Μουσείο Μπενάκη

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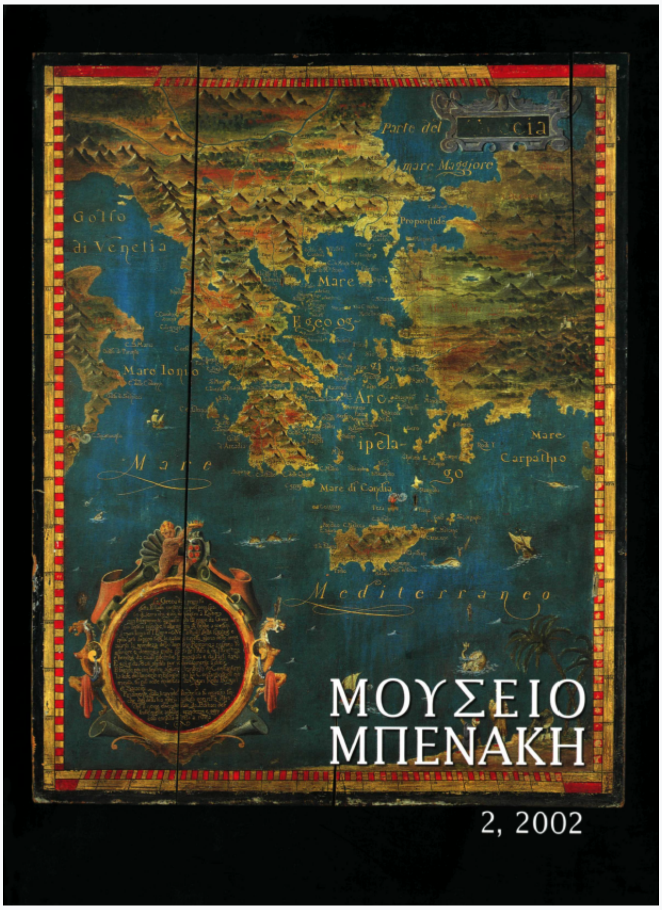

Μελέτη της τεχνικής και της σύστασης του υστερορωμαϊκού κάδου με σκηνή κυνηγιού

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Technical and chemical examination of the brass bucket with a hunting scene

THE METAL *SITULA* in the Benaki Museum (inv. no. 32553) (henceforth called "Benaki") was examined in order to correlate its techniques, composition, and findspots with the group of buckets mentioned in the article by Mundell Mango et al.[1] (henceforth "the Group").

Fig. 1 shows Benaki's present appearance, after partial restoration by gap-filling to strengthen the main body. For the same reason, a backing film can be found on the interior surface at the point where the base and vertical walls meet (fig. 2). Both these processes were carried out during earlier conservation treatments. Cracks or complete breakage near or around the base commonly occur in these objects and probably result from the technique used to produce this particular shape. For this reason, as Mundell-Mango et al.[2] point out, some of the vessels in the Group had to be repaired, as was also the case with Benaki.

Benaki was examined using several analytical techniques such as X-Ray fluorescence spectroscopy (XRF), scanning electron microscopy (SEM), X-ray radiography and metallography. Unfortunately not all these techniques were employed for the Group, where only the composition of the alloy was established.[3] Since the examination of the latter was carried out on a more empirical and archaeological basis, precise correlation with Benaki has had to be limited to the elemental composition.

Technical examination

1. X-ray Radiography.[4] X-ray radiographs of Benaki were made at the X-ray Diagnostic Center in Athens.[5] Fig. 3 is an example of a print from a X-ray negative. The X-rays revealed some hairline cracks in the body of the object and also some areas which were incomplete. The crack patterns in the wall are characteristic of a macroscopically brittle fracture. Cracks often occur since the cold metal, which is at first malleable and not yet annealed, hardens under the action of crushing forces during its shaping.[6] In Benaki, serious crack patterns exist only near the base, which may well indicate that the annealing process was generally satisfactory, with the few cracks in the body perhaps resulting from the use of an inappropriate annealing temperature.

Fig. 3 also shows the external decorative grooves visible in fig. 1. This decoration was effected by chasing. The special tools used have displaced the metal to produce a flat mat bottom and an annular dot as well as a straight groove. The X-ray negative shown in fig. 4 revealed shaded areas, which are a characteristic result of hammering.

2. Metallography.[7] Two samples less than 1mm. in size were removed from the object for sectioning. One was extracted from a position near a previous gap-filling area on the wall of the main body and the other from one of the two edges of the handle (fig. 1).

The samples aimed at being as representative as possible of the object as a whole, while at the same time conforming to the basic requirements for analysis and study, the general principles of sample preparation and the Museum's own standards,[8] although the problems of making comparisons using a limited number of small samples as representative of the overall structure of the object are well known.[9]

Fig. 1. The external appearance of the *situla*, which has been partially restored (gap filled areas) to support the whole shape of the object: a. sample selected from the body, b. sample selected from the handle.

Fig. 2. The interior surface of the *situla*. A backing film is used at the area where base and vertical walls meet to support the base.

