THE LIESEGANG EFFECT ON ANCIENT BRONZE ITEMS DISCOVERED IN ROMANIA

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Abstract

Most archaeological bronze items discovered in recent years in Moldova and Dobrogea (Romania) have corrosion crusts on their surface, concentrically or radially stratified. This phenomenon, known as the Liesegang effect, manifests itself differently in regard to its extension, stratification and disposition, according to the base alloy composition, the nature of the primary patina and the conservation state at abandonment, as well as to the soil conditions and soil aggressiveness. In our study, in which we used OM and SEM-EDX analysis, we found a 3D spatial distribution of the different Liesegang effects, each layer being formed from a separate dominant compound, contaminated with the main compound of the neighboring layer. The objects that are totally corroded, without a metallic core, it has a central gray-colored compound, which contains chlorine and l tin, with a greatly reduced composition of copper, compared to the base alloy, over which there formed mineralized layers of cuprite, malachite, azurite, nantokite, atacamite, paratacamite etc. . The morphology and distribution of the layers is determined by the shape of the original object and the processing technique used for its manufacture.

Keywords: *Ancient bronze objects; Liesegang effect; Primary, secondary and contamination patina; OM; SEM-EDX*

Introduction

In ancient bronze items from archaeological sites the Liesegang effect of the corrosion crust allows a better differentiation of basic chemical components, specific for the three periods: the manufacture and use, abandonment and the stay in the archaeological site. These surface compounds are grouped as: *primary, or noble patina*, *poor or secondary patina* and tertiary, or contamination patina [1-6].

The Primary patina is formed during the manufacturing process and in the first period of use, when chemical and electrochemical redox processes form thin continuous coatings, initially by oxides and sulfurs of Cu(I, II), then by basic carbonates of Cu(II), out of which only malachite has a protective and aesthetic function [7-11].

The secondary patina appears in the final period of use, under the influence of environmental factors with high aggressiveness, which, by competitive redox and complexation processes, acid-base assisted, mainly in the presence of the chloride anion in an acid medium and of carbon dioxide in an alkaline medium, form *nantokite* (CuCl), then *azurite* ($CU_3(OH)_2(CO_3)_2$)/*malachite* ($Cu_2(OH)_2CO_3$), *atacamite* ($Cu_2Cl(OH)_3$ - orthorhombic)/*paratacamite* ($Cu_2(OH)_3Cl$ - rhombohedral) and so on, distributed more or less evenly over the surface. Many artifacts in pre-abandonment phase suffer from thermal processes (incineration, combustion, fire etc.).

The processes of the two stages culminate in the soil, during the underground stay period, and they cause serious degradations to the metal core and form crevices and pitting holes [5, 6, 12-15].

In some bronze items, with a higher concentration of tin and lead, insufficiently mixed, a separation into small lenses of amphoteric metal occurs, those metals less active than the zinc or iron from their composition, which cause segregations to the surface of the object, where they dissolve and disperse in water, impoverishing the alloy.

Thus, the lower concentration of iron in bronze and zinc in old brass, is a very important archaeometric feature [13].

The catalyst in soil processes is the chloride anion, which, by having a very low volume, migrates into crevices and pitting holes by corrosion, in the presence of cations in a high oxidation state and of oxygen [13, 16-20].

The bronze items with Sn, Pb and Zn, in their transformation to cationic amphoteric form, in high humidity sites with cyclic variations of their conditions, exhibit the Liesegang phenomenon, due to the hydrogel coating of Sn (IV), Pb (II) and/or Zn (II), and in soils rich in phosphates, due to chlorine-apatite/hydroxy-apatite coatings, which allow direct and reverse osmosis, a recrystallization of the layered compounds from the first two patinas occurs.

In the stay period the tertiary, or contamination patina is formed in the form of new structures, continuously consuming the metallic core and which embed by monolitization minerals and various organic and inorganic materials from the surrounding environment in the corrosion crust. In time, organic matter undergoes mineralization and fossilization processes [2, 21-24].

Depending on the strength of cyclical aggression, the Liesegang effect can extend over the whole item, or just in small areas, because it grows/evolves according to the shape and complexity of the item, to the composition of the alloy and the surrounding environment, to the object manufacturing processes, to thermal processes and to subsequently suffered effects of the seasonal cycles. The basis of their formation are a series of semi-membrane hydrogels or of chlorine-apatite membranes with coating capabilities and behavior, membranes with specific permeabilities for certain cations and anions. At the transition from the wet mediums to dry ones and from dry ones to desiccant, through osmosis, those structures allow the layered recrystallization in a certain order of the components from the first two patinas: cuprite, chalcocite, nantokite, atacamite, paratacamite, malachite, azurite etc.

