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Technological and Functional Approaches Applied to Miniature Vessels with Pigment Traces: Two Middle Bronze Age Case Studies from Eastern Subcarpathians of Romania

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Abstract: Vessels with a special shape have always been a point of interest for pottery studies, especially from the perspective of the distinct functionality that these pots would have had. The ceramic typologies made for the miniature finds specific to the Middle Bronze Age in the Eastern Carpathian area include a series of such vessels attributed to the Costișa communities. Currently, the role of these pots is still under debate, being classified as ritual or special, which led to two case studies focused on investigating these miniatures. The analyzed vessels come from the Piatra Neamț—*Bâtca Doamnei* and Siliștea—*Pe Cetățuie* settlements (Neamț County), where these containers were discovered with traces of pigment or in association with colored minerals. These findings led to a series of questions related to their use, as it is known that in the Middle Bronze Age there are not many archaeological discoveries that explain the presence of pigments in the studied area. In this sense, multiplication of information was achieved by performing detailed analyses, such as optical microscopy (texture and surface details), colorimetry CIE L*a*b* (color investigation), SEM-EDX (elemental composition) and μ-FTIR (chemical compounds). The results of the interdisciplinary study led to new data on the nature of the pigment and the method of preparation, and also clues on the source of the raw material. Thus, these items illustrate the special use of miniature vessels and their probable functions.

Keywords: Middle Bronze Age; miniature vessels; pigments; SEM-EDX; CIE L*a*b*; μ-FTIR

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1. Introduction

The approach to the technology and functionality of the "ceramic packages" specific to the Middle Bronze period gained consistency through the varied and constantly improved typological contributions that have been more or less systematized. However, among the many vessels identified, a few containers stand out that, owing to their lack of use, attracted the attention of the research team. Such is the case of an older discovery like the one from Piatra Neamț—*Bâtca Doamnei*, or new one based on the careful information from the context researched at Siliștea—*Pe Cetățuie*; we propose a diversified approach to the issue. The need to explain a behavior attested from the Stone Age period [1] comes in the context of multiplying the answers regarding the destination of tiny storage containers of raw materials with such different roles. All this constitutes a new element in the approach and attempt to find multiple explanations of a behavior that is less known for the Middle Bronze period east of the Carpathians.

In this paper, we present the results of the performed analyses by optical microscopy (OM), scanning electron microscopy (SEM), coupled with energy dispersive X-ray spectroscopy (EDX), μ-FTIR and CIE L*a*b* colorimetry applied on the pigments from the Middle Bronze Age period in the Eastern Carpathians, to establish their chemical nature and preparation mode, and to identify their possible source and use.

1.1. Study Area and Archaeological Background

The study area is within eastern Romania, mainly the Subcarpathian area of Moldavia, which includes the hydrographic basin of the Bistrița River (Figure 1a) and the geographical unit called Cracău–Bistrița Depression, where the Middle Bronze discoveries are grouped (Figure 1b). Owing to the particularities of the relief and natural resources [2], such as fertile soils and pastures, but also salt springs [3], this area was intensively frequented in prehistoric times [4]. The Bistrița Valley is also an important hydrographic artery of the Subcarpathians, so some sectors register a high density of settlements. It also represents an important communication route [5] that connects the east and the west of the Eastern Carpathians, benefiting from smaller communication arteries, branched on either side of the main valley.

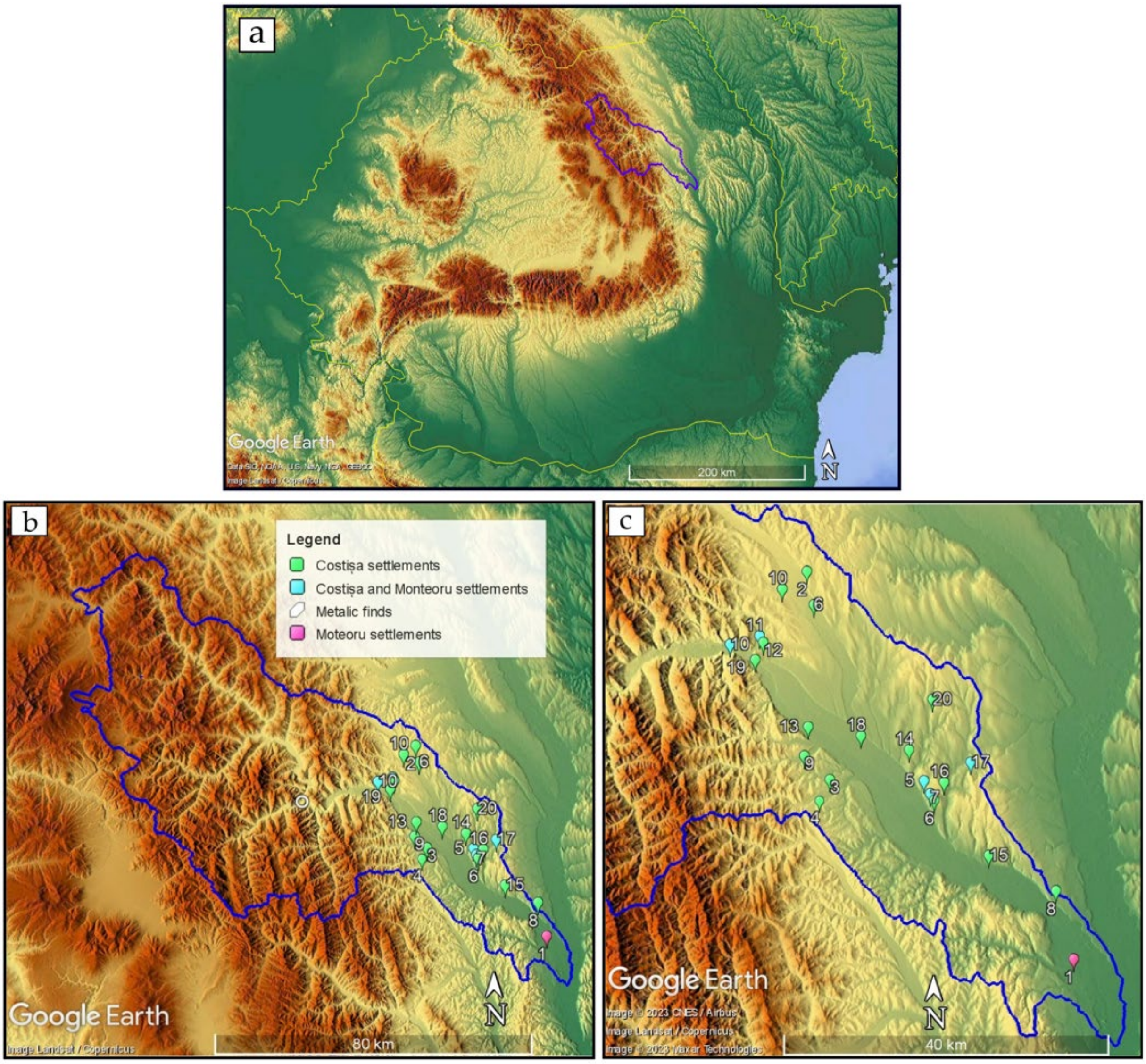


Figure 1. Bistrița River basin: (**a**) localization on Romanian territory; (**b**) discoveries specific to the Middle Bronze Age; (**c**) Costișa and Monteoru sites (1. Bacău—*Mărgineni*; 2. Bodeștii de Jos—*Cetățuia Frumușica*; 3. Borlești—*Dealul Cucului/Dealul Nucului*; 4. Borlești—*Dealul Runcu*; 5. Costișa—*Dealul Bisericii/Piciorul Moenii*; 6. Costișa—*Dealul Stanciului*; 7. Costișa—*Cetățuia*; 8. Itești—*Lac Lilieci*; 9. Luminiș—*Deleni*; 10. Piatra-Neamț—*Bâtca Doamnei*; 11. Piatra-Neamț—*Lutărie*; 12. Piatra-Neamț—*Pietricica*; 13. Piatra Șoimului—*Horodiștea/Capul Dealului*; 14. Podoleni—*Dealul Teiului*; 15. Racova; 16. Siliștea—*Vatra Satului*; 17. Siliștea—*Pe Cetățuie*; 18. Traian—*Dealul Fântânilor*; 19. Văleni—*Cetățuia*; 20 Hoisești—*La Curmătură* 1).

Although sporadic traces of habitation have been identified in the mountainous sector of the Bistrița valley, there are a series of archaeological discoveries in this area that illustrate and support the idea of using this transit space during prehistoric times (Figure 1b).

The intensity of habitation in the middle and lower basin of the Bistrița River varies from one chronological level to another, but for the Middle Bronze Age, the period of interest for this study, 20 discoveries are known, some of which were investigated by archaeological surveys and excavations or by field research (Figure 1c).

