

COPPER ALLOYS AND CYCLADIC METALLURGY DURING THE BRONZE AGE

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The Aegean basin has long been appreciated as one of the seminal and most dynamic centers of metallurgical activity during the Bronze Age. That appreciation rests not only on the volume and quality of metal objects found in the region, providing some sense of the scale of production, but on detailed laboratory investigations of the artefacts themselves which yield a wealth of data on the technologies of production.

The practice of alloying which becomes widespread in the Early Bronze II period, had already begun in the Early Bronze I period. Arsenical copper was the most popular alloy in the Aegean by that period, closely followed by tin bronze (Renfrew, 1967, 14; Charles, 1967; Branigan, 1968, 47; Muhly, 1985; Tylecote, 1991, 221). The addition of a second alloying metal to copper, either arsenic or tin, not only increases the hardness of the product. Pure copper is not easy to cast successfully as it develops gas bubbles that seriously weaken the end-product. The addition of arsenic or tin lowers the temperature at which melting occurs and improves casting by producing a more fluid melt that cools to a denser, less spongy metal. This was particularly important after the Early Bronze Age, when more complex shapes were cast in closed moulds (Tylecote, 1991, 216).

A. ARSENICAL COPPER ALLOYS

1. The production of copper-arsenic alloys.

The metallurgical advantages of copper-arsenic alloy over unalloyed copper have been described by many scholars (e.g. Charles, 1967; 1980; Coghlan, 1972; Northover, 1989; Tylecote, 1991; Zwicker, 1991) who have clearly established that the presence of arsenic in copper is particularly beneficial in enhancing its workability. In fact the new alloy has better casting properties and can more readily be worked cold or hot than unalloyed copper while having strength and hardness equivalent to those of tin bronze. It is also clearly established that with an arsenical content of up to 7%, copper alloys possessed remarkable ductility and could be readily worked hot or cold by hammering without cracking (Charles, 1967, 24). In view of its properties ancient societies are believed to have recognised it as a superior form of copper and used it extensively when arsenic concentration was over about 2% (Gale - Stos Gale - Gilmore, 1985; Budd - Ottaway, 1989).

The vital innovation of alloying prompted the production of the whole range of artefacts seen at this time. Most of them could be produced only by considerable secondary forging after the initial casting; for this as well as for its improved hardness, the copper-arsenic alloy might be «preferred». Its production constituted a distinct phase of considerable duration, lasted for approximately two millennia (roughly 3500-1500 BC) in Western Asia and Europe. A rapid growth of an interesting and distinctive Cycladic metal industry, which produced hundreds of metal objects, took place in the Early Bronze Age II period (2800-2300 BC). Many of the analysed artefacts and especially weapons were of copper alloyed with arsenic. However, there has been much speculation concerning the ancient production of copper-arsenic alloys, and many theoretical models have been proposed so far for the production of these alloys in antiquity (see Charles, 1967; McKerrell - Tylecote, 1972; Charles, 1980; Zwicker, 1980; Tylecote, 1991). Most of the researchers argue that the initial discovery of copper-arsenic alloy was unintentional, while soon after –when their properties were recognised– the ancient

metalsmiths must have been fully conscious of the efficacy of selecting and mixing different ores.

There is a broad spectrum of ore types that will contribute arsenic to copper and the availability of such minerals and ores in many of the major deposits in the earth's crust, can explain in part why arsenical copper was one of the first important alloys along with electrum in the ancient world.

The accidental discovery of arsenical copper alloys must have been reached by smelting mixed copper ores with arsenic - rich minerals. However, as many copper artefacts have more than 1%-2% As, a proportion recovered during smelting of most copper ores containing a little arsenic, it is thought that arsenic was added in some way to copper. Many attempts have been made to identify the manner in which the arsenic was introduced into the metal mixture. According to Tylecote (1967, 7) there are two possibilities:

a. The addition of minerals of high arsenic content to molten copper under reducing conditions; or

b. The selection of arsenical minerals and the direct co-smelting.

Merkel et al. (in press) in an investigation of the Precolombian production of copper-arsenic alloys, and reconstruction of the smelting process in three smelting sites at Batan Grande, Peru, review and discuss a number of theoretical models which have been proposed so far for the production of arsenical copper alloys in antiquity. The authors note from published results that experiments have been made to test those theoretical models and successfully to produce arsenical copper:

c. additions of arsenic rich minerals to molten copper

d. smelting or roasted copper sulfarsenide ores, and

e. smelting of mixed copper sulfarsenide ores with copper oxide ores

Thus, the experimental results cannot be used to rule out any of these possibilities.

2. Sources of ores -as related to origins of alloys

The production of arsenical bronzes from mixed oxidised ores of copper and arsenic might explain why arsenical bronzes were particularly common in the Aegean -Cyclades and Crete- in the Early Bronze Age, (when the smelting of sulphidic copper ores is quite unlikely) since in these two regions the oxidised ores of copper are the commonest (Brannigan, 1974, 59; McGeehan-Lyritzis, 1983; Gale - Stos Gale, 1984, 267).

Copper ore sources have been investigated on the Cycladic island of Seriphos and Kythnos; two ancient copper slag heaps on Seriphos (Avyssalos and Kefala) and one on Kythnos have been surveyed by a joint IGME / Oxford team; in each case fragments of ore found in the slag heaps prove that oxidised copper ores were smelted (Gale et al, 1985).