The layering, the nature of the coating and the extension of the Liesengag effect are often used as archaeometric authentication features, important in determining the evolution of an artifact from manufacturing to use and abandonment [16, 17, 21-25].

Our article presents the typology of Liesegang effects, with different forms of layering, the nature of coating and the extension of the effect, as highlighted in certain bronze artifacts that were recently discovered in archaeological sites in Romania, analyzed on the surface and in section by OM and SEM-EDX.

The formation mechanisms of the three patinas

The Primary patina, also named *noble patina,* due to its aesthetic and protection function [1, 8], is formed during the manufacture of the object and in the period of use, by redox, pure chemical or electrochemical processes, in the presence of oxygen from the air, of sulfur, or of hydrogen sulfide derived from the cystine and cysteine in the skin, due to manipulation, friction, thermal treatment etc. [16-24].

These coatings have a smooth, monochrome or polychrome surface, uniform and compact, and can develop small non-uniform, randomly disposed areas, if the object is abandoned in aggressive environments. Those surfaces can have specific colors, smooth and bright aspect, determined by the chemical compounds from the primary patina (red, brown, green, gray), but also by compounds from the secondary patina (blue, green, brown, red, dark and bright grey).

Among the compounds that form thin uniform layers, the most important are Cu(I and II) with anions O^{2-} and S^{2-}, which subsequently forms chloro- and hydroxo- compounds of Cu(II), susceptible to form shiny green-grey layers of malachite, in alkaline mediums and in the presence of CO_2 ($Cu_2(OH)_2CO_3$).

On the smooth surfaces of the primary patina, on very old items, one can often observe cracks, holes and crevices, caused by physical and mechanical stresses. Among these stresses, the thermal ones (burning, ritual cremations etc.) lead to intergranular or transgranular cracks, that deepen the corrosion, causing profound evolutionary effects.

Moreover, the iridescent surfaces with oriented microtextures called patterns are part of the surface damages that occur when the object is subjected to erosion by the action of underground water sources with a physical load (gravel, stones etc.) as well as of surface water sources (rivers, streams/tides, waves washed beaches, etc.). Iridescent texture patters may also result from landslides, digs and agricultural operations. Those situations can often cause serious damage, such as flattening/crushing, bending, twisting, punctures/scratches, tears/fragmentation etc.

The secondary patina, is formed in a long period, in atmospheres with CO_2 in excess or in the presence of HCO_3^-, CO_3^{2-} or SO_4^{2-}, which activate the cuprite or/and cracked *chalcocite, natochite* and hydrated forms of atacamite, forming *malachite* ($Cu_2(OH)_2CO_3$), and in some area *azurite* ($Cu_3(OH)_2(CO_3)_2$), *ceruzite* ($Pb_2(OH)_2CO_3$), *chalconite* ($CuSO_4·5H_2O$)*, antlerite* ($Cu_3(OH)_4SO_4$)*, brocantite* ($Cu_4(OH)_6SO_4$) *and/or langite* ($Cu_4(OH)_6SO_4·H_2O$)*, etc.* [12-24].

The appearance of age cracks and pitting corrosion, allows the chloride anion and the oxygen from atmosphere or from soil moisture to activate the metal surface under the noble patina, forming a series of hydroxo-complexes of Cu(II) - highly reactive, which pierce the primary patina, growing to the surface in the form of boils [14, 15]. Then they generalize on large areas, including the mineralization of other cationic and anionic species, and form the *secondary patina* [16-24].

Secondary patinas, occur often in the form of a crust, with or without protrusions, for example lamellar, lymph or flattened bulbs, flattened snail-like crack networks, honeycomb structures of different sizes, mono-or polychromatic effects, well crystallized microstructures on the outside (Fig. 1).

From the study of old bronze coins made by punching, we were able to identify some surface effects, that were little known to date (Fig. 2). Thus, in addition to the effects in the form of bulb or snail-like shapes, we highlighted certain effects of displacement or removal, processes of dissolution, resulting in large round or oval holes – having one compound of degradation (cuprite, tenorite or malachite). Moreover, we also observed in many coins a network distribution, irregular or dendritic copper passive films, crystalline microstructures,