Although not many sites specific to the Bronze Age are known in the mountainous area of the Bistrița basin, it certainly was an area of transit or resources procurement. The working hypothesis can be supported by, among other things, the existence of an intermediate site at Chirițeni (Hangu commune), where two archaeological complexes are documented and dated to the Bronze Age [6]. Such presences were also reported at Dîrțu (Hangu commune), where a stone ax attributed to the Bronze Age was discovered [7]. Isolated metal finds [8] (Bicaz—*Neagra Cocioarvei*, Bicaz—*Capșa*, Bicaz-Chei, Bistrița, Grințieș, Tulgheș, Viișoara) attributed to the Middle [9] and Late [8] Bronze Age were also reported. All these discoveries highlight the frequenting of the mountainous area by prehistoric communities. The mountainous sector is an important area for a number of raw materials such as igneous and metamorphic rocks resulting from Neogene volcanism in the Eastern Carpathians. A recent study carried out on the lithic material illustrates the presence of these types of rocks in proportion of 10–15% in the Costișa—*Cetățuia* settlement [10].

The parallelism of the valleys and hills facilitates longitudinal circulation, but the transversal routes that could have represented old connecting roads between the east Carpathian and intra-Carpathian areas are not to be excluded [11,12]. Additionally, the settlement from Păuleni—*Dâmbul Cetății* (Harghita County), dated between 1830 and 1680 B.C. [13], must be discussed; this site being relevant to the present study by its positioning in a strategic area, located to the west of the Eastern Carpathians, as well as through the presence of some discoveries relevant to the present study. In the mountainous sector, another important resource for the Eneolithic period is found [14]. This is represented by the manganese deposits in the Iacobeni area [15], these being developed over an area of approximately 60 km along Bistrița [12]. The studies carried out until now have demonstrated that these resources, could be transported on the plain roads, and were used for painting Eneolithic pottery.

Radiocarbon dating situates the Middle Bronze Age habitations in this geographic area between ca. 1950 [16] and 1620 [17] B.C. Thus, the Middle Bronze Age period is represented in this area by two cultural entities, Costișa and Monteoru, the relationship between them still being a subject of debate. In this sense, until recently, the hypothesis of conflicting relationships [18] was accepted, but recent research has shown that these two communities were contemporaneous and even cohabited [19,20] in some settlements in the Bistrița River basin, an aspect partially reflected in the pottery they produced.

The Costișa pottery typology is represented by all functional categories such as cooking vessels, those for preparation, serving and consumption; containers for storage or transportation of solid and liquid goods; drinking vessels; and multipurpose vessels. The shapes of the containers are relatively simple, high and low, having small, medium and large sizes, consisting of one to three volumes. Monteoru pottery is represented by the same functional categories, which include a greater variety of shapes. Additionally, the category of storage or liquid transport vessels contains more complex containers consisting of three to five volumes [21].

As far as our study is concerned, of the known Middle Bronze sites, miniature vessels were discovered in only five of them, namely at Costișa—*Cetățuia* [21–24], Păuleni—*Dâmbul Cetății* [25], Piatra Neamț—*Bâtca Doamnei* [26], Poduri—*Dealul Ghindaru* [26] and Siliștea—*Pe Cetățuie* [21]. Two of these settlements are outside the studied hydrographic basin, but were taken into account due to the presence of miniature vessels and their special emplacement. Although material remains of both ceramic groups are present in three of these sites, the miniature pots are specific to the Costișa community. Therefore, the

Costișa pottery includes a category of vessels that represent miniatures of functional utilitarian classes, such as those for preparation, serving and consumption (Figure 2a); those with multiple purposes (Figure 2b); drinking vessels (Figure 2c); and those for storage or transportation of liquids (Figure 2d). Most miniature vessels belong to this last category, being also known as miniature amphorae.

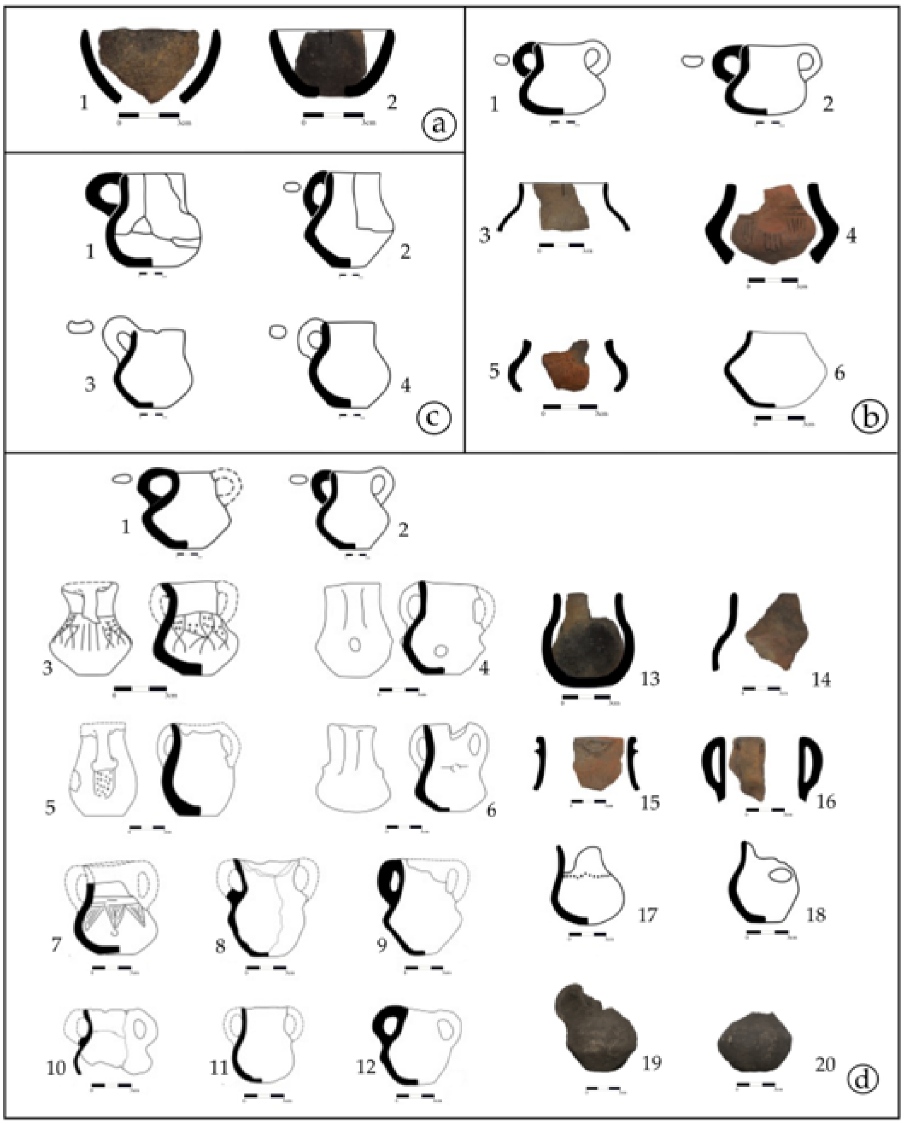


Figure 2. Costișa miniature vessels: (**a**) vessels for preparation, serving and consumption; (**b**) vessels with multiple purpose; (**c**) drinking vessels; (**d**) vessels for storage or transportation of liquids. These vessels come from the settlements of Costișa—*Cetățuia* (2 a, 1–4 b, 1–4 c, 1–2 d, 17–18 d), Păuleni—*Dâmbul Cetății* (2–7 d), Piatra Neamț—*Bâtca Doamnei* (13 d), Poduri —*Dealul Ghindaru* (6 b, 8–12 d) and Siliștea—*Pe Cetățuie* (1 a, 5 b, 14–16 d, 19–20 d). Drawings after [24,26].

It should be noted that these containers appear in the sites placed on dominant positions in the studied basin, because these settlements provided a special role of supervision or control which, along other important archaeological discoveries, could represent an aspect that can be an indication of miniature vessel functionality, and at the current research stage, seem to have been used only in dominant Costișa settlements (Figure 3).

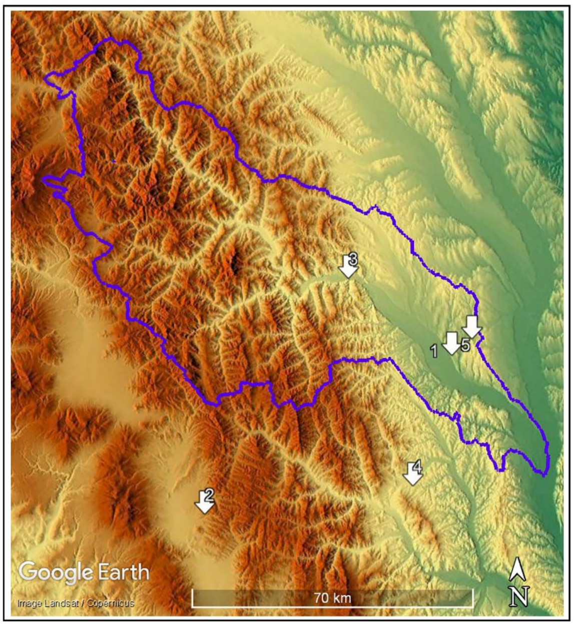


Figure 3. Costișa settlements with miniature vessels: 1. Costișa—*Cetățuia*; 2. Păuleni—*Dâmbul Cetății*; 3. Piatra Neamț—*Bâtca Doamnei*; 4. Poduri—*Dealul Ghindaru*; 5. Siliștea—*Pe Cetățuie*.