On the island of Seriphos oxidised copper ores (chrysocolla) were found on top of the headland between the bays of Mega Livadi and Koundouro, and sulphidic copper ores (iron pyrite plus chalcopyrite, together with some secondary oxidised ores) occurred at Kalavatsena, where there was much modern exploitation of copper ore. However, the antiquity of copper exploitation and of the copper smelting on Seriphos is not yet known.

On the island of Kythnos oxidised copper ores (malachite) occur within the iron ores at Milyes, Zogaki and around the bay of Ayios Ioannis. Ancient mines exist at all three localities and at Milyes and Psathi there are many vertical shafts through the marble and several entrances to the mines underground (Gale et al, 1985). At Zogaki the ancient mines are badly destroyed by the Italian exploitation in 1940-1941, but there are still remnants at the ancient galleries.

The Kythnos copper slag heap is about 150 metres above sea level at the cliff top, about two kms to the north of Cape Ioannis. Much of the slag is copper stained and it is mixed with fragments of clay furnace lining, many pottery sherds, stray pieces of oxidised copper ore (malachite in iron ore) and fragments of quartz-quartz veins are

abundant in the nearby schist outcrops and would have been ideal as a source of flux (Gale et al, 1985, 85). Copper prills of centimetre size and obsidian blades were also found within the slag heap. The discovery of obsidian tools, of primitive granite hammers, of the fine crushing of the slag to extract copper prills and the nature of the associated pottery (undecorated brownware), suggest a date in the Bronze Age.

The lead isotopic compositions of Kythnos slag and copper ore (Gale - Stos Gale, 1984, 261 figure 4) group in a field distinct from the Laurion field, and many Early Cycladic bronze artefacts (from Kythnos, Naxos, Amorgos and Kea) fall within the Kythnian field. It seems therefore that in the Early Bronze Age the most likely source of copper for the Cycladic metallurgists was the oxidised copper of the island of Kythnos with slight indications of use also of Laurion (Attica) oxidised copper ores.

3. Arsenical Coppers from the Bronze Age Cyclades: The Archaeological Evidence

Several sites in the Aegean have yielded remains of metal working. For the Cyclades the bronzes so far studied came from Amorgos, Naxos, Kythnos (or Naxos), Ayia Irini on Kea and Kastri and Chalandriani on Syros. Unfortunately the study of the Early Cycladic artefacts is hindered, because many have no known association, many have been bought on the antiquities market, and others are from early excavations which were inadequately reported (e.g. Tsountas, 1898, 1899).

The «Kythnos Hoard»

The acquisition of «ten bronze implements, found on the island of Thermia, the ancient Cythnos» was reported to the Trustees of the British Museum in 1866 (Trustees Parliamentary Reports 1866). These objects, now known as the «Kythnos Hoard» have been recognized as being of Early Cycladic manufacture, and were first fully published as such by Colin Renfrew in 1967. However, new documentary evidence as well as scientific examination reported by L. Fitton (1989), suggest that two of the ten objects are unlikely to belong, and the remaining eight can be shown to have been part of a larger hoard, consisting of 12 items, four of which are now in the National Museum, Copenhagen (CNM 3143, 3144, 3145, 3153). This newly reconstructed hoard was probably found not on Kythnos, but on the island of Naxos (Fitton, 1989).

The so-called Kythnos hoard consists of three shaft-hole axes, three massive flat axes, three narrow flat axes or chisels and an axe-adze, which may well represent a carpenter's set of tools. The various parallels of these tools seem to place the «Kythnos hoard» in the EB II period of the Aegean. The lead isotope compositions for all ten artefacts of the Kythnos hoard fall squarely within the field for copper ores and slags from Kythnos (Gale - Stos-Gale, 1984, fig. 5). According to the analytical data (Craddock, 1976) the "Kythnos hoard" is entirely of arsenical copper with practically no trace of tin.

Early Cycladic weapons: The daggers from Amorgos

The most representative type of the EBA Aegean weapons was the dagger, and Cyclades formed an important centre in the distribution of daggers. The two other types of weapons, spearheads and swords do not differentiate a lot from daggers, since the difference between spearhead and dagger in one of mounting, and in the same way the term «sword» merely implies a long dagger, of length greater than about 40cms. It seems that the dagger appears simultaneously in the Cyclades, Crete, Mainland Greece, and West Anatolia in Early Bronze Age II. However, these finds are notably more abundant in Crete and the Cyclades (especially Amorgos) than in the Mainland of Greece or West Anatolia. The Early Cycladic metal objects from Amorgos and Naxos are also without exception of tin-free arsenical copper whilst the Late Bronze Age artefacts from the same islands are of low arsenic tin bronze.

B. TIN BRONZE METALLURGY

1. The production and the sources of copper-tin alloys

Though the dominant alloy for the Aegean Early Bronze Age, especially in the

Cyclades, was arsenical copper, some metal objects found at the fortified citadel of Kastri on the island of Syros are predominantly high tin bronze (5.40%-10.8% tin) with arsenic content from 0.40% to 1.33%.

It is during EBA (4300-3500 BC) that tin bronzes become known in Anatolia. The presence of tin bronze at Thermi in Lesbos in EBA I (Lamb, 1936, 215) shows that tin-bronze technology has by this time reached the Aegean basin. This technological advance may have been a result of interaction between metallurgies in the Late Neolithic – Early Bronze I period.

The greater proportion of all tin comes today, as well as in early times, from alluvial or mineral deposits of cassiterite (SnO_2). Tylecote (1976, 14) records that early copper-based alloys from widely separated areas of Eurasia contain small amounts of tin, often together with arsenic. According to Tylecote it would be possible that most of the tin content is the result of smelting copper ore contaminated with tin minerals, although later some of this contamination could have been caused by the addition of tin bronze as scrap.

