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Article

# A Bronze Lebes from the Coastal Cemetery of the Phaleron Delta, Greece: Excavation and Conservation of the Find

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**Abstract:** The excavations carried out by the Ephorate of Antiquities of Piraeus and Islands at the cemetery in the Phaleron Delta, Attica (late 8th - 4th century B.C.), have uncovered in total 1961 burials of various types, among which the Burial 923 is of particular importance as it is the only case of secondary cremation inside a copper alloy lebes. The use of such a valuable bronze vessel, symbolizing prestige, social status and wealth, as a cinerary urn indicates the importance of this find for the interpretation of issues related to the use of the cemetery and the ritual customs of the period and makes imperative the need to preserve the object despite its significant erosion. In this paper, we will present issues related to the lifting and conservation of the bronze vessel, that was found buried within a coastal and sandy depositional environment. Also, the condition of the vessel was scientifically investigated using optical microscopy (OM), portable X-ray fluorescence (p-XRF) and X-ray diffraction (XRD) techniques. The results showed a completely mineralized bronze artefact with tin corrosion products in the core, which indicate decuprification of the copper alloy.

**Keywords:** copper alloys; copper corrosion; bronze artefacts; conservation; corrosion products; XRD analysis; Phaleron Delta semetry

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## 1. Introduction

Corrosion of bronze artefacts, found in burials, reflects a complex mechanism that generates a sequence of various corrosion product layers. The formation of this stratigraphy is a complicated process, due to various factors, such as a) the artefact's find spot environment, b) the kind and quality of its alloy and c) its manufacture technology. It is not at all uncommon to uncover similar artefacts, completely corroded, without metal core, the preservation of which is further affected by factors, such as humidity and presence of chloride ions. The latter factors cause continuation of corrosion chain reactions and gradually lead to the complete segregation of the alloy, by forming compounds of copper trihydroxychlorides. This phenomenon has been a frequent subject of study [1–4]. Though corroded, some artefacts play an important role in the understanding of their archaeological context, hence their conservation and protection are imperative, while quite often it is necessary to put them on display, irrespective of their condition of preservation.

The main objective of the article is an overall presentation of the conservation actions/works and subsequent maintenance of this unique bronze cinerary lebes from the excavation in the coastal cemetery of the Phaleron Delta, in Attica, which was put on display in the context of a recent temporary exhibition in the Archaeological Museum of Piraeus. There will be presented a preliminary study of the corrosion products stratigraphy (identification and corrosion factors). It is an exceedingly corroded bronze vase, without metal core, something that indicates decuprification of the bronze alloy.

## 2. Materials and Methods

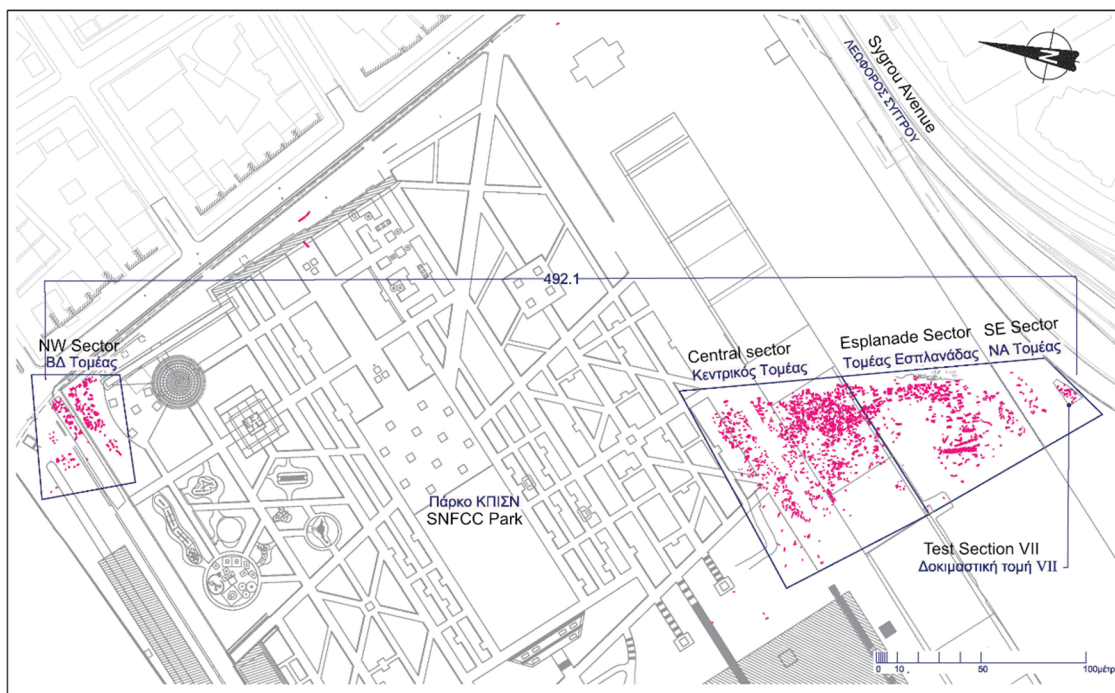
### 2.1. Excavation Data of the Find

The cemetery of the Phaleron Delta lies 4 kilometres to the south of the modern centre of Athens, the capital of Greece, expands across a large part of the coastal zone of the ancient Phaleron bay and was in use throughout an extensive chronological period of about four centuries (8<sup>th</sup> – 4<sup>th</sup> cent. B.C.) [5–8]. Its excavation was carried out by the Ephorate of Antiquities of Piraeus and Islands (EAPI) in the context of the Stavros Niarchos Foundation Cultural Centre (SNFCC) construction. The map in the Figure 1 shows the location of the Phaleron Delta in relation to Athens and the SNFCC where the cemetery was excavated.



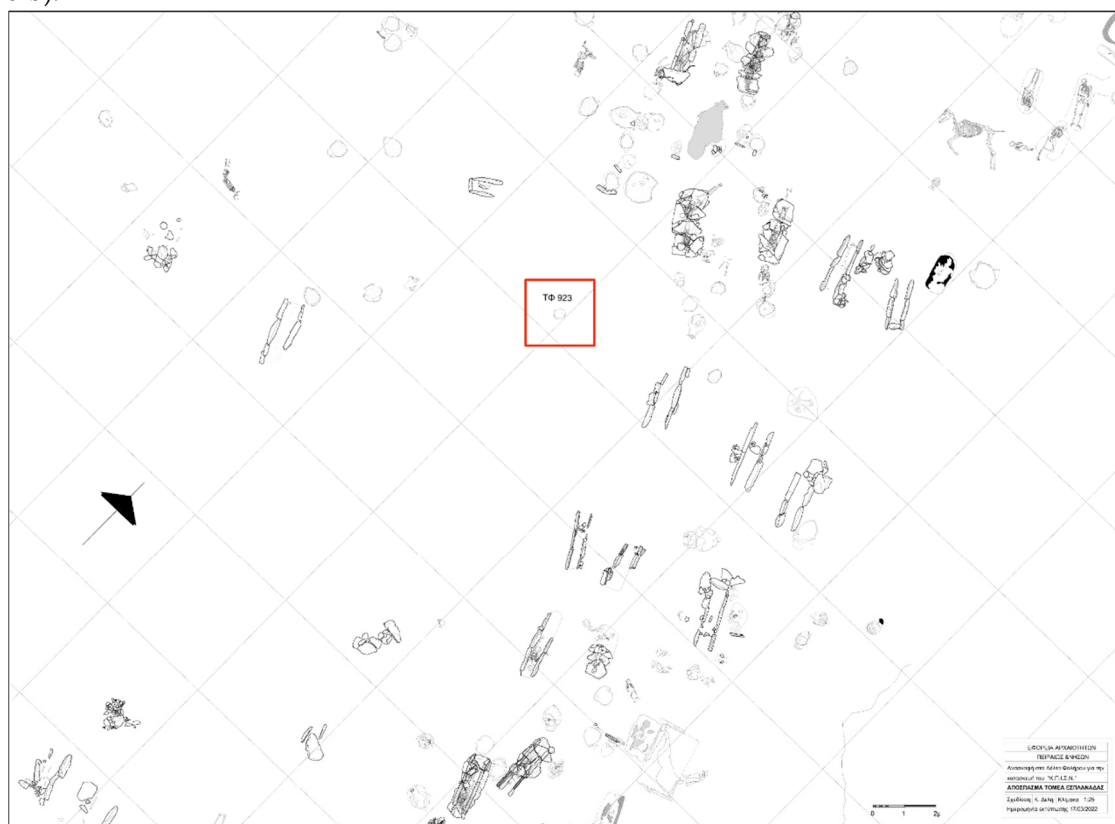
**Figure 1.** Map showing the location of the Phaleron Delta in relation to Athens. The smaller map shows the place of the SNFCC.

