ORIGINAL PAPER

ANALYSIS AND STRUCTURAL INVESTIGATIONS ON NEOLITHIC PAINTED POTTERY FROM SUPLACU DE BARCĂU/PORŢ-CORĂU ARCHAEOLOGICAL SITE

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Manuscript received: 12.03.2024; Accepted paper: 18.08.2024;
Published online: 30.09.2024.

Abstract. *The main objective of this study was the archaeometric analysis of eleven ceramic fragments discovered in the archaeological site of Suplacu de Barcău/Porț-Corău, situated in the Northwest part of Romania, more precisely in the Sylvanian Basin. The ceramic fragments come from different archaeological contexts and show a typically decoration, through black painting. The studied ceramic fragments have fine and semi-fine textures, discovered in certain stratigraphic situations: funerary contexts or household pits. All the analysed fragments belong to the Suplac type pottery. The archaeological research, both systematic and preventive, highlighted the main characteristics of the Neolithic habitation in the Sylvanian Basin, making it the subject of numerous studies until now. In the present paper, optical microscopy, scanning electron microscopy coupled with energy dispersive spectrometry (SEM-EDS) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) analyses were carried out on the batch of ceramic pieces studied, and based on the obtained results, the burning temperature of the samples was estimated. At the same time, for five clay samples – collected from archaeological sites and around the settlement – the elemental content was determined to establish the potential source of clay for the ceramic fragments.*

Keywords: *ceramic artefacts; painted pottery; clay; optical microscopy; SEM-EDS; ATR-FTIR; firing temperature.*

1. INTRODUCTION

Archaeological research from Suplacu de Barcău/ Porț-Corău is defined as the most important in the North-West of Romania, regarding the extent and the archaeological contributions as well, which became fundamental for the Neolithic and Eneolithic, providing

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https://doi.org/10.46939/J.Sci.Arts-24.3-b05

unprecedented information regarding the type of habitat, economic and especially spiritual life.

In the scientific literature, the name of the site is Porţ-Corău and is located between two administrative units, Bihor and Sălaj Counties. In this geographic area, the Barcău River, after ending a narrow path at Marca, creates a large terrace, with a favourable environment for human settlements (Fig. 1).

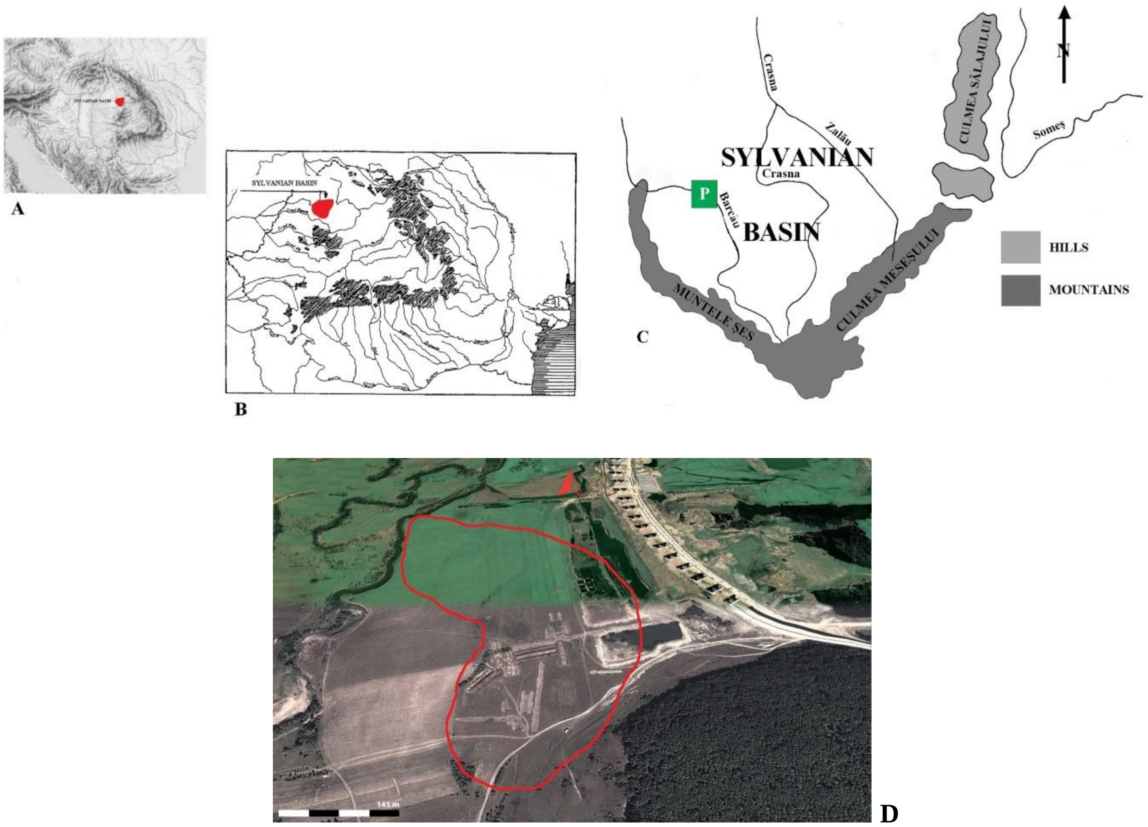


Figure 1. Suplacu de Barcau/ Porț-Corău archaeological site: A and B – site location in the Carpathian Basin [1]; C - site location in Sylvanian Basin [1]; D – Google Earth view of the site.

The site was mentioned for the first time by Emeric Salanki but extensive excavations were started only in 1973 by Doina Ignat. In 2008 the construction of the water storage from Suplac determined the necessity of starting here preventive excavations, both on the territory of Bihor and Sălaj County [2]. Findings from here would introduce in the scientific literature a new cultural group named Suplacu de Barcău [2, 3] after the eponym site, with two special characteristic components: the predilection of this community for stone manufacture (including performed axes) and biritualism. Late Neolithic communities from this geographic area, including Porț-Corău archaeological site, were used both cremation and inhumation in the funerary practice [4]. As for the stone manufacture, most of the polished stone artefacts discovered in Sălaj County come from Porţ-Corău, speaking about more than 1600 lithic artefacts which illustrates the manufacture of this raw material in the Late Neolithic, in a settlement of which members are skills in this specialized craft [5].

Archaeological research made in Bihor County [5, 6] also helped us to complete the information gathered during research made at Corău. The surface investigated had about 11000 square meters and discovered more than 700 archaeological complexes, houses, pits, graves, and fireplaces, during campaigns conducted between 2002-2003, and 2010-2012 [7-11]. In this area, there had been identified settlements belonging to Starčevo-Criș Culture, Pițcolt Group, or Coțofeni materials. Based on all the materials discovered, some attribute of the pottery can be listed: glasses, cups, bowls with very thin walls for fine pottery; pedestal vessels; bowls are preponderant: conical bowls or with slightly arched walls, vessels with slightly oblique walls that are almost straight; tempers consists of sand, micas and crushed shards; the majority of coarse pottery represented by pots or bowls has in composition sand or gravel in a small amount; well-defined and specific anthropomorphic and zoomorphic clay figurines with elements that define particular content; the painting evolves from spectacular shapes of good quality to simple black bands arranged without special attention directly on the bottom of the vessel and on the outside [2, 12].

Undoubtedly, pottery is the category that overwhelmingly predominates in archaeological discoveries. The often-huge quantities of pottery, the shapes, and especially the decoration of the vessels, characteristic of a certain area or period, determined that this category should be a priority in the concerns for defining a community with its customs and beliefs. Issues related to the funerary behaviour but also to aspects of daily life, can be identified and studied based on the evidence of pottery characteristics: manufacturing, composition, decoration, archaeological context of discovery, and by archaeometric investigation methods. Furthermore, the archaeometric investigations have implications for the identification of materials and production techniques, the establishment of origin, and their provenance, requiring for this matter the localization and characterization of the natural sources of raw materials, and the establishment of sources for obtaining them.

By getting to know the composition of raw materials used in different types of archaeological ceramic pieces, firing temperature, or tracing features of decoration, but also to determine the chemical composition of the soil/raw materials by performing analyses, making a correlation between them: clay deposits, local sediments, and ceramic composition can provide much useful information or even answers to some questions like: what kind of ceramic vessels were ritually deposited as a funeral inventory? were these pieces specially made to be deposited? were they made in a certain way compared to the usual, domestic ceramics? was the production technology different for vessels with different functionality? were they decorated differently? are those found in different contexts?

