

## Original Study

Andrea Vianello\*, Robert H. Tykot

# Investigating Technological Changes in Copper-Based Metals Using Portable XRF Analysis. A Case Study in Sicily

<https://doi.org/10.1515/opar-2017-0025>

Received February 4, 2017; accepted December 18, 2017

**Abstract:** The introduction of copper-based metals in Sicily appears to have been a particularly late and slow process. A program of pXRF analyses on early metals in Sicily has revealed the use of mostly copper, and a very late introduction of tin. Copper had been in use and extracted in northern Italy since the Late Neolithic (ca. 3500 BC), and spread across the Italian peninsula after that. Yet, copper became widespread in Sicily only in the Bronze Age (ca. 2200–1050 BC), despite some early arrivals. The story of the introduction of copper-based metals in Italy acquires a new layer of complexity and the southwestern corner is providing a fuller perspective of the transmission of metal technology across Italy. This study of about 100 artifacts from Sicily tests the hypothesis that metallurgy and metals became important at a later time compared to other Mediterranean areas.

**Keywords:** metals; Sicily; pXRF; Copper Age; Bronze Age; copper; bronze

## 1 Introduction

The study of metal artifacts in Sicily, like for the rest of Italy, has a long tradition based on typological studies and site reports (e.g. Maniscalco, 2000; Albanese Procelli, 2006; Giardino, Spera and Tusa, 2012). The particularity of the region is due primarily to the seemingly late arrival of metallurgy. Only Malta appears to have been later in the introduction of metallurgy, probably by a few generations (Evans, 1977; Giardino, 1997; Dolfini, 2014). The chronological gap between metallurgy in Latium (De Santis, 2006), as well as probably northern Campania, and Sicily is approximately of one millennium (Dolfini, 2013), a substantial period of time that cannot be justified by geographic, political or natural causes. It is possible to reach Sicily through Calabria and a short sea crossing would not have caused problems. However, Calabria also shows a similar late arrival of metallurgy pattern (Affuso and Lorusso, 2006). Alternatively, it would be possible to follow the coast navigating south, and then use the Aeolian Islands for hopping to the mainland of Sicily, in a sea route active at least since the Middle Bronze Age (ca. 1500–1250 BC; proven by Aegean-type materials in Vivara and connections with that network that included Lipari and Stromboli), if not going back to the Neolithic. Politically, there was no empire or other cohesive social entity in the area at that time capable of deterring trade, nor were there violent or savage peoples (Cazzella and Recchia, 2010; Attema, Burgers and Leusen,

---

**Article Note:** This article is a part of Topical Issue on Portable XRF in Archaeology and Museum Studies, edited by Davide Tanasi, Robert H. Tykot & Andrea Vianello

---

**\*Corresponding author: Andrea Vianello**, Department of Anthropology, University of South Florida, Tampa, FL 33620-8100 USA. Email: [avianello@usf.edu](mailto:avianello@usf.edu), [a\\_vianello@hotmail.com](mailto:a_vianello@hotmail.com)

**Robert H. Tykot**, Department of Anthropology, University of South Florida, Tampa, FL 33620-8100 USA

2012; Blake, 2014; Risch and Meller, 2015). Culturally, Calabria, Sicily and the Aeolian Islands are linked at least since the Early Neolithic (ca. 6000–5000 BC), for instance through the Stentinello pottery culture (Scarcella, Bouquillon, Leclaire, 2011). And finally, there are mines with copper and iron ores in Calabria (e.g. at Grotta della Monaca; Larocca, 2005, 2012; Geniola, Larocca and Vurro, 2006), and probably copper was mined also at Fiumedinisi, located in the Sicilian mainland, on the actively connected eastern coast of Sicily, in the Bronze Age (for a modern perspective of minerals in the area, see Donati, Stagno and Triscari, 1978; Giannitrapani, 2014, p. 24). Long-distance trade networks were indeed present since the Early Neolithic, with obsidian from Lipari being widely traded in Italy, and even on the eastern coast of the Adriatic Sea (Tykot, 2017).

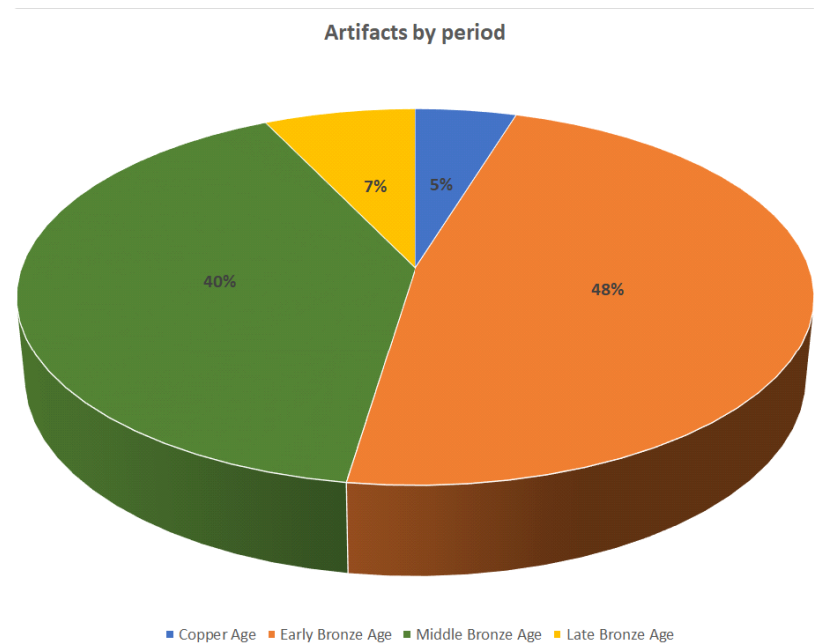
This research is testing the hypothesis that the absence of metallurgy in the region of Sicily was due to preferences for pre-existing technologies until the availability of copper and bronze. The abundant presence of obsidian (Tykot, Freund and Vianello, 2013; Freund, Tykot and Vianello, 2015) in the area and its apparent demise only at the time that metals were introduced is particularly intriguing. It is not possible to conclusively address a possible correlation between obsidian and metals, but it should be noted that many of the early copper metals were not used for cutting or slashing, like swords and daggers, but rather as ornaments. Certainly, after metals become widely available, the long-distance distribution of obsidian had less incentive, and notably the island of Lipari, the main source of obsidian, adopted metallurgy quickly likely due to its being well-connected in exchange networks which must have played a role in spreading the technology and in circulating at least raw copper (Giardino, 2000). It is not clear if obsidian as a material was preferred to copper-based metals (because of availability or efficiency) and delayed their introduction, but it can be said that in Lipari itself metallurgy replaced the obsidian industry during the Middle Bronze Age, although it is not clear why. All that the archaeological record allows us to say is that there was a switch in technologies, and it was both fast and thorough.

The focus of this publication is on technological change in the Bronze Age (the earliest cultural period with copper-based metals in the region). This research suggests that metallurgy was introduced from elsewhere, considering both the speed in the introduction and different alloys being recognized. Indigenous people manufactured metal tools and other objects according to their needs early after metallurgy was introduced, suggesting that there was no problem in acquiring the technological know-how or raw materials, but probably some localized preference. There was a conscious choice of adopting metallurgy and abandoning obsidian and lithics in general, but much more research will be needed to test any possible direct correlation. In addition to testing whether knowledge and raw materials were imported, the pXRF data enable us to discuss the possibility that introducing metallurgy so late depended on specific innovations that superseded prior technologies that had been preferred, or found adequate, until then.

## 2 Materials

Figure 1 shows the composition of the main group of materials analyzed: 4 artifacts from Copper Age contexts, 40 from Early Bronze Age contexts, 34 from Middle Bronze Age contexts, and 6 artifacts from Late Bronze Age contexts. Table 1 summarizes most data; a few analyses of jewelry or highly corroded artifacts have been excluded at this stage because they are not comparable. Unpublished or unverified artifacts have no reference number at this stage of the research. Given the aims of the research at investigating the introduction of metallurgy and early alloys, there is a strong bias against post-Middle Bronze Age artifacts, which have been largely excluded. Most contextual information is not available (but see Tusa, 1999 or Leighton, 1999 for a general overview of the sites cited within the framework of Sicilian prehistory). Many sites were excavated long ago, as early as the late nineteenth century. The only recently excavated site is Scintilia (Gulli, 2015). Most materials are conserved at the Paolo Orsi Regional Museum in Syracuse, with only a few conserved in Agrigento and Palermo. Some analyses have also been carried out in Lipari as a test, where there is a substantial assemblage. A full set of analyses has been carried out there by Alessandra Giumlia-Mair (2009; Lo Schiavo et al., 2009), and readers should refer to those data that are consistent with the results obtained just from a selection of artifacts. In Palermo, analyses have been carried out on metal objects from sites along

the Conca d'Oro, the coastal area west of the modern city. Additional information for most sites follows, in no particular order (Table 1 follows a chronological order).



