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A MULTI-ANALYTICAL APPROACH FOR THE TECHNOLOGY AND CONDITION ASSESSMENT OF BRONZE MIRRORS FROM THE ARCHAEOLOGICAL COLLECTION OF ANCIENT MESSENE, GREECE

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Abstract
Ancient Messene, located in the southern Peloponnese, is one of the most impressive and well-preserved cities of the Hellenistic-Roman period in Greece. Excavations have revealed a vast archaeological site with impressive buildings and tombs. The on-site museum houses a rich collection of copper alloy artifacts dating from the 4th century BC to the 5th century AD, including everyday objects related to the activities and customs of Messenian society. The paper presents research that employed a systematic multi-analytical approach, combining an archaeological (classification/typology) and a condition assessment with diagnostic techniques, to better understand the technological features and conservation needs of the collection. Specifically, the paper focuses on ten bronze mirrors from dated funerary contexts (3rd century BC to 1st century AD), representing four different archaeological types. These luxury items were associated with the upper class in ancient Messene. This combined approach links the mirrors in the metals collection of Ancient Messene with their archaeological context and technological features, providing insights into local and imported metalwork, the function of the objects, and their social significance within Messenian society. The technological features, such as manufacturing, decorative, and finishing techniques, were investigated using various examination and spectroscopic analytical techniques (X-ray radiography, pXRF and μXRF, and LIBS), mainly non-invasively. The evaluation of the results provided information on a) the frequency of occurrence and distribution of common and distinctive morphological and technological features (such as shape, form, plating, and decoration); b) identification of manufacturing and finishing technologies; c) conservation priorities based on condition assessment; d) dating issues and the use and function of the mirrors in relation to the everyday activities, customs, and habits in Messenian society; and e) technological evolution.

Keywords: *Hellenistic bronze mirrors; Classification; Technology and condition assessment; Conservation decision making; X-ray radiography; Spectroscopic techniques; Non-invasive analysis*

Introduction

This paper contributes to the knowledge of the technological development of metalworking in the Hellenistic Peloponnese through a systematic study of a group of copper-alloy mirrors from funerary monuments at the archaeological site of Ancient Messene in Greece.

There are no publications, to the best of the author's knowledge, on excavated material from metalworking sites of the Hellenistic period in the Peloponnese in Greece that provide information on technological development, trade and the circulation of products, or interactions in the manufacture and production of everyday-use metal artifacts. Few publications present such

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information, but these studies focus on a single artefact or a specific type of artefact of earlier periods [1]. This lack of information may be related to the destruction of significant Hellenistic production centers, such as Corinth, due to the Roman conquest and occupation. Alternatively, it may be related to the fact that the production of metal objects in other centers of the Peloponnese, such as Argos and Olympia, was connected to important sanctuaries that flourished from the Geometric to the Classical period.

Furthermore, the earliest and most relevant archaeological publications for this region and/or period [2-5] present their metal finds either in the form of simple inventory lists that do not provide information on their archaeological context since they present artifacts belonging to foreign museum collections or use a general classification system according to function and distinctive types. The basic morphological features that distinguish each type from others, or the frequency with which these features occur and their distribution within each distinctive type, are not provided. There is usually no reference to, or study of, the production technology of the objects (i.e., manufacturing techniques or alloy composition). Such information could help to identify and define technological characteristics, as well as the level of local production, which may vary from region to region.

Historical and archaeological context

Founded in 369 BC as the new capital of free and independent Messenia, the city of Messene played an important role in the historical and political events that took place after the dissolution of the state of Alexander the Great and during the Roman occupation [6]. As P. Themelis [7], professor and director of the excavations from 1986 to 2023, states, "the systematic scientific study of the buildings and finds has revealed the magnificent achievements of this social, political, and cultural center in the fields of urban planning, architecture, sculpture, ceramics, and minor arts."

A group of ten (10) mirrors, which is the focus of this study, has been excavated from important Hellenistic funerary monuments, located in the Gymnasium of Ancient Messene (K3, K5, K6 and K7). Each monument presents a different architectural style and number of burials and corresponds to a special case study [6-12] (Fig. 1).

Fig. 1. The Stadium and the Gymnasium of Ancient Messene after restoration and Funeral monument K3 after its restoration [13] (https://pacf.gr/etaireia-messiniakon-archaiologikon-spoudon-2/)

Only one mirror was excavated from a funerary monument of the Hellenistic period in the Eastern Road, belonging to six men and four women who probably fell during the capture of Messene by Navi of Sparta in 201 BC [11], [14].

The mirrors are mainly offerings for the deceased and provide significant information on the funerary customs and practices of the Hellenistic and Roman periods in Ancient Messene.

The group of mirrors

The selected sample includes 10 mirrors made of copper alloys. Casting is probably the basic manufacturing technique due to the presence of casting porosity and the thickness of the mirrors, and a lathe has been used to shape the surface, as indicated by the presence of concentric embossed and incised rings.

In Table 1 and Figure 2, the group of mirrors is presented with various information for the archaeological context and type, according to literature.

Table 1. The group of mirrors with information for the excavation context, the type, and a short description of the characteristic features (shape, surface formation, and condition) with literature references

Mirrors group	Excavation context	Type	Description
Mirror 1- M1	Hellenistic tomb, Arsinoe village [15]	‘Handle’ type	Simpler form of the 'Argive-Corinthian' type (Type ID) with incised decoration on the handle and small disc. Only representative example in the group of this early type [2], [16].
Mirror 2- M2	Hellenistic tomb, Arsinoe village [17]	Folded type IIIΓ lid	The lid completely covers the disc, as indicated by the shape of the lid periphery. Decoration with concentric and incised circles. [4]
Mirror 3- M3	Hellenistic tomb, Arsinoe village	Folded type	Decoration with plastic concentric circles and with an embossed chained spiral pattern on the edge of the disc.
Mirror 4- M4	Hellenistic tomb, Arsinoe village [18]	Folded type, IIIΓ, lid	The lid completely covers the disc, as indicated by the shape of the lid periphery. Decoration with concentric and incised circles [4].
Mirror 5- M5	Funerary monument K7, Stadium of Ancient Messene [8]	Folded type, IIIB	The circular disc has an acute thickening at the periphery [4].
Mirror 6- M6	Funerary monument K3, Stadium of Ancient Messene [8], [9]	Circular disk	Simple circular disc mounted on a base, undecorated [2], [5]. Highly reflective surface with extensive tarnishing.
Mirror 7-M7	Funerary monument K3, Stadium of Ancient Messene [8], [9]	Circular disk	Simple circular disc mounted on a base, undecorated [2], [5].
Mirror 8-M8	Funerary monument K6, Stadium of Ancient Messene [8]	Circular disk	Simple circular disc mounted on a base, decorated with a relief rosette leaf motif inscribed in double circles [2]. Highly reflective surface with extensive tarnishing.
Mirror 9- M9	Tomb 48, Eastern Road of Ancient Messene [6], [11], [14]	Circular disk	Simple circular disc mounted on a base, undecorated [2], [5], with extensive corrosion.
Mirror 10- M10	Funerary monument K5, Stadium of Ancient Messene [8], [9]	Rectangular type	Undecorated 'rectangular' type common to the Roman period. Retains the characteristic. Highly reflective surface with extensive tarnishing [2], [5].

Regarding their condition, the surface is mainly covered by dark and light green copper corrosion products and areas of black and silvery lustrous layers. The copper corrosion products form two different surfaces, one with a smooth and even surface (patina) and one with bulk layers and green pustules.

