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A STUDY ON THE DETERIORATION AND DEGRADATION OF METALLIC ARCHAEOLOGICAL ARTIFACTS

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Abstract

Our paper presents the way we used non-destructive methods - optical microscopy (OM), scanning electron microscopy, combined with energy dispersing X-ray analysis (SEM-EDX) and x-ray fluorescence (XRF) - in our research on the morphology of corrosion crusts, the distribution of primary and secondary compounds, the presence of microstructures of contamination from the archaeological site of two metallic artifacts dated to the 2nd and 3rd century A.C.: an iron buckle and a copper alloy pendant, found in the Văleni necropolis, Boteşti, Neamţ county.

Keywords: *iron and bronze artifacts; corrosion; archaeometry; OM; SEM – EDX; XRF.*

Introduction

The metallic artifacts found during the archaeological digs were particularly valuable in clarifying certain aspects, starting from the acquisition of their chemical composition - the origin of the ore, the extraction and processing of metals in order to produce alloys which were then manufactured into objects, such as jewelry items, garment accessories, weapons, tools, coins etc. - to the establishment of their authenticity and their proper classification according to cultural aspects, their function and use, or the detection of forgeries and reproductions [1-8]. Another aspect of interdisciplinary researches on museum heritage, metallic objects pertain to the way they degraded during their underground stay. In that regard, numerous studies show that the evolution from the initial state of an artifact, the one before abandonment, to the state the object was uncovered in the archaeological site is may be read from the modifications occurring over long periods of time, especially those in the corrosion crust that forms under the influence of internal and external factors and of certain natural processes, chemical and electro-chemical, or micro-biological [9-14].

The studies performed on iron, or copper alloy objects, some of which stayed for long periods in different environments (in soil, in funerary urns, ceramic vessels, others in open air) indicated a series of transformations, some major ones, that allow us to easily establish their current state of conservation reached under the influence of exogenous or endogenous factors, with or without anthropic influences. The interdisciplinary researches on copper alloy artifacts

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showed that the corrosion crusts formed during their stay are different, but according to their morphology, there are three general types (thin, medium and thick) characterized by elements specific to physical deterioration (cracks, pits etc.) and chemical alteration (primary and secondary chemical compounds). Thus, in certain copper alloy items, the shift of base metals to primary or secondary chemical compounds (oxides, chlorides, carbonates etc.) happened partially, the section revealing the metallic core covered by a brown-red copper oxide layer, over which there was a green layer consisting of copper chlorides, while other objects were completely mineralized, their shape being retained by the corrosion products [15-18].

In open air, in the presence of pollutants, of rain etc., copper alloys develop a patina that acquires different colors in time: light-green, grey-green, brown-green. The color of the patina formed on copper alloys is set by the corrosion products. Some researchers made a classification thereof, according to the elements in the copper alloy - Cu, Sn, Zn, Pb - and their reaction with rain and the duration of those modifications in their chemical composition [19-22].

Our paper presents the way we used non-destructive methods - optical microscopy (OM), scanning electron microscopy, combined with energy dispersing X-ray analysis (SEM-EDX) and x-ray fluorescence (XRF) - in our research on the morphology of corrosion crusts, the distribution of primary and secondary compounds, the presence of microstructures of contamination from the archaeological site of two metallic artifacts abandoned during funerary rituals during the 2nd and 3rd century A.C. in an incineration and an inhumation tomb in the Văleni necropolis, Boteşti, Neamț county.

Experimental

The Description of the Artifacts and Their State of Conservation

Iron buckle, with inventory no. 7460 (fig. 1a), found in an incineration tomb (M342), in a funerary urn consisting of a ceramic vessel with lid, 0.82 m underground. That urn, covered with a grey ceramic lid, also contained calcinated bones, calcedonium beads, white, red and green glass and a fragment of an iron pendant shaped as a bucket [23, 24].

Bronze pendant with inventory no. 7377 (fig. 1b), found in an inhumation tomb (M212), 0.81 m underground, together with some child teeth, a bronze coin dating from the time of the Roman emperor Domitianus (81 - 96 A.C.) and a bronze needle [23, 24]. The pendant was broken in two and one fragment preserved a nut.

Fig. 1. The artifacts: a - the Buckle; b – the Pendant

Methods and Techniques

For our analyses we used optical microscopy (OM), scanning electron microscopy coupled with X-ray spectrometry (SEM-EDX) and X-ray fluorescence (XRF).

