THE FIRST ARCHAEOOMETRIC CHARACTERIZATION OF THE LATE ROMAN PERIOD BRICKS IN THE DNIESTER RIVER BASIN IN COMPARISON WITH EARLY MEDIEVAL MATERIAL

Primera caracterización arqueométrica de ladrillos tardorromanos de la cuenca del río Dniéster y comparación con el material altomedieval

ANASTASIIA KOROKHINA *, VOLODYMYR BELSKYI **, OLEG PETRAUSKAS *, MARYANA AVRAMENKO *, NATALIA KHAMAIKO *, YURII LYTVYVENKO *** and MYKOLA ILKIV ****

ABSTRACT The paper presents the results on archaeometric characterization of a test sample of building materials from the settlements of the Late Roman period Komariv and Buzovytsia-1 in the middle course of the Dniester river. The parameters of raw material and technology of bricks from the two sites are compared and the first reconstruction of features of operational chains are offered. Also, the first comparison of the Late Roman period materials with same-function artifacts of the Middle Ages (Old Rus’ Culture) has been made. The development of petrographic and geochemical classification of archaeological building ceramics from the sites of the Central and South-West Ukraine was started. Keywords: Late Roman Time, Cherniakhiv-Syntana de Muresh Culture, Middle Ages, Old Rus’, Bricks, Building Ceramics, Eastern Europe, Archaeometry.

RESUMEN El artículo presenta los resultados de la caracterización arqueométrica de una muestra preliminar de materiales de construcción de los asentamientos de la época romana de Komariv y Buzovytsia-1 en el curso medio del río Dniéster. Se comparan los parámetros de la materia prima y la tecnología de ladrillos de los dos sitios y se ofrece la primera reconstrucción de las características de las cadenas operativas. También se ha realizado la primera comparación de los materiales del período romano tardío con los artefactos de la misma función de la Edad Media (la antigua cultura de la Rus). Se inició el desarrollo de la clasificación petrográfica y geoquímica de la cerámica de construcción arqueológica de los monumentos del centro y suroeste de Ucrania. Palabras clave: Época romana tardía, Cultura Czerniakhiv-Syntana de Muresh, Edad Media, Antigua Rus, Ladrillos, Cerámica de construcción, Europa del Este, Arqueometría.

* Institute of archaeology, NAS Ukraine, Kyiv (Ukraine). a.v.korokhina@gmail.com https://orcid.org/0000-0001-6123-6285
  oleg_petrauskas@iananu.org.ua, https://orcid.org/0000-0001-9117-4265
  mariana_avramenko@iananu.org.ua, https://orcid.org/0000-0003-1566-1648
  khamajko@gmail.com, https://orcid.org/0000-0002-7396-0315

** M.P. Semenenko Institute of geochemistry, mineralogy and ore formation NAS Ukraine, Kyiv (Ukraine). belskyi.vm@gmail.com, https://orcid.org/0000-0001-7990-1386

*** M.P. Semenenko Institute of geochemistry, mineralogy and ore formation NAS Ukraine, Kyiv (Ukraine). yurimlyt@mail.ru, https://orcid.org/0000-0001-6609-0000

**** Yu. Fedkovych Chernivtsi National University, Chernivtsi (Ukraine) ilkiv_chnu@ukr.net, https://orcid.org/0000-0002-1501-876X

http://dx.doi.org/10.30827/CPAG.v32i0.23984
INTRODUCTION

Archaeometric studies of building materials from the sites of the Eastern Europe is a scarcely researched topic. They were started in 1920s and were represented by isolated attempts at chemical or petrographic analysis of ancient building materials and mortars (for overview see: Vinogradov et al., 2019:382). The activity in the field renewed in 2000s concentrating mainly on the study of the material from the famous churches of Kiiv (Hutsuliak et al., 2007; Hutsuliak, 2010; Strilenko, Totskaia, 2012; Hutsuliak, Shevchenko, 2017). A. Vinogradov, D. Yolshin and M. Kulkova aslo conducted the comprehensive petrographic study of bricks from Caucasian temples of the 9-10th centuries (Vinogradov et al., 2019). As an outcome, the foundations of petrographic classification of Medieval building ceramics of the region were laid. As for Late Roman materials, the rarity of their finds in the south of Eastern Europe meant that research on this subject was sparse and limited to mortars of Chersonesos until recently (Krupa et al., 2007).

The necessity to carry out our study was caused by an accumulation of the collection of building ceramics during the excavations of the settlements of the Late Roman period – Komariv and Buzovytsia-1, which are in the middle reaches of the Dniester river. The both sites represent the Cherniakhiv-Syntana de Muresh culture and are located within the so-called Eastern European Barbaricum (approximately 360 km from the Danube Limes, or 250-300 km if one takes into account the borders of the Dacia province), which is of particular interest regarding the expansion of the Roman culture to the North and East (fig. 1).

The Komariv settlement, which has been investigated intermittently since the 1950s, is known in the region for the evidence of glass production (Smishko, 1964; Petrauskas, 2014b; Petrauskas and Avramenko, 2019). As for the nearby located Buzovytsia-1, the amount of material obtained from the site is much more modest. At the same time, the fieldwork conducted in 2020-2021 yielded an unexpected material, namely a significant amount of bricks (plinphos), which were deposited as accumulations on the surface and in the cultural layer.

The discovery of potential remains of brick buildings at the Buzovytsia-1 made it necessary to clarify their cultural and chronological attribution before the beginning of stationary excavations. For this purpose, authors have applied archaeometric methods aiming to compare raw material and technology features of the products from the Buzovytsia-1 and same-function artifacts from the Komariv, which were contextually related to the Late Roman time. Another block of comparative material consisted of building ceramics (bricks and tiles) of the Middle Ages, or the Old Rus’ culture, which originate from the Middle Dniester and Middle Dnieper regions. This paper highlights the first data obtained.
Fig. 1.—A) A map of Europe showing the region under study; B) Studied sites; C) Location of the Late Roman Group sites within the Cherniakhiv-Syntana de Muresh culture and concerning the Roman Empire borders; D) Location of the Old Rus’ Group sites within the Old Rus’ area and concerning the Byzantine Empire borders (the blank map for A by © Intermap, NASA, NGA, USGS | Esri Community Maps Contributors, Esri, HERE, Garmin, Foursquare, GeoTechnologies, Inc, METI/NASA, USGS; for B, C, D by A.V. Panikarskyi). Figure in color in the electronic versión.
Archaeological context

The Late Roman Group

The Cherniakhiv culture is traditionally regarded as a culture of pro-Roman influences. Such influences, as a rule, are reflected both in the import of technologies (pottery, agriculture tools, etc.) and dissemination of certain categories of Late Antique production (coins, amphorae, glassware). In recent years, however, a new record has pointed to a deeper connection between the Roman Empire and certain regions of the Barbaricum. The right bank of the Middle Dniester can be attributed to these regions. Its specificity is the import of sophisticated technologies, which required the physical presence of highly skilled masters from the Empire in a barbaric environment. The marks of such a sophisticated “imports” are traced at the sites of Buzovytysia-1 and Komariv.

The Late Roman period site complex near the village of Komariv (Chernivtsi region, Ukraine) is located in the western-north area of the Cherniakhiv culture, on the right bank of the Dniester River. It consists of a settlement with a glass production evidence (“Komariv”) and cemetery (“Komariv-1”). The settlement covering an area of approximately 35 ha occupied both slopes of a stream that flows into the Dniester after 5 km from the location. The synchronous cemetery is located on a cape of the southern bank of the stream.