The part of the cemetery that was investigated from 2012 to 2020 was conventionally divided in four excavation sectors: a) NW Sector, b) Central Sector, c) Esplanade Sector and d) SE Sector, as seen in the Figure 2.



**Figure 2.** Map of the cemetery part which was investigated from 2012 onwards and the excavation sectors (©Ephorate of Antiquities of Piraeus and Islands/Konstantina Deli).

Burial 923, referred to from now on as ΤΦ923 [9], was unearthed in the Esplanade Sector (Figure 3), within an undisturbed pure sand stratum of brown colour, overlying a grey-brown one (Figure 4a and b).



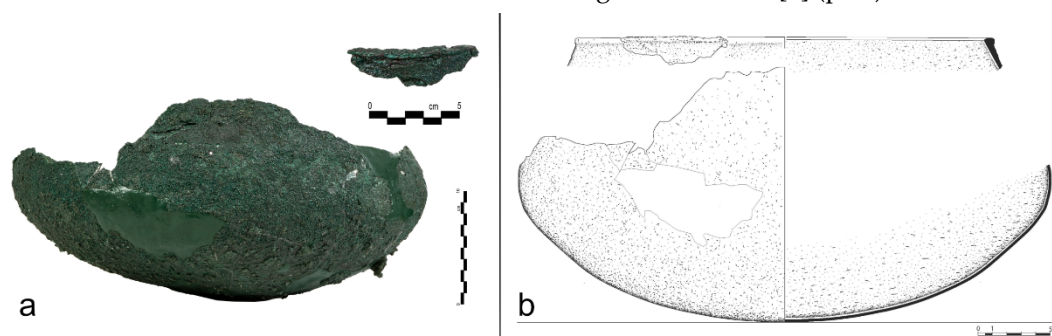
**Figure 3.** Part of the Esplanade Sector and Burial 923 marked in red (©Ephorate of Antiquities of Piraeus and Islands).



**Figure 4.** Burial 923 in situ (left) and within the limits of the square it was located in (right) (©Ephorate of Antiquities of Piraeus and Islands).

The burial was uncovered at a depth between -0,54 and -0,60 m. (measured from sea level). It was a secondary cremation of an adult, whose burnt remains were located inside a bronze lebes. Unfortunately, from the osteological finds, to which we will refer further below, it was not possible to identify the dead's gender and age. Inside the vase there were discerned right from the beginning quite a few small fragments of the lebes itself, while no grave offering was found. Remarkable is its location, since it does not border any other burial, although it was found at a relatively high level (the usual depth range of burials at Phaleron is from -0,20 to -1,20 m.). At a relatively short distance, to the north, there is a large number of pot burials and a few pit graves, all of which are dated within the 7th cent. B.C. To the east of TΦ923 there were found very few cist graves, which have been re-used, therefore their dating is not safe [9] (p.58).

The cinerary lebes of TΦ 923, under inv. no. 26142, is preserved in fragmentary condition, its maximum preserved measurements being: D. 30-33 cm., Ht. 19 cm. It received conservation treatment and was mended from bigger and smaller fragments from the lower part of the body, restored at the joints. Preserved is the lower part of the body, from the biggest diameter down to the base, as well as part of the rim. Its surface is rough and corroded, with accretions and green patina. The base is convex/rounded, without any particular configuration, and the lower body is hemispherical, slightly compressed (Figure 5). It has a slight to imperceptible rounded carination at the transition from the lower to the upper part of the body. The walls in the upper body have a subtly concave profile and converge slightly to the centre, ending in a wide mouth with slightly out-turned band rim. No handle element can be discerned and the vase is made of a single metal sheet [9] (p.58).



**Figure 5.** a) The fragmentary lebes of Burial 923 and part of its rim (©Ephorate of Antiquities of Piraeus and Islands) and b) drawing illustration of the lebes in Burial 923 (©Ephorate of Antiquities of Piraeus and Islands /Konstantina Deli).

With regard to the dating of the vase, the total absence of accompanying grave offerings renders difficult any attempt to determine it with precision. In any case, the occurrence of accompanying artefacts, which could be safely dated, would have determined a chronological *terminus ante quem* for

the lebes, but not necessarily the chronology of its manufacture and often long duration of use [9,10] (p. 124, p. 59). According to Lourentzatou, who has studied this particular burial, the chronology of the vase can be fixed, chiefly because of its proximity to safely dated funerary assemblages from the cemetery, as well as on the basis of chronological parallels (especially on the basis of the parallel from tumulus R of Gordion), to the 7th cent. B.C. [9] (p. 59).

### 2.1.1. The Special Case of TΦ923 (Burial 923)

In the Phaleron Delta cemetery, a total of 1.959 burials were found in the last excavation period (2012-2020). The prevailing funerary custom is inhumation at a percentage of 92,64 %, while, in relation to the funerary practice of cremation, the primary cremation, with one hundred and thirty burials, is more popular than the secondary cremation, which is represented by just three burials [11] (pp. 243-244). There are three reasons for which burial TΦ923 stands out as to its importance: a) it is a burial which adopts the funerary custom of cremation in a cemetery where up to now the practice of inhumation seems to be dominant, b) it belongs to the very small percentage of secondary cremations (0,15 %) and c) is the only case of secondary cremation, for which a lebes is chosen to be used as cinerary vase [9] (p. 61). According to Lourentzatou, the choice of combining the custom of cremation with the lebes as cinerary vase, supports the hypothesis that the dead was an individual of social eminence. As the same comments, the adoption of the practice of cremation indicates the intention of the dead's kin to differentiate this particular burial from the remaining ones in the cemetery. Moreover, the choice of the lebes as cinerary vase, a valuable vessel after all, symbol of prestige, social position and wealth, which could have also been an heirloom, highlights even more strongly the intention of marking out social differentiation in the cemetery. Also, the fact that burial TΦ923 was not clearly adjacent to any other burial (see Figure 3) could possibly reinforce the hypothesis that the dead belonged to an *elite* group or family, which used cremation and the valuable cinerary vase as symbols of social superiority and chose as resting place for the deceased a space, within the cemetery, but slightly remote from the rest of the graves, so as to make more apparent his/her social superiority [9] (p. 61).

