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A global approach to the authentication of ancient bronzes based on the characterization of the alloy–patina–environment system

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Abstract

The aim of this paper is to propose a general framework for improving authentication practice of ancient bronze artefacts. In a first part, the article comprehensively reviews the different approaches usually performed to authenticate bronzes, but also evidences their limitations. It is shown that even if numerous technical and fundamental scientific improvements have overcome some of the limitations encountered in the characterization of materials, properties, metal and patina are always considered as independent systems. It is evidenced that authentication requires a global approach based on the investigation of the metallic materials–patina–close environment system. On this basis the complex relationships between alloys, alteration (patinas) and environment (soil...) are successively pointed out, and investigation of the consequence of decuprification (as a global phenomenon of bronze corrosion), taking into account the coupled interactions, is discussed. An application from an example of a fake Chinese ding artefact is then given. A methodological approach is finally proposed, in which many improvements requiring further research could be integrated.

Keywords: Bronze, Authentication, Cu–Sn alloys, Decuprification, Corrosion, Patina, Methodology

1. Research aims

Authentication of ancient metals still remains an important scientific challenge that requires both strict methodology and pertinent criteria. Since metals do not possess physical properties that can be expressed as a function of time, ancient metallic artefacts cannot be directly dated. So far, to determine whether a metal artefact is ancient or not, the most valuable method is thermoluminescence, only applicable to artefacts with unsullied core material [1]. Generally no casting core material is present and metal authentication requires an interdisciplinary investigation involving several scientific methods. As pointed out by earlier studies [2,3], the objectives are to ascertain whether or not some characteristics purport to be namely ancient-made alloys with corrosion produced by environmental interaction of hundreds or thousands of years. Actually, as schematised in Fig. 1, two main approaches of scrutiny must be considered taking into account the specificities of cultural

materials (unicity, “obscure” history, limited sampling...). The first one is the “historical and artistic” approach, which is conducted in order to identify the style, the typology, the temporal origin and the history of the artefact. We will not develop this aspect here. The second approach, here called the “materials science” approach, is based on the characterization of the materials (structure and composition, fabrication and finishing techniques, alteration or patinas) in order to verify the original features of the artefacts. Despite the recent development of analytical techniques since these last decades and the new performances to elucidate the origin of objects or to identify of corrosion products, no clear and precise methodology is applied for authenticating metals. As a matter of fact, it is always easier to prove that an object is a fake than to confirm that it is an authentic one.

The purpose of this article is to propose a general methodological framework for improving the authentication practice of bronze materials (coppertin-containing alloys). The currently applied methods for the bronze authentication will be first reviewed and discussed. It will be shown that, even if efficient analytical techniques can be applied to investigate either the

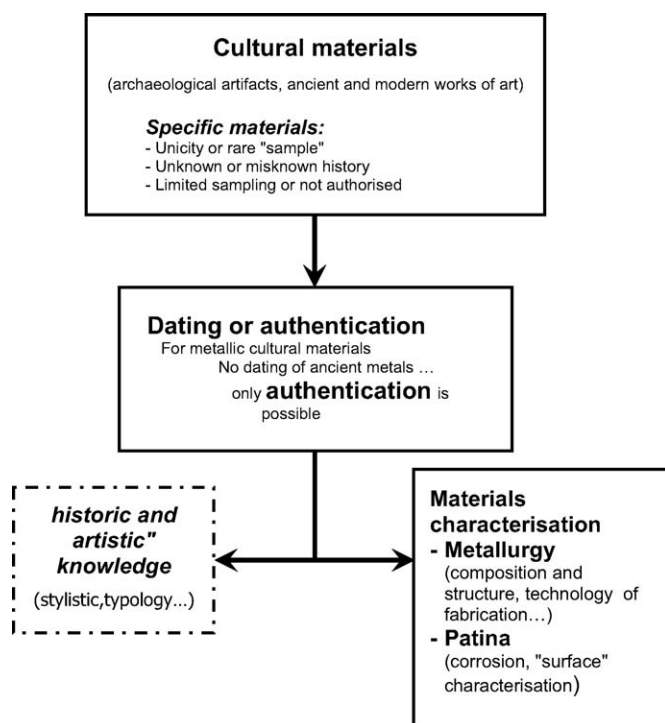


Fig. 1. Schematic process of investigation to authenticate metallic works of art.

bulk alloy or the patina, the authentication must be considered fundamentally as a global process. The great importance to consider the alloy/patina/environment as a global system in which the patina must be regarded as the result of the physical-chemical interactions between the alloy and the environment with time will be underlined. In a second part, according to some recent understanding of the corrosion phenomena of bronze involving the decuprification process, new criteria of authentication will be defined, while some others, often used today, will be critically discussed. Finally, a case study of a recent copy of an ancient Chinese bronze will illustrate the global methodology that we will propose for improving authentication of bronze artefacts.

2. Bronze authentication—a critical review

Nowadays one the classical approach to authenticate is based on the analysis of the metal composition (when pertinent metal sampling is allowed!) and on the comparison with available databases. Thus major, minor and trace elements are classically determined in order to link the composition of the unknown artefact to a known reference. For leaded bronzes, another method often used is based on the measurement of isotopic lead ratios in order to determine a probable provenance [4,5]. A further step is to investigate the patinas. Composition analysis and microstructural examination can provide identification of the corrosion products and point out whether or not they are consistent with the composition and structure of both metal and corrosive environment. Often, the mineral alteration products of the patinas are determined by X-ray diffraction or infrared spectrometry, in situ or from mechanically scraped samples, but this is only valid for the identification of

the crystallized compounds. A last recommended procedure is to investigate the microstructure of the alloy and patina from metallographic cross-sections in order to determine the origin and subsequent history of the object [6]. However, this last procedure requires metallic sampling and, in many cases, it is not feasible.

In practice, the above-mentioned approaches have severe limitations even in some cases they can bring immediate pertinent results.

For metal characterisation, the available data banks are still few in number. The recycling of bronzes that may occur in ancient metallurgy also appears a limiting factor for determining the metals, origin. However, it must be noted that for copper-based prehistoric metals, several programs have been completed [5], for example the SAM (*Studien zu den Anfängen der Metallurgie*) and now the SMAP (*das neue Stuttgarter Metalanalysenprojekt*) programs [7–9], where numerous bibliographical references for European bronzes are given. A comparison of analytical techniques between several laboratories has even been conducted and is detailed in [8], confirming the great interest of metal analyses, but also underlining the importance of the analytical procedure to obtain accurate results. The presence and concentration of alloying elements might be also used as chronological indicators. A typical example of that is given in [10]: from the Zn content in Egyptian bronzes, the (re-)attribution of different historical periods to the objects has been possible, alloys with high-Zn content being used together with brass in Egypt during the Roman period. Nevertheless, these data are also submitted to our present knowledge of the metallurgy. For example, in ancient copper alloys with very high zinc content, it has been recently shown from new simulation experiments that the practical composition limit of around 30 wt.% must be shifted up to almost 40% [11]. However, many analyses are for the most part devoted to identify the ores, but not the fabrication procedures nor authentication. Difficulties are encountered in practice when trying to determine at a global level, systematic correlations between typology, age, geographic origin and/or metallurgy [4]. For example, a recent study of Roman statues from the Vatican and Louvre Museums [12] underlined an evolution in the bronze composition with the chronology, as shown in Fig. 2. These objects are leaded bronzes. The lead content increases from the first century BC to the third AD, while the tin content remains approximately constant. This tendency is characteristic of our present knowledge and is therefore limited. For instance, what should we conclude if a Roman bronze statue of the IIIrd century AD reveals a low Pb content? In fact, historical attribution based on the composition of metals remains too often hampered by our insufficient knowledge of the history of metallurgy.

