

Article

Pottery of Early Iron Age from the Glinjeni II-La Șanț (North-Western Pontic Sea Region): Composition, Technology and Raw Material Sources

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Abstract: Transition to the Early Iron Age was marked by the appearance of innovations such as iron technology and changes in the lifestyle of local societies on the territory of the North-Western Pontic Sea region. One of the most interesting sites of this period is the Glinjeni II-La Șanț fortified settlement, located in the Middle Dniester basin (Republic of Moldova). Materials of different cultural traditions belonged to the Cozia-Saharna culture (10th–9th cc. BC) and the Basarabi-Șoldănești culture (8th–beginning of 7th cc. BC) were found on this site. The article presents the results of a multidisciplinary approach to the study of ceramic sherds from these archaeological complexes and cultural layers as well as raw clay sources from this area. The archaeometry analysis, such as the XRF-WD, the thin section analysis, SEM-EDX of ceramics, m-CT of pottery were carried out. The study of ancient pottery through a set of mineralogical and geochemical analytic methods allowed us to obtain new results about ceramic technology in different chronological periods, ceramic paste recipes and firing conditions. Correlation of archaeological and archaeometry data of ceramics from the Glinjeni II-La Șanț site gives us the possibility to differ earlier and later chronological markers in the paste recipes of pottery of 10th–beginning of 7th cc. BC in the region of the Middle Dniester basin.

Keywords: pottery of Early Iron Age; raw clay sources; archaeometry; Glinjeni II-La Șanț; North-Western Pontic Sea region; XRF-WD; thin section analysis; SEM-EDX of ceramics; m-CT of pottery

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1. Introduction

The modern analytic methods widely used in archaeology for ancient ceramic studies allow us to construct the relative chronology and to reconstruct the cultural and historical processes for the different areas of prehistoric Europe [1]. The authors had been considering these questions for a number of years in the framework of interdisciplinary projects devoted to investigations of the material culture of the Early Iron Age in Eastern Europe. The problem concerned the traditions and innovations in the different technological spheres, including the area of pottery technologies of mobile and sedentary societies of Eastern Europe involving also the western regions such as the North-Western Pontic Sea region [2–9]. The study of ancient pottery through a set of mineralogical and geochemical analytic methods gives us the possibility to obtain new interesting results about clay and temper compositions and reconstruct some of the technological processes for ceramic making such as firing conditions and determination of raw sources [10–13]. In