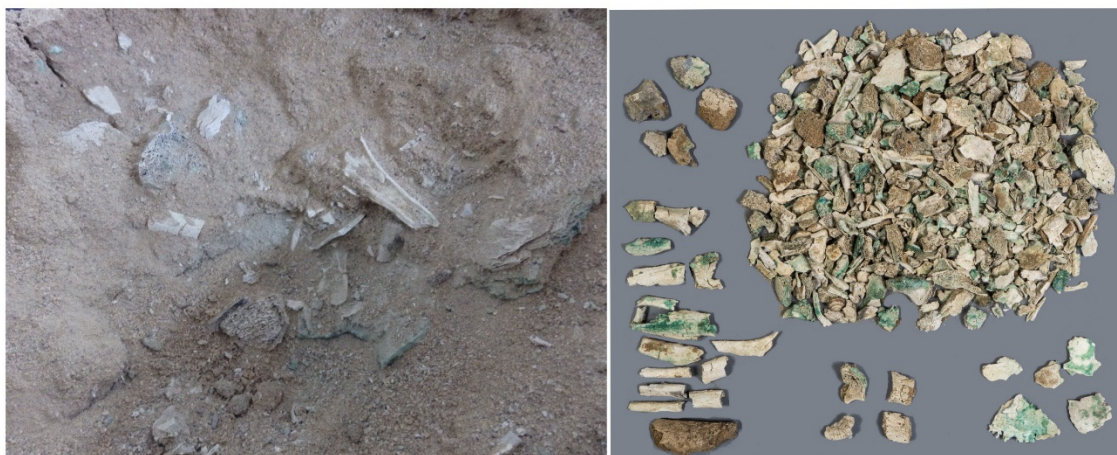
### 2.2. Lifting and Conservation Treatment

The bronze lebes was found placed directly on the ground and its interior had been filled with sand from the immediate burial environment, as a result of the subsidence of the object that covered its mouth as a kind of lid. Similar cases of using a bronze lebes with lid as cinerary vase are also known from other areas, a characteristic example being that of Kifissia [9,12] (p. 204 - fig.10,11, p. 60 - footnote 26), in our case, though, the bad state of the object's preservation was immediately recognized. For its protection and because of its advanced corrosion, it was decided to lift the find *en block* and transport it to the lab to proceed there with the digging of its interior and simultaneously with its conservation. For detaching it from the excavation field, the sandy soil material was gradually removed and, in parallel, a cast was placed on its exterior surface, made of open weave fabric soaked in a 10% w/w solution of acrylic resin in acetone, aiming at enhancing it. On the underside of the vase's base, a considerable section of the sandy sub-stratum was retained for the safety of the find during the insertion, underneath it, of a flat wooden support/lifting surface. Next came its bandage with polyethylene sheet and its placement in a box with protective Expanded Polystyrene (EPS) panels for its safe transportation (Figure 6).



**Figure 6.** Lifting stages: a) gradual removal of sandy soil material, b) application of a cast on the exterior, c) bandage with polyethylene sheet and d) preparation for the transportation to the lab (©Ephorate of Antiquities of Piraeus and Islands).

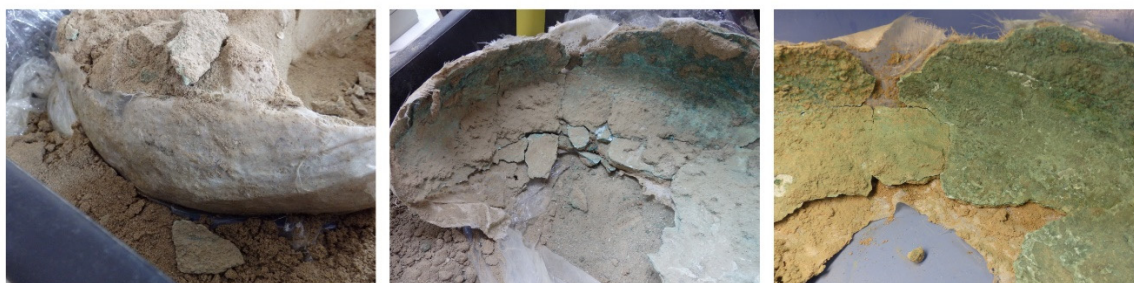
In the conservation lab, the micro-excavation in the interior of the lebes began, keeping at the same time the retaining cast on the exterior surface. The removal of the sandy fill in the excavation field was deemed unsafe a) for the integrity of the object itself, b) for reasons related to the search for other objects and materials and c) for securing the preservation of probable information [13] (pp. 54-59). In the present case, in the course of the gradual removal of soil material, apart from some fragments of the vase itself, there were uncovered only cremation remains among which parts of diaphysis and epiphysis bones, while a few cranium and vertebra fragments were also observed. The colour alterations of the bones from white to grey and beige-brown indicate the fluctuation of temperature during combustion. Bone, when subjected to fire, gradually undergoes colour alteration from brown to black and grey-blue and, in the end, reaches white colouring when exposed to temperature above 650° C (1112° F), a point of opinion convergence for most researchers [14]. The green colouring on certain bones is due to their contact with the lebes walls and to diffusion of bronze corrosion products (Figure 7).



**Figure 7.** In the course of the fill removal, remains of cremation and fragments of the vase come to light (left). Osteological material that was retrieved from the interior of the lebes. There are observed: diaphysis and epiphysis bone fragments, a few cranium and vertebra fragments, alterations in colour, diffusion of bronze corrosion products (right).

After the removal of the fill material from the lebes' interior, the vase's aggravated condition became evident. The thickness of the metal varied between 4 and 2 millimetres on the body and was decreasing towards the base, while the single preserved part of the rim had a thickness, at its upper end, of 7 millimetres. The object's lack of metallic core had resulted in minimal or zero mechanical strength. The walls were fragmented and held together by the cast that had been placed on its exterior. One side of the lebes is missing, it was possible, though, to measure its diameter at about 30 to 33 cm.

The advanced corrosion of the vase and its fragmentary state of preservation dictated such conservation interventions that would bring the artefact into a more stable physical-chemical condition. The interventions were conducted in the metal objects conservation lab of the Archaeological Museum of Piraeus and are the following: - Cleaning of the metal surface. The aim of the intervention was to remove the unstable components, which undermine the preservation and aesthetic aspect of the artefact, and to expose an as coherent as possible surface. The task was performed in dry environment by mechanical means, with the use of hand tools, which provided flexibility and secured control over the intervention's depth and extent. The equipment used in the process includes, scalpel, pins, dental tools, fiberglass scratch brush and powered by electricity lab micro-motor with the possibility of regulated rotation. Cleaning began from the internal surface of the vase, keeping in place the cast on its exterior surface (Figure 8). Then, as the cast was gradually removed with the use of acetone, the pieces supported by it were removed and cleaned with great care, on their exterior surface, each one separately.



**Figure 8.** During the fill removal and cleaning operations. On the outside, the cast kept to retain the vase fragments.