**Figure 1.** Chart showing percentages of artifacts by period. Built using data from Table 1.

**Table 1.** Values of pXRF analysis, averaged and calibrated. Some analyses repeated. Some chemical elements (impurities, restorative materials) are not detected and imprecision ( $\pm 1\%$ ) introduced by calibration on very low values results in some totals below 100%. Some sites excluded from table if alloy was found not comparable (e.g. jewelry) or results need further attention (e.g. high corrosion or patina in small artifacts). Periods: Copper Age (CA); Early Bronze Age (EBA); Middle Bronze Age (MBA); Late Bronze Age (LBA); Early Iron Age (EIA).

USF #	Site	Item	Period	Average	Cu	Sn	Pb	As	Zn	Fe	Total
16391	Chiusazza Cave	97334	CA	3	98.3	0.0	0.6	0.9	0.0	0.1	99.8
34157	Sant'Ippolito	SI1	CA		99.0	0.0	0.0	0.2	0.0	0.5	99.7
34158	Sant'Ippolito	SI2	CA		99.3	0.0	0.0	0.2	0.0	0.3	99.8
25466	Scintilia	tomb B-26	CA	2	89.2	9.5	0.1	0.2	0.8	0.1	99.9
26593	Palermo	artifact (from Boccadifalco)	EBA	6	97.4	0.0	0.6	1.1	0.5	0.1	99.7
26594	Palermo	Dagger (from Boccadifalco)	EBA	6	90.6	0.0	0.2	9.2	0.4	0.0	100.0
26595	Palermo	armilla 6866 (from Boccadifalco)	EBA	5	98.4	0.0	0.4	0.2	0.6	0.1	99.7
16350	Bernadina	Cava Bernardina tomb 12 - metal wire	EBA		95.2	2.0	1.4	0.0	0.5	0.1	99.0
16351	Bernadina	Cava Bernardina tomb 12 - spiral	EBA		97.6	0.2	1.1	0.3	0.0	0.1	99.4
16352	Bernadina	Cava Bernardina tomb 12 - bead 1	EBA		81.9	16.2	0.4	0.1	0.0	0.1	98.4
16353	Bernadina	Cava Bernardina tomb 12 - bead 2	EBA		99.6	0.0	0.0	0.2	0.0	0.1	99.6
16364	Castelluccio	Castelluccio yoke	EBA	2	99.3	0.0	0.0	0.8	0.0	0.1	99.9
16365	Castelluccio	Castelluccio sheet	EBA	6	86.9	11.0	0.5	0.3	0.1	0.2	99.0
16366	Castelluccio		EBA		93.1	3.7	1.5	0.2	0.9	0.3	99.6
16368	Castelluccio		EBA	2	91.3	1.0	0.7	0.0	5.8	0.3	96.0
16369	Castelluccio		EBA	2	98.0	0.1	0.1	0.5	0.5	0.5	99.3
16370	Castelluccio		EBA	2	99.0	0.0	0.0	0.0	0.0	0.3	99.2

USF #	Site	Item	Period	Average	Cu	Sn	Pb	As	Zn	Fe	Total
16371	Castelluccio		EBA	2	77.3	18.7	1.0	0.5	0.0	0.2	97.6
16373	Castelluccio	8920-1 Castelluccio pointed pin	EBA		80.3	17.5	0.2	0.3	0.0	0.1	98.4
16374	Castelluccio	8920-2 Castelluccio hook	EBA		89.5	9.7	0.1	0.8	0.0	0.1	100.0
16375	Castelluccio	8920	EBA	1	99.0	0.0	0.0	0.3	0.0	0.8	100.0
16377	Cava Cana Barbara		EBA	1	98.5	1.0	0.0	0.1	0.0	0.3	99.7
16378	Cava Cana Barbara		EBA	1	96.0	2.5	1.0	0.1	0.0	0.2	99.7
16381	Cava Cana Barbara		EBA	1	92.9	6.1	0.0	0.1	0.0	1.3	100.0
16382	Cava Cana Barbara		EBA	1	70.7	12.7	13.0	1.0	0.0	2.2	99.1
16383	Cava Secchiera	Cava Secchiera tomb 12 pierced necklace element 1 inv.11002	EBA	2	76.5	7.9	0.1	0.1	15.1	0.2	99.9
16384	Cava Secchiera	Cava Secchiera tomb 12 pierced necklace element 2 inv. 11003	EBA	1	94.7	4.0	0.1	0.0	0.0	1.5	100.0
16385	Cava Secchiera	Cava Secchiera tomb 1 lamina 1 8899	EBA	2	99.0	0.0	0.0	0.0	0.3	0.4	99.5
16386	Cava Secchiera	Cava Secchiera tomb 1 lamina 2 8901	EBA	1	96.5	2.6	0.0	0.4	0.0	0.2	99.8
16386	Cava Secchiera	Cava Secchiera 1-2	EBA		96.2	2.1	0.0	0.3	0.9	0.3	99.7
16386	Cava Secchiera	Cava Secchiera tomb 1 lamina 2 8901	EBA	2	96.3	2.4	0.0	0.4	0.4	0.3	99.7
16387	Cava Secchiera	Cava Secchiera tomb 6 bead 10973	EBA	1	96.9	1.6	0.0	0.3	0.0	1.0	99.8
16388	Cava Secchiera	Cava Secchiera tomb 10 bead inv. 10992	EBA	1	95.1	3.1	0.0	0.0	0.0	2.4	100.0
16389	Cava Secchiera	Cava Secchiera tomb 14 inv. 11012	EBA	1	97.5	0.0	0.0	0.1	0.0	2.8	100.0
16390	Cava Secchiera	Cava Secchiera tomb 7 hatchet-shaped pendant 10977	EBA	1	91.7	0.1	0.0	0.2	0.0	8.1	100.0
16403	Monte Racello	17453	EBA	4	98.5	0.2	0.0	0.0	0.0	0.4	99.0
16404	Monte Racello	17454	EBA	3	92.9	0.0	0.2	6.1	0.2	0.4	99.8
16405	Monte Racello	17478	EBA	2	98.9	0.2	0.0	0.6	0.0	0.2	99.8
16406	Monte Racello	17480	EBA	3	98.5	0.2	0.0	0.0	0.0	0.8	99.5
16407	Monte Racello		EBA	1	99.0	0.1	0.1	0.0	0.0	0.3	99.5
16408	Monte Racello		EBA	1	96.7	1.1	0.8	0.0	0.0	0.5	99.1
16409	Monte Racello		EBA	1	99.2	0.0	0.0	0.0	0.0	0.3	99.5
16410	Monte Racello		EBA	1	98.6	0.1	0.0	0.0	0.0	0.6	99.3
16411	Palombara Cave	96954	EBA	2	99.4	0.0	0.1	0.2	0.0	0.2	99.7
16354	Caldare	Caldare bowl 16290	MBA	5	95.9	3.1	0.4	0.3	0.2	0.1	99.9
16355	Caldare	Caldare bowl 16291	MBA	6	93.2	4.9	1.0	0.4	0.1	0.3	99.8
16356	Caldare	Caldare dagger 16292	MBA	6	95.9	3.7	0.0	0.1	0.2	0.1	99.9
16357	Caldare	Caldare dagger 16293	MBA	4	73.3	20.5	1.8	0.7	0	0.2	96.4
16395	Gela		MBA	6	85.6	12.6	0.1	0.2	0.2	0.5	99.2
16396	Gela Manfria		MBA	1	96.2	2.6	0.0	0.0	0.0	1.1	99.9
16412	Plemmyrion	Plemmyrion big sword	MBA	2	95.1	4.6	0.0	0.1	0.0	0.1	100.0
16413	Plemmyrion	Plemmyrion middle sword	MBA		94.3	4.4	0.2	0.2	0.6	0.3	99.9
16414	Plemmyrion		MBA		94.1	5.4	0.4	0.2	0.0	0.1	100.0
16415	Plemmyrion		MBA	11	85.7	10.6	0.2	0.2	1.6	0.4	98.6
16416a	Plemmyrion	Plemmyrion (5) body of small sword	MBA	1	70.3	22.6	0.2	0.5	0.0	0.5	93.6
16416b	Plemmyrion	Plemmyrion (5) rivet of small sword	MBA	2	91.5	8.5	0.0	0.2	0.0	0.1	100.0
16418	Thapsos	Thapsos dagger? 14753	MBA		94.3	5.8	0.0	0.1	0.0	0.1	100.0
16420	Thapsos	Thapsos ring	MBA		80.4	15.4	2.6	0.0	0.0	0.2	98.0
16421	Thapsos	Thapsos plaque (from dagger?)	MBA		80.3	13.4	1.4	0.6	0.0	4.2	100.0

