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In memoriam prof. dr. Liviu Oniciu

ARCHAEOMETRIC CHARACTERISATION OF THE NEOLITHIC POTTERY DISCOVERED AT ALBA IULIA-*LUMEA NOUA* ARCHAEOLOGICAL SITE (ROMANIA)

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ABSTRACT. A set of 21 Neolithic painted pottery fragments belonging to the Lumea Noua culture (5th millennium B.C.) and discovered at Alba Iulia-*Lumea Noua* (Romania) settlement were investigated in order to elucidate some aspects concerning the manufacturing technique used for the ancient pottery production. The chemical, microstructural and petrographic features of the ceramic bodies were determined by X-ray fluorescence, X-ray diffraction and optical microscopy. The preliminary obtained data were used to make inferences concerning the pottery's technology in terms of type of raw clays and firing temperatures.

Keywords: *pottery, Neolithic, Romania, X-ray fluorescence, X-ray diffraction, optical microscopy*

INTRODUCTION

Pottery analysis plays an important and multi-faceted role in the interpretation of an archaeological site, being the fundamental tool used by archaeologists for dating sites or for determining trading patterns, cultural exchanges between peoples and social structures.

In the last decades, an impressive range of analytical techniques (*i.e.* X-ray fluorescence, neutron activation analysis, SEM-EDS, X-ray diffraction, etc.) have been exploited with considerable success to produce detailed "fingerprints" that can be used to ascertain the provenance and to reconstruct the technologies used in the manufacture of the ancient artefacts [1].

Contrary to other European regions, in Romania only very few investigations on prehistoric pottery have been made using modern techniques [2-3]. Consequently, in spite of the large quantities of ancient ceramic material collected from archaeological excavations, there are still many unknown aspects about the origin and production techniques of the prehistoric pottery discovered on the actual Romanian territory.

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In the last years, one of the most controversial issues of the Romanian archaeology was related to a Neolithic painted ceramic material belonging to the "Lumea Noua" culture (first half of the 5th Millennium B. C.). "Lumea Noua" pottery was found in relatively small quantities in few settlements (Alba Iulia-*Lumea Noua*, Limba, Tartaria, Zau de Campie, Cheile Turzii) from Transylvania and the painted decoration patterns show strong analogies with the ceramic finds from Slovakia (Bükk and Raškovce cultures) [4], Hungary (Esztár and Bükk cultures) [5] and Ukraine (Diakovo culture) [6], and North-Western of Romania (Piscolt group) [7].

The present study is part of a systematic archaeometric investigation on "Lumea Noua" pottery discovered at Alba Iulia-*Lumea Noua* settlement aiming at establishing its production technology in terms of the raw materials used, forming and firing procedures. The selected pottery samples were studied by X-ray fluorescence, X-ray diffraction and optical microscopy in order to obtain chemical, mineralogical and petrographic information.

RESULTS AND DISCUSSION

Thin-sections analysis (texture and mineralogy)

The observation of the thin-section of the samples under the polarizing microscope revealed that the 21 "Lumea Noua" potsherds display aplastic inclusions of various type, abundance and grain-size. Moreover, different types of relicts of micro-fossils (*i.e.* bioclasts, bivalve, algae and foraminifera) have been identified.

According to the absence or presence of the fossil relics, the "Lumea Noua" potteries have been grouped into two main "petrographic groups". Beside bioclasts, the abundance, type and size of aplastic inclusions are other parameters used to ascertain the groups.

Group 1 consists of 9 pottery samples (LN1 – LN 9) which do not enclose bioclasts in their ceramic body (Figure 1).

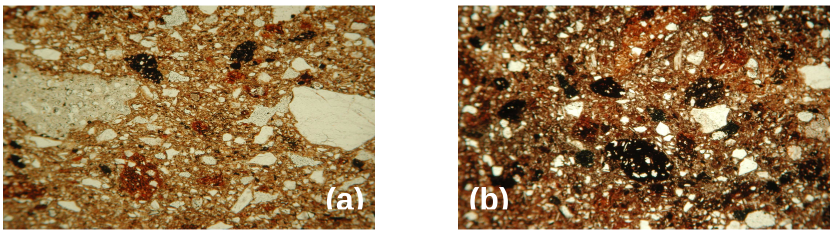

Figure 1. Thin-section of the ceramic bodies of the pottery samples belonging to group 1: (a) LN 1; (b) LN6 (40x; parallel nicol).