- **Stabilization.** The purpose of the intervention was to inhibit corrosion and achieve physical-chemical stability for the object, in a given environment, via chemical reactions. As inhibitor we used benzotriazole (BTA) of molecular formula  $C_6H_5N_3$ , a chemical substance that forms exceptionally insoluble complexes with copper [3,15] (p. 228, pp.376-381). The stabilization was carried out by immersing the object in 3% w/w solution of benzotriazole in ethyl alcohol, in room temperature. The treatment was conducted in vacuum in order to secure penetration of the solution in depth between the corrosion crusts. The excess of benzotriazole crystals was removed with ethanol and there followed desiccation.
- **Protection.** The aim of the intervention was to create a barrier between the environment and the metal surface. To this purpose, a coating of acrylic protective varnish in an organic solvent, under the trade name, Incralac Protective Lacquer, was applied, a material that contains corrosion inhibitors and absorbs the ultraviolet radiation so as not to be degraded by solar radiation [3,16] (p.384, pp. 300-312). A 15% v/v solution of Incralac in toluene was used; to obtain a uniform, of sufficient thickness coating, two applications of it were performed with brush on either side, with desiccation intervals in between.
- **Resetting.** The aim of the intervention was to reconstruct the shape of the artefact and to deal with the fractures and material losses. For the mending of the broken parts thermoplastic acrylic resin of indicative type HMG-Paraloid B72 was employed. Furthermore, the local enhancement of the structure along the joints/ binding lines on the inside, was accomplished by using fine fibrous textile made of carbon fibres, 21 gr/m<sup>2</sup>, soaked in a 7% w/w solution of thermoplastic acrylic resin Paraloid B72 in acetone. Paraloid B72 is an acrylic polymer, widely used in conservation thanks to a series of characteristics, such as ease of application, reversibility, transparency and its ability to be diluted in a series of solvents, such as ethanol, acetone and toluene. The percent concentration of the resin and the choice of solvent are adjusted depending on the manner of application (mending or consolidation) and the material (porous or not). The choice of a volatile solvent, such as acetone, impedes the penetration of the resin, which though increases when concentration is very low. In high concentration it is used as adhesive of good workability and ability to fill small voids. However, Paraloid B72 loses its properties when exposed to high temperatures, about 40° C [17], a fact that in the case of the bronze lebes is regulated by the conditions that prevail in the space where it is stored.
- **Restoration.** For binding and holding together the preserved pieces and because of the extensive losses, fillings of two-component epoxy putty, under the trade name Epoxol Putty, were applied and aesthetic restoration with water colour tubes took place. This work was deemed absolutely necessary in order to put on display the bronze lebes in the temporary exhibition entitled "Phalērothen. Between two worlds" [18] (pp. 112-113), with the aim, on one hand, to establish the required structural adequacy and, on the other hand, to render its shape and size easily recognisable. However, to secure its authenticity, the object was restored only as to the preserved part, by joining those parts whose edges were fitting together and by filling the spaces in between. The single part of the rim that was found, was presented separately, next to the body of the vase (Figure 9).



**Figure 9.** Presentation of the bronze lebes and part of its rim in the temporary exhibition of the Archaeological Museum of Piraeus (©Ephorate of Antiquities of Piraeus and Islands).

- **Passive conservation interventions.** The actions that relate to controlling the environmental parameters of the spaces where artefacts of metal alloys are exhibited or stored, are necessary for their preservation and are integrated in the framework of passive conservation interventions. In order to safeguard the stability of its state of preservation, the bronze lebes is kept in a space with controlled conditions of relative humidity and temperature, the relative humidity being maintained low, up to 45%, and temperature at 20°C with a fluctuation of about  $\pm 2^{\circ}\text{C}$  [19] (pp. 219, 227). The environmental conditions are regulated via installed air-condition and dehydration systems, while the measurements of relative humidity are recorded by an electronic device. For the storage of the lebes, acid-free paper and ethafoam sheet was used as well as a polyethylene box.

### 2.3. Examination Techniques

To investigate the condition of preservation and the layering of corrosion products on the bronze lebes, 3 fragments from the vase's body, not joining to the reconstructed part, were taken as samples. The analyses were carried out in accordance with the no. 32830/19-02-2024 permit of the Hellenic Ministry of Culture. Their examination took place after the completion of cleaning operations and the removal of soil material remains that had formed crusts of considerable thickness on both surfaces of the fragments, which were heavily corroded. Macroscopically, their surfaces were rough and covered by greenish corrosion products, with bulges, micro-cracks and flaking, in places.

Initially, the artefact's condition was evaluated by visual examination of the fragments [20] (p. 212), in the conservation lab of the Archaeological Museum of Piraeus. The fragment surfaces and their fracture sections were observed at suitable magnifications, using a portable optical microscopy device with a source of Light Emitting Diodes (LED) system, in visible light, of Dino-Lite AM7515MZT type and a Leica Microsystems – M80 stereoscope, with embedded camera of Flexacam C3 type, and micro-photos were taken.

Then, the samples were analysed with an X-ray fluorescence (p-XRF) portable device in the Archaeometry lab of the University of the Peloponnese. The p-XRF is a popular non-destructive technique for the study and elemental recognition of metallic objects [21] (pp. 109-112). A portable

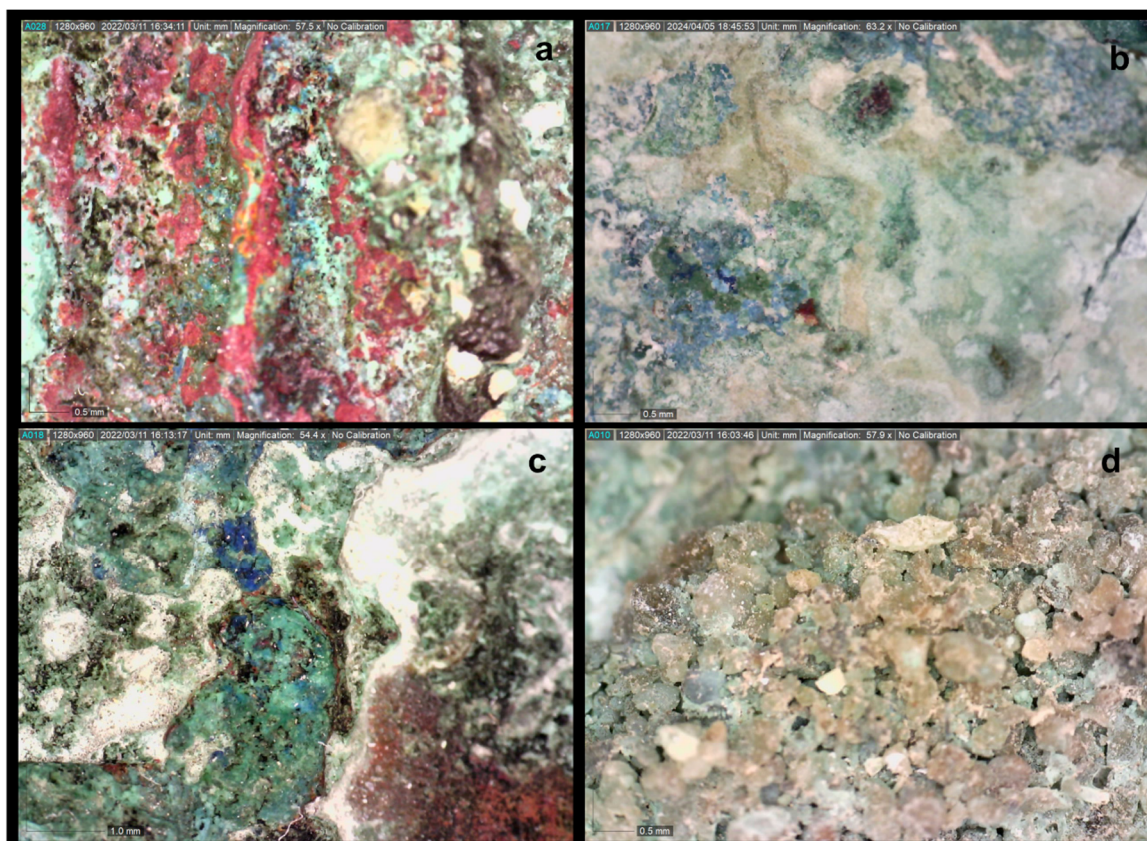
instrument was used with a detector of the Bruker Company, model Tracer 5G, accompanied by a portable mini-pump vacuum. The excitation parameters were: voltage 40kV, current 12,7 $\mu$ A, collimator 8/8 mm, filter Blank and measurement time for each analysis 90 seconds. Given that the samples under examination are completely corroded, the objective of the analysis is a first assessment of the identity of the elements that are included in the corrosion crusts of the examined surfaces and for this reason a total of 6 measurements were taken, 2 from each sample.