which developed in tight spaces, blade-like layers of copper or malachite, small nodules, cellulite structures, flattened dendridic networks or structures like an "orange peel" [25, 26].
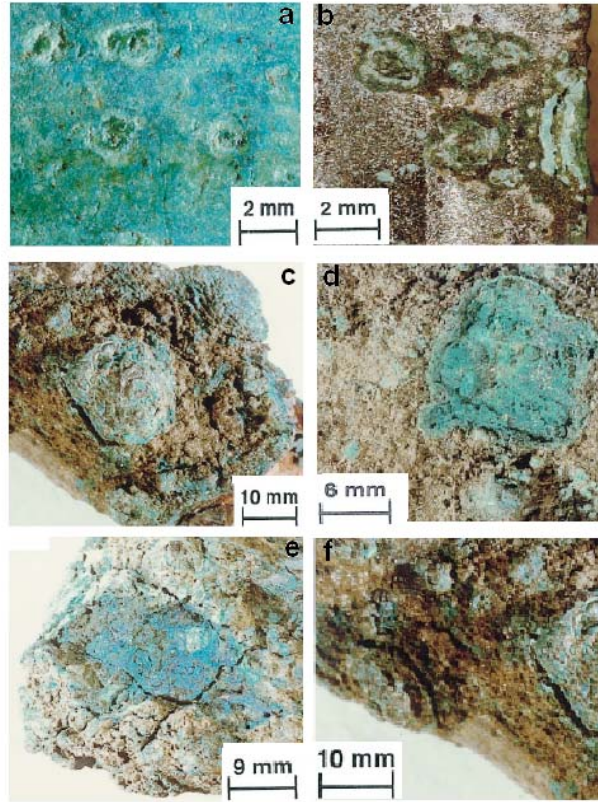

Fig. 1. Microscopic images of some copper base alloys artefacts from bronze age (1500-750 A.C.) [1, 2, 14, 15]:
a – bladders and growths; b – lamellar crusts; c - nodules, snail-like and flattened bulbs;
d – thin strips; e – superficial cracks; f – crevices.
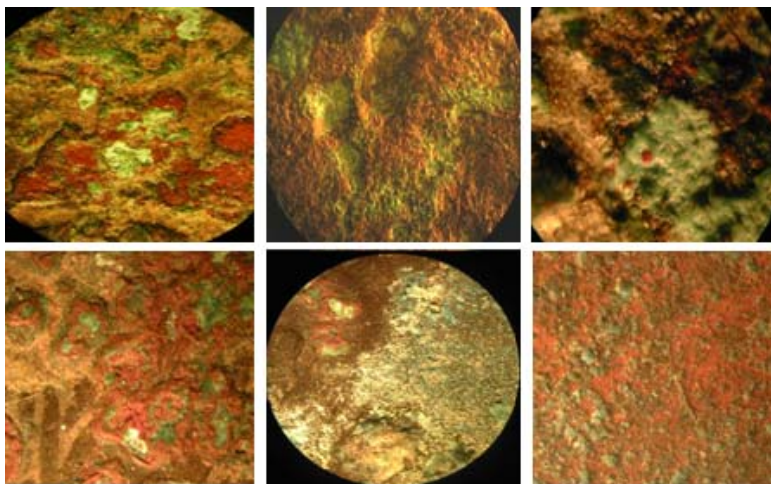
Fig. 2. Optical microscopy images with surface effects on bronze coins from Romania and Austria, 1880-1888 [4, 5, 6]

As mentioned above, a first phase in the formation of the secondary patina is the transformation of cuprite and chalcocite into malachite, azurite, atacamite, paratacamite, antlerite, brocantite and nantochite (Fig. 3).
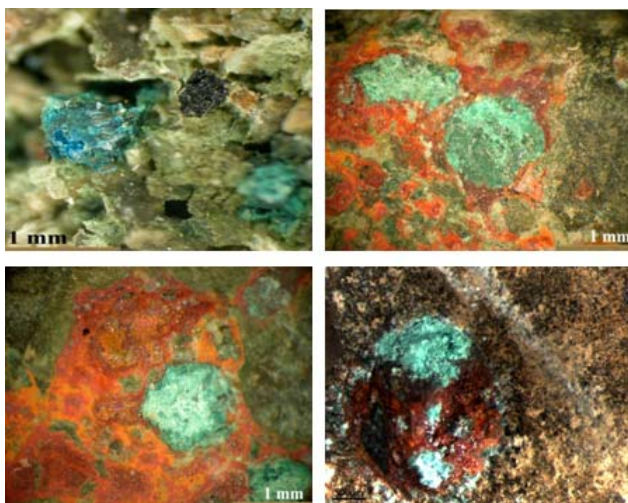
Fig. 3. Images of crusts and nodule formations of malachite, azurite, nantochit etc. on cuprite structures, as a primary effect of the degradation of bronze [26].

