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Abstract

Two metal plaques and a cock statuette belonging to a private collection and stylistically consistent with the Royal Art of Benin (Nigeria) were investigated in order to verify their authenticity. The characterization of alloys and patinas were carried out by inductively coupled plasma mass spectrometry (ICP-MS), optical microscopy (OM), scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS), and X-Ray diffraction spectrometry (XRD). Furthermore, thermal ionisation mass spectrometry (TIMS) was used to assess the abundances of lead isotopes and to attempt a dating by the measurement of 210Pb/204Pb ratio. The results showed that all three artefacts were mainly composed of low lead-brass alloys, with relatively high concentrations of zinc, antimony, cadmium and aluminum in the solid copper solution. Microstructures were mostly dendritic, typical of as-cast brasses, and characterized by recrystallized non-homogeneous twinned grains in areas corresponding to surface decorations, probably due to multiple hammering steps followed by partial annealing treatments. The matrix was composed of a cored α-Cu solid solution together with non-metallic inclusions, lead globules and Sn-rich precipitates in interdendritic spaces. On the surface of all metalworks, both copper and zinc oxides, a non-continuous layer of sulphur-containing contaminants and chloride-containing compounds, were identified. The lead isotope results were consistent with brasses produced shortly before or after 1900 A.D. Overall, the data obtained by different techniques supported the hypothesis that the three artefacts were not authentic.

Keywords	Benin brass, authentication, ICP-MS, TIMS, 210Pb/204Pb ratio
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To the Editors of
SPECTROCHIMICA ACTA PART B:
ATOMIC SPECTROSCOPY

Object: Revision of manuscript SAB_2016_30

Dear Sirs,

Thank you very much for your mail and for kindly providing comments and/or suggestions on our manuscript (SAB_2016_30). We carefully amended the manuscript according to the suggestions provided and enclose a detailed answer to the Editors' and Reviewers' comments. We hope now that the manuscript is suitable for publication on your Journal.

Best regards,

Elettra Fabbri, PhD
Corresponding author

Department of Engineering
University of Ferrara, Ferrara (Italy)

Ferrara, February 5th, 2017

ANSWERS TO THE EDITORS AND REVIEWERS:

EDITORS

1- In the revision of the manuscript please keep in mind that the scope of Spectrochimica Acta Part B is analytical atomic spectroscopy. Emphasize the spectroscopic aspects of the study. See comments of reviewer #1 regarding 210 Pb.

Following the Editors' suggestions, we have thoroughly revised the manuscript, emphasizing the spectroscopic aspects of the study and taking into account the suggestions of Reviewer #1 regarding ^{210}Pb.

2 - Please note that Elsevier accepts electronic supplementary material for online publication with the article. Several figures and/or tables may be considered for publication in an appendix. For publication of supplementary content, please check the Guide for Authors and recent issues of SAB. In the text please refer to figures in the appendix as Fig. S1 (Appendix), Table S1 (Appendix), etc.. After the Acknowledgement the following text should be inserted 'Appendix A. Supplementary data' and 'Supplementary data to this article can be found online at doi:...'. The reader can access the data online with the article.

Following the Editors' suggestions, we removed Table 3. We reported and discussed the corresponding results in the *3.4 Comparing ICP-MS and ^{210}Pb analyses* subsection.

3 - As per journal instruction, a maximum of five (5) keywords, using American spelling and avoiding general and plural terms and multiple concepts (avoid, for example, 'and', 'of'), should be provided. Please check.

Following the Editors' suggestions, we revised the keywords.

4 - Please check and correct the highlights. Highlights are a short collection of bullet points that convey the core findings and provide readers with a quick textual overview of the article. These three to five bullet points describe the essence of the research (e.g. results or conclusions) and highlight what is distinctive about it. Specifications: * Include 3 to 5 highlights. * There should be a maximum of 85 characters, including spaces, per highlight. * Only the core results of the paper should be covered.

According to the Editors' suggestions, we corrected the highlights.

5 - Please check and correct the tables. In Table 1, define "n.d.". Include the lower limit of determination. Provide information on uncertainties (plus definition of what is reported, e.g. standard deviation and number of replicates; confidence interval). Table 3: define uncertainties.

Following the Editors' suggestions, we checked and corrected the tables. In detail, "n.d." was defined in Table 1, also providing information on the lower limits of determination and uncertainties, plus their definition. The lower limits of determination and the definition of uncertainties associated with ^{210}Pb/ ^{204}Pb measurements was provided in the *Materials and methods* section.

6 - Please check and correct the figures.
Fig. 1: Provide information on dimensions or include scale.
Figs. 2-4: Provide readable scale (use larger font size).
Fig. 5: Use different symbols to improve readability in black and white printing. Check axis title and units. Use uniform notation and larger font size.

According to the Editors' suggestions, we revised and amended all figures.

7 - It is a condition of publication that all manuscripts must be written in clear and grammatically correct American or British English (but not a mixture of both). Please check and correct language. Ask help from a native English colleague or ask professional advice.

Following the Editors' suggestions, we revised all the manuscript with the help of a native American colleague.

REVIEWER #1

I'm not sure, if the problem is the language or a general misunderstanding of the Pb210 methodology. You wrote:
Dating assumptions of the metal objects are ascertained by the detection of this isotope: the absence of it could indicate that the artefact was produced in the last 100 years [23].

We thank the Reviewer for his/her relevant comment and accordingly amended the sentence as follows:

"Dating of metal objects is based on the detection of this isotope: its presence indicates that the artefact was produced in the last 100 years [24]."

The contrary is the case. The absence of the peak has no indication at all (as you mentioned later in the text: Recycling or use of very pure materials means even new material shows no peak). If the peak is present, for one of the metallic components an age below 100 years can be assumed.
In the conclusion you mention, that the detected lead and other points rise suspicion about authenticity.

