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Review article

NEW INTERDISCIPLINARY ASPECTS ON SCIENCE FOR CONSERVATION OF CULTURAL HERITAGE-II

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Abstract

The paper is the second note presenting a series of modern aspects regarding the interdisciplinarity of the science for conservation of the cultural heritage, focused on the background of the artifacts in specific contexts, the discovery in the valuing of an archaeological artifact, types of expertise and their role, and the importance of scientific investigation of newly discovered artifacts and finally archaeometric studies by identifying compounds of three typologies of patinas.

Keywords: Conservation science, Path and backgrounds, Preservation, Restoration, Display, Harnessing/Treasuring, Patina, Liesegang effect

1. Introduction

The science of conservation, as academic domain, caught the attention of many Universities and Research Institutions. Thereby, in 1996, the Polytechnic University of Valencia founded the Forum UNESCO "University and Cultural Heritage", which in a short time attracted over 260 universities with departments of specialized cultural heritage. Every year, this Forum organizes in different academic centers around the world meetings scientific on conservation, where different cases of the conservation state are presented together with various experiences of young and recognized groups and the guidelines concerning the management,

the valuing of the cultural heritage by various activities focused on discovery, acquisition, investigation, evaluation, preservation and museum display [1] [2] [3] [4] [5] [6] [7]. A special place is taken by the research which highlights new aspects concerning the internal and surface structure of archeological artefacts, on site, presenting the specific effects and processes, less known. An example, cited in this article, is the elucidation of the Liesegang stratification mechanisms by means of the two films: hydrogels based on Sn(II), Pb(IV), Zn(II) etc. or hidroxy and chlorapatite, which preserve differently the stratified compounds [8] [9] [10]. In this respect, on the basis of previous experiences developed by the author in this field, there are presented a number of issues the on background of the artifacts in specific contexts, the role of discovery in the valuing of an archaeological artifact, types of

2. The Background of the Artifacts in Specific Contexts

Any artifact of cultural heritage, from the process of making to its housing in a museum, has a background route during which continually changes the shape and appearance. Along this route, the object is part of different contexts. such as: design/creation, production, acquisition/ transfer, use or display (as applicable), loss, abandonment, theft, destruction. For archaeological artifacts the components of these paths are: discovery, restoration / preservation, exhibiting. Depending on the context, we distinguish the following routes: * normal artwork or monument (the installation, acquisition, display/use, preservation, restoration, conservation etc.). * Through abandonment, loss of use functions (the installation, operation, abandonment, archaeological discovery); * by stealing and illicit discovery; * by hiding and forgetting, followed by archaeological discovery (treasures, jewelry, money etc.). * by weather or

expertise and their role, and the importance of scientific investigation of newly discovered artifacts and finally archaeometric studies for identifying compounds of three typologies of patinas.

natural disasters damaging, followed by archaeological discovery (flooding, landslides, earthquakes, volcanic eruptions, lightning, fire, explosion etc.). * by destructions or man-made disasters, followed by archaeological discovery (explosions, fires, wars, revolutions, collapse, diving etc.); * by epidemic / pandemic diseases that caused to many rural and urban settlements to be abandoned including the monuments, than followed by archaeological discovery (e.g. for pyramids and temples of civilization Mesoamerica, there is no accepted theory today to explain their abandonment some explained bv overcrowding, some by foreign invasion, popular uprisings or the collapse of the trade routes and of the interest for the area; closer to the truth are probably the ecological assumptions, including disaster medium/droughts, epidemics and climate change).