These samples are characterized by an inhomogeneous and mainly anisotropic matrix, which contains argillaceous rock fragments. The skeleton has a sandy texture; the aplastic inclusions are around 15-20% of the ceramic body. Their mineralogical composition is represented by quartz (mono- and polycrystalline), mica (biotite or muscovite), small amounts of K-feldspars and plagioclase.

Group 2 includes 12 samples (LN 10 - LN 21) which contain different types of relicts of fossils in their ceramic body (Figure 2).

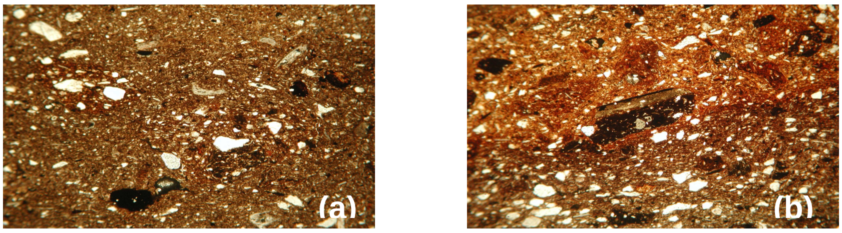

Figure 2. Thin-section of the ceramic bodies of the pottery samples belonging to the group 2: (a) LN 18; (b) LN19 (40x; parallel nicol)

The samples in group 2 have a semi-isotropic to isotropic groundmass, orange-yellow to reddish-brown in colour. Many samples have a sandwich-like structure from the colour point of view, which suggests that the firing atmosphere was not sufficiently oxidizing. A characteristic of the samples belonging to the group 2 is represented by the presence of a relatively high macro-porosity. The pores are rounded, have big dimensions and are seldom filled with secondary calcite. The rounded pores suggest that the artefacts were shaped by hands. The mineral composition of the temper is given by quartz (mono- and polycrystalline), micas, plagioclase, K-feldspars and rare and partially decomposed carbonatic rock fragments.

Under the polarizing microscope the white or light yellow slips observed on all “Lumea Noua” pottery appear as thin layers with thicknesses varying mostly between 100 and 120 μm. The thickness of the decoration layer varies between 10 and 20 μm.

Chemical composition of the ceramic bodies

The chemical composition of the ceramic bodies was determined by XRF analysis and the measured elements were Na, Mg, Al, Si, K, Ca, Ti, Fe, Mn and P expressed as oxide percentages (w/w). The P_2O_5 concentration exhibits values in a restricted range (0.18-0.50 %), except for samples LN 10 (0.95%) and LN 16 (1.37%), suggesting a possible post-depositional contamination with phosphorous during burial [8].

The IL values vary over a not very wide range, mainly between 1 and 3%, approximately. Only three samples show higher values, LN 1 (4.56%), LN 16 (6.63%) and LN 15 (6.57%), probably due to the fact that they were partially rehydrated during burial.

In order to make accurate comparisons between the chemical composition of different pottery and raw clays, the analytical data were normalised by excluding the IL and P_2O_5 values (Table 1). The silica content of the ceramic bodies is situated in the range of 61 to 73%, while the amount of alumina and iron oxide varies from 14.7 to 20% for Al_2O_3 and from 4.9 to 8% for Fe_2O_3. Most of the samples are characterized by a relatively low content of CaO (1.26 – 3.47%) and MgO (around 2%). In three samples (LN 2, LN 8, LN 11) the amount of CaO is around 4.8%, while sample LN 18 shows the highest concentration of calcium oxide (6.2%). All the samples present a low content of sodium (<1% Na_2O), while the concentration of potassium is higher and varies between 1.8 and 3.8% K_2O. The low contents in CaO are compatible with the scarcity of the calcareous micro-fossils in the ceramic paste.

Table 1.