The secondary patina often presents crystal formations on its surface (Fig. 4), as structural arrangements (3D).
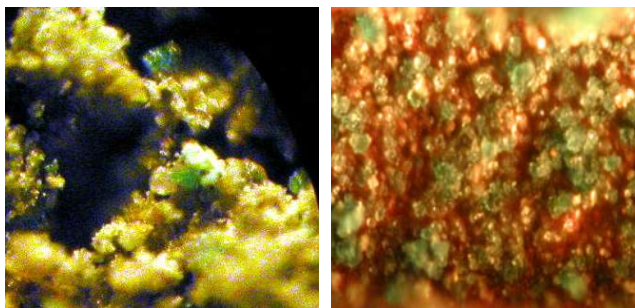
Fig. 4. Azurite microcrystallites (blue), atacamite (green), casiterite (bright white-gray), cuprite (red-brown) and malachite (green-grey) crystallized and well developed 3D [1,4-6]

The secondary patina, by developing in contact with some microstructures from the site, embeds them into the surface of the object (by processes of levigation and mineralization), forming the *tertiary, or the contamination patina* [16-24]. The tertiary patina is shaped as monolith bulks, with or without metallic core, with embedded microstructures of vegetal or animal fibers, insects etc. Those microstructures of contamination from the site have a great importance in archaeometric researches, as they highlight some aspect in ythe evolution of the artifact. Currently, bulk achaeometry requires new approaches with regard to the identification of structural components and the elucidation of the mechanisms of formation/embedding.

For example, the bulks of some coins and other Byzantine artifacts from the 9th-12th Century, found at Nufărul and Novium Dunum, Tulcea county, Romania, contain monolith structures of wood (Figs. 5-8).
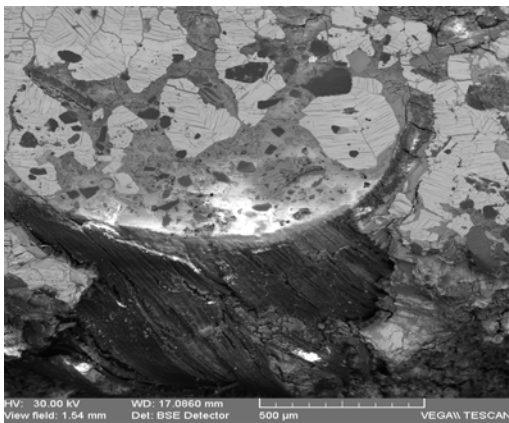
Fig. 5. Bronze plates with wood monoliths
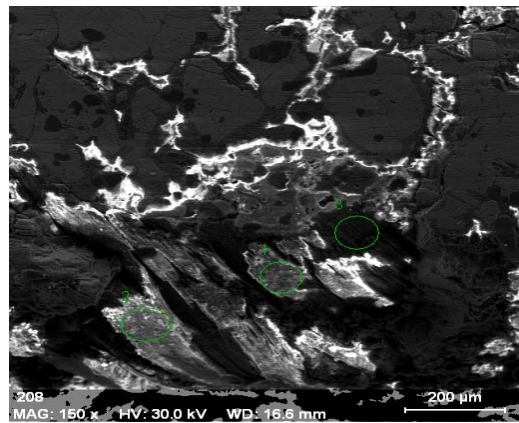(Novium Dunum, Tulcea, Romania, XII Century) [1, 2]

Fig. 6. Bronze coins with wood monoliths
(Nufărul, Tulcea, Romania, IX-X Century) [1, 2]

In figures 7 and 8 the SST of a bronze coin is presented. It has remains of wood, partially conserved.

Fig. 7. SEM image of the bronze coin *SST* (X Century), with partially conserved wood structures [1, 2]

Fig. 8. SEM image of analyzed areas [1, 2]

The data from table 1, evaluated from the spectra in Figure 9, confirm the presence of partially carbonized wood, with visible dendrological elements (microfibers and annual rings). The wood was conserved by Cu(II) compounds.

