ATR-FTIR and SEM-EDS Analyses of Lumea Noua Painted Pottery from Alba Iulia-*Lumea Noua* Neolithic Site

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This study aims to investigatea possible link between the painted pottery from the Alba Iulia-Lumea Nouã settlement and the potential clay sources identified in the proximity of the archaeological site. Sixteen samples (clay and pottery) were collected and afterwards analyzed through two analytical techniques (attenuated total reflection - Fourier transform infrared spectrometry and scanning electron microscopy coupled with energy dispersive spectrometry). The recorded data show similarities for both techniques and give preliminary information regarding the clay composition used for pottery manufacturing in middle Neolithic. Cluster analysis using Average Linkage method correlated the clay sources with the analyzed painted pottery.

Keywords: Neolithic, painted pottery, clay, ATR-FTIR, SEM-EDS

The physical and chemical composition of archaeological ceramics is significantly altered by the life cycle of the artifacts, starting with the production process and use to the post-depositional modification. As a wide range of interdisciplinary studies have already shown, in the study of ancient ceramic technology, the traditional archaeological approach based on typology, pattern ornamentation, and context analysis can certainly benefit from the cooperation with the material sciences [1-7].

In the Transilvanian Neolithic, the Lumea Noua communities are considered the creators of an elegant painted pottery. The eponym site is Alba Iulia-*LumeaNouã*, discovered by chance in 1942, while carrying out some town planning works. The Lumea Nouã settlement is located in the northeastern part of Alba Iulia city (Transilvania, Romania), and represents one of the most important Neolithic sites from the middle Mures River area [10]. The main characteristic of LumeaNoua pottery is represented by the painted decoration, applied before firing, with geometrical motifs [8-13]. From a stratigraphic point of view, the Lumea Noua pottery emerged in association with incised pottery and pedestal bowls belonging to the Vinea B culture [10]. The archaeological research revealed the presence of this distinctive painted pottery category in the following Transylvanian Neolithic sites: Alba Iulia-*Lumea Noua*, Tartaria, Limba, Cheile Turzii, Doh, ªimleu Silvaniei, Porþ [8-13]. From the chronological point of view, the Neolithic communities who have produced this type of pottery are included in the time frame 5200-4900 BC [8, 10]. The origins of this type of painted pottery are still controversial. Some scholars sustain the existence of one large culture corresponding to the middle and late Neolithic, called Zau. In this respect, the discoveries of Lumea Nouã painted pottery in the Mures valley settlements are considered imports [11, 12].

Until now, the Lumea Nouã pottery from the eponym site was analyzed using various analytical techniques such as: X-Ray Fluorescence (XRF), X-Ray Powder Diffraction (XRPD), optical microscopy (OM) and scanning electron microscopy (SEM). These methods were used to obtain complementary results regarding morphological and compositional features of the samples. There were highlighted issues concerning the pottery technology related to raw material and firing temperature [14-16].

In order to establish some correlations between clay source and pottery composition, two analytical techniques (attenuated total reflection - Fourier transform infrared spectrometry and scanning electron microscopy coupled with energy dispersive spectrometry) have been used.

Experimental part

Materials and methods

Four clay samples (i.e. C3, C4, C5 and C6) were collected starting from the average depth of 1 m below the present soil, the same depth reached by the Neolithic structures found during the archaeological excavations. The hypothesis that some of these could have functioned, at their first use, as clay pits for raw material extraction was not excluded. Other two samples (i.e. C1 and C2) were collected from the surroundings (~ 1.5 km Northeast and ~ 6.0 km South, respectively, from the settlement) and represent a possible raw material sources available to the Neolithic community from Lumea Noua. The clay samples are described in table 1.

The painted pottery samples from Lumea Noua archaeological site (fig. 1 and table 2) were excavated between 2005 and 2014. The clay samples were collected from the Lumea Noua and Limba archaeological sites or proximity, from accessible outcrops, from 2014 to 2016. The clay samples were identified on several properties: appearance, plasticity, density, color, and absence of vegetal, animal and geological impurities.

