

THE AUTHENTICATION OF OLD BRONZE COINS AND THE STRUCTURE OF THE ARCHAEOLOGICAL PATINA

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ABSTRACT

This paper presents comparative results concerning the chemical composition and mineralogical distribution of the main compounds from the structure of the archaeological patina of ancient bronze coins, which were determined by the corroboration of microchemical, IR spectrophotometry, SEM/EDAX and Colorimetric methods. The stratigraphical distribution of the chemical components in the structure of patina is caused by the pedological processes from the archaeological sites and which represents main elements used in the authentication of ancient bronze artifacts.

KEYWORDS: ancient bronze coins; pedological transformation; primary, secondary and contamination patina; archeological patina; stratified structure; authentication elements

1. Introduction

Coins and other metallic numismatic pieces often have various casuistic of *preservation state* and can be taken as valid samples for experimental analyses during the research activities. Except the *treasures* made of noble metals, the pieces made of other metals have the disadvantage of a precarious preservation state, in the worst case of *pre-collapse* – as the pieces with a very thin metallic bulk that merely preserves their shape – or of *collapse* – when the metallic bulk is completely absent and the shape can't be recognized, their authentication being almost impossible [1-7]. Among these, those made of *ancient bronze* have a *very complex composition* of the corrosion products, resulted from the reactions with *corrosion agents* (of chemical, electrochemical or microbiological nature), or by *contamination*, during the various *pedological processes* (*disgregation, segregations, cementations, monolithisations, recrystallizations etc.*). The most important problems arise for the *pieces without metallic bulk*, that during the *preliminary classification* in the yard (excavation place) were destined to the „grey fund”, in the most of cases abandoned. At the present, these pieces are a very important source of information, often being unique proofs of a technique or metallurgical tradition/period.

According to the previous studies [1-7], for the pieces of ancient bronze, both the ones with metallic

bulk and the ones without it, coming from disturbed sites or not, three types of products can be differentiated in the structure of the archaeological patina: the first ones resulted from the corrosion processes, the other ones from the acid-base processes, mainly through hydrolyses and ionic exchange, and the last ones from the processes of contamination (diffusion, segregation, deposition, etc.). These products are formed in different tapes, being characteristic to certain types of patina: the oxides and sulphides, formed since the utilization period, constitute *the primary patina*; the halogenides, oxyhydroxides, carbonates, sulphates, phosphates etc., resulted in the last period of utilization and in the first step of pedological period, define the *secondary patina*; finally those resulted from physical processes of diffusion-segregation-deposition-recrystallization are forming the *contamination patina*.

Their study allows the explanation of the inner mechanisms of formation but also the evaluation of some chronological parameters, that offers a series of elements used in authentication, such as: alloy's nature, mineral's type, technology (elaboration of the alloy and of the coin), provenience of the coin (period and place of creation), way and period of utilization and other data concerning the „time's imprint” [8, 9]. The continuous stratigraphical deepness of the site in time, from the surface, where the action of the climatic, microbiological and antropological agents is strong and cyclic, to the internal zones, where the aerobically or anaerobically conditions of the soil

alternates and the oxygen and water in soil have oscillations in time creating another different system of cyclic variation, has a very important role in the structuring of the corrosion products, of the ionic exchange or contamination products.

The last cyclic processes, although occur with a very slow rate during centuries, provoke important structural modification of the ancient patina of an object, creating a stratigraphical distribution of the three groups of products. The cyclic property of the pedological processes determine the characteristic stratification of the three patinas, that can be easily put in evidence through known stratigraphical methods.

If we compare the microstratigraphies of the archeological patinas of two coins coming from different sites - one non-disturbed and with low humidity, almost constant, and the other site situated in an area with a great mobility of subterranean water and a complex chemism - we observe the stratigraphical distribution, under the form of deposits of products specific to the three types of patina: primary, secondary and of contamination (fig. 1a) for the first coin and a deposition of the micro-crystals, not uniform in the volume phase of the archaeological patina for the second coin (fig. 1b).