Table 1. The composition of wood structures from areas 1-3 in figure 8

| Area	1		2		3	
Element	Weight [%]	Error, [%]	Weight [%]	Error, [%]	Weight [%]	Error, [%]
Carbon	6,389193	1,814477	12,18501	3,529135	7,733482	1,041857
Oxygen	35,33253	4,72851	38,85173	9,277283	30,78189	4,009206
Copper	29,53714	0,570017	11,50144	0,487489	43,06152	1,164948
Aluminum	18,78719	0,742615	26,78328	1,655008	9,274744	0,529978
Calcium	6,117853	0,176049	2,901968	0,185975	3,847487	0,154689
Iron	0,689548	0,048993	1,934821	0,149728	0,592968	0,043224
Silicon	0,864429	0,075672	2,991724	0,267102	2,065661	0,127574
Chlorine	0,155296	0,037845	0,477909	0,080947	0,627806	0,050521
Sulfur	0,110234	0,036185	0,87741	0,11058	0,668576	0,053926
Phosphorus	2,016597	0,108595	1,494708	0,159937	1,345867	0,086249
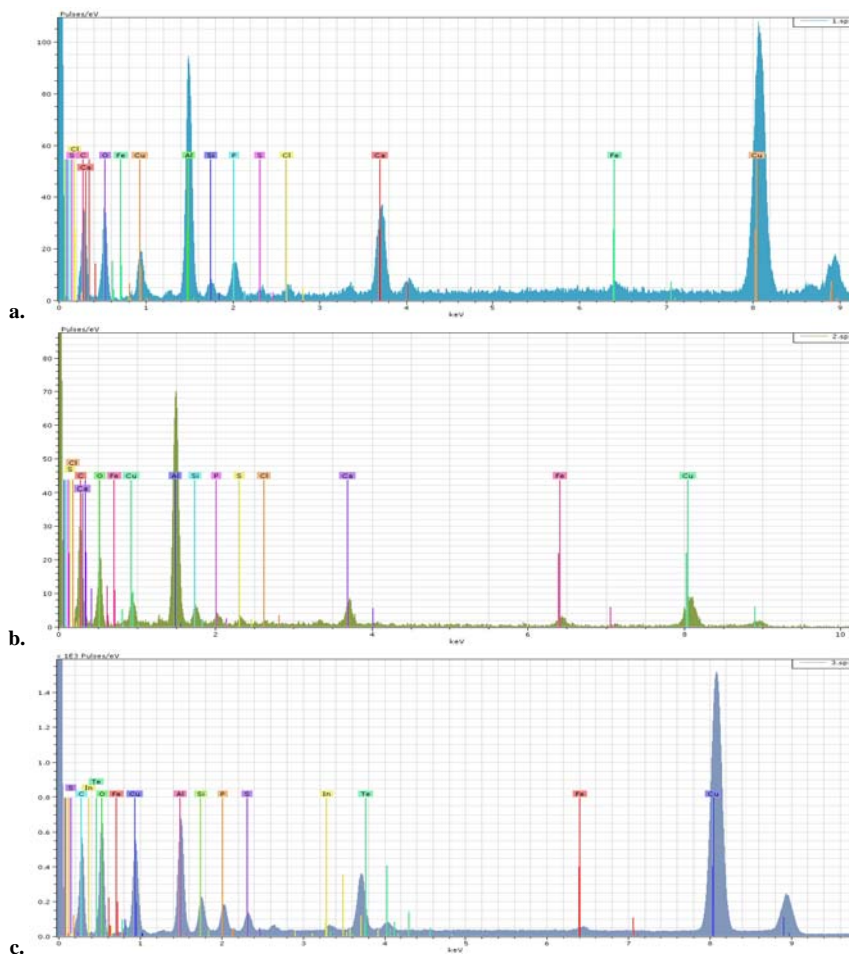
Fig. 9. EDX spectrum of area 1 (a), 2 (b) și 3(c) from figure 8.

The problem for restorers is the elucidation of the mechanism of formation for the three patinas and their distribution in the crust of corrosion.

Types of Liesegang effect

One aspect often seen on archaeological bronze items is the Liesegang effect, both on objects with metallic core and on those without. The question that still bothers scientists is linked to the elucidation of the mechanism of formation of a layered structure from the bulk section of corrosion.

Such structures have been studied in detail by a number of researchers [9-24] and by several the systematic doctoral studies [2, 27].

On most of the bulks, mainly the ones without metallic core, in the concentric stratified structures, the central pit is a grey compound, surrounded by a thick layer of red cuprite, then by a thin grayish green of malachite, after which the layers are repeatead. On the exterior we can find black layers, among the green and red thin ones [28-35].

Figures 10 to 17 present some manifestations of the Liesegang effect on bronze items recently discovered in archaeological sites in Romania [16-24].

The Liesegang layering was well observed in the fracture of two bronze coins found at Nufărul.

The cross-section images taken by optical microscopy at 50X magnification (Fig. 10a and b), and SEM images at 100X, highlight the concentric layering from the edge of the coins.
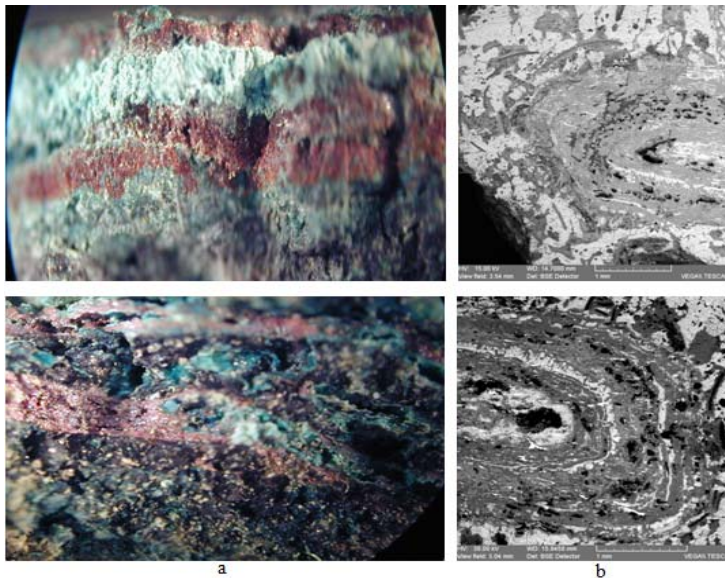
Fig. 10. Stratigraphic structure of ancient coins discovered in Nufărul [5, 6]
a – central cross-section of coin, whole 50X,
b - cross-section detail from the edge of the coin, 100X

