Abstract: This paper presents the study of three bronze socketed axes discovered in Neamț County, Romania. The surface structures and those from the interface of the corrosion layer with the metal core of the basic alloy were analyzed, in order to elucidate the nature of the materials used and the manufacturing processes. The analyses by optical microscopy (OM) and electron microscopy (SEM), coupled with X-ray spectrometry (EDX), revealed the type of their degradation during the depositional period, as a result of the processes of chemical alteration and physical damage. A series of metallurgical techniques used were also established, as well as the identification of some finishing and decoration processes that led to the establishment of the objects' functionality.

Keywords: OM; SEM-EDX; socketed axes; bronze; corrosion

1. Introduction

Researchers in the field of scientific conservation of cultural heritage pay special attention to each archaeological discovery, and in the case of an archaeological artefact, first and foremost is considered the context of the discovery, but also other aspects, such as its manufacture, use and disposal. The context of the discovery provides a series of very important data in determining the patrimonial features and functions of the artifact [1].

The evolution of the conservation state is strongly influenced by the depositional period in the archaeological site. From the beginning, the primary patina is formed. It is based on chemical redox processes (oxides, sulfides, etc.), when continuous and uniform films are formed. Due to these layers with their preservative role, it is also called the noble patina. Before the abandonment and immediately after (the final phase of the period of use and continuing with the incipient phase after the abandonment), the secondary patina, also called poor patina, is reformed over the noble one. It occurs due to the aggression of the exogenous factors, when as a result of redox electrochemical processes, assisted by acidobasic, ionic exchange and hydrolysis processes, the following are formed: oxyhydroxides, hydroxy salts, halogenates, carbonates, sulfates, phosphates, etc., which may be anhydrous or hydrated in the form of crusts, nodes and moles, concentrated in or differentiated across certain areas. For certain artifacts, in this phase they may suffer thermal effects (calcination, recrystallization, etc.) following incineration and anthropic or natural fires. In the archaeological site, over the secondary patina, tertiary or contamination patina forms, under the influence of pedological, chemical and microbiological processes (segregation, diffusion, osmosis, monolithization, fossilization, mineralization, hydration/dehydration,
The three types of structures are often difficult to identify, on artifacts from both disturbed and undisturbed sites, due to variable/oscillating aggression of exogenous factors [2–17].

It is known that the authentication of an artifact means much more than dating and identifying the metal worker and the place of manufacture. In fact, attention is paid to a number of attributes related to the origin of the raw material, the elaboration of the basic material, the manufacturing technology, the craftsman/workshop, the owner/holder, the distribution area, the way of use and the course taken until the abandonment. These aspects contribute to the determination of patrimonial elements and functions.

The old collections of some museums are composed from a series of objects that deserve a revaluation and a proper scientific valorification through modern methods, as is the case of the three socketed axes discovered in Neamț County, Romania. These objects represent single finds, accidental discoveries without a clear context; but, as far as the metal objects are rare presences, these can be reevaluated and exploited from a scientific point of view through interdisciplinary methods, in order to gain more data. These axes were analyzed using noninvasive OM and SEM-EDX techniques to evaluate their archaeometallurgical characteristics, based on the chemical composition, the morphology of the corrosion crusts and the basic alloy. The experimental data allowed to indicate the artistic techniques and the manufacturing technology involved.

The analogies of the pieces and their chronological frame indicate different cultural frameworks in three consecutive historical periods, so the main objective of this paper is to try to identify the manufacturing techniques that were used in order to follow the evolution and changes of these technologies in time in this specific area. Another objective is to investigate the depositional environment of the artifacts and its impact on their preservation through the study of corrosion products and patina to find optimal conservation solutions.