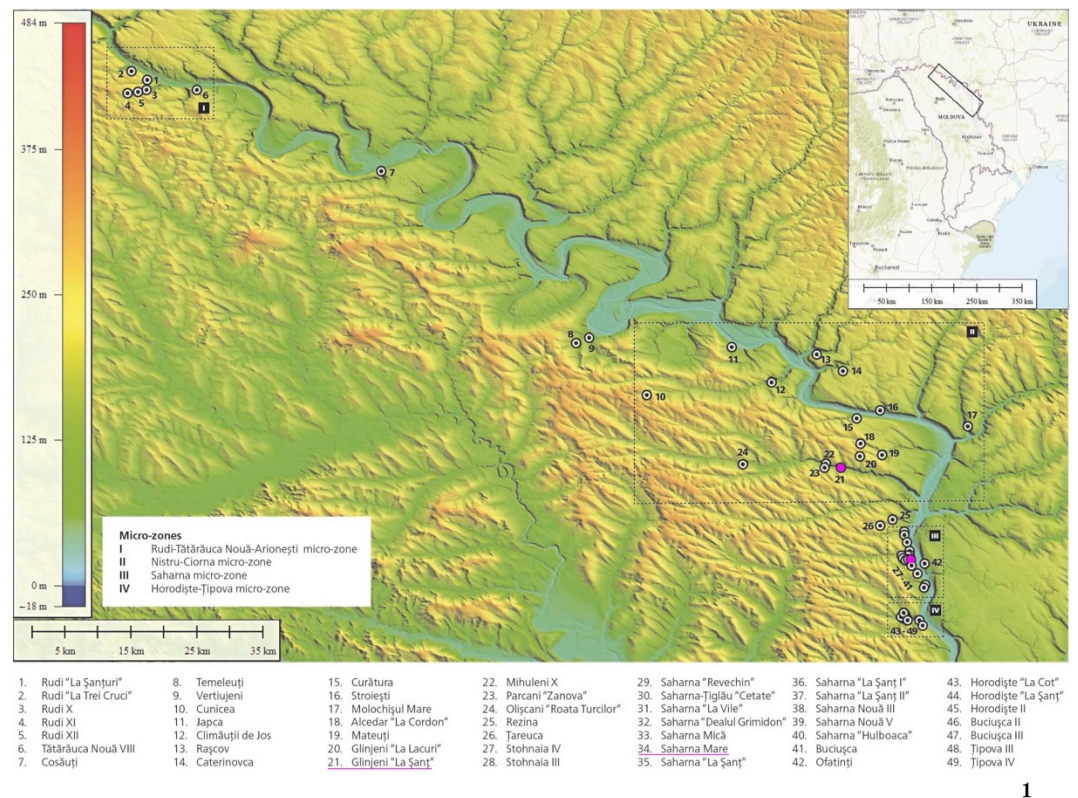
view of the above, the investigations of Early Iron Age pottery from archaeological sites of 10th–7th cc. BC in the Dniester river basin are very important. The transition to the Early Iron Age affects the appearance of not only the iron making process but also some changes in ceramic production and the development of new styles [14]. In the period of 11th–8th cc. BC, the first iron-making technologies had occurred in the Carpathian-Danube basin and the Northern Pontic Sea region. The North-Western Pontic Sea region at the beginning of 1st millennium BC was occupied by societies with different cultural traditions. The steppe cultures had local Northern-Pontic Sea or Eastern-Eurasian roots. Conversely, the forest-steppe zone of the Middle Dniester basin was inhabited by societies that were from the Carpathian Basin. During the first half of the 1st millennium BC, there were several waves of migrations and the material culture of outside tribes had some specific features, which was especially evident in the ceramic technology [15]. The first chronological schema of the Late Bronze–Early Iron Age cultures for the Middle Dniester region was based on traditional archaeological methods. The following sequence for cultural “outsider” traditions was developed: (1) Chişinău–Corlăteni, (2) Basarabi-Şoldăneşti, and (3) Cozia-Saharna [15,16]. These cultures were known as Thracian in historiography, but at present they were renamed the Carpathian-Danubian or Hallstattian [17,18]. The pottery of these cultural traditions is characterized by quality polish black or gray-black (rare light orange) walls decorated by fluting and/or a geometric carving ornament with white (rare with red) paste inlay.

At the end of the 20th century, the widescale excavations of the Glinjeni II-La Şanţ fortified settlement had been conducted (Figure 1). The archaeological materials from this site as well as other sites of the same age opened new perspectives on the existing cultural and chronological periodization [15–19]. According to stratigraphy, planography and typology of artifacts on the sites, another cultural periodization was developed: (1) Chişinău–Corlăteni, the 12th–10th cc. BC, (2) Cozia-Saharna, the 10th–9th cc. BC, and (3) Basarabi-Şoldăneşti, the 8th–beginning of 7th cc. BC. These cultural societies could coexist with each other [19,20].

Interestingly, new societies of the Basarabi-Şoldăneşti culture in ca. 800 BC settled on the places of the earlier Cozia-Saharna culture. On these settlements, numerous rebuilding houses and household constructions were registered. The old types of pottery were used, while new ceramic styles were widely distributed also. This is evidence of partial conservation of pottery technological traditions. However, the appearance of innovations in ceramic manufacture and a wide assortment of wares had considerably changed existing traditions [21,22]. These conclusions were assumed on the investigations of morphology and ornamentation of vessels. The archaeometry analysis of pottery of the Cozia-Saharna and the Basarabi-Şoldăneşti cultures has only recently been made possible [9]. This article presents the results of a multidisciplinary approach to the study of ceramic sherds from the archaeological complex and a cultural layer of the Glinjeni II-La Şanţ fortified settlement as well as raw clay sources from this area.

The main tasks set out in process of ceramic study from the Glinjeni II-La Şanţ site are: (1) studying the ceramic sherds by modern analytic methods for the reconstruction of ceramic paste composition and technological features; (2) to determine if there are any differences in composition and technology of the earlier Cozia-Saharna and later Basarabi-Şoldăneşti pottery. Some goals such as (3) to find out any causes of technological differences, whether it was chronological differences, local or import production, wares for cooking or table wares, etc.; (4) to establish the possible roots of technological traditions; (5) to clarify the question about mixing technologies in pottery making for cultures under consideration; (6) to consider if there are any analogies to pottery technology from other sites of the region, were set out as advanced investigations.