3. Context of Discovery in the Valuing of an Archaeological Artifact

In the valorization of the archaeological artifacts is interesting to use the following contexts, discussed in terms of shape and appearance during a specific period: the nature and origin of raw materials design and manufacture, acquisition/transfer, use, abandonment or loss and discovery. Among these, the context of abandonment is the most important and to which is given a special attention. It includes: * The discovery (through systematic excavations, change after agricultural operations, construction, excavation, landslides or mudslides, in silt or after flooding, old galleries or those of wild animals and

after poaching without depletion site and so on); * Photo fixing and stratigraphic survey of the levels of ironing (stratigraphic positioning and surveying); * physic-chemical Determining and microbiological load of the soil of laying and determining of the chemical composition of the crust and of some archaeometric features/deposits and base material (morphology, texture, porosity, micro-stratigraphic structure, structural components from contamination etc.). * Evaluation of transformation/process/structure effect/ composition/allotropy etc. to determine the evolution between abandonment and

discovery (soil effects), or why not, establishing specific archaeometric features before abandonment. For these reasons, it is imperative that at the discovery, the artifact should not be cleansed of crust cover until it is physically and chemically investigated and

4. Types of Expertises and their Role

Scientific investigation of cultural heritage assets is based on six types of surveys: authentication, asset evaluation, establishing conservation state, compatibility studies of new with traditional materials artistic techniques, compatibility interventions preservation and restoration. of monitoring the behavior of these interventions for a specified period (six months, one year or more, depending on the state of conservation, scale and complexity of interventions) and monitoring of conservation state throughout the period of display or storage. Among these surveys, the authentication and the establishment of the state of conservation requires corroboration of analytical methods of diverse related disciplines involved in conservation science and respectively two or more instrumental co-assisted techniques, such as: SEM-EDX, micro-FTIR and micro-Raman, X-ray fluorescence, chromatography coupled with UV-Vis spectroscopy etc. [10]. In carrying out these surveys, an important role is played by archaeometry, which by determination of the evolutionary characteristics of the materials, can establish a series of attributes that allow dating, paternity

Regarding the aspects of the evaluation of bronze artifacts from the archaeological sites in our country, under current rules and concepts of integrated conservation science, we have highlighted a number of research directions. These allowed setting *the position and role of the three ways or forms of enhancement* (purposes), the soil microbiological tested. It will be noted in detail all data related to the context of discovery. It is known that an artifact, of which the context of discovery is unknown, loses a number of factors and patrimonial functions, value rate decreasing from 30 to 80%.

(author, school/workshop, laying geographical area, source material etc.) asset evaluation and determination of conservation states. The role of scientific investigation for the harnessing of cultural heritage is undeniable. It is known that scientific investigation of newly discovered artifacts or those bought without anamnesis (with no historiographical data and unknown context of discovering) is a complex research. Thus it will bring valuable contributions which will allow three groups of evaluations: *historiographic, archaeometric and respectively for the technology and the process of making the artifact by involving the base material (gemology, ceramology, archarchaeo-dendrology, aeometallurgy, the archaeo-ethnography of fabrics). * museum display (introducing it in the museum presentation, harnessing of artifacts); * antiques trade, with the two legitimate forms (known) and illicit (monitored and maintained by the law enforcement bodies, national and international). In this context, we will show the role of scientific investigation in researching ancient bronze artifacts extracted from various archaeological sites.

4.1. Valuing the scientific investigation of newly discovered artifacts

namely: archaeometallurgy, archaeometry and historiographical studies, museum displaying, trading and assemblance / enrichment of the collections, by analyzing the involvement of various scientific activities, of the integrated conservation for the main types or groups of interest in bronze artifacts in general, fig. (1).

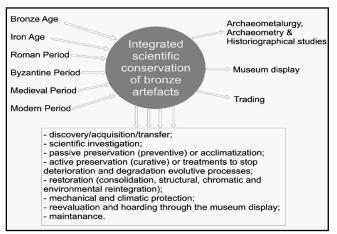


Figure (1) Graphic representation of period of interest (left), goals (right) and scientific conservation activities (bottom) of bronze artefacts.