The function of these miniature pots is unknown, but there are several hypotheses to approximate their utility: they could represent prototypes of large vessels, an aspect determined by maintaining their shapes and proportions [21], they might have played a special role within the communities that created them or they could have had a practical purpose. The first hypothesis about the special role of miniature amphorae [27] was related to the fact that some of these vessels were burned and broken. Thus, these destructions were considered intentional, being part of a possible ritual of "transition" or "killing" of the vessels. However, not all containers of this type show such damage and the burning of the pots are actually use-wear traces and not a sign of a ritual, which could indicate a different purpose, and through this paper, two case studies are highlighted that can bring clarifications and additions to this subject.

1.2. Geology and Mineralogy

The Bistrița River is one of the most important in the Eastern Carpathians because its course cuts through various geological formations that contribute to the gathering of various sediments, from the springs toward the mouth [28] (Figure 4). This sector can be divided into two subsectors with special aspects: the subsector overlapping the Crytalino–Mesozoic zone and the subsector overlapping the flysch zone [29].

Regarding our study, from a geological point of view, the height from *Bâtca Doamnei* is represented by a great variety, characteristic of the Cretaceous–Paleogene flysch zone. The Paleogene (Eocene) deposits, of Lutetian and Ypresian type, are composed of calcareous-schist flysch, which includes Sucevița strata, Jghiabul Mare strata and Straja strata, these representing the intermediate facies. The Sucevița strata consist of an alternation of greenish calcareous sandstones and greenish leafy clays. The Jghiabul Mare strata are characterized by alternations of green quartz sandstones with green clays, having intercalations of conglomerates and microconglomeratic limestones with nummulites. The Straja strata are represented by fine calcareous, gray and gray-brown sandstones and greenish and reddish shaly argillites. Paleogene deposits are also represented by sandstone flysch characterized by the Tarcău sandstone facies. The latter is represented by 10–18 m thick sandstone beds with intercalations of thickly bedded gray or green clay shales; red and green clay shales; micaceous, coaly shaly sandstones; and calcareous, glauconitic and chloritic sandstones. The Bistrița riverside is made up of Holocene deposits (Upper Holocene) containing sands, gravels, boulders and loessoid deposits [30] (Figure 4).

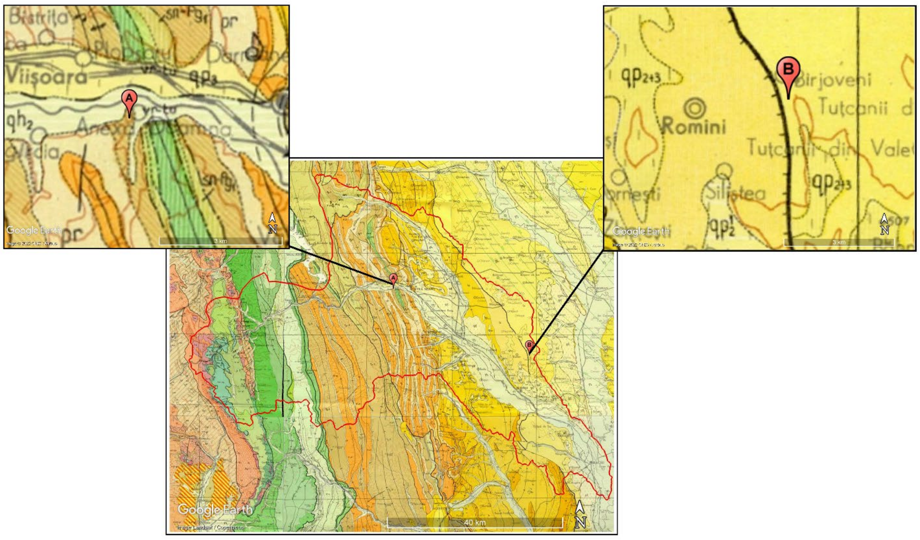


Figure 4. Geology of the Bistrița River basin and the two investigated settlements: A. Piatra Neamț—*Bâtca Doamnei* and B. Siliștea—*Pe Cetățuie* (Georeferenced Geological Map of Romania).

Quaternary deposits belonging to the Middle Pleistocene are found on the plateau of the Siliștea settlement, consisting of sands, gravels, boulders and loessoid deposits. Near the site there are Neogene Tortonian sedimentary deposits consisting of sands, marly clays, rock salt, gypsum and tuffs [30] (Figure 4).

Thus, from a geological perspective, in both settlements common clays and minerals are found, representing possible sources of raw material for house construction and pottery manufacture, and less for the presence of pigments. It is assumed that for the prehistoric periods the natural sources of ocher are generally nonspecific due to the abundance and local variability [31], and for the Middle Bronze Age period in Romania there are no studies that have considered this subject.

Ocher is a natural deposit, characterized by a variable amount of clay minerals (such as kaolinite and illite), iron oxides/hydroxides and other minerals/impurities (such as quartz, calcium carbonates, etc.), showing different colors depending on the specific nature of the Fe oxides/hydroxides present [32]. The term "ocher" is often used to describe iron-based pigments that have colors within a spectrum ranging from yellow to deep red or purple-brown [33]. Yellow ocher is generally represented by goethite (α-FeOOH) or lepidocrocite (γ-FeOOH), and red ocher by hematite and magnetite. Limonite is a generic term that corresponds to the combination of crystalline Fe(III) iron hydroxides and oxides (often goethite or mixed with lepidocrocite, hematite, etc.). The formation conditions of limonite, often considered mineraloids containing iron oxide and hydroxide, can be related to the crystallization/sedimentation process in a crust of minerals enriched in iron oxides due to environmental conditions (when minerals and their aggregates are transformed by the action of water and biological or atmospheric processes). Limonite is not a pure mineral, being represented by secondary transformations of iron oxides, often containing impurities. Mostly, it appears as a crust on the surface of other minerals, but it also appears in the form of conglomerates or crystals, which do not have a unique and defined structure and can be composed of different iron oxides and their additives (amorphous silicates, clay minerals, organic matter) [34]. However, being strongly influenced by the action of natural factors, the most widespread form of limonite is the alluvial one, identifiable on the banks of various waters, hence the popular name "swamp iron" [35]. The main coloring compound of yellow ocher is goethite, while the less stable lepidocrocite is a rarer mineral that gives ocher its color [36]. Although the predominant color is yellow, it can vary depending on the conditions of formation and composition: hematite—brown, reddish-brown; goethite—varies from yellow-brown to black; calcium carbonates—result in yellowish compounds; manganese impurities—darker tones. The range of colors also depends on the particle size (the finer the particles, the lighter the tone) and the formation conditions (temperature, amount of water, organic matter, pH during formation, etc.). For example, iron oxides are often formed by decomposition processes of Fe–Ti oxides derived from magmatic formations, and another phase classified together with ocher is jarosite. Jarosite-based yellow pigments are recognized as a special type of yellow ocher, which is considered an iron hydroxysulfate mineral. Depending on the origin area, ocher can be classified into "primary", which is in the vicinity of the parent ore and has a higher purity, and "secondary", the latter being transported away from the parent deposits by erosion and sedimentation, being less pure [36].

1.3. Case Studies from Eastern Romania

The first case study is represented by Piatra Neamț—*Bâtca Doamnei*, the settlement (Neamț County; Figure 1(10), Figure 3(3), which is located on an isolated hill on the right bank of Bistrita River (GPS: N 46°55′22″; E 26°19′22″). At this location is a well-known Dacian fortification (Iron Age), but traces of habitation on this plateau date back to the Eneolithic. Additionally, here were discovered artifacts attributed to the Middle Bronze Age and the Early Middle Ages, but without data related to stratigraphy or archaeological complexes, the site being mostly affected by subsequent human interventions [37]. As for the Middle Bronze Age habitation, this is represented by Costișa and Monteoru ceramic materials [26,37,38], without any housing structures being mentioned. In addition to the pottery, from the Piatra Neamț—*Bâtca Doamnei* site, there is also a mention of a gold ring that was discovered outside the settlement, on the western slope [37], attributed to the Middle Bronze Age communities. Moreover, from this settlement was recovered a miniature vessel [26]; the macroscopic analysis showed a reddish layer on the inner surface and several smaller spots of the same color on the outside (Figure 5).

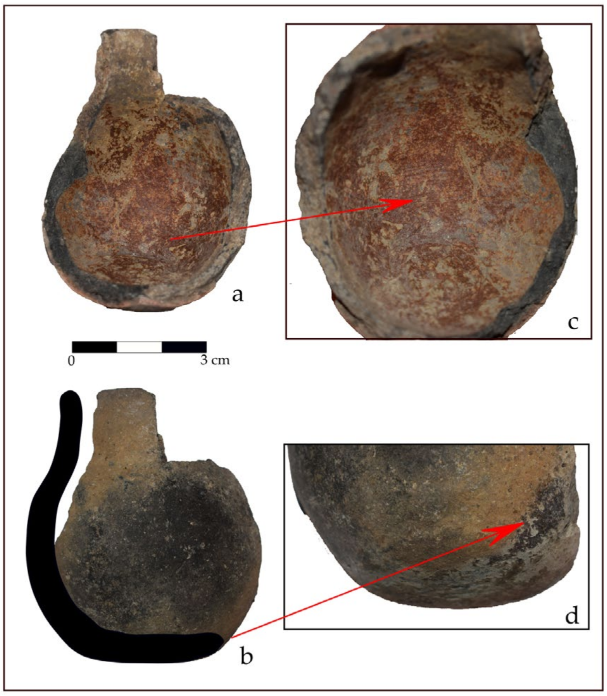


Figure 5. The miniature vessel from Piatra Neamț—*Bâtca Doamnei*: (**a**) interior of the vessel; (**b**) exterior of the vessel; (**c**) interior detail; (**d**) exterior detail.