Some limitations in the characterisation of patinas are also clearly encountered. The main crystallised compounds are identified, but corrosion compounds are more complex and their formation process is still not well understood. Gettens has already underlined this point in [13]. Accurate standards corresponding to mineral alteration products are also difficult to get. Consequently, when “unusual” results are obtained, the

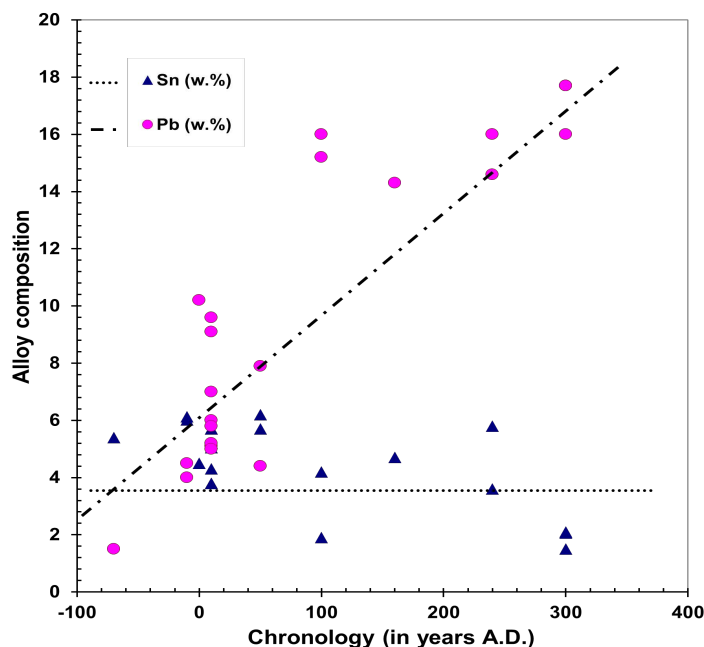


Fig. 2. Chronological evolution of Sn and Pb contents (wt.%) of Roman bronze statuary, from [12].

lack of knowledge becomes a limiting factor. A good example is revealed when amorphous products without “classical” compositions are detected in the bronze patinas such as, for example, high tin contents with Si, P, Al, Ca, Cl and Fe elements [14,15]. In such cases, are the analytical results of the corrosion products characteristic of a fake bronze? Can we assume that the object, “for good reasons”, has been intentionally patinated? Or that a higher content of Al, Si and Ca elements detected in the corroded surface has to be related to the manufacturing process, in which moulds of fired clay were used? Since this last decade, numerous analytical techniques have been applied to characterise the mineral alteration products on ancient bronzes but also on artificially corroded samples for example: X-ray photoelectron spectroscopy [16,17], Raman and infrared spectroscopies [18,19], cathodic reduction and differential scanning calorimetry [20], energy dispersive spectrometry with TOF–secondary ion mass spectroscopy or glow discharge optical emission spectrometry [21–23]. Some investigations [15, 16,23–25] at the microscopic level have been also conducted in order to determine the composition profile of the patinas. Yet, no precise relationships between the surface products, the alloy composition and the corrosive environments are evidenced. They are most often case studies in which the corrosion processes have rarely been taken into account. Application of these results is still limited for authentication. The question of intentional patination versus corrosion by natural agents also remains a recurrent one [26, p. 98].

Usually, these different approaches, considering as independent systems the substrate properties and the patinas, are concurrently conducted, but often without a real interconnection. Therefore, even if numerous and performing analytical techniques have been applied to characterize the metals or the corrosion compounds, the application of these results are still limited for authentication. A global methodological procedure for authentication, which will also integrate the previously mentioned approaches, has not been defined yet. The problem is

more centred on how to correlate all the information brought by the scientific investigations rather than to discover the single physical-chemical property that will directly bring along the solution.

Previous articles have mentioned several global characteristics of alteration on ancient copper base alloys, which could be determinant criteria for the identification of natural patina [3, 27].

They are relative to the presence of:

- a pronounced intergranular corrosion, generally in the cases of forged or hammered artefacts;
- a significant red cuprous oxide layer (cuprite marker layer) contiguous with the residual metal;
- a thick corrosion layer, assuming that with time the patina increases in thickness and porosity, which could reveal a layered, banded or periodic structure in heavily corroded objects.

Nevertheless, as already mentioned by Lewin [3] and more indirectly by Chase [26], these propositions must indicate that the patina is probably natural, but the converse of these propositions is not true. The absence of a substantial layer of cuprous oxide or intergranular corrosion does not necessarily imply that the patina is artificial [26,28]. In fact, the presence of cuprous oxide, thick corrosion layers or intergranular corrosion cannot be considered as sufficient criteria.

It is obvious that the different compositions of the corrosion products are related to the environmental conditions in which they are formed. However, most publications on characterization of corrosion compounds rarely considered the environmental factors affecting corrosion-mineral formation. In some cases, properties of corrosion products and conditions governing their formation have been investigated, but unfortunately remain inconclusive for clear authentication purposes [3,29]. Sharkey and Lewin [29] studied the formation of copper hydroxichlorides in order to determine the relative proportion of paratacamite and acatamite. The investigation of the proportion of oxygen and carbon isotopes present in some corrosion products [30] was also very indicative of the scientific tendency to find a pertinent criterion. Very interesting results were obtained by analysing malachite, but copper hydroxy compounds are “secondary products” of bronze corrosion that can precipitate during all the corrosion life of the objects [31]. In these conditions, sampling was inappropriate and no conclusion was possible at this time.

3. Propositions for a new approach of bronze authentication

The metallic artefact and its close environment must be considered as a global physical system. We cannot consider the patina independently of the characteristics of both the alloy and the global environment, because it is the result of the whole physical–chemical interactions between them. Consequently a new global approach for authentication can only

emerge if clear relationships between patina and alloy, and between patina and environment are evidenced. The alteration processes of bronzes with time must be then taken into account. On this basis, the decuprification process of bronzes can be considered as a key point for introducing new authentication criteria. It has been evidenced on archaeological objects of wide cultural and geographic origins, but also from artificially corroded synthetic materials [31–38].

Hereafter, several points of particular interest will illustrate the importance to consider the bronze artefact as a global physical-chemical system, able to be a source of knowledge of the “past”.

3.1. Relationship between alloy and patina

Many factors, such as the composition and the microstructure of bronzes, the corrosive environment features of the corrosive context(s)... can influence the chemical and structural nature of bronze patinas [28,33,39,40]. Thus, bronzes can exhibit complex and heterogeneous corroded structures. Never-

theless, independently of the alloy compositions, patinas of bronze objects have many similar morphological features, such as the presence of tin-enriched corrosion layers. As suggested by [26,32–34] and confirmed by [31,41,42], the formation process of bronze patinas in natural environments is mainly related to a decuprification phenomenon, the selective dissolution of copper, connected to an internal oxidation of the alloys. This has been evidenced since 50 years ago for ancient and historical metals [21,26,28,31–36], but also more recently for synthetic bronzes artificially corroded in aqueous solutions [24, 37,38,43].

From a practical point of view, numerous patinas can be observed on bronzes. However, in the literature, they are most often classified into two main types of patinas, according to the presence or the absence of an original surface (marker layer) preserving the original shape of the artefact [35,44,45]. A simplified model of these two types of patinas, with some of their numerous variations, has been detailed in [31]. In the first type (type 1), the original surface is visible (Figs. 3a and 3b) or simply concealed by copper-containing deposits or earthy-