The description of the Glinjeni II-La Şanţ fortified settlement, located in the forest steppe zone of the Middle Dniester river region (North-Western Pontic Sea region) and the pottery samples from this site are reported in Appendix A.



1



2



3

Figure 1. Location of the Early Iron Age fortified sites in the Middle Dniester Region (1) the Glinjeni II-La Șanț (No. 21) and Saharna Mare (No. 34) sites were marked by magenta color. Pictures of the landscape of the Dniester-Ciorna micro-zone (2) and view at the fortified settlement Glinjeni II-La Șanț (3) according to publication [23].

2. Materials and Methods

2.1. Materials—Characterization of Site and Sampling Strategy

The Glinjeni II-La Șanț fortified settlement was occupied by societies of the earlier Cozia-Saharna and the later Basarabi-Șoldănești cultures during the 10th–beginning of 7th cc. BC. This was confirmed by the constructions of both the earlier Cozia-Saharna culture and later Basarabi-Șoldănești culture found in the process of excavations. Some structures were attributed to so-called mixed complexes, which existed for a long time and were rebuilt several times. The group of so-called mixed ceramics with elements of both cultural traditions was allocated [19,21,22]. Twenty samples of ceramic sherds for

archaeometry analysis were chosen from the collection of the National Museum of History of Moldova (Chişinău, Republic of Moldova) (Figures 2 and 3).

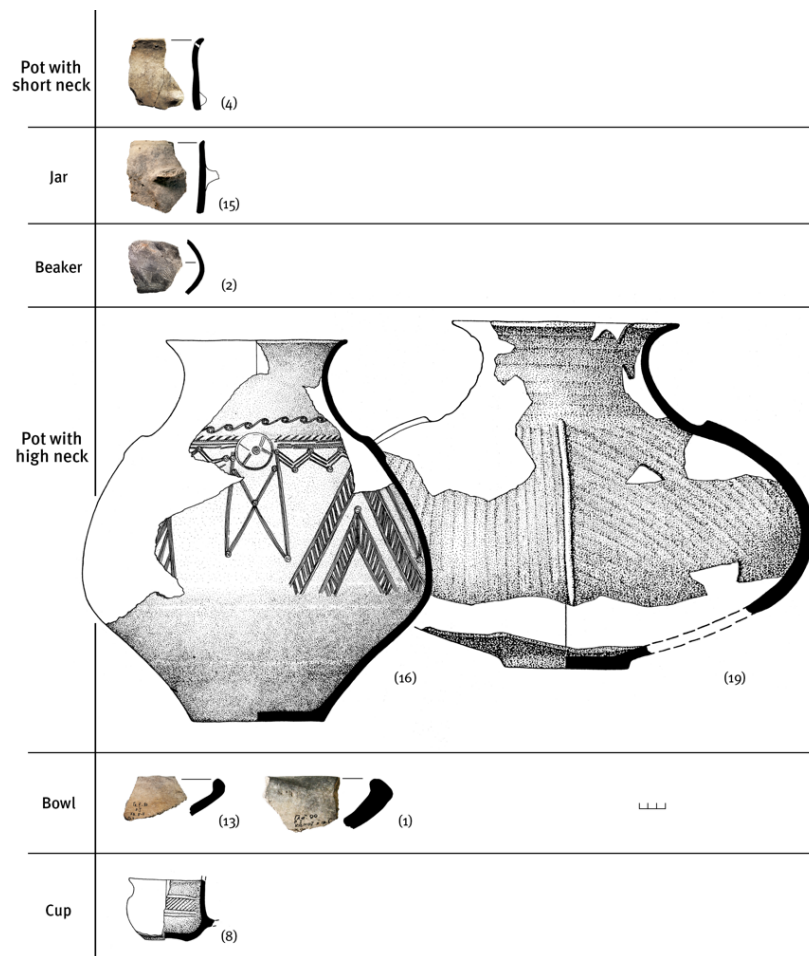


Figure 2. Glinjeni II-La Şanţ settlement. The main vessel types (types of the vessels and their numbers were assigned according to the database in [2]) and sherds that were analyzed.