From these goals, three (Archaeometalurgy, Archaeometry and Historiographical studies) have а particular importance, requiring а complex series of studies and research that is: archaeometry/authentication. For the harnessing of a bronze artifact from archaeological site, based on specific integrated conservation activities, a series of principal stages must be followed [11] [12] [13] [14] [15] [16] [17]: excavation; cleaning; scientific investigation; the coherent reconstruction of the shape from fragments; completion of form and ornament; coating for mechanical and climatic protection ; display and maintenance. It is very important to find a set of archaeometry data about the object, which can be obtained by involving modern techniques of scientific investigation, historiography and research studies of experimental archaeo-metallurgy and archeology. These data are linked on one hand to the authenticity, and secondly to the state of conservation [10]. It must be allowed the achievement of one of the three goals by scientific conservation and involvement of various specific activities shown in figure (1). The three goals of the scientific conservation for bronze artifacts [10] - * Archaeo-

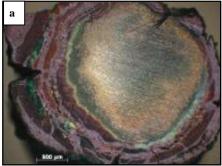
The archeological pieces of bronze that do not contain a metallic core raise the most important and metallurgy, archaeometry and historiographical study - should aim to understand the nature of the material, technology of making the artwork and the artistic technique used, possibly at the expense of formal and aesthetic issues in the context of the historical epoque (or timeframe) in which they were used; * Displaying in the museum, should be well presented so that the morphological, structural, functional. materials, technology and aesthetic features of the object, must not be overshadowed; * *Trading* in the antiquities market, should highlight the issues particularly related to aesthetic and those genuine linked to the authenticity, which are able to meet the collectors needs and the national standards on conservation of cultural heritage and archaeology. Although these features coexist to different degrees, their order of presentation is not random, their importance decreasing from the first to the third. Regarding the taken archaeology, it is into consideration the phenomenon of illegal trading with high value goods or fakes the encouraged and action of authentication by certified experts, their acquisition and classification by museums and collections of precious objects.

4.2. Archaeometric studies by identifying compounds of three patinas

complex problems in their authentication. Such pieces are often sent to the 'grey fund' and abandoned, in most cases

during the preliminary sorting. immediately after excavation. These pieces can be a very important source of information, mainly about the basic minerals and often being the unique proof of a technique or metallurgical tradition/period [17] [18] [19] [20] [21]. Speaking of old bronzes authentication, a number of archaeometric features are very important, such as: seniority patina or historical patina, mineral trace and elements contamination from the archaeological site. structure and distribution of chemical components in Liesegang layers etc. [22] [23] [24] [25] [26] [27]. On historical patina on bronze the basic chemical components are easily differentiated, specific for the three periods, grouped under the following names (terms): noble or primary patina, poor or secondary patina, contamination or tertiary patina. Primary patina is formed during the making process and in the first period of use, when chemical and electrochemical redox processes, give thin continuous films, initially by oxides and sulphides of Cu(I, II), then the basic carbonates of Cu(II), which serve as protection. Secondary patina appears in the final period of use, under the influence of factors with environmental high aggressiveness, which by competitive and complexation redox processes, acid-base assisted in the presence mainly of chloride anion in the acid medium. and carbon dioxide in the alkaline medium, form nantokite (CuCl), then azurite $(CU_{3}(OH)_{2}(CO_{3})_{2}).$ malachite (Cu₂(OH)₂CO₃), atacamite (Cu₂Cl(OH)₃orthorhombic)/paratacamite (Cu2(OH)3Clrhombohedral) and so on, distributed on the surfaces more or less evenly. Many artifacts in pre-abandonment phase suffer from thermal processes (incineration, combustion of guilt covering, devastation by fire and so on). The processes of the two stages culminate in the soil, in the laying period and forms deep degradations to the metal core and activation crevices and pitting holes. Here, besides the action of soil environment, in addition to electrochemical corrosion and microbiological processes several atypical processes act, such as: the separation of less active metals (amphoteric) in small lenses, for example tin, and the segregation of components (active metals as such as Zn, Fe, etc.) of the alloy phase volume to the surface, where they dissolve in groundwater, leaving the base alloys poorer. Today, lower concentration of iron in bronze and zinc in old brass, are very important archaeometric features. The catalyst in soil processes is chloride anion, which having very low volume, migrates in crevices and pitting holes by corrosion, in the presence of cations in high oxidation state and releases oxygen. The bronzes. where there are circular variations of the laying conditions on sites, are subject to Liesegang phenomenon, which is due to the coatings of amphoteric hydrogels of Sn (IV), Pb(II) or Zn(II) and those of chlorapatite/ hydroxyapatite, allowing osmosis recrystallization of layered compounds of the first two patinas. In the laying period the tertiary or contamination patina is formed in the form of new structures with continuous consumption of metallic core and embedding by monolitisation in the corrosion crust, minerals and various organic and inorganic materials, from the laying environment. In prolonged periods, organic materials undergo mineralization and fossilization processes. Depending on the strength of cyclical aggression, the Liesegang effect can be extended to the whole piece or just on small areas, because it grows/evolves according to the shape and complexity of the piece, the alloy composition, and the laying environment, processing the procedures of making the art piece, thermal processes and subsequently suffered periodicity and variability of seasonal cycles. The bases of its formation are a series of semi-membrane hydrogels or of chlorine-apatite membrane with coating capability and behavior of membrane with specific permeability for certain cations and anions. At the transition from the wet mediums to jellying ones and from dried