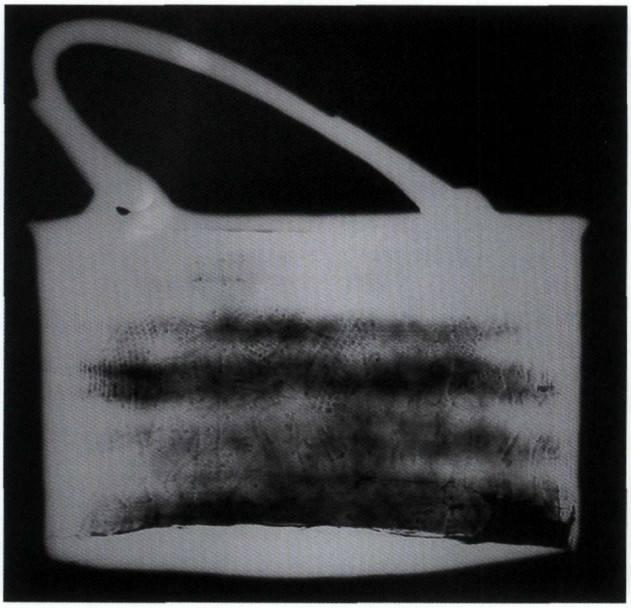
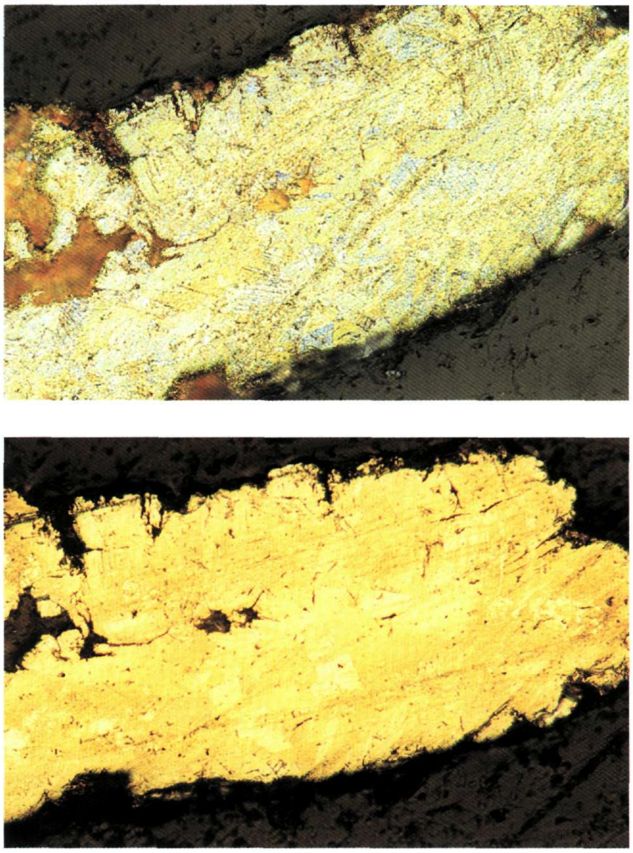
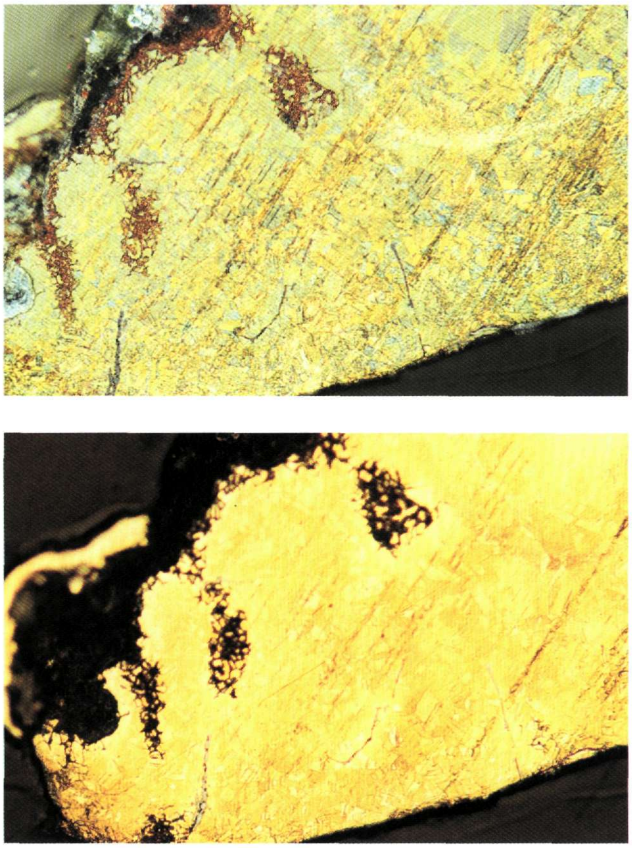


Fig. 3. X-ray image of the external appearance of the *situla*. Note the few hairline cracks, decoration tool marks and gap filled area on the right of the image.

Fig. 4. X-ray image of the interior, showing tool marks produced by hammering.



Figs 5-6. Cross section details of the body sample under bright field unpolarized illumination and polarized illumination. Etch: $FeCl_3$ x 200: a. Homogenous stucture, b. Slip lines, grain deformation, annealing twins emerging on grain boundary facets, c. Hair line cracks especially around the surface of the samples, d. Intergranular corrosion (few areas), e. No inclusions.



Figs 7-8. Cross-section details of the body sample under bright field unpolarized illumination and polarized illumination. Etch: $FeCl_3$ x 500: a. Homogenous structure, b. Equaxed grains, some annealing twins emerging on grain boundaries facets, c. Intergranular corrosion, preferentially near the upper surface of the sample, d. One internal crack, possibly due to corrosion, e. Some light gray-blue elongated inclusions.

The samples were mounted in a polyester resin block[10] and polished for subsequent examination under the optical microscope. The samples were examined under an unpolarized and polarized light with magnification ranging from x 200 to x 500 (figs 5-8).

3. SEM examination.[11] The specimens were re-polished and covered with carbon for examination under the scanning electron microscope. Both samples displayed features similar to those observed under the optical microscope, but no elongated inclusions were visible.

Technical results

1. Fabrication. All the methods mentioned above[12] confirmed the method of fabrication. The *situla* was made by hammering the metal into shape, and was raised from a single cast disc (ingot) of metal, the size of which was calculated by adding together the average diameter of the base and the height. It was then shaped by the techniques of sinking[13] and planishing.[14] The disc was first sunk in a block as far as possible, but, as Sherlock states,[15] it is planishing which can give depth to an object, and this must have been the main procedure followed here. The latter is unquestionably the more difficult technique

but according to Hodges[16] it allows a greater variety and complexity of form by varying the sizes and shapes of the stakes involved in the process. Indeed the shape of Benaki is unusual since the base is flat and the walls vertical; an expert craftsman would have been needed for this work, since the meeting-points of base and walls were apparently difficult to produce. The base seems often to have become broken or detached during hammering, and for this reason craftsmen of the period produced the base separately from the rest of the object.[17] Even where this was not done, these meeting points seem to have been so sensitive that in most buckets the bases are either broken or missing.[18]

Another possible method of shaping Benaki is spinning,[19] a technique which involves the use of the lathe. This mechanical process is consistent with the date of Benaki's manufacture,[20] and would be well suited to the production of such a deep vessel.[21] A great advantage of spinning was that it could assist in strengthening the rim or creating a more elaborate shape, both of which were sometimes difficult to achieve merely by hammering.[22] But according to Hodges,[23] only simple open shapes or closed forms could be produced by this method. He also states that while the metal is being compressed on to the form, there is a great tendency for the object to pleat, and to mitigate this problem a second tool, the backstick, was normally used to support the metal behind the burnisher.

No pleating is observable in Benaki, but a centre-mark was detected on the exterior surface, the standard indication of spinning (fig. 9). This mark can also be a sign of turning,[24] a process difficult to distinguish from spinning, and which usually leaves a second centre-mark in the interior of the object,[25] though this was not found here. If the second mark ever existed, it could have been removed by polishing the inner surface of the base. Another indication of the use of a lathe arises from the fact that both Benaki and the Group[26] have borders (fig. 10) made with an annular punch, containing inscriptions, scrolls and other motifs. These borders could only have been made with the assistance of a rotating wheel.

The fabrication of both Benaki and the Group, all of which have this particular shape, could not have been satisfactorily completed and could also give rise to cracks, unless the metal was annealed.[27] Indeed the cross-section examination of the Benaki body sample under the optical microscope proves this to be such a case. Figs 5 and 6 show evidence of heavily worked grain structure. The grains present strain lines and are deformed, probably by additional hammering at the end after the working and annealing cycles (annealing twins) in order to shape the *situla*. The structure appears fatigué and also displays slight mid-section cracking. According to Lanord[28] this is also associated with over-working during some stages of

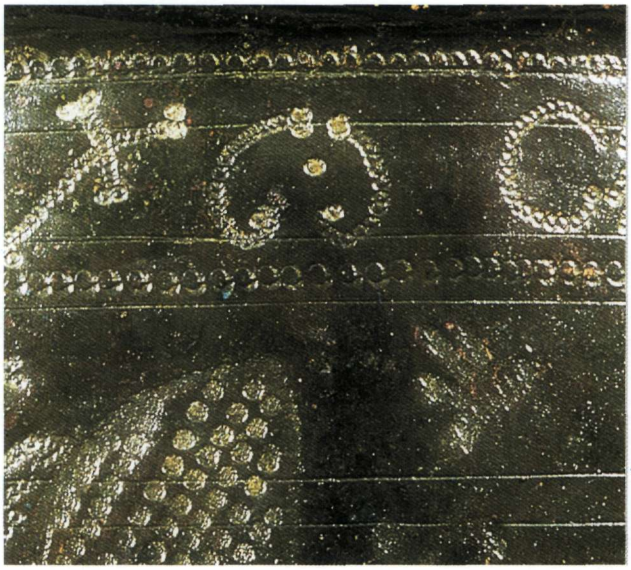


Fig. 9. Detail photo of the base (outer surface), showing the centering mark left from the use of the lathe x 25.