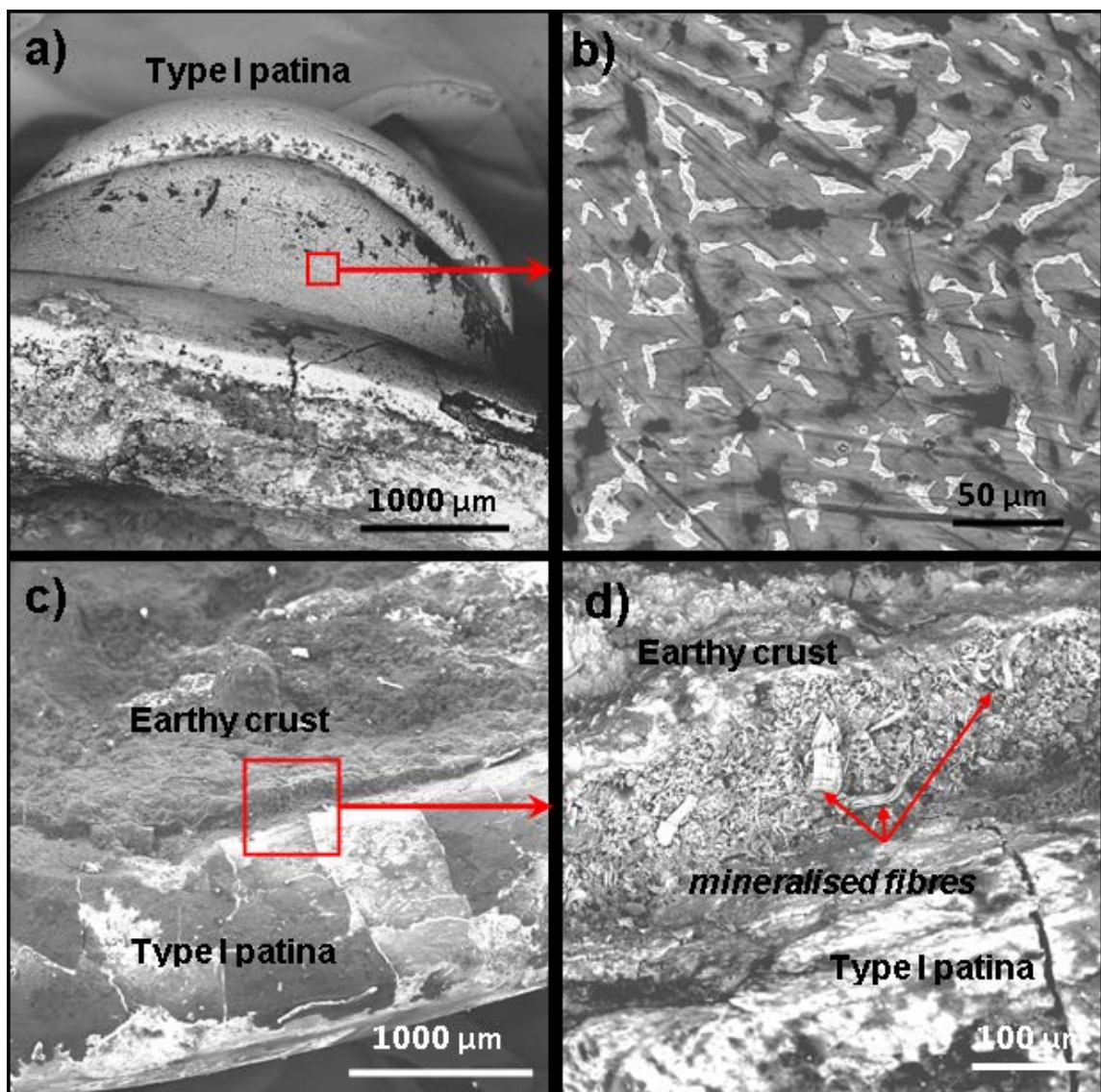


Fig. 3. SEM observation of type-1 patina (noble patina) of a Celtic bronze (3rd BC): a) general vision and b) detail of the surface revealing a ghost as-cast structure of the alloy and traces of polishing grooves. c): earthy crust deposit on type-1 surface and d) detail revealing mineralised fibres fossilised by corrosion and embedded in.

crusts (Figs. 3c and 3d). Often called « noble » patina [13], this type of patina exhibits some remarkable protective properties [46]. It is characterized by a high tin-enriched surface corrosion layer due to copper-depletion, also containing chemical compounds of the corrosive context such as carbonate, silicate, sulphate etc. For the second type of patina (type 2), when the original surface has been destroyed or deformed by severe corrosive attacks (pits, crevices, lamellar corrosion etc.; cf typical examples in [31, Fig. 8a–f]), a thicker and much more complex structure than for the type 1 is observed. Nevertheless, an internal tin-enriched layer, often linked to a remnant metallurgical structure of the alloy, is systematically evidenced as mainly connected to the presence of oxide or hydroxide compounds, with a relative enrichment in Cl content.

For authentication purposes, type-1 patina appears to be the most interesting one for defining pertinent relationships between the alloy and the patina.

As the original surface of type-1 patina is fossilized, essential information regarding the nature of the alloy (ghost dendrites for cast alloy...), the fabrication and use of the artefacts (polishing grooves (Fig. 3b), chasing marks...) are most often preserved. Consequently, surface examinations (from optical or electronic microscopy) can be an important source of knowledge to interpret signs of fabrication or daily use of the bronzes [35,47]. Even if this approach is still embryonic, a very promising way is opened for defining potential authentication criteria.

A second point of interest is that the decuprification process induces a strong enrichment in tin compounds in the surface layer due to an important selective dissolution of copper ions in the environment. This has been evidenced by elemental analysis of type-1 patinas [26,31–36], performed on cross-sections or on powders or directly in situ on the surface, mainly by EDS (energy dispersive X-ray spectrometry), on a great number of bronzes from several historic origins. Recent results [31,36]

have also revealed that the amount of dissolved copper is quite constant on the whole thickness of the surface of the tin enriched layer, but is depending on the tin content in the alloy. Therefore, as shown in Fig. 4, a relationship exists between the tin contents of the alloy and the surface layer of type-1 patinas, for a great number natural environments (soil, urban atmosphere, water lake, etc.) and independently of the historic period of the considered bronzes [31]. This result has been applied with success to the authentication of Roman portraits of Augustus and Livia in the Louvre Museum [12]. Thus, the amount of dissolved copper ions released seems to be connected to the corrosivity of the context (soil, atmosphere...) and not to the time of exposure, as it will be discussed later. The more the corrosive conditions are severe, the more copper of the bronze is dissolved and, consequently, the more tin content in the surface layer of type 1 patina is high. A dissolution factor f_{Cu} can then be defined, allowing a quantification of this phenomenon not only on ancient bronzes [31], but also on synthetic bronzes artificially corroded in laboratory experimental conditions [37,38]. Such alloy patina relationship now appears as a conventional criterion of authentication for Cu–Sn alloys; yet this relationship must therefore be only considered as a necessary criterion.

3.2. Relations between patina and corrosive environment

It is also important to consider the global influence of the environment on the nature of patinas, because most often, ancient bronzes have reached a steady state with their corrosive environment. This led to slow down or to stop the corrosion processes, such as: the dissolution of copper ions from the alloy to the corrosive context, the migration (percolation) of soil compounds into the corrosion layers and the precipitation of dissolved copper forming copper containing minerals or acting as cementing agent of earthy crusts, marine concretions, aerosol particles...

Consequently, several fundamental points will be here more particularly discussed: the effect of time, the composition and colour of patinas in relation with their environment, and the importance of the environmental factors affecting corrosion-mineral formation.

3.2.1. Time and patina thickness

The fact that a steady-state regime is reached by the objects in their environments implicitly induced that the thickness of ancient bronze patinas is not a function of the time of exposure. Patina thickness is not a pertinent criterion for authentication. This is confirmed by comparing long-term corrosion tests on copper and copper-base alloys exposed in different natural corrosive environments [48–51] with archaeological samples. As shown in Fig. 5, the corrosion penetration for the modern alloys and pure copper after less than two decades is typically between 10 and 100 μm , which is equivalent to that usually observed for type-1 patina of archaeological bronzes. The average penetration of the corrosion with respect to time of exposure follows globally a parabolic law in a great number of nat-

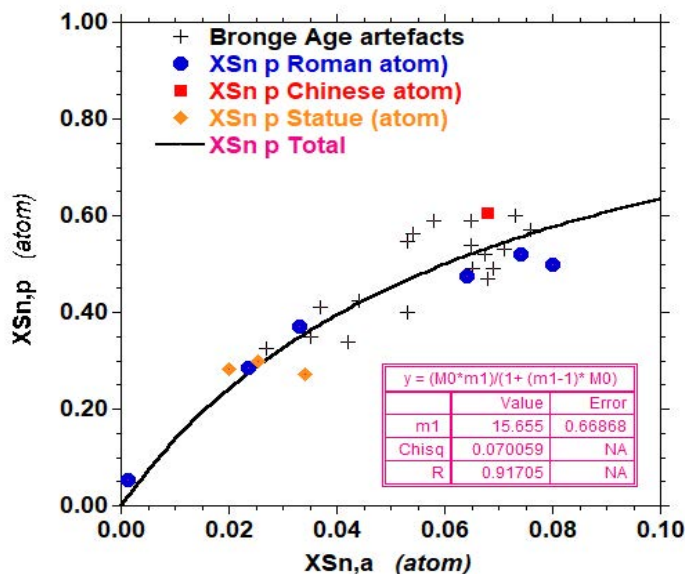


Fig. 4. Atomic fraction of tin cations in the passivating outer layer $X_{Sn,p}$ as a function of the atomic tin fraction in the alloy $X_{Sn,a}$ for bronzes of various origins and different historical periods, from [31].