USF #	Site	Item	Period	Average	Cu	Sn	Pb	As	Zn	Fe	Total
16422	Thapsos	Thapsos rivet	MBA		94.7	4.9	0.0	0.2	0.0	0.3	100.0
16423	Thapsos	Thapsos 14671	MBA		89.8	9.4	0.5	0.3	0.0	0.1	100.0
16424	Thapsos	Thapsos part of dagger 1	MBA		92.4	7.2	0.0	0.1	0.0	0.5	100.0
16425	Thapsos	Thapsos part of dagger 2	MBA		94.8	5.2	0.1	0.1	0.0	0.1	100.0
16426	Thapsos	Thapsos part of dagger 3	MBA		97.1	1.1	0.0	0.1	0.0	2.2	100.0
16427	Thapsos	Thapsos (7) bent wire	MBA		87.8	9.1	2.4	0.5	0.0	0.1	99.9
16428	Thapsos	Thapsos (7) metal sheet 1	MBA		98.7	1.3	0.0	0.1	0.0	0.1	99.9
16429	Thapsos	Thapsos (7) rounded object	MBA		95.7	4.2	0.0	0.2	0.0	0.1	100.0
16430	Thapsos	Thapsos (7) metal sheet 2	MBA		88.4	11.1	0.0	0.1	0.0	0.2	99.8
16431	Thapsos	Thapsos (8) sword	MBA		99.1	0.8	0.0	0.1	0.0	0.1	99.9
16432	Thapsos	Thapsos (8) pin 1	MBA		96.6	0.2	0.3	0.3	0.9	1.5	99.8
16433	Thapsos	Thapsos (8) pin 2	MBA		95.6	3.7	0.3	0.0	0.0	0.2	99.8
16434	Thapsos	Thapsos settlement bull 1	MBA		87.0	11.5	1.2	0.2	0.0	0.2	99.7
16435	Thapsos	Thapsos settlement bull 2	MBA		78.0	18.2	1.5	0.2	0.0	0.3	97.8
16436	Thapsos	Thapsos settlement stick with zoomorphic representations	MBA		86.5	10.9	1.8	0.5	0.0	0.4	99.8
16437	Thapsos	Thapsos settlement dagger	MBA		90.9	7.0	1.4	0.1	0.0	0.9	100.0
16438	Thapsos	Thapsos ingot from settlement	MBA		97.8	0.0	0.0	0.0	0.0	2.9	100.0
16439	Thapsos	dagger	MBA	5	93.5	6.4	0.0	0.2	0.0	0.2	100.0
16440	Thapsos	metal sheet	MBA		98.5	0.5	0.4	0.2	0.0	0.1	99.7
16358	Montagna di Caltagirone	Montagna di Caltagirone (6) sword	LBA	2	91.0	7.5	1.3	0.3	0.0	0.1	100.0
16359	Montagna di Caltagirone		LBA		92.9	5.7	1.4	0.2	0.0	0.0	100.0
16360	Montagna di Caltagirone	Montagna di Caltagirone 8-1	LBA		96.5	2.1	1.1	0.2	0.0	0.0	99.8
16361	Montagna di Caltagirone	Montagna di Caltagirone 8-2	LBA		96.8	2.5	0.6	0.1	0.0	0.1	99.8
16362	Montagna di Caltagirone	Montagna di Caltagirone 9	LBA	2	81.3	15.9	0.1	1.3	0.0	0.2	98.5
16363	Montagna di Caltagirone	Montagna di Caltagirone 10 sword	LBA	12	94.0	1.9	1.5	0.3	1.4	0.5	99.6
16392	Finocchito	F1	EIA	Cu, high Sn, some Pb, As							

**Chiusazza Cave** was used from Neolithic to Roman times – the artifact tested is probably Chalcolithic, as suggested by the curators of the Regional Museum in Syracuse. No dated (C14) stratigraphy is available. **Palombara Cave** is a karstic cave, where a few ceramic vessels dating to the Early Bronze Age have been found. Vessels are Castelluccian, but the cave and vessels are often reported to be older, without proof. **Castelluccio** is an important Early Bronze Age settlement, with several cemeteries. **Monte Racello** is a Castelluccian settlement at the top of the mountain (510 m) and lower necropolis, and dated to the Early Bronze Age. It is part of a group of sites including, W to E, Monte Tabuto, Monte Sallia, Monte Racello and Monte Raci. **Manfria** (Gela) is located in the Agrigento province, southwest of Syracuse. It is a Castelluccian settlement of the Early Bronze Age. **Cava Bernardina** is a cemetery located just west of Megara Hyblaea, where Paolo Orsi in the late 19<sup>th</sup> century found Early Bronze Age materials (Castelluccian style). Very close there are traces of a settlement that has not yet been excavated. **Caldare** is a settlement with a necropolis located about 1 km away. Most artifacts come from the necropolis. It is a Castelluccian site, Early Bronze Age, but some artifacts suggest an early presence in the Late Neolithic. Bowls and daggers, however, have been found at the tomb of San Vincenzo, near Caldare. This tomb is dated to the Middle Bronze Age, or Late Bronze Age, Thapsos culture. The settlement of Caldare continued to be active in this period. **Montagna di Caltagirone**, a settlement, has been inhabited since the Castelluccian Early Bronze Age. The swords are dated to the Late Bronze Age, or more likely to the Early Iron Age (Pantalica culture). Tusa (1999) suggests that local metal production had been influenced by Thapsos culture bronze smiths. **Valsavoia** is a large

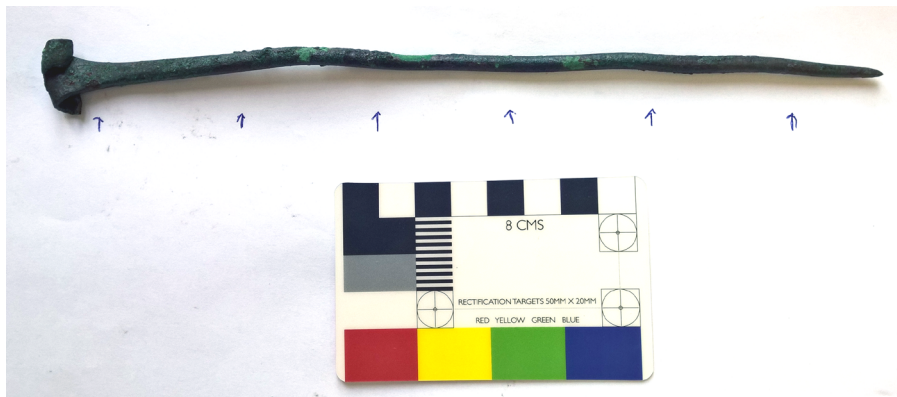
settlement with a nearby cemetery (**Cava Cana Barbara**) dated to the Early (Castelluccian) or Middle Bronze Age. The site is notable for glass and faience artifacts. **Cava Secchiera** is a cemetery dated to the Early Bronze Age. It has yielded Castellucian artifacts. **Finocchito** is a cemetery dated to the Early Iron Age. In subsequent phases Greek materials appear. **Plemmyrion** is a Late Bronze Age cemetery typical of the last phase of the Thapsos culture. **Thapsos** is a Middle Bronze Age site, on a peninsula, and a main commercial center for long-distance exchanges as well as the center of a distinctive local culture, with both a settlement and cemeteries. **Scintilia** is a Copper to Early Bronze Age necropolis located near Agrigento. **Sant'Ippolito** is an Early Bronze Age settlement located near Montagna di Caltagirone and dated Late Neolithic to Early Bronze Age, contemporary with Castelluccio.

Suspected clay molds and crucibles from Case Bastione, near Enna, have tested negative for copper and sulfur, casting some doubts on the nearly one hundred molds reported by Albanese Procelli (2006). The tests were carried out by the authors using the same pXRF. Crucibles are usually recognized more reliably (because of the metallic residue), and with one Copper Age exception from Lipari, the four others known are dated to the Early Bronze Age and divided between Manfria (near Gela) and from the Nebrodi area, confirming a slow adoption of metallurgy as deducible from the artifacts. The only two possible Copper Age sites would be therefore Lipari and Chiusazza Cave (near Syracuse), suggesting that the whole eastern coast of Sicily adopted metallurgy as a readily available technology from the Italian peninsula, almost certainly through Calabria.

### 3 Methods

This research focuses on copper-based metals from excavations, sometimes older than a century ago, which present some challenges to the present research in the form of difficulties in obtaining contextual information and records of their conservation and restoration. The materials are sparse in the territory of Sicily, and not abundant at all until the end of the Late Bronze Age. The same pXRF, a Bruker tracer III-SD, was used for all analyses. Spots of about 5x7 mm were analyzed for 30 seconds at 40 kV/1.5  $\mu$ A with no vacuum but using a filter which enhances the precision of the analyses. Calibration was based on the analysis of an extensive number of metal standards from the Smithsonian and the University of Georgia, with analytical results rendered in percent for the major elements. The strategy was to analyze artifacts at multiple points (when possible, each point about 1 cm apart or on the other side, see Fig. 2), and then assess variation in the measurements to estimate their original chemical composition. The methodological decision of analyzing multiple points were taken to recognize qualitative differences in the surface analyses caused by the patina, because limited permission from the museums prevented scraping in most cases. The preservation of the materials however plays a huge role in the reliability of surface analyses: in Sicily the dry climate has preserved copper-based metals fairly well, at least in terms of apparent degradation. In other areas, especially if moister, such a simplistic sampling strategy could easily fail due to much greater surface degradation (e.g. Nørgaard, 2017). A test done in the Aeolian Islands (cemetery of Lipari, Piazza Monfalcone, dated to the Late Bronze Age) has shown clearly that if the preservation is not as good, the pXRF produces unreliable data. The pXRF only measures at the surface, and has minimal penetration on metals. A test was run on a single artifact at the museum of Palermo (armilla 6866; Fig. 3) that had been scraped and noticed no changes between the multi-point analyses of the surface and the analyses of the scraped surface. There is visual evidence of some oxidization in all artifacts, but being relatively few and stored for very long periods, they likely have all been cleaned. Only a few, however, appear to have been treated with preservative containing zinc. Five intensive tests were made on daggers and swords in the Syracuse museum, and could not find any significant variation, partly because the objects were found in a dry and stable climate. They may have been conserved using chemical products since some intrusive zinc appears evident in some analyses, but these chemicals did not alter the ratios of copper and tin. Avoiding traces of restoration and residual rust is needed to obtain valid measurements, and while scraping may be a good practice in general, there is no evidence in the analyzed assemblages that this practice would provide any benefit at all. Furthermore, because several of these artifacts are displayed or restored, scraping is

considered by some local conservators as potentially destructive and actively opposed. Ultimately, the multi-point analyzing strategy is the best measure to detect potential problems with heterogeneity in the results. It is not advocated for this technique to be implemented universally, and there are some limits of pXRF analyses when consistency in measurements cannot be achieved, which is typically the norm. Multi-spot analyses, however, can distinguish between copper and bronze, and provide a rough estimate of the amount of tin, lead, or other intentionally elements in an alloy.