Fig. 10. Detail image of the body, showing the borders made with an annular punch on the lathe.

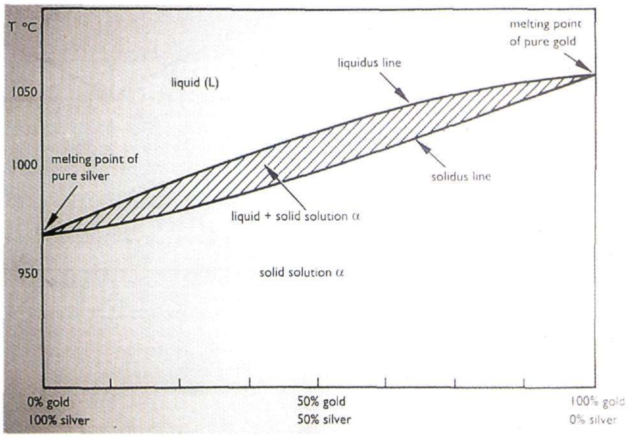


Fig. 11. Copper-zinc phase diagram by Scott (1991).

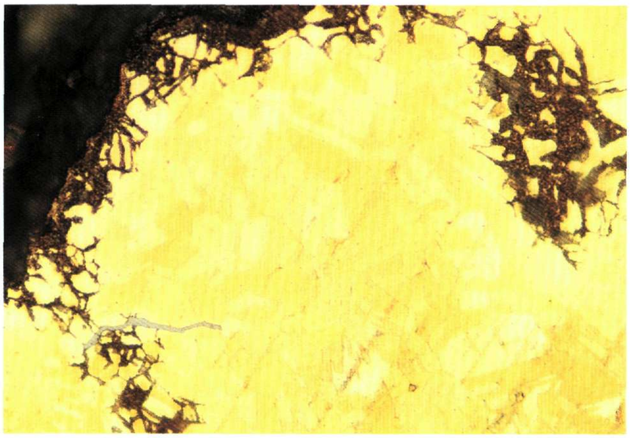


Fig. 12. The light blue elongated inclusions in cross section. Etch: $FeCl_3$ x 1000.

manufacture. Although the grains are recrystallized upon annealing, these cracks cannot be removed by subsequent working and annealing. This accords with the findings of the examination by X-ray radiography and SEM.

The handle of the *situla* was produced separately from the body, as was normally the case with buckets 'carrying' a handle. It was formed from a thick cast metal rod, hammered to shape, and is rectangular in section. According to the metallographic examination (figs 7, 8), the structure shows a well-formed re-crystallized grain matrix with annealing twins. The grains are finer but not flattened, which means that the handle was not left in a worked condition. The structure is not fatigué, as was the case with the body sample (no strain lines). This suggests that the handle of the *situla* was not heavily worked; on the contrary it displays more intergranular corrosion patterns, especially near the upper surface of the sample, which probably indicates the use of a more impure alloy.

The metallographic figures from both the handle and the body display no evidence of a second phase. No ternary mixtures occur. This conforms with the composition analysis of the metal of Benaki (see below), and thus only the study of the copper-zinc phase diagram is required. From fig. 11, we may assume that the concentration of zinc in the copper-zinc alloy must have been less than 40% since an alloy with a higher concentration, having passed below the liquidus line, will begin to precipitate out alpha grains, which are then partially attacked and converted to beta during solidification,[29] so that the resulting structure consists of alpha + beta grains.

The few, very small elongated inclusions present in the cross-section of the handle sample (fig. 12) must be impurities of the metal, which tend to segregate at the grain boundaries if the alloy is hot-worked and not cold-worked and annealed.[30] Their elongated shape probably results from the final annealing.[31] Although annealing was used, and served to remove the strain lines from the grains and to deform the grains, these inclusions do not seem to have been re-crystallized.[32] Since they were not dissolved by ferric chloride solution, they are probably, according to Scott,[33] sulfide rather than cuprite inclusions. Their composition will be discussed later.

2. Decoration. The appeal of metalwork of the culture and the chronological period of Benaki lies in its surface decoration. The various methods previously mentioned provided an opportunity to examine the marks left by the tools used to decorate it.

The surface of the object appears chased, without the removal of any metal through engraving. According to Ogden[34] and Hodges,[35] the cross-section of impressions produced by engraving is very different (fig. 13). This was observed in Benaki when examining the body sample under the optical microscope and SEM. The body sample in profile (fig. 14) shows a curve near its external surface, which is proof of the subsidence of the metal

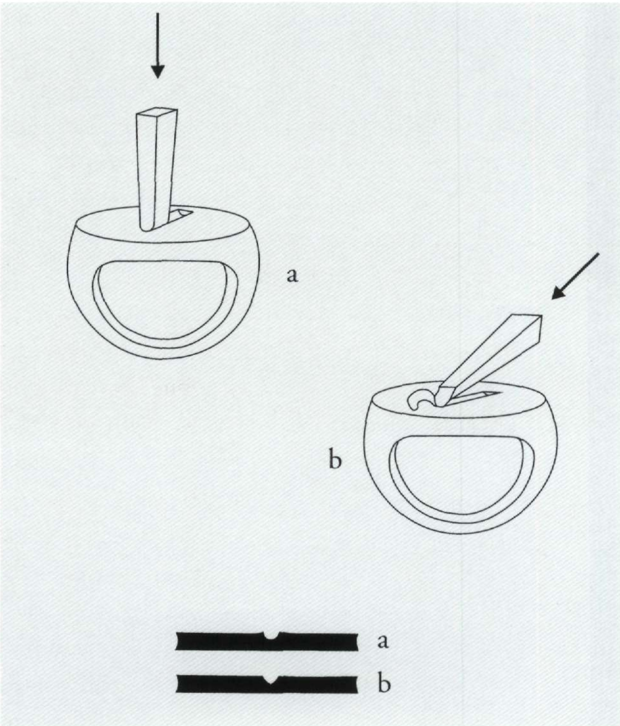


Fig. 13. The different cross-section of the impressions produced by chasing and engraving by Ogden (1982) and Hodges (1976).