Inorganic and organic groups of chemical compounds was performed by Attenuated Total Reflection - Fourier Transform Infrared spectrometry (ATR-FTIR) [17-21] using Vertex 80v spectrometer (Bruker), which adsorbs infrared radiation in 600-8000 cm^{-1} range, with high spectral

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Sample code	Sample location*	Sample description
C1	Bărăbanț, Alba Iulia (Ampoi River)	Red-brown with coarse-grain sand
C2	Limba, Ciugud Village, Alba County	Yellow-brown
C3	ALN.15.S	Brown with fine-grain sand
C4	ALN.15.S	Brown
C5	ALN.16.S	Yellow-brown
C6	ALN.14.IV	Dark-brown

Table 1
CLAY SAMPLES DESCRIPTION

** ALN-Alba Iulia-Lumea Noua; 15 - year of excavation (2015); IV/S-the number of the Trench (rescue excavation) / Systematic excavation (e.g.)*

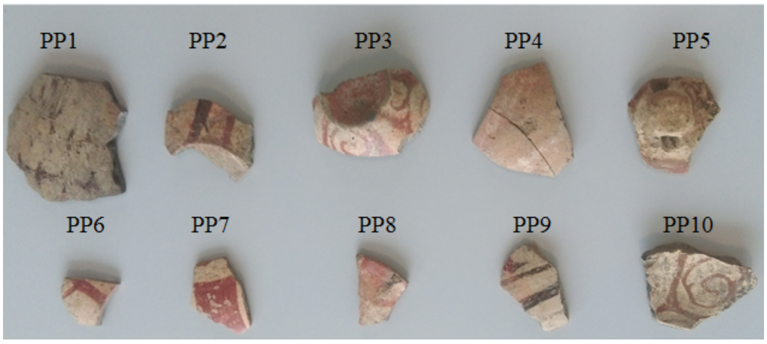

Fig. 1. Lumea Noua painted pottery samples

Sample code	Archaeological context*	Physical and archaeological characteristics
PP1	ALN.11.III; □ A; ▼ 2.10 - 2.90 m; Cx. B1.	Vessel fragment, semi-fine texture, painted decoration
PP2	ALN.12.S; □ B; ▼ 0.85 m; Cx. 004.	Vessel bottom fragment, fine texture, slip and painted decoration;
PP3	ALN.11.I; □ C; ▼ 2.10 - 2.50 m; Cx. C2.	Vessel bottom, semi-fine texture, slip and painted decoration;
PP4	ALN.14.S; □ D; ▼ 1.25 - 1.70 m; Cx. 013.	Vessel rim, fine texture, slip decoration;
PP5	ALN.14.I; □ B; ▼ 1.20 - 1.40 m; Cx. C1.	Vessel fragment, semi-fine texture, slip and painted decoration
PP6	ALN.08.I; □ A; ▼ 0.60 - 0.80 m; Cx. L1.	Vessel fragment, fine texture, slip and painted decoration
PP7	ALN.05.I; □ D; ▼ 0.80 m; Cx. L1.	Vessel rim, fine texture, slip and painted decoration

Table 2
PAINTED POTTERY SAMPLES - LOCATION AND DESCRIPTION

PP8	ALN.14.S; □ D; ▼ 2.36 m; Cx. 006.	Vessel rim, fine texture, slip and painted decoration
PP9	ALN.08.I; □ D; ▼ 1.30 - 1.60 m; Cx G8.	Vessel fragment, semi-fine texture, slip and painted decoration
PP10	ALN.14.S; □ D; ▼ 2.35 m; Cx. 006.	Vessel fragment, semi-fine texture, slip and painted decoration

** ALN-Alba Iulia-Lumea Nouã; 11 - year of excavation (2011); I/S-the number of the Trench (rescue excavation) / Systematic excavation (e.g.); ¡% - square; ¼%- depth; Cx. - feature*

resolution (0.2 cm^{-1}), good accuracy 0.1 %T and equipped with diamond ATR crystal accessory.