The misunderstanding is probably due to the above mentioned sentence. If a peak of ^{210}Pb is detected, an age below 100 years can be assumed for a metallic object, thus the absence of ^{210}Pb may indicate an artefact older than a century. However, as remarked by the Reviewer, no detectable value of ^{210}Pb does not prove authenticity because artefacts could be manufactured in modern times using scrap and/or old stocked metals.

For the discussion you should mention, that there is as a matter of principle no proof for authenticity. Unfortunately, I can't find a date for the objects only from stylistic evidence. You mention different approaches, but you don't apply them to your objects. The given possible date range (Style and manufacturing process consistent with Benin art (1440-1897 A.D.) is very broad and made it nearly impossible to separate fake from original.
If stylistic dating is 1800 or earlier one can safely assume a fake. Later than 1800 until 1850 or so it is not clear and newer means no strong discrepancy to the analysis Maybe a metal with a high Pb210 content was used.
Please add a stylistic date to give a meaning to your later discussions and conclusions.

Following the Reviewer' suggestions, we reported the different approaches we applied for dating on the basis of stylistic evidences, such as iconography and/or quality of the castings. It is known that a modern replica can be detected based on a wrong iconography. The stylistic features highlighted in the text are similar to those ascribed to most Benin objects produced during the sixteenth-seventeenth century. However, in the studied artefacts one aspect raised suspicion about the production period, i.e. the "hierarchical proportions" different from the key features of Benin art. Accordingly, we were not able to establish a reliable date for the analyzed objects.

More specific remarks:
please check grammar and wording e.g.:
…state of conservation were reported
his calculations were too old by about ... I don't think the calculation were old, but the results were off.
The name of the cited author is Pernicka (wrong at different locations)

According to the Reviewer' suggestions, we carefully checked and amended the manuscript.

Please rewrite the part about Pb210 and be careful to make clear, what absence and present of the Pb210 peak means.

Following the Reviewer' suggestions, we rewrote the part about ^{210}Pb, including a more detailed explanation of the meaning of absence and presence of the ^{210}Pb peak.

For table 1 and 2 please give uncertainties of the measurements.

According to the Reviewer' suggestions, we included uncertainties of the measurements in Table 1 and 2.

At the end a principle remark. The provenance information: "two metal plaques and a cock statuette belonging to a private collection" is not sufficient.

According to the private collector, the artefacts were purchased in West Africa. Unfortunately, no other information was available on the origin of the objects under investigation.

Additionally, it remains unclear, why this objects have been analyzed. Was it to prove authenticity? Was it to demonstrate the technique?

The aim of the study was to prove the authenticity of the artefacts, so we added clarifying remarks in the manuscript.

In summary I suggest a major revision to clear the open questions and to structure the text in a more comprehensive way. Especially the question 'why?' should be addressed extensive and a description of the objects and there provenance should be included.

Following the Reviewer' suggestions, we attempted to answer all questions and reorganized the entire manuscript in a clearer way. We also added a more detailed description of the objects in the *Materials and methods* section.

REVIEWER #2

This paper concerns the study of three metallic artefacts believed to have been produced in the kingdom of Benin. In order to establish the authenticity of the samples, several experimental techniques have been applied. The article is well written and I was delighted by the clear and exhaustive description of the state of art of the techniques available for dating. The methodological approach followed appear to be complete and coherent and the paper is very interesting. For all these reasons I recommend it for publication.

We thank the Reviewer for his/her favorable comments and his/her positive evaluation. We are glad for his/her appreciation of our study.

Abstract

Two metal plaques and a cock statuette belonging to a private collection and stylistically consistent with the Royal Art of Benin (Nigeria) were investigated in order to verify their authenticity. The characterization of alloys and patinas were carried out by inductively coupled plasma mass spectrometry (ICP-MS), optical microscopy (OM), scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS), and X-Ray diffraction spectrometry (XRD). Furthermore, thermal ionisation mass spectrometry (TIMS) was used to assess the abundances of lead isotopes and to attempt a dating by the measurement of ^{210}Pb/^{204}Pb ratio.

The results showed that all three artefacts were mainly composed of low lead-brass alloys, with relatively high concentrations of zinc, antimony, cadmium and aluminum in the solid copper solution. Microstructures were mostly dendritic, typical of as-cast brasses, and characterized by recrystallized non-homogeneous twinned grains in areas corresponding to surface decorations, probably due to multiple hammering steps followed by partial annealing treatments. The matrix was composed of a cored α-Cu solid solution together with non-metallic inclusions, lead globules and Sn-rich precipitates in interdendritic spaces. On the surface of all metalworks, both copper and zinc oxides, a non-continuous layer of sulphur-containing contaminants and chloride-containing compounds, were identified. The lead isotope results were consistent with brasses produced shortly before or after 1900 A.D. Overall, the data obtained by different techniques supported the hypothesis that the three artefacts were not authentic.

AUTHENTICITY OF BENIN METALWORKS EVALUATED BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY AND LEAD ISOTOPE ANALYSES

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Keywords: Benin brass, authentication, ICP-MS, TIMS, ^{210}Pb/^{204}Pb ratio

1. Introduction

Two metal plaques and a metallic statuette of a cock in a good state of conservation, purchased in West Africa by a private collector and apparently consistent with the Royal Art of Benin (Nigeria), were conferred to Department of Engineering of the University of Ferrara (Ferrara, Italy) in order to verify their authenticity. No other information was available on the origin of these artefacts.

Attempts to reconstruct the history of Benin art have been made along five decades. The manufacture of copper-based alloy castings from Benin City (capital of the Kingdom of Benin) covered about four hundred years [1-7]. Based on oral tradition, Egharevba [8] stated that the transfer of knowledge of the *cire perdue* technique from the Yoruba city of Ife to Benin was completed at the end of the thirteenth century, but Bradbury maintained that this transfer occurred about a century after [9]. Later investigations on the relationships between Ife and Benin alloys by emission spectrography did not yield clear results [10].