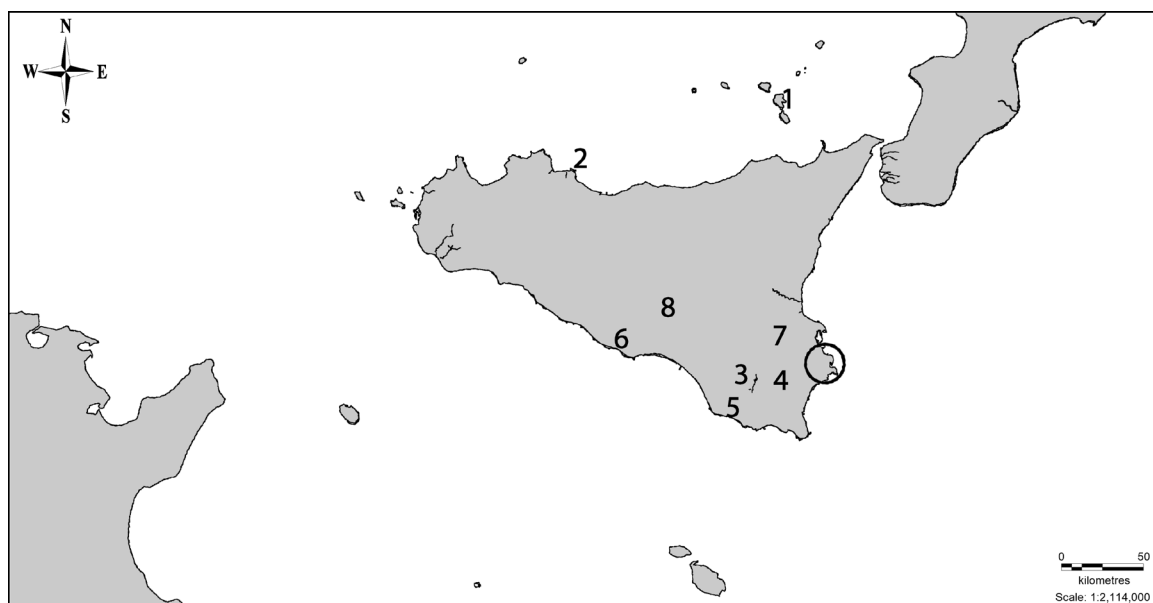
**Figure 2.** Example of multi-point analysis, artifact from Palermo (26593).



**Figure 3.** Test to remove patina on armilla 6866 from Palermo.

In a few cases, there were peaks of zinc in the detection, which suggest the use of some preservative varnish. In general, zinc peaks help recognizing problematic spots, which are removed from our interpretation. Zinc values are recorded and reported, but need to be understood as evidence of change in the composition due to chemical preservatives, and not intentional use in pre-Roman times. Multi-point analyses are specifically aimed at recognizing interferences from corrosion and modern preservatives, and provide values that are robust and representative of the actual composition of the ancient artifacts. There is now an extensive literature in support of this methodology (Orfanou and Rehren, 2015; Scott et al., 2015) with investigations carried out in the Americas (e.g. Dussubieux and Walker, 2015; Garrido and Li, 2017), as well as in Europe (e.g. Dylan, 2012; Peterson et al., 2017; Powell et al., 2017), including the Mediterranean (e.g. Charalambous, 2014; Charalambous et al., 2014). All this past experience has been applied to this research, beginning with the aims and research questions that match the capabilities of the technique: for instance there is no attempt to track the provenance or movements of copper, and the focus rests on technological issues related to the recognized alloys. The contexts do not allow a precise chronological seriation, but all sites are known well enough to know the main period of use, which likely applies to most artifacts from that site. The stratigraphic layers for long-lived caves are known, while all other sites do not last very long. The spatial distribution (Fig. 4) of the sites across Sicily supports the idea of the technology being imported

along with the raw materials because most artifacts have been found in Lipari (northeastern Sicily), which was connected to Calabria and the Tyrrhenian side of the Italian peninsula, and in the southeastern corner, which was connected with the Ionian side of the peninsula as well as with the Aegean. This makes most likely an introduction from the Italian peninsula. Alternative paths would have been possible, for example the Bell Beaker culture entered western Sicily (Tusa, 2001) from Sardinia in the Copper Age (and Sardinia had an earlier and more developed metallurgical tradition), while central Sicily would have been a likely candidate for indigenous development thanks to its mines of sulfur, or the district rich in minerals between Messina and Catania in eastern Sicily.



**Figure 4.** Map of Sicily with main sites listed: 1 Lipari; 2 Palermo; 3 Montagna di Caltagirone; 4 Monte Racello; 5 Gela; 6 Scintilia; 7 Finocchito; 8 Caldare. Circled area includes: Bernardina; Castelluccio; Cava Secchiera; Thapsos; Cava Cana Barbara; Plemmyrion.

## 4 Results

This research on early copper metal use in Sicily is still in progress, while much work is still required to determine with some precision the contexts and types of artifacts that have been targeted for this preliminary study. The chemical composition of these artifacts is the only data that is available at present and offered in this publication. Future effort will add materials that are not part of this specific research and therefore have not been included here (e.g. materials from the museum of Sant'Angelo Muxaro, which are dated to the Iron Age) and more analyses may be carried out in Sicily and the neighboring region of Calabria. The task at hand is recognizing technological differences that can clarify the development of metallurgy in the region. As an example of the type of patterns that was being looked for, a pattern typical of native development (smelting done locally representing the natural ore, then purified to increase concentrations of the main element such as copper, finally progressing in more functional and artificial alloys such as bronze) or a pattern of technological transfer (alloys always available).

The data have been summarized in Table 1. This includes a univocal number for the analysis issued by the Laboratory for Archaeological Sciences & Technology at the Department of Anthropology of the University of South Florida (site name, artifact description or identification, calibrated where possible, compositional data [copper, tin, lead, arsenic, zinc and iron], and a short comment when possible). More contextual information needs to be added to the table to be in final form, particularly on individual artifacts and contexts. At this stage, there is information on most artifacts, and a near complete list of



detected alloys, which is sufficient for our current scope of interest. The preliminary character of this publication enables presenting all individual analyses for scrutiny, including re-runs and multiple spots, together with averages for single artifacts. The sensitivity of the instrumental analysis allowed us to follow the common rule that values above 1% are indicative of alloys and not natural heterogeneity in the smelted raw material. For the purpose of this study, such values that meant artificial inclusion of that element were targeted, and therefore tiny values that could be the result of natural processes at the formation of the ore or after production can be ignored. Non-destructive surface analysis is not suitable to provide exact quantities of the original chemical bulk composition, but it is adequate for the aims of recognizing intentionally added alloys and estimating the amounts.

## 5 Discussion

The results in Table 1 show that the oldest “copper” artifacts found in Sicily were not made only of plain copper, but also copper intentionally mixed with tin or arsenic. The non-destructive use of pXRF is not ideal to identify the original chemical composition of corroded or altered objects with high precision (all elements), but it can provide a robust description of the alloyed object and therefore the technology employed. For non-copper-based metallic artifacts, especially jewelry, it is not possible at this point to produce calibrated numeric values, due to the matrix effects of X-ray penetration, and therefore the relevant data have been omitted at this stage of the research although identification of the composition is possible from visual assessment of graphs showing the energy and area of the secondary X-ray peaks. Tables 2–5 group the data after a preliminary typological and functional analysis (not using the final values after averaging the spots, expunging problematic data after repeated analyses as in Table 1, which is still a work in progress, but chemical variations for typological analysis are sufficiently accurate for comparison and use data from the main series of analyses). The tables present mostly unalloyed copper artifacts; bronze and other copper-based alloys; vessels; and weapons. The decision to use two different datasets depends on some refinements to Table 1, including the addition of four artifacts, which are insufficient to change any conclusion. For 19 artifacts, tin, lead and arsenic are absent or present in very low quantities (<0.5%). Lead is present in 39 artifacts, but only 23 have it in percentages of at least 0.5%. Arsenic is virtually absent in concentrations of >1%, except for four ornaments. It seems however that arsenical copper was used, for example in an EBA dagger from Boccadifalco (Palermo).