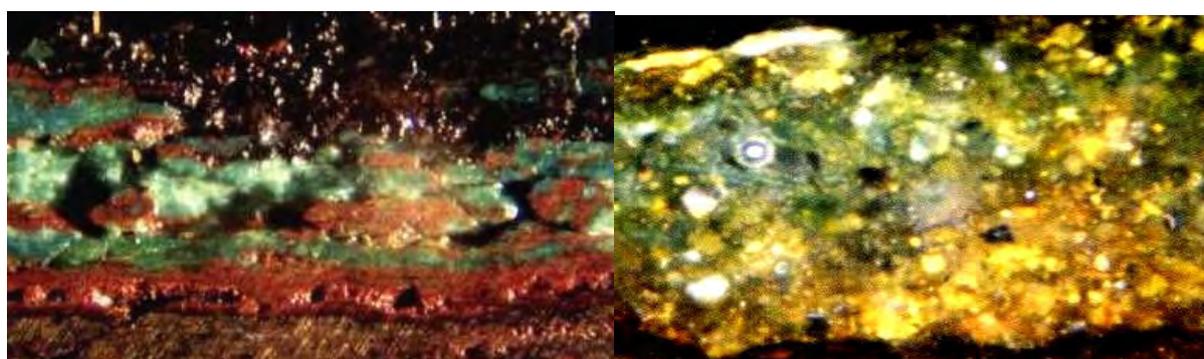


Fig. 1. Microstratigraphical structure of the archaeological patina:

- a* – patina for the coin coming from an archaeological non disturbed site and with low humidity;
b – patina for the coin coming from an archaeological site with a fluctuant chemism provoked by the abundant subterranean water.

If in the case of a non-disturbed site, we can easily draw up structural-phenomenological correlations for chronological evaluations, for the second one, the study of the parameters implied in such correlations requires complex analyses through co-assisting systems or corroboration of new methods and techniques, of great resolution.

So, the stratigraphical morphology of the most of the archaeological patinas of the ancient bronze pieces have a *sandwich* structure, characteristic to the *Liesegang effect* [9], in which the layers of primary patina are overlapped or partially interposed with the ones of the secondary patina. The layers of contamination products, formed during chemical chronological processes that occur in the heterogeneous systems liquid-solid, with a sequential formation of products with characteristic morphology, are also named „*Liesegang rings*”. In the case of bronze coins, the primary patina contains layers of *cuprite* or *cuprite/tenorite* and *sulphides*, the secondary patina of *malachite/azurite*, overlapped or alterned with layers of *atacamite/paratacamite* and *brochantite/anthlerite* and of contamination products: *ankerite*, *gypsum*, *silicates* and *caolinite*

interposed with *cassiterite*, resulted from the segregation and diffusion processes in the inferior layers.

The paper studies the comparative chemical and mineralogical distribution for two bronze coins of the byzantine period - one with metallic bulk and the other one without it - with the help of *modern methods of microstratigraphical analysis*, such as: microchemical tests, IR spectroscopy, SEM/EDAX and reflection colorimetry, that allow the determination of chronological characteristics used for their authentication.

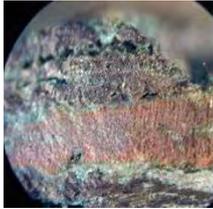
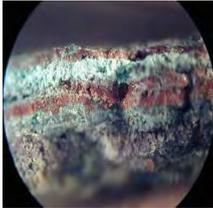
2. Experimental

2.1. Coins taken into study

The study was done on two ancient coins (IV-V century) – M1 and M2 - discovered in the archaeological site Nufărul, Tulcea county, in 2000, initially classified for the *grey fund*; one of them conserves the metallic bulk and the other one is without it.

The table 1 gives the images and the shape of the two coins, together with the microstratigraphy of the sections in the break and polished, observed with the optical microscope at a magnifying power of 40X.

Table 1. State and aspect of the coins and metallic bulks

	Image of the coin	Shape of the coin	Cross-section in break/polished (40X)	State of the metallic bulk
M1		Flat, thick		Thick, affected by corrosion after the removal from the site; advanced segregation processes with holes and fissures between phases
M2		Flat, thick		Thick, discontinuous, sponge shape, strongly affected by corrosion after the removal from the site; nonuniform distribution of the pores and small holes

2.2. Micro-chemical and stratigraphical analysis

Both the cross-sections and the surfaces of the coins were analyzed by optical microscopy using a OLYMPUS CX21 microscope under reflected light (Vis), followed by micro-chemical tests.

The micro-photographies were taken with an OLYMPUS C990zoom digital camera, adapted to the microscope.

The nature of the corrosion products and of the contaminants was established by micro-chemical reactions on surfaces or cross-sections, in a native state or after mechanical or chemical cleaning (nital attack).

The nature of the structural components of the corrosion products and contaminants, formed in concentrated areas as beautifully colored crystals, was directly attributed, based on color and crystallographic system [9].

2.3. Colorimetry by reflection

The colorimetric study was done by selecting on the surface of the coins the areas with corrosion

products and the area with an uniform passivated patina.

A digital colorimeter with two types of optical devices (based on optical fibers) with different illumination geometries and observation angles, coupled with a computer with which the values R G B of the CIE colorimetric triangle were established. The analyzed areas were covered with *mylar* (PET), foreseen of small holes that delimit the measuring areas.

The number of 3-5 points is corresponding to the comparison areas (basic alloy and patina). In each point the transducer was positioned directly on the material, protecting in this way its color from the contact.