Chemical composition of the "Lumea Noua" pottery samples and of the raw materials (wt% after normalization)

Sample		SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O
Group 1	LN 1	70.95	16.22	0.87	4.93	0.07	1.94	2.16	0.84	2.01
	LN 2	63.00	18.76	0.84	6.73	0.12	2.19	4.47	0.68	3.21
	LN 4	61.97	19.20	0.80	7.62	0.15	2.60	3.47	0.91	3.19
	LN 6	67.34	17.21	0.83	6.23	0.12	2.30	1.55	1.02	3.40
	LN 7	64.41	18.81	0.86	7.08	0.08	2.47	1.92	0.98	3.38
	LN 8	61.67	18.49	0.84	6.68	0.13	2.69	4.88	1.03	3.59
	LN 9	73.01	14.76	0.78	5.92	0.12	1.52	1.26	0.80	1.82
	Average	*66.05*	*17.64*	*0.85*	*6.46*	*0.11*	*2.25*	*2.81*	*0.89*	*2.94*
	st. dev.	*±4.51*	*±1.65*	*±0.04*	*±0.87*	*±0.03*	*±0.41*	*±1.45*	*±0.13*	*±0.72*
Group 2	LN 10	68.73	15.39	0.76	5.19	0.05	1.94	3.44	0.70	3.80
	LN 11	62.43	18.45	0.73	6.96	0.22	2.33	4.80	0.55	3.54
	LN 12	67.36	18.51	0.77	6.39	0.12	1.86	1.62	0.64	2.73
	LN 14	63.62	18.77	0.88	7.28	0.06	2.56	2.13	1.12	3.58
	LN 15	66.21	18.01	0.81	8.02	0.05	1.75	2.16	0.39	2.59
	LN 16	65.33	17.35	0.81	7.01	0.09	1.99	2.99	0.65	3.78
	LN 17	66.89	16.93	0.81	6.62	0.17	2.42	2.03	0.94	3.18
	LN 18	62.69	18.02	0.81	5.75	0.08	2.26	6.22	0.71	3.45
	LN 19	66.19	18.56	0.86	6.13	0.06	2.29	1.93	0.80	3.16
	LN 20	63.50	19.50	0.79	6.48	0.06	2.15	3.36	0.59	3.57
	LN 21	63.11	19.90	0.82	7.37	0.13	2.19	2.45	0.85	3.17
	Average	*65.10*	*18.13*	*0.80*	*6.66*	*0.10*	*2.16*	*3.01*	*0.72*	*3.32*
	st. dev.	*±2.14*	*±1.24*	*±0.04*	*±0.80*	*±0.06*	*±0.25*	*±1.40*	*±0.20*	*±0.40*
Clay	LC	62.40	20.63	0.99	6.40	0.08	2.97	1.92	1.48	3.13
	BC	66.10	16.61	0.62	4.47	0.09	1.93	7.06	0.75	2.38
	RC	66.52	23.13	1.24	7.36	0.06	0.23	0.51	0.14	0.80
	YC	83.89	11.93	0.66	2.70	0.05	0.06	0.30	0.15	0.26

As it regards the raw clay samples, it is evident that they are very different to each other. For example, silica and alumina contents of the samples LC, BC and RC are very similar to those of the pottery, while the sample YC exhibits a very high concentration over 80% of silica and a very low value of alumina (about 12%).

In order to compare the chemical data relative to the two groups of potsherds with those of local raw materials, variation diagrams between pairs of significant elements were used (Figure 3).