In the second half of the twentieth century the settlement was excavated by Markiian Yu. Smishko and Yuliia L. Shhapova (Smishko, 1964; Shhapova, 1978; Petrauskas, 2014b). In 2012, the investigations were renewed by the stuff of the Institute of Archaeology of the National Academy of Sciences of Ukraine, since 2014 — in collaboration with German scholars. By 2021, over 5000 m² has been excavated and 73 objects of the Late Roman period have been explored on the settlement.

The main types of structures discovered are: on-surface daub buildings, semi-dugouts, houses on a stone foundation, pottery kilns and a glass fusing one, hearths, pits for public and production purposes, etc. The inventory includes local and Antique tableware, Roman and Bosporan coins, details of clothing and adornments (fibulae, buckles), tools (axes, hammers, etc.), weapons (spurs, arrowheads, spearheads) and so on. The chronology of the site is set within the range of the stages B₂\C₁ and D₁\D₂, that corresponds to the edge of 2/3 – mid-5 century (fig. 2A) (Petrauskas, 2014a; Petrauskas, 2014b:87-116; Rumyantseva, 2014).

Glass artifacts found at the Komariv consist of glassware debris (cups, bowls, jars), beads, window glass and gambling tokens. Glassware is divided into two large groups, provisionally attributed as the “Antique-type” and “Cherniakhiv-type”. In the Komariv, there are artifacts that represent all the stages of glass production – boiling/remelting, forming and decoration (fig. 2B). The question as to whether the glass was melted on the site is a subject of debate (Smishko, 1964:67-80; Shhapova, 1978:230-242; Petrauskas, 2014b:87-116; Rumyantseva, 2016, 2017).
A specific category of artifacts is the building remains represented by bricks, roof tiles, window glass. Bricks was used, *inter alia*, in the construction of the glass melting furnace (fig. 2C). In other buildings, bricks and tiles were used in varying amounts and didn’t form structures. Their fragments are found in both on-surface and deepened buildings. Komariv’s bricks are square (about 30x30cm) or rectangular (about 13x25cm) with a thickness of 3-7 cm. End planes are level with smooth outer surfaces and humpy inner ones. Some specimens have diagonal strips of three or four lines on the face. The bricks are yellow, red or brown and mostly has a coarse admixture. Roof tiles are made of yellow or red mass almost without coarse admixture, their faces are level, back sides are rough with large ridges, one their edge is thickened and obliquely cut, the thickness is 2-2.5 cm. Tiles found at the the site are represented solely by the *tegula* type.

Comparing to other Cherniakhiv settlements, Komariv looks like a trading post with high-tech crafts mainly of Antique origin. Our research allows to distinguish at least four their types —glassmaking, pottery, iron— and jewelry making. Of no doubts, supplementary crafts, *e.g.* charcoal and lime burning, leather processing and weaving, *etc.*, were also practiced on the settlement. This peculiarity distinguishes it from other craft centres of the Late Roman period from the barbaric territories of Europe, as a rule, producing a single type of products.

The Buzovysia-1 settlement is situated on both slopes of a gully along which a stream flows into the Dniester river. The area of the settlement is over 65 hectares. It has been known since the 1950s, but focused research has started in 2014. The distance between Komariv and Buzovysia-1 is about 4 km and they are located on the neighboring tributaries of the Dniester.

In 2020, during surveys at the settlement six accumulations of archaeological material were rediscovered above the boundary of the cultural layer. These consisted of bricks, mortar and lime fragments, Antique amphorae, Cherniakhiv-type wheel-made grayware, a large number of iron nails, Cherniakhiv and Roman imported metal wares and others (fig. 2D).

The building remains belong to the following types: (1) mortar, with lime binder and sand, pebble and grog admixture; (2) stone, which is represented by a local limestone; (3) bricks that constitute the bulk of the building remains and could be divided into the following subtypes: (a) rounded, with an approximate diameter of 23 cm and thickness of 8 cm; (b) rectangular, with a short side length of 15-18.5 cm, long side length of 30 cm and width of 4-6 cm; (c) squared, with sides of approximately 30/35 cm and a height of 4.5 to 6.5 cm.

Face surfaces of the bricks are smoothed, sometimes with traces of cutting of a redundant clay. The end faces are smoothed or slightly humped, backsides are humped, often bear the impressions of the forming box. Square bricks are often decorated/marked with one to four diagonally crossed lines on the face surface.

1. Attributed by Dr. Bohdan T. Ridush.
Fig. 2.—Materials from the settlement of Komariv (A-B) and Buzovytsia-1 (C): A) Chronological scheme of the Komariv settlement; B) Artefacts of the main stages of glass production on the Komariv settlement; C) Brick sample and a glass melting kiln made with the use of bricks from the Komariv settlement (after: Smishko, 1964); D) Artefacts of Cherniakhiv and Roman origin from the Buzovytsia-1 settlement. Figure in color in the electronic versión.
Bricks of the second and third types are similar to those found at the Komariv; the artefacts of the third type, moreover, have analogies in another Cherniakhiv site – the Kamianka Anchekrak (Magomedov, 1987:21), which is in the nearby of the ancient city of Olbia. Bricks of the first type have analogies only among the materials of Roman provinces. Such products had a narrow function as supportive pillars for a warm floor – *hypocaustum* (e.g.: Konestra et al., 2020:96; pl. 2; 4-5).

Excavations in 2021 confirmed the presence of a structure built using bricks. Its type could not be determined due to the limited scope of work. Given the material found in the filling, especially, fragments of the late Forlimpopoli type amphorae, the object could be dated up to the second half of the 3rd – early 4th century AD.

*The Old Rus’ Group*

Today, sites representing the Old Rus’ culture provide evidence of about 200 monumental buildings of the 10th – 13th centuries AD where bricks were extensively used in the construction. It is believed that this tradition originated in the Byzantine school. For the Southern part of this area (Kyiv, Chernihiv), a significant variability in paste composition of bricks was noted (Yolshin, 2010, 2017). In the far South-West (Middle Dniester basin), however, stone construction was predominantly practised using only decorative floor tiles as building ceramics.

Findings from the two sites (Kyiv and Vasyliv) which are located in different regions were included to our sample (fig. 1). The Middle Dnieper region is represented by samples from the 35 Spaska Street on the Podil district in the city of Kyiv. This part of the town served as a market and manufacturing area in the Old-Rus’ time. Archaeological excavations here were held throughout 2007, 2008, and 2011 by Mykhailo A. Sagaidak and Natalia V. Khamaido, during which three homesteads of the 11th – early 13th century have been excavated (Sagaydak et al., 2009, 2012).