Technical information (shapes or decoration of household or usual pottery) compared to funeral inventory, will come to unravel aspects related to spiritual and social life. Pottery discovered during the archaeological excavations carried out in this area was already published but studies were limited to describing and presenting stratigraphy in general. A truthful image of social life and spiritual culture cannot be provided without analysing, interpreting, and comparing these artefacts in the light of their archaeological context and functionality.

There is not much information about the chemical composition of the pottery and only a few studies on the painted decoration of the Neolithic and Eneolithic pottery in the region of Transylvania and Banat [13-19]. Chemical analysis of archaeological artefacts, whether organic or inorganic, is a real challenge due to their complex composition. Their study has been possible in recent years due to the development of modern techniques and due to the evolution of technologies.

2. MATERIALS AND METHODS

2.1. MATERIALS

In order to be able to establish differences, and similarities, or to make correlations, a number of 11 ceramic fragments from Corău were analysed. All fragments are painted with black, specific to the Suplac group, but two of them present some red pigment traces. The painted decoration is well-preserved, on some parts but on others only the trace of the decoration is preserved.

The selected pottery belongs to the fine and semi-fine category, coming from different contexts: pits, agglomeration of vessels, and graves. The fragments are distinct parts of the vessels: the bottom, rim, and body of the vessel. In Table 1 are concatenated and tagged as sample catalogue the pottery and the information related to them as they were inventoried.

Table 1. Porț - Corău site (preventive excavations) – Sample catalogue

S (*the number of the trench*)	**Cx *(context)***	**□ *(square)***	**▼ *(depth) [m]***	***Inventory number***	**Sample No.** (short presentation)
S3/2010	61/1 /2010 inhumation grave	50 -52	0.89	477/2011	 **Sample 1** (Suplac group pottery) - Fine ceramic vessel bottom fragment with painted decoration marks.
S3/2010	61/1 /2010 inhumation grave	50 -52	0.89	479/2011	 **Sample 2** (Suplac group pottery) - Fine ceramic vessel fragment with painted decoration marks.
S3/2010	61/1 /2010 inhumation grave	50 -52	0.89	478/2011	 **Sample 3** (Suplac group pottery) - Fine ceramic vessel fragment with painted decoration marks.
S3/2010	66 /2010 pit - deposition of ceramic fragments, possibly a funerary context.	64-65.2/0-1	1	1156/2011	 **Sample 4** (Suplac group pottery) - Fine ceramic vessel rim fragment with painted decoration marks.

S (*the number of the trench*)	**Cx** (*context*)	□ (*square*)	▼ (*depth*) *[m]*	*Inventory number*	**Sample No.** (short presentation)
S6/2011	8 /2011 pit	14-17	0.60 - 1.60	2375/2011	 **Sample 5** (Suplac group pottery) - Fine ceramic vessel rim fragment with painted decoration and handle.
S9/2011	48 pit	11-13	0.40 - 1.66	2701/2011	 **Sample 6** (Suplac group pottery) - Fine ceramic vessel rim fragment with painted decoration on white slip.
S9/2011	48 pit	11-13	0.40 - 1.66	2701/2011	 **Sample 6a** (Suplac pottery) - Fine ceramic vessel rim fragment with painted decoration on red slip.
S6/2011	36/2011 pit	-	0.65 - 0.85	2433/2011	 **Sample 7** (Suplac group pottery) - Fine ceramic vessel fragment with painted decoration
S5/2010	136/2010 pit	-	0.80 - 1.70	1198/2011	 **Sample 8** (Suplac group pottery) - Fine ceramic vessel fragment with painted decoration on red slip.
S22/2012	149/1/2012 pit	-	-	1507/2013	 **Sample 9** (Suplac group pottery) - Fine ceramic vessel fragment with painted decoration and pierced handle.

S (*the number of the trench)*	Cx *(context)*	□ (*square)*	▼ (*depth) [m]*	*Inventory number*	**Sample No.** (short presentation)
S23/2012	213/2012 pit	-	-	4045/2013	 **Sample 10** (Suplac group pottery) - Fine ceramic vessel fragment with painted decoration.

S – the number of the trench; Cx – context; □ – excavation square; ▼ *– depth.*

The 11 painted pottery samples belonging to Suplac Group communities display a typical black decoration consisting of lines of different thickness that follows parts of the pot or form linear motifs. The black-painted decoration is applied directly on the ceramic body on red or white slips. The vessel fragments are made of fine ceramic, well fired, with fine non-organic tempers added: fine sand, and quartz, after which is applied the ornament.

Five clay samples (i.e. C1-C5) were collected as follows: C1 and C2 were collected from the surroundings (Southern and South-eastern parts outside of the archaeological site), while C3-C5 were collected from the archaeological excavations. Bintintan et al. [17] have mentioned that some of this sample could have functioned, at their first use, as clay pits for raw material extraction.

Until now, the pottery of Suplac Group has been analysed regarding the composition of the black matter used on painted decoration of the pottery found at Porț-Corău; for that study samples of this material were used, analysed by GC-MS and FTIR spectroscopy. The results showed that the black layer was composed of a mixture of birch bark tar and natural bitumen, predominantly composed of birch bark tar [20].

2.2. ANALYTICAL TECHNIQUES

To accomplish the archaeometric characterization, the ceramic fragments required some complementary methods for compositional and morphological analysis. Therefore, were investigated by optical microscopy (OM), scanning electron microscopy coupled with energy dispersion spectroscopy (SEM-EDS), and attenuated total reflection - Fourier transform infrared spectroscopy (ATR-FTIR).

Optical microscopy represents a non-invasive solution for micro-scale analysis which gives information regarding the matter surface, its particularity as the colour, texture, density, inclusions, the quality of a manufacturing process, and so on. The microscope used for investigations in this case is Stemi 2000-c (Carl Zeiss Microscopy GmbH, Jena, Germany) with a magnification of 6.5X. The images presented in this study were acquired using an Axiocam 105 digital camera and processed by Zen Software (Carl Zeiss proprietary software). OM analysis is important to pinpoint the relevant aspects that could create the premises for a more complex investigation regarding the morphological and chemical structure of the samples.

In addition, ceramic samples were analysed by scanning electron microscopy coupled with energy dispersion spectroscopy, using SU-70 SEM (Hitachi, Ibaraki, Japan) coupled with UltraDry EDS (Thermo Fisher Scientific, Waltham, MA, USA). One of its main characteristics is that operates in ultra-high vacuum (10^{-8} Pa) and uses a ZrO/W Shottky-type electron gun. For surface morphology, an acceleration voltage (Vacc) of 1 kV was necessary. Additionally, it was performed the elemental analysis at 25 kV (Vacc). The equipment performs at ultra-high resolution (1 nm / 15 kV and 1.6 nm / 1 kV) and provides high-quality images in a magnification range between 30X and 800000X. In respect of qualitative and quantitative analysis, UltraDry EDS allows detection from Be (Z=4) to Pu (94) on point, rectangle, line, etc., and gives the distribution maps of the elements.

A complementary Fourier transform infrared spectroscopy technique was used for the investigations of inorganic and organic groups of chemical compounds. The analyses were performed using a Vertex 80v spectrometer (Bruker Optics GmbH & Co. KG, Ettlingen, Germany) equipped with diamond ATR crystal (4000-400 cm^{-1}), defined mainly by a high spectral resolution of 0.2 cm^{-1} and good accuracy (0.1%T).

The clay samples were analysed by ATR-FTIR (already described in this section) and wavelength dispersive X-ray fluorescence (WD-XRF). XRF technique provides qualitative and quantitative analysis (*i.e.*, elemental content of the clay samples) and, for this, Supermini200 spectrometer (Rigaku, Osaka, Japan) was used.

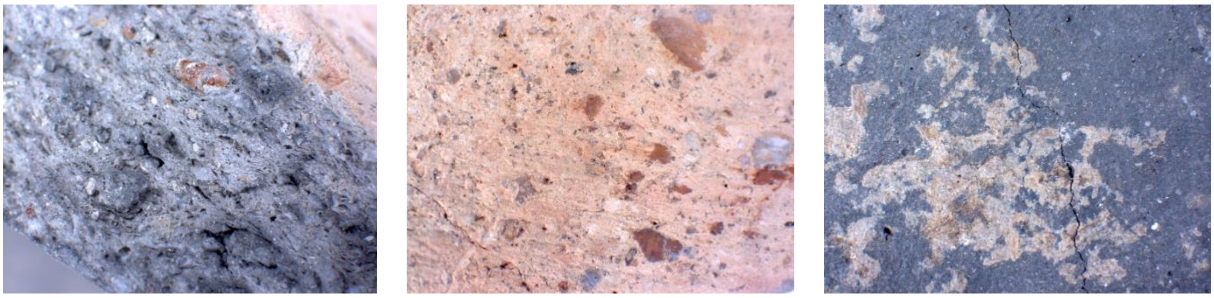
2.3. DATA ANALYSIS

The obtained data were used to estimate the firing temperature – according to Velraj et al. [21, 22] and Bintintan et al. [17]. The potential source(s) of clay for the ceramic samples were established by Hierarchical Cluster Analysis (dendrogram) using SPSS Statistics.