Clay and pottery samples were investigated using SU-70 SEM (Hitachi) coupled with UltraDry EDS (Thermo Scientific) [22]. This equipment operates in ultra-high vacuum (10^{-8} Pa) and the electron gun is ZrO/W Shottky type. For morphology investigation the acceleration voltage (Vacc) was set at 1 kV for clay and 20 kV for pottery. The elemental analysis was performed at 15 kV for clay and 25 kV for pottery. SU-70 present an ultra-high resolution (1 nm / 15 kV and 1.6 nm / 1 kV) and provide high quality images in SEM magnification range (30x-800000x). UltraDry EDS allow qualitative and quantitative analysis from Be (Z=4) to Pu (94) on point, rectangle, line etc. and offers elemental distribution maps [23].

Results and discussions

The FTIR spectral data (table 3) of the MIR-region of clay samples show only little variation and generally the highest absorbance (strong signal) at wavenumbers between 990 and 1002 cm^{-1}. This region of the spectrum as well as regions between 644 and 692 cm^{-1} and centered at 800 cm^{-1} can be attributed to absorbance caused by SiO or organic material. In C3 – C6 clay samples, organic compounds are only minor constituents, whilst material containing SiO was dominant. Within the recorded spectra of all six clay samples presented a weak absorbance centered on 3619-3698 cm^{-1} which can be mostly attributed to hydroxyl vibrations. Molecules present in organic substances show absorbance in a large part of the whole MIR-region. Absorbance around 1600 cm^{-1} region is characteristic for CO bonds, such as those originating from carbonates or carboxyl-groups of humic substances. Also, the values presented in all clay samples, around 1430 cm^{-1} can be attributed to C-H aliphatic group from humic acids.

FTIR data (table 4) of painted pottery samples provide the first clues on the clay sources used in manufacturing process. Thus, the PP1 sample is the only one which presents a different FTIR spectrum comparative with all other obtained spectra. Also, the medium peak at 2360 cm^{-1}, was not found in any other clay or pottery samples, and can be attributed to the OH_{st}, NH_{st}, SH_{st} or even SiH_{st} groups. According with the spectral data for both category of samples (clay and pottery) presented in tables 3 and 4, it can be concluded that the chemical composition is quite similar (hydroxyl, carbonyl, aliphatic and SiO groups). FTIR spectral data are in well compliance with EDS and statistical results.

Table 3
INFRARED SPECTRAL DATA OF CLAY SAMPLES

Clay sample	ATR-FTIR spectrometry	
	Wavenumber [cm^{-1}]	Relative Intensity*
C1	3696/3619/1638/1435/1163/994/911/874/832/796/777/754/692/	w/w/w/w/w/s/w/w/w/w/w/w/w/
C2	3696/3619/1633/1429/990/912/876/796/777/692/	w/w/w/w/s/w/w/w/w/w/
C3	3698/3620/1798/1637/1429/1162/1002/873/796/777/713/693/646/	w/w/w/w/s/w/s/s/w/w/w/w/w/
C4	3695/3619/1797/1640/1424/1162/1000/916/872/796/777/713/693/644/	w/w/w/w/s/m/s/w/s/w/w/w/w/w
C5	3696/3619/1635/1431/1162/995/912/796/777/692/642/	w/w/w/w/w/s/w/w/w/w/w/
C6	3697/3619/1634/1432/989/912/795/777/692/645/	w/w/w/w/s/w/w/w/w/w/