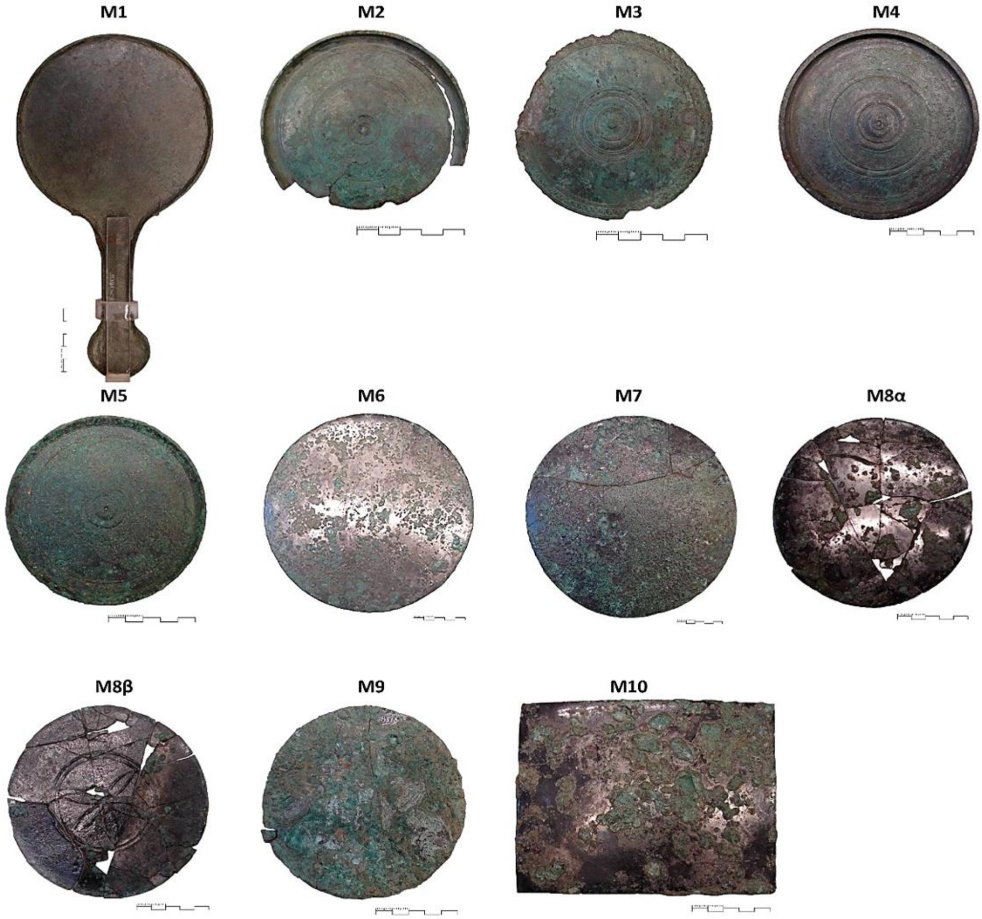

Fig. 2. The group of mirrors from the collection of Ancient Messene Museum [19]

Aim of the research

After the macroscopic examination, the different manufacturing and decorative features, as well as the presence of uneven surface corrosion and/or patination layers, were documented. The following questions were raised related to the possible alloy compositions to better understand the technology and condition of the artifacts:

1. Manufacturing: What is the composition of the alloys?

2. Decoration: What type of decoration and technique was used? Is there any surface decoration sealed under or within the corrosion layers?

3. Dating: Does the relative dating of the object based on the excavation context agree with the analytical examination based on the alloy composition?

4. Corrosion stratigraphy: Can the extent and thickness of the corrosion layers be measured? What is the nature/composition of the corrosion layers/products? Is there evidence of active corrosion? Are there cracks sealed in the corrosion layers? What is the original surface of the corroded mirrors?

To answer these questions, non-invasive scientific techniques were applied within the framework of an EU project, PROMET, one of the first EU projects to focus on developing compact instrumentation for on-site analysis while also investing in the development of multi-analytical and complementary methodologies for the systematic study of CH collections so as to overcome legal restrictions regarding sampling and transfer of objects out of laboratories and museums [20-24].

This paper describes the multi-analytical study of this campaign in Ancient Messene with the aim to design and implement an effective management policy and conservation approach. The study focused on objects of everyday use (tools and instruments, door and furniture fittings, toiletry artifacts, weapons, vessels, etc.). The methodological approach developed was applied to a selected representative sample of 873 iron and copper alloy objects from the site.

Specifically, the case study of mirrors is presented, as they are finds that are dated and retain their archaeological value, represent the stylistic evolution of this type in the Hellenistic and Roman periods, and come from burials of important families of ancient Messene.

The study involves a selection of ten mirrors with well-defined technological features and the application of scientific diagnostic techniques and statistical processing tools according to stylistic criteria. The aim is to address the following issues:
(a) frequency and distribution of common and distinctive features;
(b) manufacturing and finishing techniques;
(c) condition (stratigraphy and type of corrosion products) and conservation decision-making;
(d) dating issues and their use and function in relation to the daily activities, customs and traditions of ancient Messinian society;
(e) technological evolution for bronzes in the region.

This multidisciplinary approach aims to enhance both the understanding of the technological profile of a period and/or a site (manufacturing alloys and forming and decorative techniques) and the identification of the problems and needs associated with the preservation of the metal findings.

Materials and Methods

The technology and condition assessment methodological approach includes the following:

1) Classification and clustering into smaller and distinct groups based on technological/morphological features [25].

2) Examination of different technological/morphological features by visual inspection and classification of objects based on statistical analysis of the frequency of occurrence and distribution of these features (Burt frequency tables, classification trees, and frequency diagrams).

3) Application of mainly non-invasive, portable diagnostic techniques such as X-ray radiography, portable X-ray fluorescence (pXRF), micro-X-ray fluorescence (μXRF), and laser-induced breakdown spectroscopy (LIBS). These are used to determine the manufacturing technology (e.g., alloy composition, manufacturing processes, decorative and finishing techniques) and condition (e.g., corrosion products, corrosion stratigraphy, and residual metal core) of the objects. Objects and spots/areas for diagnostic examination were selected based on classification by technological/morphological features.

Classification and clustering

Two general principles were used in the classification and clustering process. Identity is established based on clearly identifiable features with a recurring appearance and their combination. In general, it is best to classify the material under study based on clear and easily identifiable features that can be obtained by simple visual observation [26], [27].

The classification of mirrors was based on the frequency of occurrence and distribution of intrinsic morphological features such as shape and extrinsic morphological features such as surface decoration and plating. Their presence indicates and/or implies the use of a specific manufacturing and processing technique.

This type of classification is referred to as a 'technology survey,' the aim of which is to study artifact types based on morphological (or technological) features and to classify them according to selected features [28], [29].

As ‘technology surveys’ use similar criteria to archaeological typologies, they should be compared with them and take archaeological information into account. The difference is that 'technology surveys' do not give names, and the classification types are described in terms of morphological features that distinguish one group from another, the presence or absence of which is important for the classification of an artifact into the given type.

The classification process used a combination of the principles of 'phenotypic' or morphological typology and functional taxonomy [26]. 'Phenotypic' or morphological typology involves types that can be identified by combinations of intrinsic features that create a group. The selection of features or types is made with the sole aim of description. Visible and distinct features such as size, shape, color, and decoration play an important role in the identification of types [26]. Taxonomy refers to the process of grouping discrete basic types into larger sets (clusters) or separating them into smaller types or both [30].

The classification was made by selecting intrinsic features (shape: circular/rectangular, disk periphery configuration, handle) and extrinsic features (decoration, plating), separating the mirrors by visual observation on the basis of these characteristics in smaller types, and using Burt frequency tables [28], classification trees, and pie charts presenting the frequency of occurrence and distribution of selected and distinctive features that separate the artifacts of the particular type into characteristic smaller types.