The brick fragments sampled were found in the lower part of the infill of the Homestead 1, on the floorboards of the burned-out wooden frame construction (Feature 7/27) measured about 7×5 m. The finds from the infill of the construction consisted of numbers of copper-casting remnants (fragments of crucibles, slag, scrap, flattened ingots, drops of copper alloy and copper foundry waste), iron objects, small pieces of gold, and a fragment of a crucible with the gold drops, gold threads and a woolen gold-embroidered burnt fabric. The fragments of amber and rock crystals with traces of cutting mark the jewelry production. Glass beads, bracelets, finger-rings, lamps, glassware, fragments of bottles, a gilded piece of glass mosaic, and the fragments of lustre-ware were also discovered, as well as the sword with inscription of BENEDICTUS-type, copper-alloy belt ornaments and rings, which were probably the sword-belt details (fig. 3). All the finds belong to the widely dated period of the 12th – early 13th centuries. A number of pottery-finds dates the Horizon 5 more narrowly to the second half of 12th century (Sagaydak et al., 2015:26-30).
Fig. 3.—Materials from 35 Spaska Street, the city of Kyiv (Feature 7/27 and Horizon 5): A) Finds of gold; B) Feature 7/27 and the bricks found there; C) Amber, burned amber and cutted rock crystal; D) Artifacts of imported origin: glass ware and ornaments, glazed and lustre ware, sword of BENEDICTUS-type; E) Copper-casting and glass-making evidences; F) Floor-tiles and bricks; G) Smalt. Figure in color in the electronic versión.
All the bricks were fragmented, some had traces of mortar. Denis D. Yolshin identified them as reusable ones and dated by visual characteristics to the turn of the 11th-12th century and to the early 12th century (Yolshin, 2017).

The Middle Dniester region is represented by the city of Vasyliv located 70 km to the west of the aforementioned Late Roman sites. As it was noted, in the Middle Ages it was stone building that mainly practiced in the region, though, we were able to investigate tiles found on the outskirts of the Vasyliv Church, which is dated to the 12-13th century (Dovzhenok et al., 1975:264-265).

AIMS, MATERIALS AND METHODS

The research addresses the following aims:

(1) to carry out the first comparative study of raw material and technology features of the building material from the Buzovysia and Komariv, as well as from the Late Roman and Old Rus’ groups. Thus, the potential of archaeometric data for cultural and chronological attribution of artifacts could be tested
(2) to start the petrographic and geochemical database for the material under consideration
(3) to give the description of the chaînes opératoires for building ceramic within each cultural and chronological group
(4) to test procedures and methods for archaeological building materials analysis.

For the analysis of the Late Roman Group, visual observation, petrography, X-ray diffraction (XRD) and SEM-EDS analysis were used, while elemental analysis was omitted for the Old Rus’ artifacts.

The primary technological characterization, apart from the naked eye observation, included the fixation of physical traits of the products – surface colour, colour pattern of cross-sections, Mohs hardness, surface feel and fracture type (Whitbread, 2017).

Petrographic analysis was carried out according to the methodology adapted to archaeological ceramics (Quinn, 2022). We used the classical technique for investigation of transparent ceramic thin sections (30 μm thickness) in transmitted polarized light, as well as quantitative analysis of non-plastic inclusions. Image processing and quantitative analysis were performed using SmartGrain software (Takanari et al., 2016), statistical procedures were carried out in the R (R Core Team, 2013). Granulometric categories were determined according to the Udden-Wentworth classification (Wentworth, 1922).
XRD analysis\(^2\) was carried out on an automatic diffractometer DRON-3M with cobalt irradiation (CoK\(_\alpha\) = 1.78892 Å). Measurements were taken in an angle range of 4-75 °2\(\theta\), with a scanning step of 0.05 deg/sec. The International Center for Diffraction Data (ICDD) database PDF-2 of 2003 was used to diagnose minerals using the PCPDFWIN program.

During the SEM-EDS analysis, we investigated ceramic polished sections cut perpendicularly to artifact surfaces, covered with a graphite coating. Elemental composition of clay matrix was determined as an average of five measurements for each sample. The analysis was performed on the JCM-733B electronic microanalyzer (JEOL, Japan) with the following parameters: accelerating voltage of 20.00 kV, current strength – 20 nA, probe locality – 2-3 μm\(^3\). The following reference materials were used for estimating mineral quantities: jadeit – for Na, diopside – for Si, Mg and Ca, augite – for Al and Fe, biotite – for Ca and Ti, manganite – for Mn. Secondary electron images were used to observe microstructural features of the micromass.

Sample within the Late Roman Group consists of 11 items. Of these, 6 are from Buzovytsia-1 and 5 – from Komariv. Komariv’s sample also includes 2 fragments of artifacts with specific features of the paste (the LR-F-4 Fabric), which attribution as “bricks” is in question. The Old Rus’ Group includes 6 items: 4 brick fragments from Kyiv and 2 tile fragments from Vasyliv.

During the last field season, surveys of raw materials in the vicinity of the Komariv village have been renewed for the purposes of ceramic studies, as well as laboratory firing experiments (in progress). Namely, one sample of clayey raw material collected from the modern quarry in the village was analyzed within to the sample. It has been previously moistened, hand-formed in a briquette and fired in a muffle furnace at a T of 700°C in an oxidizing atmosphere with a soaking time of 1 hour.

Typological and contextual attribution of the samples, their basic physical traits and methods used for the analysis are shown in tables 1 and 4.

During the classification, the taxons have been marked by letter-ciphers and numbers as follows: LR — Late Roman Group; OR — Old Rus’ Group; F — fabric; P — petrogroup; E — group on elemental composition. For example: LR-F-1 stands for the “Late Roman Group, Fabric 1”, etc. Thus, several parallel classifications have been created within each cultural and chronological group.

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2. The measurements were made by Dr. Olena Ye. Hrechanovs’ka (M.P. Semenenko Institute of geochemistry, mineralogy and ore mining of the National Academy of Sciences of Ukraine).

3. SEM-photos were taken by Dr. Volodymyr M. Belskyi and Yuriy O. Lytvynenko (M.P. Semenenko Institute of geochemistry, mineralogy and ore mining of the National Academy of Sciences of Ukraine) on the JCM-6200M electronic microanalyzer.
RESULTS

Archaeometric characterization of the Late Roman Group

Macro-features

A data on the physical characteristics of the samples are shown in table 1. Three groups are distinguished by the colour of the surfaces: (1) orange ones with a tendency towards red or burgundy (K-2, K-4, B-2-2, B-3-2); (2) bright orange ones (K-3, B-2-3, B-2-4, B-3-1). The B-2-3 sample is characteristic for orange (oxidized) surfaces and gray, weakly oxidized core; (3) pale-orange ones (K-1, K-5, B-2-1).

Colour patterns often show heterogeneity within an artifact. Some of them have gray, incompletely oxidized core (K-1, B-2-3, B-2-4, B-3-2). In other cases, the colour unevenness is caused, on the contrary, by the stronger impact of heating, thus, zones of more intensive reddish shade can be seen in cross-sections (e.g., for B-2-1).

The Mohs hardness ranges from 3 to 5, and for the fine-textured samples (K-3, K-4) it stands at 2. Surfaces are rough, harsh or powdery (depending on the presence and texture of the coarse fraction of inclusions). Fractures are respectively hackly, granular or earthy.

Fabric and petrographic classification

Since the two classifications coincide, they will be described jointly. The division is based primarily on the characteristics of the coarse inclusions (temper). However, of course, the data provided are preliminary due to small samples and must be supplemented by further research.

We distinguish four fabrics and correspondent petrographic groups: (1) with dark-gray shale (LR-F-1, LR-P-1); (2) with reddish shale (LR-F-2, LR-P-2); (3) with polycrystalline sand and pebble (LR-F-2, LR-P-2); (4) untempered (LR-F-4, LR-P-4) (fig. 4).