3. RESULTS AND DISCUSSION

3.1. OPTICAL MICROSCOPY (OM)

The OM revealed various aspects about ceramic fragments as that in some cases the structure proved to be dense and compact, and in others coarse and amorphous, furthermore, some samples had cracks, striations, inclusions, or dislocation of minerals. All these aspects will be discussed one by one in the following lines.



edge **background** **black pigment**

Figure 2. Sample 1 - Optical microscopy (6.5X)

Sample 1 shows a coarse and amorphous structure, dark coloured with inclusions on the edge; also, fine cracks on the front side. The predominant is a reddish cream colour, otherwise quite often found in ceramics, and a black pigment as can be seen in Fig. 2 - black pigment. The texture of the surface highlights several aspects related to the process of execution and manufacturing of ceramics, such as the presence of transverse lines (striations) as a probable result of clay processing.

edge **background**

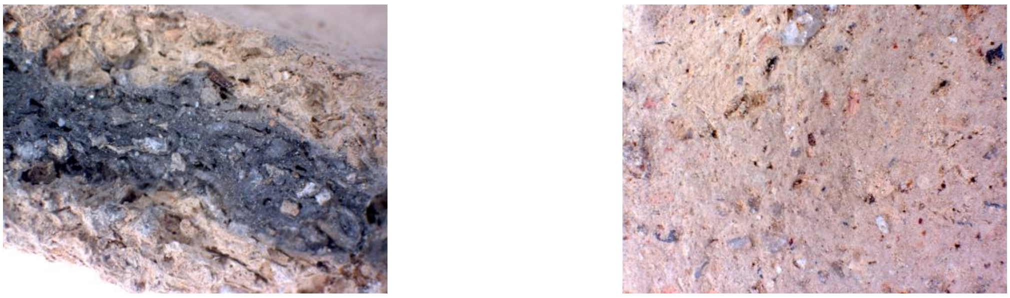
Figure 3. Sample 2 - Optical microscopy (6.5X)

Sample 2 has a fairly dense texture of reddish colour with black variations in places that can be found on the edge or the front side of it (Fig. 3); this time the presence of striations can be observed on the surface of the ceramic. Their depth is more pronounced than in the case of sample 1, an aspect caused probably either by the low clay moisture or by the minerals present in clay that left traces in the manufacturing process. The sample shows some fine cracks on its surface.

edge **background**

Figure 4. Sample 3 - Optical microscopy (6.5X)

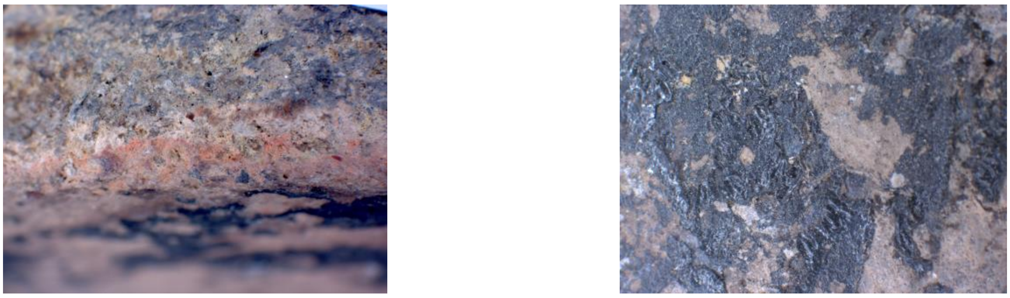
Sample 3 has a predominant cream colour, except for the edge, which is dark grey (Fig. 4). Regarding the granulation, it can state that it is close to sample 1, but the material is more compact and contains mineral inclusions of different colours but also cracks.



edge **background**

Figure 5. Sample 4 - Optical microscopy (6.5X)

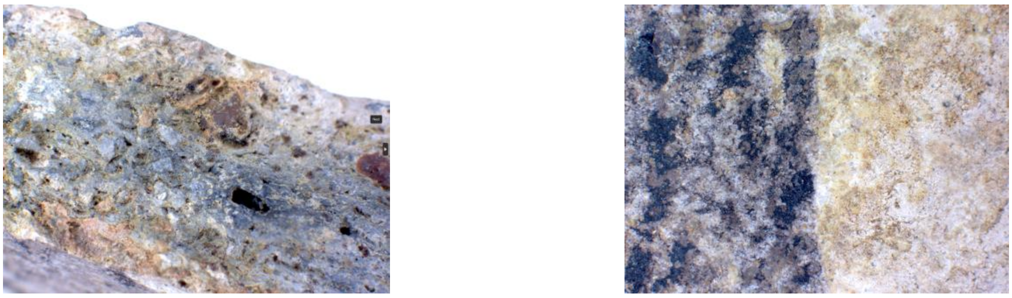
Sample 4 is characterized by a relatively large grain on the edge, an aspect that places it in front of the first 3 samples from this point of view, overall, the colour is cream except for the edge where are visible some cream-black layers, and for the first time, the cracks so common in the previously studied samples are missing (Fig. 5). Surprisingly the striations are missing as well, and the texture seems more homogeneous.



edge background and black pigment

Figure 6. Sample 5 - Optical microscopy (6.5X)

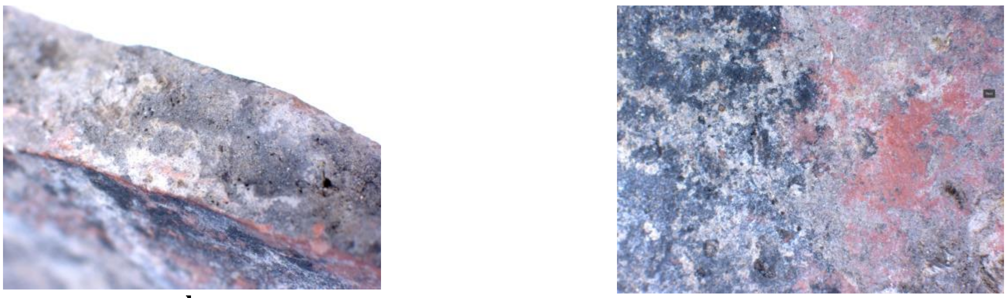
Sample 5 shows a relatively dense and compact structure on the edge, with a reddish colour in places and black influences, but among which a predominant cream colour can be distinguished, mainly representing the natural background on which a black pigment assimilated as part of a decorative process was applied (Fig. 6). This pigment has an uneven glassy texture and is applied more coarsely in certain areas.



edge black pigment (left side), background (right side)

Figure 7. Sample 6 - Optical microscopy (6.5X)

Sample 6 has a relatively large granular structure on the edge, dark in colour in the centre and brown or yellowish white at the ends, as can be seen in Fig. 7 - edge. In the second image, the natural yellow-white background and the black pigment are highlighted. Regarding the outer face of the sample, an irregular surface without striations and the absence of cracks can be highlighted.



edge black pigment (left side), red pigment (right side)

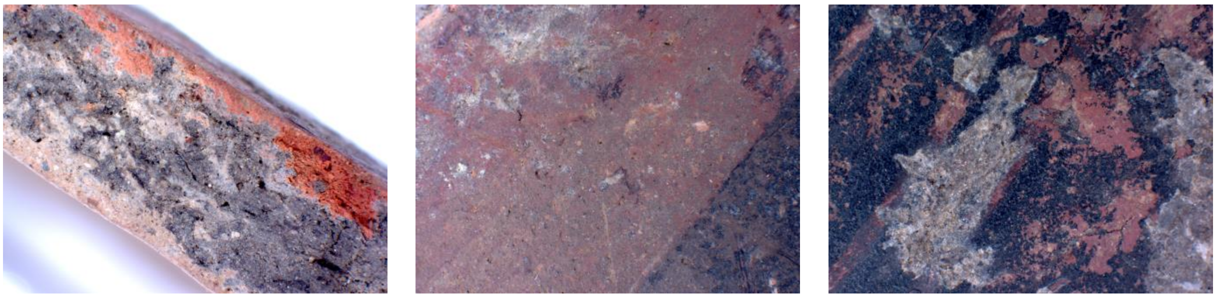
Figure 8. Sample 6a - Optical microscopy (6.5X)