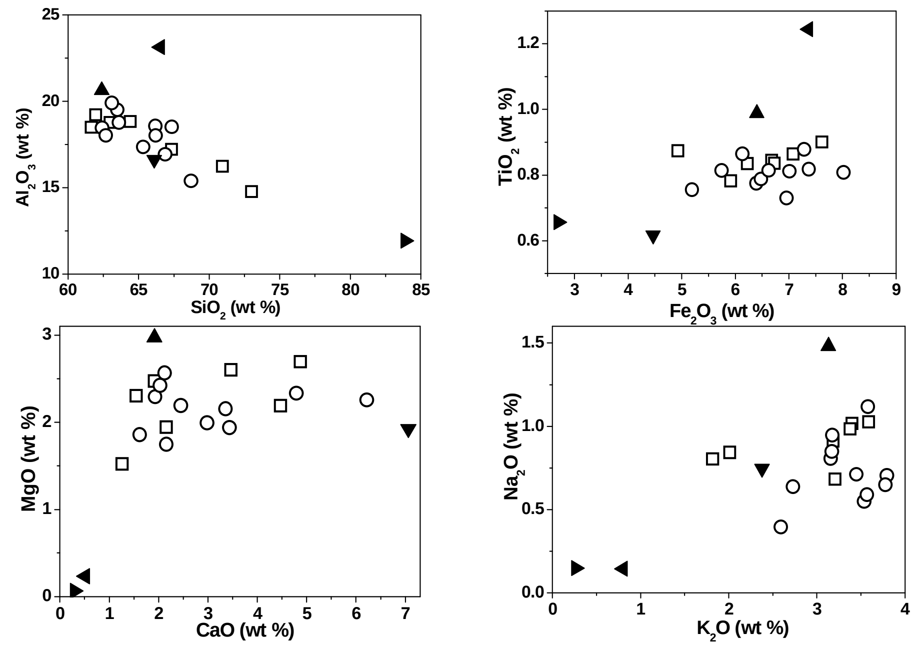

Figure 3. Chemical composition of the samples belonging to the two groups and of the raw clays represented in different binary diagrams: (□) Group 1; (○) Group 2; (▲) LC; (▼) BC; (◄) RC; (►) YC.

The results of the two ceramic groups show that the samples are chemically heterogeneous, and they do not evidence the two groups obtained by petrographic examination.

The differences in the chemical composition of the pottery samples allow rejecting the hypothesis of the use of a unique but very heterogeneous sediment for the pottery-making. The more reliable hypotheses are the following:

(i) two sources of raw clay materials, with and without microfossils respectively, were used with the addition of the same type of temper;

(ii) it was a unique source of raw clay material, not containing microfossils, which is modified adding temper with or without microfossils.

The comparison between pottery and clays does not show any overlap for RC and YC, while LC and BC should not be retained incompatible, especially if we take into account that the introduction of temper can modify the whole chemical composition in a significant way. But it is obvious that deeper investigations on the local clays composition are required in order to identify the correct hypothesis.

In a previous study [9] it has been established that the slip of the "Lumea Noua" pottery consists of carbonatic clay with a high content of illite, while iron-rich materials have been used for the painted decorations.

Mineralogical composition of the ceramic bodies

The mineral phases identified in the XRD patterns of representative pottery samples from each petrographic group are reported in Table 2.

Table 2.

Mineralogical composition of the "Lumea Noua" pottery samples and of the raw materials as determined from the XRD patterns

Sample		Qtz	Ill	Chl	Cc	K	Pl	Kfs	Other phases	Temp (^0C)
Clay	LC	xxxx	xx	xx	xx	tr.	xx	tr.	Mo (tr.)	----
	BC	xxx	x	-	x	tr.	-	x	-	----
	RC	xxx	tr.	-	-	xx	-	-	Go (tr.)	----
	YC	xxxx	tr.	-	-	xx	-	-	-	----
Group 1	LN 1	xxxx	x	-	-	-	xx	x	Mo	700-800
	LN 6	xxxx	xx	-	-	-	xx	-	He	850-900
	LN 7	xxxx	x	tr.	-	tr.	xx	tr.	-	~600
	LN 8	xxxx	x	-	-	-	x	x	-	850-900
Group 2	LN 10	xxxx	xx	-	x	-	xx	x	Do (tr.)	600-700
	LN 11	xxxx	xx	-	x	-	x	-	Do	600-700
	LN 12	xxxx	x	-	-	-	x	x	-	850-900
	LN 18	xxxx	x	-	-	-	xx	-	-	850-900
	LN 21	xxxx	xx	-	-	-	xx	x	-	850-900

Gr. – group; Qtz – quartz; Ill – illite; Chl – chlorite; Cc – calcite; Pl – plagioclase; K – kaolinite; Kfs – K-feldspar; Mo – Montmorillonite Do – dolomite; He – hematite; Go – goethite; tr. – traces.