The low tin alloys can be found in nearly all early civilizations of the world (Tylecote 1976, table 11) and might have initially been an accidental product since, as mentioned above some copper deposits, could have produced a natural tin bronze with a few percent tin. Charles (1980, 173) shows that some gossans may also contain tin; if used for fluxing in copper smelting they might introduced tin at about the 1% to 3% level.

Where the ores already contain arsenic and tin contamination has taken place, we find the so-called arsenical bronzes with 1%-2% Sn and 1%-4% As (e.g. No 16166 chisel from Kastri containing 1.94% Sn and 0.92% As). The effect of tin and arsenic on the mechanical properties is more or less additive, and it is found that cold-worked alloys of this type are a good deal stronger than pure or slightly impure coppers. The «addition» of 1% Sn in solid solution would confer about the same increase in hardness upon workings as 1% As. It seems clear however, that bronzes containing greater than about 5% of tin must mostly be deliberate alloys which as mentioned by Charles (1980, 174-5) are easily produced by adding cassiterite to the surface of molten copper via a slag under charcoal in a crucible. This is an easier process than reducing the cassiterite separately to tin and then adding the tin to copper. The recognition of the «ideal» tin-bronze, and the more controlled use of tin, seems to be reflected in the upper limits of the alloying range, which lie between 8% and 10%. However, a precise percentage of tin was not critical as the final hardness was achieved by work-hardening.

As tin deposits are something of a rarity, tin had ordinarily to be traded from the few localities, where it occurred in workable quantities, to be added deliberately to the copper melt. In the Aegean tin sources are more in doubt and the existence of tin-bronzes does tend to confirm the view that there have been sources of copper ores yielding metal with 1%-3% Sn.

However, the Aegean tin problem remains a central one for the Bronze Age, since no tin sources whatever are known in the area (Muhly, 1973, 271). The question is where did the tin used in the area ultimately come from?

The best evidence for the tin used in the Aegean comes from the classical period and concerns the tin of Cornwall (Diodorus Siculus, V 22). It would be possible that the Cornish tin plays the same role in the Bronze Age that it did in the Iron Age. Muhly (1973, 336) argues that Cornish tin came into the Aegean by a network of trade routes which developed out of a trade in amber and faience, a trade in which the manufactured goods of the Aegean basin, especially the products of the Mycenaean bronze industry were exchanged for the raw materials of the western Europe. However, there is no evidence for this trade before 1600 BC.

In the East Aegean tin-bronze was more common in the Early Bronze II period (2800-2300 BC). Though the evidence is inconclusive the most likely source for the Early Bronze Aegean would seem to be some alluvial deposits of tin, in or near the Troad (Renfrew, 1967, 13; Muhly, 1973, 337). This would explain its early occurrence and fre-

quency in the Troad, and seems a more probable explanation than some hypothetical and distant tin trade for which one can only hazard a guess.

2. Kastri on Syros : Tin-Bronze Artefacts in an Early Cycladic Context

The settlement of Kastri on the Cycladic island of Syros, was first excavated and published by Tsountas in 1899, and systematically excavated later by Bossert in 1967. The bronze objects found at the fortified hill-top site of Kastri, comprised tool hoard containing 2 pins, 2 awls, 8 chisels and a saw; in other parts of the site were found 2 small daggers, 2 flat axes and a spearhead. Bossert (1967, 65-67) discussed the spearhead at length and showed that it had very close Anatolian comparisons of Troy II times. Branigan has further shown that some of the objects from the tool hoard have good parallels in Anatolian objects excavated at Troy and Thermi and Lesbos. Kastri seems to have been inhabited for a relatively short period in the later Early Bronze Age II (EC II) or earlier EB III period (circa 2300-2700 BC). It should be noted that the archaeometallurgical evidence from Kastri supports only the melting and casting of bronze and lead at the site; there is no evidence for extractive metallurgy. The chemical analyses of 16 metal artefacts from Kastri, made by Gale et al (1984; 1985), show that 69% of these objects are high tin bronzes. Bossert in an earlier study had already noted their «anomalous» alloy composition in an Aegean context (Bossert, 1967, 63, note 22).

Lead isotope analyses (Gale - Stos-Gale, 1984, 41-42) have shown that all the tin bronzes found at Kastri are made of copper from two sources not represented amongst other analysed Cycladic artefacts. Nevertheless the two objects from Kastri shown by lead isotope analysis to be the Kythnian copper are both of arsenical copper containing over 2% arsenic with no tin. It seems that the high tin bronzes from Kastri do not represent the technology available in the Cyclades at that time, though the picture is still far from being complete (Bossert, 1967, 63; Gale - Stos-Gale, 1986, 24). It is at Troy where one sees a striking predominance of tin bronzes in EBA times (Renfrew, 1972, 313; Branigan, 1974, 64; de Jesus, 1980, 101). The similarities in alloy compositions between Troy and Kastri together with the striking similarities in isotopic composition may suggest that the analysed objects from Kastri would be Trojan (or Anatolian) both in alloy type and in the provenance of the copper (Gale - Stos Gale, 196, 28).