The surface microstructures were studied with a Zeiss Imager a1M microscope, at magnifications of 10X and 200X, coupled to a AXIOCAM camera and using dedicated software and an Olympus SZ60 microscope, at magnifications of 10-60X.

We used a VEGA II LSH SEM microscope, made by Tescan, The Czech Republic, coupled with an QUANTAX QX2 EDX detector, made by BRUKER/ROENTEC, Germany, to identify the elemental composition and the placement of the microstructures on the surface of items.

X-ray fluorescence analysis was performed with a portable INNOV-X system with a 35 kV wolfram anticatode tube, 40 μA, a 30 seconds exposure time and data processing was done by a specialized software.

Results and Discussions

The buckle had a complex corrosion crust, discontinuous, composed of plane coating formations (Fig. 2a), embossed ones (Fig. 2b) and a series of mixed structural components shaped as whole and broken alveoli (Fig. 2c). The plane coating formations and the embossed ones resulted from the incineration, while the alveoli appeared both from incineration and from metabolic processes during the stay.

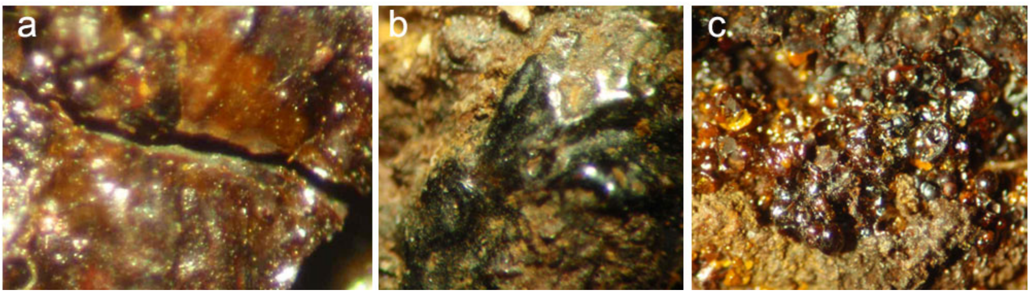

Fig. 2. Formations in the corrosion crust (50X): a - coating structures, b - embossed coating formations, c - cracks in the corrosion crust

In the areas with coating and embossed structures the corrosion crust of the external layer resembles a film that follows the shape of the object precisely and it has no deposits of chemical compounds. The destruction of coating or embossed structures, mostly by cracking, leads to interactions of the environment with the metallic alloy, resulting in the formation of primary, secondary and tertiary compounds of iron.

Moreover, the corrosion crust featured formations of alveoli (fig. 3), resulted from thermal processes and from certain micro-biological actions. Those formations were whole or broken, the whole ones having similar shapes, but different colors, red (fig. 3a), yellow (fig. 3b). The broken alveoli were filled with materials from the soil and by monolithization they formed a discontinuous corrosion crust (fig 3d) and other microstructures included from the soil.

X-ray spectrometry revealed the elements in the corrosion crust of the buckle: Fe, Cu, Mn, Ti, Zr, Co. Thus, Fe belongs to the processed alloy and the presence of the elements Ti, Mn, Zr, as indicated by the XRF spectrum (fig. 4), was attributed to other materials in the urn.