Sample 6a is highlighted by a very compact structure with fine granulation (probably the raw material was previously strained before use) – Fig. 8. In the first image, it can be distinguished that two thin layers of red and black pigment are applied on a natural background. In the same image is noticed an uneven distribution of colours in which dark grey predominates, but can also be found brown, white, cream, or reddish. On the front side, it has a mixture of red and black in which the black comes from the pigment used, but the possibility that the red colour is also a pigment is not excluded. Nevertheless, it could be added as well that the presence of red colour may occur as a natural result of the burning process.

edge **black pigment**

Figure 9. Sample 7 - Optical microscopy (6.5X)

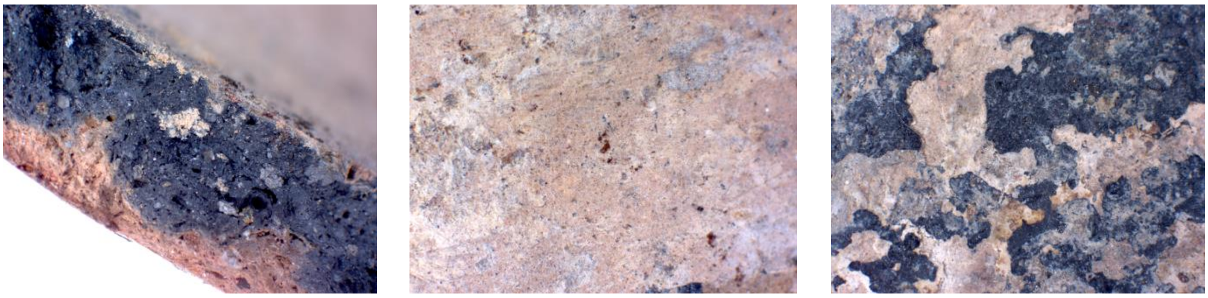
Sample 7 has a surprisingly quite compact structure and with not so fine granulation as in other cases. On the edge (Fig 9 left image) the predominant colour is brown with some white-grey calcareous kind of textures. The image on the right highlights the black pigment applied to the front side of the sample as well as the large grain of the substrate.



edge **background** **black pigment**

Figure 10. Sample 8 - Optical microscopy (6.5X)

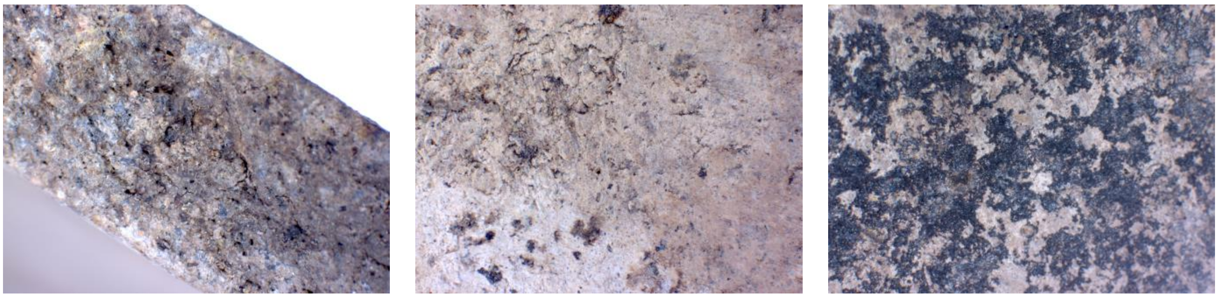
Sample 8 shows a dark colour on the edge surface (especially in the centre) and reddish or cream at the extremities. The structure is quite dense, the grain being slightly larger than in the case of the previous sample. The reddish colour is also present on the side of the sample, where shades of grey and white yellow can also be found in places, but a black pigment is applied over the predominant red. Although it has a compact structure in general, some cracks can be observed in the optical microscopy analysis. The black pigment (Fig. 10 - black pigment) can be characterized as a mixture of an amorphous and glassy mass that most likely went through a thermal process of melting followed by solidification. It is not excluded that the ceramic after the firing process has generated the vitrification effect of the pigment. In the case of this sample, no streaks were observed.



edge **background** **black pigment**

Figure 11. Sample 9 - Optical microscopy (6.5X)

Sample 9 does not have a very dense structure; moreover, it shows a medium graining in relation to the previous samples (Fig 11 - edge) and a dark colour unevenly distributed on the edge, but also a reddish and cream colour. On the side, you can distinguish the cream colour that also gives the natural background of the sample over which a black pigment has been applied. No cracks are noticed, only dislocations of minerals on the surface of the sample and fine striations probably due to the manufacturing process.



edge **background** **black pigment**

Figure 12. Sample 10 - Optical microscopy (6.5X)

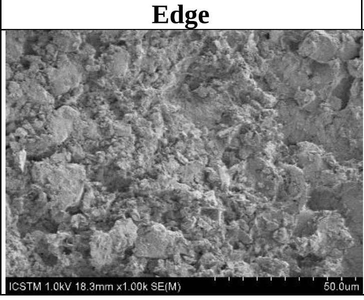
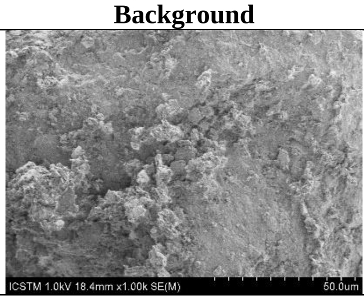
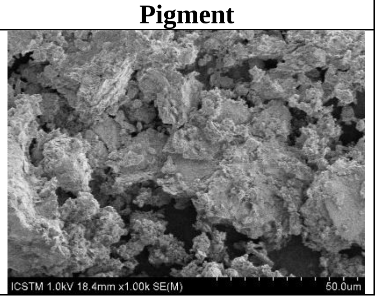
Sample 10 has a granular structure of medium to large sizes, as can be seen in Fig. 12 - edge where there are variations of grey and cream. On the side face, we distinguish a natural cream-colored background and a dense but uneven surface in places due to dislocations of material, over which, a black pigment was applied.