Diagnostic examination

A portable radiography system was used with the following elements [31]:

1.A second-hand military control unit and tube transformer head, X-Ray Apparatus 15 mA, Mobile-Portable, Stock No.-6-013-680, manufactured by Picker X-Ray Corp., Waite MFG. DIV., Cleveland, Ohio, USA.

2.A portable film processor Curix 60/CP1000, type 9462, 230V/50/60Hz, manufactured by Agfa-Gevaert N.V., Belgium.

The portable Millibeam XRF spectrometer consists of a Rh-anode side window low-power X-ray tube (50 kV, 1 mA, 75 μm Be window), a PIN X-ray detector (165 eV FWHM at Mn Kα, Amptek Inc.) with a 500-μm nominal crystal thickness, and a battery-powered MCA card. The spot of the excitation beam at the sample position is approximately 3 mm in diameter. The analysis of the metal alloys was performed at an operating high voltage of 40 kV [20]. The pXRF quantitative analysis is based on a theoretical model (Fundamental Parameter Approach) that correlates characteristic X-ray line intensities and concentrations through a set of well-defined non-linear equations [32].

The μXRF spectrometer head consists of an optical element (polycapillary lens, IfG), a laser pointer, and a color CCD camera for visual inspection of individual analysis areas. The spectrometer consists of a low-power, air-cooled Rh-anode X-ray tube and a silicon drift detector (145 eV FWHM at MnKa, Bruker-AXS). Three different stepper motors coupled to the spectrometer head allow its three-dimensional movement. Single-colored areas were selected and examined by line scans. 2D elemental mapping was then performed in selected areas characterized by intense local variations in both color and texture, exhibiting spatial resolution per analysis spot of about 80×80 μm^2 [33], [34].

The LIBS system used for the analysis is model LMNT-II, which consists of a hand-held probe containing the laser head, optics to guide, attenuate, and focus the laser beam on the sample, and an optical fiber to transmit the plasma plume emission to the spectrograph, which is housed in the main unit together with the laser power supply. The laser (passively Q-switched Nd:YAG) emits 8 ns pulses at 1064 nm with an energy of up to 15 mJ/pulse, which, when focused, probes a measurement spot of approximately 200 μm in diameter. The spectrograph (HR4000, Ocean Optics Inc.) covers the spectral range 270-650 nm with a spectral resolution of about 0.5 nm and uses a 3648-element CCD array detector [21]. LIBS ablates by successive pulses the selected corroded surfaces to the metal core, forming a crater with estimated dimensions of 120×120 μm^2, and it is characterized as a virtually non-destructive elemental technique [32], [35], [36].

A combined application of μXRF and LIBS using a single-mode analysis methodology was carried out on mirror M8 [33]. LIBS was first applied to remove material by successive pulses from the surface to the metal core, and after a certain number of pulses, μXRF mapping was performed in the ablated area, both providing the elemental intensities versus depth.

For pXRF analysis regarding the composition of the manufactured alloys, an area of 1 cm in diameter was selected where there was no decoration or plating. The soil deposits and the corrosion layers were removed with a scalpel and an electric-powered wheel at the level of the metal core, forming a 'cleaned' area to be used for the qualitative and quantitative measurement of the alloy and as a reference area for the surface measurements with μXRF and the stratigraphic measurements with LIBS.

Results

Classification and clustering

Figure 3 shows the classification of mirrors based on selected morphological/technological features, such as shape, disk circumference shape, presence of a handle, plating, and decoration, and the Burt Frequency Table (Table 2) shows the frequency of their distribution and occurrence. Each type is described by discrete morphological features formed by the application of a specific technique and/or process.

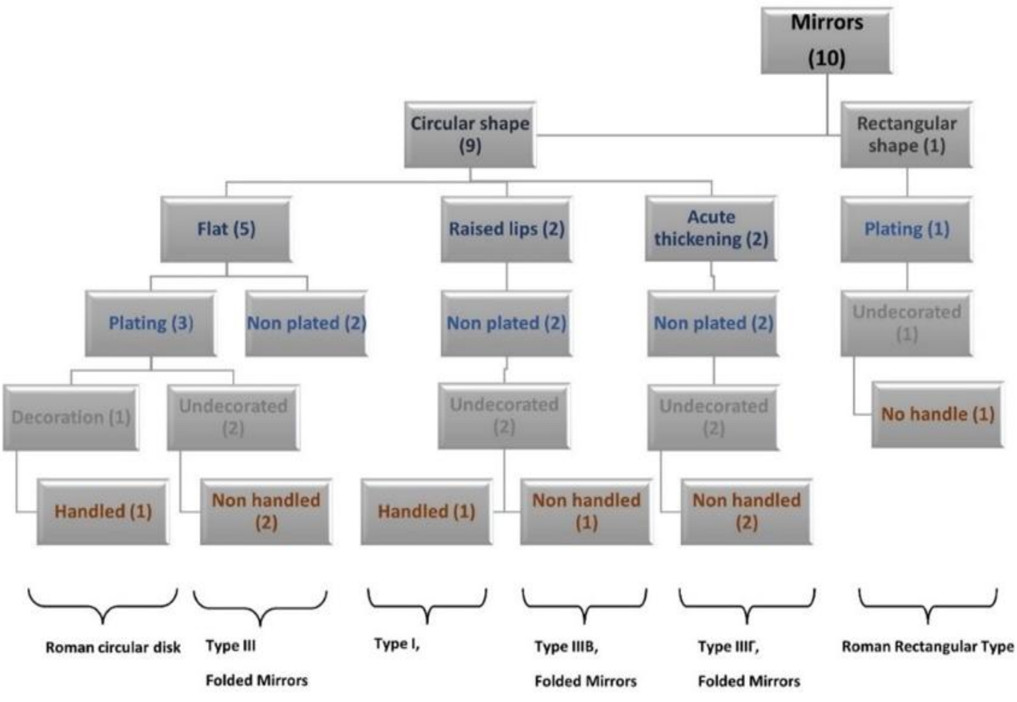

Fig. 3. Classification Dendrogram of the mirrors' sample [19]

The technological types that the dendrogram describes from the second separation level ('circular and rectangular shape') and onwards present the same characteristics as the archaeological typological classification of the mirrors, presented in relevant publications (Type IΔ, Type III with subtypes IIIB and IIIΓ, and Roman mirrors).

Table 2. Burt's frequency table of the mirrors' sample [19]

Mirrors			Shape				Handle		Plating		Decoration	
			Circular			Rectangular	Yes	No	Yes	No	Yes	No
			Flat	Raised lips	Acute thickening							
Shape	Circular	Flat	**5**	0	0	0	0	5	3	2	2	3
		Raised lips	/	**2**	0	0	0	2	0	2	2	0
		Acute thickening	/	/	**2**	0	1	1	0	2	2	0
	Rectangular		/	/	/	**1**	0	1	1	0	0	1
Handle	Yes		/	/	/	/	**1**	0	0	1	1	0
	No		/	/	/	/	/	**9**	4	5	5	4
Plating	Yes		/	/	/	/	/	/	**4**	0	1	3
	No		/	/	/	/	/	/	/	**6**	5	1
Decoration	Yes		/	/	/	/	/	/	//	/	**6**	0
	No		/	/	/	/	/	/	/	/	/	**4**

Technology

The radiographic results are presented in Figure 4 and summarized in Table 3, where the observation of specific features of the radiographs, such as the presence and extent of casting porosity, the shape of the disc circumference, the presence of a central pin hole, the representation of concentric circles, and the presence of white spots, correlated with literature references [41], [42], provided various direct information on the manufacturing process and indirect information on the qualitative composition of the cast alloys.