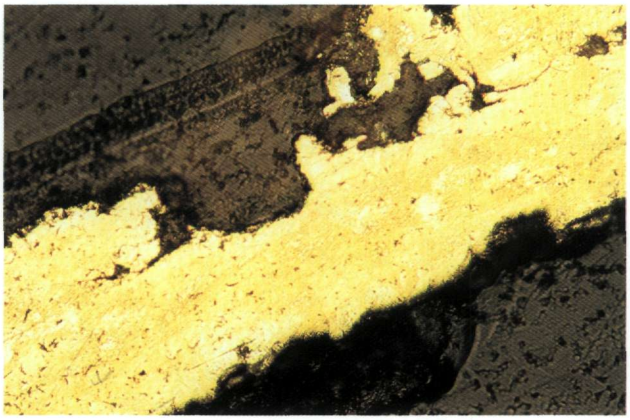


Fig. 14. The subsidence of the metal under the force of a chasing tool. The hairline cracks around it arise from heavy working of this area.

under the pressure of a chasing tool. Hairline cracks around it also indicate a heavily worked area.

Figs 15-18 illustrate the various types of marks left by the chasing tools, and suggest that four different tools were used, each of which produced a series of repeated impressions on the metal surface. However it is also possible that a single tool could have produced this variety of textures if applied in differing ways. For example, the similar circular marks on Sassanian silver vessels (AD 226-651), described by Harper and Meyers,[36] could have arisen as a result of the circular tool being held at an angle to the surface and not perpendicularly to it.

Chemical analysis

1. XRF analysis.[37] One very small area from the lower part of the Benaki body was well polished (to remove corrosion products) for analysis by XRF at the Democritos Laboratory of Archaeometry, N.C.S.R. in Athens.[38] The purpose of using this technique was to make a preliminary estimate of the composition of Benaki and to correlate the analysis results with those from the five other objects of possibly the same origin which were also analysed by XRF by Oddy and Craddock.[39] The results are given in Table 1 (fig. 19) with the analysis results taken from the body, handle and / or base of the buckets in the group.

The metal composition of Benaki is 82% copper, 17% zinc and very small amounts of other elements. If we consider the qualitative results from the body composition, it can be seen that Benaki and the group of five buckets are extreme examples of this variety of composition in which the tin and lead[40] contents are so negligible that the alloy must be considered to be brass.[41] Trace elements such as chromium, calcium, sulphur and arsenic identified in Benaki have not been detected in the other buckets. Conversely, trace elements such as antimony and silver, identified in the group, were not found in the body composition of Benaki. Despite the above, if we correlate the quantitative analysis results of Benaki with those from the group, it can be seen that their percentage cluster is minimal.

2. SEM analysis. The small polished specimens extracted from the body and the handle for technical examination were also chemically studied by scanning electron microscope at the scientific research laboratories

Figs 15-18. The characteristic marks left by the chasing tools.

of the Institute of Archaeology, University College, London.[42] The purpose of this examination was to correlate the chemical analysis results by SEM with those given by XRF. In addition, SEM investigations were carried out to identify possible compositional differences among areas that could not be approached by XRF (bulk) and to correlate these results to make them more representative. Sometimes corrosion products which have passed through the metal surface, or been subjected to several technical processes, cannot give representative data when a chemical analysis method is only applied on the surface.[43] The results are presented in Table 2 for both the body and the handle samples. According to Table 2, the measurements provide similar analytical results to those taken by XRF spectrometry. In addition, by comparing the overall measurements of the two samples, the SEM analysis results for the handle sample show two additional elements, iron and nickel.

As far as the inclusions are concerned (see above, Technical Examination), they were not detected in the handle sample by SEM as they were under the optical microscope, and it was difficult to analyse them without knowing their specific position. Nevertheless, after the figures from the metallographic examination were printed, a chemical analysis of the limited area, which included one inclusion, was attempted. The compositional results given for this area seem to confirm our first estimation that these might be sulfide inclusions. Table 2 also gives the chemical analysis results. As can be seen, sulphur appears as one of the main elements. The presence of sulphur explains the appearance of the light blue inclusions in the cross section (fig. 12). Although the sulphur content is small, this amount appears to segregate in copper since its solubility in copper is almost nil.[44]

Chemical analysis results

In general, the chemical analysis of Benaki conforms with the composition results for the Group, as regards both the body and the handle. The evidence of both XRF and SEM accords with the metallographic evidence that in both samples the alloy is single-phased. It also fits the copper-zinc phase diagram mentioned previously. The brass of Benaki accordingly belongs to the category of alpha brasses, which were in use particularly in earlier times.[45]

From the 1st century BC onwards brass made an increasing impact on the world of the coppersmith,[46] so that by the 7th century AD it was probably the most important alloy. As mentioned by Oddy and Craddock,[47] brass was of great significance in the metalwork of Byzantine Egypt, where hammered objects such as buckets are usually made of unadulterated brass. The ancient Greek word for brass, mentioned by Aristotle, was *oreichalkos* ('golden' or more likely 'mountain copper'),[48] and according to Plato, *oreichalkos* ranked second only to gold as a precious metal among the inhabitants of Atlantis.[49] These references show that brass was used in pre-Roman times,[50] and also that brass was valued more highly than bronze, as is also apparent from brass and bronze coinage[51] before the time of Diocletian (AD 286-305).

The preference for brass over bronze was also based on its properties. Copper base alloys in earlier, and especially Roman, times contain both zinc and tin.[52] But according to Utchract[53] and Tylecote,[54] there was a tendency for wrought copper alloys to contain more zinc than tin, while the opposite is the case in cast alloys. Brass was therefore used not only for coinage but also for personal ornaments[55] and decorative metal work.[56] The metal used for such work needed to be highly ductile and of good colour, and chemical analysis of the alloys used for working has accordingly shown a 80% level of copper and an 18% level of zinc.[57]

The alloy used for wrought brass usually contained about 11 to 28% zinc. The zinc content of Benaki and the Group correspond to this significant cluster, which could be achieved by using the cementation[58] process to make the alloy.[59]

Many of the textual references indicate that the process originated in Asia Minor, in the region of Phrygia, near zinc deposits which are known to have been worked in antiquity.[60] The maximum zinc content that could be obtained by this process was 28%.[61] This amount conforms with the alloying of copper with zinc oxide (calamine), and not with metallic zinc where the final product (brass) would contain a higher percentage, comparable to modern brass or commercial high zinc brass.[62]

Although the cementation process was a much more efficient method than the use of metallic zinc, it presented some disadvantages. A small amount of the zinc vapour, which copper retains by absorption during the process, could eventually be lost. According to Tylecote[63] it would not be as easy to obtain such an accurate control over composition as when zinc was added in metal-

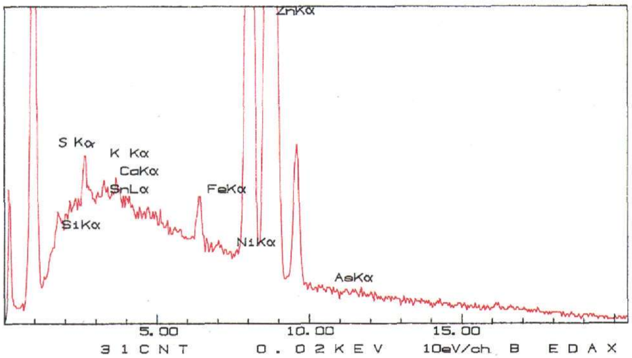


Fig. 19. The corresponding X-ray Fluorescence spectrum of the Benaki bucket.