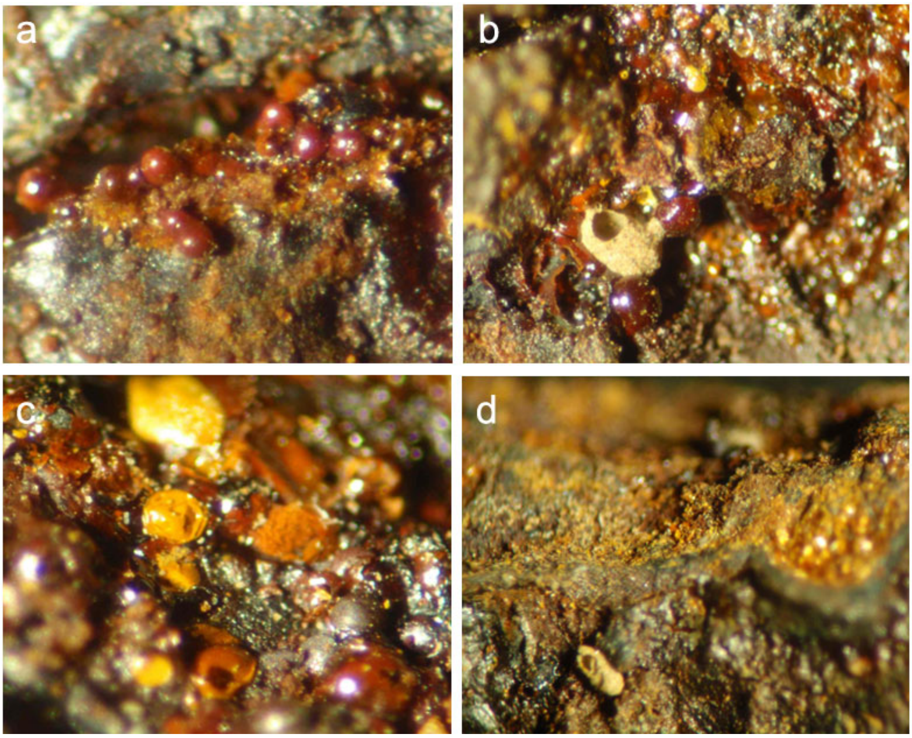

Fig. 3. Alveoli formations (50X): a - whole; b - whole and broken; c - broken and monolithized; d - microstructures from the soil

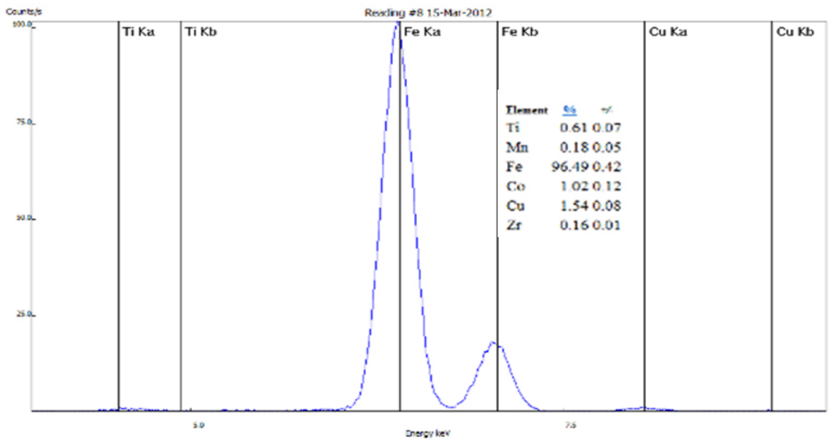

Fig. 4. XRF spectrum of the buckle

The pendant was a representative item for the study of deterioration and degradation processes occurring during the stay period. The modifications in the chemical composition of the processed alloy, the primary or secondary chemical compounds that formed, made a primary patina, which subsequently turned into an uneven corrosion crust. The product resulted from corrosion were then involved in processes of monolithization and mineralization, together with other materials from the soil. The primary and secondary products were unevenly distributed (Fig. 5a) and the microstructures from the surrounding environment covered the details of the decorations on the surface of the object (Fig. 5b). Moreover, elements of physical deterioration were visible, as surface effects, holes, pits and cracks (Fig. 5c) caused by mechanical-physical stress and by crumbling and erosion processes.

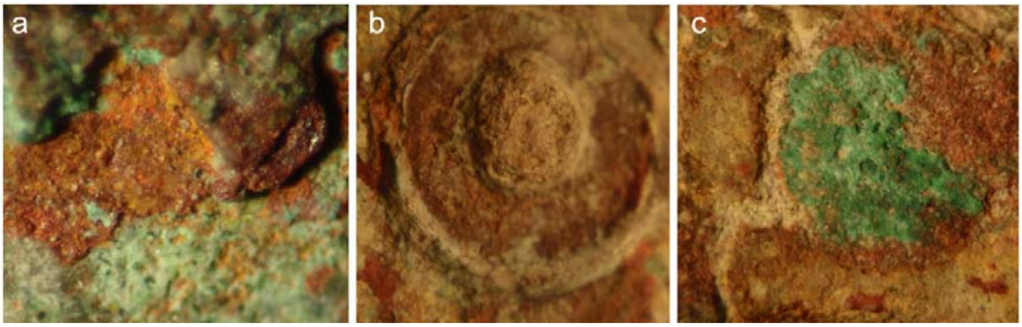

Fig. 5. The morphology of the corrosion crust: a - distribution of the chemical compounds in the corrosion crust, b - microstructures in the corrosion crust, c - pits and craters in the corrosion crust

Figure 6 presents the unevenness of the corrosion crust and the EDX spectrum revealed the elements in the processed alloy (Cu, Sn, Zn, Pb, Fe) as well as the elements Al, C, O, that were found both in the primary and secondary chemical compounds and in the microstructures from the soil.