C. ANALYSES OF THE METAL ARTEFACTS: DISCUSSION OF THE RESULTS

There have been several large scale analytical projects devoted to metalwork of the Aegean Bronze Age. Notable are the analyses of about 100 Greek Bronze Age samples recorded by Junghans et al. (1968), which are included in their coverage of the metalwork of the European Bronze Age, the analyses of over 300 Bronze Age and Geometric Greek bronzes published by Craddock (1976) and the analyses of 120 metal objects from Poliochni on Lemnos carried out by Pernicka et al. (1990). There are also reported projects including smaller numbers of analyses such as that published by Renfrew (1967) on Cycladic metalwork from the collections of the Ashmolean Museum, Oxford, and the British School of Archaeology at Athens; various analyses made by Gale and Stos-Gale (1984; 1985) especially on Cycladic metal artefacts, the remaining slag and metallic prills and copper ore surface collected at the ancient sites. Analyses of five copper axes from Finlay Collection of the British School at Athens were published by Phelps et al. (1979). The results and the conclusions from these projects are very important and often form useful comparative material.

The chemical analyses of the objects from the Kythnos hoard (Craddock, 1976) show all to be of arsenical copper with tin contents never above 0.5% and arsenic ranging from 1.25% to 6.20% (Craddock, 1976, 98). Lead, silver, iron and nickel are the most frequent impurities. The Amorgos figures which should be broadly contemporary with those from Kythnos, show a marked preponderance of arsenical alloys (3%-9%), in which very little, if not at all tin is found (Branigan, 1974, 71; Renfrew, 1967, 20; Craddock, 1976, Lab.

Nos: 956, 1391, 1392, 1393, 1394). Indeed, the only two artefacts with more than traces of tin also have the lowest arsenic contents -1.1% and 1.5% respectively- so that here too, less than 2% of arsenic might be indicative of a natural alloy (Table 1).

Of six Early Bronze Age artefacts from Naxos, five have significant quantities of arsenic (greater than 2%), (Bossert, 1967, 76; Stephanos, 1905, 225; Jungans et al. 1968, Nos 16158, 16159, 16160, 16161, 16162). The same pattern is repeated at Ayia Irini, Kea, where the EC metal objects are without exception of tin-free arsenical copper (Gale and Stos-Gale 1984).

Two metal artefacts from Chalandriani (EC II or EC IIIA) are both low tin arsenical bronzes; the punch no 16125 has 4.1% As and 0.3% Sn, while the tweezers no 16157 have 3.9% As and 0.5% Sn. Electron microprobe analyses and neutron activation analyses (Gale et al. 1985, 148) of 16 of the bronze artefacts from Kastri, Syros have shown that 69% of these objects are made of high tin bronze (1.94%-10.8% Sn), a proportion paralleled at this period only in Troy and other Anatolian sites (de Jesus 1980, 101).

The analyses of the objects from Kastri show also that the tin bronzes amongst them contain arsenic at levels ranging from 0.4% to 1.33%, whilst the two objects containing over 2% arsenic contain virtually no tin (Table 1). It seems clear that the objects from Kastri are quite unlikely all other Early Cycladic copper alloy artefacts yet analysed, both in alloy type and in the provenance of their copper. Gale and Stos-Gale (1985) suggest that the 16 analysed objects from Kastri are Trojan (Anatolian) both in alloy type and in the provenance of copper; moreover many of these objects are also of Trojan (or Anatolian) typology.

Eight Late Bronze Age objects from Amorgos and Naxos are of low arsenic tin bronze. The range of tin is from 5.2% to 8.8% with an average of 7.025%. Although the LBA sample size may not appear to be representative of the total number of bronzes recovered in the Aegean, certain comments and comparisons can be made from the results of the compositional analyses. As expected, tin is the major alloying metal in LBA Cycladic artefacts.

A variety of types of artefacts are represented among the analysed samples. With this in mind, the analytical data were used to investigate whether correlations existed between composition and function of the artefact. The compositional analysis of 17 EC axes show that only two have less than 1% arsenic. The range of arsenic is from 0.45% to 6.20% with an average of 2.76%. This could suggest that the deliberate alloy was being used for the EC axes as they needed to be taut as well as hard. The four LBA axes include three of tin bronze with between 7.3% and 6.6% tin and one of arsenical copper with 3.4% arsenic and traces of lead (0.25%).

The daggers obviously are used differently from axes, and less control was exercised over the alloy used to produce them. This is reflected in the arsenic content of the 21 Early Cycladic daggers analysed in the three projects, with ranges from traces (natural «alloy») to 9.5% (deliberate alloy), (mean content 3.078%). Nearly 30% of the analysed daggers have less than 1% arsenic, and no particular range of arsenic content seems to have been preferred.

A similar situation is encountered in the MC daggers, although a satisfactory comparison is difficult owing to the small sample size. The three LBA daggers from Amorgos are of tin bronze with between 6.1% and 8.3% tin. They also contain small quantities of arsenic (0.79%-1.00%). And lead (0.4%-2.2%). It is not uncommon for artefacts made during the long period of change from arsenic to tin alloys with copper to have appreciable quantities of both metals (Charles, 1967; Craddock, 1976, 99). The analyses of the LBA daggers suggest an improvement in the effective use of tin, which may be interpreted as an improvement in refining and alloy control, or a combination of these two with several other factors.

From the 11 Early Cycladic chisels included in this study, 9 came from Kastri, Syros and they are all tin bronzes. All but one have more than 5% tin. The chisel no 16166 contains low and equal amounts of tin and arsenic (1.94% and 0.92% respectively).