The macroscopic analysis revealed that the exterior of the vessel is strongly affected by secondary firing, and on the unaffected areas the pot has two shades of brown, which, along with the fresh section, indicates a reducing firing atmosphere. The paste contains small inclusions represented by subrounded grog with a low frequency (5–10%) [39]. Microscopic analysis of the paste indicates the presence of quartz and iron oxides, while

SEM analysis illustrates good homogeneity of the component microgranules, without traces of vitrification, which indicates firing temperatures below 750–800 °C. The physicochemical analyses of the paste showed that the clay used in the manufacture of the vessel is slightly calcareous kaolinite, and other minerals present in the raw material were also identified, such as quartz, muscovite, feldspars and magnetite. The results of the analyses indicate that the firing temperature exceeded 500 °C, and the presence of carbonates in the ceramic paste suggests temperatures below 750–800 °C, as demonstrated by the SEM micrographs [21].

The vessel's exterior is very well finished, without decoration, while on the inside are visible traces of vegetal fibers, being carelessly smoothed. Additionally, on the inner surface, toward the base, a thick reddish layer is visible and on the outside a few smaller spots of the same color. It is important to mention that the reddish layer on the inside corresponds perfectly to the burned surface on the outside, both reaching the same area of the vessel, which could represent an important clue regarding the vessel functionality.

The second case study is represented by the site from Siliștea—*Pe Cetățuie* (Români commune, Neamț County; Figure 1(17), Figure 3(5) which is located on a high promontory (GPS: N 46°47′43.81″; E 26°43′33.00″), with good visibility toward the surrounding landscape [40]. The settlement is naturally protected on three sides by steep slopes; the defensive system was completed with an anthropogenic ditch of appreciable dimensions [5]. Here, a single habitation layer was discovered, in which archaeological materials of Costișa and Monteoru archaeological cultures were discovered, with no stratigraphic differences, thus indicating cohabitation of the two contemporary Middle Bronze Age communities [5,16]. During the archaeological research from Siliștea—*Pe Cetățuie* settlement (2000-present), several unburned rectangular housing structures were discovered, represented by large-sized sandstones that formed the basis of some supporting pillars, along with red-burnt sandstones and fragments of adobe and ceramic fragments [41]. Additionally, elements were discovered that indicate the practice of a foundation ritual of these constructions. In this sense, four such situations were discovered in which, under the large-sized sandstones, were whole pots or in situ broken vessels, together with animal osteological remains that represented fragments of meat offerings [19,41–44]. As for the archaeological materiality in this settlement, there are a multitude of bone artifacts (awls, pendants, arrowheads); stone artifacts (axes, curved knives/*Krummesser*, arrowheads, grinders) and clay fragments (spindle whorls) [42]; several metal objects, represented by six *Noppenringe* [18,40,41]; and a simple ring, a bracelet and a small ring fragment [43]. The metal pieces showed similarities with those from Central Europe, thus illustrating the existence of contacts or relationships of the eastern Carpathian communities with the Middle Danube area [22]. Regarding the pottery, complete functional packages were identified for both communities, but for the Costișa pottery several miniature vessels were discovered, one of them being in a special context, in the proximity of the hearth, considered the "heart" of the dwellings, next to a lump of yellow ochre (Figure 6), which may explain the functionality of these containers. Moreover, a consistent amount of whitish material remains, represented by calcium carbonate, which was also identified near the hearth [43]. The macroscopic analysis of the vessel from Siliștea—*Pe Cetățuie* did not provide a series of data as complex as those from *Bâtca Doamnei*, an aspect determined by the need to keep the vessel intact for analyzing the contents. However, it was found that the vessel had been broken almost in half since ancient times, without being able to make assumptions about the intentionality of this damage. In terms of manufacturing technology, the pot was found to have a carefully finished exterior, most likely fired in a reducing atmosphere. The archaeometric observations related to the vessel from Siliștea—*Pe Cetățuie* could not be carried out, an aspect determined by the impossibility of sampling, but the information could be extrapolated from those obtained from the *Bâtca Doamnei* settlement, assuming a similar temperature range. Additionally, based on a ceramic assemblage from this settlement that was analyzed in a previous study [45], it was possible to establish that most of the vessels were fired at temperatures between 700 and 750 °C.

Figure 6. The miniature vessel from Siliștea—*Pe Cetățuie* settlement: (**a**) context of the discovery and (**b**,**c**) details.

2. Materials and Methods

The proposed work methodology includes macro- and microscopic analysis of the vessels, color measurements and two interdisciplinary analyses such as SEM-EDX and μ-FTIR, designed to provide details of the elemental composition and chemical compounds present both in the clay and on the surfaces. The main focus of the study is represented by the chemical analysis of the pigments.

The microscopic investigations allow the detailing of certain characteristics of the pigment, data related to structure and microstructure, and the identification of minerals and use-wear traces. The microscopic analysis was performed with a Zeiss Imager.a1M microscope with a built-in AXIOCAM camera, which uses AxionVisionRelease 4.7.1 software.

SEM-EDX analysis provides information on the microstructure and elemental composition of the studied pigments. In this study, an electron microscope with an SEM scan was used, model VEGA II LSH, produced in the Czech Republic by TESCAN, coupled with an EDX detector, QUANTAX QX2, produced in Germany by BRUKER/ROENTEC.

FTIR analysis offers information on functional groups identified in the samples, completing the compositional results. The spectroscopic analysis was recorded with an FTIR spectrophotometer coupled with a HYPERION 1000 microscope from Bruker Optik, Germany (Rudolf-Plank-Straße 27, 76275 Ettlingen, Germania). The FTIR spectrophotometer is of the TENSOR 27 type, which is predominantly suitable for measurements in near-IR. The standard detector is DLaTGS and covers the spectral range 7500–370 cm^{-1}, working at room temperature. For completely nondestructive measurements, the TENSOR 27 spectrophotometer is connected to the HYPERION 1000 microscope, and, usually, the solid samples are analyzed in reflection mode.

Thus, by means of SEM-EDX and μ-FTIR techniques, we wanted to obtain data regarding the elemental composition of the pigment, the preparation technique and the source of these colored minerals.

The colors were analyzed with a model NR 10QC precision colorimeter, produced by 3NH Technology Co., Ltd. (F/6,Block 5B, Skyworth Inno Valley, Tangtou 1st Road, Shiyan, Baoan District, Shenzhen, China), China, which displays the recorded data directly onscreen with the possibility of computer transfer. It has a 4 mm opening. The measurement accuracy is ±1.

The classification of the analyzed pots as patrimony artifacts required some restriction regarding the sampling. Thus, the samples that were taken were very small (1–2 cm), which limited the mineralogical thin-section analysis, thus the mineralogical investigation of the paste could not be carried out due to the destructive nature of this method, the observations being restricted in this sense only to elementary investigations.

3. Results

3.1. Optical and Scanning Electron Microscopy

Following the optical microscopy analysis of the vessel from *Bâtca Doamnei*, it was observed that the inner layer is monolithized on the vessel wall and has a glossy appearance (Figure 7c,d), which excludes the possibility of contamination over time, while on the outer surface the appearance of the reddish spots is matte, indicating rather some ”staining” during the use of the container (Figure 7a,b).

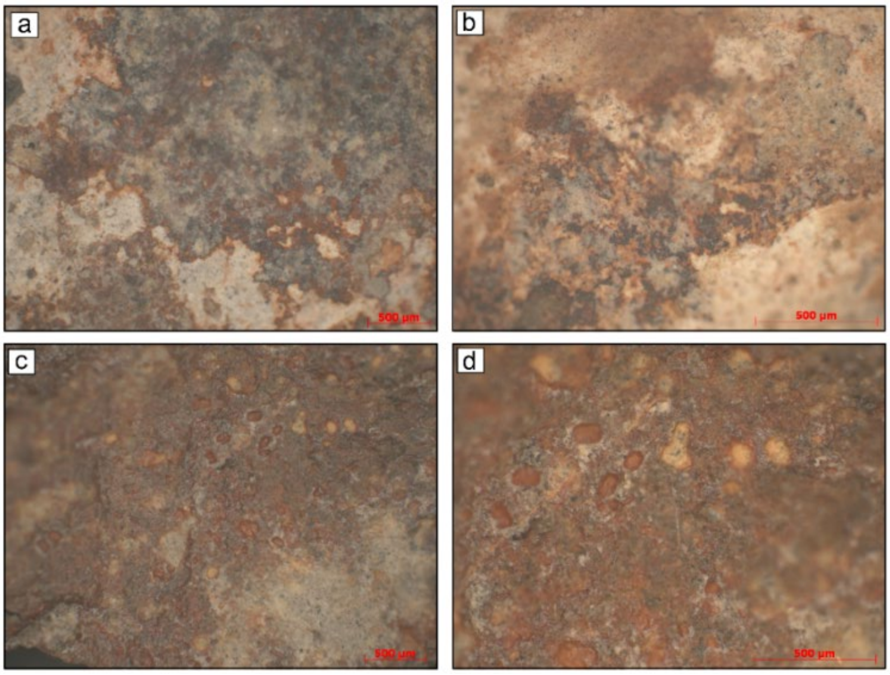


Figure 7. OM images for the red pigment from *Bâtca Doamnei*: (**a**,**b**) vessel exterior; (**c**,**d**) vessel interior ((**a**,**c**) 50×; (**b**,**d**) 10×).