In petrogroup LR-P-1, the share of non-plastic inclusions is 20-30% of the area in perpendicular cross-cuts (fig. 5A-B). The share of the coarse fraction (0.25-6 mm) varies in between 50-75%. Shale predominates (fig. 5C-D), while micritic clots, polycrystalline quartz, colorless fibrous mineral (actinolith or fibrolith?), bioclast (shell) are accessory. The fine fraction (<0.5 mm) is constituted of predominant quartz and feldspars, polycrystalline quartz, chert, muscovite, calcite, sedimentary lithoclasts and inclusions as accessories. The matrix makes up 65-75% of the area; it’s calcareous, moderately birefrigent (sample K-1) or optically inactive, sintered (rest of the samples), homogeneous, with inclusions. The presence of calcareous sediments (carbonate clots and “ghosts”, sparite inclusions, micrites dispersed in the matrix) should be noted (e.g., fig. 5B). The voids take 5-10% and are represented by micro-channels, and coarse planar voids and vughs (caused by shrinkage).
<table>
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<th>Individual #</th>
<th>Category / morphology</th>
<th>Site / context</th>
<th>Surface color (general name)</th>
<th>Cross-cut color pattern</th>
<th>Surface feel</th>
<th>Hardness (after Mohs scale)</th>
<th>Fracture Methods applied</th>
<th>Petrogroup #</th>
<th>EDS group #</th>
<th>Petrogroup description</th>
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<td>completely oxidized</td>
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<td>LR-E-1</td>
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<td>completely oxidized</td>
<td>powdery</td>
<td>4</td>
<td>hackly</td>
<td>petrography, SEM-EDS, XRD</td>
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<td>hackly</td>
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<td>hackly</td>
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<td>LR-E-1</td>
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TABLE 1: CONTEXTUAL, MORPHOLOGICAL AND PHYSICAL CHARACTERISTICS OF THE LATE ROMAN GROUP SAMPLES
Fig. 4.—Characteristic samples of building ceramics of the Late Roman Group: A) Sample K-1; B) Sample B-2-4; C) Sample B-2-4, cross-cut; D) Sample B-2-2; E) Sample K-2, cross-cut; F) Sample K-5; G) Sample B-3-1; H) Sample B-3-1, cross-cut; I) Sample K-3; J) Sample K-4; K) Sample K-3, cross-cut. Lines over the images indicate places of thin sectioning. Figure in color in the electronic versión.
Fig. 5.—Photomicrographs of thin sections of the Late Roman Group ceramics: A-B) Paste of petrogroup LR-P-1; C-D) Shale inclusions, petrogroup LR-P-1; E-F) Paste of petrogroup LR-P-2; G-H) Shale inclusions, petrogroup LR-P-2. Scalebar length = 0.1 cm. Figure in color in the electronic versión.
The characteristics of petrogroup LR-P-2 are quite similar to the previous one. Though, some peculiarities of sample B-2-2 included to the group should be mentioned: it is slightly richer in aplastics where feldspars dominate over quartz, a high concentration of muscovite is noted, while carbonates are heavily decomposed (fig. 5E-F). The distinctive feature of the group is that all the shale have bloating voids (fig. 5G), some inclusions are exceptionally optically active (fig. 5H). The colour of the shale, obviously, was determined by the intensity of firing, thus, in some samples reddish shale is confined to intensively heated areas and the dark-gray one – on less heated zones.

Petrogroup LR-P-3, while sharing common features with the previous two, is distinguished by the presence of polymictic sand and pebbles as a temper (fig. 6A-D). It’s artificial origin is established basing on a bimodal distribution of sand size. The mode of the coarse fraction stands at the “medium sand”, though it also includes pebbles (up to 5 mm) composed of diverse sedimentary lithoclasts (siltstone, sandstone, mudstone, quartzite-sandstone, flint, slate, debris) – the so-called “Volynian pebbles” (fig. 6A-F). In a small amount, sand could have accidentally gotten into the paste due to co-presence with clay in some outcrops observed in the vicinity of the site.

Petrogroup LR-P-4 is markedly different from the previous ones. Here, the aplastics constitute about 10-20% of the area (fig. 6G). They are represented by a single moderately sorted fine fraction (<0.5 mm) where quartz predominates, and feldspars, biotite, fibrous colorless mineral, opaques and iron-rich nodules act as accessories. The matrix makes up 75-80%, is non-calcareous, optically inactive (sintered), homogeneous, with opaques (fig. 6H) and iron-rich nodules. The voids occupy 5-10% and are represented by micro-channels and coarse channels caused by gas releasing.

The sample of clay collected in the vicinity of the Komariv settlement (raw material #1, the outcrop coordinates: N48.5661072274213, E26.98251736425914) has no such specific features that would allow it to be unambiguously compared with the raw material of any of the petrogroups. In briquette, fired at 700°C, in an oxidising atmosphere and with one hour soaking time, its characteristics are as follows. The inclusions take 20%; from close spaced to open spaced; poorly sorted. Some coarse inclusions (c. 25% of the area, <1 mm in size) represented by polymictic sand and pebble are probably an accidental admixture taken with a clay. In the fine fraction (<0.5 mm), quartz predominates, while polycrystalline quartz, feldspars, pertites and muscovite are accessories. The matrix constitutes 80% of the mass, non-calcareous, with a low optical activity, homogeneous, with very rare opaques. The voids take less than 5%, represented by micro— and meso-channels, and by coarse vughs (caused by insufficient compaction of the paste during moulding).

In general, there is a high similarity between the first, second and third petrogroups, with some variations in physical parameters, composition and concentration of inclusions. In all the cases, the coarse admixture which characterizes the groups is artificial. The share of natural clasts (the fine fraction) can range from 5% (silty
Fig. 6.—Photomicrographs of thin sections of the Late Roman Group ceramics: A) Paste of petrogroup LR-P-3; B-F) Inclusions of sedimentary rocks in petrogroup LR-P-3; B) Quartzite (lower left) and unspecified lithoclast (upper right); C) Slate; D) Mudstone; E) Opaque nodule; F) Fragment of sedimentary lithoclast with carbonate cement; G-H) Paste of petrogroup LR-P-4. Scalebar length = 0.1 cm. Figure in color in the electronic versión.
clay) to 15%, with the highest concentration (20%) in the sample K-4 and clay from the Komariv’s quarry. Petrographic specificity is noted for the petrogroup LR-P-4, while its individuals also vary in proportion and size of natural clastic inclusions.

**X-Ray diffraction analysis**

One or two characteristic samples for each petrogroup were selected for the XRD analysis (fig. 7A-D). The common phases are quartz and alkali feldspars. Albite and illite/muscovite are found in most of the samples, while calcite seems to be common for petrogroup LR-P-1 (fig. 7A). The content of feldspar (alkali + albite) in K-1, K-4, B-3-1 is found to be insignificant (fig. 7A lower, C-D), in K-2 and B-2-3 – medium (fig. 7A upper, B lower), in B-2-2 – the highest (here, probably, it exceeds quartz). The B-2-2 sample has the highest illite/muscovite content (fig. 7D upper).