The range of the tin content in the tin bronzes is from 5.4% to 10.8% with an average of 7.34%. The optimal tin content in bronze to give maximum hardness without undue brittleness is about 10% (Tylecote, 1976, 15). The 8 chisels from Kastri might have been deliberate alloys containing sufficient tin, tended to satisfy this requirement. As it was mentioned above, tin bronzes seem to have been rarely used in the EBA Cyclades, because of the lack of tin in the area. However, the objects from Kastri are predominantly high tin bronzes and their inclusion has tended to confuse previous discussions of the Early Cycladic bronze technology (Muhly 1985; Gale and Stos-Gale 1986). The two other chisels from Naxos are of tin-free arsenical copper containing 5.7% and 3.4% arsenic.

The relative control of the composition of the Bronze Age Cycladic axes and chisels and correlation between alloying metal content(s) and function of artefact, suggest a relative degree of sophistication in the selection and in the controlled use of arsenic and tin. During the Early Bronze Age the arsenic content in copper alloys provided the required hardness in the Cycladic tools and weapons while in the Late Bronze Age tin became more widely used.

D. CONCLUSIONS

One of the most interesting characteristics of the Early Aegean metallurgy is that it combines both copper-arsenic and copper-tin alloys, the two being used together almost simultaneously but distinctly. The evidence available at present suggests that arsenical copper and tin bronze were used for the same types of object. However there do not appear to be many mixtures of arsenical copper with tin bronze (i.e. remelts of scrap), as in very few cases does arsenic occur with tin bronze in any amount higher than a trace (i.e. <1% which results from refining). Likewise, no tin occurs in any amount higher than a trace in the arsenical coppers. It is evident from the analyses that tin and arsenic are not associated, and thus not confused by the ancient metallurgists of the Cyclades. This may be indicative of two distinct Bronze Age "traditions" of metallurgy, one based on the production of arsenical copper and the other on tin bronze. Both alloys were used occasionally for the same type of object, but copper as well. There does not seem to be any particular methodological use of one alloy or just copper for any particular type of object. This would seem to question claims by some authors that tin bronze or arsenical copper were necessary for intricate castings or certain types of metalworking (Tylecote, 1991).

Summing up the evidence, it is reasonable to suggest that arsenical bronzes continued in use in most of the Early Bronze Age Aegean sites, long after the advantages of tin bronze were recognized, perhaps because of the scarcity of tin in this area (Renfrew, 1967; Muhly, 1973). However we cannot be always sure whether arsenical bronzes were produced accidentally or otherwise. The point at which one distinguishes between deliberately or accidentally produced alloy is still disputed for the Cyclades.

From the available literature it is obvious that there is still a great deal of work to be done to demonstrate how arsenical copper alloys were produced and whether they were deliberately created and selectively used. However, in view of the evidence provided so far, it seems quite likely that arsenical copper alloys found as artefacts in the Aegean Bronze Age culture was at first the accidental result of smelting though their properties resulted in their being selected as an especially good sort of copper for casting and cold working to produce a tougher metal. The method of production was obviously dependent to some extent on local ores, sources and minerals. Arsenical bronzes in the Cyclades were achieved in smelting rather than in subsequent phases of production. Research emphasis should be placed more upon the selection of alloy type for specific function or object types. The controversy between deliberate or accidental alloying should be more focused upon the chronology from the archaeological evidence, proportions of each alloy at given sites, and evidence for extractive metallurgy.