The traditional brass castings from Benin included vessels, regalia, altarpieces, bells, heads, animal figures and plaques. According to oral tradition, plaques were first produced in the early sixteenth century, during the period of Portuguese contact with Benin [11], as decorations for the royal palace to proclaim and glorify the prestige of the king together with the ceremonial life of the court. In 1897, during a punitive expedition against the kingdom, the British removed many plaques and other artefacts from the royal palace and most of them were sold in Europe at government auctions to dealers, private collectors and museums [12,13].

The plaques were examined from a stylistic point of view by Fagg in 1963, who dated them according to evidence of European clothing and weapons together with changes in regalia as early as 1485, and as late as the beginning of the eighteenth century based on historical reports by travelers who visited the royal palace after its rebuilding. The author also suggested a style sequence from thinner to thicker and coarser castings, and from a more naturalistic and restrained aesthetics to a less naturalistic, flamboyant one [14,15]. Fagg identified three periods in the Benin memorial heads, the Early, Middle and Late Period, and attributed the plaques from mid-sixteenth century to the first quarter of the seventeenth century [14,15]. More recent studies on the Benin art collection of the Metropolitan Museum of Art in New York identified a typical foliate pattern with four leaves (*ebe-ame* design) on the front background, and a composition of figures according to "hierarchical proportions" (heads larger than bodies and size of figures reflecting the social status (position in the court)) [16,17]. Based on these criteria, the plaques were dated to the Middle Period.

Due to the growing interest in traditional African art for aesthetic and anthropological reasons [18], the proliferation of fakes has dramatically increased in Benin art in the last thirty years, making it necessary to verify the authenticity of artefacts by scientific methods [19-22]. Although direct dating of metals is not possible, analytical approaches are available to check the authenticity of ancient metal objects, such as thermoluminescence (TL), lead isotopes (^{210}Pb), analysis of trace and main elements, and investigation about the alloy-patina-environment system.

Initially applied for analysis of ancient pottery, TL was also found suitable for other materials, such as the core from lost wax metal castings, a mixture of clay and charcoal sometimes trapped inside the castings [23]. The clay core of Benin objects was traditionally removed from the interior of heads and from the reverse side of plaques; thus, an attempt to date the artefacts by TL is rather difficult [24]. Tunis [25] reported TL data from two plaques considered the last examples of rectangular bas-relief casting, but complained about the lack of physical data and detailed experimental results. On the contrary, Willett and Fleming [23] dated by TL twelve pieces excavated in 1938 at Wunmonije Compound (Nigeria) and the results were consistent with historical interpretation based only on style [26].

The method of lead isotopes is also used since the late 1960s in archaeology and geology to provide answers to several questions. The ratios between the three lead isotopes ^{206}Pb, ^{207}Pb, ^{208}Pb and ^{204}Pb are used as a fingerprint of ore deposits. The first three isotopes are formed by a well-known process of natural decay of uranium and thorium; conversely, the ^{204}Pb, the only non-radiogenic one, can be used like an index of lead impurity in the sample [27,28]. The first applications of this dating technique were for measurements of age of minerals in meteorites and terrestrial rocks [29], but in archaeological studies the intermediate members of the decay (e.g. ^{210}Pb and ^{214}Pb) are usually ignored because of their relatively short half-life [30].

The first archaeometric use of ^{210}Pb was proposed by Keisch in 1968 to ascertain whether a metal object was ancient or not [31,32]. The experimental procedure was later described in detail by Pernicka et al. [33]. The technique is based on natural radioactivity of ^{210}Pb, which has a very short lifetime (22.3 years). Dating of metal objects is based on the detection of this isotope: its presence indicates that the artefact was produced in the last 100 years [24]. However, the absence of ^{210}Pb does not necessarily provide a proof of authenticity, since ancient metals could be used in modern times to produce a forgery [31]. Schwab et al. [34] compared analytical data on twenty-seven Benin castings from the "Stiftung Situation Kunst" private collection (Bochum, Germany) and six Benin artefacts from the collection of the Reiss-Engelhorn-Museen (REM) in Mannheim (Germany). All the pieces from the museum collection showed no ^{210}Pb activity, whereas African pieces from the private collection had a clear activity of ^{210}Pb.

The analysis of main and trace elements in brass castings from Benin may be a useful dating tool, because some elements and their amounts could be fingerprints of specific historical times [24,35-37]. A main role is played by trace elements that represent natural impurities, such as iron, nickel and bismuth. Other trace elements, such as aluminum, phosphorous and silicon were sometimes intentionally added to alloys to improve their performances: however, some of them are not generally included in modern alloys or are used in completely different amounts, therefore the production period of artefacts may be evaluated by the combination of results obtained from all the above analyses.

The last criterion for the authentication of metal objects was expressed by Robbiola et al. [38,39], who stated that a global approach to relationships between metallic substrate/patina and the patina/corrosive environment should be considered to improve understanding of everyday usage and reconstruction of the corrosion processes of artefacts. A process to be considered is decuprification, often leading to two types of structures in the same object. In a patina of Type I the original surface of the artefact is preserved, while in a patina of Type II the original shape is no more identifiable, because of localized or intensely general metal dissolution or macroscopic deposits [40]. The authors proposed two authentication criteria: the first one was based on the relationship between the tin content in the alloy and in the Type I corrosion structure, the second one was based on the fact that compounds in the patina show traces of the environment to which the bronze was exposed.

This study investigates the composition and alloy microstructures of the two Benin plaques and the cock statuette. Inductively coupled plasma mass spectrometry (ICP-MS) and scanning electron microscopy coupled with energy dispersion spectroscopy (SEM/EDS) were used to determine the chemical composition with minimally invasive methods. The manufacturing procedures were also investigated by optical microscopy (OM). Studies of the main corrosion products and of patina stratification were carried out by SEM/EDS and X-Ray diffraction (XRD) technique. An attempt was made to date the artefacts by thermal ionization mass spectrometry (TIMS), measuring the ^{210}Pb/^{204}Pb ratio. The results were compared to those collected by quantitative alloy analyses, in order to assess whether the artefacts were modern replicas of objects from Benin.