Figure 11 highlights the discontinuity of the external layers of the stratigrafic section, under the influence of pedological perturbations (disturbed site).
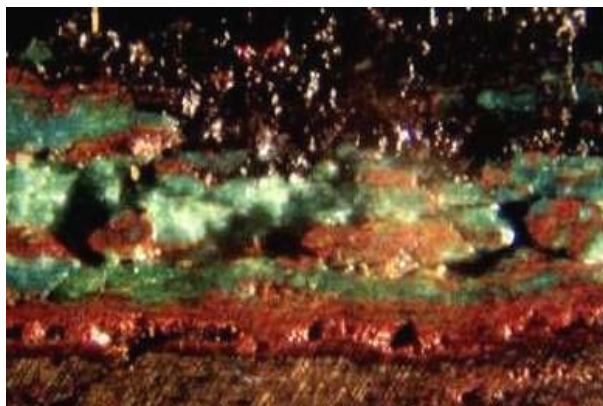
Fig. 11. 400X image of a Liesegang layering on a bronze coin from Ibida, Romania [1, 4-6]

In figure 12 we can see a unique stratification of a bronze artifact, also from Ibida (a needle in transversal section of a brass clip forged in torsade), which presents the Liesegang effect – concentric but discontinuously at a level of four crossed crevices, produced by mechanical processing and dehydration.
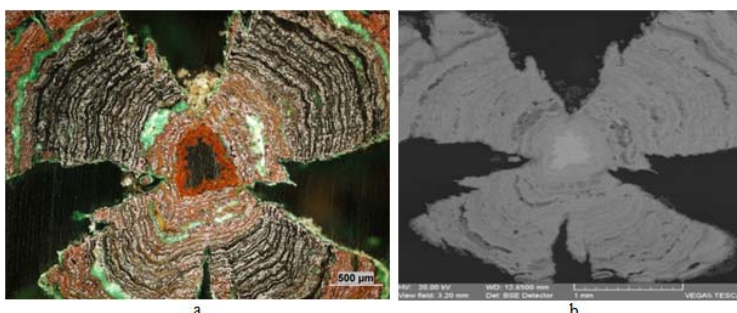

Fig. 12. *SST* images of object Ib06_09 [1, 2]: a – optical stereomicroscopy (100X);
b – SEM image (100X), with alternating structure of cuprite, cassiterite, azurite and malachite.

In figure 13 the SEM detail of a stratified structure of a central area can be observed, with the arrangement of the main compounds (a) and a mapping of the chemical elements (b), highlighting the metallic core of Cu-Sn, on which we can find the rich layer of Sn and poor one of Cu, by segregation, after which there follow the nantochite cuprite, atacamite, malachite, azurite layer etc.
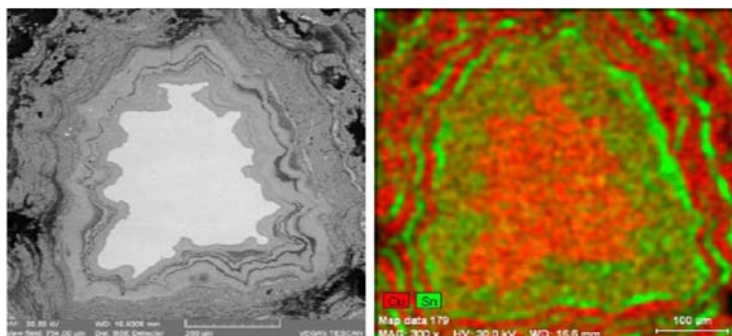

Fig. 13. Detail of the core of sample from figure 12. Arrangement of layers of tin, responsible for generating coating hydrogels leading to the Liesegang effect [1, 2]