The coarse and granular texture observed in the radiographs (Fig. 3), apart from mirror 9, which is heavily corroded, and the thickness of the mirrors indicate that casting in an open mold is the main manufacturing technique [31], [41], and the use of copper alloys with tin and lead [43].

XRF analysis provided quantitative analytical results identifying copper (Cu), tin (Sn), and lead (Pb) in mirrors 2, 3, 6, 7, 8, 9, and 10. Iron (Fe), arsenic (As), and antimony (Sb) are present as trace elements at concentrations < 1% due to impurities or aggregates in the original ore. XRF results are summarized in Table 4 [19], [21] and described below.

Table 3. Technological features from the observation of radiographs

Mirror	Casting	Lathe	Forging	Amount of Sn*	Amount of Pb*
1/ Type I (Handle Type)	X		X		
2/ Type IIIΓ	X	X	X	-	-
3/ Type III	X	X			
4/ Type IIIΓ	X	X			
5/ Type IIIB	X	X		+	-
6/ Simple disk	X			+	+
7/ Simple disk	X			+	
8/ Simple disk	X	X		+	
9/ Simple disk	X			+	
10/ Rectangular type	X			+	

Where: * (+) indicates high Sn > 11% and (-) low < 9%.
** (+) indicates high Pb > 6% and (-) low < 3%.

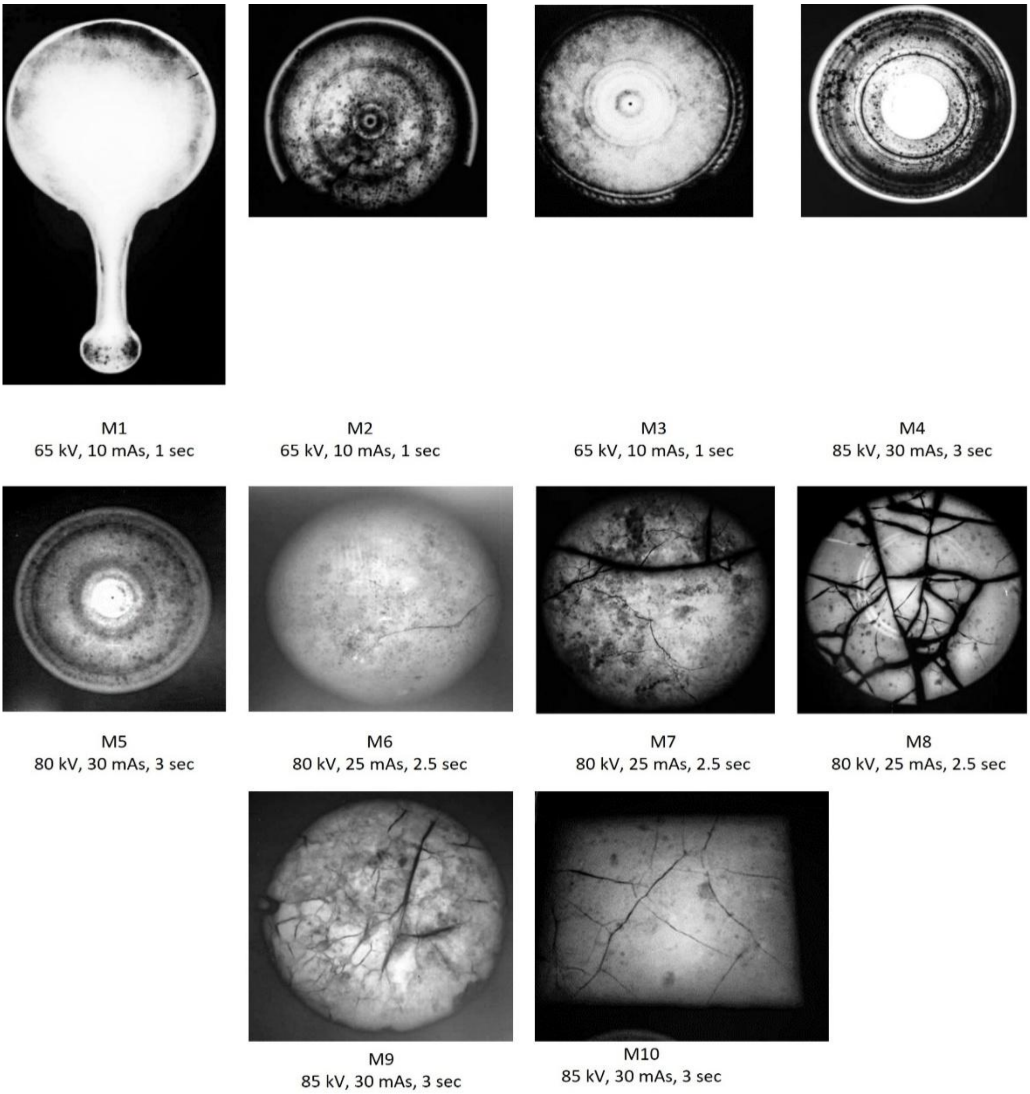

Fig. 4. Radiography images of the mirrors' samples. The general operating parameters are distance of the X-ray tube from the radiographic plate 75 cm, correction of the local line voltage to 70kV [19], [31]

Table 4. Elemental compositional results in wt.% by portable millibeam XRF spectrometer [19]

Mirror	Cu%	Sn%	Pb%	Fe%	As%	Sb%
1/ Type I (Handle Type)	89.2 (±0.3)	10.4 (±0.2)	0.3 (±0.1)	0.2 (±0.02)	<0.02	<0.15
2/ Type IIIГ	88.6 (±0.2)	6.6 (±0.2)	4.8 (±0.1)	0.1 (±0.05)	_	<0.14
3/ Type III	86.5 (±0.2)	9.8 (±0.2)	3.7 (±0.1)	0.04 (±0.01)	<0.06	<0.14
4/ Type IIIΓ	86.3 (±0.3)	12.3 (±0.2)	0.4 (±0.05)	1.0 (±0.04)	<0.09	<0.18
5/ Type IIIB	84.1 (±0.3)	15.2 (±0.2)	0.2 (±0.02)	0.4 (±0.02)	0.1 (±0.04)	<0.17
6/ Simple disk	70.2 (±0.3)	22.9 (±0.3)	6.8 (±0.02)	0.2 (±0.02)	_	<0.2
7/ Simple disk	68.2 (±0.3)	26.5 (±0.3)	5.1 (±0.02)	0.2 (±0.02)	<0.15	<0.22
8/ Simple disk	71.4 (±0.2)	23.1 (±0.3)	4.4 (±0.04)	0.7 (±0.04)	0.3 (±0.1)	<0.17
9/ Simple disk	69.4 (±0.3)	25.5 (±0.3)	4.9 (±0.02)	0.2 (±0.02)	_	<0.2
10/ Rectangular type	70.6 (±0.3)	26.3 (±0.3)	3.4 (±0.01)	0.1 (±0.01)	<0.03	<0.21

According to Figure 4 and Tables 3 and 4, the following information is documented:

Mirror 1 with handle (type IΔ) was made in a single casting from a typical Cu-Sn alloy (bronze) [42] with a negligible presence of lead. The Sn percentage is relatively high and is typical of mirrors whose reflection properties are accomplished via polishing of the surface of an unleaded copper-tin alloy [42]. The single casting is supported by the absence in the radiography of a sign of joining between the handle and the circular disc. The edges of the disc are forged, as evidenced by the thinning of the metal at the point of rotation. The surface decoration of the mirror, engraved and punched, is flat and preserved in the green corrosion patina.