2. Materials and Methods

2.1. Description of the Artifacts

The three bronze socketed axes (Figure 1) analyzed were selected from the collections of the History and Ethnography Museum in Târgu Neamț, presenting specific differences in shape, size, ornamentation and site aggression/conservation status. The artifacts were discovered in the eastern part of Romania, namely in the sub-Carpathian area of Neamț county (Figure 2), a rich area in salt springs (brine) that attracted prehistoric communities, exploiting the area’s resources since the Chalcolithic and which continue to be processed even today [18–21]. Thus, these bronze artifacts could represent goods obtained after the exchange with salt and may indicate a chief that oversaw and protected the area and the resources. Even if these objects represent accidental discoveries, without a clear context, the archaeometallurgical study could lead to new information about their use and symbolism.
Socketed axe A (Figure 1A), inventory no. 4649, was discovered in 1965 on the territory of Tibucani, Neamț County, Romania. The piece was discovered on the bank of a creek, within a settlement of the Noua Culture \[22,23\]. The piece has a length of 124 mm, 0.413 kg weight, a blade width of 45 mm, the depth of the fixing orifice is 76 mm, the diameter of the fixing orifice is 35 mm × 23 mm, the length of the attachment loop is 37 mm and its diameter is 6 mm × 5 mm. The item has a massive body; the upper edge is thick, and it is oval in plane and is provided with a small loop for attaching. The blade is slightly curved, and on the sides the burrs of casting in the bivalve pattern are observed. On the main faces, below the upper edge, there is a perforated alveoli and colorizations/traces of use. The entire surface of the item is covered by a consistent patina, colored in malachite green, dispersed under tenorite layers and sprinkled with small azurite points, in deepened surface areas. From a typological point of view, this artifact can be included, according to some specialists, in the eastern version of the Transylvanian Socketed Axe \[24\] or in the C3 version (according to a broader classification based on morphological criteria of the

Figure 1. Images of the three socketed axes and the analyzed areas (A) inventory no. 4649 (B) inventory no. 2113, (C) inventory no. 4650.

Figure 2. Geographic location of the discoveries, Neamț county, Romania: A and C—Tibucani; B—Tg. Neamț (Google Earth 2020).
Socketed axe B (Figure 1B), inventory no. 2113, was discovered by chance in 1957 on the territory of Târgu Neamț, Romania [26]. The item is small in size and has a slightly trapezoidal body. It is equipped with an attaching loop. The piece has a length of 70 mm, 0.142 kg weight, a blade width of 40 mm, the diameter of the fixing orifice is 22 mm × 27 mm, the depth of the fixing orifice is 40 mm, the length of the attachment loop is 43 mm and its diameter is 5 mm × 5 mm. The upper edge is straight, thick and oval in plane, and it preserves the burrs from casting. Below the edge there is a cast ornament, consisting of six oblique ribs, and on the body of the item, inside the trapezoidal facets, there are four others vertically arranged ribs, which confer certain aesthetics, with a rank attribute [27]. The cutting edge is slightly arched and shows, like the other socketed axe, visible use wear marks. The entire surface of the item is covered with a blue-azure patina, with small white areas of stannite, below malachite green and tenorite black layers, over which there are brown-gray crusts of nantokite. The main analogies for this artifact are found at Brza Palanca, Serbia [22]; Jupalnic, Mehedinți county, Romania [22,29]; and Pietrosu, Buzău county, Romania [22,29].

Considering the fact that similar specimens have been identified in the middle part of the Danube, it is supposed that this item also originated in that area and it could have reached the submontane area of Neamț, either through the mountain passes towards Transylvania or through the curve of the Carpathians. On the basis of the abovementioned analogies, but also in the absence of a clear archaeological context, for the item from Târgu Neamț we can admit a dating as from the beginning of the Early Iron Age, at the Ha A2–Ha B2 level (Hallstattzeit); from a cultural point of view, it must be associated with the Corlăteni-Chisinau Culture (11th–9th c. BCE) [30].