Fig. 1. Photographic images of brass artefacts under investigation: (a) rectangular plaque portraying two figures kneeling on both sides of a central figure armed with an axe; (b) rectangular plaque portraying the king of Benin on horseback with three attendants; (c) statuette of a cock.

2. Material and methods

The investigated artefacts are shown in Fig. 1 (a-c). Both rectangular plaques portray small static groups arranged around a central figure. The first one (34.5 cm in height, 30.5 cm in width and with thickness ranging from 0.5 to 4.0 cm) (Fig. 1a), called "Axe", depicts two attendants kneeling on both sides of a central figure armed with an axe. The second one (31.0 cm in height, 36.5 cm in width and with thickness ranging from 0.5 to 3.0 cm), called "Horse", portrays the king of Benin on horseback with three attendants (Fig. 1b). The statuette of the cock consists of a hollow casting 49.5 cm in height, 13.5 cm in width and 3.0 cm in thickness (Fig. 1c).

As the majority of the objects belonging to the sixteenth-seventeenth century, the plaques depict the ceremonial life of the court. The castings are coarse and characterized by a limited naturalistic representation. The background on the front of both plaques, engraved with a typical foliate pattern with four leaves (*ebe-ame* design), was consistent with Benin objects produced in the Middle Period [14,15,17]. However, a stylistic detail of the iconography raised suspicion about production period, because the "hierarchical proportions", a key feature of Benin art, were not respected. In plaques verified as authentic and belonging to the sixteenth-seventeenth century, the heads of figures were larger than the rest of the body and the size of figures reflected their importance within the composition [17]. This criterion was unmet since the figures in the two plaques were portrayed with a similar size (Fig. 1(a, b)). Concerning the cock statuette, it was apparently made from the same cast of the base, as the majority of Benin sculptures and statuettes manufactured after the first use of the *cire perdue* technique and reported in literature [24,33].

To preserve artefacts from damage, investigations were carried out on fragments collected from the back of the plaque and from the interior of the cock statuette. The chemical composition and microstructure of the alloys was determined on some representative fragments of the longitudinal section (sample observed in the direction of the metal surface) and of the cross section (sample observed across the thickness of the metal). The fragments were mounted in resin, polished and analyzed by conventional metallographic observations. Surface investigations after chemical etching (in $FeCl_3$/HCl hydro-alcoholic solution) were performed by Leica MEF4M optical microscope (OM) (Leica, Wetzlar, Germany) according to a previously described procedure [41], to identify the alloy microstructure. Analyses of polished surfaces were carried out by a ZEISS EVO MA 15 scanning electron microscope (SEM) (ZEISS, Oberkochen, Germany) coupled to energy dispersion spectroscopy (EDS) to evaluate alloy composition.

The composition of alloys was determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) of major and trace elements after acid digestion. The composition and distribution of major and trace elements were evaluated by laser ablation system (LSX-200+, CETAC, Omaha, NE 68144, USA) coupled to inductively coupled plasma mass spectrometer (ELAN 9000, Perkin Elmer SCIEX, Concord, Ontario, Canada). An LSX-200+ system at 266 nm UV laser (Nd-YAG, solid state, Q-switched) with maximum energy up to 6 mJ/pulse and a pulse repetition rate from 1 to 20 Hz with a viewing CCD camera system was used for laser ablation.

Samples in cross section and in non-etched conditions were also used to investigate the thickness of the patina and the stratification of corrosion products. The identification of corrosion compounds was carried out by non-destructive surface analyses (SEM/EDS, XRD). The XRD spectra were acquired by using a Cu Kα radiation source with a 40 kV accelerating voltage and a 40 mA filament current: θ-2θ scans from 8° to 90° were performed, with a 0.02° step size and a 10 s dwell time.

To assess the presence of ^{210}Pb, a standard chemical procedure to separate lead from matrix was set up by an ion-exchange separation technique. The measurements were performed by Finningan MAT 262 multi-collector Thermal Ionization Mass Spectrometer (TIMS) (Finningan MAT, Bremen, Germany) on both standard NIST SRM 981 and on samples from the plaques and from the cock statuette in order to correct isotope fractionation. The detection limit was 0.0001 for the ^{210}Pb/^{204}Pb, ^{208}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{206}Pb/^{204}Pb ratios. Each sample was measured in triplicate. Experimental values correspond to the median ± double standard deviation. The data acquisition followed a strict procedure: the filament was heated for 15 minutes at 100 mA/minute, then at 30 mA/minute until the filament temperature reached 1100 °C and the current 2200 mA. Filament heating was then stopped and data acquisition started after the slow decrease of signal. The ion beam of each mass number was collected by a fixed Faraday cup. The filament heating time was approximately 30 minutes and the data acquisition time was about 35 minutes for each measurement.

3. Results and discussion

3.1 Composition of the alloys

The composition of alloys in the artefacts measured by ICP-MS and by SEM/EDS is respectively reported in Table 1 and in Table 2. The artefacts are mainly composed of low-lead brass alloys (Cu≈65-72 wt.%, Zn≈23-29 wt.%, Pb≈2-3.5 wt.%) with low concentrations of tin, nickel, iron, manganese, aluminum, antimony, arsenic and cadmium.

Table 1

Composition of the alloys (measured by ICP-MS, wt.%) of fragments collected from the back of the plaques and from the interior of the cock statuette. Each sample was measured in triplicate. Accuracy was lower than 15% for all elements. The detection limits were 1-10 ppb for Al and Fe, and less than 0.1 ppb for Sb, As, Cd, Mn, Ni, Pb, Sn, Cu and Zn. Experimental values correspond to the median ± relative standard deviation.

