at all, in the sense that the use of the Monte Carlo simulations has been proposed in the past (Trojek *et al*. 2010; Trojek 2011; Gardner & Doster 1979; Gardner & Doster 1982a; Gardner & Doster 1982b; Fernandez 1989; Schoonjans *et al*. 2012; Vincze *et al*.1993; Bottigli *et al*. 2004; Golosio *et al*. 2014). The novelty is the speed of the Monte Carlo simulation that allows real-time simulation and the capability to simulate irregular surfaces. The Monte Carlo code used here is called *XRMC* (Bottigli *et al*. 2004; Golosio *et al*. 2014). It is a very versatile code able to simulate a wide range of X-Ray experiments, from XRF to phase contrast. As mentioned before, it is also able to simulate irregular surfaces and a version which will be able to introduce a tridimensional reproduction of the real surface of the sample in the simulation is under development.

The quantitative procedure used here is structured in the following steps. The first step is the experimental setup described in the language of XRMC. The code requires the structure and composition of the sample, the position of the sample, the detector and the X-Ray source and their spectroscopic characteristics. Then the experimental XRF spectrum is acquired. The experimental setup used for the measurements reported here is a custom portable model composed of a silver anode X-Ray tube working at 40 kVp and 5-10 mA and a SDD detector. The geometry can be chosen according to the accessibility of the zone to be analyzed, but usually the detector is placed orthogonally to the sample surface, while the X-Ray tube forms an angle of about 30° with respect to the detector, both 2-3 cm away from the surface. After the experimental measurement, the spectrum is also simulated by the Monte Carlo code. The two spectra are then compared superimposing each to other: if any difference is observed the structure and/or the composition of the sample introduced in the Monte Carlo is changed. This procedure is iteratively repeated until the simulated spectrum is a perfect reproduction of the experimental one, within the statistical fluctuations. In the last iterations a chi-squared test is also performed to help the user in the evaluation. In principle this procedure could be made automatically, but the high number of variables involved in this problem is, in our opinion, so too hard to perform it without the user supervision. Some attempts in such direction are been done in PyMCA, a well-known quantitative estimation code (Solé *et al.* 2007; Schoonjans *et al.* 2013). This approach has been extensively tested on reference samples as well as real Cultural Heritage objects such as a couple of identical pieces of the same provenience, of which only one has been restored, and even in this case the results obtained were similar (Brunetti *et al.* 2016b). Based on these tests, the error on the concentration estimation is about 5% for the chemical element with concentrations larger than 1%, and around 30% for concentration around 100 ppm. The minimum detectable concentration is around 20 ppm. The capability to perform analysis before restoration is of particular importance because sometimes, for example, a silver enrichment of the sample surface can be produced by the restoration technique itself (Moreno-Suárez *et al.* 2016). Of course, the signal emitted by the inner layer must be able to reach the surface of the sample and to be detected, this means that this technique cannot be applicable to sample with a too thick, in XRF sense, patina.

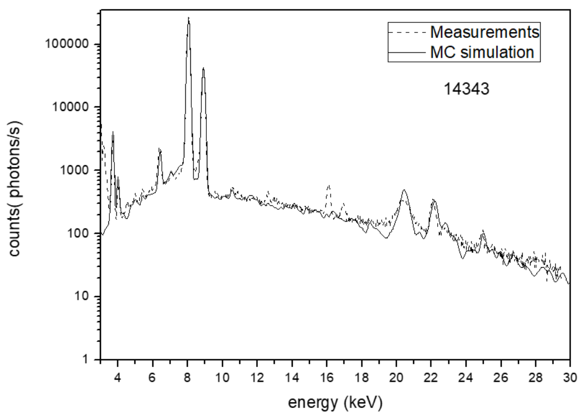

Figure 3. XRF measurements of sample 12343.

3. RESULTS

The results obtained on all the samples analyzed are reported in table I. However, in order to show how the procedure works, two examples will be discussed in detail. In figure 3 the measured and simulated spectra of sample 14343 is depicted. The model utilized is a two layer one. The first layer, the patina, is 300 μm thick and is essentially formed by incrustation with calcium and iron as the majority elements. The bulk part is almost pure copper (98.3%) with a low amount of silver (0.5%) and lead (0.1%). The pile-up peaks are due to the detector (too high dead time) and for this reason are not simulated.