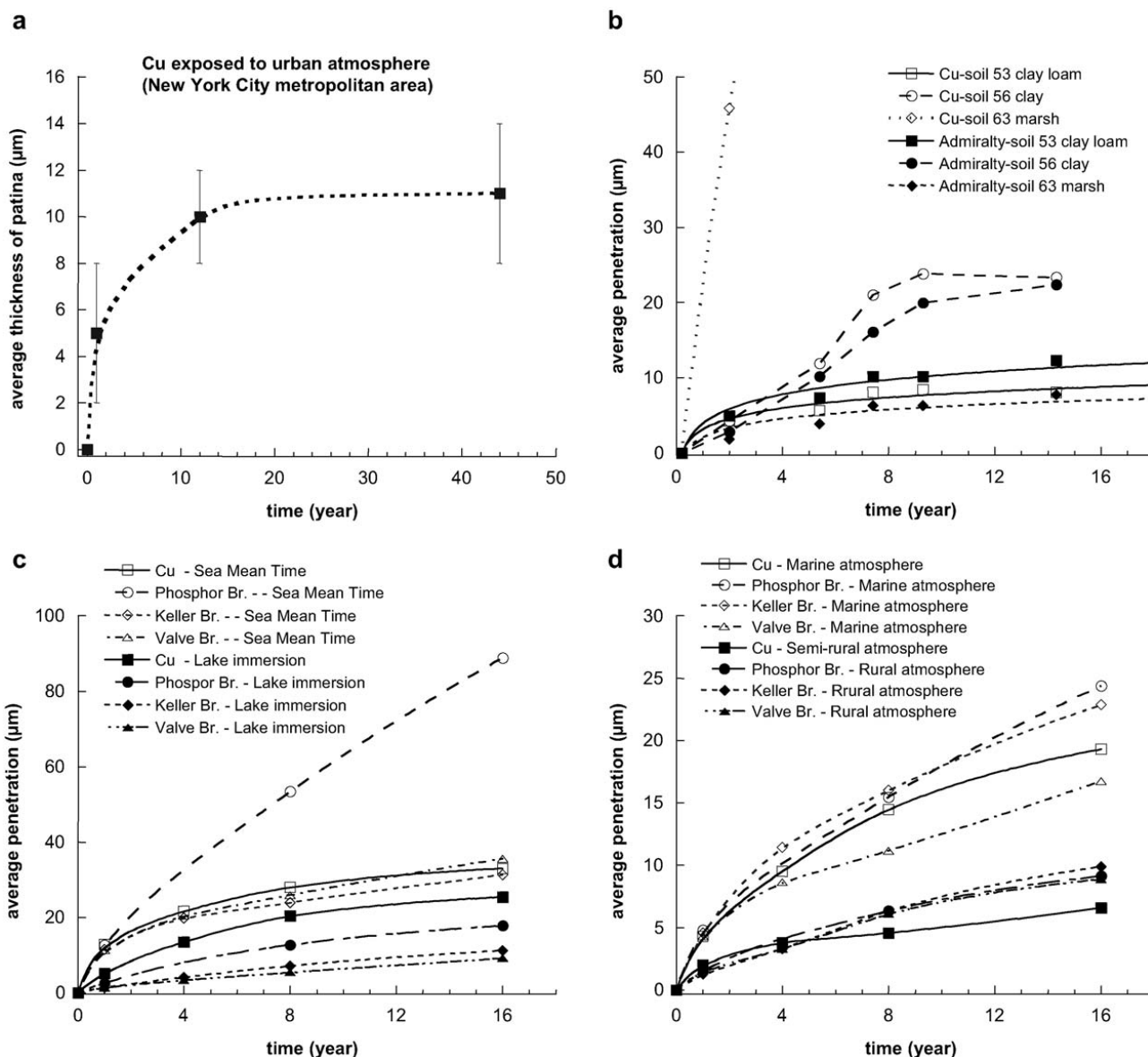


Fig. 5. Time corrosion curves (average penetration deduced from weight loss measurements) for pure copper and copper alloys exposed to natural environments a) outdoor urban atmosphere [49], b) soil burial [48], c) and d) water immersion and outdoor atmosphere [50]. Alloys composition in wt. %: Admiralty (71.3Cu–1.3Sn–27.4Zn), Phosphor bronze (95.75Cu–4Sn–0.25P), Keller bronze (85Cu–5Sn–5Zn–5Pb) and Valve bronze (88Cu–6Sn–3Zn–2Pb–1Ni).

ural environmental conditions. Consequently, type-1 patinas of bronze build up in a relatively short period of time (several decades) in natural environments. The case of thicker patinas, also often observed on ancient bronze, is usually the consequence of localized attacks or a non-uniform generalised corrosion (type-2 patina). These thicker patinas could form during the early stage of exposure, but more generally can form intermittently up to the present (as, for example, in the case of the bronze disease [52]). Consequently, type-2 patinas are also not related to the duration of corrosion and to the age of the object. The general assumption that thin (thick) patinas necessarily imply recent (ancient) objects is wrong.

3.2.2. Composition and colour of patinas in relation with their environment

For pure-copper-containing minerals, it must be recalled that the copper corrosion products formed under natural conditions or artificially often exhibit similar colours: red for Cu(I)

oxide, green to blue for Cu(II) compounds, etc. In fact, the patina colours are directly connected to the nature of the corrosive environment and not to the composition of the bronze alloys [28,31]. Consequently, the patina colouration cannot be considered as a valid criterion providing a quick identification of typical corrosion products useful for authentication.

However, for type-1 patina (“noble patina”) of buried artefacts, the colour appears strongly influenced by the presence of incorporated soil components [31]. The more the patinas incorporate soil compounds, the more the patinas will be coloured from grey to dark green, to green and to blue. Furthermore, it has been evidenced that:

- the “noble” patinas bear the imprint of the soil type in which the bronze has been buried;
- the earthy crusts on patinas, containing copper ions, must be considered as the “geological alteration” of a soil caused by the presence of a metallic material.

Thus the relative proportion between the elements (Ca, Si, Al) used to classify soils (calcareous, sandy, clayey...) is expected to be similar in both the surface layer of type-1 patinas (metal corrosion products) and the earthy crusts (soil corrosion products).

Such chemical behaviour has been verified by analysing Roman portraits [12] and a Celtic object [47], both found in clayey sandy soils in France. Fig. 6 shows the chemical composition in soil elements (Al/Cu, Si/Cu and Ca/Cu ratios) of the type 1 corrosion products and of the earthy crusts, directly in contact with the type 1 patina. It must be underlined that the repeatability is fairly good despite of the fact that the sampling technique was different. For the Roman objects, results were obtained by EDS/SEM from around 15 analyses of both scraped samples and cross-sections, while the Celtic bronze was analysed in situ on around 40 points on the surface. A good analytical correlation appears between the patinas and the earthy crusts, confirming the patinas were really formed in a clayey sandy soil. This result must be validated on other bronzes, but it already appears as an interesting criterion to be investigated. Furthermore from a practical authentication purpose, if earthy crusts have been simply put on an artificially patinated bronze, such correlation between corrosion products and soil crusts should not be observed.

3.2.3. Environmental factors affecting corrosion-mineral formation

The importance of taking into account the environmental factors affecting corrosion-mineral formation has been demonstrated by Schweizer [28]. From the study of ancient bronzes corroded under anaerobic conditions, he evidenced the close link existing between the composition of patinas and the environments in which they are formed. He used these information to determine under what sort of environmental condi-

tions the patinas grew and to evidence the biography of these artefacts.