Socketed axe C (Figure 1C), inventory no. 4650, was accidentally discovered on the territory of the village of Țibucani, Neamț county, Romania [23]. It is a small specimen with an elongated body. The piece has a length of 78 mm, 0.54 kg weight, a blade width of 37 mm, the diameter of the fixing orifice is 20 mm × 14 mm, the depth of the fixing orifice is 50 mm, the length of the attachment loop is 21 mm and its diameter is 2 mm. The upper edge is straight, slightly thickened and oval in plane. The item was provided with an attachment loop, broken during the period of use. Below the upper edge there are three horizontal ribs. The lower part of the item is flared, and the cutting edge is slightly arched. The surface of the artifact is covered with a black tenorite layer, uniform in thickness, which contains superficially dispersed small spots of azurite and malachite, over which there are brown-gray crusts of nantokite. The main analogies for this artifact are found in bronze deposits and singular discoveries, such as those from Rădeni, Neamț county, Romania [23]; Floreni, Vaslui county, Romania [31]; Sămbăta Nouă, Tulcea county, Romania [29]; Techirghiol, Constanța county, Romania [29]; Câpușu de Câmpie, Mureș county, Romania [29]; Rusu, Sibiu county, Romania [32]; Iara II, Cluj county, Romania [29]; Boldesti, Prahova county, Romania [29]; Ciunga, Alba county, Romania [33]; Obreja, Alba county, Romania [34]; Valea Mare, Vaslui county, Romania [34]; and Dupliska, Ukraine [35]. Similar examples are known at the level of the Gyermely and Hajdúbőszörmény bronze deposits horizons, as shown by specimens from Szendrőlád, Hungary [36]; Jászkarajenő, Hungary [36]; Balmazújváros, Hungary [37]; Nádudvar-Bojárhollós, Hungary [37]; and Polgár, Hungary [37].

On the basis of the abovementioned analogies, the item from
Tibucani can be framed chronologically in the Early Iron Age, between Ha B1 and Ha B2, or even in Ha B3 (Hallstattzeit), in the 10th–8th c. BCE.

2.2. Methods of Analysis

The three artifacts were studied by surface optic microscopy (OM) without any sampling to obtain information about the resulting crusts from alterations of the base alloy and those from incorporation and monolithization in the ground (identifying similarities or differences in appearance and color and homogeneity of the chemical compounds from the primary, secondary or tertiary patina). A ZEISS-type optical microscope with video camera and computer co-assistance was used for the analyses. The samples were analyzed by reflection at different magnification orders (×50 and ×100) in dark field.

For elemental and microstructural analyses, the samples were collected non-destructively from the fixing orifice and from areas with destruction, being studied the areas with corrosion and the metal alloy (samples from the metal interface). All samples were studied through scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX). A SEM microscope, model VEGA II LSH, produced by TESCAN Czech Republic, coupled with an EDX detector, type QUANTAX QX2, manufactured by BRUKER/ROENTEC Germany, was used in the analyses. The microscope, controlled by a computer, has a tungsten filament electron cannon that can achieve a resolution of 3 nm at 30 kV, with a magnification between ×30 and ×1,000,000 in the “resolution” operating mode, an acceleration voltage between 200 V and 30 kV and scanning speed between 200 ns and 10 ms per pixel. The working pressure was less than 1 × 10⁻² Pa. Quantax QX2 is an EDX detector used for the qualitative and quantitative micro analyses. The EDX detector was a third-generation, X-flash-type detector. The images obtained for the analyzed samples were made up of secondary electrons (SE) or backscattered electrons (BSE) at magnifications between ×200 and ×1000.

2.3. Areas of Analyses

Figure 1 shows four analyzed areas for each socketed axe, one for the identification of the processed alloy and three representatives for the conservation status, which allow to highlight the effects of the deterioration and degradation resulting from the use and abandonment periods, in particular the morpho-structural components of the three patinas (noble, poor and contamination).

3. Results and Discussions

From the microphotographs obtained by OM for the representative areas, each of the three analyzed socketed axes show interesting characteristics in terms of corrosion and use.

Specifically, socketed axe A has a relatively uniform, thin layer of corrosion on the surface, completely covering the metal core (Figure 3a). Near the blade, in the outer layer, there were identified traces of deep scratches (Figure 3b), attributed to the use of the item before deposition, and at the interface of the metal core were found chemical compounds resulting from the corrosion processes occurring on the base alloy, namely, copper oxides—red—and the basic copper carbonates—green (Figure 3c).
Figure 3. OM images of the three representative areas of the surface of the socketed axes: (a) uniformity of the corrosion layer for axe A; (b) scratches caused by use before deposition for axe A; (c) the oxides and basic carbonates of copper for axe A; (d) disposal of the corrosion products in the patina for axe B; (e) the basic carbonates and copper oxides for axe B; (f) copper oxides for axe B; (g–i) the corrosion layer with the disposal of the chemical compounds of the patina for axe C.

Socketed axe B presents a corrosion layer distributed very heterogeneously over the entire surface of the item (Figure 3d), in which deposits of the basic carbonates and copper oxides were randomly located on the micro-zones in the form of crusts (Figure 3e), and at the interface with the metal core were found thin layers of copper oxides, also disposed unevenly (Figure 3f).

