ANALYSIS AND STRUCTURAL INVESTIGATIONS ON EARLY ENEOLITHIC FOENI PAINTED POTTERY FROM ALBA IULIA – LUMEA NOUA ARCHAEOLOGICAL SITE

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Abstract. The present research is based on the use of analytical techniques on Early Eneolithic painted pottery of Foeni cultural group. The research is focused on providing information about the provenance and nature of some of the raw materials used in the manufacture of ceramic production from Alba Iulia – Lumea Noua archaeological site. In this paper, 17 pottery samples belonging to the Foeni group, which present a refined painted decoration exclusively in reddish or ruby-brown colours, as well as 6 clay samples, were analyzed. The most appropriate and holistic approach for both ceramic and clay investigation is through synergistic use of non-destructive (e.g. FTIR and SEM-EDS) methods combined with other analytical techniques and physical forms of examination. The analysis was carried out in order to be able to distinguish the locally manufactured painted pottery from those imported.

Key words: painted pottery, Foeni culture, Alba Iulia-Lumea Noua site, FTIR, SEM-EDS.

1. INTRODUCTION

The recent decades have seen the emergence of cultural heritage science as a new direction for understanding the history and traditions of different countries, with a special emphasis on preserving heritage. Recent years have witnessed the development of different analytical techniques into the archaeological approaches, which has significantly enhanced preservation practices, affording a deepened
understanding of materials’ properties and degradation processes of ancient pottery. Today, the optical microscopy [1] is corroborated with various advanced techniques for separation and chemical identification, for high magnification and analysis of microstructure [2–4], and imaging using nuclear magnetic resonance [5], thermal neutrons [6], and a large range of electromagnetic radiation [7–11].

Therefore, the properties of prehistoric pottery are significantly altered by the life cycle of some artifacts. The structural and compositional changes of the clay begin as early as the production process, and continue throughout the use of ceramic objects discovered in the excavation, adding to the influence of post-deposition conditions in the soil [12]. As a result, the traditional archaeological (i.e. typological, stylistic and by context) research of Neolithic and Eneolithic pottery should benefit from the real information that archaeometric analyses bring to light [4, 12].

The Foeni group is individualized in the area of Banat and Transylvania by ceramic technology production in comparison with other late Neolithic cultures [13–15]. Until now, 27 Foeni sites have been identified by archaeological research, of which we mention the most important in the intra-Carpathian area: Alba Iulia – Lumea Noua, Daia Romana – Paraut, Mintia – Gerhart, Păuca – Homm, Petresti – Groapa Galbena, Pianu de Jos – Podei, Zau de Campie – La Gradinita [16]. Relevant discoveries belonging to the Foeni communities in Transylvania have been made in Alba Iulia-Lumea Noua archaeological site, where the research revealed dwellings and pit houses, typically pottery artefacts, an enclosure, and anthropomorphic and zoomorphic burnt clay figurines [17]. Radiocarbon data from this settlement indicates a timeframe between 4650–4450 BC [17, 18], which means the beginning of the Eneolithic period in Transylvania [18].

Until now, the pottery of Foeni group has been at the forefront of archaeometric research regarding the chemical composition of the clay and firing temperatures [17] but not in terms of chemical structure of mineral pigments used to decorate the surfaces by painting. Most of the information on this issue stems from stylistic observations, and was complemented by the analogies offered by neighboring cultural areas which were more intensively investigated in this direction. As the studies show, the research of the last ten years has been constantly pursuing the widening of knowledge about the Foeni discoveries in Transylvania; therefore this paper envisaged analytical methods (i.e. FTIR and SEM-EDS) based on non-invasive techniques, hence avoiding sampling and sample destruction. The combination of both techniques was chosen in accordance with the material being analyzed, the information needed, and the sensitivity required. As mentioned above, the rotational-vibrational spectroscopy was combined with microstructural analysis, where the distribution of elements in the various components was mapped.
2. MATERIAL AND METHODS

The 17 fine painted pottery samples (Table 1 and Figure 1) belonging to Foeni communities display a very typical, refined reddish or ruby-brown decoration, consisting of parallel lines that form angular motifs, all applied directly (no slip) on the ceramic body as background. This distinctive ornament is applied before firing and the thin surface of the vessels is remarkably well burnished and fired. For protection against contamination, each sample was placed in its own well-labelled sterile plastic container according to Perkins and Chalmers requirements [19, 20].