ones by the desiccant, these structures allow through osmosis the layered recrystallization in a certain order of the components from the first two patinas. Some manifestations of Liesegang effect



on bronze pieces was recently discovered in archaeological sites in Romania as presented in fig. (2- 9) [22] [23] [24] [25] [26] [27] [28] [29] [30] [31] [32] [33] [34] [35] [36].

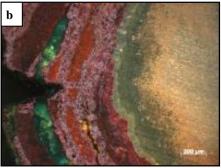


Figure (2) microscopic image of the cross section of a needle clip \underline{a} whole 50X, \underline{b} detail 100X

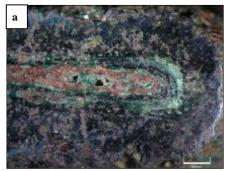
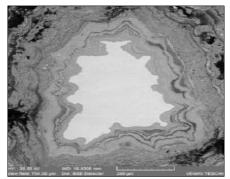




Figure (3) stratigraphic structure of ancient coins discovered in Nufărul <u>a</u>, whole 50X, <u>b</u> detail 100X



Figure (4) OM image of a needle in transversal section of a brass clips forged in torsade



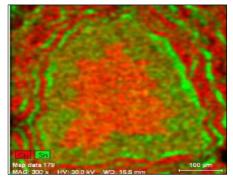


Figure (5) arrangement of layers of tin, responsible for generating coatings hydrogels leading to Liesegang effect

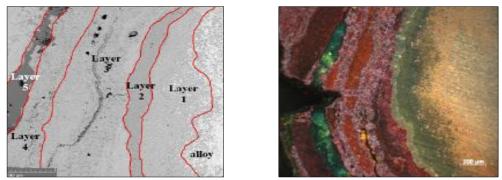


Figure (6) layered arrangement of corrosion products from soil processes

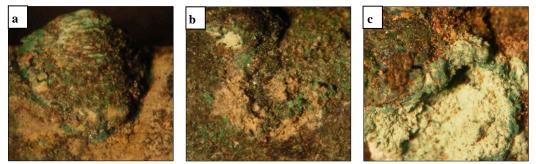


Figure (7) discontinuous forms of Liesegang effect with film-forming hydrogels <u>a</u> concentric distribution to a rivet of the same material with the support, revealed at the surface; <u>b</u> distributions in a semi-ring with rivet hole; <u>c</u> Liesegang effect structural disturbed by pedological process

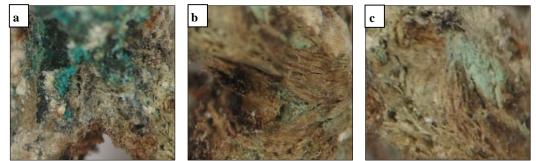


Figure (8) discontinuous forms of Liesegang effect with film-forming hydroxy and chlorine based apatite <u>a</u> Lisegang structures segregation of corrosion products on the surface of the piece, <u>b</u> Honeycomb membranes of chlorapatite remaining after removal of the Liesegang stratified compounds, <u>c</u> Honeycomb membranes of hydroxyapatite partially deserted by Liesegang stratified compounds.