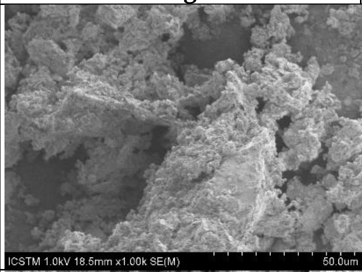
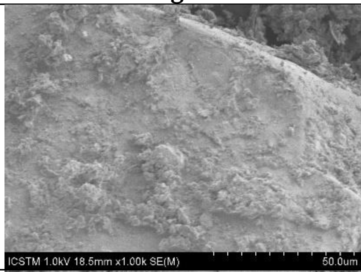
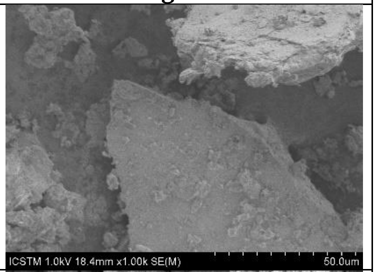
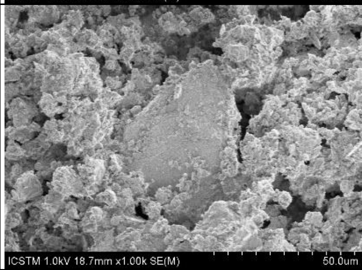
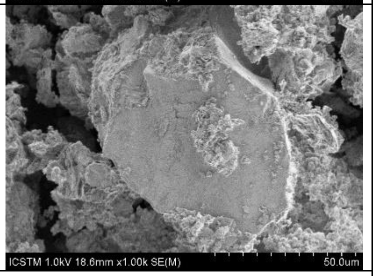
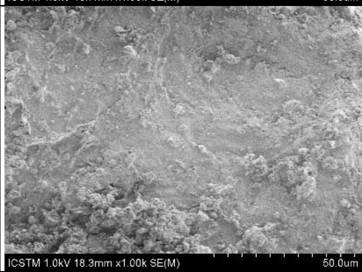
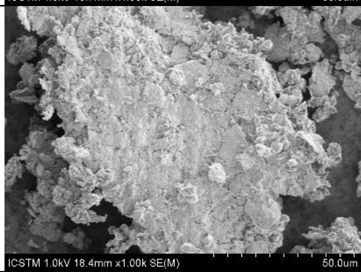
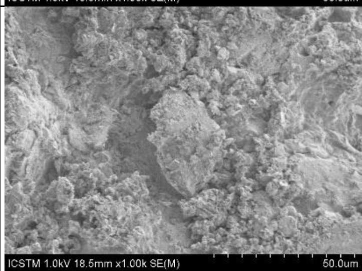
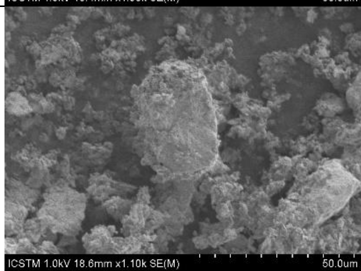
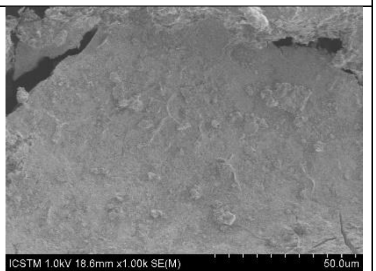
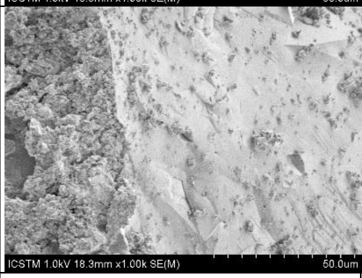
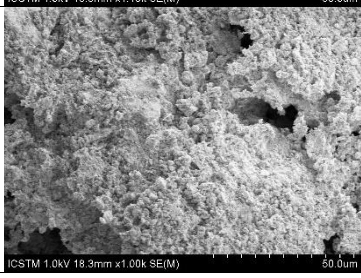
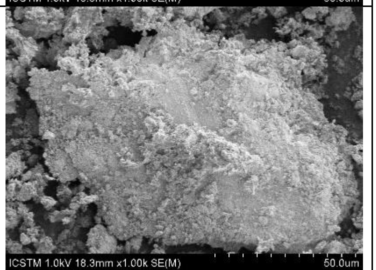
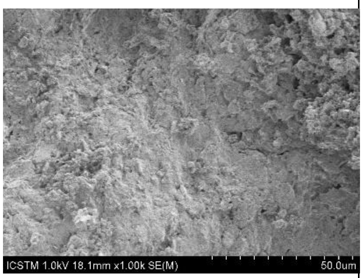
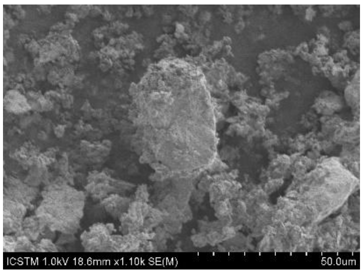
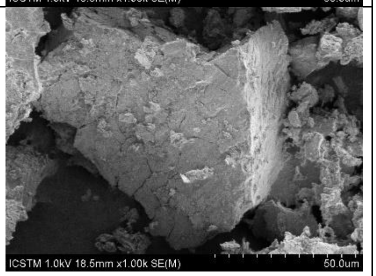
In general, the ceramic fragments had some similarities in the aspect of colour and granular structure but also differences which can probably be attributed to the entire process of selection and processing of the clay, the firing temperatures to which it was subjected, and ending with the pigment applied as a colour ornament.

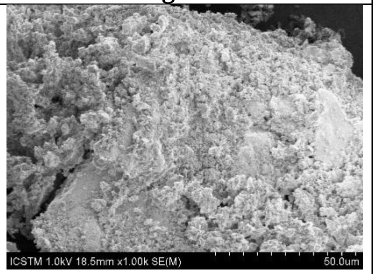
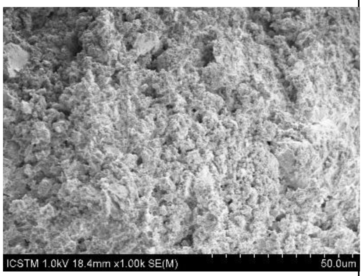
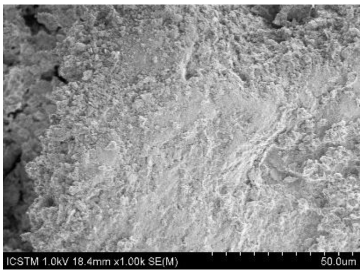
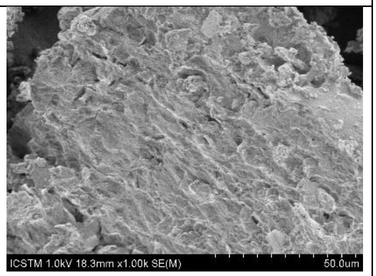
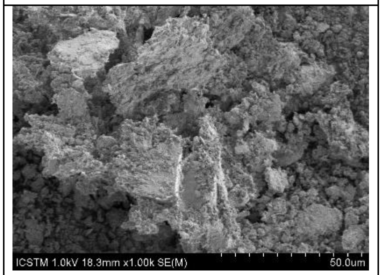
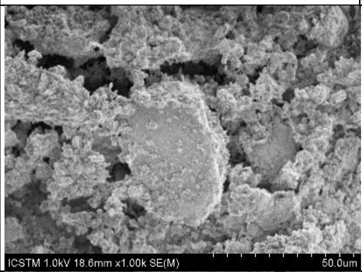
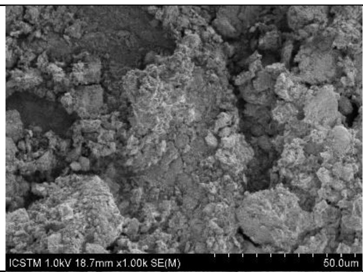
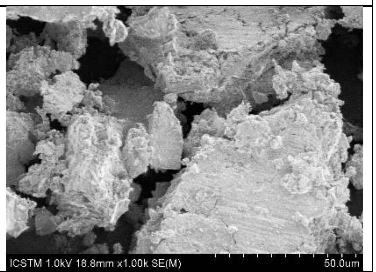
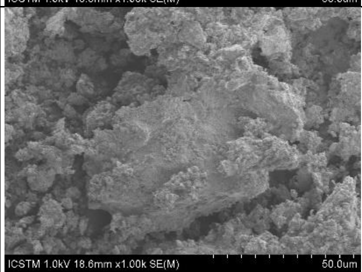
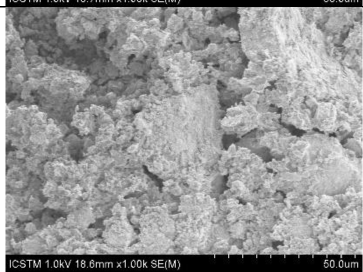
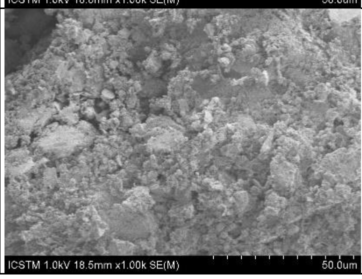
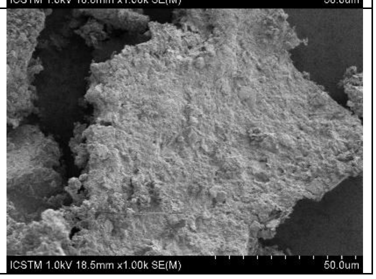
3.2. SCANNING ELECTRON MICROSCOPY COUPLED WITH ENERGY DISPERSIVE SPECTROMETRY (SEM-EDS)

The ceramic samples studied by SEM-EDS were taken both on the edge of the ceramic fragments, on their background, from the red engobe on the surface, and from the black layer with which they were decorated (Table 2).

Table 2. Samples morphology using SEM

Sample	Edge	Background	Pigment
1			

Sample	Edge	Background	Pigment
2			
3			
4			Without pigment
5			
6			
6a			 black

Sample	Edge	Background	Pigment
			 red
7			 black
			 red
8			
9			
10			

The profile of these artefacts is completed by highlighting the morphological characteristics of the samples through SEM images. The SEM morphology images obtained for the selected ceramic fragments show us a lamellar structure, for samples 2, 3, 4, 5, and 7, a lamellar structure with granular inclusions for samples 6a, 8, and 9, and a granular structure for samples 1, 6, and 10. Furthermore considering SEM results, the samples are mostly compact, without plant, animal, or geological impurities. In the case of the pictorial matter layer, the images show a predominantly lamellar structure for the black pigment. For the red pigment found on samples 7 and 6a, a lamellar structure can also be observed.