Table 1
Painted pottery samples – location and description

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Archaeological context*</th>
<th>Physical and archaeological characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALN.14.I; □A; ▼1.30–1.50 m; Cx. C1</td>
<td>ALN.06.V; □I; SIII; ▼0.95–1.10 m</td>
<td>Vessel fragment, fine texture, painted decoration</td>
</tr>
<tr>
<td>ALN.15.I; □C; ▼2.30 m; Cx. 006</td>
<td>ALN.05.III; □A; ▼1.00 m</td>
<td>Vessel fragment, fine texture, painted decoration</td>
</tr>
<tr>
<td>ALN.14.I; □A; ▼1.30–1.50 m; Cx. C1</td>
<td>ALN.06.V; □I; ▼0.60–0.90 m</td>
<td>Vessel fragment, fine texture, painted decoration</td>
</tr>
<tr>
<td>ALN.15.I; □C; ▼2.30 m; Cx. 006</td>
<td>ALN.05.III; □A; ▼1.00 m</td>
<td>Vessel fragment, fine texture, painted decoration</td>
</tr>
<tr>
<td>ALN.14.I; □A; ▼0.90–1.10 m</td>
<td>ALN.14.V; □C; ▼0.50–0.75 m</td>
<td>Vessel fragment, fine texture, painted decoration</td>
</tr>
<tr>
<td>ALN.14.I; □E; ▼0.95 m</td>
<td>ALN.06.V; □I; SII; ▼1.50 m; Cx.C1</td>
<td>Vessel fragment, fine texture, painted decoration</td>
</tr>
<tr>
<td>ALN.15.I; □E; ▼1.20–1.45 m; Cx. 007</td>
<td>ALN.14.IV; □ A; ▼1.00 m</td>
<td>Vessel fragment, fine texture, painted decoration</td>
</tr>
<tr>
<td>ALN.14.I; □BD; ▼1.40–1.60 m; Cx. C1</td>
<td>ALN.06.V; □I; SII; ▼1.70–1.80 m</td>
<td>Vessel fragment, fine texture, painted decoration</td>
</tr>
<tr>
<td>ALN.05.III; □ A; ▼1.70 m; Cx. G1</td>
<td>ALN.06.V; □I; SII; ▼1.70–1.80 m</td>
<td>Vessel fragment, fine texture, painted decoration</td>
</tr>
<tr>
<td>ALN.14.I; □B; ▼0.40–0.60 m</td>
<td>ALN.06.V; □I; SII; ▼1.70–1.80 m</td>
<td>Vessel fragment, fine texture, painted decoration</td>
</tr>
<tr>
<td>ALN.14.I; □A; ▼1.10–1.30 m</td>
<td>ALN.06.V; □I; SII; ▼1.70–1.80 m</td>
<td>Vessel fragment, fine texture, painted decoration</td>
</tr>
</tbody>
</table>

ALN – Alba Iulia – Lumea Nouă; 15 – year of excavation (2015); IV/S-the number of the Trench (rescue excavation) / Systematic excavation (e.g.); □ – square; ▼ – depth; Cx. – feature

Qualitative FTIR spectroscopy is a valuable analytical tool that allows for the identification of organic and inorganic compounds. The absorption bands in a recorded FTIR spectrum exhibit three important parameters: frequency, shape, and intensity. The band positions or frequencies, indicate the presence of certain functional groups.

Band assignment of functional group in the mid-infrared region (*i.e. MIR, 4000–1500 cm\(^{-1}\)) is easy attributed, while assigning a band to a group in the fingerprint region (*i.e. near-infrared region, NIR, 1500–500 cm\(^{-1}\)) may be difficult, since many
types of functional groups absorb at similar wavenumbers in this region [4, 21–25]. The relative intensity of a band provides information on the amount and type of specific functional group present in a compound [26, 27]. Inorganic and organic groups of chemical compounds were performed by Attenuated Total Reflection – Fourier Transform Infrared spectrometry (ATR-FTIR) using Vertex 80v spectrometer (Bruker) equipped with diamond ATR crystal accessory. For inorganic materials, FTIR spectroscopy is often used in conjunction with either SEM-EDS to give much more direct compositional information.

Pottery samples were investigated using SU70 SEM (Hitachi) coupled with UltraDry EDS (Thermo Scientific) [4, 28, 29]. This equipment operates in ultrahigh 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 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.
3. RESULTS AND DISCUSSION

Inorganic substances are found as base materials from ceramic as pigments, thickeners and fillers, polishers (talc, alum, carbonates), stabilizers and neutralizers, and unwanted reaction products (corrosion, weathering crusts, salt deposits). Organic materials in pottery may have either natural or synthetic sources. Both plants and animals generate natural products (cellulose, hair, skin, resin, gum, dye, oil, protein, wax) that are themselves complex mixtures of chemical compounds, even before being used as substances for art objects.