Another point must be underlined regarding the strong effect of the environment on the nature of patinas. As the bronze corrosion process leads to a preferential dissolution of copper ions into the environment, exogenous elements- e.g.- coming from the environment- can be entrapped in the corrosion layers or mineralised. Traces of textiles or leather (Fig. 3c and d), insects, woods or even pure organic matters may reveal numerous pertinent historical information- which today could be studied. A typical example has been recently illustrated on mineralised textile fibres [53]. This new aspect appears to be of primary importance and should be explored more systematically for future authentication applications. The *micro-archaeology* of corroded surfaces could prove to be a source of new criteria.

The understanding of the interactions between environmental conditions and patina's nature, combined with the *micro-archaeology* of patinas, should lead to strong pertinent knowledge of the history of the object and consequently to its authentication.

3.3. Correlations between morphology and composition

This last part intends to show how the patina's investigation related to both the alloy and the environment may give numerous results, especially in cases of restored or composite artefacts. This point is illustrated by a typical example of expertise performed on a ding bronze, presently in a private collection.

3.3.1. Global examination of the bronze object

As shown in Fig. 7, the object is an ancient-looking tripod vessel consisting of spherical basin with two suspension rings. It purports to be of the type excavated at the Shang period site (1300–1100 BC) in Dayangzhou, Xin'gan, Jiangxi Province, China. Inside the basin, there is an archaic inscription, stylistically and historically in total agreement with its supposed age. In fact, this *ding* is a very good copy. The original one has been recently identified during an exhibition of Chinese art in Washington DC and belonging to the Jiangxi Provincial Museum in China and [54].

Looking on the surface appearance, the fake bronze exhibits an unevenly corroded surface, partially cleaned. Uniform patina, dark green, is observed on the decoration and its 3 feet (thickness of several 100 μm). Numerous rough mineral green crusts on dark green patina and also earthy compounds are present all over. They appear thicker in some places, such as the bottom of the basin, inside and outside of the rim, at the top of the legs and around the feet. Some powdery pale green compounds are also present, looking as classical compounds observed on localized attacks such as in case of bronze disease.

The patina appeared to be consisting of corrosion layers but by closer visual inspection, no clear corrosion stratigraphy was evidenced. Nevertheless, this patina could be interpreted at first sight as a type-1 patina, with copper-product deposits on it, with some punctual and enlarged localised type-2 corrosion.

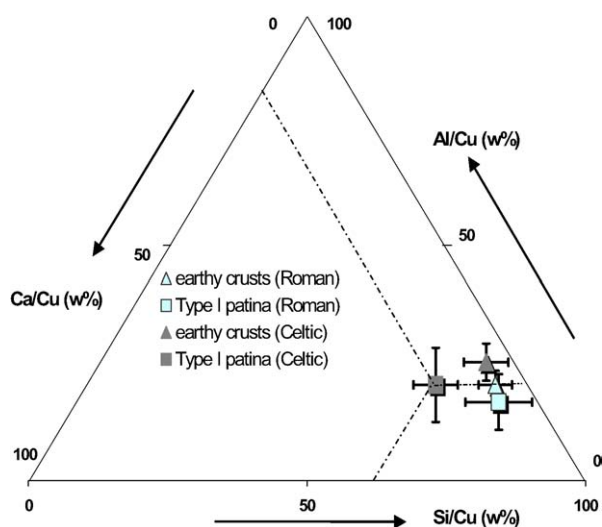


Fig. 6. Comparison of the composition of type-1 patinas and earthy crusts of Roman bronzes [12] and of a Celtic bronze (IIIrd BC) [35] both found in clayey sandy soils: ternary diagram (Al/Cu, Si/Cu, Ca/Cu). The error bars are the standard deviations ($\times 2$) of the mean value of the analyses, obtained on scraped corrosion products samples and cross-sections for the Roman bronzes or in situ for the Celtic bronze (EDS analysis).

3.3.2. Scientific investigation

No X-ray radiography was possible and no cross-section was allowed, thus after the visual examination, seven samples were selected for authentication from scraping off “surface” points (Fig. 7). These samples were put on a carbon tape on a holder before examination by SEM (scanning electron microscopy) coupled with an EDS (energy dispersive X-ray spectroscopy, semi-quantitative analyses, Ge detector with an ultra-thin window, beam intensity 20 kV).

In order to verify the relationships between the alloy, the patina and the environment (soil in this case) for the entire object (basin and feet), a study was conducted in order to determine:

- the nature of the alloy (one sample (0.5×0.5 mm) taken from 1 foot);
- the nature of patina (dark green patina upper green crusts, earthy crusts);
- the composition of the earthy crusts;

and then to relate all the data for interpretation.

The results are as follows:

- alloy composition: the alloy is a quaternary bronze, with an unusually high- Zn content (in wt.%: Sn 6–10%, Zn 10–15%, Ni 1–2% and Fe < 1%), but without lead. From this result, we can already conclude that the alloy composition of the sampled leg is an anachronism: high-Zn bronzes do not historically exist in China at this period [6] therefore confirming that this object is a fake, which will be further evidenced from the corrosion investigation;

- patina: it has a complex nature. The main characteristic is the presence of different compounds mixed together and mainly related to chloride anions. The dark green patina (supposed to be a type-1 patina) corresponds to a three-layer structure. The external surface (Fig. 8a) is an organic layer with some traces of other elements, as shown by the EDS spectrum (Fig. 8, spectrum 1). Under this organic layer, a green layer is visible by optical microscopy and contains a complex porous mixture of various mineral grains (Fig. 8b). Here the particularity is the high Pb content (lead was not found in the alloy), associated with Cl–O–Cu compounds (Fig. 8, spectrum 2). The third layer (Fig. 8c: details of Fig. 8b) in contact with the alloy is also porous and complex. Numerous mineral grains (spherical of a few μm diameter, rectangular or trapezoidal of 10–20 μm length) are observed. They are mainly Cu–Cl–O–Zn compounds, with noticeable amounts of Si–S–K–Ca elements (Fig. 8, spectrum 3a) or only with traces of Sn and Ni and Ti (Fig. 8, spectrum 3b). Also lying on the alloy, some organic compounds, similar to those observed in the first layer, are embedded into these mineral products. The green crusts (supposed to be copper corrosion products on the dark green patina) contain mainly the elements Zn–O–Cl–Cu–Al, with pure crystallites of Zn–O–Cl compounds. The pulverous pale green product is a complex mixture of compounds containing S–Cl–K–Ca–Cu–Zn–Al–Si–O–(C), but also of pure crystallites of Ca–S–O (probably calcium sulphate, plaster?) and Pb–Cl compounds;
- soil crusts: Classical compounds with Al, Si, Mg, K, Ca and Fe are detected, which are all elements typically found in a clayey soil, but they only contain traces of Cu element.

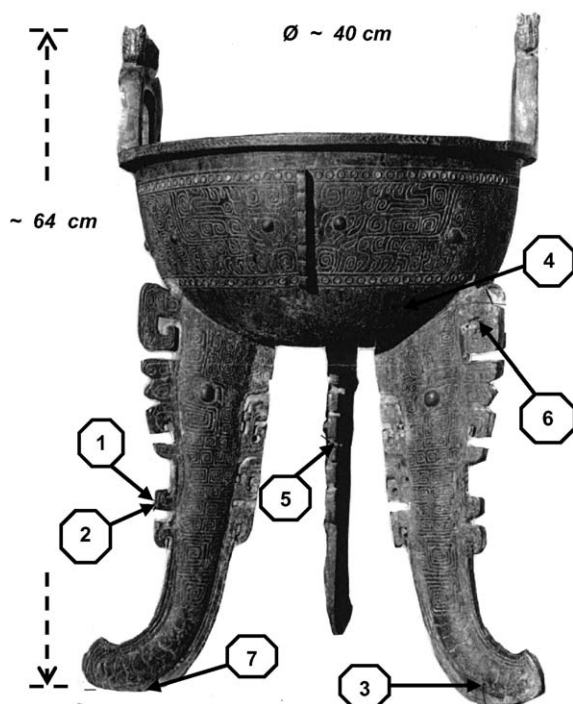


Fig. 7. Fake ancient Chinese bronze (*ding*, Shang period) and sampling localisation.