The SEM micrographs of the pigment from *Bâtca Doamnei* show its morphology and distribution, both on the inner surface (Figure 8a,b) in the form of a continuous crust, with fine cracks caused by degradation through time, and on the outer surface where only small spots are visible (Figure 8c,d), corresponding to the use-wear stains. Thus, by the means of this method, the macro- and microscopic observations regarding the pigment are strengthened, highlighting the fact that the identified reddish layer is not the result of subsequent contamination, but represents traces of a deliberate action of preparation and use of these pigments. Thus, a possible explanation is that the mineral pigment would have been dispersed in an aqueous solution together with a natural organic binder [1] and mixed using a heating source. When the vessel was no longer used, the solvent evaporated and the pigment monolithized on the inner surface of the vessel, creating the consistent red layer. The hypothesis of using a heating source in the pigment mixture is also supported by the macroscopic observations of the secondary burnings visible on the outside of the vessel.

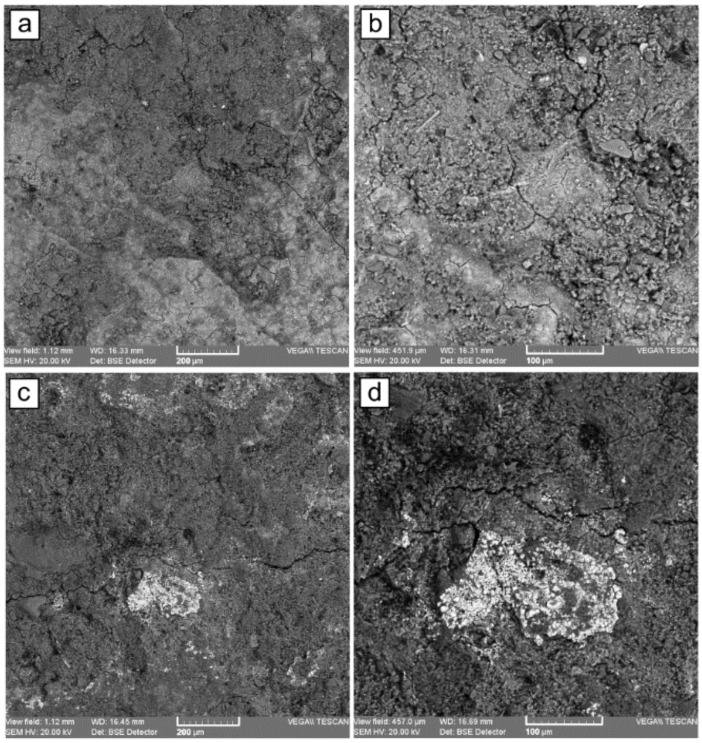


Figure 8. SEM micrographs for the pigment from *Bâtca Doamnei*: (**a**,**b**) interior; (**c**,**d**) exterior ((**a**,**c**) 200× magnification; (**b**,**d**) 500× magnification).

In the case of the yellow ocher from the Siliștea—*Pe Cetățuie* settlement, the microscopic analysis (Figure 9) revealed fine-grained mineral components, represented mainly by quartz and iron oxides, with limonite also identified in the form of quartz granules with yellow color. Precise identification of the mineralogical and chemical composition of the pigment was carried out by means of compositional analysis. The shape of the particles is varies; they are predominantly subrounded and subangular, suggesting a secondary mineral mixture affected by erosion factors.

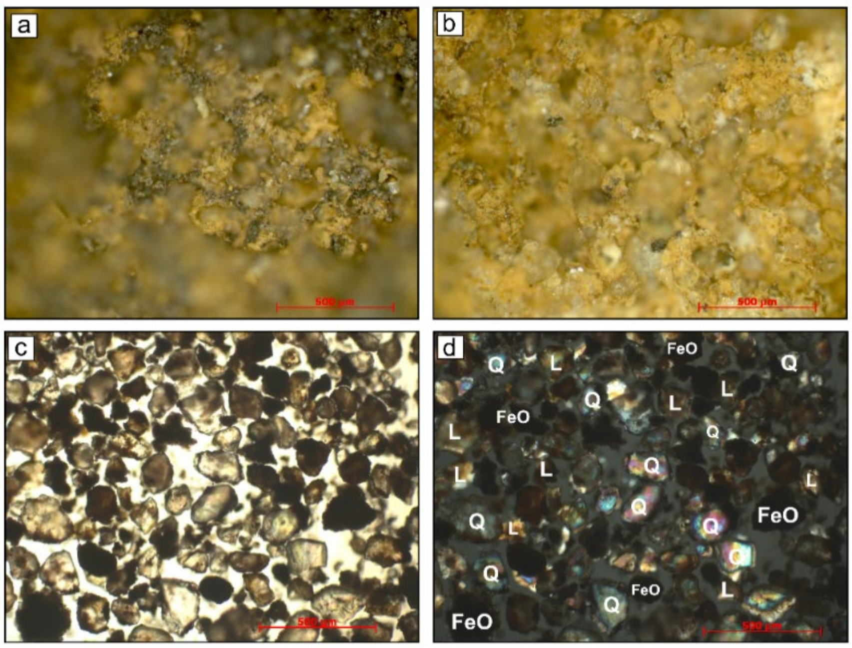


Figure 9. OM images of yellow pigment in reflection (**a**,**b**) and transmission (**c**,**d**) (50 and 100× magnification): Q—quartz; FeO—iron oxide; L—limonite (**c**)—parallel Nicols; (**d**)—crossed Nicols.

The SEM analysis of the yellow pigment from Siliștea highlights the existence of individual quartz grains of different shapes and sizes, limonite [46] being visible in the form of a thin layer on these particles. Thus, the morphology of the pigment sample indicates an alluvial nature, which is a clue as to its area of origin (Figure 10).

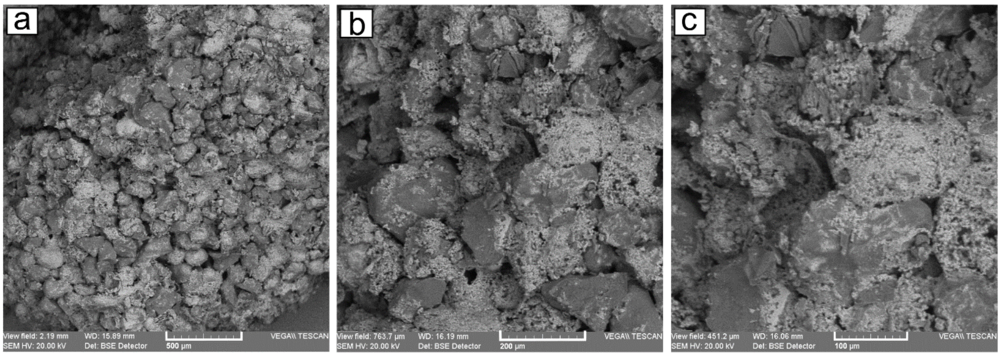


Figure 10. SEM micrographs for the yellow pigment from Siliștea—*Pe Cetățuie*: (**a**) 100×; (**b**) 300×; (**c**) 500×.

3.2. Colorimetric Analysis

CIE L*a*b* analysis was performed on six areas for each pigment sample. Thus, in the case of both samples, the highest values are L* (luminosity), which are between 43 and 51, and the values of the coordinates a* (green–red axis) and b* (blue–yellow) vary depending on the sample. In the case of the red pigment from *Bâtca Doamnei,* the values of the two coordinates are close, a* having values of 7 and b* of 12 (Figure 11). On the other hand, considerable differences are noticed in the case of the yellow pigment, where the values of the a* coordinate are 13, and those of the b* coordinate are 30 (Figure 12).

Based on the colorimetric results, a series of comparisons can be made indicating the mineral nature of the pigment. Thus, it was highlighted that in the case of the a* coordinate, values below 17 indicate the predominant presence of goethite (yellow), those above 30 indicate pure hematite (red), and those between 20 and 35 indicate a mixture of goethite with hematite (orange) [47,48]. Therefore, based on these values, both analyzed samples are represented by an ocher with a predominant content of goethite, a result that is also verified through compositional investigations.