* *s-strong; m-medium; w-weak.*

Painted pottery sample	ATR-FTIR spectrometry	
	Wavenumber [cm^{-1}]	Relative Intensity
PP1	2360/999/796/777/694/657/648/	m/s/w/w/w/w/w
PP2	1548/1478/1462/1441/1427/992/874/795/777/712/694/	w/w/w/w/w/s/w/w/w/w/w/
PP3	1640/1002/796/777/722/693/646/	w/s/w/w/w/w/w/
PP4	1432/986/875/796/776/712/693/	w/s/w/w/w/w/w/
PP5	1638/1431/1005/797/778/721/693/	w/w/s/w/w/w/w/
PP6	1632/995/797/778/722/694/647/	w/s/w/w/w/w/w/
PP7	1632/1441/998/795/777/715/693/643/	w/w/s/w/w/w/w/w/
PP8	992/796/778/717/693/645/	s/w/w/w/w/w/
PP9	1426/996/987/875/796/777/712/694/647/	w/s/w/w/w/w/w/w/w/
PP10	1452/984/876/795/776/714/693/	w/s/w/w/w/w/w/

* *s-strong; m-medium; w-weak.*

Table 4
INFRARED SPECTRAL DATA OF PAINTED POTTERY SAMPLES

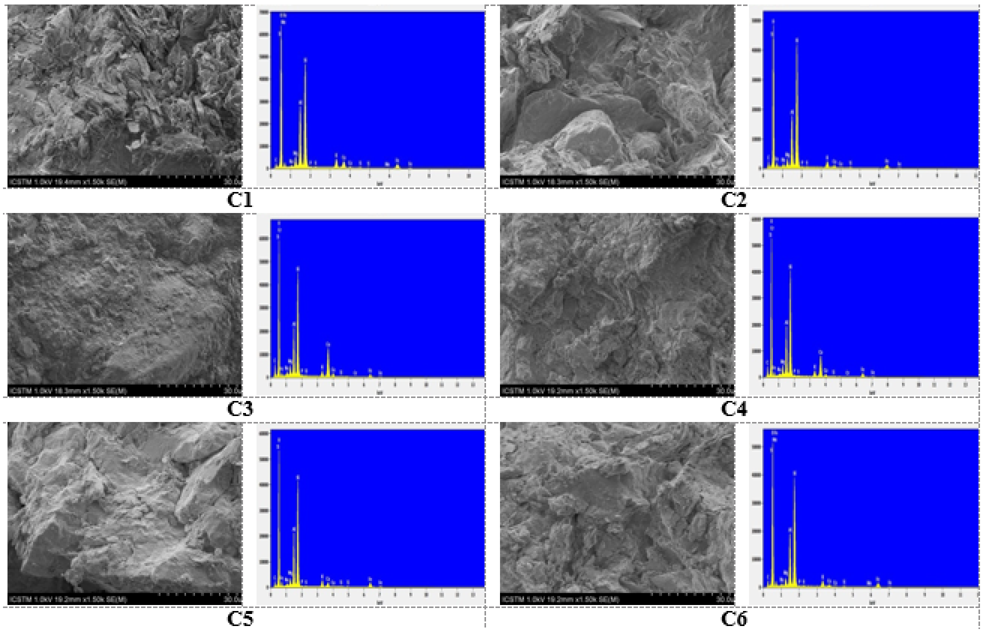

Fig. 2. SEM-EDS analysis of clay samples

Table 5
ELEMENTAL CONTENT OF CLAY AND PAINTED POTTERY SAMPLES

Samples		Elemental weight [%]										
		C	O	Na	Mg	Al	Si	P	K	Ca	Ti	Fe
Clay	C 1	4.87 ±0.09	52.95 ±0.27	0.39 ±0.02	1.61 ±0.02	9.35 ±0.05	18.51 ±0.07	0.14 ±0.01	2.69 ±0.02	2.52 ±0.03	0.47 ±0.02	6.23 ±0.09
	C 2	7.35 ±0.12	53.19 ±0.27	0.76 ±0.02	1.26 ±0.02	7.73 ±0.04	21.24 ±0.08	0.16 ±0.02	1.94 ±0.03	0.76 ±0.03	0.35 ±0.02	5.09 ±0.10
	C 3	10.19 ±0.08	54.90 ±0.26	0.54 ±0.02	1.23 ±0.02	5.78 ±0.03	13.89 ±0.05	0.21 ±0.02	1.17 ±0.02	8.30 ±0.05	0.31 ±0.02	3.13 ±0.07
	C 4	9.47 ±0.08	51.40 ±0.49	0.36 ±0.01	1.44 ±0.02	6.83 ±0.04	16.38 ±0.06	0.17 ±0.01	1.56 ±0.03	7.01 ±0.05	0.32 ±0.03	4.82 ±0.09