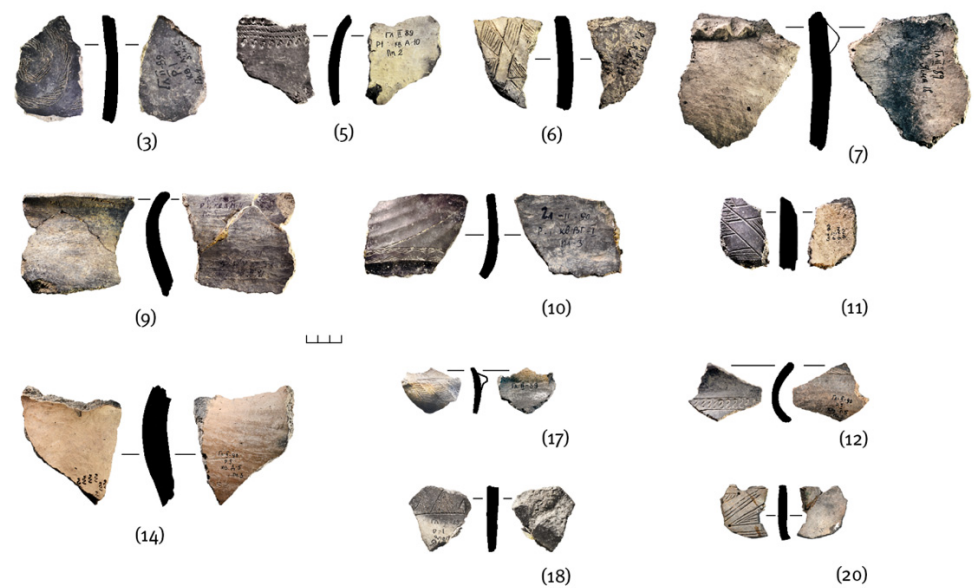


Figure 3. Glinjeni II-La Şanţ settlement. The ceramic sherds that had been analyzed (numbering is in accordance to the database in [2]).

In accordance with the ceramic database developed as a part of the Volkswagen Foundation project [2], the numeration of samples was from 1 to 20 (see also Table 1).

Table 1. Sampled ceramics from complexes and cultural level in the Glinjeni II-La Şanţ settlement. Modified from published database <https://doi.org/10.5281/zenodo.3521608> accessed on 29 October 2019. Key: * SPb—Saint Petersburg (Russia).