Mirror 2 (type III lid) shows the characteristic coarse and granular texture of the casting, indicating the use of an alloy with a low tin content or a very low lead content. The presence of a central hole and symmetrical rings indicates the use of a lathe for forming. The vertical circumference is formed by forging, as indicated by the shape and the thickness. Mirror 3 (Type III lid) was formed and decorated in a lathe, as indicated by the central hole, the deep engraving of the plastic rings, and the decorative chain motif, which is clearly visible in the radiograph but not macroscopically due to surface corrosion. The XRF analysis of Mirror 2 (lid) and 3 showed that they were made of a typical Cu-Sn alloy with the presence of lead. The tin percentage is typical for Hellenistic mirrors. Hellenistic mirrors manufactured with this type of alloy, with a significant presence of lead, were tin plated [4].

Mirror 4 (type III lid) was also formed and decorated on a lathe, and its rings show intensive plasticity compared to mirrors 2 and 3. The thickness of the vertical circumference and the thickness of the disc at the junction suggest that the circumference was not formed by hammering. Mirror 5 (Type IIIB) was formed on a lathe, based on the form of the circumference and the presence of engraved and plastic concentric rings. The radiograph indicates the use of an alloy with a relatively high tin content. The presence of large casting pores indicates a minimal percentage of lead in the casting alloy [42], [43], [44]. The XRF analysis of Mirrors 4 and 5 showed that they were made of a typical Cu-Sn alloy, like Mirror 1, with a negligible amount of lead, explaining the increased porosity depicted on the radiographs.

Mirrors 6, 7, 8, 9, and 10 (Roman mirrors) show similar features: the characteristic texture of the casting (presence of pores) and the use of an alloy with a high tin content. Mirror 6 has intense white areas, indicating a higher percentage of lead in the alloy. Mirror 8, the only one with decoration, was shaped with a lathe and decorated with concentric rings, while the central decorative rosette must have been stamped (imprinted) on the mold. The radiograph of mirror 9 showed that the artifact has no decoration and no concentric circles, which usually decorate the discs. The XRF analysis of mirrors 6-10 showed that they were made of a copper alloy with high tin percentages (22.9-26.5%) and lead, representing the technology of 'high-tin bronze mirrors' known from the Han dynasty in China and very popular items during the Roman period. Their manufacture involves a surface enrichment process with tin. Studies [45], [46], [47] suggest that mirrors during the Roman period were made from copper alloys with high levels of tin and lead. By adjusting the thermal parameters during the casting process, a tin-enriched phase was developed, giving the mirror the reflective surface [48].

Analysis with μXRF was performed among different single-colored areas of mirrors 6 and 10, showing the variation of the mean elemental intensities of Sn-Lα, Cu-Kα, Pb-Lα, and Sn-Kα characteristic X-rays. The elemental intensities have been normalized to the corresponding ones measured on a pre-cleaned area. The measurements of each color were obtained by means of linear scans that covered an overall 10 mm distance with a 500 μm step size. The silverish and black areas are characterized by an increase of the mean elemental intensities of Sn-Kα and Sn-Lα characteristic X-rays compared with the clean area, corresponding to the metal core (Fig. 5). These results suggest the presence of a tin enrichment process of surface layers.

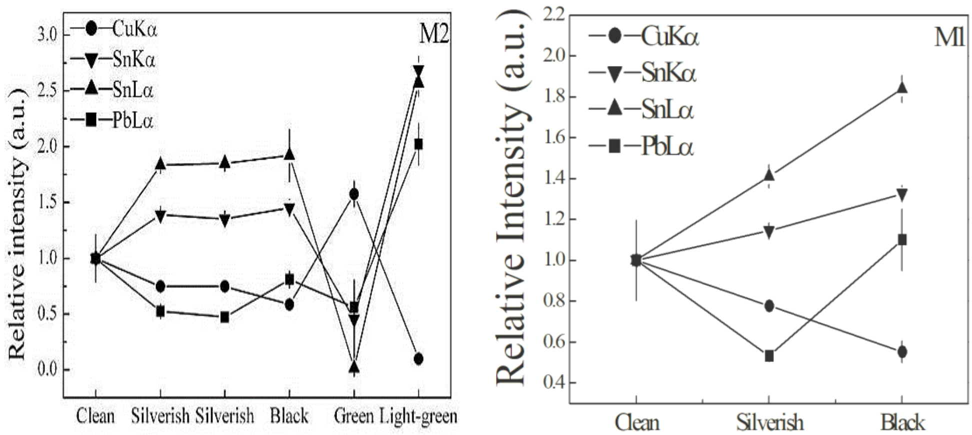

Fig. 5. Linear scans of different single-colored areas on mirror M6 (left) and M10 (right) [19]

Condition assessment

The radiographic images, the μXRF linear and area scans, and LIBS stratigraphic analysis show the following:

- For Mirror 1, the radiograph revealed small internal cracks sealed beneath the corrosion layers (see Fig. 4, M1). The surface is uniformly covered with a smooth, even 'patina' of green corrosion products, as well as areas of red corrosion products, which are most likely composed of cuprite. Visual and microscopic examinations were performed on the corrosion products due to the presence of this uniform 'noble' patina, probably with cuprite and malachite formation.

- For Mirror 2, the radiograph revealed areas near the edges and within the missing section where the metal core was partially preserved (see Fig. 4, M2). Microscopic observation indicated the presence of cuprite, dense and even green corrosion products, probably malachite, and elements from the burial environment.

- For Mirror 3 the radiograph indicated areas, particularly near the edges of the mirror, where the metal core is partially preserved (see Fig. 4, M3). Microscopic observation indicated the presence of cuprite and dense and even green corrosion products.

- Mirror 4 retains a shiny and smooth 'black' surface layer, corresponding to the first stage of corrosion of the polished surface, due to the formation of solid tin oxides during the burial of the object [49].

- For Mirror 5, the radiograph revealed a thin, radial crack extending from the center to the periphery. The surface is uniformly covered with an even, smooth 'patina' of black and green corrosion products. Microscopic observation indicated the presence of cuprite and dense and even green corrosion products.

- For Mirror 6 the μXRF results of 'linear' (Fig. 5) and 'area' (Fig 6) scans for the 'black' area show no clear differentiation from the 'silver' area, suggesting that the tarnish represents a first micromolecular corrosion layer on the tin-enriched surface. In Figure 6, hot color areas represent higher intensities of the respective characteristic X-ray lines. The differentiation of cold/hot colors among the individual elemental graphs evidences a rather inhomogeneous distribution of different corrosion products based on the corresponding elements. The pale green areas characterized by a significant increase in PbLα intensity and a dramatic decrease in CuKα intensity may represent lead corrosion products and a selective decuprification process [50].

The presence iron can be explained by contamination from the burial environment. Finally, in the green areas, the increase in CuKa intensity and the absence of chlorine or sulfur suggest that a copper carbonate is the main corrosion product, confirmed by XRD analysis. According to the literature, the corrosion products of alloys with high tin and lead contents are characterized by a complex microchemical structure [51-58], where a surface enriched in tin oxides due to corrosion may be present, as well as lead globules due to selective corrosion, and finally, iron and quartz from soil contamination.