Figure 14 highlights a Liesegang structure on a cross-section for a needle clip from Ibida, with a well conserved metallic core. It has a similar distribution of the corrosion compounds – in concentric layers and deep cracks resulted from dehydration. Around the metallic core, which has on the exterior a concentration of Sn and Pb (matte gray), followed by a thin layer of cassiterite (dirty white, shiny), over which there is cuprite (brick-red) and cuprite with coveline (blue-magenta), followed by a thin layer of malachite (green), after which the layers succeed one another in a similar way towards the surface of the crust.
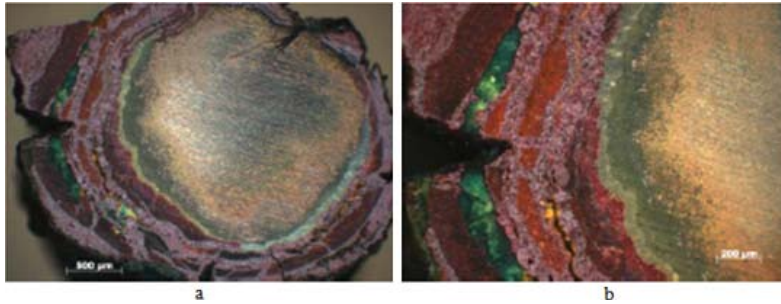
Fig. 14. Microscopic image of the cross section of a needle clip:
a - whole 50X, b - detail 100X [1, 2]

Figure 15 presents the elemental analysis by SEM-EDX of the layers in figure 14b, indicating the delineation and marking the metal core from the concentric layers as well preserved.
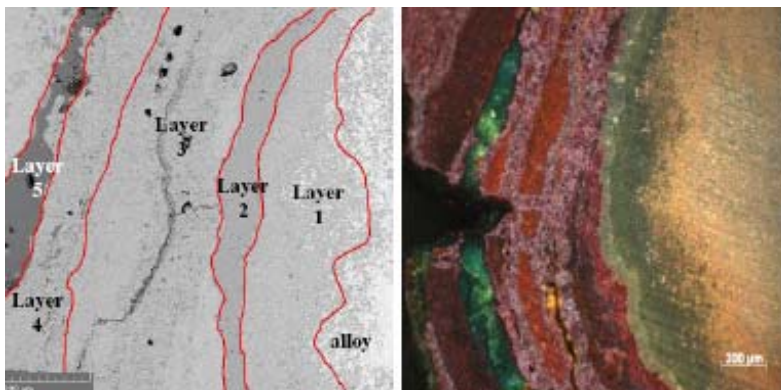
Fig. 15. Detail of the image from figure 14b. Layered arrangement of corrosion products from soil processes [1, 2]

The SEM-EDX of the dirty white central area from figure 15 proves that it contains a high quantity of Sn (~72%), unpurified with Cu (9%) and Pb(5%) and between layers with Cl(18%) and respectively O (22%)

The composition in Pb and Sn is similar to the alloy concentration, due to the low segregation of the metals, compared to Cu.

In contrast, the analysis of the first, brick red layer (1) of cuprite, , between the layers of blue-magenta of coveline shows a high concentration of Cu (76%), O (10%) and S (8%) and a low concentration of Sn (6%). The green malachite layer (2) is rich in Cu (62%) and O (22%), Sn, Pb and Cl having low variable concentrations. As we go to the exterior (layers 3, 4 and 5) the concentration of Cl^-, O^{2-} and S^{2-} anions increases, contrary to that of Pb and Sn. We speak

here about hydroxo-chloride of Cu(II) (paratacamite and atacamite), *coveline* (CuS), *chalcocite* (Cu$_2$S), hydroxo-sulphides of Cu(II) (*chalconite* - CuSO$_4$·5H$_2$O, *antlerite* - Cu$_3$(OH)$_4$SO$_4$), *brocantite* - Cu$_4$(OH)$_6$SO$_4$ *and langite* - Cu$_4$(OH)$_6$SO$_4$·H$_2$O). For samples without a metallic core, on the exterior we can often find other thick layers of *malachite* (Cu$_2$(OH)$_2$CO$_3$), and in some areas *azurite* (Cu$_3$(OH)$_2$(CO$_3$)$_2$) [28-35].

In figure 16, we can see three atypical cases of the Liesegang effect, formed by semi-membrane hydrogels, identified on a shield fragment. The Liesegang effect is locally developed in a bulb (a) and as a half-ring (b) and it has a disturbed stratification (c).
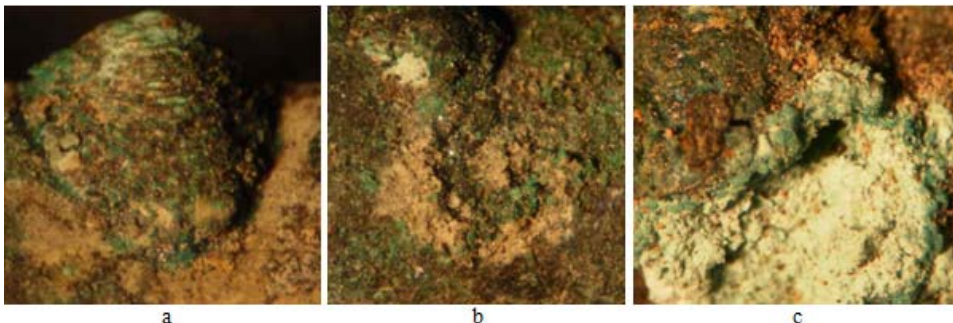
Fig. 16. Discontinuous forms of Liesegang effect with coating hydrogels [16, 17]:
a. Concentric distribution on a rivet of the same material as the support, revealed at the surface;
b. Distributions in a semi-ring with rivet hole;
c. Liesegang effect structurally disturbed by pedological processes