Socketed axe C presents a discontinuous, thin layer of corrosion with unevenly arranged deposits of oxides (cuprite/tenorite), chlorides (nantochite) and copper basic carbonates (malachite/azurite), cassiterite and silver veins, unevenly distributed in the form of crusts or thin layers (Figure 3g–i).

SEM-EDX analyses were performed on both the surface corrosion layer and the stratigraphic structure at the interface with the base alloy to highlight the correlation between the chemical composition of the artifact, the nature of the corrosion products and the elements taken from the soil (contamination).

From the SEM micrographs of the corrosion layer of socketed axe A (Figure 4S1-1, S1-2 and S1-3) was identified a structure with a non-homogeneous distribution, characterized by the presence of cracks, microcavities and microphases differentiated as superficial structures in the form of irregularly shaped granules.
The EDX analyses of these surfaces identified the chemical elements corresponding to the basic alloy (Cu and Sn) and the ore impurities (Pb and Fe), as well as the elements of the corrosion products (C, O and Cl) and of the contamination from the soil, such as Si, Al, Mg, P and S (Table 1). This composition shows that the artifact has undergone corrosion and segregation processes under the influence of an environment with fluctuating humidity and temperature, rich in oxygen and carbon dioxide, in the presence of alkaline and alkaline-earth cations, phosphates, carbonates, aluminosilicates and silicon dioxide (quartz micro-crystallites).

The SEM micrographs of the corrosion layer of socketed axe B, also performed on three representative areas, are shown in Figure 4(S2-1,S2-2,S2-3). Through the analyses, the surface structures, with a non-homogeneous granulometric distribution of the corrosion crusts and metallic micro-phases with uneven geometric profiles, can be observed.

The elemental EDX analyzes of the corrosion layer of socketed axe B, performed on the three areas (S2-1, S2-2 and S2-3), corresponding to the SEM micrographs in Figure 4, is shown in Table 1.

Thus, in samples S2-1 and S2-3 were highlighted the chemical elements corresponding to the basic alloy (Cu and Sn), and the micro-elements from the ore were based on Ni, Pb and Fe. Instead, the sample S2-2 contains corrosion products of the copper, in the form of basic carbonates and oxides, but also iron oxides, possibly from contamination, because the Fe concentration is quite high (14.23%).
Table 1. Chemical composition of the surface structures for socketed axes A (S1), B (S2) and C (S3).

| Samples | Elemental Composition—Weight Percent (%) |
|---------|-----------------------------------------|
|         | Cu  | Sn  | Pb  | Fe  | Ag  | Ni  | Si  | Al  | Ca  | Mg  | K   | O   | S   | C   | P   | Cl  |
| S1-1    | 17.07 | 21.69 | 0.14 | 1.69 | -   | -   | 1.84 | 0.40 | -   | 0.12 | -   | 40.61 | 0.15 | 14.30 | 1.34 | 0.63 |
| S1-2    | 16.03 | 24.59 | 0.09 | 2.66 | -   | -   | 3.99 | 1.70 | -   | 0.31 | -   | 44.37 | 0.13 | 4.93  | 1.07 | 0.13 |
| S1-3    | 21.11 | 23.45 | 0.11 | 1.49 | -   | -   | 1.19 | 0.10 | -   | 0.35 | -   | 45.25 | 0.07 | 4.88  | 1.91 | 0.09 |
| S2-1    | 64.59 | 3.11  | 0.14 | 1.71 | -   | 1.38 | 0.01 | 0.01 | -   | 0.04 | -   | 26.51 | 0.01 | 2.34  | 0.15 | -   |
| S2-2    | 23.39 | -     | -    | 14.23 | -   | -   | 0.45 | 0.23 | 0.75 | -   | 0.47 | 42.71 | 0.27 | 17.00 | 0.17 | 0.33 |
| S2-3    | 68.43 | 1.57  | 0.14 | 0.83 | -   | 1.36 | 0.02 | 0.03 | -   | -   | -   | 25.69 | 0.02 | 1.89  | 0.02 | -   |
| S3-1    | 32.31 | 17.38 | 1.09 | 0.72 | -   | -   | 1.98 | 0.52 | -   | 0.67 | -   | 37.30 | -   | 6.35  | 1.30 | 0.38 |
| S3-2A   | 34.99 | 11.07 | 1.09 | -   | 5.65 | -   | 0.82 | 0.09 | -   | 0.72 | -   | 39.75 | 0.66 | 4.61  | 0.55 | -   |
| S3-2B   | 46.17 | 11.81 | 0.49 | -   | -   | -   | 0.91 | 0.02 | -   | 0.40 | -   | 36.44 | 0.02 | 3.17  | 0.57 | -   |
| S3-3A   | 33.35 | 16.48 | 0.29 | -   | 4.44 | -   | 1.14 | 0.14 | -   | 0.78 | -   | 40.12 | 0.43 | 1.87  | 0.96 | -   |
| S3-3B   | 9.24  | -     | -    | 35.41 | -   | -   | 0.42 | 0.09 | -   | 0.31 | -   | 28.28 | 4.63 | 21.62 | -   | -   |
| S3-3C   | 36.12 | 12.95 | 1.15 | -   | -   | -   | 1.44 | 0.27 | -   | 0.09 | -   | 40.59 | -   | 3.55  | 1.09 | -   |