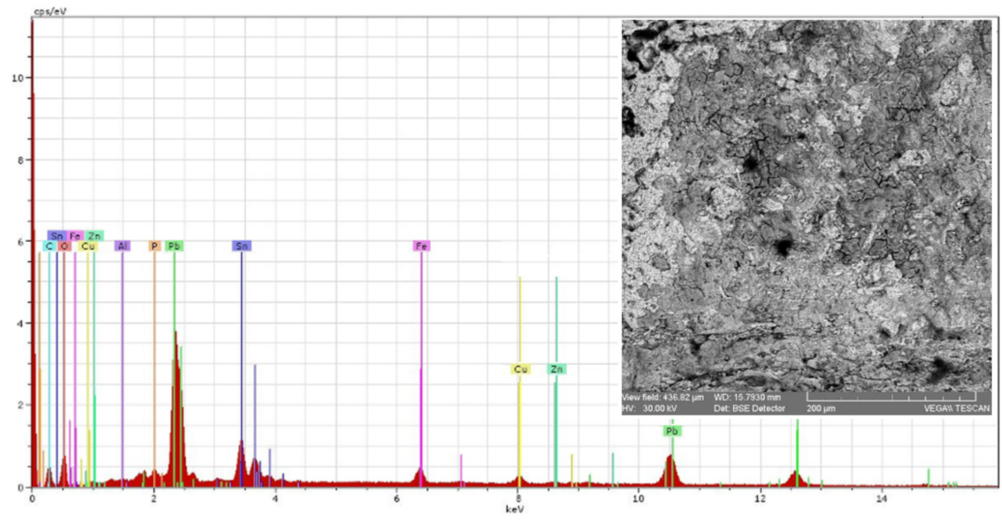

Fig. 6. The EDX spectrum and the SEM image (500X) of the corrosion crust of the pendant

An important role in the process of alteration and deterioration of metallic artifacts is played by the quality of the alloy, but also by the process of manufacture. In that regard, part of the elements characteristic to processes of physical deterioration are enhanced by corrosion processes and in the case of volume corrosion, there occur cracks, pits, craters etc.

The nut area revealed under microscopic observation the presence of certain structures attributed to the manufacture procedure. Thus, in the corrosion crust we identified several formations resembling beads (Fig. 7). The elements established according to the EDX spectrum (Fig. 8) were Cu, Sn, Pb, corresponding to the base alloy, C, O, as found in primary and secondary chemical compounds and Al, in microstructures from the soil.

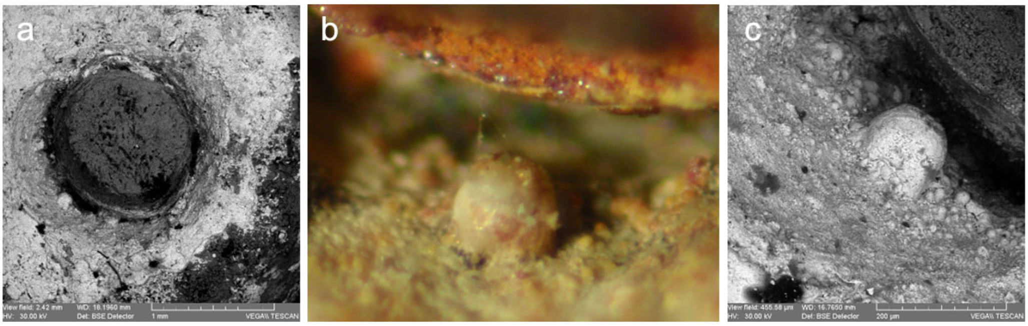

Fig. 7. Bead formations:
a - SEM microphotogram of the formation near the nut - overview (100X BSE);
b - optical microphotogram (50X); c - SEM microphotogram (500X BSE)