To determine the equivalent firing temperatures, the presence or absence of certain mineral phases is of fundamental importance. For example, calcite decrystallisation is associated with a temperature of 800-900°C (although it depends on many factors — both the firing conditions and duration as well as the amount and form of calcite). The peak of illite/muscovite — the most common among the clay minerals — disappears between 900-950°C. It should be noted that no explicit amorphous phase and high-temperature minerals characteristic of carbonate clays (gehlenite, diopside, wolastonite), whose formation begins at temperatures above 800-850°C, were documented in our samples. Such features point at the fact the slight difference in the phase composition (presence/absence of calcite, albite and illite/muscovite) can be attributed to the varying degree of the heating impact on the products (Rice, 1987:102-104; Cultrone et al., 2001; Albero, 2014:95, fig. 12:1; Quinn, 2022:fig. 9.37). Sample B-2-2 is distinguished by its mineralogical composition, which confirms the previous observations.

**Microstructure and elemental analysis (SEM-EDS)**

The SEM-images of fresh breaks and polished sections of the samples in a secondary electron mode allowed to observe the degree of matrix vitrification. We used the classification of degrees of vitrification proposed basing on the results of experimental firings (Maniatis and Tite, 1981).

Micromass of the majority of the samples show continuous vitrification (CV, fig. 7E), less often – extensive vitrification (V). K-2 and B-2-3 show signs of continuous vitrification, with formation of dominantly fine (>4 μm) bloating pores, or CV/FB (fig. 7F). To correlate these features with other technological peculiarities, a more representative sample should be analysed.

The average composition of the samples matrix is shown in table 2. Clustering have allowed to identify three groups of samples with close chemical composition...
Fig. 7.—Diffractograms and SEM-images (secondary electron mode) of the Late Roman Group samples: A) Samples B-2-3 (upper), K-1 (lower); B) Samples B-2-2 (upper), K-2 (lower); C) Sample B-3-1; D) Sample K-4; E) Sample B-2-2, fresh break (example of continuously vitrified matrix, CV); F) Sample B-3-2, polished section (example of continuously vitrified matrix with bloating voids, CV(FB)).
<table>
<thead>
<tr>
<th>Sample</th>
<th>Na₂O</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>P₂O₅</th>
<th>K₂O</th>
<th>CaO</th>
<th>TiO₂</th>
<th>MnO</th>
<th>FeO</th>
<th>Summ</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-2-1</td>
<td>0.4 (106.31)</td>
<td>4.6 (5.74)</td>
<td>17.0 (1.97)</td>
<td>58.2 (0.87)</td>
<td>0.0 (3.09)</td>
<td>3.4 (2.08)</td>
<td>7.9 (33.25)</td>
<td>4.0 (106.34)</td>
<td>0.1 (2.82)</td>
<td>6.9 (18.07)</td>
<td>100</td>
</tr>
<tr>
<td>B-2-2</td>
<td>0.3 (127.37)</td>
<td>2.1 (10.37)</td>
<td>24.1 (1.37)</td>
<td>59.1 (0.78)</td>
<td>0.2 (756.63)</td>
<td>6.7 (1.89)</td>
<td>0.5 (19.13)</td>
<td>1.6 (9.59)</td>
<td>0.0 (345.89)</td>
<td>5.4 (3.13)</td>
<td>100</td>
</tr>
<tr>
<td>B-2-3</td>
<td>0.4 (609.40)</td>
<td>3.5 (7.50)</td>
<td>18.7 (1.82)</td>
<td>58.7 (0.83)</td>
<td>0.4 (139.92)</td>
<td>3.9 (3.45)</td>
<td>3.9 (4.82)</td>
<td>0.8 (74.76)</td>
<td>0.1 (61.69)</td>
<td>9.7 (2.41)</td>
<td>100</td>
</tr>
<tr>
<td>B-2-4</td>
<td>0.6 (360.79)</td>
<td>3.5 (6.44)</td>
<td>17.0 (1.77)</td>
<td>62.3 (0.76)</td>
<td>0.5 (36.32)</td>
<td>3.4 (2.60)</td>
<td>6.6 (7.30)</td>
<td>0.2 (146.82)</td>
<td>0.0 (353.58)</td>
<td>5.8 (2.76)</td>
<td>100</td>
</tr>
<tr>
<td>B-3-1</td>
<td>0.2 (100.78)</td>
<td>2.9 (7.38)</td>
<td>19.9 (1.45)</td>
<td>60.2 (0.71)</td>
<td>0.7 (27.35)</td>
<td>4.0 (2.49)</td>
<td>4.2 (3.69)</td>
<td>0.8 (17.32)</td>
<td>0.1 (270.43)</td>
<td>7.0 (2.46)</td>
<td>100</td>
</tr>
<tr>
<td>B-3-2</td>
<td>0.6 (99.29)</td>
<td>3.1 (7.15)</td>
<td>20.2 (1.50)</td>
<td>56.8 (0.77)</td>
<td>0.4 (77.04)</td>
<td>3.7 (2.52)</td>
<td>7.8 (1.91)</td>
<td>0.7 (20.03)</td>
<td>0.1 (241.25)</td>
<td>6.8 (2.49)</td>
<td>100</td>
</tr>
<tr>
<td>K-1</td>
<td>0.4 (295.65)</td>
<td>3.4 (7.19)</td>
<td>19.8 (1.81)</td>
<td>57.9 (0.91)</td>
<td>1.2 (17.56)</td>
<td>3.3 (3.23)</td>
<td>6.6 (2.25)</td>
<td>0.3 (63.63)</td>
<td>0.1 (444.71)</td>
<td>6.9 (2.88)</td>
<td>100</td>
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<tr>
<td>K-2</td>
<td>0.5 (181.53)</td>
<td>2.9 (7.90)</td>
<td>18.7 (1.79)</td>
<td>61.1 (0.85)</td>
<td>0.4 (837.43)</td>
<td>4.2 (3.04)</td>
<td>5.6 (2.47)</td>
<td>0.6 (19.75)</td>
<td>0.2 (90.01)</td>
<td>6.0 (3.05)</td>
<td>100</td>
</tr>
<tr>
<td>K-3</td>
<td>1.8 (35.22)</td>
<td>2.0 (11.71)</td>
<td>20.1 (1.86)</td>
<td>66.1 (0.88)</td>
<td>1.2 (18.41)</td>
<td>3.0 (3.55)</td>
<td>1.5 (6.66)</td>
<td>0.3 (44.12)</td>
<td>0.0 (172.33)</td>
<td>3.7 (4.26)</td>
<td>100</td>
</tr>
<tr>
<td>K-4</td>
<td>0.3 (121.942)</td>
<td>1.7 (13.914)</td>
<td>15.2 (2.202)</td>
<td>72.6 (0.802)</td>
<td>0.8 (26.17)</td>
<td>2.9 (3.642)</td>
<td>1.2 (7.836)</td>
<td>0.3 (58.538)</td>
<td>0.2 (53.558)</td>
<td>4.9 (3.648)</td>
<td>100</td>
</tr>
<tr>
<td>K-5</td>
<td>0.1 (1192.42)</td>
<td>3.2 (10.84)</td>
<td>20.2 (1.82)</td>
<td>55.7 (0.92)</td>
<td>0.9 (19.08)</td>
<td>4.4 (3.19)</td>
<td>9.9 (9.64)</td>
<td>0.3 (21.31)</td>
<td>0.1 (98.8)</td>
<td>5.0 (2.61)</td>
<td>100</td>
</tr>
<tr>
<td>Raw clay #1</td>
<td>0.1 (174.94)</td>
<td>2.2 (8.658)</td>
<td>21.9 (2.146)</td>
<td>62.2 (1.05)</td>
<td>1.1 (24.862)</td>
<td>3.5 (2.326)</td>
<td>0.9 (2.33)</td>
<td>0.5 (385.756)</td>
<td>0.1 (82.69)</td>
<td>7.3 (3.558)</td>
<td>100</td>
</tr>
</tbody>
</table>

**TABLE 2**
ELEMENTAL COMPOSITION OF THE LATE ROMAN GROUP SAMPLES (EDS ANALYSIS). AVERAGE VALUES FOR 5-POINT MEASURES
The Average Analytical Error is Given in Parentheses.
of their matrix (fig. 8A). In the absence of data on the bulk of minor and trace elements, elemental classification is considered to be preliminary, reflecting the mineralogical composition of the clayey matrix.