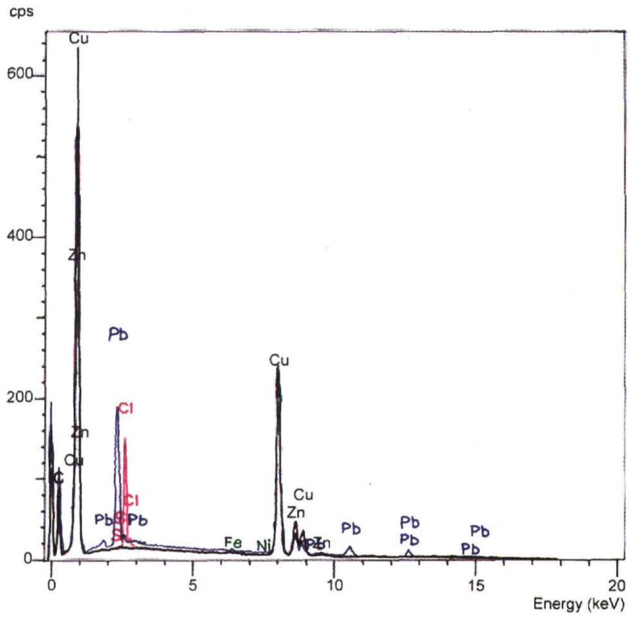


Fig. 20. The corresponding Scanning Electron Microscopy spectrums of the Benaki bucket
→ Analysis of the body (overall area)
→ Analysis of the handle (overall area)
→ Analysis of the elongated inclusion (detection of sulphur)
→ Analysis of the handle (limited area-detection of lead).

BUCKETS	ELEMENTS %											
	copper	lead	tin	zinc	silver	nichel	iron	antimony	chromium	arsenic	sulphur	calcium
BROMESWELL BUCKET												
body	79.4	0.14	0.03	20.0	0.02	0.22	0.12	0.02	-	-	-	-
handle	78.5	0.88	0.17	19.7	0.01	0.40	0.34	0.01	-	-	-	-
ANIMAL FRIEZE BUCKET (no. 7) 1988, 10-1,1												
body	79.4	0.28	0.51	19.3	0.03	0.26	0.11	0.02	-	-	-	-
base	78.8	0.23	0.46	20.0	0.01	0.30	0.10	0.05	-	-	-	-
handle	68.7	1.50	0.28	28.4	0.01	0.57	0.49	0.01	-	-	-	-
CHESSELL DOWN BUCKET, grave 45 (no. 6) 1867, 7-29, 136.												
lug	76.0	0.03	0.2	22.8	0.02	0.15	0.15	-	-	-	-	-
handle	82.0	0.35	0.1	17.0	0.01	0.4	0.21	-	-	-	-	-
CHESSELL DOWN BUCKET, grave 26 1869,10-11,10												
handle	82.0	0.08	0.45	16.8	0.12	0.15	0.32	0.09	-	-	-	-
ASHMOLEAN BUCKET (NO. 4) 1975.308												
body	79.5	-	-	18.0	0.01	0.14	1.45	0.02	-	-	-	-
handle	68.0	5.1	-	26.9	0.07	0.13	0.09	trace	-	-	-	-
BENAKI MUSEUM BUCKET												
body	82.1	-	0.5	17.5	-	0.2	0.2	-	<0.4	0.05	0.2	100 500 ppm

Table 1. X-ray fluorescence analysis of the Benaki bucket, together with earlier analysis of five comparative buckets by Oddy and Craddock (1983).

AREA ANALYZED	ELEMENTS%						
	Copper	Zinc	Iron	Nickel	Sulphur	Lead	Chloride
BODY SAMPLE							
Overall area	81.77	18.23	-	-	-	-	-
Limited area	84.82	15.18	-	-	-	-	-
HANDLE SAMPLE							
Overall area	81.99	17.01	0.48	0.49	-	-	-
Limited area	81.53	18.47	-	-			
Elongated inclusion	81.92	1.16	-	-	0.41	-	16.19
Limited area	70.31	15.00	-	-	-	14.66	-

Table 2. Scanning Electron Microscopy analysis of the Benaki bucket: a. Two indicative analysis results of one overall and one limited one of the body sample, b. Four analysis measurements of the handle sample. Each area analyzed also presents trace elements which indicate the use of a more impure metal for the handle manufacture.

lic form. A variety of zinc content in copper alloys for the manufacture of similar objects could therefore be detected.

In addition the cementation process allows impurities from the zinc ore to become incorporated into the alloy.[64] This problem is a possible explanation of the presence of so many elements in the composition of the buckets, though it may also be connected with the other major constituent used (copper), where many impurities could have been incorporated from the copper ore. It could also result from the use of scrap metal derived from many sources.

In addition to the study of the alloying metals, the smaller quantities of metal can sometimes be useful in pointing to an individual source of supply.[65] Indeed trace elements have recently been used satisfactorily to provenance studies of metals,[66] associating a metal artifact with a metal ore or recycling process, even though some scientists disagree with their value.[67] However in Benaki as in many other cases, the situation is far more complicated as we are dealing with an alloyed metal whose lesser components could derive from many sources.

Sulphur

Sulphur was detected both by XRF and by SEM. This seems to confirm our first estimation that the elongated inclusions revealed under the optical microscope are sulfide inclusions.[68] Sulphur as a component has connections with copper, specifically with the copper ore chalcopyrite CuFeS which changes to sulfide, sulfate, carbonate, hydroxide and oxide ores.[69] According to Hauptmann et al.,[70] sulfide inclusions can be found in slags from the smelting of copper ores. Muhly et al.[71] also refer to the finding of inclusions in oxhide ingots, such as those from Gelidonya.

The amount of sulphur detected in Benaki was small. Muhly et al.[72] suggest that if the sulphur content is small, the ore used for the production of copper was probably a fairly well weathered ore (azurite or malachite). Conversely Hauptmann et al.[73] suggest that a low sulphur content and other trace elements, together with the existence of cuprite (Cu_2O) identified in raw and copper ingots, such as those from Maysar, indicate the refining of the raw copper from sulfide ores produced before the casting of these ingots. Such a combination was detected in

Benaki's alloy, although cuprite was empirically detected (polarized light). Sulfide ores were mainly found in Cyprus and Sardinia.[74] Hauptmann et al.[75] believe that the copper deposits from Oman are similar in origin and comparable in form and type with the famous copper deposits in Cyprus.

Iron

According to Tylecote[76] the iron content of a copper zinc alloy is related to the copper used. He also believes that the iron and zinc content was related and that iron was a product of infiltration, having been precipitated by zinc from percolating water in a form suitable for its preservation.

Cowell and La Niece[77] claim that iron could be incorporated into the alloy from impurities from the zinc ore and this would adversely affect its mechanical and corrosion-resistant properties. Conversely Michel and Asaro[78] suggest that its presence is more connected with the use of old scrap metal.

However the former theory enables us to recognise brass made by the cementation process in the Benaki *situla*. In addition the low zinc content (<28%) combined with an high iron content leads to the same conclusion.[79]

Indeed the iron content given for the composition of the Benaki *situla* and the other buckets is high and corresponds to the percentage detected in some Sardinian oxhide ingots[80] (the Uluburum or the Encomi ingots).[81] This amount ranges from 0.1% to 4.6%, which also indicates that the copper was probably not refined or multiple recycled.[82]

Tin

The small amount of tin indicates that the metal used for alloying was zinc.[83] This increasing use of zinc probably reflects the scarcity of tin in the eastern Mediterranean following the break-up of the Roman empire and the loss of the tin mines in both Spain and Cornwall.[84] Oddy and Craddock[85] refer to the wide distribution of sources of zinc in Asia Minor, which were probably first exploited in Roman times and were certainly extensively used in the Islamic period. They believe that the small amount of tin in these buckets may reflect the introduction of some Roman scrap metal into the crucibles. Muhly[86] agrees, claiming that a product with 1-2% tin content indicates the re-melting of scrap metal.