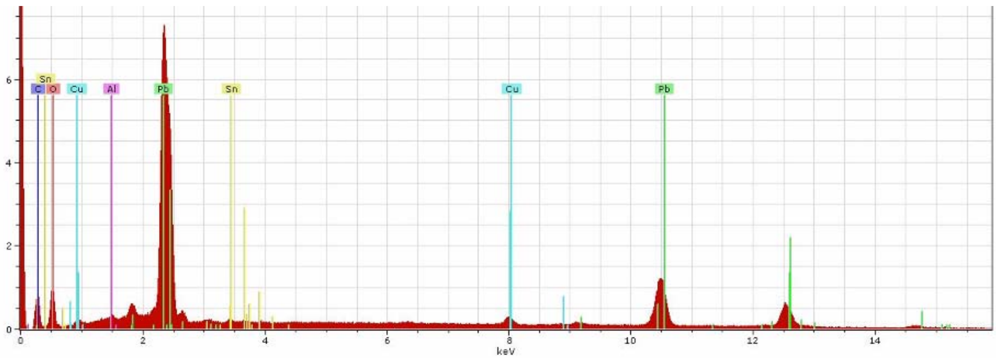

Fig. 8. EDX spectrum of the corrosion crust with beads formations

In the corrosion crust of the nut we identified crack and pits, as physical deterioration effects (Fig. 9). The elements established according to the EDX spectrum correspond to the composition of the base alloy (Cu, Sn, Zn, Pb), the primary and secondary chemical compounds (Cl, C, O) and of the microstructures from the soil (Si, Al).

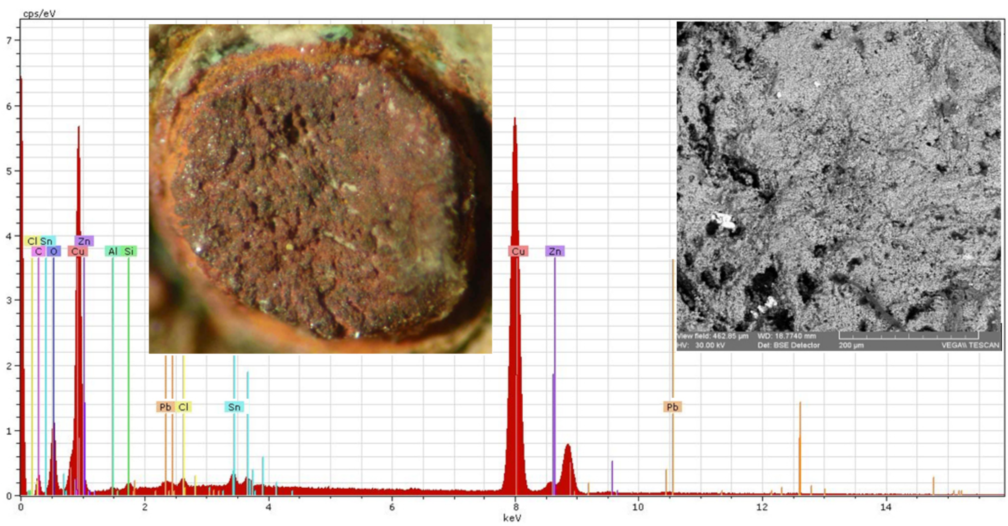

Fig. 9. The EDX spectrum, the OM (20X) and SEM image (500X BSE) of the corrosion crust of the nut

Figure 10 reveals the morphology of the corrosion crust near the nut, the distribution of the primary and secondary compounds and the microstructures from the soil. The elements established according to the EDX spectrum were: Cu, Sn, Zn, Pb, from the base alloy, Fe from impurities in the alloy, P and Al from the soil and C and O from primary and secondary chemical compounds.