Table 2 lists the artifacts that were made of copper and not alloyed. It is based on very high percentages of copper without any significant amounts of metals used for alloys (intentionally added non-copper metals are not <1%). The only ingot tested has been found to match the signature for pure copper.

Table 3 lists the artifacts made of bronze (Cu + Sn) or other copper alloys (e.g. with As, Pb). It is a simple, unsophisticated division that shows clearly how copper alloys are present in the archaeological record since the Early Bronze Age, and supports the view that metals were introduced in the region only after alloys and more elaborated shapes became available from elsewhere. A preliminary typological and functional study has also grouped some artifacts by their function. All the values for Tables 2–5 can be checked on Table 1.

Table 4 lists the vessels, which appear consistently of unalloyed copper except for one metal sheet from Thapsos, which is made of tin bronze. This means that if unalloyed copper was widespread or prevailed in the Middle Bronze Age, by the next period tin bronze was already known and in common use. The vessels (Table 4), bowls in particular, show that there was little difference in technology between the Thapsos and Caldare assemblages, they clearly had access to tin and knew that smaller quantities produce a robust bronze, higher amounts a hardened metal. There is no evidence of a progression from unalloyed copper to arsenical and tin bronze, even with limited chronological insight.

Table 5 examines swords and daggers, which range from the Late Bronze Age (Thapsos) to the Early Iron Age (Plemmyrion). There are swords in unalloyed copper at both sites, and therefore both dates. This suggests that some swords were not meant to be used in battle. For instance, swords from Thapsos in unalloyed copper would be inefficient against the Caldare dagger, from the same period but of possible

Cypriot provenance (Mosso, 1908; De Miro, 1999; Lo Schiavo, Macnamara and Vagnetti, 1985; Graziadio, 1998). Swords of later periods in high percentage of copper are unlikely to have been made then, and may represent heirlooms from previous periods. Only four out of 18 swords and daggers are in tin bronze with higher percentages of tin (>15%) than the rest, and only six have lead in percentage >1% (intrusive or from recycling). The Caldare daggers are particularly significant, since their composition is very different despite belonging to an assemblage of probable Cypriote origin. One dagger (16356) has a high percentage of copper and some tin (3.7%), while the other (16357) has much higher tin (20.5%) and some lead in it (1.8%). The accompanying Caldare bowls are probably made of unalloyed copper, or just with traces from recycling (only destructive analyses can provide exact quantities). Although copper weapons can be functional, and can be preserved in time as heirlooms, the presence in the same assemblage of very different alloys for weapons suggests different uses, particularly a ceremonial one for weapons with high copper content that were disadvantaged in front of similar weapons using tin bronze. It is not possible to talk of progressive technological improvement or different needs in different areas. Half of the swords (dated Middle Bronze Age to Early Iron Age) have high copper contents, and are less functional if pitted against the other half, which spans the exact same period and areas. Six out of nine (out of 18 weapons in total) have a meaningful percentage of lead (>1.5%), which reduced melting temperature if the lead was added deliberately in antiquity (it could also be an unintended result of recycling). It can be safely assumed that weapons used the most advanced technology available, and were prepared for either warfare or ceremonial purposes. Tin sources were not available in Sicily or nearby regions, and therefore it had to be imported through long-distance exchange. It is however present in some artifacts from the earliest contexts, such as at Scintilia (Late Copper Age to Early Bronze Age) and at Castelluccio (Early Bronze Age). There is no significant gap between the introduction of unalloyed copper and tin bronze availability in Sicily, so that the presence of copper artifacts may be intentional (e.g. ingots) or due to difficulties in sourcing enough tin, but do represent a stage in the local development of copper-based metallurgy.

The earliest metals, from Chiusazza and Palombara Caves near Syracuse, and from Sant'Ippolito (near Montagna di Caltagirone), are dated Early Bronze Age, if not Copper Age for the caves, and they are made of unalloyed copper (roughly 98% copper, 1% arsenic and 0.5% lead for the dagger from Chiusazza; 99% copper for Palombara and Sant'Ippolito). In Castelluccio, dated Early to Middle Bronze Age, there are two sheets of tin bronze from tomb 22 (e.g. 16365, 11% Sn). Unalloyed copper artifacts arrived in small quantities by the Early Bronze Age, but tin bronze was already known by the Middle Bronze Age, if not at the same period. This excludes an indigenous discovery of metallurgy or local development of an imported technique because there would be a period in which substantial amounts were produced in unalloyed copper ore or some development in the production of particular alloys. In Sicily, multiple types of advanced alloys appear very early in the archaeological record, as the analyses prove. The newly found desire for copper-based metals might have played some role in establishing a long-distance exchange network, but the particular alloys used in Sicily suggest an indigenous production to satisfy local needs, but using imported technological know-how. The vessels and ingot show the ability to access from early times unalloyed copper of good quality, comparable with that of Aegean ingots, which have been found in many Sardinian sites of the Late Bronze Age (Lo Schiavo et al., 2009). The presence of Eastern Mediterranean copper oxide ingots in the Central Mediterranean was not the first introduction of metals in general, nor were they a technological step up, although they potentially were seen as valuable unalloyed copper available for production of tin bronzes as needed (without any evidence of use so far).

The weapons show the ability to produce alloys with 2 metals from the beginning, and some knowledge of lead copper that was rare but present from the beginning. Arsenic copper was also used from the earliest times. The conclusion can only be that metals and metallurgical know-how were both imported at the same time. Determining the provenance of some artifacts could prove interesting for future research, but the mediated introduction of metallurgy and apparent high frequency of recycling, along with the absence of a clear indigenous metallurgical development, will prove most certainly that metals could have come from either the northern Italian peninsula or the Aegean, and tin came from even further afar. Finding the precise location is of little significance, because by the Middle Bronze

Age the exchange network in which the ancient Sicilians participated included the whole Mediterranean (van Wijngaarden, 2002; Vianello, 2005; Broodbank, 2013). Rather, Sicily stayed on the margins of metallurgy and exchange networks trafficking metals, and benefited from them only very late as they expanded in closer regions and the technology matured. Even the possibly Middle Bronze Age Caldare assemblage, suggesting a connection with Cyprus as is the case for Thapsos tomb D (Voza, 1973a, 1973b), is not extraordinary, since Cypriot copper reached the farther island of Sardinia no later than one or two generations after their arrival. The Caldare assemblage shows a workmanship that is of the highest quality, and it is therefore not surprising that Aegean metals could have been preferred. Without an indigenous development (except for recycling), and modest amounts of metals until the end of the Bronze Age, it is unlikely that the ancient Sicilians were searching for metals or offered a ripe market for enterprising merchants from the Aegean, given the distances involved. It seems more a case of exchange networks becoming longer and accessing more areas, certainly affecting the economy of traders and the new cultures involved, but it is important to consider that the lack of local productions implies reliance on imported finished products for the most part, whose availability was scarce.

Considering the weapons, after accepting that some must have been ceremonial given the contemporaneity of efficient alloys and unalloyed copper, which is significant if one's life depends on it, the conclusion is that many metal tools and half of the weapons in Bronze Age Sicily were probably prestige items, or at least not used for regular warfare, as it has been proven unlikely at Montagna di Caltagirone (Tanasi, 2008). The pXRF analyses of metals prove that even in presence of metal weapons in many later tombs, the quality and typology varied too much for even a small army at a major settlement, unlike in the Aegean and elsewhere.

**Table 2.** Artifacts that are most likely made with copper, with no intentional alloys.

Sample	Item	Type	Period
0753-1	Monte Racello tomb 4 - 0745	mixed	EBA
Bernadina 12-5-4	Cava Bernardina tomb 12 - bead 2 inv. 8663	mixed	EBA
Cava Secchiera tomb 1 - 1-3	Cava Secchiera tomb 1 lamina 1 8899	mixed	EBA
7-5 unmarked	Monte Racello tomb 4 - X (unmarked)	mixed	EBA
8-3	Monte Racello fragment	mixed	EBA
17453-7-2	Monte Racello tomb 4	mixed	EBA
Castelluccio 1	Castelluccio t. 22 yoke of scale 8875	mixed	EBA
17478	Monte Racello tomb 5	mixed	EBA
1745X	Monte Racello tomb 4 - 1740	mixed	EBA
17453	Monte Racello tomb 4	mixed	EBA
17480	Monte Racello tomb 5 dagger	dagger	EBA
Cava Cana Barbara 6	Cava Cana Barbara t. 6 pierced bead (2-6)	mixed	EBA
Castelluccio	Castelluccio various	mixed	EBA
Bernadina 12-5-2	Cava Bernardina tomb 12 - spiral inv. 8663	mixed	EBA
Cava Secchiera tomb 14 - 2	Cava Secchiera tomb 14 inv. 11012	mixed	EBA
Thapsos 8-1	Thapsos (8) sword inv. 14742 tomb 37	sword	MBA
Thapsos 7-2	Thapsos (7) metal sheet 1 tomb 38	vessel	MBA
14783	Thapsos bowl (sheet) tomb 57	vessel	MBA
Thapsos ingot	Thapsos ingot from settlement	ingot	MBA