For the detection of corrosion products, the technique of X-ray diffractometry (XRD) was employed. In the context of the XRD technique, two samples of 0,5 gr powder each, from two fragments, were taken, by mechanical means. The mineralogical analysis of the fragment's corrosion products was performed at the Laboratory of Archaeometry (University of the Peloponnese) by means of X-ray Powder Diffraction (XRPD), employing a Bruker D2 PHASER diffractometer, with Cu-K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) operating at 30 kV/10 mA, on a 2-80° 2 $\theta$ , equipped with a Bruker LYNXEYE XE-TX detector. The qualitative mineralogical analysis was carried out using the DIFFRAC.EVA software based on the ICDD (International Centre for Diffraction Data) Powder Diffraction File (2006 version). This method has often been used for the detection of corrosion products in ancient artifacts made by copper alloys [22–27].

### 3. Results

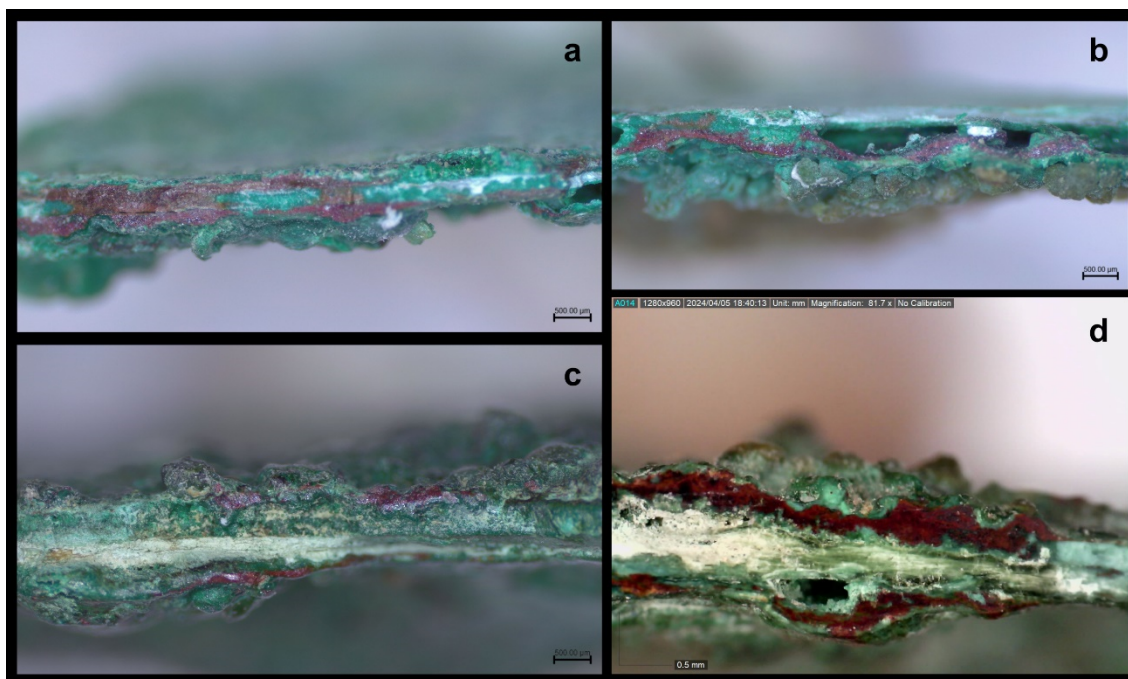
In the analysis of the samples with the p-XRF technique, the elements copper and tin as well as the elements lead, antimony, iron and nickel, were recorded. Since the surfaces under examination consist solely of corrosion products crusts, no quantitative analyses of the measurements were conducted. Moreover, the lack of metal core does not allow for the determination of the chemical composition of the alloy. However, we can conclude that for the manufacture of the vase a binary copper-tin (Cu-Sn) alloy has been used.

The observation of the fragments via optical microscopy showed that the entire artefact has been turned into corrosion products and there was no sign of metal core preservation in their section. The surface corrosion layers principally contained products of red, green and off-white/whitish colour, while, in places, there were additionally observed products of blue, dark-black and orange colour, as well as accretions of soil material remains (Figure 10a-c).



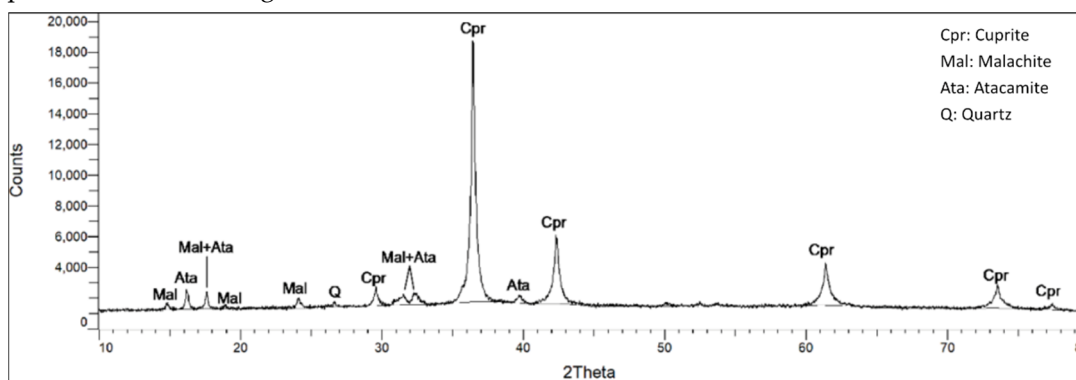
**Figure 10.** Images from the surface of the fragments under examination. Colour gradations of corrosion products (a-c) and accretions of soil material and corrosion products (d) (Dino digital microscopy, magnification 57.5, 63.2, 54.4 and 57.9X).