| Sample No. | Reference Code of the Depository | Kind of Feature; Trench, Sector; Depth (m), Position | Archaeological Culture; Dating of Sampled Ceramics | Vessel Form; Measurement (cm) | Colour Outer/Inner Surface |
|-------------|--|---|--|--|--|
| Hlinjeni 1 | ГЛ II-90, Р I, кв. HO I, II, ПЛ./ШТ. 5 | Cultural layer; I, sq. H,O -I,II; layer 5 (ca. 1 m) | Cozia-Saharna culture; 10th–9th cent. BC | Bowl; type I; Dr. ca. 22–24 | Dark and light gray, smoothed/ black, polished (burnished) |
| Hlinjeni 2 | ГЛ II-89, Р-I, яма 36 | Pit No. 36; I; sq. Б,В-9; undetermined | Cozia-Saharna culture; 10th–9th cent. BC | Beaker | Dark gray, spotted/dark gray, good polished (burnished) |
| Hlinjeni 3 | ГЛ II-89, Р. I, кв. Л-М 3; 4; 5, ПЛ./ШТ. 4 | Cultural layer; I; sq. Л,М-3,4,5; layer 4 (ca. 0.60–0.80 m) | Basarabi-Şoldăneşti culture; 8th–beginning of 7th cent. BC | Jug (or small pot with high neck) | Black/ black |
| Hlinjeni 4 | ГЛ II-89, Р. I, кв. В-9, ПЛ./ШТ. 2 | Cultural layer; I; sq. В-9; layer 2 (ca. 0.20–0.40 m) | Cozia-Saharna culture; 10th–9th cent. BC | Pot with short neck; type III | Light gray-orange/gray-orange, polished (burnished) |
| Hlinjeni 5 | ГЛ II-89, Р. I, кв. А-10, ПЛ./ШТ. 2 | Cultural layer; I; sq. А-10; layer 2 (ca. 0.20–0.40 m) | Basarabi-Şoldăneşti culture; 8th–beginning of 7th cent. BC | Indeterminable type: jug or small pot with high neck (?) | Black/light gray, polished (burnished) |
| Hlinjeni 6 | ГЛ II-89, Р. I, яма 18 | Pit No. 18; I; sq. 3,Ж-7,8; undetermined | Cozia-Saharna culture; 10th–9th cent. BC | Indeterminable type: small pot with high neck (?) | Gray-orange/gray, polished (burnished) |
| Hlinjeni 7 | ГЛ II-89, Р. I, яма 18 | Pit No. 18; I; sq. 3,Ж-7,8; undetermined | Cozia-Saharna culture; 10th–9th cent. BC | Pot with short neck; type III oder type IV | Gray-orange/black gray-orange, spotted |
| Hlinjeni 8 | ГЛ II-89, Р. I | Cultural layer; I; undetermined | Cozia-Saharna culture; 10th–9th cent. BC | Cup, Type I; H 6,6, Dr 7,5, Db 8,6, Dbt 4,3 | Black gray/black gray, polished (burnished) |
| Hlinjeni 9 | ГЛ II-89, Р. I, кв. Л-М 4, ПЛ./ШТ. 5 | Cultural layer; I; sq. Л,М-4; layer 5 (ca. 0.80–1.00 m) | Cozia-Saharna culture; 10th–9th cent. BC | Pot with short neck; type III | Gray-orange/black gray, polished (burnished) |
| Hlinjeni 10 | Л II-90, Р. I, кв. ВГ-I, ПЛ./ШТ. 3 | Cultural layer; I; sq. В,Г-I; layer 3 (ca. 0.40–0.60 m) | Basarabi-Şoldăneşti culture; 8th–beginning of 7th cent. BC | Jug | Black/dark gray |
| Hlinjeni 11 | ГЛ II-90, Р. I, яма 144, дно | Pit No. 144; sq. А,Б-12,13; I; pits bottom (1.65 m) | Cozia-Saharna culture; 10th–9th cent. BC | Pot with high neck; type I | Black/light orange |
| Hlinjeni 12 | ГЛ II-90, Р. I, кв. Г-5, ПЛ./ШТ. 2 | Cultural layer; I; sq. Г-5; layer 2 (ca. 0.20–0.40 m) | Cozia-Saharna culture; 10th–9th cent. BC | Indeterminable type: big cup (?); type I | Black/dark gray-orange, polished (burnished) |
| Hlinjeni 13 | ГЛ II-90, Р. I, кв. Б-4, ПЛ./ШТ. 4 | Cultural layer; I; sq. Б-4; layer 4 (ca. 0.60–0.80 m) | Basarabi-Şoldăneşti culture; 8th–beginning of 7th cent. BC | Bowl; Type I | Gray-orange/black |
| Hlinjeni 14 | ГЛ II-90, Р. I, кв. Д-5, ПЛ./ШТ. 3 | Cultural layer; I; sq. Д-5; layer 3 (ca. 0.40–0.60 m) | Cozia-Saharna culture; 10th–9th cent. BC | Indeterminable type: pot with high neck (?) | Orange/orange, polished (burnished) |
| Hlinjeni 15 | ГЛ II-89, Р. I, яма 18 | Pit No. 18; sq. 3,Ж-7,8; I; undetermined | Cozia-Saharna culture; 10th–9th cent. BC | Jar; type II | Dark gray-orange, spotted/ dark gray-orange, spotted |
| Hlinjeni 16 | Л II-90, Р. I, яма 126 | Pit No. 126; I; sq. а,А-5,6; undetermined | Cozia-Saharna culture; 10th–9th cent. BC | Pot with high neck; type II | Black/dark gray, good polished (burnished) |
| Hlinjeni 17 | ГЛ II-89, Р. I, р.с. 3 | Cultural layer; I; undetermined | Cozia-Saharna culture; 10th–9th cent. BC | Cup; type III | Dark gray-orange, spotted/ black, spotted |
| Hlinjeni 18 | ГЛ II-89, Р. I, яма 14 | Pit No. 14; sq. А,Б-11; I; undetermined | Cozia-Saharna culture; 10th–9th cent. BC | Pot with high neck; type I | Dark and light gray/dark gray, polished (burnished) |
| Hlinjeni 19 | ГЛ II-90, Р. I, яма 126 | Pit No. 126; sq. а,А-5,6; I; undetermined | Basarabi-Şoldăneşti culture; 8th–beginning of 7th cent. BC | Pot with high neck | Dark gray/gray, polished (burnished) |
| Hlinjeni 20 | ГЛ II-90, Р. I | Cultural layer; I; undetermined | Basarabi-Şoldăneşti culture; 8th–beginning of 7th cent. BC | Indeterminable type: pot with high neck (?) | Gray/light gray |