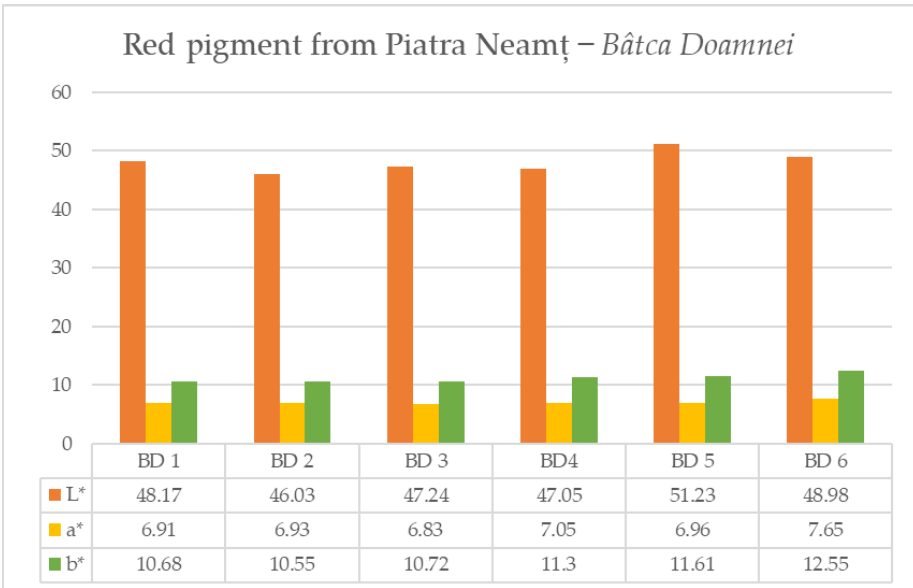


Figure 11. CIE L*a*b* colorimetry for the red pigment from Piatra Neamț—*Bâtca Doamnei*.

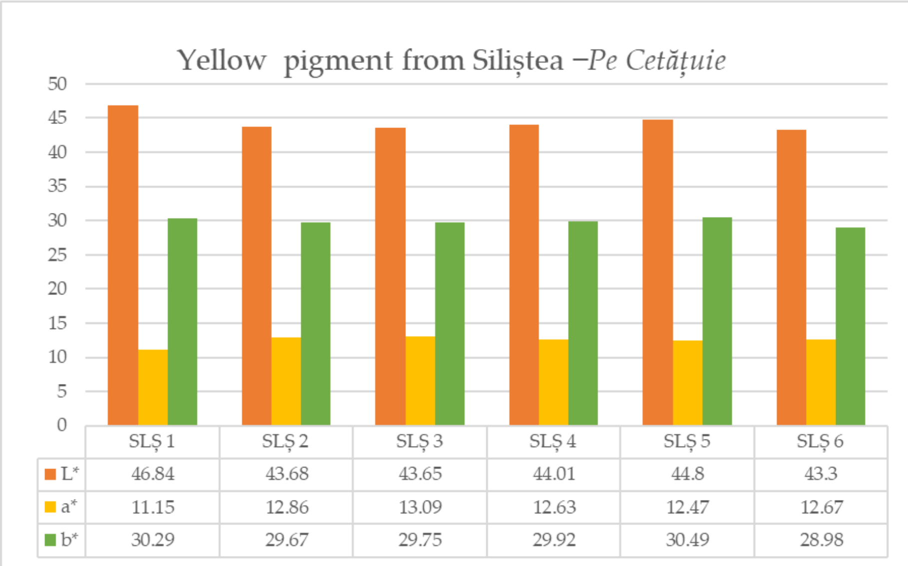


Figure 12. CIE L*a*b* colorimetry for the red pigment from Siliștea—*Pe Cetățuie*.

Another method for identifying the types of pigments, presented in specialized literature [49], is based on the use of the Munsell Soil Color Charts. Thus, based on this, the 2.5YR4/6 color established for the red pigment is attributed to jarosite, and 10YR5/6 corresponding to the yellow pigment would indicate maghemite. Maghemite is a yellowish-brown mineral that forms in sediments and soils and is commonly found in association with other minerals such as magnetite, lepidocrocite and goethite [50].

3.3. Compositional Analysis (EDX and μ-FTIR)

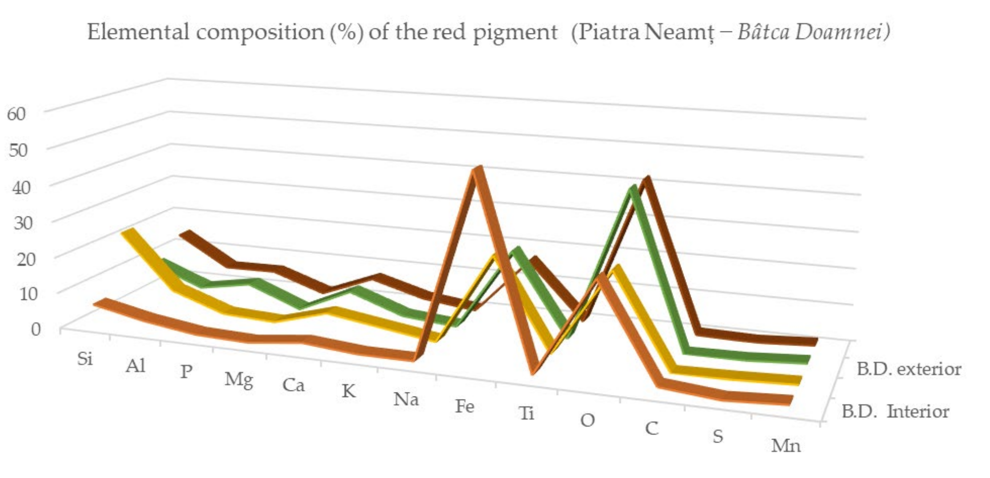
The EDX analysis of the pigment from *Bâtca Doamnei* was carried out on two areas of the pigment, both for the inner layer and for the small outer spots (Figure 13). Thus, a series of elements attributed to aluminosilicates was identified, but also appreciable concentrations of iron (26.3–51.9%), both on the inside red layer of the vessel and on its outer spots (16.7–23.3%), possibly red ocher rich in iron [32]. Appreciable traces of manganese (0.96–1.29%) and sulfur (0.19–0.48%) are also present on both surfaces, these coming from the minerals present in the pigment. The presence of these elements can be connected with minerals such as jarosite ($KFe_3(SO_4)_2(OH)_6$) and jacobsite ($Mn^{2+}Fe^{3+}{}_2O_4$) [51]. Additionally, based on the appreciable concentration of iron, the presence of goethite (α-FeO(OH)) and lepidocrocite (γ-FeO(OH)) can be assumed, an aspect that is also verified by means of infrared spectroscopy.

The elemental composition of the yellow pigment from Siliștea—*Pe Cetățuie* was obtained by analyzing three areas of a lump of mineral sample (Figure 14), identifying elements specific to aluminosilicates and appreciable concentrations of iron (31–50%), manganese (0.33–0.76%) and sulfur (0.12–0.30%). Additionally, in this case, the presence of jarosite and possibly jacobsite is noted. Moreover, the presence of goethite and lepidocrocite is also highlighted.

The μ-FTIR analysis for the sample from the *Bâtca Doamnei* settlement was performed for both surfaces (Figure 15), for the consistent inner layer on the inside and for the reddish spots on the outside. Based on the characteristic vibrational groups, we were able to establish the nature of the compounds present in the pigment.

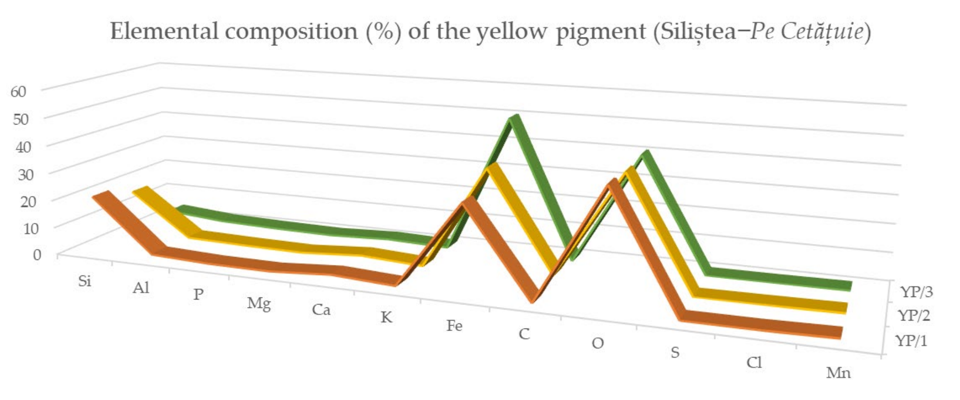
In addition to the peaks attributed to absorbed water [51,52], such as those in the range 4000–3000 cm^{-1} and at 1682 cm^{-1}, the one specific to kaolinite [46,51,53] at 3528 cm^{-1} is highlighted.

The obvious peaks at 2926 and 2859 cm^{-1} correspond to organic compounds that contain C-H bonds [52,54–58] and appear only on the inner surface of the container, probably corresponding to some organic components used in the preparation of the pigment that remained impregnated on the vessel. This aspect also supports the macro- and microscopic observations regarding the preparation of the pigment using an organic binder. Carbonates [59,60] are visible in the 1300–1500 cm^{-1} range, and were identified only on the inner surface by the presence of an intense peak around the 1300 cm^{-1}.