Spectral data show a high absorbance which can be attributed to 990–1003 cm⁻¹ band (Figure 2). The peak around 1600 cm⁻¹ can be assigned for CO bound specific to all Foeni pottery samples (F1-F17) and prove the presence of carbonates and/or carboxyl group of humic acids.

![FTIR overlay spectra for pottery samples.](image1)

![FTIR overlay spectra for clay samples.](image2)
FTIR data corroborated with SEM images have generated the firing temperature predictions for pottery samples (Table 2). The band corresponding to kaolinite dehydroxilation is present in samples F1, F3, F5-F8, F11-F14, F16-F17, in the range of 872–876 cm$^{-1}$ and indicates a temperature of around 800 °C.

The bands corresponding to Si-O bonds, in the ranges of 775–778 cm$^{-1}$ and 692–694 cm$^{-1}$, respectively, signal the presence of quartz in all pottery samples. Gehlenite, a soro-silicate with Ca$_2$Al[AlSiO$_7$] formula and often used as refractory material is evidenced by the band assigned to Si-O-Si bond (643–648 cm$^{-1}$) in the samples: F1, F3, and F5–F9. Unlike samples containing gehlenite, the Fe-O bond (from hematite) was observed only in samples F2, F15, and F17. The presence of hematite is characterized by the peaks around the values of 530–534 cm$^{-1}$, which indicate the formation of iron oxides during the combustion process and, implicitly, a firing temperature which exceed 600 °C (Figure 2 and Table 2).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Clay type (1)</th>
<th>Vitrification stage (2)</th>
<th>Firing temperature [25] predicted by SEM [°C]</th>
<th>Band 875 cm$^{-1}$ (3)</th>
<th>Band 535 cm$^{-1}$ (4)</th>
<th>Firing temperature [26] predicted by FTIR [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>NC</td>
<td>IV</td>
<td>800–850</td>
<td>DC</td>
<td>NH</td>
<td>&gt;800</td>
</tr>
<tr>
<td>F2</td>
<td>NC</td>
<td>IV</td>
<td>800–850</td>
<td>C</td>
<td>H</td>
<td>&gt;600</td>
</tr>
<tr>
<td>F3</td>
<td>C</td>
<td>IV</td>
<td>800–850</td>
<td>DC</td>
<td>NH</td>
<td>&gt;800</td>
</tr>
<tr>
<td>F4</td>
<td>C</td>
<td>IV</td>
<td>800–850</td>
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</tr>
<tr>
<td>F5</td>
<td>C</td>
<td>IV</td>
<td>800–850</td>
<td>DC</td>
<td>NH</td>
<td>&gt;800</td>
</tr>
<tr>
<td>F6</td>
<td>C</td>
<td>IV</td>
<td>800–850</td>
<td>DC</td>
<td>NH</td>
<td>&gt;800</td>
</tr>
<tr>
<td>F7</td>
<td>C</td>
<td>CV</td>
<td>850–950</td>
<td>DC</td>
<td>NH</td>
<td>&gt;800</td>
</tr>
<tr>
<td>F8</td>
<td>NC</td>
<td>CV</td>
<td>850–950</td>
<td>DC</td>
<td>NH</td>
<td>&gt;800</td>
</tr>
<tr>
<td>F9</td>
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<td>IV</td>
<td>800–850</td>
<td>C</td>
<td>NH</td>
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<tr>
<td>F10</td>
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<td>F11</td>
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<td>DC</td>
<td>NH</td>
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<td>DC</td>
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<td>F13</td>
<td>NC</td>
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<td>DC</td>
<td>NH</td>
<td>&gt;800</td>
</tr>
<tr>
<td>F14</td>
<td>NC</td>
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<td>&lt;800</td>
<td>DC</td>
<td>NH</td>
<td>&gt;800</td>
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<tr>
<td>F15</td>
<td>C</td>
<td>CV</td>
<td>850–950</td>
<td>C</td>
<td>H</td>
<td>&gt;600</td>
</tr>
<tr>
<td>F16</td>
<td>C</td>
<td>CV</td>
<td>850–950</td>
<td>DC</td>
<td>NH</td>
<td>&gt;800</td>
</tr>
<tr>
<td>F17</td>
<td>C</td>
<td>CV</td>
<td>850–950</td>
<td>DC</td>
<td>H</td>
<td>&gt;800</td>
</tr>
</tbody>
</table>

(1) Calcareous (C)/ Non-calcareous (NC); (2) NV – Unobserved Vitrification; IV – Initial Vitrification stage; CV – Continuous Vitrification stage; (3) DC – with signal, C – without signal; (4) H – with signal, NH – without signal.