The EDS data (Table 3) revealed a similar composition of the ceramic samples, in all 11 samples a large amount of oxygen (O) is present because this element forms chemical bonds with the other elements detected during the analyses: silicon dioxide/quartz (SiO_2), aluminium oxide (Al_2O_3), an element that enters the composition of clays in the form of aluminosilicates and ferric oxide (Fe_2O_3). Smaller amounts of K, Ca, Ti, and Mg are followed as a percentage of Si since ceramics is a material based on different types of silicates, these being the majority compounds in the structure of this material.

At the chemical level, the presence of iron (Fe) was found in all analysed samples, the concentration values (<8.21%) being variable and generally low. For the red pigment, identified in two of the samples (6a and 7), a high percentage of Fe is observed (11.02% and 7.88%, respectively) due to the presence of Fe_2O_3 iron oxides. It should be noted that the recorded values, correlated with the visual observations on the materials, do not confirm that the intensity of the colour tone is closely related to the amount of Fe content. The black pigments are characterized by Fe content from 0% to 8.21% and high carbon content (i.e., 12.77-44.95%) which was a clue of charcoal usage for this colour. The back pigments from samples 9 and 10 presents low content of Mn, which can come from $(Mn_x,Fe_{1-x})_3O_4$ according to Uda et al. [23].

Regarding the presence of Al, it may be stated that higher values are found in all samples and range between the values of 4.11% - 10.81% (aluminosilicates being the basic constituents of clays). Potassium (K) is found in all the samples, but in low percentages (between 1.04% and 3.04%) by reaching into the composition of the clays in the form of potassium carbonate (K_2CO_3). The content of manganese (Mn) was recorded in samples 7, 9, and 10 (<1.33%). In the case of the last two, its presence may be attributed to the black pigment (MnO_2 – brown-black solid compound). Calcium (Ca) concentrations range from 0.84% to 5.18% – higher values are detected in the pigment of the samples. The EDS results showed a high content of silicon (Si), a chemical element that is included in the composition of silicates, the major compounds of clay: silicon dioxide (SiO_2), their values in the analysed samples being between 5.39% and 26.01%. In the case of pigment analyses, this element has lower values than those present in the paste, by 2 to 10%.

3.3. FOURIER-TRANSFORM INFRARED SPECTROSCOPY

The sample spectra collected by FTIR techniques were similar (Fig. 13), with few differences between edge, background, and pigments – because pigments were obtained by coloured clays. The bands observed in the FT-IR spectra at 995-1000 cm^{-1} are due to Si-O bonds (silicates, aluminosilicates, and quartz).

The presence of absorption bands at 794-795 cm^{-1}, 780-781 $cm^{-1,}$ and 695 cm^{-1} indicates the presence of quartz in all the studied samples while the bands in the range of 713-722 cm^{-1} are due to the presence of carbonates. The absorption band appearing at 668 cm^{-1} is due to the presence of anorthite. The presence of bands around the values of 583 cm^{-1} and 540 cm^{-1} is due to the presence of magnetite and hematite respectively (Fe-O bonds) (weakly observed in the spectra, but it was present in all samples). The presence of birch bark tar (2850, 2919, 1458 cm^{-1}) or bitumen (3500, 2950-2855, 1600, 1455, 1376 cm^{-1}) was not identified, as the studied samples did not present the specific absorption bands [20, 24].

Table 3. Elemental content of samples determined by SEM-EDS, expressed as wt.%±error.

Sample	Elements															
	C	O	F	Mg	Al	Si	P	K	Ca	Ti	Mn	Fe	Ba	Ir	Nb	Au
1-edge	4.90±0.10	49.97±0.26	nd	0.90±0.02	9.53±0.07	24.27±0.11	0.74±0.004	2.61±0.04	1.60±0.04	0.80±0.11	nd	5.60±0.32	nd	nd	nd	nd
1-background	5.88±0.10	45.37±0.24	nd	0.77±0.03	9.95±0.07	26.01±0.12	nd	2.74±0.08	1.43±0.08	0.80±0.06	nd	4.49±0.28	nd	2.56±0.14	nd	nd
1-pigment	13.94±0.13	45.08±0.24	nd	0.46±0.03	9.55±0.06	20.12±0.10	1.01±0.04	2.41±0.06	0.84±0.04	0.64±0.05	nd	5.95±0.27	nd	nd	nd	nd
2-edge	11.17±0.12	45.43±0.24	nd	0.45±0.03	9.77±0.06	18.55±0.10	3.15±0.05	2.17±0.04	1.67±0.04	0.77±0.06	nd	6.88±0.27	nd	nd	nd	nd
2-background	25.30±0.14	41.27±0.21	0.00±0.00	0.26±0.01	6.61±0.04	13.89±0.07	1.86±0.03	1.32±0.02	0.88±0.03	0.48±0.04	nd	8.13±0.15	nd	nd	nd	nd
2-pigment	33.45±0.16	36.53±0.19	0.36±0.36	0.36±0.02	4.63±0.03	13.78±0.06	nd	1.32±0.02	0.93±0.04	0.42±0.03	nd	8.21±1.74	nd	nd	nd	nd
3-edge	10.72±0.10	45.62±0.23	nd	0.66±0.02	9.63±0.05	21.69±0.09	1.49±0.04	1.95±0.05	1.47±0.03	0.81±0.05	nd	5.97±0.22	nd	nd	nd	nd
3-background	24.02±0.15	41.17±0.22	0.00±0.00	0.50±0.01	7.14±0.05	17.74±0.08	nd	1.43±0.03	0.87±0.03	0.53±0.05	nd	6.60±0.16	nd	nd	nd	nd
3-pigment	12.77±0.10	45.08±0.23	nd	0.69±0.02	7.89±0.05	19.28±0.08	1.78±0.04	1.95±0.05	4.60±0.08	0.70±0.04	nd	5.34±0.21	nd	nd	nd	nd
4-edge	7.57±0.08	46.72±0.23	nd	0.95±0.02	10.81±0.05	20.63±0.08	2.81±0.04	2.43±0.05	1.91±0.05	0.74±0.04	nd	5.42±0.20	nd	nd	nd	nd
4-background	28.11±0.16	40.74±0.21	0.00±0.00	0.64±0.02	5.92±0.04	14.72±0.07	nd	1.39±0.02	0.70±0.03	0.32±0.04	nd	6.86±0.15	nd	nd	nd	0.60±0.05
5-edge	9.77±0.08	44.87±0.22	nd	0.65±0.02	7.92±0.04	17.92±0.08	2.89±0.04	2.09±0.03	4.28±0.06	0.64±0.07	nd	8.97±0.20	nd	nd	nd	nd
5-background	34.30±0.18	37.57±0.21	1.78±0.74	0.32±0.01	5.43±0.04	12.26±0.06	nd	1.49±0.03	0.60±0.03	0.43±0.04	nd	5.82±2.37	nd	nd	nd	nd
5-pigment	36.70±0.19	39.65±0.22	nd	0.42±0.02	5.90±0.04	11.83±0.06	nd	1.70±0.06	2.67±0.08	nd	nd	0.40±0.16	nd	nd	0.72±0.06	nd
6-edge	19.34±0.14	44.15±0.23	0.00±0.00	0.60±0.02	6.72±0.05	20.51±0.09	nd	1.63±0.03	1.38±0.06	0.42±0.04	nd	5.26±0.17	nd	nd	nd	nd
6-background	24.59±0.13	42.63±0.22	0.00±0.00	0.42±0.02	4.76±0.03	15.61±0.06	nd	1.75±0.04	5.18±0.06	0.42±0.06	nnd	4.64±0.13	nd	nd	nd	nd
6-pigment	25.87±0.14	40.45±0.22	0.77±0.73	0.51±0.02	5.63±0.04	15.56±0.07	nd	2.07±0.05	2.65±0.03	nd	nd	6.49±2.31	nd	nd	nd	nd
6a-edge	3.32±0.04	49.68±0.24	nd	0.74±0.02	10.61±0.05	24.35±0.09	nd	2.21±0.04	2.03±0.05	0.46±0.03	mnd	6.60±0.21	nd	nd	nd	nd
6a-background	17.28±0.12	43.53±0.22	0.05±0.05	0.52±0.02	7.10±0.05	20.32±0.08	nd	2.04±0.03	2.55±0.03	0.41±0.04	nd	5.74±0.20	nd	nd	nd	0.45±0.06
6a-red pigment	23.10±0.13	39.96±0.21	0.88±0.69	0.44±0.01	5.27±0.04	15.26±0.06	nd	1.20±0.04	2.07±0.05	0.39±0.06	nd	11.02±2.20	nd	nd	nd	0.43±0.05
6a-black pigment	26.62±0.14	40.65±0.21	0.00±0.00	0.48±0.02	5.01±0.04	14.43±0.06	nd	1.49±0.05	4.07±0.07	nd	nd	7.25±0.16	nd	nd	nd	nd
7a-edge	8.82±0.10	46.56±0.24	nd	0.93±0.03	9.03±0.06	20.92±0.09	1.60±0.04	2.66±0.06	2.98±0.04	0.63±0.09	nd	5.88±0.27	nd	nd	nd	nd
7a-background	11.40±0.12	42.36±0.25	nd	0.87±0.03	7.88±0.06	18.28±0.09	0.94±0.04	3.02±0.07	2.00±0.04	0.51±0.05	1.33±0.15	11.41±0.34	nd	nd	nd	nd
7a-red pigment	6.82±0.08	45.41±0.23	nd	1.06±0.02	9.34±0.05	21.54±0.09	nd	2.97±0.06	2.08±0.03	0.70±0.08	nd	7.88±0.24	nd	2.20±0.11	nd	nd
7a-black pigment	37.86±0.19	40.42±0.22	nd	0.51±0.02	4.73±0.04	11.11±0.06	nd	1.57±0.05	2.80±0.07	0.33±0.04	nd	0.26±0.17	nd	nd	nd	0.41±0.04
8-edge	17.97±0.13	42.52±0.22	0.00±0.00	0.61±0.03	8.70±0.06	16.33±0.09	2.11±0.04	2.05±0.03	1.63±0.04	0.67±0.09	nd	7.41±0.18	nd	nd	nd	nd
8-background	32.72±0.16	37.23±0.20	1.22±0.56	0.31±0.02	6.07±0.04	12.00±0.05	nd	1.40±0.04	0.94±0.02	0.48±0.06	nd	7.37±1.78	nd	nd	nd	0.27±0.05
8-pigment	37.37±0.18	41.55±0.23	nd	0.54±0.02	5.32±0.05	10.94±0.06	nd	1.57±0.06	2.44±0.08	nd	nd	0.26±0.19	nd	nd	nd	nd
9-edge	15.74±0.11	43.19±0.22	0.00±0.00	0.59±0.02	8.33±0.05	17.77±0.08	1.84±0.04	2.10±0.03	2.35±0.03	0.63±0.04	nd	7.45±0.16	nd	nd	nd	nd
9-background	10.99±0.09	44.74±0.22	nd	0.38±0.02	9.19±0.05	19.43±0.08	2.66±0.04	2.39±0.03	1.99±0.03	0.74±0.07	nd	7.48±0.21	nd	nd	nd	nd
9-pigment	38.35±0.18	39.28±0.20	0.00±0.00	0.38±0.01	6.29±0.04	5.39±0.04	4.43±0.04	1.04±0.02	3.34±0.05	0.21±0.04	0.60±0.09	0.00±0.00	0.71±0.11	nd	nd	nd
10-edge	16.09±0.11	43.90±0.22	0.00±0.00	0.72±0.01	7.49±0.05	18.21±0.08	1.07±0.03	2.05±0.05	2.45±0.03	0.62±0.08	nd	7.41±0.15	nd	nd	nd	nd
10-background	19.47±0.13	42.39±0.23	0.19±0.07	0.63±0.02	6.96±0.05	20.10±0.09	nd	3.04±0.04	1.49±0.04	0.43±0.04	nd	4.22±0.22	nd	nd	nd	1.09±0.07
10-pigment	44.95±0.21	33.52±0.19	nd	0.32±0.02	4.11±0.03	9.72±0.05	nd	1.46±0.05	1.68±0.03	0.25±0.04	0.98±0.11	3.00±0.14	nd	nd	nd	nd