Object	**Sb**	**±**	**As**	**±**	**Al**	**±**	**Cd**	**±**	**Mn**	**±**	**Fe**	**±**	**Ni**	**±**	**Pb**	**±**	**Sn**	**±**	**Cu**	**±**	**Zn**	**±**
Axe	0.004	0.30	n.d.	-	0.54	0.05	0.0040	0.15	0.45	0.05	0.35	0.10	0.44	0.15	2.34	0.10	0.17	0.10	69.99	0.05	25.72	0.05
Horse	0.050	0.30	0.006	0.50	0.25	0.05	0.0020	0.15	0.18	0.05	0.19	0.10	0.25	0.15	3.46	0.10	1.54	0.10	65.00	0.05	29.01	0.05
Cock statuette	0.023	0.30	n.d.	-	0.15	0.05	0.0018	0.15	n.d.	-	0.21	0.10	0.23	0.15	2.97	0.10	1.35	0.10	71.86	0.05	23.15	0.05

n.d. = not detected

Table 2

Semi-quantitative elemental composition of wide areas (1.0 x 0.5 mm^2) of the alloys (measured by EDS, wt.% ± an estimate of the standard deviation in the integrated peak area) of the three fragments collected from the back of the plaques and from the interior of the cock statuette. Each area was measured in triplicate.

Object	**O**	**±**	**Al**	**±**	**Mn**	**±**	**Fe**	**±**	**Ni**	**±**	**Pb**	**±**	**Sn**	**±**	**Cu**	**±**	**Zn**	**±**
Axe	1.15	0.13	0.51	0.06	0.36	0.05	0.57	0.05	0.56	0.07	1.77	0.17	2.19	0.10	66.19	0.28	26.70	0.23
Horse	1.29	0.12	0.49	0.05	0.24	0.05	0.27	0.05	0.46	0.06	1.16	0.15	1.76	0.09	64.36	0.24	29.97	0.21
Cock statuette	1.53	0.12	1.12	0.06	0.09	0.04	0.59	0.05	0.54	0.06	0.89	0.15	2.70	0.09	67.52	0.24	25.02	0.20

The majority of "Benin bronzes" were made of brass or gunmetal alloy, a quaternary alloy containing copper, zinc, tin and lead. Several authors discussed the use of abundance of the three main alloying elements in the alloy (zinc, tin and lead) as an indicator of the provenance or relative age of the metallic object [36,37]. The Zn content was widely used as a chronological indicator for brasses [42,43], even though the Zn content alone is not sufficient to identify forgeries. In Europe, before the production of zinc as a single metal in ancient and Mediaeval times, brass was exclusively produced by the reduction of zinc ore (zinc oxide or zinc carbonate) mixed with charcoal at about 1000 °C and the diffusion of metallic zinc vapors into the copper metal (cementation process). The cementation produced a rather pure α-brass, with an upper limit of Zn 28-32 in weight [1,44]. Newbury et al. [45] showed it was possible to manufacture brasses with over 40% Zn in weight by performing the cementation process under laboratory conditions (e.g. in very small quantities and at very short reduction times); these data were in contrast with historical reports about the cementation brass production techniques [43]. The process was abandoned around the half of nineteenth century [43], when the speltering process completely replaced cementation as the main manufacture technique for brass alloys.

It is known that the Zn percentage of Benin artefacts tend to rise along centuries. In objects dated before the eighteenth century the Zn percentage is usually less than 20%. From the sixteenth century onwards, Zn occasionally increases up to 30% and exceeds this value in Benin works made at the end of the eighteenth century by the addition of metallic zinc [33,35]. Considering the "Horse" plaque, the amount of Zn was slightly above the conventional limit of 28%, but for the "Axe" plaque and for the cock statuette the Zn content range was 23-26%. Unfortunately, it is not possible to prove the authenticity of the last two objects by only considering this parameter.

The alloys also contain small amounts of Pb (2-3.5% in weight), Sn (0.2-1.5% in weight), Ni (0.2-0.45% in weight), Fe (0.2-0.35% in weight) and traces of As, Sb and Cd. In ancient copper-based alloys, a Sn content lower than 1% could be due to recycling or to the use of tin-containing ores [46]: the Benin brasses from the nineteenth century were characterized by very low concentrations of Sn and As (Sn<0.25% and As<0.10%, respectively) [24]. Lead percentages lower than 5% were generally ascribed to copper or zinc ores and were not considered a deliberate addition to the alloy in order to improve the features of molten metal [1].

In pre-industrial copper-based alloys, the presence of Fe and Ni was probably due to poor smelting conditions. Pernicka et al. [33] reported that, although commonly detected in prehistoric metal artefacts, high Ni percentages were almost unknown in Benin castings made before the twentieth century [35]. Conversely, Riederer [24] established a time-dependent relationship between Zn and Ni, Sb and As: according to this author, Benin metalworks should be considered older than 400 years when the Ni content is more than 0.2%; the Ni percentages over 0.5% are typical of artefacts made after the sixteenth century.

The concentrations of trace elements are also important in attempts to date Benin brass objects because of their variation in amount during historical times. For example, ancient objects are characterized by high amounts of trace elements [24]. As shown in Table 1, in all artefacts the amount of Sb is below 0.05% in weight, whereas As and Cd are barely detectable (≤0.006% in weight). An Sb content below 0.1%, or lower than 0.05% is a reliable evidence for a later manufacture [24]. Cadmium was a typical trace element included in brasses because of the industrial distillation of metallic zinc. According to Riederer [24], Benin brasses from the XIX century are characterized by a Cd concentration above 0.002%.

Manganese and aluminum are also interesting. Most brasses produced in the twentieth century were characterized by small amounts of these *lithophile* elements, unambiguous indicators of modern industrial alloys [33,47]. In many industrial brasses manganese is added to improve wear and resistance to oxidation in copper-based alloys, but its percentage is usually kept below 0.1% because of the negative effects on dezincification [48].