N°	Surface aspect	Description of sample
1	dark green	rough, compact and thick but, after scraping, pulverous sample
2	dark crust	quite smooth, taken with a dark green underlayer (~ 1 not thick), in contact with alloy low or not altered
3	dark crust	quite smooth, taken with dark green products on brown and "alloy"
4	dark green product	~1 but here thinner; surrounded by black crust
5	pale green	porous and pulverulent
6	earthy crust and green product	rough and compact
7	alloy	light gold color

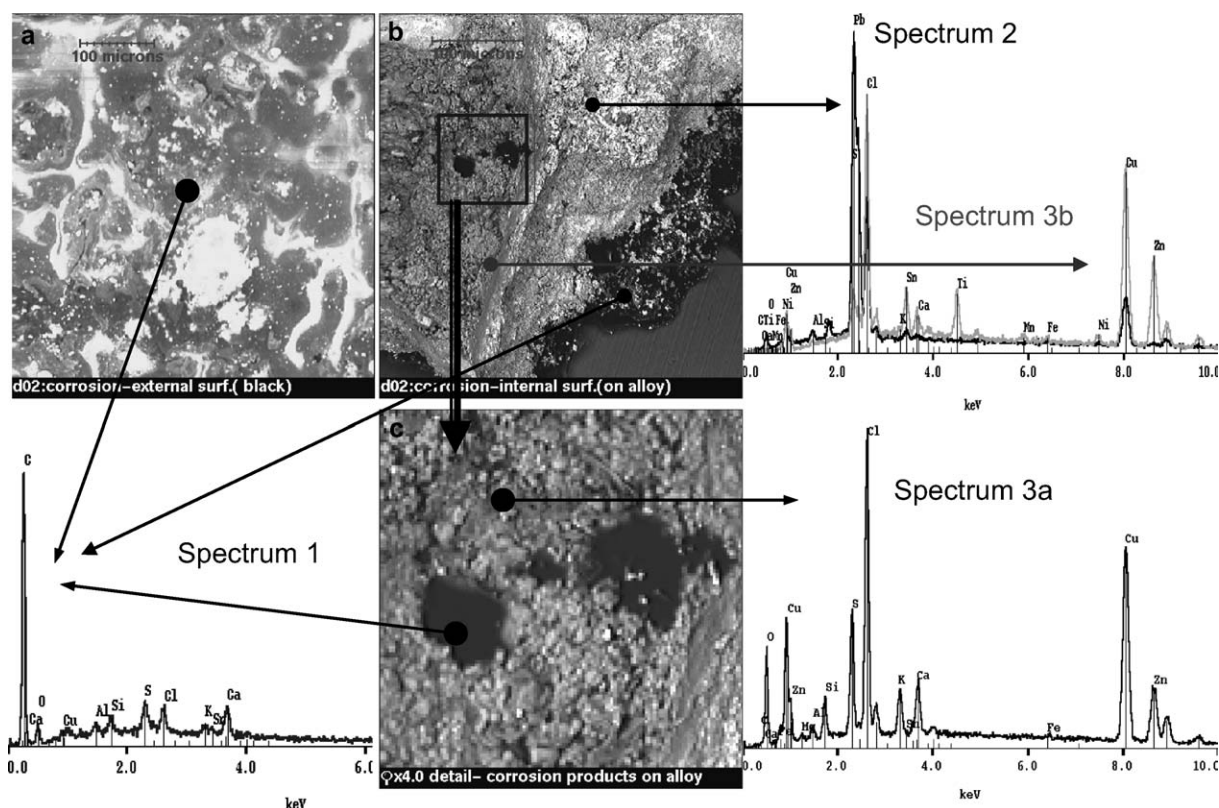


Fig. 8. Fake Chinese *ding*: SEM examination and EDS analysis of patina sample No 2: a) organic film (outer layer) b) observation from the internal part revealing a three-layer structure, c) detail of the organic matter embedded in the inner corrosion layer in the vicinity of the bulk alloy. Patina is here a mixture of crystallised grains of different compositions.

3.3.3. Application of authentication criteria and interpretation

Consequently, these results clearly reveal that no connection exists between the compositions of the alloy, the patinas and the earthy crusts. In fact the patina is not the result of a natural corrosion process:

- the patina (dark patina and green crusts) does not exhibit the normal characteristics (composition and structure) of type-1 patina structure previously defined;
- the decuprification phenomena are not observed (no relative Sn enrichment in the patina and no copper products in the earthy crust);
- the high level of lead content in the corrosion layer is unexpected, especially since no lead was detected in the alloy;
- the absence of correlation between the soil and patina compositions reveals that the soil crusts have been intentionally added on the surface.

The dark green patina, on all the different parts of the bronze, is characteristic of an organic coating with a colouration treatment covering mineral grains poorly coalesced, which are not the consequences of natural corrosion. It corresponds to an artificial treatment of patination made of successive deposits of zinc, copper and lead chlorides products associated to mineral extenders followed by an organic coating. The presence of an organic coating could be attributed to a drastic

“restoration” of the whole object. However, as similar organic coatings are embedded inside the internal corrosion layer, even the internal part of the patina on the alloy would be supposed to have been removed and “restored”. This is incoherent with the fact that the object is in a good state of conservation, and with the fact that superficial pale green corrosion products looking as type-2 corrosion were still present and finally that the earthy crusts have been added on the dark green patina. Furthermore as the alloy has an anachronistic composition due to its high zinc content, the whole results clearly show that this *ding* bronze is not original. Thus, the supposed “restoration” exhibits all the characteristics of an intentional treatment that gives an ancient aspect to a fake bronze buried into a modern soil.

So, in this case, even if structural examinations from cross-sections or complementary analyses such as infrared spectrometry or X-ray diffraction could have been pertinent to characterize more deeply the “alteration” nature, a minimal but adapted sampling can be sufficient to determine a counterfeiting if the whole set of the information, brought by the alloy patina environment system is considered.

4. Global methodology for bronze authentication

Authentication requires a clear methodological protocol to be set. According to the new data shown and discussed in this

article, an update of the usual approach appears possible. As shown in Fig. 9, the proposed synthetic procedure incorporates four necessary steps to reach a final conclusion:

- a first global examination;
- a scientific investigation with a well-defined sampling strategy and using complementary analyses (composition, structure and physico-chemical properties);

- a first synthesis of the analytical results from the application of the authentication criteria;
- a global interpretation of the analytical results taking into account the criteria above defined and also incorporating the stylistic, artistic and technologic data.

Obviously, the choice of the investigation methods should vary according to the specificity of each investigated bronze