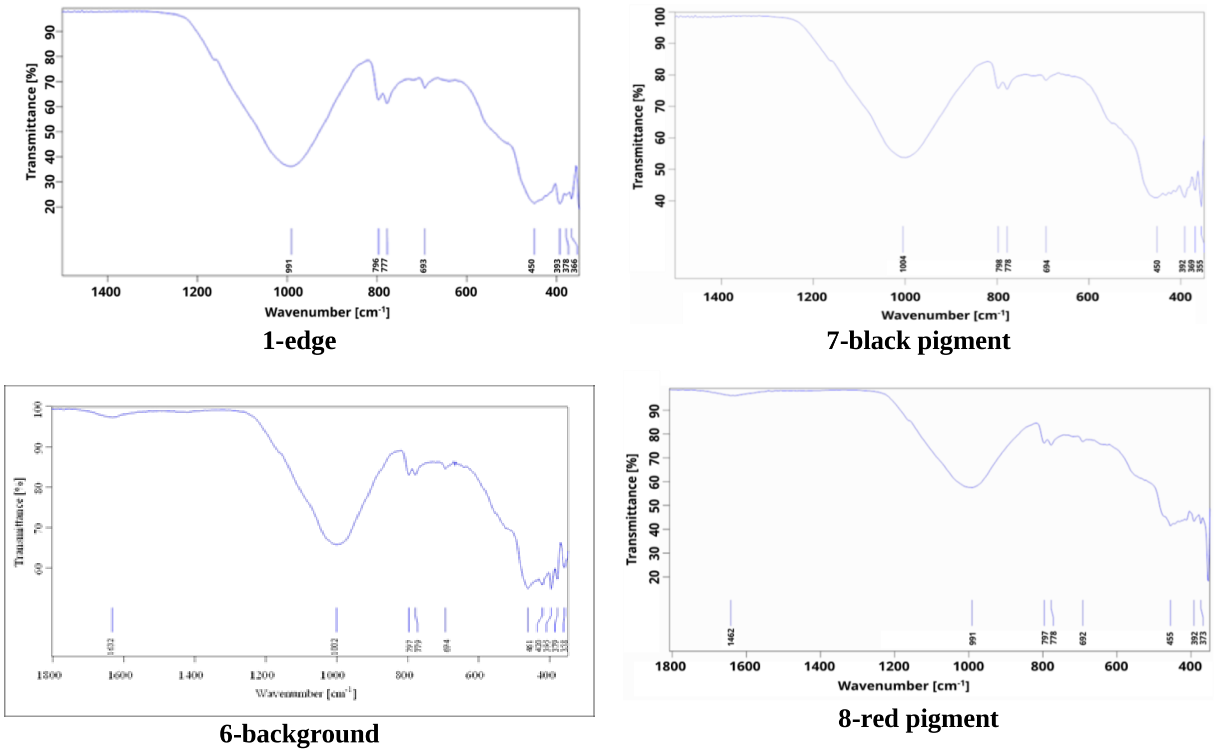


Figure 13. FTIR spectra of some selected sub-samples.

3.4. FIRING TEMPERATURE

The firing temperature of ceramic samples is identified based on the presence or absence of certain mineral phases in the studied samples. Quartz and feldspar mineral groups are stable even at high temperatures and therefore cannot be considered for estimating firing temperature conditions (Table 4). The presence of kaolinite in the samples suggests that the firing temperature was not sufficient to complete the decomposition of these minerals, indicating that firing did not exceed 650°C.

Table 4. Determination of the firing temperature

Sample	Clay type	Vitrification stage	Estimated temperature-vitrification (SEM)	875 cm^{-1} band	535 cm^{-1} band	Estimated temperature (FTIR)	Firing temperature
1	C	Initiated	800-850°C	No	Yes	>600°C	800-850°C
2	C	Initiated	800-850°C	Yes	Yes	>800°C	800-850°C
3	C	Initiated	800-850°C	Yes	Yes	>800°C	800-850°C
4	C	Initiated	800-850°C	Yes	Yes	>800°C	800-850°C
5	C	Uninitiated	<800°C	No	Yes	>600°C	600-800°C
6	C	Initiated	800-850°C	No	Yes	>600°C	800-850°C
6a	C	Uninitiated	<800°C	No	Yes	>600°C	600-800°C
7	C	Uninitiated	<800°C	No	Yes	>600°C	600-800°C
8	C	Uninitiated	<800°C	No	Yes	>600°C	600-800°C
9	C	Uninitiated	<800°C	No	Yes	>600°C	600-800°C
10	C	Initiated	800-850°C	No	Yes	>600°C	800-850°C

The presence of calcite indicates that it has not been decomposed and the firing temperature of the sample is below 850°C. If calcium carbonate is present (875 cm^{-1} corresponding to CO_3^{2-}) the firing temperature is higher than 800°C. The presence of hematite (535 cm^{-1} corresponding to the Fe-O bond) in the ceramic samples indicates that they were fired in an oxidizing atmosphere at temperatures higher than 600°C.