Conversely tin could have been an accidental product. It may be connected with the copper used in the production of the brass, and in particular with the copper ores, even though they very rarely contain a significant amount of tin.[87] But according to Gale et al.,[88] where this does occur, a tin content of up to 3% can be detected in the copper smelted from them. Tin may also be introduced into the alloy due to gossans (which may also contain tin) being used as a flux during the copper smelting.[89]

This distinction confirms the difficulties faced when discussing the re-melting cycles of copper according to the amount of tin present in the copper alloy.[90]

Nickel

The nickel content often depends on the copper which has been used in the alloy.[91] According to Hauptmann et al.,[92] nickel is also associated with the Cu-Fe sulfide ores. The nickel is always concentrated in the iron sulfide phases in the matte, which of course are slagged. In this case, the nickel content of the metal is much lower than in the ore and the nickel content of the slag is higher. Nickel is divided equally between the slag and smelted copper.[93]

In the composition of both Benaki and the Group, the nickel content clusters between 0.1% and 5.7%. A similar concentration of nickel was detected in copper ingots from a Maysar hoard as well as some of the artifacts from Ras al-Hamza, which seemed to correspond with the trace element pattern of many copper ores from Oman.[94]

Hall[95] claims that a high concentration of nickel can indicate the use of scrap metal. Conversely, it has been suggested that this high nickel content arises from its enrichment during smelting,[96] as is the case today with arsenic during the smelting of ores found at Timna.[97]

In Benaki the arsenic content is very small, and this could indicate that refining was carried out in a crucible.

Lead

Lead was detected in the composition of the Benaki handle sample only (Table 2), as was also the case with the Ashmolean bucket. This confirms once again the difficulty noted by Oddy and Craddock[98] in studying the variations in the lead content. In general the quantity of lead in the buckets is small, and this may indicate that it was not an addition to improve the fluidity of the alloy in the moulds.[99] According to Oddy et al.[100] the existence of a small amount of lead must have been the result of its introduction into the copper alloy as an impurity in both the copper and the zinc from the parent ores. Conversely it has been suggested that a larger proportion could also pass into the copper metal produced in this way.[101] These conflicting theories make the position somewhat confused.

Conclusion

The application of all the techniques described above has enabled us to make a technical and compositional examination of Benaki and to confirm the hypothesis that it belongs to the group of buckets studied by Mundell-Mango et al.[102] and Oddy and Craddock.[103]

The *situla* was fabricated by sinking and, more especially, by raising either manually (planishing) or mechanically (spinning). Cold-working and annealing was used for a more satisfactory result. The final working to make the body of the vessel, including the external decoration, resulted in substantial work-hardening residual deformation in its microstructure and some internal residual stresses. This phenomenon was not noticed in the handle. The final polishing and the double borders containing inscriptions were completed on a lathe. Decoration was made with chasing tools.

The composition analysis indicates a metal made of copper and zinc with several trace elements. The composition of the alloy, together with the concentration of the zinc element, demonstrates that the alloy was produced by the cementation process. The study of the main alloying elements and trace elements could not provide a definite answer to the provenance of the material. As with other cases, it is not clear whether the incorporation of the trace elements was accidental or intentional. Was the material re-cycled, imported, or produced from parent ores near the workshops? And what about the two main alloying metals, copper and zinc? It was not possible to find an answer which would confirm the existence of a central point for the production and distribution of the buckets.

However the iconography and historical sources suggest that the eastern Mediterranean played a central role in the distribution of the buckets. Compositional studies may also confirm the use of the important sources of ores from that area. Oman, Asia Minor, Cyprus may well have provided the bulk of the material used in their fabrication, in the form either of the primary product (ores) or the secondary product (scrap, traded material). There has been a recent resurgence of interest in the development of ancient metallurgy in the Eastern Mediterranean, particularly Anatolia,[104] and further studies will be of great assistance in identifying metal sources of more recent periods.

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NOTES

1. As mentioned, the techniques, composition, iconography and findspots of all the buckets appear similar and give clues to the date, origin and use of this copper-alloy group: M. Mundell-Mango, C. Mango, A. Care Evans, M. Hughes, A 6th century Mediterranean bucket from Bromeswell Parish, Suffolk, *Antiquity* 63 (1989) 295-311.

2. *Ibid.*

3. Oddy and Craddock have used X-ray fluorescence for a similar purpose, as part of an on-going study of the composition of East Mediterranean copper alloys, W. A. Oddy, P. T. Craddock, Scientific examination of the Coptic bowl and related Coptic metalwork found in Anglo-Saxon contexts, in: B. Mitford (ed.), *The Sutton Hoo ship-burial* (London 1983) 753-57.

4. X-ray radiography is familiar from its medical use, but, on the basis of the different densities of materials, it offers the possibility of obtaining an insight into the internal structure not only of the human body but also of antiquities and paintings. An X-ray sensitive film (or more than one in the case of three-dimensional objects) is thus impregnated with the relative intensities of the rays that emerge from the several materials.

5. Diagnostic Center, 99 Sokratous and Davaki Streets, Kallithea, Athens.

6. D. A. Scott, *Metallography and Microstructure of Ancient and Historic Metals* (Getty Museum 1991).

7. A method of examination of polished sections of metallic materials using a microscope that reflects light passing through the objective lens onto the specimen surface. The structure of the section can thus be studied as the reflected light passes back through the objective lens to the eyepiece.

8. The conservators of the metals laboratory at the Benaki Museum insist on the extraction of samples small in number and size.

9. Scott (n. 6) 57-58.

10. Neotex, 42-45 Victoros Ougo Street, Metaxourgio, Athens.

11. A method based on a beam which interacts with the metal sample and creates various signals (secondary electrons, internal currents etc.) all of which can be appropriately detected. These signals, in synchronism with an electron beam, can form an image highly magnified and with a great depth of field. With ancillary detectors, the instrument is capable of elemental analysis.

12. The use of the binocular microscope (an initial approach), X-ray radiography, optical microscope and SEM, assisted our study by elucidating the technological data concerning the Benaki *situla.*

13. Sheet metal hammered either on the flat surface of an anvil or into a shallow concave depression cut into the surface of the anvil.

14. Repeated hammering on the outer surface, the work being done over a small dome-headed stake or anvil.

15. D. Sherlock, Silver and silversmithing, in: D. Strong, D. Brown (eds), *Roman Crafts* (London 1976) 11-23.

16. H. Hodges, *Artifacts: An introduction to early materials and technology* (London 1976).

17. C. E. Snow, T. D. Weisser, A technical study of the Hama Treasure at the Walters Art Gallery, in: *Greek, Roman Metalware* (Baltimore 1997).