| | Location | Description | Date | Provenance | As % | Sn % | Pb % |
|----|--------------|------------------|-----------|--------------|-------|-------|-------|
| 1 | BM 12.31.10 | Axe Adze | EC II | Kythnos | 3.00 | 0.40 | 5.10 |
| 2 | BM 12.31.7 | Shaft-hole Axe | EC II | Kythnos | 2.10 | — | 0.14 |
| 3 | BM 12.31.8 | Shaft-hole Axe | EC II | Kythnos | 2.00 | — | 0.090 |
| 4 | BM 12.31.9 | Shaft-hole Axe | EC II | Kythnos | 3.80 | — | 0.430 |
| 5 | BM 12.31.1 | Flat Axe | EC II | Kythnos | 2.30 | — | 0.140 |
| 6 | BM 12.31.2 | Flat Axe | EC II | Kythnos | 1.25 | — | 0.050 |
| 7 | BM 12.31.3 | Flat Axe | EC II | Kythnos | 3.40 | — | 0.080 |
| 8 | BM 12.31.4 | Flat Axe(chisel) | EC II | Kythnos | 4.60 | — | 0.080 |
| 9 | BM 12.31.5 | Flat Axe(chisel) | EC II | Kythnos | 6.20 | — | 0.080 |
| 10 | BM 12.31.6 | Flat Axe(chisel) | EC II | Kythnos | 3.60 | — | 0.350 |
| 11 | BM 12.31.54 | Dagger Class V | MC | Amorgos | 4.80 | 0.450 | 0.120 |
| 12 | BM 12.31.55 | Dagger Class IIa | EC II | Amorgos | 6.20 | 0.12 | 0.250 |
| 13 | BM 12.31.56 | Dagger Class IIa | EC II | Amorgos | 6.20 | 0.25 | 0.020 |
| 14 | BM 12.31.57 | Dagger Class IIb | EC II | Amorgos | 2.40 | 0.30 | 0.250 |
| 15 | BM 12.31.58 | Dagger Class Va | EC II-III | Amorgos | 4.50 | 0.15 | 0.450 |
| 16 | BM 8.23.5 | Axe Adze | EC II | Amorgos | 2.60 | — | 0.240 |
| 17 | BM 12.31.85 | Flat Axe(chisel) | EC II | Amorgos | 0.450 | — | 0.020 |
| 18 | A 1927.1357 | Flat Axe | (EC II) | Amorgos | — | <0.1 | 0.11 |
| 19 | AE 236 | Flat Axe | (EC II) | Amorgos | 1.1 | 0.85 | 0.13 |
| 20 | A 1927.1362 | Sickle | LBA | Amorgos | 0.66 | 5.5 | 1.1 |
| 21 | AE 237 | Dagger Class IIa | EC II | Amorgos | — | — | 0.5 |
| 22 | A 1927.1361 | Dagger Class IIa | EC II | Amorgos | — | — | 0.45 |
| 23 | AE 233 | Dagger Class IIc | EC II | Amorgos | 1.5 | 0.24 | 0.13 |
| 24 | AE 231 | Dagger Class IId | EC II | Amorgos | 3.5 | — | 0.1 |
| 25 | AE 238 | Dagger Class Va | EC II-III | Amorgos | 4.9 | — | — |
| 26 | AE 240 | Dagger Class Va | EC II-III | Amorgos | — | — | 0.54 |
| 27 | A 1927.1360 | Dagger Class Va | EC II-III | Amorgos | — | — | 0.38 |
| 28 | AE 230 | Dagger Class Va | EC II-III | Amorgos | — | — | — |
| 29 | AE 239 | Dagger Class Va | EC II-III | Amorgos | 9.5 | — | 0.054 |
| 30 | AE 252 | Dagger Class Va | EC II-III | Amorgos | 9.5 | — | 0.19 |
| 31 | A 1927.1358 | Dagger Class Va | EC II-III | Amorgos | — | 0.27 | 2.6 |
| 32 | A 1927.1359 | Dagger Class Vb | EC III | Amorgos | 8.7 | — | 0.19 |
| 33 | AE 234 | Dagger Class VI | (EC III) | Amorgos | — | 0.18 | 0.17 |
| 34 | AE 235 | Dagger Class VI | (EC III) | Amorgos | — | 4.4 | 0.93 |
| 35 | AE 241 | Dagger Class VII | (MC) | Amorgos | — | — | 1.2 |
| 36 | AE 242 | Dagger Class VII | (MC) | Amorgos | 7.7 | — | 0.024 |
| 37 | BSA B181,B | Dagger Class VII | (LBA) | Amorgos | 0.79 | 8.3 | 2.2 |
| 38 | BSA B181,C | Dagger Class VII | (LBA) | Amorgos | 1.0 | 6.1 | 0.64 |
| 39 | BSA B181,A | Dagger Class VII | (LBA) | Amorgos | 1.0 | 6.7 | 0.4 |
| 40 | A 1927.2968 | Shaft-hole Axe | (LBA) | Amorgos | — | 8.8 | 0.59 |
| 41 | AE 86 | Axe Adze | LBA | Naxos | 0.79 | 7.3 | 0.26 |
| 42 | AE 87 | Axe Adze | LBA | Naxos | — | 8.3 | 2.1 |
| 43 | A 1910.618 | Flat Axe | (LBA) | (Paros) | 3.4 | — | 0.25 |
| 44 | Nax 4.11.61 | Chisel | (EBA) | Naxos | -5.7 | 0 | 0 |
| 45 | Nax 1685 | Double Axe | (EBA) | Naxos | 1.45 | 0 | 0.77 |
| 46 | Nax 1686 | Flat Axe | (EBA) | Naxos | 4.6 | 0 | 0.12 |
| 47 | Nax 1684 | Chisel | (EBA) | Naxos | 3.4 | 0 | 0.65 |
| 48 | Nax 1687 | Flat Axe | (EBA) | Naxos | 4.6 | (TR) | 0.12 |
| 49 | Nax 248 | Tweezers | (LBA) | Katsoprinas | 0.11 | 5.2 | 0.07 |
| 50 | Erm.Syros201 | Punch | EC II | Chalandriani | 4.1 | 0.3 | 0.28 |
| 51 | Erm.Syros203 | Tweezers | EC II | Chalandriani | 3.9 | 0.5 | <0.1 |
| 52 | Erm.Syros200 | Spearhead | EC II B | Kastri Syros | 0.66 | 8.1 | - |
| 53 | Erm.K 62/11 | Chisel | EC II B | Kastri Syros | 1.00 | 10.8 | - |
| 54 | Erm.K 62/12 | Chisel | EC II B | Kastri Syros | 1.33 | 8.14 | - |
| 55 | Erm.K 62/13 | Chisel | EC II B | Kastri Syros | 0.92 | 1.94 | - |
| 56 | Erm.K 62/14 | Chisel | EC II B | Kastri Syros | 1.04 | 6.2 | - |
| 57 | Erm.K 62/15 | Chisel | EC II B | Kastri Syros | 0.72 | 8.3 | - |
| 58 | Erm.K 62/16 | Chisel | EC II B | Kastri Syros | 0.40 | 7.7 | - |
| 59 | Erm.K 62/17 | Chisel | EC II B | Kastri Syros | 0.73 | 6.4 | - |
| 60 | Erm.K 62/18 | Sawblade | EC II B | Kastri Syros | 1.08 | 0.53 | - |
| 61 | Erm.K 62/19 | Chisel | EC II B | Kastri Syros | 0.91 | 5.4 | - |
| 62 | Erm.K 62/20 | Chisel | EC II B | Kastri Syros | 1.09 | 5.8 | - |
| 63 | Erm.K 62/21 | Punch | EC II B | Kastri Syros | 1.21 | 7.2 | - |
| 64 | Erm.K 62/27 | Dagger(small) | EC II B | Kastri Syros | 2.28 | 0.02 | - |
| 65 | Erm.K 62/28 | Hoe | EC II B | Kastri Syros | 2.38 | 0.07 | - |
| 66 | Erm.K 62/29 | Punch | EC II B | Kastri Syros | 1.73 | 0.05 | - |

FIG.1 Location, Description, Date, Provenance and analytical results for copper alloy artefacts from the Cyclades.