It is well known that during firing the clays decompose and chemical reactions occur which lead to the formation of new microcrystalline mineral phases, which depend mainly on the composition of clays, the kiln atmosphere and the firing temperature [10]. The firing temperatures can be estimated by the mineralogy of the potsherd bodies, assuming that the phase association present in the sample reflects the one formed during firing and that no important changes occurred during burial.

A temperature interval was assigned to each of the investigated potsherds on the basis of the minerals present in the assemblage identified by XRD and taking into consideration the thin-section observations.

As can be seen from Table 2, many investigated "Lumea Noua" samples were fired at 850-900^{0}C. In the case of LN 10 and LN 11, the absence of chlorite and the contemporaneous presence of dolomite and calcite indicate a low firing temperature between 600 and 700^{0}C.

Since kaolinite loses its stability rather abruptly at 550–600^{0}C, for sample LN 7 a lower firing temperature (around 600^{0}C) was hypothesized.

EXPERIMENTAL SECTION

Description of the pottery samples

A set of 21 pottery fragments belonging to the "Lumea Noua" culture, were selected as experimental samples. They were supplied from the collection of the "1 Decembrie 1918" University. Examples of "Lumea Noua" potsherds are presented in Figure 4.

LN 1

LN 10

LN 18

N 1

Figure 4. Examples of pottery samples belonging to "Lumea Noua" culture

Macroscopically, the potsherds consisting of rim or fragment of vessels are covered with a white or a white-yellowish slip and decorated with red, red-orange to purple or brown bands or geometrical models. In some cases, parallel black lines are also drawn on the slip.

In addition, four samples of different local clays, named "Limba Clay" (LC), "Brown Clay" (BC), "Red Clay" (RC) and "Yellow Clay" (YC), originating from natural deposits situated in the surroundings of the archaeological site have also been investigated.

Methods

All samples were analyzed from the petrographic, chemical and mineralogical points of view.

The microscopic examination by transmitted polarized light was carried out on pottery thin-sections using a Leitz Laborlux 11 POL optical microscope. The main goal was to discriminate among groups of pottery having similar "ceramic fabrics".

The chemical composition of the ceramic bodies (for major and minor elements) and of the raw clays was determined using a Philips PW 1480 XRF spectrometer. The test specimens were obtained by cutting small pieces from each ceramic fragment. After removing the slip and decoration layers by a lancet, the cut pieces were ground to powder in an agate mortar and a quantity of 0.5 grams of powder was used to prepare the tablets by pressing it on a boric acid support at approximately 2000 kg/cm^2. The chemical data were completed by determining the ignition loss (IL) of the dried sample after calcination at 1000^0C.

The mineral composition was estimated using a SIEMENS X-ray diffractometer with copper anticathode, scanning an angular range between 4° and 64° 2 θ with a step of 2°/min.

CONCLUSIONS

The results of the archaeometrical investigations on "Lumea Noua" artefacts allowed the individualization of two different types of ceramic body with and without microfossils respectively. In spite of this, all the artefacts could be probably retained of local provenance.

The samples are chemically heterogeneous, suggesting that different starting raw clay materials were used for their production.

Archaeometric data allowed "reconstructing" the stages used to produce the "Lumea Noua" artefacts; the proposed flow-manufacturing processes consists of: (i) preparation of the paste by mixing raw clays, (probably illitic clays) with temper (quartz - feldspatic sand) and water; (ii) shaping the clays by hands pressure; (iii) smoothening and partial drying; (iv) application of the slip, consisting very probably of a fine-grained carbonatic clay with high illite content; (v) polishing the surface; (vi) painting using iron-rich materials; (vii) final drying and (viii) firing at temperatures between 600 and 900^0C.

Further and more detailed investigations on different clays sources and on other "Lumea Noua" pottery collected from the archaeological sites from Transylvania will allow us to identify the raw materials used and to ascertain exactly their origin or to discriminate between sources.

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