18. Mundell-Mango et al. (n. 1).

19. Mechanical form of raising which requires the use of the lathe, Sherlock (n. 15) 15-16.

20. Sherlock (n. 15).

21. Hodges (n. 16) 74.

22. R. Ward, *Islamic metalwork* (London 1983).

23. Hodges (n. 16) 74.

24. The object is set up on the lathe and a sharp tool is held against the metal to remove any irregularities on the surface.

25. Hodges (n. 16) 75.

26. Mundell-Mango et al. (n. 1).

27. This happens because the metal, which at first was malleable when cold worked, subsequently hardens, thus leading to distortion of the crystal structure: Sherlock (n. 15) 13. The annealing process thus becomes necessary to allow the metal to reshape itself and to restore its softness and malleability.

28. A. F. Lanord, *Ancient metals structure and characteristics* (Rome 1980).

29. Scott (n. 6) 20.

30. *Ibid.*

31. D. Dungworth, *Report on the chemical analysis and metallographic examination of copper alloy samples from Tell Selekkahire, Syria* (Sheffield 1999).

32. Scott (n. 6) 101.

33. *Ibid.*

34. S. Ogden, *Jewellery of the ancient world* (New York 1982).

35. Hodges (n. 16) 79.

36. P. O. Harper, P. Meyers, *Silver vessels of the Sassanian Period* (New York 1981).

37. A non-destructive method of analysis since it does not require sampling. An X-ray beam is aimed at a small area around 2mm. in diameter on the artifact's surface. The interaction of the X-rays with metal causes other (fluorescence) X-rays to be generated, which are detected as a spectrum. The energies of these fluorescence X-rays are specific to the elemental composition of the object.

38. Laboratory of Material Analysis, Institute of Nuclear Physics N.C.S.R. "Demokritos".

39. Oddy, Craddock (n. 3) 753-56.

40. Lead was only discovered in the composition of the handle of the Benaki bucket.

41. P. T. Craddock, The composition of the copper alloys used by the Greek, Etruscan and Roman civilizations. The origins and early use of brass, *Journal of Archaeological Science* 5 (1978) 1-16.

42. University College, 31/34 Gordon Square, London WC1.

43. S. Bowman, *Science and the Past* (London 1991) 187.

44. J. D. Muhly, T. S. Wheeler, R. Maddin, The Cape Celidonya shipwreck and the Bronze Age metals trade in the Eastern Mediterranean, *Journal of Field Archaeology* 4 (1977) 353-62.

45. Scott (n. 6) 19-20.

46. P. T. Craddock, Zinc in Classical Antiquity, in: P. T. Craddock (ed.), *2000 years of Zinc and Brass* (London 1990) 1-6.

47. Oddy, Craddock (n. 3).

48. It was a "brilliant and white copper made by mixing

zinc and copper with a peculiar earth origin as calmia from the store of Euxine": Copper Development Association, *Copper through the ages* (London 1962).

49. Craddock (n. 41).

50. Indeed the chemical analysis of three brasses which date to the 3rd century BC (11.8% of zinc and only 0.7% of tin) suggest that zinc has totally replaced tin as the alloying metal with copper: P. T. Craddock, The first brass: some early claims reconsidered, *MASCA Journal* 1,1 (1978) 4-5.

51. Oddy, Craddock (n. 3).

52. Craddock (n. 41).

53. O. Untracht, *Metal techniques for Craftsmen* (New York 1975) 18.

54. R. F. Tylecote, *Metallurgy in Archaeology* (London 1962).

55. J. Bayley, Brass and brooches in Roman Britain, *MASCA Journal* 3,6 (1985) 189-91; *id.*, The production of brass in antiquity with particular reference to Roman Britain, in: Craddock (n. 46) 7-28.

56. J. Bayley, The production of brass in antiquity with particular reference to Roman Britain, in: Craddock (n. 46) 7-28.

57. Copper Development Association (n. 48).

58. Granulated copper packet in close crucibles with calcined zinc ore (zinc oxide) and charcoal and heated to 1000° C. The zinc oxide was reduced to zinc in situ and dissolved into copper.

59. Craddock (n. 50).

60. M. Cowell, S. La Niece, Metalwork: Artifice and Artistry, in: S. Bowman (ed.), *Science and the Past* (London 1991) 74-98.

61. O. Werner, F. Willet, The composition of brasses from JFE and BENIN, *Archaeometry* 17 (1975) 141-56.

62. Tylecote (n. 54).

63. *Ibid.*

64. Cowell, La Niece (n. 60) 81.

65. According to DeBruin et al., trace element concentrations can be a much more important tool in comparing the characteristics of an object of unknown origin with the characteristics of reference objects or of raw materials from unknown origins, M. DeBruin, P. Korthoven, A. Steen, J. Houtman, R. Duin, The use of trace element concentrations in the identification of objects, *Archaeometry* 18 (1976) 75-83.

66. M. Hall, Comments on oxhide ingots, recycling and the Mediterranean metals trade, *Journal of Mediterranean Archaeology* 8,1 (1995) 42-44.

67. P. Budd, A. M. Pollard, B. Scaife, R. C. Thomas, Oxhide ingots, recycling and the Mediterranean metals trade, *Journal of Mediterranean Archaeology* 8,1 (1995) 1-32.

68. See the section on Fabrication.

69. J. D. Muhly, Beyond Typology: Aegean metallurgy in its historical context, in: N. C. Wilkie, W. D. E. Coulson (eds), *Contributions to Aegean Archaeology* (Minnesota 1985) 109-41.

70. A. Hauptmann, G. Weisgerber, H. G. Bachmann, Early copper metallurgy in Oman, in: R. Maddin (ed.), *Beginnings and Use of Metals and Alloys* (1986) 34 -51.

71. Muhly et al. (n. 44).

72. *Ibid.*

73. Hauptmann et al. (n. 70) 36.

74. N. H. Gale, Z. A. Stos-Gale, G. R. Gilmore, Alloy types and copper sources of Anatolian copper alloy artifacts, *Anatolian Studies* 35 (1985) 143-73.

75. Hauptmann et al. (n. 70) 35.

76. The frequent appearance of iron in Bronze Age artifacts is due to unintentional use of Cu-Fe sulfide ores where Cu-Fe sulfide particles remain in the copper, Tylecote (n. 54).

77. Cowell, La Niece (n. 60) 81.

78. H. V. Michel, F. Asaro, Chemical study of the plate of brass, *Archaeometry* 21 (1979) 3-20.

79. Cowell, La Niece (n. 60) 81.

80. F. LoSchiavo, Early metallurgy in Sardinia, in: A. Hauptmann, E. Pernicka, W. A. Wagner (eds), *Old World Archaeometallurgy* (Bochum 1989).

81. N. H. Gale, Z. A. Stos-Gale, Comments on oxhide ingots, recycling and the Mediterranean metals trade, *Journal of Mediterranean Archaeology* 8,1 (1995) 33-41.

82. According to LoSchiavo a low iron content present in the copper ingots would have been the result of a fire-refined process, LoSchiavo (n. 81). Merkel also suggests that this amount is due to multiple remelting cycles, J. F. Merkel, Ore benefication during the late Bronze Age / early Iron Age at Timna, Israel, *MASCA Journal* 3 (1985) 164-70.

83. Oddy and Craddock mention that in the 6th and 7th c. AD copper alloys in the Mediterranean area normally contain appreciable quantities of zinc: Oddy, Craddock (n. 3) 757.