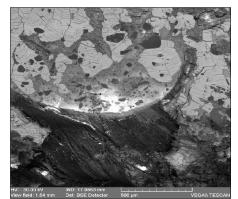


Figure (9) macroscopic and SEM image of the SST-bronze coin (Xth century), inside which are noticed partially preserved wooden structures

Regarding authentication, some archaeometrical characteristics can be focused as: ancient patina, microelements from ore and from site contamination, structure and distribution of chemical compounds from Liesegang effect etc. Regarding the ancient patina bronzes. the main chemical of compounds are easy to identify, being grouped in three types: primary patina, secondary patina and the contamination patina. The first one is formed in the making and usage period of the artifact, by chemical and electrochemical redox processes, when thin continuous layers of oxides and sulphides of Cu(I, II) are formed. Secondary patina is formed in the second period of usage under the influence of the high aggressivity environment factors by redox and acidbase competitive processes. The processes take place under the presence of Cl⁻ in acid environment and CO₂ in alkaline environment. Then the nantokite lead to malachite and azurite, which have irregular surface distributions. The processes culminates with the forming of "buboes" [21] and the activation of the crevices and pitting holes by the

dissolution of small lens of active metal. and the segregation of some components from the volume phase of the alloy through surface, followed by dissolution and/or forming of the monolith with the contamination structures from site. Thus the compounds are continuously forming with partial or total destruction of the metallic core. In the sites with cyclic activities of the environmental factors, the Liesegang effect usually appears. This evolves depending on the shape and complexity of the sample, the composition of the alloy and of the site, the obtaining procedures or the thermal processes after that and the variability of the seasonal cycles. Responsible for the Liesegang effect are the hydrogells of the amphotere metals with coating capacity and the behavior of membrane permeability specific to some cations and anions. At the solution/gel transition these structures allow by osmosis the stratified recrystallization of some compounds like: cuprite, nantokite, malachite and azurite [26] [27] [28] [29], [30].

5. Conclusions

When dealing with the valorization of the archaeological artifacts it is very important to know and identify a series of issues, discussed in terms of shape and appearance during a specific period: the nature and origin of raw materials, design and manufacture acquisition/transfer, use, abandonment or loss and discovery. To this respect, we have highlighted a number of research directions, which allowed setting the position and role of the three ways or forms enhancement (purposes), namely: archaeo-metallurgy, archaeometry of and historiographical studies, museum displaying, trading and assemblance/enrichment of the collections. These were done by analyzing the involvement of various scientific activities. of the integrated conservation for the main types or groups of interest in bronze artifacts in general. The archaeological pieces of bronze that do not contain any residual metallic core raise the most important and complex problems in their authentication. Such pieces are often destined to the 'grey fund' and abandoned in most cases during the preliminary selection. immediately after excavation. They can be a very important source of information, mainly about the basic mineral; often being the unique proofs of a technique or metallurgical tradition/period. In this regard, the research presents the three structural components of the archaeological patina identified in the corrosion bulk section of bronzes, namely: primary or noble patina (oxides, sulphurs etc.), resulting from chemical (dry environmental) and/or electrochemical (humid environment) redox processes, formed during the period of the object making and during the use of the object; secondary or poor patina - appearing in the final stage of the use and continuing in early stage after abandonment, by redox and coordination processes, assisted by acid - base processes, by ion exchange, hydrolysis (oxihydroxides, halogens, carbonates, sulphates, phosphates etc.) and/or thermal processes (calcination, recrystallization etc.); tertiary or contamination patina, formed in the archaeological site under the influence of soil/pedological processes (segregation, diffusion, osmosis / electroosmosis,

monolithisation, disolution / recrystallization, hydration / dehydration etc.). The three types of structures are identified for both items coming from disturbed or undisturbed sites. These forms are different regarding the typology by extension, morphology and stratification, depending on the nature of the film formed (hydrogels and hydroxyapatite), on the composition of alloys and also on the soil aggresivity and site conditions. Effects were highlighted in bronze artefacts recently discovered in archaeological sites from Romania.

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