Because the colorimetric analysis was applied on a non-shining surface, with rough areas, using the same light spot projected in one point, 3-5 determinations were done, in order to eliminate the errors of the measure.

The colorimetric calculation was done on the average spectrum of each point, for which the

standard deviation was successively determined. It has to be said that the analyzed areas were first cleaned with aqueous and alcohol solutions and for the alloy a side area with active corrosion was chosen for being treated with nitric acid (40%) in order to remove the corrosion layer from the metal.

After the nital attack with acid, the coin was attentively cleaned with water and acetone and afterwards desiccated on filter papers.

2.4. IR Spectroscopy

The IR analysis was done using fine dispersed samples as KBr pellets. The IR spectra were registered in the field of 200-4000 cm^{-1} , using a SPECORD M80 Carl Zeiss Jena spectrophotometer [10 - 14].

2.5. Scanning Electron Microscopy and Xray Spectrometry (SEM/EDAX)

Scanning Electron Microscopy was done with an electron microscope HITACHI S2600N with EDAX spectrometer, with two functions:

- Image analysis with secondary electron detector (SE): resolution: up to 4.0 nm;
- Element mapping with energy dispersive x-ray spectrometer (EDAX): up to 8 elements simultaneously are displayed and automatically overlaid.

The present study was done at an accelerating power of 15,0 kV, in the field of magnifying orders of 250-300x, with the distribution mapping of 8 elements from the surface composition of the two coins [15].

3. Results and discussions

As we saw, during the deposition in an archaeological site, the metallic pieces degrade and deteriorate, under the action of two types of pedological processes [19 - 23]:

- *chemical interactions* (chemical, electrochemical and microbiological corrosion; ionic exchange; hydrolyses; carbonatations; phosphatations, etc.), that lead to *surface products* creating the *primary and secondary patinas*;

- *physical-mechanical interactions* (osmosis, segregation, recrystallization, hydration/dehydration of physically-bounded water, monolithysation, deposition, erosion, deformation, fessuration etc.), among which the physical ones lead to *contamination products* as adherent deposits, that are called *contamination patina*.

Both the products of the first two patinas and those of the contamination patina, are subject in time

to various processes, with formation of new phases, that can be used for a chronological evaluation. From these points of view, the differentiating analysis of the compounds resulted from the primary and secondary patina and of those from the contamination patina, indicates important clues in the authentication of ancient metallic artefacts.

The formation of heavily soluble compounds as consequence of the chemically charged subterranean or meteoric waters actions leads to contaminations with uniform dispersion in the volume phase of the surface layers of compounds, as in the case of double salts.

There is also another series of processes, such as monolithisations, that can create zonal concentrations of contamination products, easily determined through instrumental methods, such as in the case of cassiterite.

The metals with a pronounced amphoteroous character, such as Sn and Pb, by transformation in saline oxides, acquire the capacity of ionic exchange, forming masked deposits of mixed products (saline oxides) resulted from corrosion and by contamination, being hardly observed by optical methods.

3.1. Mineralogical composition of the surface structure of ancient bronze coins

3.1.1. Micro-chemical qualitative analysis

During the formation of the *archaeological patina* each metal of the ancient basic alloy (copper, zinc, tin, lead, iron etc.) forms specific products resulted from pedological processes and the bronze coins are characterized by a great number of mineral species, that are given in the table 2. The chemism of these products is quite well differentiated, in function of *exogeneous* agents, related to the climatic environment, to the site's place and its aggressive character etc., but also of the *endogenous* ones, related to the alloy elaboration, to the originary mineral and the metallurgical technology.

Analyzing data from the table 2, it can be observed that from a mineralogical point of view and as concentration and distribution of the products in the volume phase of the archaeological patina is concerned, there is a correlation for the two coins – with a basic alloy made of Cu, Sn and Pb – subject to redox processes with formation of Cu(I), Cu(II), Sn(IV), Pb(II), Pb(III) oxides and Cu(I), Sn(II) sulphides and afterwards to acid-base processes with formation of hydroxycarbonates, hydroxyhalogenides and hydroxysulphates and finally to processes of contamination with gypsum, calcite and quartz.