Table 1.

| Fe % | Ni % | Sb % | Ag % | Bi % | Zn % | Au % |
|-------|-------|--------|--------|-------|-------|--------|
| (TR) | 0.650 | 0.07 | 0.060 | 0.150 | — | — |
| 0.050 | 0.060 | 0.07 | 0.060 | 0.150 | — | — |
| — | 0.095 | 0.15 | 0.070 | 0.280 | — | — |
| 0.080 | 0.520 | (TR) | 0.080 | 0.780 | — | — |
| 0.070 | 0.035 | (TR) | 0.050 | 0.150 | — | — |
| — | 0.040 | — | 0.020 | (TR) | — | — |
| — | 0.025 | 0.10 | 0.120 | 0.065 | — | — |
| 0.050 | 0.400 | 0.10 | 0.050 | 0.100 | — | — |
| (TR) | — | 0.14 | 0.050 | 0.050 | — | — |
| — | 0.030 | (TR) | 0.070 | (TR) | — | — |
| 0.020 | 0.045 | 0.01 | 0.040 | — | — | — |
| 0.060 | 0.060 | 0.16 | 0.015 | 0.015 | — | — |
| 0.015 | 0.070 | 0.02 | 0.010 | 0.004 | — | — |
| 0.150 | 0.320 | 0.13 | 0.060 | 0.500 | — | — |
| 0.010 | 0.050 | 0.04 | 0.025 | 0.001 | — | — |
| 0.120 | 0.120 | 0.10 | 0.050 | 0.600 | — | — |
| 0.025 | (TR) | — | 0.012 | (TR) | 0.020 | — |
| 0.034 | 0.018 | — | 0.32 | <0.01 | 0.16 | — |
| 1.9 | 0.11 | — | 0.088 | 0.080 | — | — |
| 0.028 | 0.046 | — | <0.005 | <0.01 | — | — |
| — | 0.072 | — | 0.037 | <0.01 | 5.1 | — |
| — | 0.18 | — | 0.029 | <0.01 | — | — |
| 0.56 | 0.30 | — | 0.051 | <0.01 | — | — |
| 0.38 | 0.012 | — | 0.022 | <0.01 | — | — |
| 0.11 | 0.029 | — | 0.064 | <0.01 | — | — |
| 0.023 | 0.15 | — | 0.022 | <0.01 | 0.14 | — |
| 0.018 | 0.13 | 0.12 | 0.18 | <0.01 | — | — |
| 0.070 | 0.032 | — | 0.0054 | <0.01 | — | — |
| — | 0.23 | 0.18 | 0.03 | 0.04 | — | — |
| — | 0.045 | — | 0.032 | 0.011 | — | — |
| 0.50 | 0.063 | — | 0.057 | <0.01 | — | — |
| — | 0.024 | — | 0.04 | <0.01 | — | — |
| 0.30 | 0.058 | — | 0.023 | <0.01 | — | — |
| 0.18 | 0.036 | — | 0.066 | <0.01 | 0.15 | — |
| 0.020 | 0.067 | — | 0.036 | <0.01 | 0.40 | — |
| — | <0.01 | — | 0.073 | <0.01 | — | — |
| + | 0.16 | (TR) | 0.17 | 0.01 | 0 | 0 |
| ++ | 0.12 | 0 | 0.02 | (TR) | 0 | 0 |
| + | 0.06 | (TR) | 0.19 | 0 | 0 | 0 |
| 0.038 | 0.12 | 0.14 | 0.078 | <0.01 | — | — |
| 0.055 | 0.026 | — | <0.005 | <0.01 | — | — |
| 0.084 | 0.062 | — | 0.011 | <0.01 | — | — |
| — | 0.66 | — | 0.018 | 0.32 | — | — |
| + | <0.01 | -0.007 | <0.01 | (TR) | 0 | 0 |
| (TR) | 0.01 | 0.02 | 0.01 | (TR) | 0 | 0 |
| (TR) | 0.02 | 0.1 | 0.04 | 0.022 | 0 | 0 |
| 0 | 0.09 | 0.04 | 0.16 | 0.057 | 0 | 0 |
| 0 | 0.14 | 0.04 | 0.24 | 0.024 | 0 | 0 |
| + | 0.01 | 0.08 | 0.09 | 0.008 | 0 | 0 |
| <0.1 | <0.1 | <0.3 | <0.1 | 0.038 | 0 | 0 |
| 0.16 | 0.1 | <0.3 | <0.1 | 0 | 0 | 0 |
| 0.02 | 0.18 | 0.037 | 0.760 | 0.066 | <.009 | .00271 |
| 0.30 | 0.23 | .0849 | .0600 | 0.016 | <.01 | .00181 |
| 0.24 | 0.13 | .0732 | .0740 | 0.11 | .011 | .0030 |
| 0.02 | 0.23 | .0600 | 5.5800 | 0.065 | <.03 | .0053 |
| 0.05 | 0.29 | .0523 | .5200 | 0.15 | <.008 | .0050 |
| 0.34 | 0.27 | .1230 | .0220 | 0.016 | <.01 | .00094 |
| 0.08 | 0.31 | .0317 | .0676 | 0.058 | <.01 | .00296 |
| 0.20 | 0.27 | .0592 | .0838 | 0.14 | <.005 | .00298 |
| 0.07 | 0.14 | .0820 | .0323 | 0.22 | <.01 | .00107 |
| 0.21 | 0.23 | .0414 | .0533 | 0.061 | <.003 | .0060 |
| 0.34 | 0.23 | .0495 | .0440 | 0.036 | <.006 | .00135 |
| 0.3 | 0.18 | .0990 | .0535 | 0.12 | <.02 | .00253 |
| 0.05 | 0.31 | .1305 | .0380 | 0.25 | .005 | .00021 |
| 0.20 | 0.04 | .0337 | .0307 | 0.006 | .008 | .00068 |
| 0.06 | 0.43 | .1155 | .0413 | 0.21 | <.008 | .00051 |