In the fracture sections the following were observed: a) In most cases, a layer of red colour and of small uneven thickness, was detected in the centre, which was surrounded by chiefly green corrosion products. This inner part, which also contained red and sometimes green corrosion products, was in reality the metal part that had been completely mineralized [26]. Furthermore, in the compact red corrosion layers, colour gradations were observed, a parameter that indicates probable differentiation as to tin content in them, a fact that will be referred to in the discussion further below. b) Patches of green colour interrupted the red layer, in places. c) Soil remains had intruded, in some cases, at a greater depth in the corrosion layers. d) An off-white/whitish phase, which was surrounded by layers of red and green colour, was sometimes discerned in the centre of the fragments and sometimes between the corrosion layers. This phase was unstable and in powdery state, while, in some cases, seemed to have retreated interrupting the layer sequence of corrosion products and creating void spaces in the layering. These off-white layers also appear to have caused surface flaking, as their remains were observed, in places, in the areas where surface corrosion flaking had retreated. e) Corrosion products of light green vitreous colour, with evident bulges, were observed in the interior of the structure of corrosion layers (Figure 11a-d).

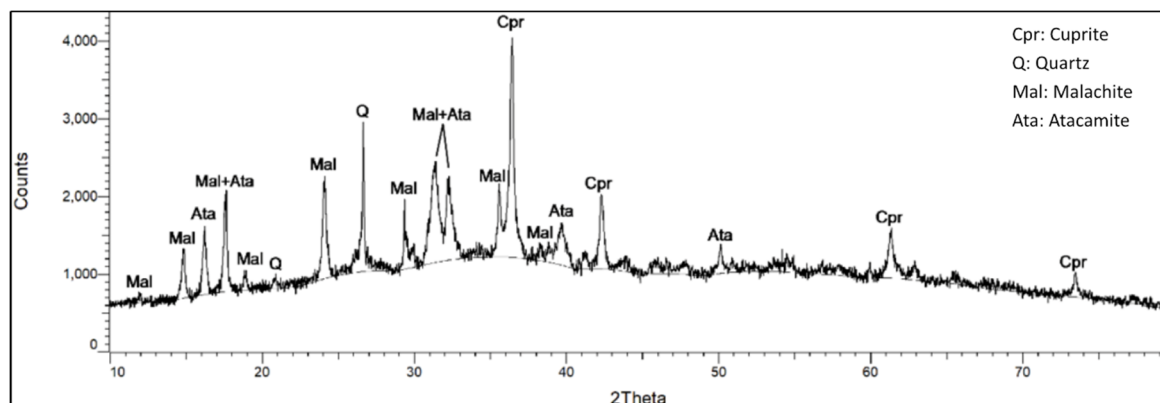


**Figure 11.** Images of the fracture sections. a and b) Red and green corrosion layers in the centre of the fragments (Leica Microsystems – M80, Magnification camera 0.8X/Visual magnification 20X). c) Off-white phase in powdery state and soil remains among the corrosion products (Leica Microsystems – M80, Magnification camera 0.8X/Visual magnification 20X). d) Corrosion products of light green colour and unstable formations of off-white colour (Dino digital microscopy, magnification 81.7X).

The qualitative analysis of two samples by the XRD technique showed that in the corrosion products of the bronze lebes from the Phaleron Delta there were detected cuprite ( $\text{Cu}_2\text{O}$ ), malachite ( $\text{Cu}_2\text{CO}_3(\text{OH})_2$ ) and atacamite ( $\text{Cu}_2(\text{OH})_3\text{Cl}$ ). The quartz ( $\text{SiO}_2$ ), which was also recorded, derived from remains of soil material that had penetrated in the porous structure of the corrosion in the course of the long period of time the artefact remained buried. The absence of tin compounds, such as oxide of tin - cassiterite ( $\text{SnO}_2$ ), from the diffractograms, is related to the difficulty in the detection of these compounds by the method of XRD, because of their very low crystallinity or amorphous structure in the bronze patinas [23,26,28]. As a result, it was attested that the main corrosion products that were documented in the examined samples were copper (I) oxide (cuprite), basic copper carbonate hydroxide salt (malachite) and copper trihydroxychloride (atacamite). The diffractograms of the two samples are seen in the Figures 12 and 13.



**Figure 12.** Diffractogram of the first examined sample. It contains cuprite (Cpr), malachite (Mal), atacamite (Ata) and quartz (Q).



**Figure 13.** Diffractogram of the second examined sample. It shows peaks that correspond to those of cuprite (Cpr), quartz (Q), malachite (Mal) and atacamite (Ata).

#### 4. Discussion

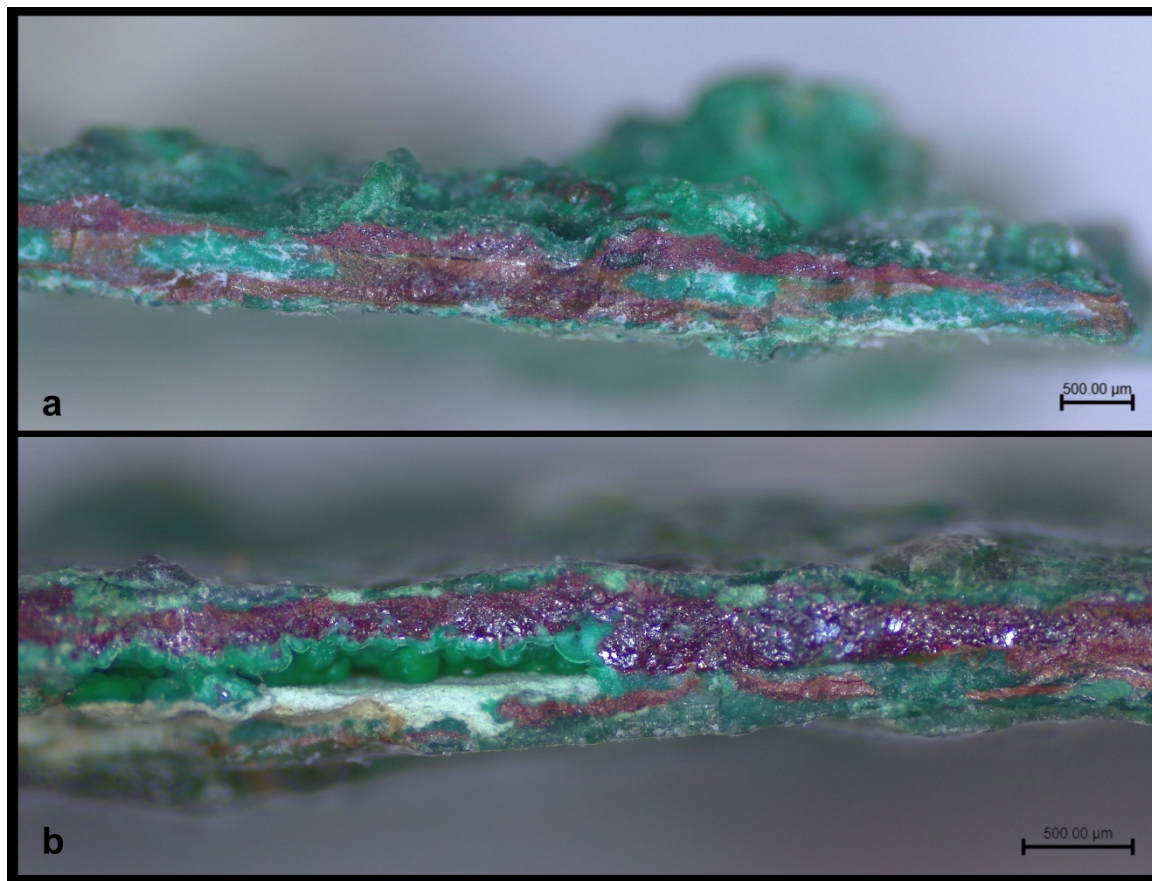
The corrosion of artifacts made of copper alloys in archaeological environments depends as much on endogenous factors, such as the nature of the alloy, the heterogeneity of its components and the method of processing, as on exogenous ones that determine the interaction of the finds with the burial environment, such as soil pH, conductivity, humidity and presence of ions [29,30]. Moreover, corrosion may affect to a greater extent certain areas of the artifact and manifests itself more intensively and at higher rates in areas where the metal is thinner, when there are discontinuities of the metallic surface, around cracks and micro-cracking as well as along the borders of the alloy grains and inclusions [15,29,31] (p. 217, p.93, pp. 387-397). Hammering and cold forming process for the manufacture of objects made of copper alloys, causes the elongation of metal grains, via the intense compression forces they have been subjected to [32,33] (pp. 83-105, pp. 334-335), resulting in their becoming more prone to corrosion processes. Thus, oxidation processes are accelerated, while corrosion penetrates in depth and develops along the borders of the grains, causing pericrystalline corrosion and intergranular cracks [24,29,34].