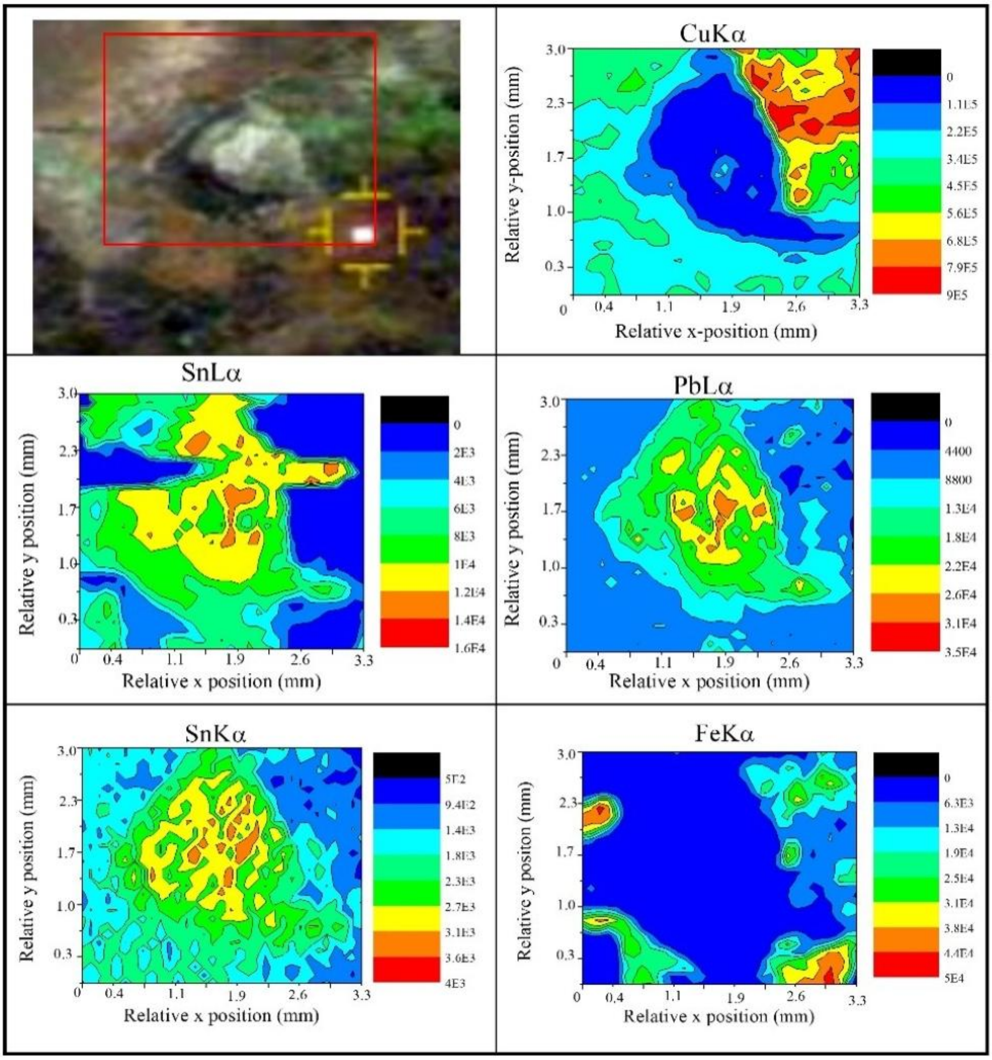

Fig. 6. Area X-ray intensity maps with μXRF that indicate the variation of the elemental content in a selected area of M6. The scanned area is 3×3 mm². The step size used was 100 μm [21]

-For Mirror 7, the radiograph revealed a network of cracks sealed beneath the corrosion layers and areas near the edges where the metal core was partially preserved. It also revealed evidence of a former conservation treatment involving the adhesion of detached fragments. Visual observation (macro- and micro-) revealed areas with cuprite and smooth green corrosion products, probably malachite. It is evident that the cuprite forms an initial micromolecular corrosion layer in direct contact with the metal core [53-58] in areas where the plating is not maintained, and then, in a second phase, malachite is formed due to interaction with the burial environment. The surface green corrosion layers also include deposits from the soil. Plating can be seen by macroscopic observation in isolated areas where a 'silvery' layer is visible. The 'black' areas correspond to corrosion products, probably solid tin oxides (cassiterite) [59], representing the first stage of alteration of the tin-enriched mirror surface.

- For Mirror 8, according to Kantarelou et al. 2007, the spectra obtained by LIBS and μXRF (Fig. 7) show the same elemental profile for the alloy elements contained either in the metal core or in the corrosion layers. The elements Cu, Pb, and Sn were determined by both techniques. A rather superficial or inhomogeneous presence of Ca in the 'black' patina was detected only by the LIBS technique, probably due to soil contamination.

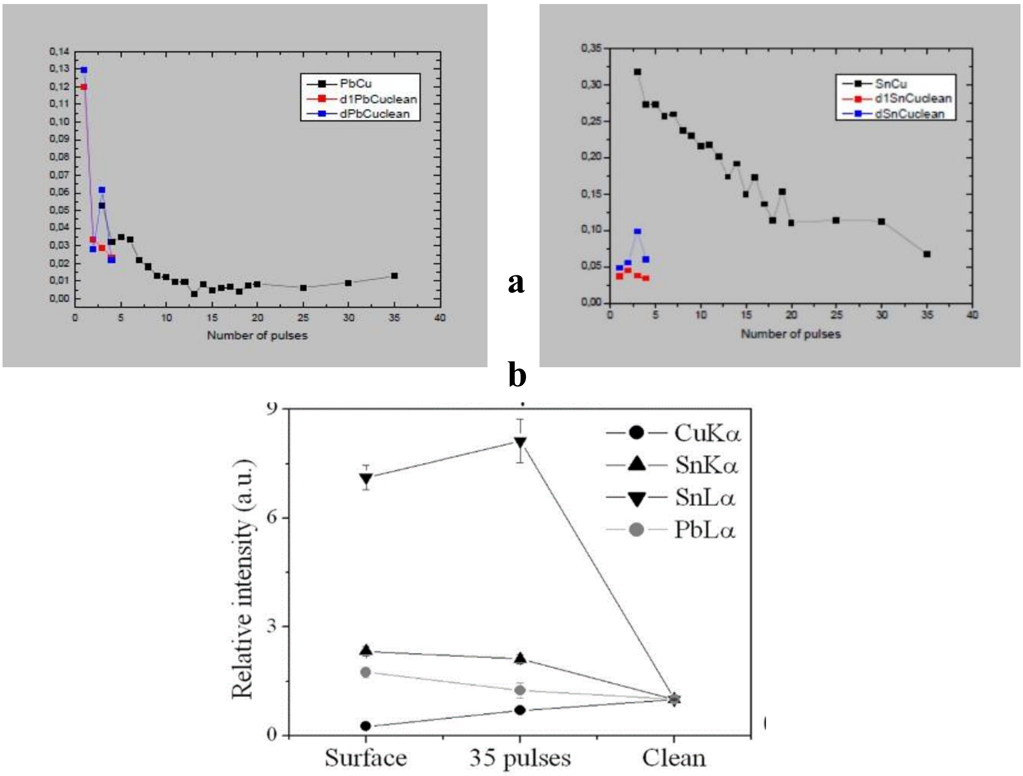

Fig. 7. (a) LIBS results from the analysis of the lustrous 'black' surface of Mirror 8, presenting the variation of the intensity of the Sn/Cu ratio and Pb/Cu, respectively, versus depth in comparison with two clean areas corresponding to the metallic core, and (b) Variation of the elemental intensities of Sn-La, Cu-Ka, Pb-La, and Sn-Ka characteristic X-ray lines between different monochromatic regions of the mirror surface, correlated with the LIBS results after 35 pulses [33]

The combination of μXRF and LIBS results from the analysis of the 'black' patina, where LIBS spectra were obtained on a spot area evaporated with 35 consecutive pulses, followed by mapping of the area by μXRF, showed that even after 35 pulses, a Sn-enriched corrosion layer remains, while the Cu intensity has increased relative to the surface. The relative intensities of Sn/Cu and Pb/Cu in the LIBS spectra measured for a certain number of pulses in the "black" patina gradually correspond to the ratios obtained from the analysis of the metal core, confirming the Sn surface enrichment and the processes of decuprification and lead leaching throughout the depth of the corrosion layers. After 10 pulses, the presence of Pb is minimal.