**Table 3.** Artifacts made of tin bronze or other copper alloys.

Sample	Item	Type	Period
Cava Secchiera tomb 6 - 10973	Cava Secchiera tomb 6 beads 10973	mixed	EBA
Cava Secchiera tomb 1 - 1-4	Cava Secchiera tomb 1 lamina 2 8901	mixed	EBA
Cava Cana Barbara 7 - 19145	Cava Cana Barbara t. 6 rod (2-7)	mixed	EBA
Castelluccio	Castelluccio various including yoke plus 8874, 8876 averaged, excl. 4	mixed	EBA
10977	Cava Secchiera tomb 7 hatchet-shaped pendant 10977	mixed	EBA
Bernadina 12-5-1	Cava Bernardina tomb 12 - metal wire inv. 8662	mixed	EBA
Cava Secchiera tomb 10 - 2-9	Cava Secchiera tomb 10 bead inv. 10992	mixed	EBA
Cava Secchiera 2	Cava Secchiera tomb 12 pierced necklace element 2 inv. 11003	mixed	EBA
17454	Monte Racello tomb 4	mixed	EBA
Cava Cana Barbara 10 - 19145	Cava Cana Barbara t. 6 - 19145 (2-10) fragmentary object	mixed	EBA
8874	Castelluccio	mixed	EBA
8876	Castelluccio	mixed	EBA
Bernadina 12-5-3	Cava Bernardina tomb 12 - bead 1 inv. 8663	mixed	EBA
Cava Secchiera 1	Cava Secchiera tomb 12 pierced necklace element 1 inv. 11002	mixed	EBA
19148	Cava Cana Barbara t. 9 dagger inv. 19148	dagger	EBA
Thapsos 8-2	Thapsos (8) pin 1 inv. 14743 tomb 37	mixed	MBA
Caldare bowl 16290	Caldare bowl 16290	vessel	MBA
Caldare dagger 16292	Caldare dagger 16292	dagger	MBA
Thapsos 7-3	Thapsos (7) rounded object tomb 38	mixed	MBA
Thapsos 8-3	Thapsos (8) pin 2 inv. 14743 tomb 37	mixed	MBA
	Thapsos part of dagger	dagger	MBA
Thapsos 1b-4	Thapsos rivet tomb 10	sword	MBA
P middle sword	Plemmyrion middle sword	sword	MBA
Thapsos 1-14753	Thapsos dagger 14753 tomb 41	dagger	MBA
Plemmirium - 2	Plemmyrion stick tomb 10	mixed	MBA
Thapsos 1c	Thapsos part of dagger tomb 7	dagger	MBA
Caldare bowl 16291	Caldare bowl 16291	vessel	MBA
Thapsos D - Voza 4	Thapsos settlement dagger inv. 63839	dagger	MBA
Thapsos 1c-1	Thapsos 14674 tomb 7	mixed	MBA
Thapsos 7-4	Thapsos (7) metal sheet 2 tomb 38	vessel	MBA
Thapsos 7-1	Thapsos (7) bent wire tomb 38 inv. 14750	mixed	MBA
Thapsos D - Voza 1	Thapsos settlement bull 1	mixed	MBA
Thapsos D - Voza 3	Thapsos settlement stick with zoomorphic representations inv. 63836	mixed	MBA
Gela sword 45526	Gela sword 45526	sword	MBA
Plemmirium 1	Plemmyrion sword tomb 44 inv. 17143	sword	MBA
Thapsos 1b-3	Thapsos plaque (from dagger?) tomb 10	dagger	MBA
	Plemmyrion (5) body of small sword tomb 12	sword	MBA
Thapsos 1b-2 ring	Thapsos ring tomb 10	ring	MBA
Thapsos D - Voza 2	Thapsos settlement bull 2	mixed	MBA
Caldare dagger 16293	Caldare dagger 16293	dagger	MBA
Thapsos 1b-1	Thapsos wire tomb 10	mixed	MBA
Gela sword	Gela sword purchase inv. 23798	sword	MBA
P big sword	Plemmyrion body of big sword tomb 20	sword	MBA
8-2	Montagna di Caltagirone 8-2	sword	LBA
8-1	Montagna di Caltagirone 8-1	sword	LBA
Montagna di Caltagirone 7 - 22222	Montagna di Caltagirone 7	sword	LBA
Montagna di Caltagirone 10	Montagna di Caltagirone 10	sword	LBA
Montagna di Caltagirone 6 - 22221	Montagna di Caltagirone (6) sword	sword	LBA
Montagna di Caltagirone 9	Montagna di Caltagirone 9	sword	LBA

**Table 4.** Metal vessels made of tin bronze or other copper alloys. Two from Thapsos, where the tested ingot has been found, are probably produced directly from ingot metal. Two from Caldare, suspected to be of Cypriot origin, are made of bronze alloy. A further vessel from Thapsos presents an excess of tin, perhaps the result of chemical modifications that have altered the analyzed surface, or an attempt to produce bronze alloy with a large amount of tin, typical of some weapons.

Sample	Item	Type	Period
Thapsos 7-2	Thapsos (7) metal sheet 1 tomb 38	vessel	MBA
14783	Thapsos bowl (sheet) tomb 57	vessel	MBA
Caldare bowl 16290	Caldare bowl 16290	vessel	MBA
Caldare bowl 16291	Caldare bowl 16291	vessel	MBA
Thapsos 7-4	Thapsos (7) metal sheet 2 tomb 38	vessel	MBA

**Table 5.** Weapons made of tin bronze or more ductile copper. The two Caldare daggers have very different amounts of tin and lead used to produce the alloy, probably one (16292) was ceremonial and one (16293) was functional.

Sample	Item	Type	Period
17480	Monte Racello tomb 5 dagger	dagger	EBA
19148	Cava Cana Barbara t. 9 dagger inv. 19148	dagger	EBA
Thapsos 8-1	Thapsos (8) sword inv. 14742 tomb 37	sword	MBA
Caldare dagger 16292	Caldare dagger 16292	dagger	MBA
P big sword	Plemmyrion body of big sword tomb 20	sword	MBA
Thapsos 1c	Thapsos part of dagger tomb 7	dagger	MBA
Thapsos 1b-4	Thapsos rivet tomb 10	sword	MBA
Thapsos 1-14753	Thapsos dagger 14753 tomb 41	dagger	MBA
P middle sword	Plemmyrion middle sword	sword	MBA
Thapsos D - Voza 4	Thapsos settlement dagger inv. 63839	dagger	MBA
	Thapsos part of dagger	dagger	MBA
Gela sword 45526	Gela sword 45526	sword	MBA
Plemmirium 1	Plemmyrion sword tomb 44 inv. 17143	sword	MBA
Thapsos 1b-3	Thapsos plaque (from dagger?) tomb 10	dagger	MBA
	Plemmyrion (5) body of small sword tomb 12	sword	MBA
Caldare dagger 16293	Caldare dagger 16293	dagger	MBA
Gela sword	Gela sword purchase inv. 23798	sword	MBA
Montagna di Caltagirone 9	Montagna di Caltagirone 9	sword	LBA

## 6 Conclusions

A monograph is planned; agreements with local authorities and permissions restrict discussion of some individual artifacts here. It has been known for some time that tin bronze was introduced already during the initial stages of the Bronze Age in Sicily, following a brief period of unalloyed copper tools (Maniscalco, 2000). The present results confirm that unalloyed copper, up to 99%, is present in some of the earliest contexts, including Cava Bernardina, Cava Secchiera, Castelluccio, Palombara Cave and Monte Racello. These sites are all located on the eastern coast, which is the supposed point of arrival of metallurgy in Sicily from Calabria. Until the local Middle Bronze Age, which corresponds to the early phases of Late Helladic III (Late Helladic III A pottery is the earliest found in local Middle Bronze Age contexts; Vianello, 2005), highly unalloyed copper and arsenic bronze was commonly used in the Mediterranean. The use of much recycled

metals can be excluded until the local Middle Bronze Age – something evident in the Late Bronze Age – because the copper is unalloyed in early metals. Lipari, where a Copper Age crucible was found (Albanese Procelli, 2006, p. 183), shows varied compositions in the metals from the Late Bronze Age hoard, itself a proof of recycling, supporting the hypothesis that by the Late Bronze Age metals had been produced long enough and in such quantities to make recycling viable. The presence of arsenic does not seem connected to a particular type of production, as suggested by Lechtman (1996), despite the presence of jewelry and sheets (Castelluccio and Thapsos), nor is “dirty copper”, but rather unalloyed copper produced by people who also alloyed it with arsenic and lead, leaving some traces. It seems plausible however that arsenical bronze was also used deliberately, as there is evidence of this at Monte Racello, Palermo and Lipari.