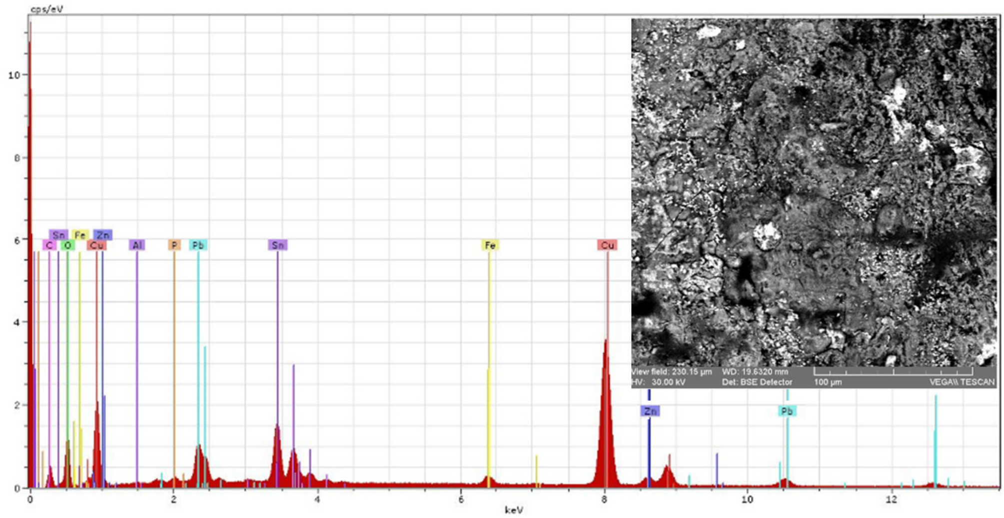

Fig. 10. The corrosion crust near the nut: a - SEM image (500x BSE); b - EDX spectrum

The XRF analysis of the corrosion crust of the pendant revealed the elements Cu, Sn, Zn, Pb, Fe, corresponding to the base alloy (Fig. 11).

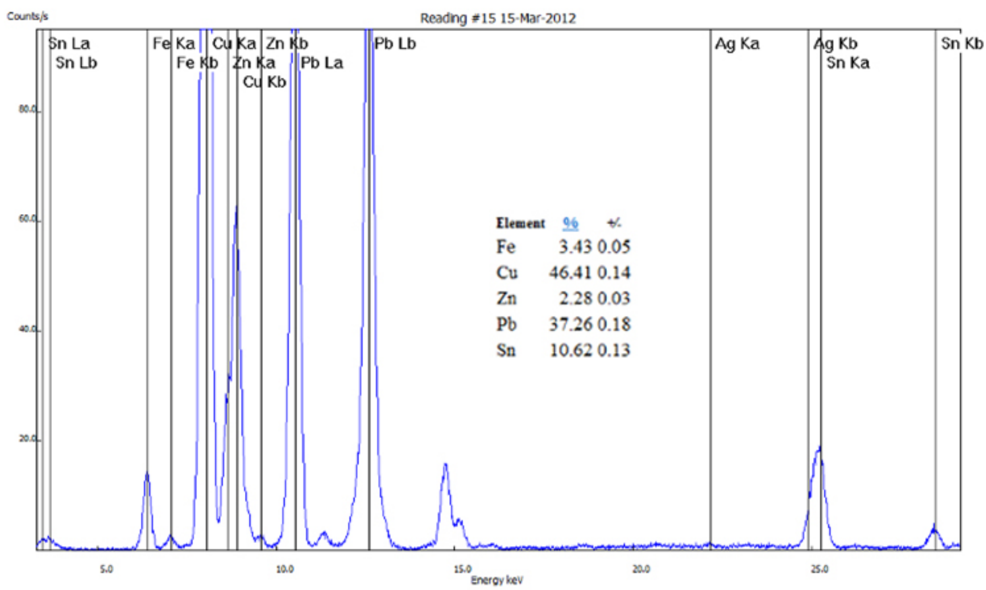

Fig. 11. XRF spectrum of the pendant

Conclusions

The corrosion crusts formed on metallic artifacts are characterized by the presence of primary and secondary chemical compounds deposits and microstructures from the soil. In the case of the iron artifact found in the incineration tomb the corrosion crust presented elements indicating the modifications of its state from before abandonment, formations from the physical deterioration process, plane coating formations and embossed ones resulted from the incineration and alveoli that appeared both from incineration and from metabolic processes during the stay. In time the broken alveoli were filled with materials from the soil and by monolithization they formed a discontinuous corrosion crust (fig. 3d) and other microstructures included from the soil.

In the case of the pendant we observed the unevenness of the corrosion crust, as well as the distribution of the primary and secondary chemical compounds and of the microstructures from the soil. Moreover, our SEM-EDX and XRF analyses revealed the elements in the base alloy (Cu, Sn, Zn, Pb, Fe), as well as the elements Al, C, O from primary and secondary chemical compounds and from soil microstructures.

Acknowledgements

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