Table 2. Chemical compounds determined by IR spectroscopy and XRD in the corrosion products and contaminants

Mineral phase	Chemical formula	Color and aspect	Density (g/cm ³)	Relative Molar Volume	M1	M2
Cuprite	Cu ₂ O	Brick-Red, with gray-brownish or yellowish to orange tones	6,00	1,67	++++	+++
Tenorite	CuO	Black-gray to brown	6,40	1,75	+++	++
Chalcocite	Cu ₂ S	Pb-like gray, with metallic brightness	5,60	1,99	+	++
Tin sulphid	SnS	Black	5,22	1,77	+	++
Malachite	CuCO ₃ · Cu(OH) ₂ or Cu ₂ (OH) ₂ CO ₃	Green, with a characteristic vitreous aspect	4,00	3,88	+++	+++
Azurite	2CuCO ₃ · Cu(OH) ₂ or Cu ₃ (OH) ₂ (CO ₃) ₂	Dark blue	3,88	4,16	+	++
Athacamite	Cu ₂ (OH) ₃ Cl · nH ₂ O or CuCl ₂ · 3Cu(OH) ₂ · nH ₂ O	Emerald-green with more or less dark tones in function of n and with a vitreous aspect	3,75	5,32	++	+++
Cassiterite	SnO ₂	Shiny white	6,95	1,33	+	++
Minium	Pb ₃ O ₄	Red	9,10	1,37	++	+++
Gypsum	CaSO ₄ · 2H ₂ O	White-gray	2,32	2,84	+	++
Quartz	SiO ₂	Translucid gray	2,653	1,94	+	++
Calcite	CaCO ₃	White-gray	2,71	1,43	+	++

3.1.2. Colorimetric analysis by reflection

Based on the experimental results of microchemical analysis, regarding the chemical nature of the corrosion products mainly as beautifully

colored minerals, the areas for the colorimetric analysis by reflection were selected under an OLYMPUS CX21 optical microscope (fig. 4).

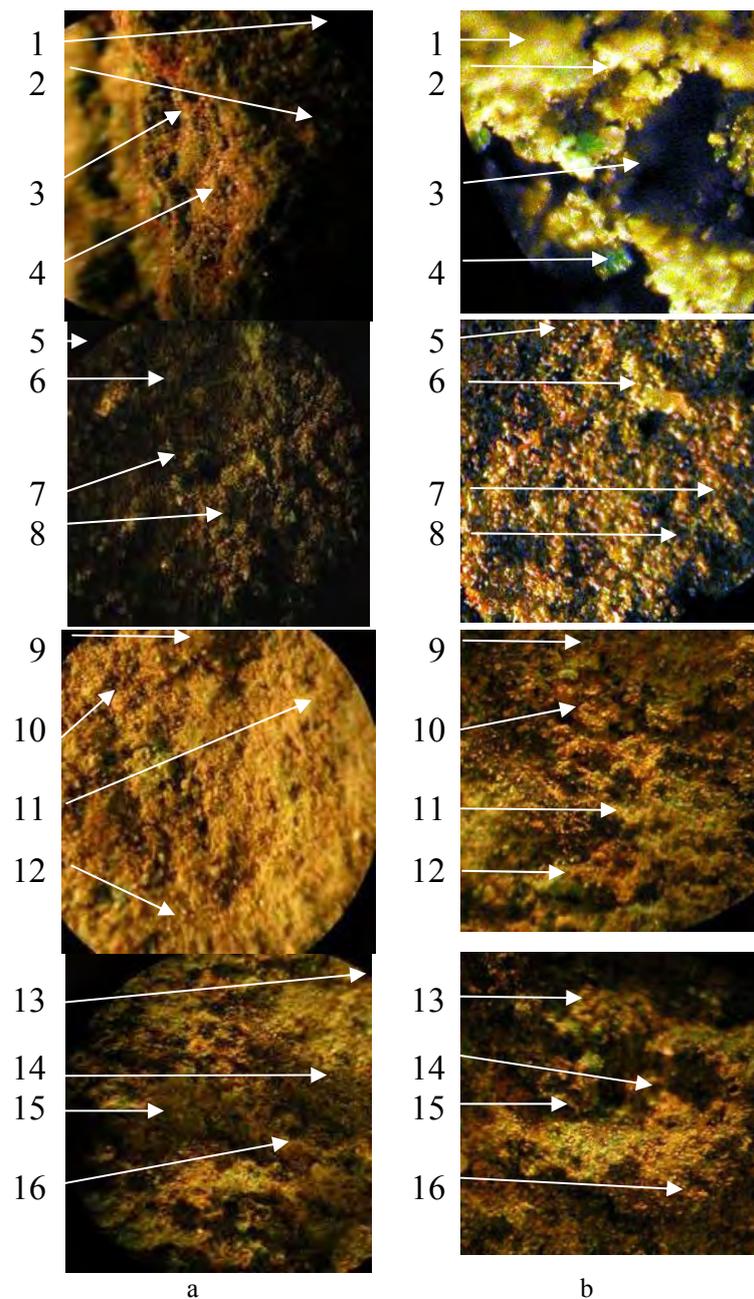


Fig.4. Sampling areas for the colorimetric analysis: a – M1, b – M2

The points selected for analysis are represented by mineralogical entities more or less unpurified, both during the corrosion processes and by contamination after the pedological processes (recrystallizations, dehydrations, segregations, osmoses, carbonations, sulphations, chlorination etc.).