The introduction of tin bronze appears dated to the transitional period between local Early Bronze Age and Middle Bronze Age (early Late Helladic III, ca. 16<sup>th</sup> century BC). This is evident from its presence in Castelluccio (also in a sheet), and Cava Bernardina. Scintilia provides a useful depositional context, which is both relatively early, dated to the local Early Bronze Age, and from a funerary context that suggests early removal without recycling. There tin represents between 5% and 10% of the bronze. Tin bronze in that range is found in Castelluccio, Thapsos, Gela, Caldare, Plemmyrion, Cava Secchiera, Montagna di Caltagirone and Caldare, which is a good grouping of sites representing the eastern coast and Agrigento in the local Middle Bronze Age. There is also one artifact detected (and probably a few more among what it was not analyzed) from the late Ausonian 2 hoard in Lipari, suggesting that recycling was relatively new by then. Higher amounts of tin are present already in Thapsos, particularly from the settlement (figurines), which continued in the local Late Bronze Age, and these percentages are confirmed also at the complex cemetery of the Plemmyrion, which is dated to the Late Bronze Age (mainly) and continues into the Early Iron Age, with a beginning perhaps between local Middle and Late Bronze Age. The figurines in Thapsos use a bronze alloy with copper, tin and lead typically used in some weapons and a few items of jewelry, confirming that this three-metals alloy remained very precious and relatively rare throughout the whole Bronze Age.

The main objective of this preliminary overview of the research has been to demonstrate from the study of about 100 artifacts (84 reported here with values) the different alloys and compositions of the earliest metal artifacts found across Sicily. There are very few dating possibly to the Copper Age, with a substantially larger number dating to the Early and Middle Bronze Age. The materials from Lipari have been excluded, but they would increase the total for these two periods. Later periods have been deliberately ignored as they fall outside the scopes of the research, and those data are useful for comparative purposes. The result of this investigation shows evidence of a sudden increase in quantities, which marks an abrupt adoption of metallurgy. The compositional analysis using a pXRF shows a variety of advanced alloys being introduced soon after the first metal artifacts appear in the archaeological record, as well as the presence of ingots of unalloyed copper and some copper artifacts, which are more frequent in the earliest periods. The functional and typological analysis demonstrates however that there was no experimentation in Sicily: particular classes of artifacts are made using a limited number of copper-based alloys (arsenic and tin), and this demonstrates some advanced knowledge of metallurgy and prior experience in determining which alloys work best for different artifacts. As a result, the case for the importation of metallurgy and metals is very strong. In Sicily, this happened particularly late, and it seems connected to the availability of ingots ready for use and functional weapons made of tin bronze (harder than unalloyed copper). Despite the high variability in forms and alloys, these are the two most advanced technological advancements present at the time of the introduction of metallurgy, and it is possible to conclude this preliminary study suggesting that either or both developments were the technological change that convinced the ancient Sicilians to embrace metallurgy.

**Acknowledgments:** We thank all staff at Sicilian museums for their kind support. Dr. Anita Crispino at the Regional Archaeological Museum Paolo Orsi in Syracuse, and the director, Dr. Beatrice Basile, have been fundamental in obtaining access to the core materials for this study. Dr. Domenica Gulli has been most supportive for accessing the materials from Agrigento, kindly also providing some materials from the newly discovered site of Scintilia. Dr. Vittoria Schimmenti, Dr. Giuseppa Carrubbo and the director, Dr. Francesca Spatafora, have supported us in our work at the Regional Archaeological Museum Antonino Salinas in Palermo. We wish to thank also the Sicilian people for their warm hospitality during the research.

## References

- Affuso, A., & Lorusso, P. (2006). Produzione materiale e circolazione dei beni nella Basilicata ionica tra Bronzo tardo e prima età del Ferro. In Cocchi Genick D. (Ed.), *Materie prime e scambi nella preistoria italiana*. Atti della XXXIX Riunione Scientifica dell'Istituto Italiano di Preistoria e Protostoria, Firenze, 25-27 novembre 2004, vol. III. (pp. 1349–1359). Firenze: Istituto Italiano di Preistoria e Protostoria.
- Albanese Procetti, R.M. (2006). Artigianato metallurgico nella Sicilia protostorica. In A. Cardarelli, M. Pacciarelli, A. Vanzetti, *Studi di protostoria in onore di Renato Peroni*. (pp. 183–189). Firenze: All'Insegna del Giglio.
- Attema, P., Burgers, G.J., & Leusen, M.V. (2012). *Regional pathways to complexity: settlement and land-use dynamics in early Italy from the Bronze Age to the Republican period*. Amsterdam: Amsterdam University Press.
- Blake, E. (2014). *Social networks and regional identity in Bronze Age Italy*. New York, NY: Cambridge University Press.
- Broodbank, C. (2013). *The Making of the Middle Sea: A History of the Mediterranean from the Beginning to the Emergence of the Classical World*. Oxford: Oxford University Press.
- Cazzella, A., & Recchia, G. (2010). The 'Mycenaean' in the central Mediterranean, a comparison between the Adriatic and the Tyrrhenian seaways. *Pasiphae*, 3, 27–40.
- Charalambous, A. (2014). pXRF analysis of Cypriot copper alloy artefacts dating to the Late Bronze and the Iron Age. In V. Kassianidou & M. Dikomitou-Eliadou (Eds.), *The Narnia Project- Integrating approaches to Ancient Material Studies*. (pp. 134–145). Cyprus: University of Cyprus.
- Charalambous, A., Kassianidou, V., & Papasavvas, G. (2014). A compositional study of Cypriot bronzes dating to the Early Iron Age using portable X-ray fluorescence spectrometry (pXRF). *Journal of Archaeological Science*, 46, 205–216. DOI: <https://doi.org/10.1016/j.jas.2014.03.006>
- De Miro, E. (1999). Archai della Sicilia greca. Presenze egeo-cipriote sulla costa meridionale dell'isola. L'emporio miceneo di Cannatello. *Publications de l'École française de Rome*, 251(1), 71–81.
- De Santis, A. (2006). Evidenza di contatti fra il Lazio protostorico e le regioni limitrofe sulla base della circolazione dei materiali metallici: ipotesi possibili. In Cocchi Genick D. (Ed.), *Materie prime e scambi nella preistoria italiana*. Atti della XXXIX Riunione Scientifica dell'Istituto Italiano di Preistoria e Protostoria, Firenze, 25-27 novembre 2004, vol. III. (pp. 1361–1378). Firenze: Istituto Italiano di Preistoria e Protostoria.
- Dolfini, A. (2013). The emergence of metallurgy in the central Mediterranean region: A new model. *European Journal of Archaeology*, 16(1), 21–62. DOI: <https://doi.org/10.1179/1461957112Y.0000000023>
- Dolfini, A. (2014). Early metallurgy in the central Mediterranean. In Roberts, B., Thornton, C. (Ed.), *Archaeometallurgy in Global Perspective*. (pp. 473–506). New York, USA: Springer.
- Donati, G., Stagno, F., & Triscari, M. (1978). Ricerche sulle manifestazioni metallifere dei M. Peloritani. III) Giacimenti delle C.de S. Carlo, Montagne e viciniori, presso Fiumedinisi (Messina). *Atti Accademia Peloritana Pericolanti, Classe Scienze Matematiche Fisiche Naturali*, 56, 177–238.
- Dussubieux, L., & Walder, H. (2015). Identifying American native and European smelted coppers with pXRF: a case study of artifacts from the Upper Great Lakes region. *Journal of Archaeological Science*, 59, 169–178. DOI: <https://doi.org/10.1016/j.jas.2015.04.011>
- Dylan, S. (2012). Handheld X-ray fluorescence analysis of Renaissance bronzes: Practical approaches to quantification and acquisition. In A. N. Shugar & J. L. Mass (Eds.), *Studies in Archaeological Sciences Handheld XRF for Art and Archaeology*. (pp. 37–74). Leuven: Leuven University Press.
- Evans, J.D. (1977). Island archaeology in the Mediterranean: Problems and opportunities. *World Archaeology*, 9, 12–26.
- Freund, K.P., Tykot, R.H., & Vianello, A. (2015). Blade production and the consumption of obsidian in Stentinello period Neolithic Sicily. *Comptes Rendus Palevol*, 14, 207–217.
- Garrido, F., & Li, T. (2017). A handheld XRF study of Late Horizon metal artifacts: implications for technological choices and political intervention in Copiapó, northern Chile. *Archaeological and Anthropological Sciences*, 9, 935–942.
- Geniola, A., Larocca, F., & Vurro, F. (2006). Approvvigionamento di risorse minerarie nella Grotta della Monaca (Sant'Agata di Esaro - Cosenza). In Cocchi Genick D. (Ed.), *Materie prime e scambi nella preistoria italiana*. Atti della XXXIX Riunione Scientifica dell'Istituto Italiano di Preistoria e Protostoria, Firenze, 25-27 novembre 2004, vol. III. (pp. 1349–1359). Firenze: Istituto Italiano di Preistoria e Protostoria.
- Giannitrapani, E. (2014). Cultura materiale, modi di produzione e organizzazione sociale della più antica metallurgia nella Sicilia preistorica. In Soprintendenza di Agrigento (Ed.), *Le opere e i giorni*. (pp. 9–36). Agrigento: Regione Siciliana.
- Giardino, C. (1997). La metallotecnica nella Sicilia pre-protostorica. In S. Tusa (Ed.), *Prima Sicilia: alle origini della società siciliana*. (pp. 404–414). Palermo: Regione siciliana, Assessorato al turismo.
- Giardino, C. (2000). Sicilian Hoards and Protohistoric Metal Trade in the Central West Mediterranean. In *Metals make the world go round: the supply and circulation of metals in Bronze Age Europe*. Proceedings of a conference held at the University of Birmingham in June 1997. (pp. 99–107) Oxford: Oxbow Books.
- Giardino, C., Spera, V., & Tusa, S. (2012). Nuovi dati sulla metallurgia della Sicilia occidentale nell'età del Bronzo. In *Dai cicli agli ecisti: società e territorio nella Sicilia preistorica e protostorica*. Atti della XLI Riunione Scientifica dell'Istituto