	Si	Al	P	Mg	Ca	K	Na	Fe	Ti	O	C	S	Mn
B.D. Interior	6.21	3.18	1.07	0.59	2.33	1.03	0.99	51.91	1.06	27.5	1.88	0.48	1.4
B.D. interior	22.73	7.41	2.3	1.57	5.77	3.51	1.24	26.35	1.5	25.45	0	0.34	0.96
B.D. exterior	9.62	3.91	6.48	0.65	7.4	2.08	0.74	23.37	0.73	42.89	0	0.26	1.29
B.D. exterior	14.57	5.92	6.07	1.02	6.87	2.66	0.78	16.7	0.89	42.07	0.53	0.19	1.13

Figure 13. The elemental composition of the red pigment from the Piatra Neamt—*Bâtca Doamnei* settlement.



	Si	Al	P	Mg	Ca	K	Fe	C	O	S	Cl	Mn
YP/1	20.77	1.54	0.63	0.48	1.9	0.64	31.25	0.25	41.16	0.3	0.32	0.76
YP/2	16.97	1.3	0.76	0.43	1.82	0.48	37.37	2.32	39.92	0.12	0.28	0.54
YP/3	3.49	1.58	0.9	0.52	1.3	0.53	50.11	0.39	40.54	0.16	0.16	0.33

Figure 14. The elemental composition of the yellow pigment from the Siliștea—*Pe Cetățuie* settlement.

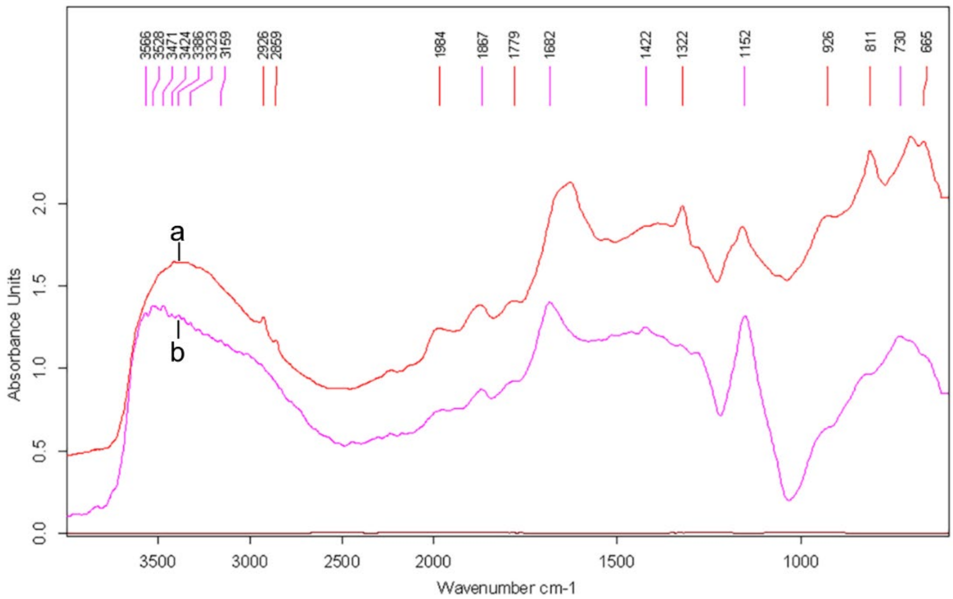


Figure 15. FTIR spectrum for the red pigment from Piatra Neamt-*Bâtca Doamnei* (a-interior; b-exterior).

Silicates are represented by the intense peaks at 1984 and 1867 cm^{-1}, these being more intense in the case of the interior. Additionally, muscovite [61,62] was identified by the peak at 811 cm^{-1}, being more visible on the inner surface and more flattened on the exterior one. The presence of feldspars [56] was noticed through the weak peak at 1779 cm^{-1}, indicating that the pigment used is of a mineral nature, with aluminosilicates in its composition.

The flattened peak at 1422 cm^{-1} and the medium one at 665 cm^{-1} are attributed to jarosite [63], identifiable on both surfaces, and the intense peak at 1152 cm^{-1} is attributed to lepidocrocite [64]. The peak at 926 cm^{-1} corresponds to magnetite [65], and the peak at 730 cm^{-1} can be attributed to goethite [66].

The µ-FTIR analysis of the yellow pigment from Siliștea—*Pe Cetățuie* (Figure 16) revealed the existence of similar compounds to those identified in the pigment from Bâtca Doamnei. In addition to the peaks attributed to absorbed water [52,66], such as those in the range 4000–3000 cm^{-1} and at 1619 cm^{-1}, the presence of kaolinite [46,51,53] is highlighted by the specific peaks at 3618 and 913 cm^{-1}.

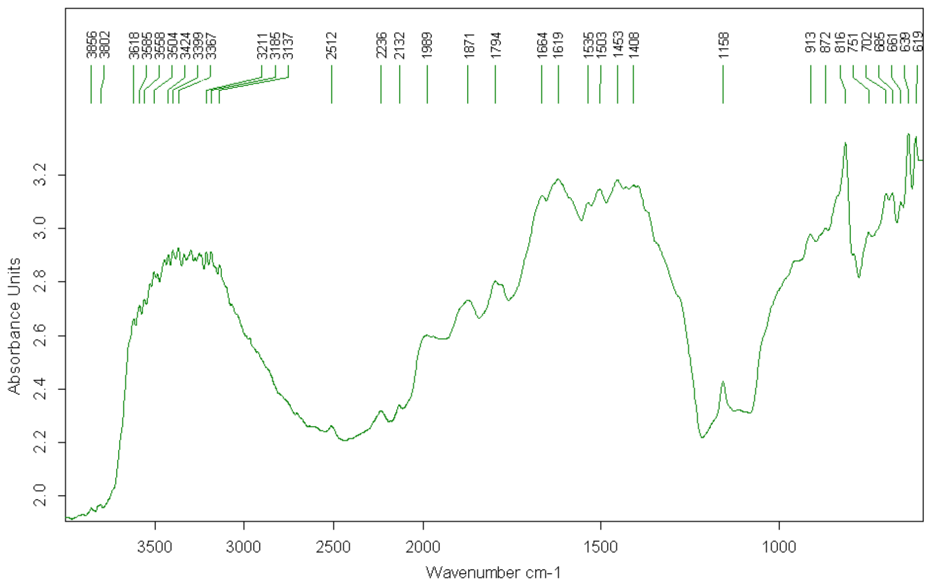


Figure 16. FTIR spectrum for the yellow pigment from the Siliștea-*Pe Cetățuie* settlement.

Carbonates [50,60] are visible by the presence of several peaks in the range 1300–1500 cm^{-1}, and calcite is visible at 2512 and 872 cm^{-1} [56].

Silicates are represented by the intense peaks at 1989 and 1871 cm^{-1} [66], and by the specific peaks of quartz at 2236, 2132 and 702 cm^{-1}, and those attributed to muscovite at 816 cm^{-1}. Feldspars [56] are also visible at 1794 cm^{-1}. As in the case of the red pigment from the *Bâtca Doamnei* settlement, the presence of silicates and feldspars indicates the mineral nature of this pigment.

The peaks at 1664 and 661 cm^{-1} are attributed to jarosite [63], those at 1158 and 751 cm^{-1} are specific to lepidocrocite [64], and goethite [64] is visible at 913 and 639 cm^{-1}. Moreover, the peak at 685 cm^{-1} is attributed to manganese oxides [46], and the one at 619 cm^{-1} to iron oxides [65], all of these minerals being specific to the analyzed yellow pigment.

Thus, the scientific investigations (OM, CIE L*a*b*, SEM-EDX, µ-FTIR) carried out for the two samples revealed the presence of natural pigments, which contain minerals such as goethite, lepidocrocite, jarosite and jacobsite. Carbonates, calcite, iron and manganese oxides have also been identified. Moreover, the kaolinitic nature of the pigment was highlighted, being present aluminosilicates such as quartz, muscovite and feldspars.

4. Discussion

The interdisciplinary analyses carried out for the pigment discovered on the miniature vessel from Piatra Neamț—*Bâtca Doamnei* provided a series of important data from an archaeological and physicochemical point of view. Thus, to obtain a red substance, a mineral pigment was used, which, most likely, was mixed with an inorganic (water) and/or organic solvent (blood, milk, glue, egg, etc.). This hypothesis is also supported by the secondary burns visible on the vessel exterior, suggesting the use of a heat source, which would have facilitated a stage in the preparation of the substances. Thus, the pigment preparation and use definitely points to a conscious component of the Middle Bronze Age communities that has been unknown up to this point. In this case, the traces of pigment on the vessel from *Bâtca Doamnei* would suggest the use of these colored substances for purposes beyond the mundane sphere, an argument in this regard being the type and size of the container. The same can be deduced for the settlement at Siliștea—*Pe Cetățuie*, where the archaeological discovery indicates a pre-use stage of the vessel and the pigment.

The use of pigments in the Bronze Age is known, in very few cases, for the central–western area of Romania. Here, there are some mentions of a ceramic fragment painted with three oblique lines and a white dot [67,68]. There is also a mention of a vessel with a horizontal band made by painting with graphite [69], and a large container, on the surface of which reddish-brick colored spots were identified [70]. The cases where traces of pigments or painting appear on Bronze Age vessels are very few, rudimentarily illustrated and without compositional analysis, no basis of comparison being available for the sample analyzed in this paper.