The technical innovations at the end of the nineteenth century allowed the extraction of aluminum on a large scale for armaments. Aluminum in the range of 0.2-0.7% was added to promote casting, to reduce zinc evaporation and to improve the mechanical properties of the alloy [49]. Aluminum also improved corrosion resistance and made the surface metal smoother and more homogeneous [50]. Together with iron and silicon, aluminum is also one of the main components of clayey soils [39]; thus, its presence in alloys could also be due to the interactions with mold wall (for as-cast objects) or with the burial soil. In the studied artefacts, the presence of aluminum detected by ICP-MS in samples (≈0.5% in weight for the "Axe" plaque, ≈0.25% in weight for the "Horse" plaque and ≈0.15% in weight for the cock statuette) could be explained by soil components not completely removed. However, SEM/EDS analyses were carried out on the core metal, untouched by environmental contamination: aluminum was again detected in the solid solution with the α-Cu matrix, since the aluminum percentage in the alloy was lower than the solubility limit, i.e. 9.4% for aluminum in copper (Table 2). Presumably, aluminum was added to the alloys on purpose, suggesting that the artefacts were produced in modern times [49].

3.2 Alloy microstructure

Optical images of the alloy microstructure are reported in Fig. 2. The cock statuette and both plaques show a mostly dendritic microstructure (Fig. 2a and Fig. 2b), typical of as-cast brasses [51]. Concerning the plaques, the presence of recrystallized non-homogeneous twinned grains in areas corresponding to surface decoration (Fig. 2c) was probably due to multiple cycles of hammering and annealing (usually between 500 °C to 800 °C for copper-based alloys), performed in order to emphasize the details of adornments and restore metal workability and toughness [52].

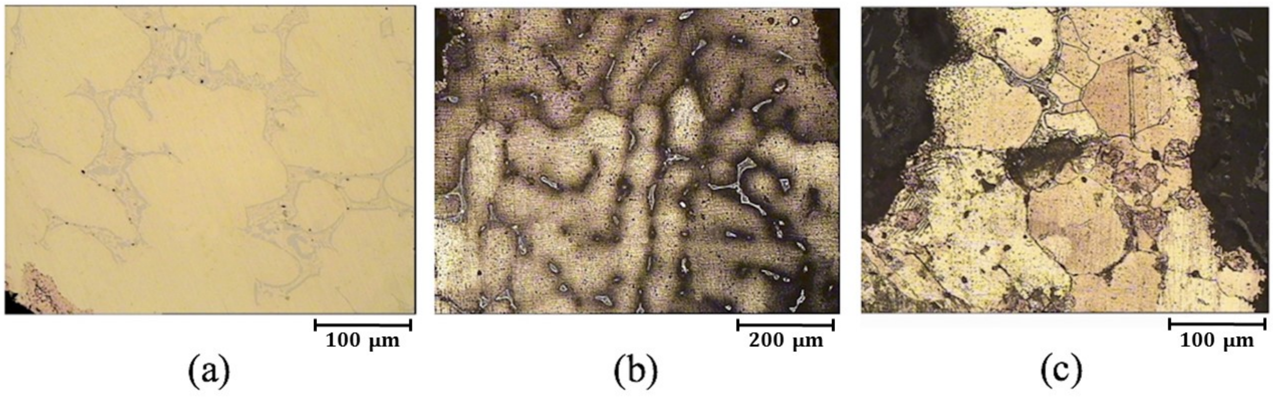

Fig. 2. Optical images of the alloy microstructure: (a) Cu-Zn-Sn interdentritic phase together with some metallic lead (insoluble in copper) on polished surfaces of the cock statuette; (b) dendritic structure on etching surfaces of the "Horse" plaque; (c) non-homogenous grains structure with thermal twin bands on the etching surfaces of the "Axe" plaque.

The single-phase microstructure of the matrix was composed of a cored α-Cu solid solution, resulting from a zinc content lower than the solubility limit in copper (about 35% Zn at room temperature) (Tables 1 and 2). In all cases, non-metallic inclusions and lead globular precipitates (insoluble in copper [52]) were also visible in interdendritic spaces. The EDS maps evidenced iron phosphide inclusions (Fig. 3). Iron phosphides in copper are rather uncommon [51]. As far as known, only Miller [53] reported a bimetallic nodule from Phalaborwa (South Africa) in which the copper layer included dendrites of a copper-iron sulphide forming a eutectic system with copper, copper-iron sulphide inclusions with a mesh-like appearance and light-blue iron phosphides. Other studies [54,55] showed that the presence of iron phosphides in copper from Fayan (Jordan) could be explained by the use of phosphorous-rich charcoal from Arabah (phosphorous content up to 10%) or by phosphorous-rich ores. Some authors remarked that even if bronzes discovered at Igbo Ukwu (Nigeria) were probably smelted and alloyed in West Africa, brasses were obtained from the eleventh century on, through Arabian trans-Saharian trade, in exchange for slaves and gold. The local industry consequently died out because of Arab competition [1,35].

Regardless of the examined fragment, EDS maps show that aluminum is almost completely dissolved into the copper-rich matrix, as already mentioned when discussing the composition of the alloys (Section 3.1). Finally, the presence of tin in interdendritic areas of alloys is probably due to micro-segregation phenomena [56,57].