For socketed axe C, analyses were also performed on three representative areas, corresponding to the SEM micrographs in Figure 4, namely, the areas S3-1, S3-2 and S3-3. The three SEM micrographs of the corrosion layer of socketed axe C, shown in Figure 4, have completely different surface structures. The micrograph S3-1 shows the presence of cavities formed by dissolution in the presence of groundwater and crusts with coarse granulometry, incorporating contamination inclusions. Crusts S3-2 and S3-3, taken from two representative areas on socketed axe C, have very similar structural profiles, with cracks resulting from contraction and the conglomerate incorporates, in addition to corrosion products and ground contamination components. In addition, silver has been identified, and that seems to have come from the silvering process because it appears concentrated on certain areas only on the surface and it is not present in the composition of the alloy [38].

In all three samples, the chemical elements of the base alloy—Cu and Sn (Table 1)—were identified alongside the microelements originating in the ore and soil compounds from depositional processes. In sample S3-1, besides Pb and Fe as micro-elements from the ore, many contamination elements from the soil are also present (Si, Al, Mg, P, C and O). Instead, Ag was identified in the S3-2 and S3-3 samples. For this reason, several analyses were made and it was found that Ag originates from the silvering of the socketed axe. Moreover, the results highlighted the compounds resulting from the alteration processes (redox, acido-base and complexation) of the base alloy during the deposition, namely, the oxides and copper carbonates, tin, lead, iron and nickel, together with the superficial contamination structures corresponding to the elements Si, Al, Mg, P, S, C and O.

From the SEM micrographs (Figure 5) of the three socketed axes, performed on clean areas, without corrosion or contamination products, for socketed axe A one can see a homogeneous structure of the basic alloy (Figure 5S1) containing Cu (88.84%) and Sn (5.92%), as alloying elements from the ore, and Pb (0.73 %) and Fe (0.75%) as alloying microelements, also from ore. The oxygen (40.62%) comes from the newly formed oxides. Instead, socketed axe B and C show voids, microcracks and microphases that are differentiated, with a complex granulometry, randomly distributed.
The chemical composition of socketed axe B indicates the presence of Cu (91.29%), Sn (1.14%), Pb (0.66%), Fe (2.32%), O and Ni (1.00%), and socketed axe C have 88.22% Cu, 5.76% Sn, 1.21% Pb, 1.01% Ni and 3.80% O. The correlation between the data obtained for the three socketed axes indicates that they come from different production areas and the raw materials are, most likely, from different sources. Their manufacturing technologies are close (making the alloy by smelting ores, pouring into bivalve moulds, finishing, ornamentation through polishing and/or gilding), with socketed axe C being special because it was ornamented by silvering. From an archaeological point of view, this is a very important aspect that illustrates the function of the artifact, namely the prestigious one. This aspect is also supported by the lack of traces of use wear on the surface of the artifact, but which are present in socketed axes A and B.

The three socketed axes also differ constructively and functionally, in terms of ornamentation and size, and in terms of conservation status; they can be discussed in relation to the composition of the base alloy, the aggressiveness of the site, the age of the artifact and the depositional period.