Figure 17 presents 3 atypical cases of the Liesegang effect, developed by continuous crystal reformation processes, under the influence of membranes of chloride-/hydroxo-apatites, identified on an ancient bronze object discovered in Gabăra, Neamț county, Romania: Liesegang effect with separation of the corrosion products on the surface of the crust (a); honeycomb membranes of chloro-apatite remaining after removal of the Liesegang stratified compounds (b) and honeycomb membranes of hydroxy-apatite partially deserted by Liesegang stratified compounds.
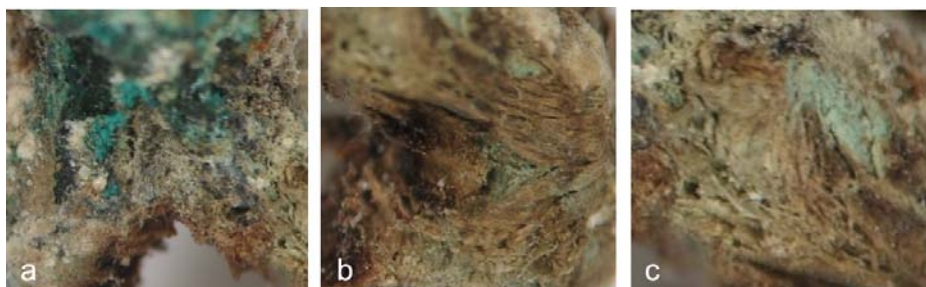
Fig. 17. Discontinuous forms of Liesegang effect with film-forming hydroxy and chloride based apatites [16, 17]: a. Lisegang structure segregation of corrosion products on the surface of the item;
b. Honeycomb membranes of chlor-apatite remaining after removal of the Liesegang stratified compounds;
c. Honeycomb membranes of hydroxyl-apatite partially deserted by Liesegang stratified compounds

The above Liesegang structures (Figs. 16 and 17) are based on two different mechanisms of formation, indicated by the presence of thin layers of hydrogel-based amphoteric metallic oxy-hydroxide (Sn, Pb and Zn) and coatings of chloride- and hydroxyl-apatites. The first conserve the Liesegang stratification (Fig. 6), as hydrogels are membrane systems susceptible to direct osmosis, while the others are not, because chloride- or hidroxo-apatites form pseudo-

membrane systems susceptible to direct and reverse osmosis, which allows the dissolution of the layered compounds and their release into the fluid - ground water, remaining cavity structures. Of course, soil aggressiveness and the cyclical factors of the underground stay period also play an important role.

Conclusions

For the valorization of archaeological artifacts it is very important to know the following 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.

We have highlighted a number of research directions, which allowed establishing *the position and role of the three ways or forms of enhancement* (purposes), namely: *archaeo-metallurgy, archaeometry* and *historiographical studies*, *museum displaying*, *trading* and *acquisition/enrichment* of 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.

The archaeological bronze items that do not contain any residual metallic core raise some very important and complex problems in regard to their authentication. Such items are often destined for the 'grey fund' and abandoned, in most cases, during preliminary selection, immediately after excavation. Those items can be a very important source of information, mainly about the basic alloy and often as unique proofs of a specific technique or metallurgical tradition/period. In that regard, our research presents the three structural components of the archaeological patina identified in the section of the corrosion bulk of bronze items, namely: *primary* or *noble patina* (oxides, sulfurs etc.), resulting from chemical (dry environment) and/or electrochemical (humid environment) redox processes, formed during the period of manufacture and during use of an object, *secondary,* or *poor patina* – appearing in the final stage of use and continuing into the early, after abandonment stage, by redox and coordination processes, assisted by acid – base processes, by ion exchange, hydrolysis (oxihydroxides, halogens, carbonates, sulphates, phosphates etc.) and/or thermal (calcination, recrystallization etc.) and the last patina, the *tertiary* or *contamination patina*, formed in the archaeological site under the influence of soil/pedological processes (segregation, diffusion, osmosis/electro-osmosis, monolithization, dissolution/recrystallization, hydration/dehydration etc.).

The three types of structures are present in items coming from both disturbed and undisturbed sites.

These forms are of different typologies, according to their extension, morphology and stratification, depending on the nature of the coating that formed (hydrogels and hydroxyapatite), on the composition of alloys and also on the soil aggressiveness and on site conditions.

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