| Sample No. | Technique/ Pattern of Ornamentation | Incrustation | Photography/ Drawing | Sampled Part of Vessel | ANALYZES | | | | | | | | Comments Chemistry | |
|-------------|--|--------------|-------------------------|------------------------------|-------------------|---------------|----------|-----------------------|-----------------|------|------|---------|-----------------------|--------------------|
| | | | | | WD-XRF (SPb) * | m-CT (SPb) | Porosity | Rest/ org. Mass | Thin Section | XRD | DTA | ED X | | |
| Hlinjeni 1 | Fluted/geometric | No | Yes/no | Rim | Done | Done | Done | Rest | Done | | | | Done | |
| Hlinjeni 2 | Incised/geometric | No | Yes/no | Wall | Done | Done | Done | Rest | Done | Done | | | Done | SEM-EDX |
| Hlinjeni 3 | Incised/geometric | Yes | Yes/Yes | Wall | Done | Done | Done | Rest | Done | Done | Done | Done | Done | SEM-EDX |
| Hlinjeni 4 | Relief/vertically rectangular moulded knob | No | Yes/no | Rim and wall | Done | Done | Done | Rest | Done | Done | | | Done | SEM-EDX |
| Hlinjeni 5 | Fine toothed and S- like stamps/geometric | No | Yes/ Yes | Wall | Done | Done | Done | Rest | Done | Done | Done | Done | Done | |
| Hlinjeni 6 | Incised/geometric | No | Yes/no | Wall | Done | Done | Done | Rest | Done | | | | | |
| Hlinjeni 7 | Relief/high roller | No | Yes/no | Wall | Done | Done | Done | Rest | Done | | | | Done | |
| Hlinjeni 8 | Incised/geometric | No | Yes/Yes | Rim and wall | Done | Done | Done | 3.5 | Done | | | | | |
| Hlinjeni 9 | Relief/vertically rectangular moulded knob | No | Yes/no | Rim | Done | Done | Done | Rest | Done | | | | Done | |
| Hlinjeni 10 | Fine toothed stamp, fluted/geometric | Yes | Yes/Yes | Wall | Done | Done | Done | Rest | Done | Done | Done | Done | Done | SEM-EDX; TG-DTA |
| Hlinjeni 11 | Incised/geometric | No | Yes/Yes | Wall | Done | Done | Done | Small | Done | | | | Done | |
| Hlinjeni 12 | Fine toothed and S- like stamps/geometric | No | Yes/no | Wall | Done | Done | Done | 4.2 | Done | | | | Done | SEM-EDX |
| Hlinjeni 13 | Fluted | No | Yes/no | Rim | Done | | Done | 5.6 | Done | | | | | |
| Hlinjeni 14 | W-like stamp/geometric | No | Yes/no | Wall | Done | Done | Done | Rest | Done | | | | Done | |
| Hlinjeni 15 | Relief/vertically rectangular moulded knob | No | Yes/no | Rim and wall | Done | Done | Done | Rest | Done | | | | Done | |
| Hlinjeni 16 | Fine toothed stamp/geometric | No | Yes/Yes | Wall | Done | Done | Done | Rest | Done | | | | Done | SEM-EDX |
| Hlinjeni 17 | Incised/geometric | No | Yes/Yes | Wall | Done | Done | Done | 3.5 | Done | | | | Done | |
| Hlinjeni 18 | Incised/geometric | No | Yes/Yes | Wall | Done | | Done | 18.4 | Done | | | | | |
| Hlinjeni 19 | Fluted | No | Yes/Yes | Wall | Done | Done | Done | Rest | Done | | | | | |
| Hlinjeni 20 | Incised/geometric | No | Yes/no | Wall | Done | Done | Done | Rest | Done | | | | Done | |

Even though there are classifications of the Cozia-Saharna and the Basarabi-Şoldăneşti types of pottery for this region [20,21], in this article, we are using the applied classification based on the most significant and universal characteristics of vessel shapes [3]. The 10 clay specimens were sampled from outcrops on the shores of Dniester valley, near the Glinjeni II-La Şanţ and Saharna Mare sites (Figures 1, 4 and 5).