The 'black' patina layer showed an enriched Sn concentration compared to the metal core, which gradually decreased from its maximum surface value to a minimum at the bottom of the LIBS crater. Cu showed a significant decrease in the corrosion layers, with its concentration gradually increasing with depth.

It is clear from these observations that the 'silver' and 'black' areas are characterized by Sn enrichment due to the manufacturing process and the formation of a solid layer of tin oxides as the first stage of alteration of the reflective surface. The formation of lead corrosion products on the surface is documented, accompanied by a selective decuprification process.

-For Mirror 9, the radiographic image (see Fig. 4, M9) revealed an extensive network of cracks covered by layers of corrosion and thick soil deposits, as well as areas where the metal core is partially preserved. Microscopic observation of the corrosion layers indicated soil depositions and smooth green corrosion products.

- For Mirror 10, the μXRF analysis (Fig. 5) shows that the areas of tarnishing are characterized by an increase in the characteristic X-ray intensities of tin compared to the 'silvery' areas, as well as an increase in the characteristic X-ray intensity of lead. These correspond to the first stage of alteration of the 'silver' area where coarse tin corrosion products are formed during burial and are accompanied by lead corrosion products.

The presence of calcium throughout the depth of the corrosion stratigraphy is attributed to soil deposits from the burial environment and their adsorption in the corrosion layers. Microscopic observation indicated the presence of cuprite and dense and even green corrosion products.

Discussion

The results from the implementation of the multi-analytical approach provided direct and indirect information related to the technology (materials and techniques), condition (corrosion stratigraphy and products), conservation needs, value of the mirrors (dating, use, and authenticity), and their relation to the technological evolution of the site.

Classification and clustering

The mirrors are divided into four types according to their archaeological typology: Type IΔ (with handle—the 'Argive-Corinthian' type), Types IIIB and IIIΓ of the folded mirror type, the single disc type, and the rectangular mirror type.

The classification of the group of mirrors determined the occurrence and distribution of discrete morphological features in the sample.

Nine (9) of the mirrors are circular. These are divided into characteristic subgroups: four (4) are simple flat discs; two (2) are circular discs with raised lips at right angles; and two (2) are circular discs with sharply thickened edges. One (1) of these has a handle. Nine mirrors are handle-less. Six (6) mirrors show no signs of surface plating, while four (4) retain a highly reflective, silvery surface of considerable thickness. Six (6) mirrors are plain with no surface decoration, such as engraving, embossing, repoussé, or punching.

Technology

The mirrors are made of bronze alloys, with the main alloying elements copper and tin. Tin, depending on its percentage, forms three characteristic groups of alloys (all compositions in wt. %):

1. Typical bronzes with a tin content of up to 10% (Mirrors 2 and 3).

2. Bronzes with a tin content of 10-15% (Mirrors 1, 4, and 5).
3. Bronzes with tin content > 22.5% (Mirrors 6-10).

The third element is lead. Less than 2.5% is considered incidental and may be due to the original ore used (Mirrors 1, 4, and 5). Above 2.5%, it is a deliberate addition and improves the ductility of the alloy (Mirrors 2 and 3, 6-10).

The mirrors are all made by the open-mold casting technique; their decoration is mainly done by lathe to form plastic and incised rings, and only one mirror (M1) is decorated by the punched and incised technique. In the case of mirrors in which the circular disc has a rim (M1 and M5) or in the case of folding mirror lids (M2 and M4) with a vertical rim, the shaping is mainly done by forging.

There are three ways to obtain the reflective surface with tin. By plating (M2 and M3), by polishing the surface of an unleaded alloy (M1, M4, and M5), and by surface enrichment treatment (M6-10)

Combining the compositional results of the alloys and the manufacturing and forming techniques, it appears that there is a relationship between them that highlights technological issues.

Mirrors with a low, almost zero, lead content are easy to polish to produce the mirror surface and to form on a lathe [42]. Mirrors 4 and 5 show greater plasticity in the rings and deeper etchings. In contrast, mirrors such as 2 and 3 with a lead content of 3.8-4.7% are lathe-formed, but the rings and etchings are more superficial.

Mirrors with a low tin content, such as 2, or a minimal lead content, such as 4 and 5, present more pores, which are also visible macroscopically.

Mirrors with a high tin content produce an outer surface of considerable thickness, enriched with tin.

Condition assessment

Based on the diagnostic study of corrosion stratigraphy and the identification of corrosion products in the samples, it is evident that the formation and composition of the corrosion layers are related to manufacturing technology and the composition of the alloys. The corrosion products are stable, consisting of copper oxides and carbonates, lead carbonates, and tin oxides. Tin enrichment, decuprification, and lead leaching characterize the corrosion stratigraphy from the metal core to the surface corrosion layers [50-60]. Elements from the soil of the burial environment are present throughout the corrosion layers and can be identified even in contact with the metal core.

Considering the results of the condition assessment with examination and spectroscopic analytical techniques, mainly non-invasive, and the exhibition needs of the museum, the mirrors should be treated as they represent the typology of this group through four centuries and are impressive objects for display according to their technological characteristics and archaeological value.

The aim of a proper treatment procedure is to preserve passive and stable corrosion products (such as cuprite and malachite) and to produce a smooth, uniform surface that preserves the archaeological value and surface-forming techniques. Since no chloride compounds were detected with XRF and μXRF, the proposed conservation approach is cleaning by mild and controlled mechanical methods with magnifying lenses and/or under the stereomicroscope to remove soil deposits and bulky and powdery products, with the possibility of applying solvent-based gels selectively to facilitate mechanical removal.

Archaeological information: dating, use and function

Finally, interesting information was obtained in relation to the archaeological value (dating and authenticity) and the use and function of the mirrors in relation to everyday activities, customs, and habits of the Messenian society.

By correlating literature references [42], pXRF elemental composition results, and dating of the mirrors based on the excavation context, a sequence emerges that shows a chronological evolution and a clear distinction between the Hellenistic and Roman periods and clarifies the relative dating, since mirrors 1-4 do not retain the information of the excavation context, and mirrors 5-8 and 10 come from funerary monuments used from the 2nd century BC to the 2nd century AD. This information is presented in Table 5. The first line, labeled 'DATING,' indicates the time period during which the mirrors were manufactured and used, as determined by their alloy composition and, where applicable, the archaeological context. In the Hellenistic period, two categories of bronze alloys, with or without lead, characterize the production of mirrors. In the Roman period, bronze alloys with a high percentage of tin characterize the production of mirrors.

Table 5. Presentation of mirrors based on their dating (type and archaeological environment) and the chronological evolution of the alloys

DATING	**3rd BC**	**3rd-2nd BC**	**2nd BC**	**1st BC**	**1st BC-1st AD**	**1st AD**
MIRRORS	M2- Type IIIΓ	M1- Type IΔ	M9- Roman type	M5- Type IIIB	M6- Roman type	M10-Roman type
	M3- Type III				M7- Roman type	
	M4- Type IIIΓ				M8- Roman type	
ALLOYS	M2 Leaded bronze	Bronze	High-tin bronze	Bronze	High-tin bronze	High-tin bronze
	M3 Leaded bronze					
	M4- Bronze					

Mirrors 2, 3, and 4 date from the 3rd century BC. They belong to Type III, which flourished until the middle of the 3rd century BC, and they are made of alloys that are characteristic of the Hellenistic period. According to the chronological study of the alloys shown in Craddock's publication, mirrors 2 and 3 can be dated to an earlier period in the 3rd century BC than mirror 4.