Based on the results obtained, it can be emphasized that the corrosion products were formed by redox, acid–basic and complexation reactions, which have an important role in hydric processes (hydration/drying). These occurred at the surface of the alloy and in the fixing orifices. Over time, due to cyclic variations in humidity and temperature, corrosion layers or crusts have undergone contraction, segregation and diffusion processes. These processes have been accelerated by the differences in chemical load of the groundwater and the presence of hydrogel coatings of Sn (II), Pb (II) and Fe (II), whose instability did not lead to the Liesegang phenomenon (this phenomenon is characterized by the appearance of concentric formations of corrosion products resulting from structural reform) [10,11,13,15,27,39] but to coarse structures similar to crusts and moles [6,7], with uneven distributions. Moreover, under the influence of the chemical and electrochemical potentials at the interfaces, they led to processes of segregation and diffusion of some components from the volume phase into the corrosion structures, respectively, between them and the depositional environment, and vice versa. These lead to cracks, voids, cavities and contamination by incorporating the microstructures from the archaeological site during the deposition.

The high content of Sn in the corrosion crusts of socketed axes A and C highlights a high rate of segregation and diffusion from the volume phase of the alloy to the surface, under the influence of electrochemical potentials activated by the chemical loading of the groundwater, differentiated according to variations and differences of the cryptoclimate (internal parameters of the depositional environment) and microclimate parameters (external parameters from the soil surface). These potentials occur in high-porosity sites of sandstone systems. In contrast, for socketed axe B, these potentials are greatly diminished, coming from a site semi-protected by waterproof structures.
Compared to other bronze age artifacts, the high content of the base alloy in Sn and Pb demonstrates that soil aggression has been greatly differentiated in the case of the three socketed axes. The strongest aggressiveness of the laying environment is in the case of socketed axe C, which has resulted in the total destruction of the silver coating and the formation of a thin layer of cuprite and malachite. Then there is socketed axe A, in the case of which the aggression has led to a high rate of segregation and diffusion of Fe from the volume phase to the surface (found in the corrosion compounds). Socketed axe B has laid in a sandstone site, with high porosity, where superficial altering processes of the base alloy were very strong, leading to thick corrosion layers and crusts over the passive malachite layer. Porosity also allowed a strong contamination explained by the high concentration of Fe (14.23%) in the corrosion products.

4. Conclusions

A series of historical and chemical conclusions can be drawn based on the results obtained by corroborating the OM and SEM-EDX analyses of the basic alloy and the compounds from the corrosion films and crusts of the three socketed axes.

The data obtained for the three socketed axes show that they come from different areas and periods, and in their manufacturing process, probably, copper ores from different sources were used. They were made by casting in bivalve molds made of siliceous stone or clay, and the presence of burrs and holes proves some casting defects. Important differences in the manufacturing technology were not observed between the three objects across the three chronological periods, indicating the same metallurgical techniques.

Corrosion products were formed by redox, acido-base and complexation reactions, and the presence of phosphate anions and oxyhydroxides led to the formation of films over the primary and secondary patina structures, with a semi-membrane effect, which allowed the formation of crusts, moles and thin coarse structures, overlayed and/or interleaved with the contamination structures. The aggressiveness of the depositional environment was different for each artifact; the most aggressive was that of socketed axe C, followed by socketed axe A and socketed axe B.

The socketed axe C is special because it was decorated by silvering, which illustrates its functionality as a prestigious object; its function was also supported by the presence of the decoration. Decoration is found also on socketed axe B, an aspect that could indicate the same symbolic functionality, but the presence of the wear traces also indicates its use as a tool or weapon. Socketed axe A has only use wear traces, indicating a practical use rather than a symbolic one.

The shape of the artifacts and the composition of the alloy demonstrate that the three socketed axes come from different areas and distinct chronological stages. Socketed axe A is specific to the Late Bronze Age, being framed in the Noua Culture; socketed axe B can be classified in chronological stage Ha A2–Ha B2, and from a cultural point of view it is associated with the Corlăteni-Chișinău Culture; and socketed axe C can be framed chronologically between Ha B1 and Ha B2, or even Ha B3 (10th–8th c. BCE). This cultural and chronological variety could support the hypothesis of salt exchanges and the existence of an elite that controlled these resources in the eastern sub-Carpathians area of Romania.

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