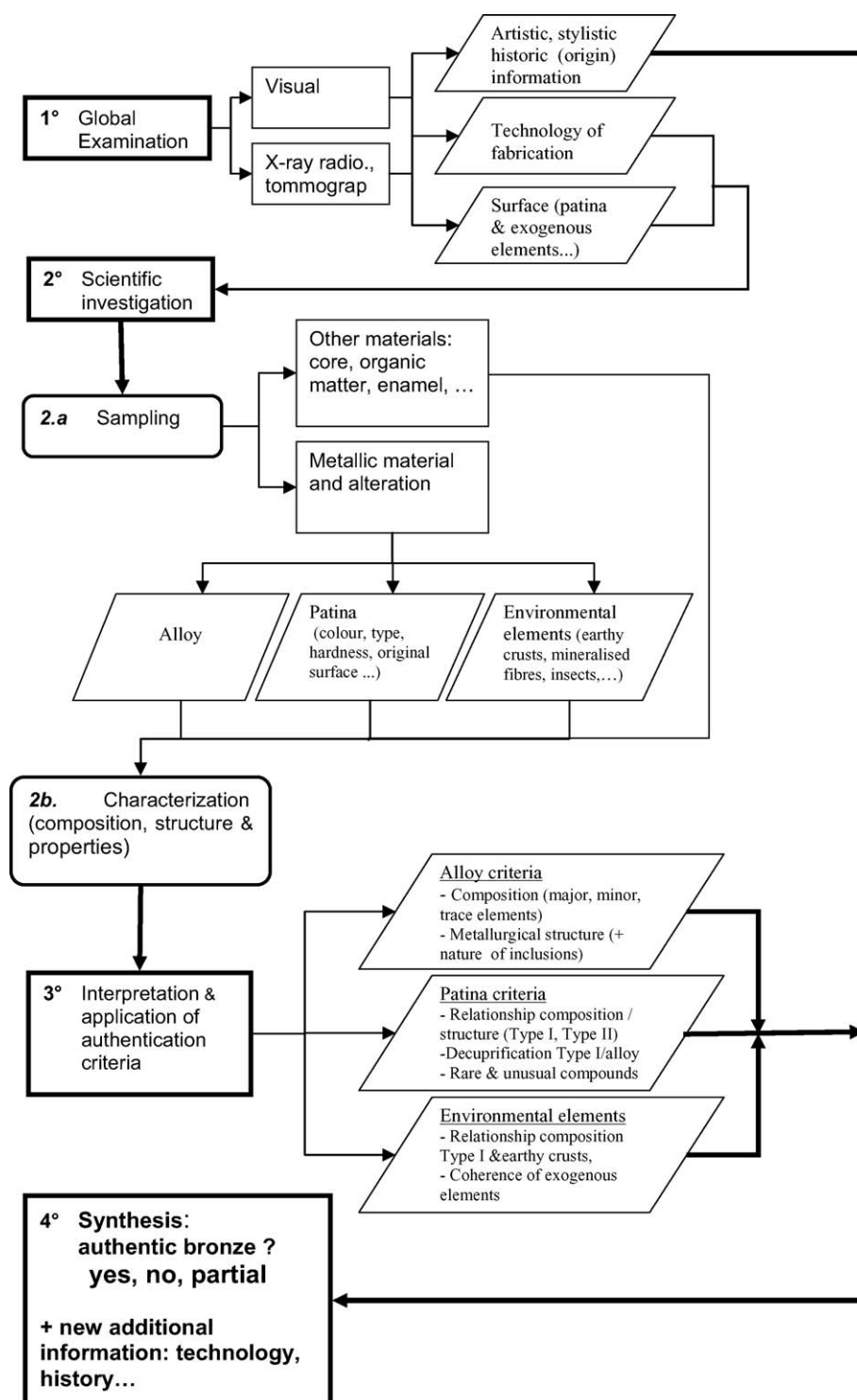


Fig. 9. Global methodological procedure for authentication of bronze artefacts.

and the characterisation facilities available. Nevertheless, some fundamental techniques appear mandatory. One could be the use of SEM and X-ray analysis for promptly obtaining information on morphology and elemental composition, which could be very complex in case of fake. It can be easily carried out on scrapped samples or by in situ non-destructive measurements, as cross-sections are often not allowed. An essential aspect is the obligation to analyse both the alloy and the alteration in order to get a clear idea of the structure of the complete system: alloy/patina/environment. Finally, it must be underlined that historical, stylistic and technological data are still necessary to conclude for authentication.

5. Conclusion

This article highlights the importance to consider the alloy patina environment as a global system for performing a pertinent authentication. It has been proved that the bronze patina reveals numerous traces of physical-chemical interactions between the metallic substrate and its environment and can be considered as pertinent historical material evidence. It is proposed that authentication requires a global approach in which the relationships between patinas alloys and patinas environment must be characterized. It has been pointed out that the corrosion processes of bronzes and more specifically the decuprification process must be taken into account.

On this basis, several new criteria have been proposed. The first one is related to the relationship between the tin content in the alloy and in the “noble” patinas (type-I corrosion structure). The second criterion is connected to the fact that a strong relationship exists between copper compound deposits and the corrosive context. The corrosion products of the “noble” patina bear the imprint of the type of soil and more generally of the environment in which the bronze corroded. Furthermore, this approach for authentication applications could be not only a way to read and interpret signs of everyday usage, but also to retrace the corrosion “biography” of the artefacts.

It has also been evidenced that neither the thickness nor the colour of the patina can be used as criteria of authentication.

The example of the fake Chinese *ding* revealed the importance of appropriate sampling. So even though complementary analyses have not been performed, the analytical results on the surface patinas, of the alloy and of the fictitious corrosive environment, are sufficient to confirm that this artefact is not original. It has been shown that the patinas are not produced in a buried context, although earthy crusts were present.

A global approach to the authentication of bronze artefacts has been proposed, which should give numerous determining results, even for restored artefacts.

However, we are still striving to identify better criteria for identifying the counterfeiting of patinas and to evidence the differences between natural/artificial and ancient/recent patinas. A better theoretical understanding of the corrosion process are expected to open new fields improving the authentication procedure. This ambition is indispensable if we wish to in-

crease our knowledge of metallurgical techniques and respond to authentication but also to conservation challenges.

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References

- [1] B. Pichler, A. Vendl, Authentication of a Renaissance bronze statue, in: Recent Advances in the conservation and analysis of artifacts, Summer Schools Press, University of London, 1987, pp. 169–171.
- [2] W.J. Young, Authentication of works of art, in: S. Doeringer, D.G. Mitten, A. Steinberg (Eds.), Art and Technology—A symposium on classical bronzes, M.I.T. press, Cambridge, MA, 1970, pp. 85–94.
- [3] S.Z. Lewin, A new approach to establishing the authenticity of patinas on copper-base artifacts, in: J. Young (Ed.), Application of Science in Examination of Works of Art, MA, Boston, 1970, pp. 62–66.
- [4] D. Attanasio, G. Bultrini, G.M. Ingo, The possibility of provenancing a series of bronze punic coins found at Tharros (Western Sardinia) using the literature lead isotope database, Archaeometry 43 (4) (2001) 529–547.
- [5] E. Pernicka, Whither metal analysis in archaeology?, in: C. Mordant, M. Pernot, V. Rychner (Eds.), L’atelier du bronzier en Europe du XX^e au VIII^e siècle avant notre ère, Bronze’96, Tome I, Comité des Travaux Historiques et Scientifiques, Paris, 1998, pp. 259–267.
- [6] W.T. Chase, Chinese bronzes and microstructure, in: Proc. BUMA IV Forum, Jan.16-17 1996, Japan Inst. of Metals Pub., Sendai, Japan, 2001, pp. 9–23.
- [7] E. Sangmeister, Metallanalysen in der Archäologie : erfahrungen aus 45 Jahren Forschung, in: ibidem [5], pp. 9–18.
- [8] J.P. Northover, V. Rychner, Bronze analysis: experience of a comparative programme, in: ibidem [5], pp. 19–33.
- [9] R. Krause, E. Pernicka, Frühbronzezeitliche Kupfersorten im Alpenvorland und ihr archäologischer Kontext, in: ibidem [5], pp. 191–202.
- [10] G. Vittiglio, K. Janssens, B. Vekemans, F. Adams, A. Oost, A compact small-beam XRF instruments for in-situ analysis of objects of historical and/or artistic values, Spectrochimica Acta B 54 (1999) 1697–1710.
- [11] J.-M. Welter, the zinc content of brass: a chronological indicator, Techné 18 (2003) 27–36.
- [12] L. Robbiola, L.-P. Hurtel, Standard nature of the passive layers of buried archaeological bronze - The example of two Roman half-length portraits, in: I. MacLeod, S. Pennec, L. Robbiola (Eds.), METAL 95, James & James Science Publ., London, 1997, pp. 109–117.
- [13] R.J. Gettens, Patina: noble and vile, in: ibidem [2], pp. 57–72.
- [14] N.D. Meeks, Surface studies of Roman bronze mirrors, comparative high-tin bronze Dark Age material and black Chinese mirrors, in: R.M. Farquhar et al. (Eds.), Proceedings of the 26th Int. Archaeometry Symposium, University of Toronto, May 1988, The Archaeometry Laboratory, 1988, pp. 124–127.
- [15] F. Colao, R. Fantoni, V. Lazic, V. Spizzichino, Laser-induced breakdown spectroscopy for semi-quantitative and quantitative analyses of artworks—application on multi-layered ceramics and copper based alloys, Spectrochim. Acta B 57 (2002) 1219–1234.
- [16] E. Paparazzo, L. Moretto, X-ray photoelectron spectroscopy and scanning Auger microscopy studies of bronzes from the collection of the Vatican museums, Vacuum 55 (1999) 59–70.