	C 5	6.32 ±0.08	52.66 ±0.26	0.65 ±0.02	1.24 ±0.02	8.49 ±0.05	19.41 ±0.07	0.18 ±0.01	1.94 ±0.03	1.55 ±0.03	0.45 ±0.02	6.97 ±0.11
	C 6	6.71 ±0.08	53.79 ±0.27	0.53 ±0.02	1.24 ±0.02	8.24 ±0.05	19.51 ±0.08	0.16 ±0.01	1.99 ±0.02	0.79 ±0.03	0.47 ±0.03	6.17 ±0.11
Painted pottery	PP1	5.29 ±0.17	43.36 ±3.06	0.59 ±0.02	1.27 ±0.03	9.24 ±0.05	26.32 ±0.10	0.25 ±0.02	3.27 ±0.03	1.79 ±0.03	0.56 ±0.02	7.75 ±0.07
	PP2	5.53±0. 13	54.19 ±0.28	0.60 ±0.02	1.05 ±0.02	7.63 ±0.04	20.77 ±0.08	0.22 ±0.02	2.10 ±0.02	3.34 ±0.03	0.35 ±0.02	4.11 ±0.04
	PP3	9.27 ±0.15	52.72 ±0.28	0.60 ±0.03	1.10 ±0.02	7.40 ±0.04	21.47 ±0.08	0.19 ±0.02	1.82 ±0.02	1.02 ±0.02	0.47 ±0.02	3.89 ±0.04
	PP4	9.58 ±0.14	52.40 ±0.28	0.59 ±0.02	0.90 ±0.02	6.76 ±0.04	18.51 ±0.07	0.19 ±0.01	1.75 ±0.02	5.33 ±0.03	0.35 ±0.02	3.56 ±0.04
	PP5	5.64 ±0.13	57.20 ±0.29	0.51 ±0.02	1.09 ±0.02	6.77 ±0.04	21.10 ±0.08	0.23 ±0.02	1.26 ±0.02	1.39 ±0.02	0.34 ±0.01	4.48 ±0.04
	PP6	3.66 ±0.17	49.66 ±0.26	0.68 ±0.03	1.21 ±0.03	9.63 ±0.05	22.37 ±0.08	0.21 ±0.01	2.53 ±0.02	1.28 ±0.02	0.57 ±0.02	8.02 ±0.06
	PP7	11.35 ±0.15	51.89 ±0.27	0.74 ±0.02	1.47 ±0.02	7.51 ±0.04	18.63 ±0.07	0.12 ±0.01	1.93 ±0.02	1.33 ±0.02	0.41 ±0.01	4.62 ±0.04
	PP8	10.23 ±0.19	51.96 ±0.27	0.97 ±0.03	1.06 ±0.02	7.57 ±0.04	20.02 ±0.07	0.13 ±0.01	1.97 ±0.02	1.34 ±0.02	0.38 ±0.02	4.19 ±0.04
	PP9	4.70 ±0.11	50.20 ±0.26	0.42 ±0.02	1.00 ±0.02	7.53 ±0.04	20.38 ±0.08	0.18 ±0.02	2.62 ±0.03	6.11 ±0.04	0.60 ±0.01	6.06 ±0.05
	PP10	3.63 ±0.22	52.92 ±0.27	0.81 ±0.03	1.43 ±0.02	7.64 ±0.04	21.16 ±0.08	0.32 ±0.02	1.85 ±0.02	4.18 ±0.03	0.51 ±0.02	5.26 ±0.05