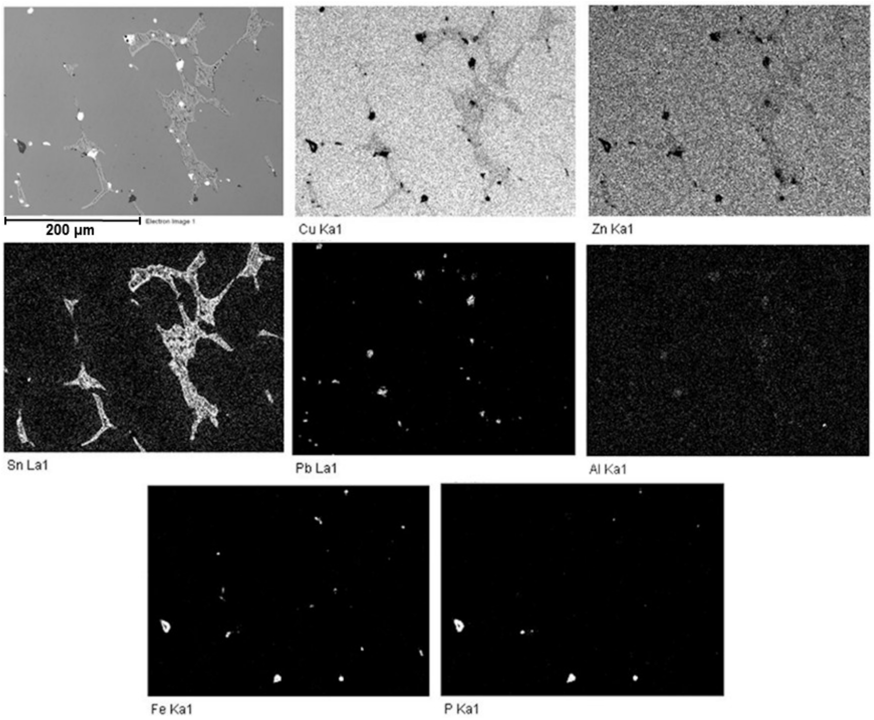

Fig. 3. SEM image (upper left corner) and EDS maps of elemental distribution in the “Axe” plaque (cross section), representative of the microstructural features of the alloy.

3.3 Characterization of the corrosion phenomena

It is interesting to note that the stratigraphy of crusts detected on the surface of both plaques and of the cock statuette is almost the same. For example, Fig. 4 shows SEM/EDS mapping of the cross section of the “Axe” plaque and the thin layer of corrosion products. An inner and porous re-deposited copper layer was recognizable, overlain by a non-uniform scale of non-uniformly distributed chloride and sulphur compounds, mixed with sand or dust. The thin copper-rich layer at the metal/corrosion products interface suggests that the dezincification process did not occur to a significant extent and the cross section also does not show any sign of corrosion attack below the surface, towards the core metal. Dezincification is generally caused by a selective dissolution of zinc and followed by a specific deposition of copper on the metal surface. The extent of dezincification depends on several factors, among which zinc content, corrosive agents and the presence in the alloy of elements (such as Sn) known to inhibit this corrosion attack [58]. Several studies [33,34,59-63] dealing with the corrosion of Benin castings reported that the original artefacts were generally placed outdoors, thus the surface corrosion was caused by interactions with the tropical environment of Nigeria, everyday usage or former restoration and conservation treatments. The metal surface was mostly characterized by compounds containing sulphur contaminants or chlorine species, strictly dependent on local atmospheric composition. The presence of fatty-acid salts was then attributed to the decomposition of protective coatings based on palmitic/stearic/oleic acid, applied during the use of metalworks.

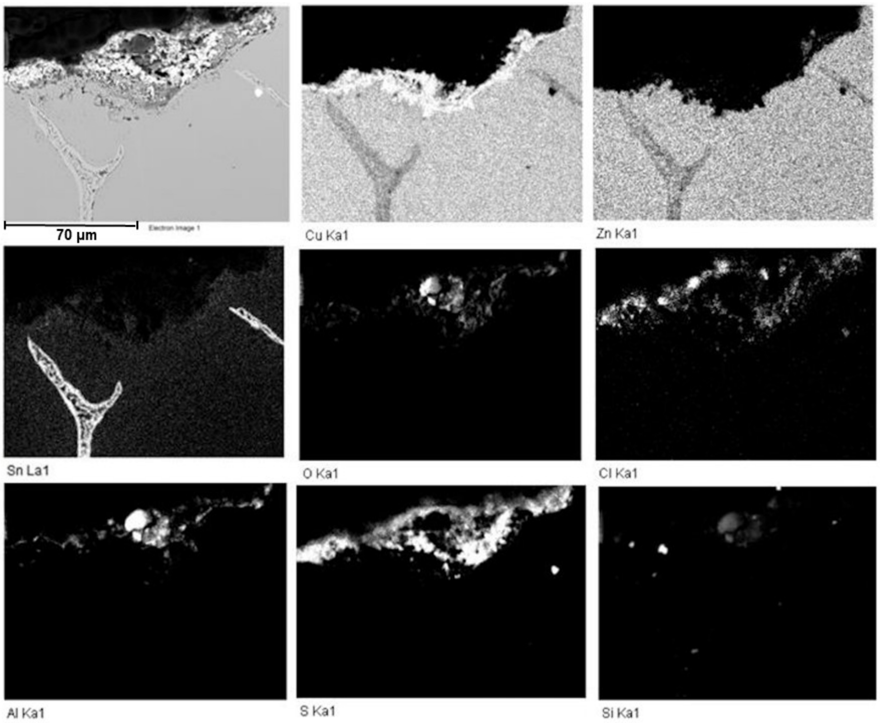

Fig. 4. SEM image (upper left corner) and EDS maps of elemental distribution on the patina cross section of the “Axe” plaque.

The corrosion powders collected from inlaid regions of the decorations of all artefacts were identified by XRD (Fig. 5) as mainly composed of copper and zinc oxides, tenorite (CuO), cuprite (Cu_2O) and zincite (ZnO). The corrosion layers of a brass surface are generally composed of copper oxides, copper chlorides and sulphates occurring in natural archaeological patinas in outdoor environments [33,64]. Tenorite is however rather uncommon as a component of natural patinas: moreover, for kinetic reasons it is very rarely found in comparison to cuprite, although the Pourbaix diagram predicts tenorite stability in a wide potential/pH region [65]. The authors found this alteration product in a previous work about a local fragmentation of an Achaemenid bronze bowl [66]: the artefact was characterized by complex corrosion layers produced during burial, with the surprising substitution of cuprite by the tenorite layer. In this case, the authors excluded that the presence of tenorite could be due to heating between 400 °C and 600 °C, in a highly oxidizing atmosphere or to an intentional patination process applied for aesthetical reasons. The only possible explanation was a prolonged local contact with highly alkaline substances.

Zincite was completely unknown before the studies of Schwab et al. and Pernicka et al. [33,34]. Conversely, the formation of zincite requires brass heating in air and is therefore an indicator of high temperature scaling. Zincite could be preserved on the surface of objects since it was collected from inlaid regions in which the leaching process was inhibited.