The LR-E-1 Group comprises most of the Buzovytsia and Komariv’s samples. Group LR-E-2 includes sample B-2-2 which mineralogical peculiarity has been noted earlier, and the raw clay sample#1. They are distinguished by high SiO$_2$, Al$_2$O$_3$ and K$_2$O (B-2-2), low MgO and the lowest CaO. Group LR-E-3 includes samples of petrogroup LR-P-4, its peculiarities are high SiO$_2$ (K-3) and relatively low CaO and FeO. Moreover, the elemental composition of each “atypical” sample has its own specifics (fig. 8B). Though, the chemical classification is consistent with other technological observations, with the accumulation of data the groups probably will be reformatted.

Archaeometric characterization of the Old Rus’ Group

Macro-features

As it has already been mentioned, the samples of the Group are quite diverse in their visual features (table 3). This technological variability looks so significant that, out of context, it would be logical to associate the different fabrics with different technological traditions. Within the “pilot” scope of our study, we have selected only a few of the available varieties of the Old Rus’ bricks from the 35 Spaska Street excavation, but have not exhausted their diversity.

Almost all the parameters (colour, feel, fracture, hardness) were highly variable due to the use of different types of clay, as well as to the practice of their mixing. Particularly striking is the difference in the hardness values ranging from “2” to “6”. In contrast to the Late Roman materials, the cross-cuts of all items are fully oxidised.

Fabric and petrographic classification

The classification is based on the parameters of raw material and technology (table 4). We have identified five fabrics and corresponding petrogroups: (1) slag and grog tempered (OR-F-1, OR-P-1); (2) heterogeneous lumpy (OR-F-2, OR-P-2); (3) silty, heterogeneous, argillaceous rock tempered (OR-F-3, OR-P-3); (4) gritty, limestone tempered (OR-F-4, OR-P-4); (5) untempered (OR-F-5, OR-P-5) (fig. 9). Each group/sample has specificity both in terms of material and technology, resulting in variations in the parameters of the non-plastic inclusions.

Petrogroup OR-P-1 is characterized by bimodal aplastic distribution which make up 20-20% of the area (fig. 10A-B). The coarse fraction (0.1-3.5 mm) constitute only 5%, is represented by predominant slag debris (fig. 10G) and accessory grog. The fine fraction (<1 mm) consists of predominant angular quartz. Feldspars,
polycrystalline quartz, chert, mullite and hematite clots as accessories. The matrix occupies 75%, is non-calcareuos, optically almost inactive (sintered), heterogeneous, with white and dark-red lumps. The use of a non-ferrugineous (kaolinite) clay with the scarce addition of a ferrugineous one is admitted in a handsample. The voids are micro-channels, and a few coarse vughs (caused by burnout of the organics).

Fig. 8.—Results of matrix elemental composition analysis by SEM-EDS: A) Cluster dendrogram (for non-normalized data); B) Ternary plot for some major elements. Figure in color in the electronic versión.
### TABLE 3
CONTEXTUAL, MORPHOLOGICAL AND PHYSICAL CHARACTERISTICS OF THE OLD RUS’ GROUP SAMPLES

<table>
<thead>
<tr>
<th>Individual #</th>
<th>Category / morphology</th>
<th>Site / context</th>
<th>Surface color (general name)</th>
<th>Cross-cut color pattern</th>
<th>Hardness (after Mohs scale)</th>
<th>Surface feel</th>
<th>Fracture</th>
<th>Methods applied</th>
<th>Petrogroup #</th>
<th>EDS group #</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sp-1</td>
<td>brick / square or rectangular</td>
<td>Kyiv / Spaska-35, cultural layer</td>
<td>pale yellow to whitish</td>
<td>completely oxidized</td>
<td>4</td>
<td>powdery</td>
<td>earthy</td>
<td>petrography, XRD</td>
<td>OR-P-1, slag and grog tempered</td>
<td>-</td>
</tr>
<tr>
<td>Sp-2</td>
<td>brick / square or rectangular</td>
<td>Kyiv / Spaska-35, cultural layer</td>
<td>orange to pale yellow</td>
<td>completely oxidized</td>
<td>2</td>
<td>powdery</td>
<td>earthy</td>
<td>petrography, XRD</td>
<td>OR-P-2, heterogeneous, lumpy</td>
<td>-</td>
</tr>
<tr>
<td>Sp-3</td>
<td>brick / square or rectangular</td>
<td>Kyiv / Spaska-35, cultural layer</td>
<td>pink to pale pink</td>
<td>completely oxidized</td>
<td>5</td>
<td>harsh</td>
<td>earthy</td>
<td>petrography, XRD</td>
<td>OR-P-3, silty, heterogeneous, with argillaceous temper</td>
<td>-</td>
</tr>
<tr>
<td>Sp-4</td>
<td>brick / square or rectangular</td>
<td>Kyiv / Spaska-35, cultural layer</td>
<td>grayish-brown</td>
<td>completely oxidized</td>
<td>6</td>
<td>harsh</td>
<td>granular</td>
<td>petrography, XRD</td>
<td>OR-P-4, gritty, limestone tempered</td>
<td>-</td>
</tr>
<tr>
<td>Vas-1</td>
<td>tile / rectangular</td>
<td>Vasyliv / surveys</td>
<td>orange</td>
<td>completely oxidized</td>
<td>3</td>
<td>rough, little bit powdery</td>
<td>earthy</td>
<td>petrography, XRD</td>
<td>OR-P-5, untempered</td>
<td>-</td>
</tr>
<tr>
<td>Vas-2</td>
<td>tile / rectangular</td>
<td>Vasyliv / surveys</td>
<td>orange</td>
<td>completely oxidized</td>
<td>4</td>
<td>rough, little bit powdery</td>
<td>earthy</td>
<td>petrography</td>
<td>OR-P-5, untempered</td>
<td>-</td>
</tr>
</tbody>
</table>
TABLE 4
ARCHAEOMETRIC CHARACTERISTICS OF THE SAMPLES.

Minerals Abbreviations After: (Kretz, 1983; With Additions By: Whitney & Evans, 2010). LR-F#, OR-F# – fabric cipher; LR-P#, OR-P# – petrographic group cipher; LR-E#, OR-E# – compositional group cipher; Qz – quartz; Afs – alkali feldspar; Ill/Ms – illite/muscovite; Ab – albite; Cal – calcite; Mul – mullite; Crs – cristobalite; V – extensive vitrification; CV(CB) – continuous vitrification with coarse bloating pores.