** In some samples were identify Mn, Cr, S and Cl, but the content was lower than 0.01%.*

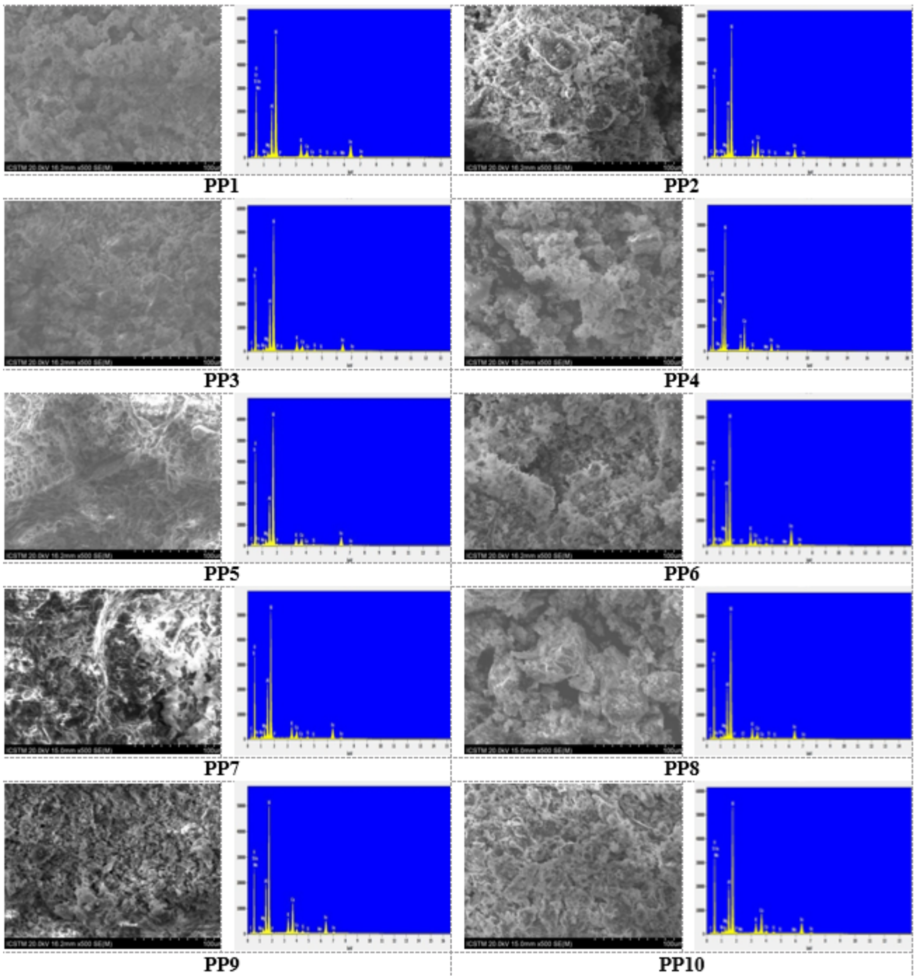

Fig. 3. SEM-EDS analysis of painted pottery samples

SEM images (fig. 2) obtained on clay samples concluded that: C1 present a lamellar structure, within C2 and C6 shown a granular structure with lamellar inclusions as well; granular structure with coarse inclusions was found on C3, C4 and C5samples. All samples are clean, without vegetal, animal and geological impurities. EDS results (fig. 2 and table 5) have shown that Si (13.89-21.24 %), Al (5.78-9.35 %) and Fe (3.13-6.97 %) are the major constituents of clay samples, but also have been recorded elements as: Mg (1.23-1.61 %), Ca (0.76-8.30 %), Na (0.36-0.76 %), Ti (0.31-0.47 %), and K (1.17-2.69 %).