With regard to the condition the Phaleron bronze lebes was found in, the aforementioned factors have played an important role, along with the immediate burial environment, which is the sandy coast of the Phaleron bay. The Phaleron Delta, according to historical sources that are evidently confirmed by current geological studies, lies in the wider region of the Halipedon, a Greek name the etymology of which is analysed as follows:  $\alpha\lambda\varsigma$  (salt) +  $\pi\epsilon\delta\acute{\iota}\omicron\nu$  (field). The Halipedon seems to have consisted of marshy areas, which, depending on the prevailing conditions, were drying up and re-emerging from time to time, with brackish waters and formations of coastal dunes, which extended across a large part of the narrow sandy strip of the bay, being a soil factor characterized by accumulation of quartz or limestone sedimentation sand [35] (pp. 136-158). All this evidence leads directly to the conclusion that in the area where the examined bronze lebes was found, prevail two important corrosive factors, as to artefacts of copper alloys: presence of humidity and circulation of chloride ions in aqueous solutions. Furthermore, access to oxygen, an element necessary for the occurrence of the corrosion phenomenon, is favoured in sandy soil, while, differentiations in the quantity of oxygen, due to the different granulometry which can occur, in places, in corresponding soil types, enhance considerably the progress of the phenomenon [36]. Furthermore, water as solvent and carrier of salts operates as an essential factor in the corrosion of archaeological finds. The impact of humidity and circulation of water increase the rate of corrosion, especially in cases of burial at small distance from the sea. In the present case, the depth level of the find and its proximity to the sea front intensify the phenomenon of corrosion, mainly because of the presence of chloride salts. Chloride ions facilitate the corrosion of bronze, as they pass through its protective oxides, forming microscopic, non-coherent atacamite–paratacamite crystals [15,37]. In conclusion, the sandy environment of the lebes burial place could be considered as “aggressive”, since it is characterized

by the ability to retain humidity but also water from rainfall and from the water table, promoting the circulation of ions and hence salt solutions.

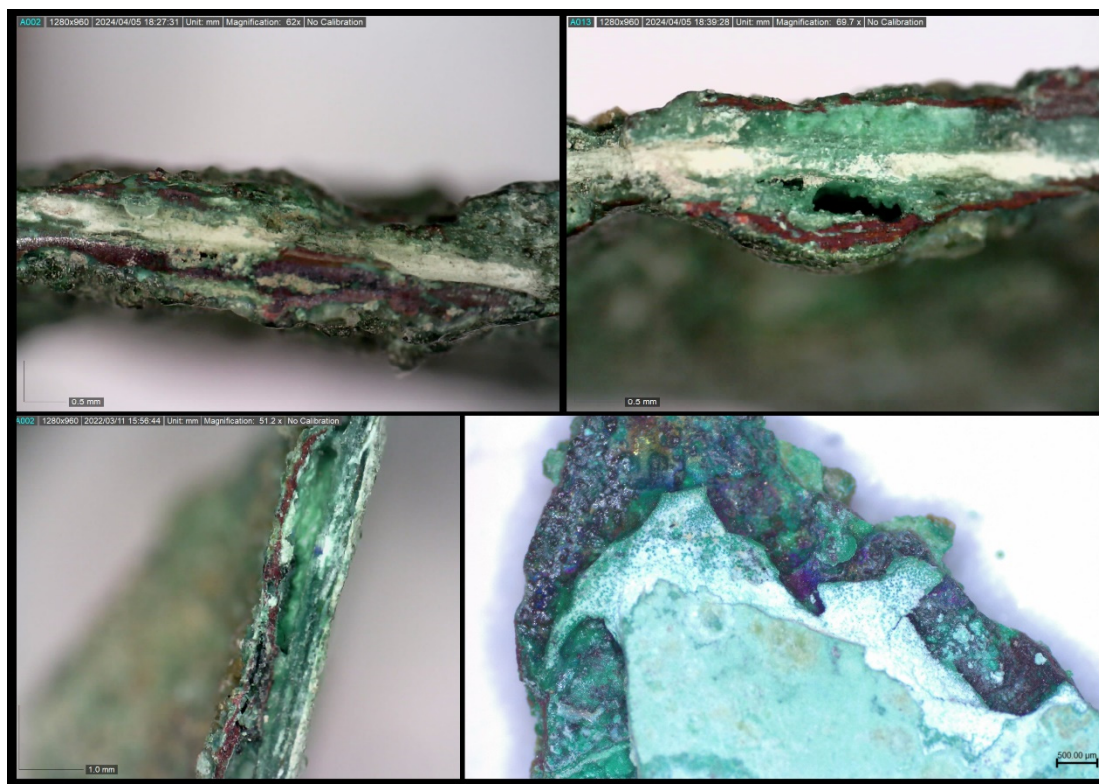
Regarding the manufacture alloy of the bronze lebes, the lack of metal core did not allow the determination of its chemical composition through quantitative analysis by the p-XRF method. Nevertheless, the qualitative analysis by this technique led us to the conclusion that this is a binary copper – tin alloy. These kinds of alloys are frequent in the Greek area and were in use for a long period of time [38]. From the viewpoint of processing, they can be subjected to cold hammering, while the hardening of the alloy by this technique, requires a high tin content for the produced object to have durability and for deformations not to be caused during its use [39] (pp. 283-284). As to the existence of lead, an element that was also detected by the p-XRF analysis, it is well known that for an alloy to be suitable to be processed by cold hammering, there is need for a uniform distribution of this element in the metal mass and its content should not exceed 2% [38]. In relation to iron, the existence of which would have had a particularly adverse effect on the process of cold hammering [33,40] (pp. 51-54, pp. 673-676), its presence is usually reinforced owing to corrosion and the intrusion of soil material. Worth mentioning, at this point, is that in the Phaleron Delta cemetery a bronze double axe of the same chronological period has been uncovered, made of good quality copper and tin alloy [41] (pp. 101-114). These two finds (the bronze double axe and the bronze lebes) are valuable artefacts and unique occurrences in this particular excavation, and play an important role in the reading of their archaeological context as a whole.