<table>
<thead>
<tr>
<th>Individual #</th>
<th>Fabric #</th>
<th>Petrogroup #</th>
<th>Phase composition (XRD)</th>
<th>EDS group #</th>
<th>Microstructure type</th>
<th>Recipe</th>
<th>Equivalent firing temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-2-1</td>
<td>LR-F-3</td>
<td>LR-P-3</td>
<td>-</td>
<td>LR-E-1</td>
<td>CV</td>
<td>clay+polymin. sand/pebbles</td>
<td>?</td>
</tr>
<tr>
<td>B-2-2</td>
<td>LR-F-2</td>
<td>LR-P-2</td>
<td>Qz, Afs, Ill/Ms, Ab</td>
<td>LR-E-2</td>
<td>CV</td>
<td>clay+shale</td>
<td>850-900</td>
</tr>
<tr>
<td>B-2-3</td>
<td>LR-F-1</td>
<td>LR-P-1</td>
<td>Qz, Afs, Ill/Ms, Cal, Ab</td>
<td>LR-E-1</td>
<td>V</td>
<td>clay+shale</td>
<td>750-800</td>
</tr>
<tr>
<td>B-2-4</td>
<td>LR-F-1</td>
<td>LR-P-1</td>
<td>-</td>
<td>LR-E-1</td>
<td>CV</td>
<td>clay+shale</td>
<td>?</td>
</tr>
<tr>
<td>B-3-1</td>
<td>LR-F-3</td>
<td>LR-P-3</td>
<td>Qz, Afs, Ab</td>
<td>LR-E-1</td>
<td>CV</td>
<td>clay+polymin. sand/pebbles</td>
<td>&gt;900?</td>
</tr>
<tr>
<td>B-3-2</td>
<td>LR-F-1</td>
<td>LR-P-1</td>
<td>-</td>
<td>LR-E-1</td>
<td>CV/FB</td>
<td>clay+shale</td>
<td>?</td>
</tr>
<tr>
<td>K-1</td>
<td>LR-F-1</td>
<td>LR-P-1</td>
<td>Qz, Afs, Ill/Ms, Cal</td>
<td>LR-E-1</td>
<td>V</td>
<td>clay+shale</td>
<td>750-800</td>
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<tr>
<td>K-2</td>
<td>LR-F-2</td>
<td>LR-P-2</td>
<td>Qz, Afs, Ab</td>
<td>LR-E-1</td>
<td>CV(FB)</td>
<td>clay+shale</td>
<td>&gt;900?</td>
</tr>
<tr>
<td>K-3</td>
<td>LR-F-4</td>
<td>LR-P-4</td>
<td>-</td>
<td>LR-E-3</td>
<td>CV</td>
<td>clay (processed?)</td>
<td>?</td>
</tr>
<tr>
<td>K-4</td>
<td>LR-F-4</td>
<td>LR-P-4</td>
<td>Qz, Afs, Ab</td>
<td>LR-E-3</td>
<td>CV</td>
<td>Clay (processed?)</td>
<td>&gt;900?</td>
</tr>
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<td>K-5</td>
<td>LR-F-3</td>
<td>LR-P-3</td>
<td>-</td>
<td>LR-E-1</td>
<td>V</td>
<td>clay+polymin. and pebbles</td>
<td>?</td>
</tr>
<tr>
<td>Sp-1</td>
<td>OR-F-1</td>
<td>OR-P-1</td>
<td>Qz, Afs, Mul, Crs</td>
<td>-</td>
<td>-</td>
<td>two clays+slag and grog+organics</td>
<td>&gt;1000</td>
</tr>
<tr>
<td>Sp-2</td>
<td>OR-F-2</td>
<td>OR-P-2</td>
<td>Qz, Ab, Ill/Ms</td>
<td>-</td>
<td>-</td>
<td>three clays (wet and dry) + organics</td>
<td>800-900</td>
</tr>
<tr>
<td>Sp-3</td>
<td>OR-F-3</td>
<td>OR-P-3</td>
<td>Qz, Afs</td>
<td>-</td>
<td>-</td>
<td>two clays+argillaceous temper+organics</td>
<td>800-900</td>
</tr>
<tr>
<td>Sp-4</td>
<td>OR-F-4</td>
<td>OR-P-4</td>
<td>Qz, Mul, amorphous phase</td>
<td>-</td>
<td>-</td>
<td>clay+limestone</td>
<td>&gt;1000</td>
</tr>
<tr>
<td>Vas-1</td>
<td>OR-F-5</td>
<td>OR-P-5</td>
<td>Ill/Mus, Qz, Ab</td>
<td>-</td>
<td>-</td>
<td>clay (processed?)</td>
<td>800-900</td>
</tr>
<tr>
<td>Vas-2</td>
<td>OR-F-5</td>
<td>OR-P-5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>clay (processed?)</td>
<td>800-900</td>
</tr>
</tbody>
</table>
Petrogroup OR-P-2 has 10-15% of non-plastic inclusions (fig. 10C-D). The differently coloured lumps, taking of about 35%, could have a twofold interpretation: as a temper of a dry crushed clay, or in terms of an attempt to mix several types of clayey material, some of which were in a dry or semi-dry state. Here we accept the second solution. The fine (natural) fraction of inclusions (<1 mm) consists of predominant quartz, frequent feldspars, muscovite and hematite, accessory biotite and sedimentary lithoclasts. The matrix which occupies 80-85% is non-calcareous, slightly optically active, heterogeneous, with lumps of clay, frequent hematite clots and rare texture concentration features. The voids are the same as in the previous group.

In petrogroup OR-P-3 inclusions take 10% (fig. 10E-F). The coarse fraction (<22 mm) constitutes 35% and is represented by predominant argillaceous rock
Fig. 10.—Photomicrographs of thin sections of the Old Rus’ Group ceramics: A-B) Paste of petrogroup OR-P-1; C-D) Paste of petrogroup OR-P-2; E-F) Paste of petrogroup OR-P-3; G) Slag inclusion, petrogroup OR-P-1; H) Argillaceous inclusion, petrogroup OR-P-3. Scalebar length = 0.1 cm. Figure in color in the electronic versión.
(fig. 10H) and accessory opaques. The fine fraction (<1 mm) is represented by predominant quartz and accessory feldspars, muscovite, polycrystalline quartz and biotite. The matrix occupies c. 80%; it’s non-calcareous, slightly optically active, heterogeneous, with differently coloured streaks and swirls. Thus, Sp-3 sample was produced from a mixture of two types of wet clay. The voids are micro-, meso-, macro-channels, coarse vughs and planar voids (caused by burnout of the organics and shrinkage).

Petrogroup OR-P-4 has the highest concentration of non-plastic inclusions, 35-40% (fig. 11A-B). The coarse fraction (<25 mm) takes 55% of inclusions, and is represented by fragments of limestone. They are rich in quartz grit, partly melted and demonstrate meso-vesicles (bloating voids). In the fine fraction (<1 mm), quartz grit predominates, mullite is frequent and polycrystalline quartz is accessory. The matrix takes c. 50%, is non-calcareous, vitrified, highly heterogeneous (vitrified micromass areas bound with limestone debris). Micro-porosity is uncommon due to the matrix vitrification, but the sample is saturated with medium and coarse vesicles and planar (overfiring) voids.