The presence of a low corrosion rate and the absence of artificial patination, which in itself raised suspicions, nevertheless were not sufficient to determine whether the original patinas were removed or whether the artefacts were well preserved.

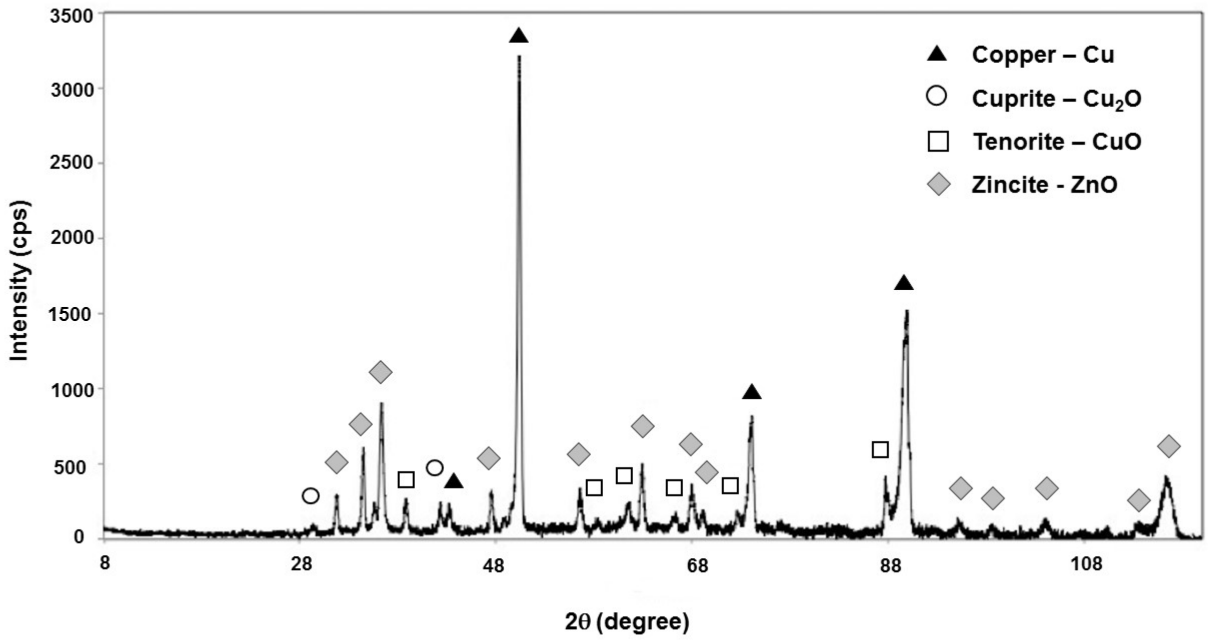

Fig. 5. Representative XRD spectrum of the corrosion products on the "Horse" plaque.

3.4 Comparing ICP-MS and ^{210}Pb analyses

The ^{210}Pb/^{204}Pb ratio was used to date the artefacts, as described in the Materials and methods section. The results were compared to the quantitative ones obtained by ICP-MS analyses and to literature databases [24]. Small average amounts of ^{210}Pb were detected in the "Axe" plaque (^{210}Pb/^{204}Pb = 0.000207 ± 0.000043) and in the cock statuette (^{210}Pb/^{204}Pb = 0.000190 ± 0.000037). According to previously published data [24,33] these objects were undoubtedly produced in the last 100 years. However, no detectable ^{210}Pb value was obtained for the "Horse" plaque, despite the suspicious contents of zinc, aluminum, antimony and cadmium detected by ICP-MS. The absence of ^{210}Pb could indicate that this artefact is older than a century, but, as previously mentioned, an undetectable value of ^{210}Pb does not guarantee authenticity. According to Pernicka et al. [33], the "Horse" plaque could have been manufactured in the early twentieth century using scrap and/or old stocked metals.

Overall, the results of ^{210}Pb generally support those obtained by ICP-MS and are comparable to those published by Riederer in his extensive database on Benin artefacts [24]. The data could therefore indicate brasses produced shortly before or after 1900 A.D.

Although it was not the main purpose of the study, it is interesting to note that the ratios between the three different lead isotopes are almost the same for all artefacts (on average, ^{208}Pb/^{204}Pb = 38.284 ± 0.038, ^{207}Pb/^{204}Pb = 15.683 ± 0.012, ^{206}Pb/^{204}Pb = 18.195 ± 0.009). These data support the hypothesis that the artefacts were produced using the same ores. The values are also comparable to those obtained by W. Snoek et al. [67], who studied some copper-alloy archaeological artefacts from Tell Ahmar (Syria).

4. Conclusions

Chemical analyses by inductively coupled plasma mass spectrometry and a combination of conventional metallography with lead isotope measurements were used to assess the authenticity of artefacts apparently belonging to the Royal Art of Benin. Some results allowed to raise suspicion about the authenticity of the objects:

- ∴ Some aspects of iconography and style were similar to those of most Benin objects produced during the sixteenth-seventeenth century. However, the absence of "hierarchical proportions" assigned the artefacts rather to modern replicas.
- ∴ In all cases, the high percentage of Zn (above 20% in weight), an amount of Sb exceeding 0.1%, a Cd content higher than 0.002% and the presence of metallic aluminum in solid solution with copper suggest that the alloys are compatible with modern brass compositions.
- ∴ On all artefacts, the extent of the dezincification process, the low corrosion rate and the absence of artificial patination do not allow to assess whether the original patinas were removed or whether the artefacts were well preserved.
- ∴ The measurements of the $^{210}Pb/^{204}Pb$ ratio were mostly in agreement with those obtained by ICP-MS quantitative analyses of alloys and comparable to previous literature data.
- ∴ Overall, the data collected on the three artefacts indicate brasses produced shortly before or after 1900 A.D.

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Highlights

- Two metal plaques and a metallic cock belonging to a private collection.
- Suspicious contents of aluminum, antimony and cadmium.
- ^{210}Pb amounts indicative of brasses produced shortly before or after 1900 A.D.