The colorimetry has the advantage that allows a punctual analysis of the color of the microcrystallites. In this respect, the mineralogical phases, studied also with other methods, were identified in their major part (table 3).

Table 3. The colorimetric results (RGB) for the minerals in the structure of the patina analyzed by groups of coins

Nr. crt.	Mineral	M1			Mineral	M2		
		R	G	B		R	G	B
1	Quartz	231	241	123	Calcite	231	246	57
2	Cup rite	137	52	8	Malachite	75	140	14
3	Malachite	64	126	22	Malachite	58	117	51
4	Cup rite	141	47	6	Calcite	251	241	109
5	Anglesite	106	83	0	Cup rite	211	55	0
6	Gypsum	246	258	142	Cup rite	215	82	15
7	Tenorite	214	107	27	Calcite	255	236	209
8	Calcite	211	181	61	Quartz	216	157	39
9	Tenorite	182	102	6	Minium	220	125	41
10	Cup rite	192	65	18	Tenorite	175	88	9
11	Gypsum	247	253	152	Calcocite	125	114	22
12	Cup rite	151	47	0	Tenorite	160	116	7
13	Gypsum	244	252	120	Malachite	84	108	24
14	Cup rite	181	52	17	Thin sulphide	32	54	12
15	Tenorite	186	107	12	Cup rite	142	68	17
16	Cup rite	139	58	7	Gypsum	240	251	115

3.1.3. Analysis through IR spectroscopy

Figure 5 gives the IR spectra for the two coins taken into study and the table 3 attribute the fields of characteristic group vibrations to the predominant

chemical species from the composition of the archaeological patina. In this case, a certain similitude can be observed for the two coins.

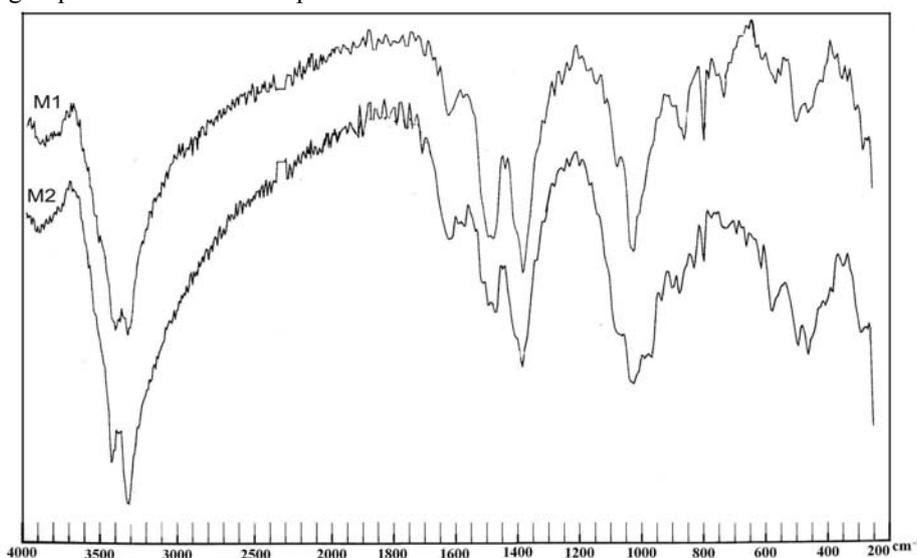


Fig. 5. IR spectra of the two coins.

Table 4. Characteristic group vibrations for the main chemical species

Sample	Mineral	Predominant species	Characteristic vibrations of group (cm ⁻¹)
MA1	Sulphide/Stannate Cuprite Tenorite Silico-aluminate Athacamite/Parathacamite Quartz Malachite Gypsum Malachite	S ²⁻ / SnO ₃ ²⁻ Cu ₂ O CuO SiO ₃ ²⁻ / AlO ₂ ⁻ SO ₄ ²⁻ SiO ₂ CO ₃ ²⁻ CaSO ₄ ·2H ₂ O HO ⁻	270 – 310l, 330l, 400s, 500s, 790m, 800l, 1050vs, 1100s 1400p, 1500s, 1610s, 3370p, 3450s
MA3	Sulphide/Stannate Cuprite Tenorite Silico-aluminate Athacamite/Parathacamite Quartz Malachite Gypsum Malachite	S ²⁻ / SnO ₃ ²⁻ Cu ₂ O CuO SiO ₃ ²⁻ / AlO ₂ ⁻ SO ₄ ²⁻ SiO ₂ CO ₃ ²⁻ CaSO ₄ ·2H ₂ O HO ⁻	250 – 270m 330s, 400s, 500s, 630p, 850m, 1000p, 1050s, 1100s, 1400p, 1500s, 1640s, 3350s, 3450s

Intensity of vibration: vs. – very strong, s – strong, m - medium, l – low, str – straight, br – broad.