In C3–C6 clay samples, organic compounds are only minor constituents, whilst material containing SiO was dominant (Figure 3). Within the recorded spectra, all six clay samples presented a weak absorbance centred 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 (Figure 3).

Based on the obtained data and established type of clay, in strong dependence with Ca content (Ca > 5%: F3-F7, F11, F12, F15-F17) and the vitrification stage observed in the SEM images can estimate that firing temperature for the Foeni specific samples is within the range of 850–900°C (Table 2).

Previous SEM-EDS results for clay were presented in earlier research, and these results can be summarized as follows: C1 (1.5 km NE, Barabant, Alba county) present a lamellar structure, within C2 (6 km S, Limba, Ciugud, Alba county) and C6 (Alba Iulia – Lumea Noua: Trench IV/2014) shown a granular structure with lamellar inclusions as well; granular structure with coarse inclusions was found on C3–C4 (Alba Iulia – Lumea Noua: Systematic excavation/2015) and C5 (Alba Iulia – Lumea Noua: Systematic excavation/2016) samples. All samples are clean, without vegetal, animal and geological impurities [4]. EDS results 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 %).

Starting from morphology and elemental composition of clay, were assigned the main elements in Foeni pottery. In this respect, SEM images (Figure 4) highlights the presence of iron in several minerals such as hematite, magnetite and limonite.
Fig. 4 – SEM images and EDS spectra of pottery samples.
Considering the clay grains with rounding edges, observed by SEM images on painted pottery (Figure 4), it was observed that samples have not reached the vitrification stage. Also, these samples are low refractory and fired in oxidizing atmosphere (at T < 800 °C), according to Velraj et al. [30, 31] and Table 2. From EDS data (Figure 4) it 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 elements are 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 %).

Cluster analysis is mainly used for group’s identification of objects having similar characteristics (i.e. chemical profile). In this research, the cluster analysis was used to identify the clay source underlying painted pottery samples. Based on the elemental compositions of the clay and pottery samples, the dendrogram was achieved through the Ward Linkage method (Figure 5). The different elemental content was expected to bring together the samples in multiple groups. The role of cluster analysis, as well as the minor elements content, is to provide information about the origin and manufacturing process of archaeological samples.

Fig. 5 – Dendrogram of clay and Foeni painted pottery samples obtained from cluster analysis using Ward Linkage method.
The dendrogram of Foeni painted pottery reveals that F1, F8-F10, and F13-F14 could have been obtained from C5 / C6 clay samples, while F2-F7, F11-F12, and F15-F16 could have been obtained from C3 / C4 or C5 / C6 clay samples. The absence of correlation between painted pottery samples and C1 / C2 strengthens the hypothesis that all investigated samples were manufactured from local clay sources.

4. CONCLUSIONS

The current investigation into the Foeni pottery adds valuable information to previous research. According to the spectral data for both sample categories (clay and Foeni pottery) it can be concluded that the chemical composition is quite similar (hydroxyl, carbonyl, aliphatic and SiO groups). FTIR data are in good compliance with EDS and statistical results. These results confirm an obvious link between Foeni painted pottery and local source (C3-C4 and C5-C6) at Alba Iulia – Lumea Noua archaeological site. Their possible concomitant use in the pottery manufacture was underlined by existence of two distinct chemical groups for samples belonging of Foeni cultural group, as revealed by cluster analysis.

For the F17 sample, first established as a ceramic import from Dimini Culture [17, 32], the processing of this statistical data did not confirm this hypothesis. By the correlations with local clay sources, the pottery fragment did not individualize itself within the evaluated lot and it does not confirm yet the cultural affiliation it was initially credited with. At this point of the research, the observed aspect does not constitute a limit to the investigation methods themselves, but rather suggests the low relevancy of the archaeometric analyzes that were applied on single fragments (the assertion is generally valid for the numerically reduced samples). The expanding of the research by adding new ceramic samples would allow a more accurate delineation of the chemical profile of the group.

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