84. *Ibid.*

85. *Ibid.*

86. Muhly et al. (n. 44).

87. Gale et al. (n. 81).

88. *Ibid.*

89. J. A. Charles, The coming of copper and copper-base

alloys and iron: a metallurgical sequence, in: T. A. Wertime, J. D. Muhly (eds), *The Coming of the Age of Iron* (Yale 1980).

90. Gale, Stos-Gale (n. 81).

91. Werner, Willett (n. 61).

92. Hauptmann et al. (n. 70) 41.

93. Hall (n. 66).

94. Hauptmann et al. (n. 70) 41.

95. Hall (n. 66).

96. Hauptman et al. (n. 70) 46.

97. Merkel (n. 83) 168.

98. Oddy, Craddock (n. 3) 755-57.

99. Scott (n. 6) 24.

100. W. A. Oddy, S. LaNiece, N. Stratford, *Romanesque Metalwork* (London 1986).

101. R. F. Tylecote, H. A. Ghachavi, P. J. Boydell, Partitioning of trace elements during the smelting of copper, *Journal of Archaeological Science* 4 (1977) 305-33.

102. Mundell-Mango et al. (n. 1).

103. Oddy, Craddock (n. 3).

104. Gale et al. (n. 81) 144.

ΔΕΣΠΟΙΝΑ ΚΟΤΖΑΜΑΝΗ

Μελέτη της τεχνικής και της σύστασης του υστερορωμαϊκού κάδου με σκηνή κυνηγιού

Ο μεταλλικός κάδος με αρ. ευρ. 32553 που ανήκει στο Μουσείο Μπενάκη, μελετήθηκε με σκοπό να εξεταστεί η τεχνική κατασκευής και διακόσμησής του όπως και η σύσταση του μετάλλου κατασκευής, με σκοπό τα αποτελέσματα της εξέτασης να συγκριθούν με την ομάδα παρόμοιων κάδων στην οποία έχουν αναφερθεί η M. Mundell-Mango σε συνεργασία με άλλους ερευνητές.

Χρησιμοποιήθηκαν διάφορες μέθοδοι ανάλυσης όπως Ακτινογράφηση, Φθορισμός με ακτίνες X (XRF), Ηλεκτρονικό Μικροσκόπιο Σάρωσης (SEM) και Μεταλλογραφικό μικροσκόπιο. Δυστυχώς από τις μεθόδους αυτές, μόνο ο φθορισμός ακτινών X είχε εφαρμοστεί για την εξέταση των υπόλοιπων κάδων.

Πιο συγκεκριμένα η προσέγγιση των άλλων τομέων όπως η διαμόρφωση ή και η διακόσμηση, ήταν περισσότερο εμπειρική και βάσει αρχαιολογικών δεδομένων, και έτσι η πλησιέστερη σύγκριση της ομάδας των κάδων με τον κάδο του Μουσείου Μπενάκη, στηρίχτηκε ως επί το πλείστον στα αποτελέσματα της ανάλυσης της σύστασής τους.

Πράγματι, η εφαρμογή των παραπάνω μεθόδων, δύο από τις οποίες απαιτούσαν την εξαγωγή δείγματος, επιβεβαίωσαν ότι ο κάδος του Μουσείου Μπενάκη ανήκει στην ομάδα των κάδων που μελετήθηκαν από τους Mundell-Mango et al. και τους Oddy και Craddock.

Ο κάδος μορφοποιήθηκε με σφυρηλάτηση από την εσωτερική πλευρά και κυρίως από την εξωτερική με το χέρι (πιθανολογείται και η χρήση τόρνου). Το υλικό κατασκευής υποβλήθηκε σε μια σειρά από διαδοχικές ψυχρές κατεργασίες και ανοπτήσεις, δίνοντας έτσι το επιθυμητό αποτέλεσμα. Οι τελικές διεργασίες για την κατασκευή του σώματος του κάδου, συμπεριλαμβάνοντας και τη διακόσμησή του, είχαν ως αποτέλεσμα την ουσιαστική παραμένουσα παραμόρφωση στη μικροδομή του και ορισμένες παραμένουσες εσωτερικές καταπονήσεις. Το φαινόμενο αυτό δεν παρατηρήθηκε στο δείγμα που αφαιρέθηκε από τη λαβή του κάδου. Το τελικό φινίρισμα (γυάλισμα) και οι διπλές διαχωριστικές γραμμές που δημιουργήθηκαν για να οριοθετήσουν την επιγραφή στην εξωτερική επιφάνεια, πραγματοποιήθηκαν στον τόρνο. Για τη διακόσμησή του χρησιμοποιήθηκαν διαφορετικά είδη καλεμιών.

Τα αποτελέσματα της ανάλυσης της σύστασης του μετάλλου, προσδιόρισαν ένα κράμα κατασκευασμένο από χαλκό και ψευδάργυρο (ορείχαλκος) με την παρουσία και διάφορων άλλων ιχνοστοιχείων. Η σύσταση του κράματος αυτού καθώς και το ποσοστό συγκέντρωσης του ψευδαργύρου μέσα σε αυτό, υποδηλώνει ότι ο ορείχαλκος ήταν μάλλον προϊόν της αναγωγικής ενσωμάτωσης ψευδαργύρου με χαλκό (cementation process).

Η εξέταση των βασικών στοιχείων κραμάτωσης του ορείχαλκου και των διάφορων ιχνοστοιχείων, δεν μπόρεσαν να αποδείξουν με βεβαιότητα την προέλευση του υλικού κατασκευής του κάδου. Τα αποτελέσματα δείχνουν ότι η ύπαρξη των στοιχείων αυτών ταλαντεύεται μεταξύ της τυχαίας και της συνειδητής ενσωμάτωσης. Το υλικό ήταν προϊόν ανακύκλωσης, ήταν εμπορεύσιμο ή ήταν πρωτογενές που είχε παραχθεί σε κοντινά εργαστήρια; Και ποιο από τα δύο μέταλλα ο χαλκός ή ο ψευδάργυρος; Τα ερωτήματα αυτά δεν μπόρεσαν να υποδείξουν κάποιο συγκεκριμένο κέντρο παραγωγής του ορείχαλκου για την κατασκευή αυτού του κάδου καθώς και των υπολοίπων.

Σύμφωνα με εικονογραφικές και ιστορικές αναφορές η Ανατολική Μεσόγειος έχει παίξει σημαντικό ρόλο στην παραγωγή των κάδων. Οι μελέτες της σύστασης του ορείχαλκου γενικότερα, μπορούν να επιβεβαιώσουν τη χρήση αξιοσημείωτων πηγών του μεταλλεύματος στην περιοχή αυτή. Το Ομάν, η Μικρά Ασία, η Κύπρος μπορούσαν να προμηθεύσουν το υλικό για την κατασκευή των κάδων ως πρωτογενές (ορυκτό) ή δευτερογενές (ανακυκλωμένο, εμπορεύσιμο). Τελευταία εκδηλώνεται ένα έντονο ενδιαφέρον για την εξέλιξη της αρχαίας μεταλλουργίας στην Ανατολική Μεσόγειο και συγκεκριμένα στην Ανατολή, αλλά θα ήταν πραγματικά ενδιαφέρον να προσδιοριστούν πηγές για νεότερες χρονολογικές περιόδους.