- [17] R. Schlesinger, H. Klewe-Nebenius, M. Bruns, Characterization of artificially produced copper and bronze patina by XPS, *Surf. Interface Anal.* 30 (2000) 135–139.
- [18] L.I. McCann, K. Trentelman, T. Possley, B. Golding, Corrosion of ancient Chinese bronze money trees studied by Raman Microscopy, *J. Raman Spectrosc.* 30 (1999) 121–132.
- [19] R.L. Frost, P.E. Williams, W. Martens, J.T. Klopogge, Raman spectroscopy of the polyanionic copper(II) minerals buttenbachite and connellite: implications for studies of ancient copper objects and bronzes, *J. Raman Spectrosc.* 33 (2002) 752–757.
- [20] A. López-Delgado, J.M. Bastida, M.P. Alonso, F.A. López, Influence of acetic and formic vapours on patinated artistic bronze, *J. Mater. Science Lett.* 16 (1997) 776–779.
- [21] M. Wadsak, I. Constantinides, G. Vittiglio, A. Adriaens, K. Janssens, M. Schreiner, F.C. Adams, P. Brunella, M. Wuttman, Multianalytical study of patina formed on archaeological metal objects from Bliesbruck-Reinheim, *Microchim. Acta* 133 (2000) 159–164.
- [22] G.M. Ingo, E. Angelini, G. Bultrini, I. Calliari, M. Dabala, T. De Caro, Study of long-term corrosion layers grown on high-tin leaded bronzes by means of the combined use of GDOES and SEM + EDS, *Surf. Interface Anal.* 34 (2002) 337–342.
- [23] I. De Ryck, A. Adriaens, E. Pantos, F. Adams, A comparison of microbeam techniques for the analysis of corroded ancient bronze objects, *The Analyst* 128 (2003) 1104–1109.
- [24] I. Constantinides, A. Adriaens, F. Adams, Surface characterization of artificial layers on copper alloy reference materials, *Appl. Surf. Sci.* 189 (2002) 90–101.
- [25] F. Noli, P. Misaelides, A. Hatzidimitriou, E. Pavlidou, M. Kokkoris, Investigation of artificially produced and natural copper patina layers, *J. Mater. Chem.* 13 (2003) 114–120.
- [26] W.T. Chase, Chinese bronzes: casting, finishing, patination and corrosion, in: D.A. Scott, J. Podany, B.B. Considine (Eds.), *Ancient and Historic Metals: Conservation and Scientific Research*, The Getty Conservation Inst., Los Angeles CA, 1994, pp. 85–117.
- [27] S.Z. Lewin, S.M. Alexander, The composition and structure of natural patinas, Part I copper and copper alloys, section A: AATA supplement, 6 (4) 1967 – section B: AATA supplement, 7 (1) 1968.
- [28] F. Schweizer, Bronze objects from lake sites: from patina to “biography”, in: *ibidem* [26], pp. 33–50.
- [29] J.B. Sharkey, S.Z. Lewin, Conditions governing the formation of atacamite and paratacamite, *Am. Mineral.* 56 (1971) 179–193 (January–February).
- [30] A.W. Smith, Stable carbon and oxygen isotope ratios of malachite from the patinas of ancient bronze objects, *Archaeometry* 20 (2) (1978) 123–133.
- [31] L. Robbiola, J.-M. Blengino, C. Fiaud, Morphology and mechanisms of formation of natural patinas on archaeological CuSn alloys, *Corros. Sci.* 40 (1998) 2083–2111.
- [32] R.J. Gettens, The corrosion products of an ancient Chinese bronze, *J. Chem. Educ.* (February 1951) 67–71.
- [33] W. Geilmann, Verwitterung von Bronzen im Sandboden, *Angew. Chem.* 68 (1956) 201–212.
- [34] T. Stambolov, *The Corrosion and Conservation of Metallic Antiquities and Works of Art*, Central Research Laboratory for Objects of Art and Science, CL Publication, Amsterdam, 1985 (236 p.).
- [35] D.A. Scott, An examination of the patina and corrosion morphology of some Roman bronzes, *J. Am. Institute Conserv.* 33 (1) (1994) 1–23.
- [36] A. Dorigo, C. Fiaud, J.-P. Labbé, L. Robbiola, P. Brunella, H. Böcking, Characterization of the corrosion structures of Roman copper alloys, in: W. Mourey, L. Robbiola (Eds.), *METAL 98*, James & James Science Publ., London, 1998, pp. 145–151.
- [37] L. Robbiola, R. Portier, Electron microscopy and EDX analysis in the investigation of the decuprification phenomena in CuSn alloys: a comparison between archaeological and synthetic bronzes, in: *Proc. 14th ICEM Electron Microscopy*, Vol. III, Inst. of Physics Publ., London, 1998, pp. 289–290.
- [38] L. Robbiola, N. Pereira, K. Thauray, C. Fiaud, J.-P. Labbé, Decuprification phenomenon of CuSn alloys in aqueous solution at nearly neutral pH condition, in: *ibidem* [36], pp. 136–144.
- [39] R.F. Tylecote, The effects of soil conditions on the long-term corrosion of buried tin-bronzes and copper, *J. Archaeol. Sci.* 6 (1979) 345–368.
- [40] A.G. Nord, E. Mattson, K. Tronner, Factors influencing the long-term corrosion of bronze artefacts in soil, *Protect. of Metals* 41 (2005) 339–346.
- [41] L. Robbiola, C. Fiaud, S. Pennec, New model of outdoor bronzes corrosion and its implication for conservation, *Proceedings of the 10th ICOM Meeting*, Washington, vol. II (1993), pp. 796–802.
- [42] P. Piccardo, Setting up an investigation method for corrosion of ancient burial bronze objects, *Microscopy & analysis*, Rolston Gordon Communications, n° 63, 2000, pp. 13–15.
- [43] L. Tommesani, G. Brunoro, G.L. Garagnani, R. Montanari, R. Volterri, Corrosion behaviour of modern bronzes simulating historical alloys, *Revue d'Archéométrie* 21 (1997) 131–139.
- [44] R.M. Organ, The current status of the treatment of corroded metal artifacts, in: B.F. Brown, et al. (Eds.), *Corrosion and Metal artifacts*, NBS Special publication No 479, Washington DC, US, July 1977, pp. 107–142.
- [45] R. Bertholon, The original surface of corroded metallic archaeological objects: characterization and location, *Rev. Met. Paris* 9 (2001) 817–823.
- [46] L. Soto, J.P. Franey, T.E. Graedel, G.W. Kammlott, On the corrosion resistance of certain ancient Chinese bronze artifacts, *Corros. Sci.* 23 (1983) 241–250.
- [47] L. Robbiola, D. Vilbert, T. Lejars, D. Bourgarit, B. Mille, Characterization of a buried archaeological bronze from the Celtic tomb n° 1002 of La fosse Cotharet-France (Roissy-en-France), in: I. MacLeod, J.M. Theile, C. Degriy (Eds.), *Western Australian Museum, Pub., METAL 2001*, Perth, 2004, pp. 237–242.
- [48] M. Romanoff, Underground corrosion, *National Bureau of Standards Circular* 579, Washington DC, 1957 (227 p.).
- [49] J.P. Franey, M.E. Davis, Metallographic studies of the copper patina formed in the atmosphere, *Corrosion Science* 27 (7) (1987) 659–668.
- [50] C.R. Southwell, J.D. Bultman, A.L. Alexander, Corrosion of metals in tropical environments—Final reports of 16-year exposures, *Mater. Performance* 15 (7) (1976) 9–25.
- [51] I. Geld, C. McCaul, Long term corrosion tests in Rondout reservoir, New York, *Mater. Performance* 17 (5) (1978) 27–33.
- [52] D.A. Scott, Bronze disease: a review of some chemical problems and the role of relative humidity, *J. Am. Institute Conserv.* 29 (1990) 193–206.
- [53] C. Moulherat, M. Tengberg, J.-F. Haquet, B. Mille, First Evidence of Cotton at Neolithic Mehrgarh, Pakistan: Analysis of Mineralized Fibres from a Copper Bead, *J. Archaeol. Sci.* 29 (2002) 1393–1401.
- [54] *The golden age of Chinese archaeology—celebrated discoveries from the People Republic of China*, Editors Office, National Gallery of Art, Washington DC, No 60 1999, p. 196.