In the assessment of the lebes fragments' condition, via optical microscopy, it was observed that the developing corrosion layers had formed rough and uneven crusts. In the areas, where corrosion had advanced at a faster pace, bulges of corrosion products had been produced, while often soil material remains were observed in hard to remove accretions of corrosion products. Through the XRD analysis, it was attested that the corrosion layers are composed of cuprite, malachite and atacamite, while there was also recognised the presence of quartz as a result of sand intrusion from the burial environment. As far as cuprite goes, apart from the characteristic red colour, which is its principal hue, can also appear in hues of different intensity, which vary from orange to yellow [24,28], a fact that was observed, as well, in the microscopic observation of the examined lebes fragments (Figure 14a). Colour gradations in the cuprite layers occur depending on the alteration of the Cu/Sn ratio and, more precisely, the lighter red colour indicates corrosion areas or bands rich in tin, while, as the colour gets darker, the content in copper increases [23,24,26]. Also microscopically, there were observed a) small areas of black to grey colour, between the cuprite layers, which may derive from bivalent copper oxides, tenorite and b) corrosion products of blue colour, which appear rarely, and are associated with copper carbonate salts, azurite [15] (pp. 216-217). These two compounds (tenorite and azurite) did not produce a detectable sign in the XRD technique, probably due to their limited and fragmentary appearance in the examined bronze vase fragments. Moreover, no tin compounds were documented, despite the fact that the existence of this element in the examined fragments was recorded by the p-XRF technique. This is due to the scarcely crystalline to amorphous structure of these compounds, a fact that renders infeasible their characterization through X-ray diffraction analysis [23,26]. In general, in the completely corroded bronze artefacts, without metal core, as the bronze lebes from Phaleron, the composition of the inner corrosion layers depends on the alloy's original composition, namely its content in tin, which, as mentioned above, is responsible for colour gradations in the red compact layers, and on the presence of chloride, the quantity of which influences the hue of the green layers [25,26]. In the course of the corrosion process, the layers of cuprite lose their coherence and break down because of the penetration of chloride ions and the formation of copper chloride compounds in the inner corrosion layer [23], a phenomenon that was observed in several cases in the fragments under examination (Figure 14b).



**Figure 14.** a) Colour gradations in the cuprite layers (Leica Microsystems – M80, Magnification camera 0.8X/Visual magnification 20X). b) Atacamite formations of light green vitreous colour between corrosion layers (Leica Microsystems – M80, Magnification camera 1.3X/Visual magnification 30X).

The microscopic observation, especially in fracture areas, ascertained, as well, the existence of unstable layers between the corrosion products, which show an off-white/whitish hue and which cause disruption of the material, surface detachments and segregation of the artefact (Figure 15).



**Figure 15.** Unstable off-white corrosion layers that cause disruption, flaking and segregation of the artefact.

These off-white phases are tin-rich and their formation is due to the process of decuprification or selective leaching of Cu, in which the copper ions are dissolved and removed from the metallic structure, while, at the same time, the tin in the inner part of the alloy is oxidized [23–26,28,42]. The quantity of copper that will leach from the metal's structure, will subsequently react with the anions contained in the soil (in our case chloride and carbonate ones) and will be deposited on the external surface of the artefact [3]. The reaction of the dissolved copper with chloride ions leads to the formation of copper trihydroxichlorides, which seriously undermine the integrity of artefacts made of copper alloys, by causing rashes of powdery texture [15,37].

On the basis of the microscopic observations and analyses that were conducted, the corrosion mechanism of the bronze lebes from the Phaleron Delta is apparently an outcome of the interaction of copper with chloride anions, which come from the burial environment. This process is known as “bronze disease” and is correlated to the action of active corrosion on copper alloys. The more the concentration of chloride and humidity in the burial soil is, the more intensive the corrosion becomes, and, in this particular case, the high water table of the area the lebes was found in, and its proximity to the sea, attest to the presence of these two corrosive factors. The development of the above mentioned phenomenon has led to the complete corrosion of the artefact under examination, as it has caused the dissolution of a considerable quantity of copper, which is the main component of its alloy, through the process of decuprification. The ongoing process a) of dissolution – re-deposition of copper and b) of the reaction of copper with chloride ions from the burial environment, has increased the thickness of the corroded artefact with the formation of porous and friable layers of corrosion products [24,26].

For the upcoming research of the bronze lebes, scheduled also is the examination of the corrosion layers by other analytical techniques, such as SEM/EDS. Moreover, its comparative study with other bronze artefacts from the same cemetery, on one hand, will contribute to the understanding of the state of preservation and the causes of corrosion, and, on the other hand, to the choice of interventions suitable for the treatment of active corrosion and their conservation/preservation.

## 5. Conclusions

The method to be chosen for the lifting of the finds from the excavation field is considered to be of vital importance for the preservation of sensitive materials, evidence and information. For this reason, in the case of the bronze lebes we adopted the practice of lifting it *en block* from the sandy soil of the Phaleron Delta. Furthermore, the mechanical cleaning that was performed, is the only method that can be applied for the removal of soil remains and the revival of the surface of a completely corroded bronze artefact. On the other hand, in order to suppress the advance of corrosion and preserve the bronze vase, it was deemed absolutely necessary to conduct interventions, both of active conservation treatments with the use of corrosion inhibitors, and of passive conservation treatments by regulating relative humidity and by keeping or storing it in suitable environmental conditions. Furthermore, the uniqueness of an artefact within the archaeological context it has been found in, often necessitates its reconstruction, with the aim, on one hand, to study it, and, on the other hand, to potentially include it in an exhibition. In the present case, the resetting of the bronze lebes was conducted on the principle of minimum possible intervention, safeguarding its authenticity and, at the same time, its structural adequacy, enabling, as well, the general public to read and absorb information on its use, shape and size.

The preliminary research on the condition of the lebes from the Phaleron Delta showed that this is a completely mineralized bronze artefact, without metal core. The main elements that compose the corrosion products are cuprite, malachite and atacamite, while no compounds of tin oxides were identified, since their detection is difficult by the XRD method. Microscopically, there were observed exceptionally unstable and friable corrosion areas that indicate decuprification of the alloy, an activity that is connected to the phenomenon of active corrosion, which is called "bronze disease". This form of corrosion is associated with the environment of the place where the bronze artefact was found, which is the Phaleron bay. The high level of humidity in the coastal burial environment, which, it should be noted, from time to time, in antiquity, was saturated with brackish waters and turned into a wetland, promoted the mobility of the copper from the alloy. Furthermore, the high concentration of chloride and the continual reactions of copper with chloride in the presence of humidity and oxygen caused the formation of copper trihydroxichlorides and have led to complete segregation of parts of the lebes. In conclusion, the water as a carrier of ions constitutes the principal corrosion factor for the bronze artefact, while, the depth level of the find and its proximity to the sea front, intensify the phenomenon of corrosion by accelerating the process of decuprification and active corrosion. The scheduled archaeometric analyses of the bronze lebes corrosion layers, including the SEM/EDS technique, and comparison of the corrosion with other bronze artefacts from the same excavation will contribute to further investigation of the state of preservation of the bronze finds that have been unearthed in the exceedingly aggressive environment of the Phaleron Delta cemetery, in Attica.

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