3.5. ELEMENTAL CONTENT OF CLAYS

The clay samples show the major components as SiO_2, Al_2O_3, Fe_2O_3, and K_2O according to data in Table 5. In the firing process, these clays are transformed in slightly reddish ceramic due to the presence of significant content of iron (~5%). The minor components of the analysed clay samples are TiO_2, MgO, CaO, and P_2O_5. The elemental contents were similar for all five samples, with just a few variations.

Table 5. Elemental content of clay samples determined by WD-XRF.

Elements (line) [wt.%]	→Oxide	Samples				
		C1	**C2**	**C3**	**C4**	**C5**
Mg (Kα)	MgO	0.67	0.72	0.69	0.90	0.93
Al (Kα)	Al_2O_3	8.54	9.16	9.28	10.48	10.38
Si (Kα)	SiO_2	32.19	32.27	31.96	30.46	29.28
P (Kα)	P_2O_5	0.11	0.07	0.20	0.19	0.43
K (Kα)	K_2O	2.41	2.31	2.37	2.43	1.01
Ca (Kα)	CaO	0.53	0.35	0.71	0.71	0.60
Ti (Kα)	TiO_2	0.80	0.68	0.72	0.73	0.71
Fe (Kα)	Fe_2O_3	5.60	4.52	4.27	4.85	5.86
Other minor elements		S, Mn, Zn	Na, S, Cl, Cr, Mn	Na, S, Mn, Zn	Na, S, Cl, Mn	Na, S, Cl, Mn, Zn

The main element of the clays, silicon, recorded values between 29.28 and 32.27%. The other major components: aluminium ranges from 8.54 to 10.48%, while iron ranges from 4.27 to 5.86%. The magnesium content was in the range of 0.67-0.93%, calcium was in the range of 0.35-0.71%, and titanium was in the range of 0.68-0.80%. Potassium and phosphorous were recorded in value between 1.01 and 2.43%, and 0.07 and 0.43%, respectively. The elemental contents were similar for all five samples with just a few variations and the obtained data were used in the next subsection.

3.6. DATA ANALYSIS

To establish the potential clay source for the ceramic fragments, the hierarchical clustering method was used and a dendrogram using Average Linkage (between Groups) was generated (Fig. 15). This method allows identifying the similarity between ceramic fragments and clay samples.

Fig. 15 shows two ceramic clusters (cluster 1: ceramic samples 2, 5, 8, 9, and 10; cluster 2: ceramic samples: 1, 3, 4, 6, 6a, and 7) and one clay cluster (all clay samples) were identified. At the same time, strong similarities between C1-C3 and C4-C5 were observed.

Regarding the ceramic samples, strong similarities between samples 8-10 and samples 3, 4, and 7 were observed. This fact can lead to the conclusion that these ceramic fragments were made from the same material.

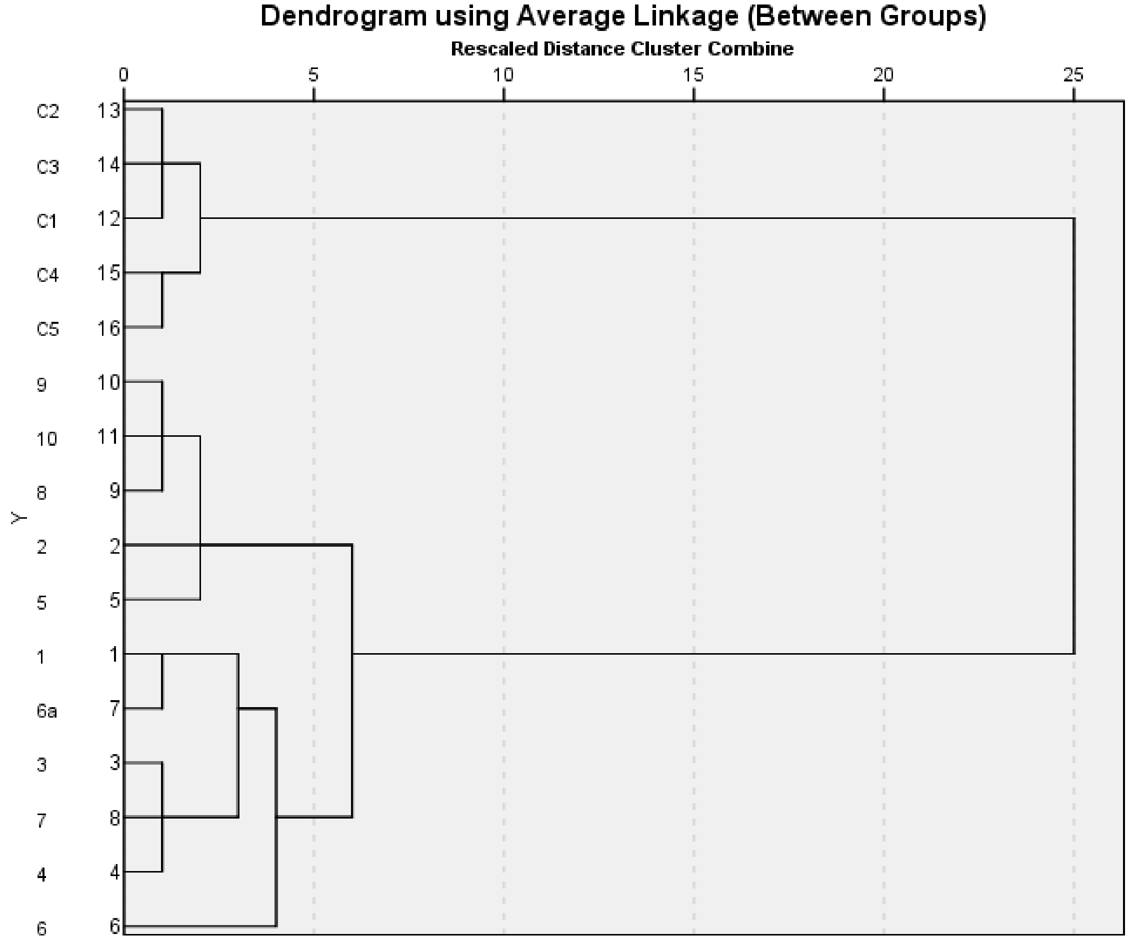


Figure 15. The Hierarchical Cluster Analysis (Dendrogram) obtained from the elemental content of the analysed samples (ceramic fragments and clays).

However, taking into account the elemental content and hierarchical cluster analysis it can be assumed that all analysed ceramic samples were made locally – using clays from / or around the settlement. The clay samples were collected not far from the archaeological site due to the fact that the area is surrounded in the present time by an artificial lake and the forest.

4. CONCLUSIONS

The archaeometric results obtained on the 11 samples studied confirm that the pottery from different contexts do not show major differences either in terms of the composition of the paste, the manufacturing process, or the method of decoration. Since there were no distinct absorption bands in the examined samples, bitumen or birch bark tar could not be recognised in the black pigment sub-samples, but a high carbon content was observed, highlighting charcoal usage.

However, for a better interpretation, statistical analysis (cluster analysis) was performed to identify the similarities between ceramic and clay samples. These results do not constitute the definitive conclusion of the study but must be supplemented with the results of future archaeometric analyses applied to a larger number of samples. Expanding the research, by adding a new batch of ceramic fragments and clay samples, would allow a more precise delimitation of the chemical profile of the ceramic artefacts, the firing (firing) temperature, and the technological process of their manufacture.

Acknowledgements: *For Anamaria Carstea (Elekes) and Mihai Gligor this work was supported by a doctoral grant financed by "1 Decembrie 1918" University of Alba Iulia. For Valahia University of Targoviste co-authors this work was funded by the project CNFIS-FDI-2024-F-0002 Sustainable Development of Research and Innovation Activities – Component in Increasing Institutional Capacity (Sustain-R&I), financed by the Romanian Ministry of Education.*

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