Mirror 1 dates from the 2nd–3rd century BC. It belongs to Type I, the earliest type, which was in use until late antiquity and is made of an alloy typical of the Hellenistic period.

Mirror 9 dates from the 2nd century BC. Due to its high tin content, it is classified as a Roman mirror and may represent an early introduction, as mirrors of this type first appeared in the Roman world in the 2nd century BC, probably originating from an Italian center. Therefore, the mirror could be dated to the end of the 2nd century BC.

Mirror 5 dates from the 1st century BC. It belongs to Type IIIB and is made of an alloy typical of the Hellenistic period. Compared to the other folded mirrors in the group, it is a late example, but it may have been manufactured earlier. It has been dated based on its archaeological context, in which it had secondary use as an offering following its primary use as a toiletry item.

Mirrors 6, 7, and 8 date from the Roman period of Messene and are made of the high-tin bronze alloys that are typical of Roman mirrors.

Mirror 10 dates from the early 1st century AD and has similar characteristics.

All the mirrors were found in Hellenistic and Roman tombs. They were placed as offerings, probably for dead women, as literature states that from the 6th century BC and during the Hellenistic and Roman periods, they were toiletry objects of daily use for women [2], [61].

Mirrors 1-4 are from Hellenistic burials that have been disturbed by previous investigations, and there is no evidence of their archaeological context.

Mirrors 5-8 and 10 come from burials in the Stadium-Gymnasium area, belonging to prominent Messenian and Roman families (such as members of the families of Aristomenes Dionysius and Theon Nikiratos in tomb K3), and Mirror 9 comes from tomb 48 on the Eastern Road.

All these artifacts were found in places where they had a second use, that of a funerary offering, a personal object that accompanied the deceased woman to continue her adornment in the underworld.

Their original use was as mirrors for daily grooming. Judging by the types represented in the selected sample, there seems to be a tendency and choice of holders towards an object that is simple, utilitarian, and easy to carry. There is also a preference for circular and more traditional shapes, although rectangular mirrors have been found in Etruscan houses in southern Italy since the 4th century BC [56]. The finds do not show elaborate decoration and are simple examples of the type they represent. The presence of four simple discs indicates this tendency. It could be said that the everyday life of the local society was characterized by austerity, practicality, and simplicity. The tendencies of projection and display to stimulate 'national' sentiments and to gain recognition are through public monumental architecture of grandiose building projects and large-scale sculptures and inscribed monuments. From the 1st century BC, there is a trend towards more decorative and/or luxurious objects. This change is due to the penetration and peaceful settlement of foreign elements, initially of Roman origin; their assimilation by local society; and their peaceful coexistence over a long period [19]. As Themelis says, "Messene had growth, social and economic, thanks to the long Pax Romana" [62].

However, the small number of mirrors found and the fact that they come mainly from rich burials of members of the upper classes suggest that for the women of ancient Messene, the mirror was not an everyday utilitarian object produced in local workshops but a luxury item, the possession of which probably marked the social status of the owner and conferred prestige. Obviously, to obtain it, one would have ordered it from a Peloponnesian workshop outside ancient Messene or from a Roman workshop. For this reason, it was considered a symbolic object that represented the class, origin, and social level of its owner and therefore followed her into the afterlife.

A primary distinction could be made between imported and domestic products [19]. Mirror 1 belongs to Type IΔ, which has also been described as 'Peloponnesian' or 'Argo-Corinthian,' since Argos and Corinth are regarded as major production centers from the beginning of the 6th century BC. It is probably an imported object or an object made in Ancient Messene and influenced by another Peloponnesian center. Mirrors 2-5 belong to type III of folded mirrors. In particular, type IIIB (5) and IIIΓ (2 and 4) were mainly made in Corinth. So, like mirror 1, they are either imported works, probably from a Corinthian workshop, or domestic works under the influence of Corinthian workshops. Mirrors 6-10 belong to the type of Roman high-tin bronze mirrors and were probably imported from a Roman production center.

However, all these hypotheses could be supplemented by the suggestion of migration and working in a local workshop of a craftsman from Corinth or from a center in the Roman region. This feature of migration for work by craftsmen is, moreover, a characteristic of the organization of production in the Hellenistic period.

In any case, their study is important for our understanding of Hellenistic bronze objects in the Peloponnese. Important production centers such as Corinth were destroyed during the Roman invasion, so this study provides insights into metalworking and local production organization in the Hellenistic period.

Conclusions

The results and advantages of applying a systematic multi-analytical approach for the study of mirrors can be summarized as follows:

a) The classification process applied can be characterized as hierarchical, since the group of mirrors is divided into successive discrete subgroups by a continuous process of bilateral division based on the morphological features that allow distinction.

As a classification system and given that the selected material has not been previously studied and may be enriched after new excavations, it is an open and dynamic system, offering the possibility of including new features and consequently new types or subtypes, as well as revising and/or redefining old ones.

The ancient Messene collection contained more mirrors, but these were not selected because they were not intact. The excavation of the site is ongoing.

b) The analysis of the composition of the alloys and the determination of shaping and forming techniques used in the production of the mirrors indicates a very good knowledge of the properties of copper alloys and the use of the secondary alloying elements, tin and lead, in order to decorate and/or plate the mirrors and improve a number of properties relating to the ductility, toughness, elasticity, and workability of the alloys and the production of objects with different surface characteristics.

c) The evaluation of the condition can highlight problems and needs and provide information for the design of an appropriate integrated conservation and protection program. The Ancient Messene collection had more mirrors, but they were not selected, as they were not preserved intact. Only five small fragments were preserved from the disks, which had dimensions of around 5 cm^2. Their fragmentary preservation does not help to identify and attribute them to a specific type.

d) This study has demonstrated the analytical capabilities of portable, mainly non-invasive techniques as a diagnostic and characterization tool for initial assessments and *in-situ* analysis, overcoming problems related to sampling and authorization licenses. In particular, the μXRF technique, which uses linear and area scans, provides analytical information on the surface elemental distribution. This technique can be used for non-destructive initial screening analysis to identify corrosion mechanisms and products, as well as manufacturing techniques. LIBS provided multi-element analysis results within seconds. It does not require sample preparation, and although it is characterized as micro-destructive, it offers close-to-microscopic spatial resolution and the possibility of in-depth profile analysis. Combining μXRF and LIBS was highly complementary, maximizing the information obtained when analyzing an inhomogeneous corrosion layer and determining the surface and in-depth distribution of corrosion-related elements. This study has demonstrated that mobile instrumentation can offer versatility and enable the analysis of a broad variety of objects in different locations, offering information for the design and implementation of a conservation plan and overcoming the need for sampling, which could compromise the noble patina that most mirrors preserve.

e) In conclusion, given that Ancient Messene is the only archaeological park in Greece that is open to the public and the best-preserved Hellenistic site in the Peloponnese, it is important to study and publish the everyday objects (the 'Minor' Objects as they are classified in archaeological catalogues) found there. Currently, these objects are being 'lost' due to the priority given to activities related to the study, conservation, and restoration of monumental structures, sculptures, and epigraphic material and are kept in storage. However, studying these objects systematically sheds light on aspects of everyday public and private life, as well as the technological development of the site.

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