3.1.4. SEM-EDAX analysis

SEM microscopy put in evidence for the two coins a rough structure on their surface, non-homogeneous, with uneven relief and microfessures, and mineral deposits resulted from depositions and monolithisation but also from segregation in the volume phase.

The coin M2 has many pores and micro-crystals non uniform distributed on the surface.

On the same surface area where the SEM microphotography was taken, EDAX microanalysis was done, the results indicating the presence, together with copper, of some other alloy elements of the originary minerals specific to the ancient bronze, such as Pb, but also of anions resulted from corrosion and ionic exchange processes, such as carbonates,

sulphates and chlorides and the contamination products based on Si, Ca, K, Mg.

The difference between the two coins consists of a different distribution of the elements specific to anions and contamination products.

Analyzing the comparative distribution of atoms in the surface structures, it can be done a clear distinction between atoms from alloy and those resulted from corrosion and ionic exchange or the ones of contamination. The first ones have an uniform distribution (Cu, Sn, Pb, Cl etc.) but the other ones have a zonal concentration (Si, Ca, Al, Cl etc.). The apparent uniformity in the distribution of atoms of Ca and Cl is explained as effect of segregation, ionic exchange and insolubilization under the form of double salts.

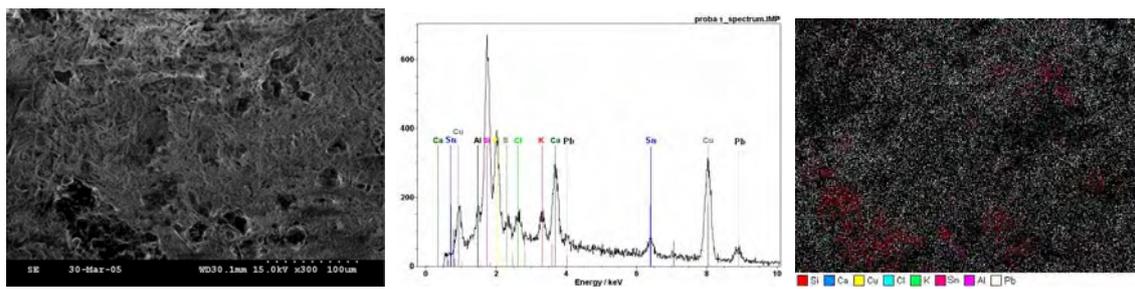


Fig. 6. SEM microscopy coupled with EDAX microanalysis for coin M1

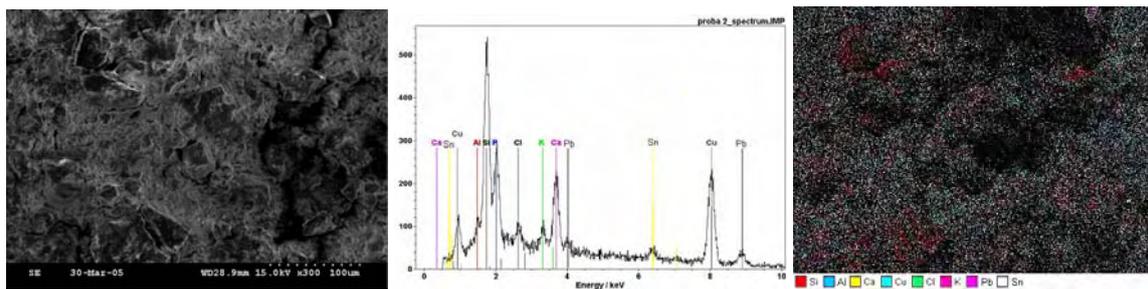


Fig. 7. SEM microscopy coupled with EDAX microanalysis for coin M2

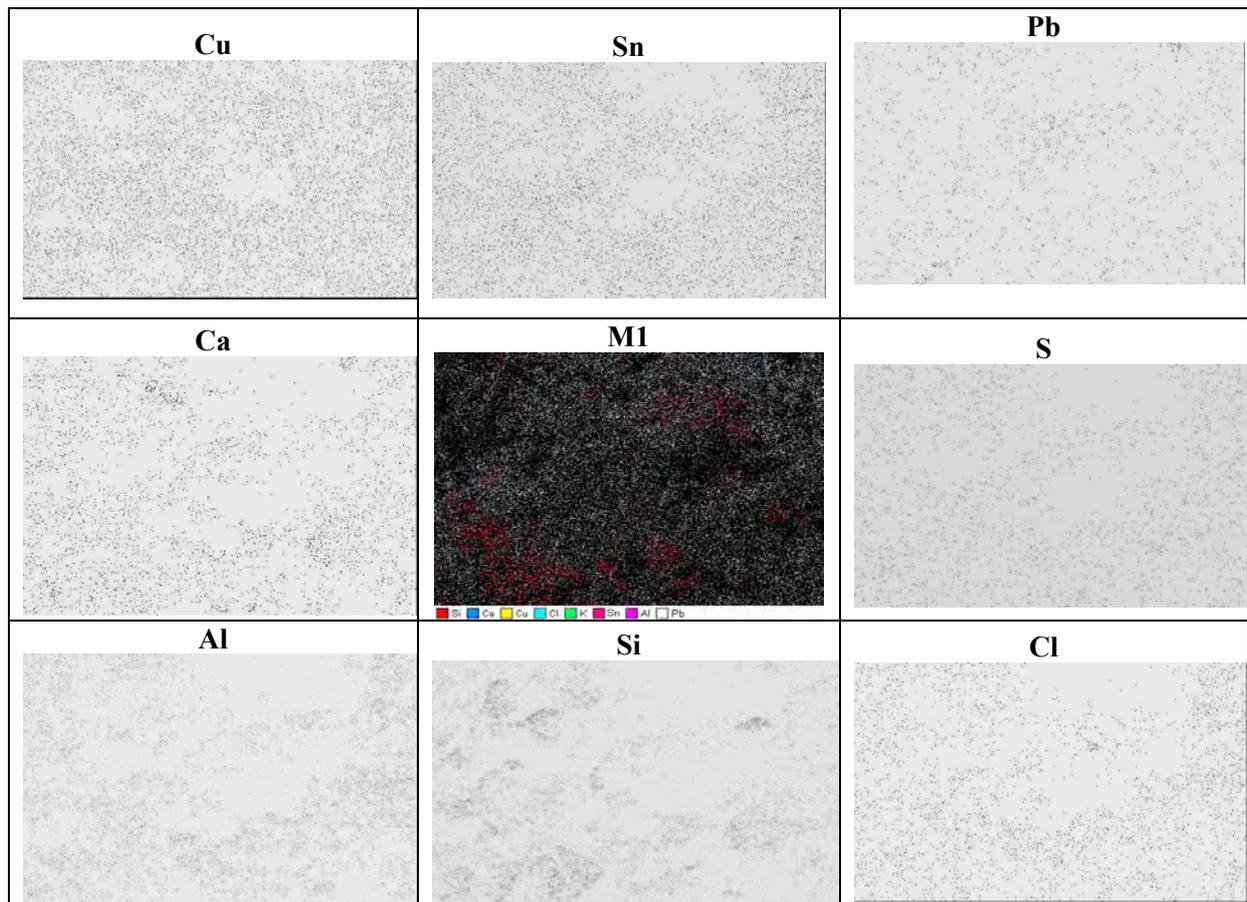


Fig. 8. Comparative distribution of atoms on the surface of coin M1

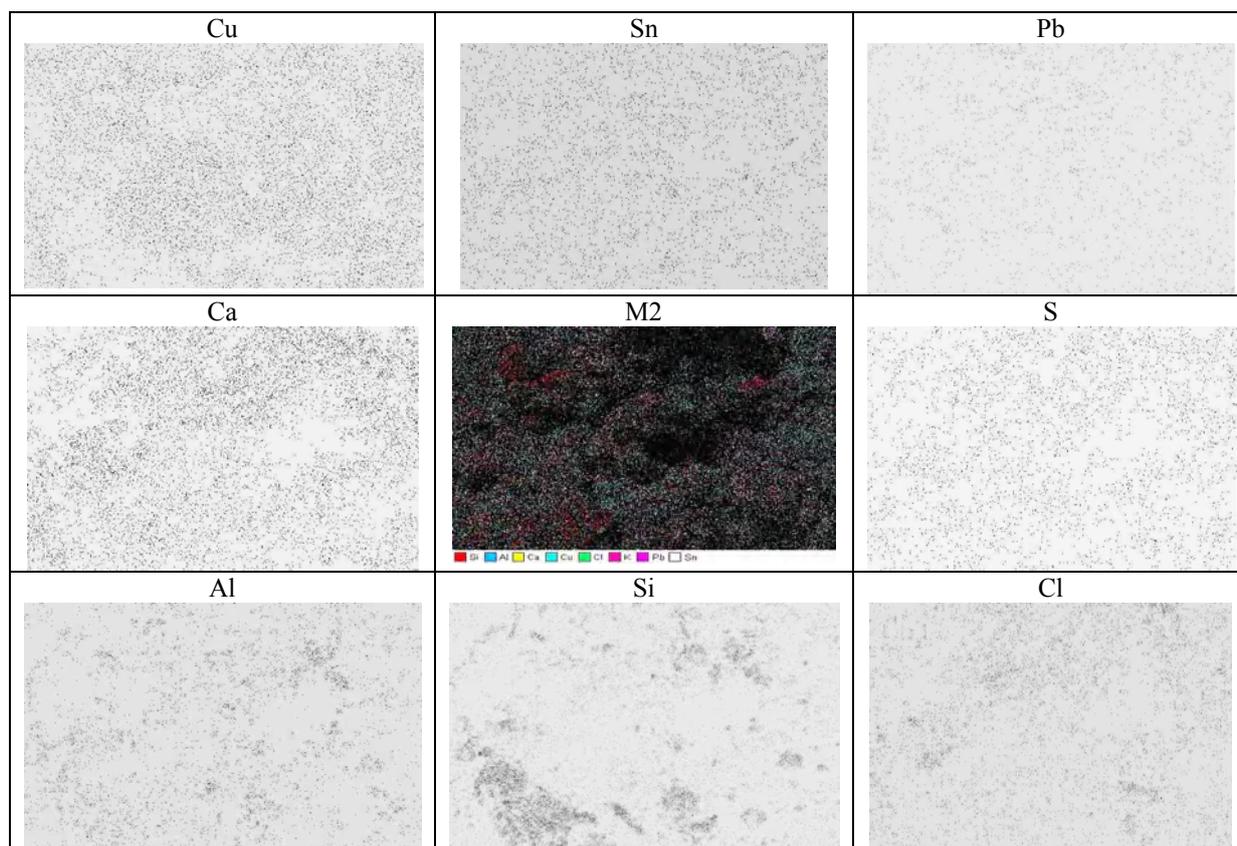


Fig. 9. Comparative distribution of atoms on the surface of coin M2