The sample 14342 (Figure 4) has been also modeled as a two layer one. The incrustation layer has the same thickness as the previous one, but its composition, of calcium and copper oxide, is slightly different. More interesting is the composition of the bulk where a copper (84,9%) and silver (15%) have been found together with a small amount of As (0.1%).

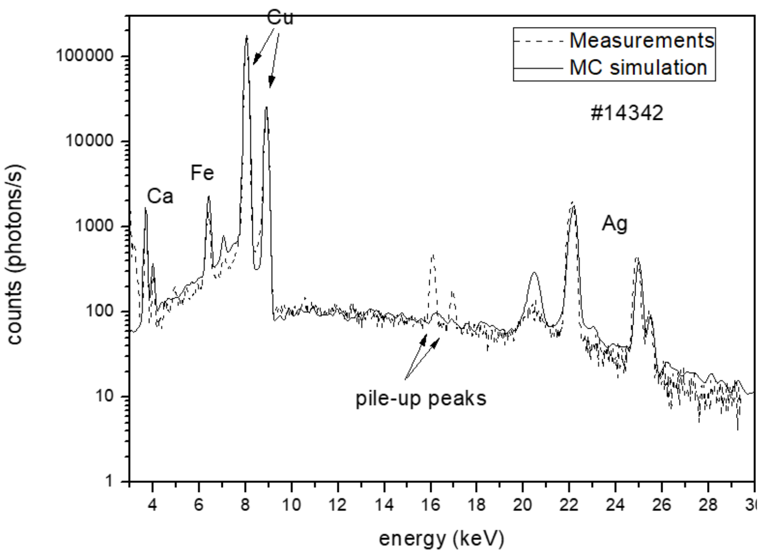

Figure 4. XRF measurements of sample 14342.

4. DISCUSSION

The finds under examination are displayed in the Archeological Museum of Sassari; archive records suggest that they have not been subjected to any preservative treatments. The results of the analyses generally show a composition of pure copper. Arsenic (As) is present in very low percentages (0,1%-0,4%), except for in sample 14344 (1%). This is a fragmented artefact, difficult to identify or date.

In 5 of the artefacts As was either absent or present in percentages too low to be detectable. Lead (Pb) is also present in some of the objects, in quantities of lower than 1%, except for in samples 14344 (1%) and 14349 (3%). Such low percentages of As and Pb should not be considered as intentional additions, rather they are probably natural components of the minerals used. Silver (Ag) is present in almost all of the objects in varying degrees. In several examples the concentration is fairly high, reaching as much as

Inventory N.	Chemical elements (%)							
	Ca	Fe	Cu	Zn	As	Ag	Sn	Pb
14339			98.9		0.1	1.0		
14340	2.4	0.3	96.2		0.4	0.3		0.4
14341		0.5	98.6			0.5		0.4
14342			84.9		0.1	15		
14343	1.0	0.1	98.3			0.5		0.1
14344	1.0	0.07	97.0		1.0	0.3	0.5	1.0
14345	1.0	0.1	98.2		0.15	0.1		0.4
14346	0.1	0.05	99.3		0.3	0.3		
14347	0.7	0.1	98.9			0.3		
14348			87.7		0.1	12		0.2
14349			93.5			3.5		3.0
14350	4.9	0.7	92.7		0.1	1.6		
14351			96.5			3.5		
14352		2.0	97.6	0.2	0.1	1.0		

Table I. Results of XRF analyses.

15% in sample 14342. In these cases it is improbable that the presence is casual; it seems more likely that the inclusion was intentional, perhaps with the aim of providing a chromatic effect, as has been suggested in the case of the dagger of Casanuova at S. Biagio (De Angelis 1995-1996; Melis 2014). A similar hypothesis has been formulated in relation to the intentional inclusion of arsenic in copper objects, with the objective of not only improving its mechanical characteristics but also to change the typical colour of copper in order to make it more similar to silver (Dolfini 2013, Giardino 2012, Giumla Mair 2005, Ottaway & Roberts 2008, Pearce 2007).

The question marks and issues raised by these preliminary results, the anomalies thus revealed and the difficulties in dating some of these artefacts together provide an indication of the route to take in furthering archaeological research, including any contribution that can be made through further archaeometric studies.

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A few short months from his passing, kind thoughts and gratitude go to Prof. Ercole Contu, who entrusted Maria Grazia Melis with the work of processing the finds from Monte d'Accoddi.

We wish to extend our thanks to Giovanni Carboni for his invaluable advice.

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