It should be noted that for the Costișa and Monteoru pottery, the actual presence of some pigments on the vessels is not documented until now, an aspect that requires detailed future studies of vessel surfaces to identify such traces. Therefore, in the attempt to interpret the possible use of the identified pigment, three possible hypotheses are outlined: the first involves the use of pigments for painting the vessels after firing, the second might suggest the coloring of some fabrics, and the third would involve the use of these pigments for body painting for purposes unknown at present, but which are probably related to the spiritual sphere of these communities. However, symbolic uses are usually cultural constructs and invisible from an archaeological point of view, as they leave no empirical evidence behind and are therefore difficult to demonstrate [1].

The use of various dye raw materials for practical purposes and beyond in prehistoric times has also been inferred based on a mixture of archaeological, ethnographic and experimental observations [35]. The presence of some traces of red ocher was also noted for the Costișa settlement, where following a microscopic study of a curved stone knife (*Krummesser*) the presence of this mineral was highlighted [71]. Moreover, in an interdisciplinary study carried out for the Costișa pottery from the *Cetățuia* settlement, it is mentioned the possible existence of some pigments that have in their composition, in addition to an appreciable amount of iron, traces of manganese [72], which would correspond to the results obtained in this study, also indicating in this case the use of pigments, but without making the connection with a miniature pot. It is important to mention the fact that in the case of the Costișa communities, the funeral ritual is not precisely known, as several disparate human osteological fragments were discovered in some settlements, such as those from Siliștea [73] or Costișa [74].

Thus, the association of pigments with miniature vessels and stone knives may indicate the use of these colored minerals in the case of some rituals, an explanation that seems plausible, especially in the absence of other archaeological evidence to indicate other functionality. Additionally, the identification of some founding rituals supports the existence of such practices which, together with the presence of pigments, indicate an active spiritual life, based on specific rituals, but which cannot be associated with funeral rituals, which are still insufficiently known. Moreover, the presence of miniature vessels and pigments in prominent settlements with some prestige objects indicates the existence of elite, which may have been engaged in a series of religious rituals involving the use of pigments. However, ethnographic accounts suggest that the boundaries between the symbolic and practical domains are often blurred, and both can coexist in the same object, tradition or practice [1].

As mentioned, identifying the sources of pigment used in the Middle Bronze Age is a great challenge, but through physicochemical analyses and archaeological finds, some important directions can be drawn. Thus, regarding the area of provenance of the red pigment from *Bâtca Doamnei*, based on current information, three possible sources of jarosite located in the Eastern Carpathians can be indicated (Figure 17), in the counties of Suceava (Iacobeni), Harghita (Sântimbru-Băi) and Covasna (Baraolt).

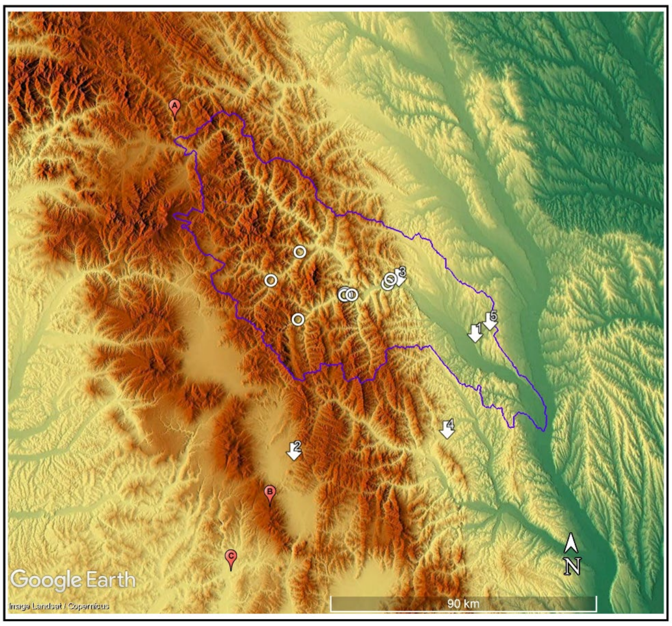


Figure 17. Map of the settlements (white arrows) with miniature vessels (1. Costișa—*Cetățuia*; 2. Păuleni—*Dâmbul Cetății*; 3. Piatra Neamț—*Bâtca Doamnei*; 4. Poduri—*Dealul Ghindaru*; 5. Siliștea—*Pe Cetățuie*), metal finds from the area of interest (white circle) and the current sources of ocher exploitation (A. Iacobeni; B. Sîntimbru-Băi; C. Baraolt).

Of these, only in the Iacobeni area is the presence of jarosite and jacobsite, a mineral mixture that would correspond to the results obtained from these case studies. Regarding the area of provenance of the pigment, some studies indicate a possible source of manganese pigments in the sedimentary–metamorphic ores of the Eastern Carpathians, the Bistriței Mountains region, the Iacobeni area [15,75]. Furthermore, the investigation of iron–manganese ratios [14] could be used to identify the possible source of origin, the following values being highlighted: 1/20—normal values for common soils; under 1/10–3/10—values for the Iacobeni area and 8/10–10/10—values for the Kryvyi Rih area. Thus, based on our ratios, which are 1/2–1/8, their source can be established, and according to the results obtained after comparing these values, the provenance of the pigments used was identified as being from the Iacobeni area. Moreover, in the absence of more detailed analyses on a reference sample, it is premature to indicate the source of raw material as the Iacobeni area. At this time, without further detailed investigation, we maintain the necessary scientific reservations regarding the source of the pigment, since our results could only be supported by circumstantial evidence at this point. However, the distance from the settlement to the possible indicated area would have allowed the pigments to be extracted. The hypothesis can also be supported by the mentioned archaeological discoveries, which demonstrate that the workspace was frequented by prehistoric communities to obtain raw materials. Next, regarding the limonite from the Siliștea—*Pe Cetățuie* settlement, the alluvial nature was established, but there are no mineral deposits in the vicinity of the area that would allow its formation. Thus, the yellow pigment was brought from other areas and processed for use. In this sense, the color obtained would be yellow, but the discovery from the *Bâtca Doamnei* settlement suggests a preference for the red color. Moreover, hot preparation of this pigment may indicate that the yellow ocher was transformed into red ocher by heating to temperatures above approx. 250 °C [32], which could be the case in the Siliștea settlement. In this case, from a technological point of view, two possible stages of pigment processing were identified, one represented by the raw material (yellow ocher) and the other represented by the finished product (red ocher).

In the case of the pigment from *Bâtca Doamnei*, if the Iacobeni area can be indicated for the more widespread limonite, based on elementary arguments, gravimetric ratios and circumstantial evidence, then the source is uncertain. However, the areas where this pigment can be present are found in the spreading area of the Costișa communities, as well as the transit ones, which would have allowed the use and extraction of colored minerals. Thus, covering the distance and acquiring such goods could be achieved by the direct travel of these routes by certain individuals, most likely specialized in the extraction of pigments, there being also the possibility of intermediaries or perhaps even some itinerant merchants, who would have facilitated access to these special products. Therefore, one can deduce the importance of this resource, which involves a considerable effort, and the purpose for which it was used. It also can be highlighted the possible existence of exchange relations based on pigments, in addition to other goods such as salt or the products made of bronze, which also require the inclusion of a cultural transfer as an indispensable element of the interpretation of the results obtained.

5. Conclusions

Interdisciplinary analyses of pigments and miniature vessels suggest the existence of lesser-known customs for the Middle Bronze Age communities east of the Carpathians. The analysis of the contents of the miniature vessel from *Bâtca Doamnei* shows that a mineral pigment was used, prepared using heat, to obtain a red substance, also using an organic solvent, which would have facilitated the mixing of the pigment and would have also influenced its quality. The community from Siliștea would have had to follow the same steps in processing the yellow pigment to give consistency to the obtained substance. In this case, the association between pigments and miniature vessels would suggest the use of these colored mixtures beyond household purposes, an argument in this sense being the type and size of the vessel. The use of pigments on Bronze Age ceramics is known, in very few cases, for the central–western area of Romania, being documented for vessels of various shapes and sizes, without any other miniature container with such residues being known. The fact that the pigment appears in association with such vessels from the Bistrița basin indicates and supports the idea of a special function for these containers, with or without traces of destruction. There are a few isolated cases that can open the discussion regarding the special destination of some colored minerals used intensively in the preceding period of the Early Bronze Age, as well as the possibility of a custom survival. Therefore, in an attempt to explain the possible use of the identified pigment, we outlined three hypotheses. The first of these involves the use of dyes for painting vessels after firing. The following one may suggest the dyeing of some fabrics, activities possible but unlikely due to the small amount of pigment resulting from such a miniature vessel. Additionally, we consider the use of these pigments as cosmetic products, an aspect that can be considered as a mundane or ritual activity. The third hypothesis, and the most plausible, considering the type, shape and size of the vessel, would involve the use of these pigments for body painting for various purposes, which are most likely related to the beliefs and rituals of these communities. This idea could also explain the effort for procuring the pigments, and processing them into miniature vessels with a symbolic functionality. In the proposed case studies, we opted for the integration of archaeological data with physical and chemical data in order to search for reasoned answers regarding the consumption and destination of different materiality.

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