Based on these observations, the SEM microscopy, coupled with EDAX microanalysis can be well correlated with the data obtained from microchemical and spectroscopical analyses.

4. Conclusions

For the ancient bronze coins and other metallic pieces discovered in the archaeological sites, a detailed analysis can put in evidence a series of structural elements specific to the archaeological patina, that allow chronological evaluation and differentiations as the alloy, area of creation and period of utilization etc. are concerned.

Each piece, at the abandon or when lost, has a *specific ancient patina*, that contains only the *primary patina* (for the objects in the utilization period) or only the *primary patina* interposed with the *secondary one* (for the objects out of use but non-abandoned). During the permanence in the site, the pedological processes are causing continuous physical and chemical transformations to the surface of the piece, the contamination patina being overlapped on the primary and secondary ones.

When the processes are on surface, under the influence of climatic agents, the ancient patina conserves quite well the shape of the object, but when the stratigraphical deepening begins, the pedological cyclic processes lead to the segregation into different layers of the compounds resulted from the three types of reactions: redox, acid-base and physical-mechanical, that create a monolithic complex of the three patinas: primary, secondary and of contamination. In function of the mechanical fluctuations of the site (non-disturbed or disturbed), the archaeological patina can have compositions and mineralogical distributions with specific dispersions: stratified or not. The detailed study of the structural characteristics of the archaeological patina allows the identification of structural-phenomenological correlations.