In petrogroup OR-P-5 (peculiar to tiles), the share of aplastics is 25-30%, from moderately to poorly sorted (fig. 11C-D). The maximum inclusion size is 0.5-1 mm. Quartz predominates, while polycrystalline quartz, feldspars, chert, muscovite, biotite and metamorphic rock are accessories. The matrix occupies c. 65-70%, is non-calcareous, optically active or with relics of optical activity, homogeneous, with very few texture concentration features and opaques. The voids are scarce and represented by micro-channels and medium planar and channels (caused by gas releasing and shrinkage).

Summarizing the observations on petro-features, the trend towards admixing poorly crushed and unsieved temper (products of iron-working, limestone, dry clay) to brick paste is quite clear in the Old Rus’ Group technological tradition. Its another striking feature is an unthorough mixing of different sorts of clay in different proportions and state, that causes heterogeneity of the matrix (in colour, texture etc.). A small number (approx. 5%) of characteristic coarse pores in these samples indicate the presence of a burned-out plant admixture. The Sp-4 is peculiar for heavily “sanded” clay and vitrified matrix. Tiny glassy debris is common for the paste. This as well as the high quartz content caused significant hardness of the mass. The Fifth fabric and petrogroup doesn’t have coarse inclusions, except for ceramoclasts probably of natural origin.

X-Ray diffraction analysis

In terms of phase composition, the Middle Ages samples demonstrate individual features. From the point of the reconstruction of equivalent firing temperatures, the diffractograms can be divided into two groups. The first one demonstrates signs associated with the impact of temperatures in the range of 800-900°C, the second one points on temperatures higher than 1000°C.
The first group is characterized by the absence of secondary phase signals and signs of clay vitrification (fig. 11B,C,E). The presence of illite/muscovite is common. Its decrystallization is known to last up to 950-1000°C (Quinn, 2022: fig. 9.37), though, the neoformation is also possible (Albero, 2014: 90-91). This suggests that the part of the “Old Rus’ Group” pieces was impacted by the heating energy approximately equivalent to that achieved during the firing of the Late Roman bricks.

The second group is characterized by the presence of high-temperature phases – mullite, β-cristobalite, as well as the amorphous phase (Sp-4) (fig. 11A,D). Mullite is usually detected from 1050°C in kaolinite and at lower temperatures in smectite and illite clays (Rice, 1987:90-92; Rodriguez-Navarro et al., 2003). Extensive forming of the glassy phase in the Sp-4 can be explained by the presence of the limestone temper: carbonates (comprising Ca and Mg) act as a flux, causing matrix melting at temperatures close to 800°C (Maniatis, Tite, 1981; Cultrone et al., 2001:630). Stable cristobalite, which was detected in the Sp-1, is formed at above 1470°C, namely from silicium dioxide released from mullite nucleation. However, the presence of K₂O can lower this threshold (Rice, 1987:91-92, 95; Albero, 2014: fig. 12:1).
Fig. 12.—Diffractograms of selected samples of the Old Rus’ Group: A) Sample Sp-1; B) Sample Sp-2; C) Sample Sp-3; D) Sample Sp-4; E) Sample Vas-1.
DISCUSSION AND CONCLUSIONS

The main result of the research is the beginning of petrographic and geochemical classification of archaeological building ceramics from sites of the Central and South-Eastern Ukraine. We also consider it possible to give early answers to the questions posed at the beginning of the work.

(1) Is the technology of the Buzovytzia-1 and Komariv settlements consistent? The data obtained seem to be sufficient to give a positive answer to this question. Not only the range of technological features behind which the system can be seen, but also the parameters of their variability are common for the two sites. This indicates technological and, quite probably, raw material similarity of most of the bricks analyzed. The commonalities are: the presence of three of four petrographic groups on both the sites; compositional similarity; similarity in phase patterns and other data.

(2) The Late Roman Group: features of the chaînes opératoires. The use of two different technological procedures for the production of the building ceramics in question has to be noted.

The first one is associated with the First, Second and Third petro-groups and related to brick production. The slightly calcareous, medium/fine grained, moderately sanded clays were mainly used. Their principal feature is a carbonate component related to the composition of the proto-lith of the clay. Fine fraction of non-plastic inclusions consists of quartz, feldspars, calcite and sedimentary lithoclasts with calcitic cement, skeletal remains of microfauna. “Heavy” minerals are quite rare. Mineralogical and petrographic traits of the raw material and temper correspond to geological features of the eastern-north part of the Volyn-Podillia Plate, where investigated sites are located (Syplivyi et al., 1974). Specific is the clay of the B-2-2 sample which also demonstrates the distinctive chemical composition, close to that of the clay sample#1.

The paste was tempered with a mineral admixture. The presence of an organic temper in a relatively liquid state is under question. The temper is argillaceous rock (shale) or sand with pebbles – the material which was probably available in an immediate vicinity of the clay outcrops. Common concentration of the coarse fraction is 15-20% by area, the inclusion size does not exceed 5 mm. Equant shale particles are well oriented towards the broad faces of the bricks, which indirectly indicates the use of molds and a fluid state of the paste. Imprints of mould boxes are also often visible on the backsides of the pieces. The void area, which may be assigned to burnt organic component, does not exceed 5%.

The products were fired in an oxidizing atmosphere. Variations in the presence/absence of calcite, illite/muscovite, the absence of amorphous phase and indicative high-temperature minerals, indicate that the maximum temperatures oscillated around 800-950°C. High-temperature firing is
also attested by the strong vitrification, bloating pores in the matrix and shale inclusions, absence of calcite signals in some samples. Judging by the brick colour, the soaking time hardly exceeded one hour. For the First Fabric, probably associated with the presence of calcite, the temperature range is set at 750-800°C. For those samples which demonstrate signals of illite/muscovite (without calcite), it is assumed to stand at 850-900°C, for those without clay mineral signals – at >900°C. However, some of these samples show signs of continuous vitrification and even a bloating pores formation (“incipient pores”), which is interpreted as a sign of a fast heating rate during firing (Maniatis and Tite 1981:61).

The other type of operational chain for the Late Roman Group is related to the Fourth Fabric – the products with unspecified function. They are distinguished by the absence of temper and organics, and the use of non-calcareous clays which differ from the bulk of the samples by the composition of the silicate matrix.

(3) A comparison of the Late Roman and Old Rus’ groups. Can archaeometric data be an argument for the cultural-chronological expertise? Not forgetting that the samples are small, let us note the obvious potential of the data obtained for such kind of speculations (table 4).

Ceramics of the Late Roman settlements seem to be more uniform in terms of technology. The clay mixing and an organic (vegetal) temper is uncommon. Despite of somewhat similar type of particular temper (argillaceous inclusions), its concentration in the Late Roman products is noticeably higher. The intensity of firing (or repeated firing?) is statistically higher for the Medieval products, although some of them seem to fall in a temperature range of 800-900°C.

The information obtained needs to be refined during investigation of representative samples, which we hope will be the basis for larger scale projects. The latter may include a number of issues that have not yet been developed, such as: (1) the ways of disseminating of the Late Roman building technologies in the Eastern Barbaricum, the mechanisms of their adaption and evolution in a new ethno-cultural environment; (2) the same questions posed regarding the development of the technology of the Old Rus’ time; (3) investigation of general trends and specific scenarios of ceramic technology evolution in a wide spatial and chronological range.

ACKNOWLEDGEMENTS

The authors are grateful to two anonymous reviewers for their valuable and interesting comments, which helped to improve the paper.
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