Considering the clay grains with rounding edges, observed by SEM images on painted pottery (fig. 3), it was observed that samples have not reached the vitrification stage. Also, these samples are low refractory and it is possible to be fired in oxidizing atmosphere (at T < 800 °C), according to Velraj et al [24]. From EDS data (fig. 3 and table 5) can be observed that major constituents are Si (18.51-26.32 %), Al (6.76-9.63 %) and Fe (3.56-8.02 %) and the minor elementsare Ca (1.02-6.11 %), Mg (0.90-1.47 %), K (1.26-3.27 %), Na (0.42-0.97 %), and Ti (0.34-0.60 %).

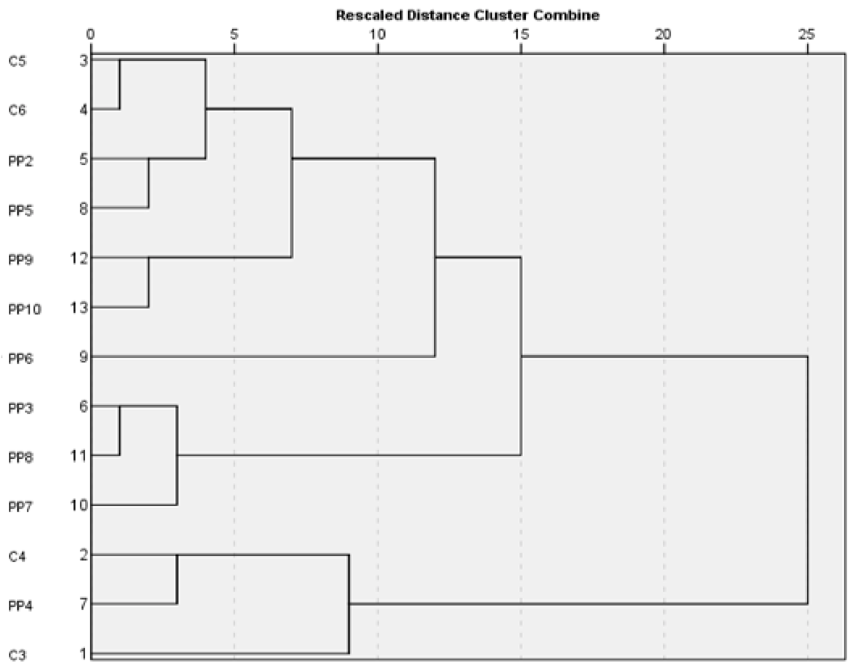

Fig. 4. Dendrogram of clay and Lumea Noua painted pottery samples obtained from cluster analysis using Average Linkage method

Cluster analysis of clay and painted pottery samples

Cluster analysis is used, usually, to identify groups of objects with similar characteristics (i.e. chemical profile). In this paper, the cluster analysis was used to identify the clay source underlying painted pottery samples. Using the elemental compositions of clay and painted pottery samples, determined by EDS, the dendrogram through Average Linkage method (fig. 4) was achieved.

The different content was expected to group the analyzed samples in multiple groups. The cluster analysis and the minor elements content have the role to provide the provenance and the obtaining technology of archaeological samples. The dendrogram reveals that: PP4 could have been obtained from clay samples C3 or C4; PP2, PP3, PP5-PP10 could have been obtained from clay samples C5 or C6. The absence of correlation between PP1 sample and clay samples strengthens the hypothesis that PP1 may have been brought from other locations or obtained through mixing some existent soils in the area during the ordinary manufacturing process of ceramics.

Conclusions

Despite the limited numbers of samples, the archaeometric results indicate that there is a obvious link between the analyzed Lumea Noua painted pottery and two of the selected clay sources from Alba Iulia-*Lumea Noua* archaeological site. Some of the local clay sources could have been considered the suitable raw material used for the Lumea Noua pottery type production. However, further determinations performed on a larger set of painted ceramic samples are needed in order to confirm this state of the research.

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