The present study analyses two coins of IV-V century d.C, discovered in 2000, in the site of Nufărul, Tulcea county, initially classified for the *grey fund*, because of their precarious preservation state (thin and fragile metallic bulk or very thin, discontinuous and even absent). These coins were discovered separately in the site. The main question about them is to establish the emission period and the circulation area.

Using a system of four modern techniques: optical microscopy, reflection colorimetry, IR spectroscopy and SEM/EDAX, the following aspects were put in evidence:

- The coins are part of the same lot, because of the basic alloy composition, and have the same age, even the preservation state of the metallic bulk is different, this aspect being considered a result of the different aggressivity of the soil;
- The correlation of data resulted from the microchemical analyses coupled with the mineralogical and colorimetric ones with the data obtained from the IR spectroscopy and SEM/EDAX allowed to establish the similitude between the two coins, with a basic alloy made of the same mineral, as for the byzantine coins of Dobrogea, containing in their composition Cu, Sn and Pb;
- Furthermore, the method of scanning electronic microscopy (SEM) coupled with the X ray spectrometry, EDAX type, has proved successful to differentiate the chemical products from the primary and secondary patinas versus the contamination ones, using the dispersion mapping of atoms.

The study will allow, after a deeper analysis of the composition, structural and thermal behavior of the main components of the archaeological patina, the determination of other chronological characteristics, that will be the object of further papers. The analyses will include the techniques coupled with SEM/EDAX for the microstratigraphical sections and the use of thermogravimetry for establishing the evolution of kinetic parameters in function of temperature and transformation degree.

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