- Italiano di Preistoria e Protostoria, San Cipirello (PA), 16-19 novembre 2006. (pp. 697–708). Firenze: Istituto Italiano di Preistoria e Protostoria.
- Giumlia-Mair, A. (2009). The hoard under the II hut on the acropolis of Lipari. A metallurgical study. In Lo Schiavo F., Maddin R., Muhly J.D., Giumlia-Mair A. (Eds.), *Oxhide Ingots in the Central Mediterranean*, Biblioteca di Antichità Cipriote 8. (pp. 161–221). Roma: ICEVO-CNR.
- Graziadio, G. (1998). Le presenze cipriote in Italia nel quadro del commercio mediterraneo dei secoli XIV e XIII a.C. *Studi classici e orientali*, 46(2), 681–719.
- Gullì, D. (Ed.). (2015). *Storie Sepolte. Riti, culti e vita quotidiana all'alba del IV millennio a.C. La necropoli di contrada Scintilia di Favara, Agrigento*. Soprintendenza per i Beni Culturali e Ambientali Agrigento.
- Larocca, F. (Ed.). (2005). *La miniera pre-protostorica di Grotta della Monaca (Sant'Agata di Esaro, Cosenza)*. Roseto Capo Spulico: Centro Regionale di Speleologia Enzo dei Medici.
- Larocca, F. (2012). Grotta della Monaca (Calabria, Italia Meridionale): Una miniera neolitica per l'estrazione dell'ocra. In: Borrell, M. et al. (Eds.), *Xarxes al Neolític. Circulació i intercanvi de materiès, productes i idees a la Mediterrània occidental (VII-III millenni aC)*. Actes Congrès Internacional, Gavà/Bellaterra, 2-4 febrer 2011. (pp. 249–256). Rubricatum 5.
- Lechtman, H. (1996). Arsenic bronze: Dirty copper or chosen alloy? A view from the Americas. *Journal of Field Archaeology*, 23, 477–514. DOI: <https://doi.org/10.1179/009346996791973774>
- Leighton, R. (1999). *Sicily before History. An Archaeological Survey from the Palaeolithic to the Iron Age*. Bristol: Bristol Classical Press.
- Liritzis, I. and Zacharias, N. (2013). Portable XRF of archaeological artifacts: Current research, potentials and limitations. In M.S. Shackley (Ed.), *X-ray Fluorescence Spectrometry (XRF) in Geoarchaeology*. (pp. 109–142). New York: Springer.
- Lo Schiavo, F., Macnamara, E., & Vagnetti, L. (1985). Late Cypriot imports to Italy and their influence on local bronzework. *Papers of the British School at Rome*, 53, 1–71.
- Lo Schiavo, F., Giumlia-Mair, A., & Albanese Procelli, R.M. (2009). Oxhide ingots in Sicily. In F. Lo Schiavo, J. Muhly, R. Maddin, A. Giumlia-Mair (Eds.), *Oxhide ingots in the central Mediterranean*, Biblioteca di Antichità Cipriote 8. (pp. 135–221). Roma: ICEVO-CNR.
- Lo Schiavo, F., Muhly, J.D., Maddin, R., & Giumlia-Mair, A. (Eds.). (2009). *Oxhide Ingots in the Central Mediterranean*. Roma: A.G. Leventis Foundation.
- Maniscalco, L. (2000). Osservazioni sulla produzione metallurgica in Sicilia nell'Antica Età del Bronzo. *Sicilia Archeologica*, 33(98), 159–166.
- Mosso, A. (1908). Villaggi preistorici di Caldare e Cannatello presso Girgenti. *Monumenti Antichi*, 18, 573–690.
- Nørgaard, H. (2017). Portable XRF on prehistoric bronze artefacts: Limitations and use for the detection of Bronze Age metal workshops. *Open Archaeology*, 3(1), 101–122. DOI: <https://doi.org/10.1515/opar-2017-0006>
- Orfanou, V., & Rehren, T. (2015). A (not so) dangerous method: pXRF vs. EPMA-WDS analyses of copper-based artefacts. *Archaeological and Anthropological Sciences*, 7, 387–397.
- Peterson, D. L., Dudgeon, J. V., Tromp, M., & Bobokhyan, A. (2017). LA-ICP-MS analysis of prehistoric copper and bronze metalwork from Armenia. In L. Dussubieux, M. Golitko & B. Gratuze (Eds.), *Recent Advances in Laser Ablation ICP-MS for Archaeology*. (pp. 115–133). Berlin, Heidelberg: Springer-Verlag.
- Powell, W., Mathur, R., Bankoff, H. A., Mason, A., Bulatović, A., Filipović, V., & Godfrey, L. (2017). Digging deeper: Insights into metallurgical transitions in European prehistory through copper isotopes. *Journal of Archaeological Science*, 88, 37–46. DOI: <https://doi.org/10.1016/j.jas.2017.06.012>
- Risch, R., & Meller, H., (2015). December. Change and continuity in Europe and the Mediterranean around 1600 bc. *Proceedings of the Prehistoric Society*, 81, 239–264.
- Scarcella, S., Bouquillon A., & Leclaire A. (2011). Neolithic facies of Stentinello culture: Analysis and comparison of ceramics from Capo Alfiere (Calabria) and Perriere Sottano (Sicily). In I. Turbanti-Memmi (Eds.), *Proceedings of the 37th International Symposium on Archaeometry, 13th - 16th May 2008, Siena, Italy*. (pp. 153–158). Berlin, Heidelberg: Springer.
- Scott, R.B., Eekelers, K., Fredericks, L., & Degryse, P. (2015). A methodology for qualitative archaeometallurgical fieldwork using a handheld X-ray fluorescence spectrometer. *STAR: Science & Technology of Archaeological Research*, 1(2), 70–80. DOI: <https://doi.org/10.1080/20548923.2016.1183941>
- Shugar, A.N. (2013). Portable X-ray fluorescence and archaeology: Limitations of the instrument and suggested methods to achieve desired results. In R.A. Armitage and J.H. Burton (Eds.), *Archaeological Chemistry VIII. ACS Symposium Series 1147*. (pp. 173–195).
- Tanasi, D. (2008). *La Necropoli Protostorica di Montagna di Caltagirone (CT)*. Polimetrica.
- Tusa, S. (1999). *La Sicilia nella Preistoria*. Palermo: Sellerio Editore.
- Tusa, S. (2001). Mediterranean perspective and cultural integrity of Sicilian Bell Beakers. In *Bell Beakers today: pottery, people, culture, symbols in Prehistoric Europe. Proceedings of the International Colloquium Riva del Garda (Trento, Italy) 11–16 May 1998*. (pp. 173–186).



- Tykot, R.H. (2016). Using non-destructive portable X-ray fluorescence spectrometers on stone, ceramics, metals, and other materials in museums: Advantages and limitations. *Applied Spectroscopy*, 70(1), 42–56. doi: <https://doi.org/10.1177/0003702815616745>
- Tykot, R.H. (2017). A decade of portable (hand-held) X-ray fluorescence spectrometer analysis of obsidian in the Mediterranean: Many advantages and few limitations. *MRS Advances*, 2(33-34), 1769–1784. DOI: <https://doi.org/10.1557/adv.2017.148>
- Tykot, R.H., Freund, K.P., & Vianello, A. (2013). Source analysis of prehistoric obsidian artifacts in Sicily (Italy) using pXRF. In R.A. Armitage & J.H. Burton (Eds.), *Archaeological Chemistry VIII*. (pp. 195–210). ACS Symposium Series 1147.
- Vianello, A. (2005). *Late Bronze Age Mycenaean and Italic Products in the West Mediterranean: a Social and Economic Analysis*. Oxford: Archaeopress.
- Van Wijngaarden, G.J. (2002). *Use and Appreciation of Mycenaean Pottery in the Levant, Cyprus and Italy (ca. 1600-1200 BC)*. Amsterdam: Amsterdam University Press.
- Voza, G. (1973a). Thapsos. *Archeologia nella Sicilia Sud-orientale*, Napoli, 30–52.
- Voza, G. (1973b). Thapsos: resoconto sulle campagne di scavo del 1970-71. In *Atti XV Riunione Scientifica dell'Istituto Italiano di Preistoria e Protostoria*. (pp. 133–157). Firenze.