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ΠΕΡΙΛΗΨΗ

ΤΑ ΚΡΑΜΑΤΑ ΧΑΛΚΟΥ ΣΤΗ ΜΕΤΑΛΛΟΥΡΓΙΑ ΤΩΝ ΚΥΚΛΑΔΩΝ ΚΑΤΑ ΤΗ ΧΑΛΚΟΚΡΑΤΙΑ

Α. ΚΑΤΣΑ

Ο Αιγαιακός χώρος έχει θεωρηθεί ως ένα από τα σημαντικά κέντρα μεταλλουργικών δραστηριοτήτων σε όλη τη Χαλκοκρατία. Η εκτίμηση αυτή δεν βασίστηκε μόνο στην ποσότητα και στην ποιότητα των μεταλλικών αντικειμένων που βρέθηκαν στην ευρύτερη περιοχή και που αποδεικνύει την κλίμακα της παραγωγής, αλλά και σε εργαστηριακές έρευνες των ίδιων των τεχνέργων οι οποίες βοήθησαν στη διερεύνηση και κατανόηση της τεχνολογίας για την παραγωγή τους. Η μελέτη αυτή βασίστηκε σε δημοσιευμένες χημικές αναλύσεις αρχαίων μεταλλικών ευρημάτων που προέρχονται από τις Κυκλάδες και εκτίθενται σε ελληνικά και ξένα μουσεία, προκειμένου να εξετάσει τη μετάβαση από τη μεταλλουργική τεχνική παραγωγής χαλκού στην τεχνολογία των κραμάτων, η οποία εξαπλώθηκε στην Πρωτοκυκλαδική ΙΙ περίοδο (2800-2300 π.Χ.), ενώ είχε ήδη αρχίσει να εφαρμόζεται στην Πρωτοκυκλαδική Ι.

Στην πρώιμη Χαλκοκρατία χρησιμοποιούνται σχεδόν ταυτόχρονα τα κράματα αρσενικούχου και κασσιτερούχου χαλκού που αντιπροσωπεύουν δύο διαφορετικές

μεταλλουργικές παραδόσεις. Ο αρσενικούχος χαλκός ήταν το πιο διαδεδομένο κράμα στο Αιγαίο αυτήν την εποχή, ενώ δεν άργησε η χρήση του κασσιτερούχου χαλκού. Η προσθήκη ενός άλλου μετάλλου, αρσενικού ή κασσίτερου στο χαλκό όχι μόνο αυξάνει τη σκληρότητα του παραγόμενου τεχνέργου αλλά κατεβάζει το σημείο τήξεως διευκολύνοντας τη χύτευση.

Τα δύο κράματα του χαλκού, όπως και ο καθαρός χαλκός, χρησιμοποιήθηκαν για την κατασκευή ίδιων αντικειμένων, και δεν προκύπτει από την έρευνα κάποια ιδιαίτερη χρήση ενός συγκεκριμένου κράματος ή καθαρού χαλκού για ιδιαίτερους τύπους εργαλείων ή όπλων. Τα αρσενικούχα χαλκά συνέχισαν να χρησιμοποιούνται στους περισσότερους κυκλαδικούς οικισμούς της εποχής της Χαλκοκρατίας για αρκετό διάστημα αφότου είχαν αναγνωρισθεί τα πλεονεκτήματα των κασσιτερούχων κραμάτων, γεγονός που οφείλεται μάλλον στο ότι τα μεταλλεύματα του κασσίτερου σπανίζουν στην περιοχή σε αντίθεση με τα αρσενικούχα μεταλλεύματα του χαλκού που απαντώνται στις Κυκλάδες και στην Κρήτη.

Όσον αφορά στην παραγωγή των κραμάτων του χαλκού, δεν μπορεί κανείς να είναι σίγουρος αν οφείλεται σε επιλογή των μεταλλοτεχνιτών ή σε τυχαίο αποτέλεσμα που προήλθε από τη σύνθεση των μεταλλευμάτων. Ωστόσο, από τη μέχρι σήμερα έρευνα, φαίνεται πιθανόν ότι τα αρσενικούχα κράματα του χαλκού που χρησιμοποιήθηκαν στην κατασκευή των περισσότερων μεταλλικών αντικειμένων στις Κυκλάδες, την εποχή της Χαλκοκρατίας, ήταν αρχικά τυχαίο προϊόν εκκαμίνευσης και όταν έγιναν γνωστές οι ιδιότητές τους, αναζητήθηκαν τα μεταλλεύματα που θα έδιναν το ζητούμενο κράμα. Η μέθοδος παραγωγής των κραμάτων αυτών εξαρτιόταν από τα ορυκτά και μεταλλεύματα που υπήρχαν στο υπέδαφος της κάθε περιοχής.