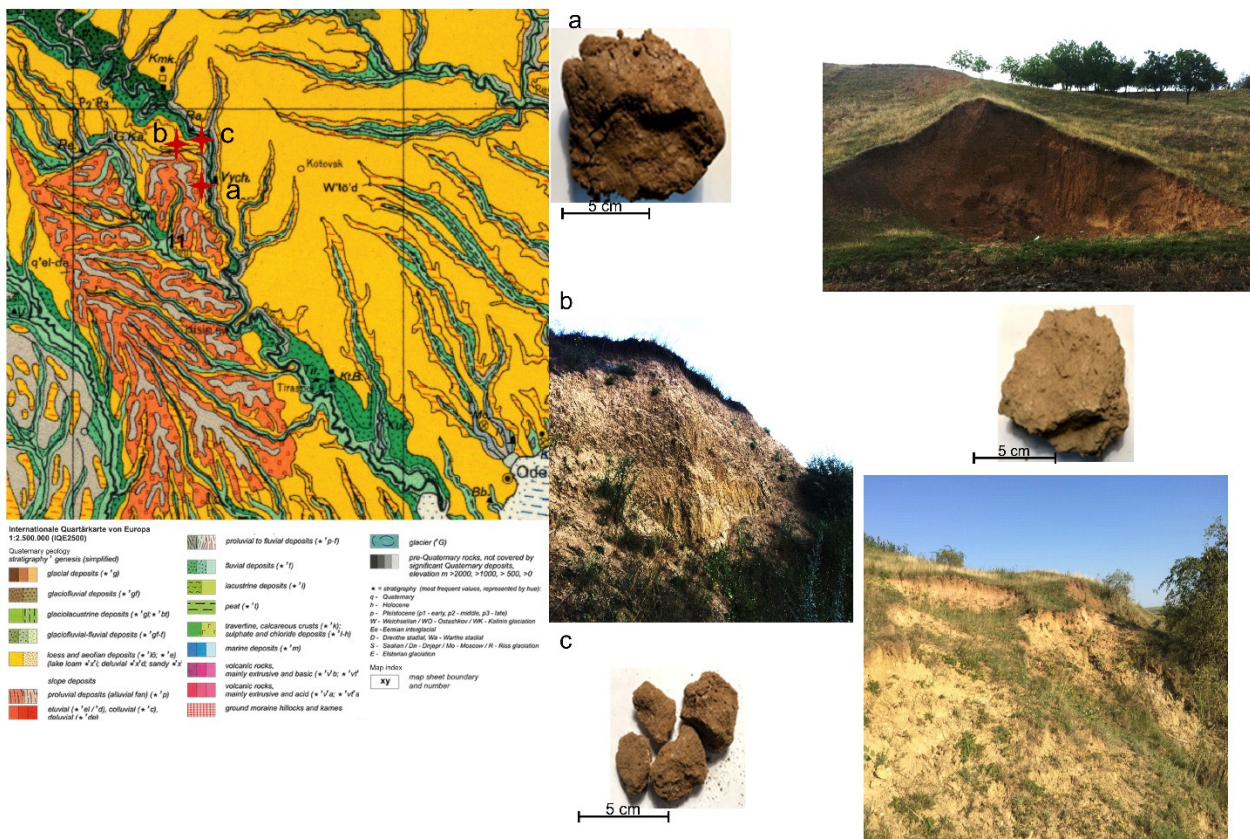


Figure 4. Map of quaternary deposits in the Moldova region (according to <https://geoviewer.bgr.de/mapapps4/resources/apps/geoviewer/index.html> accessed on: 26 July 2018) and places of outcrops of clay sediments (a) Glinjeni II-La Şanţ, (b) Saharna Mare, (c) Şoldăneşti, * stratigraphy (most frequent values, represented by hue).

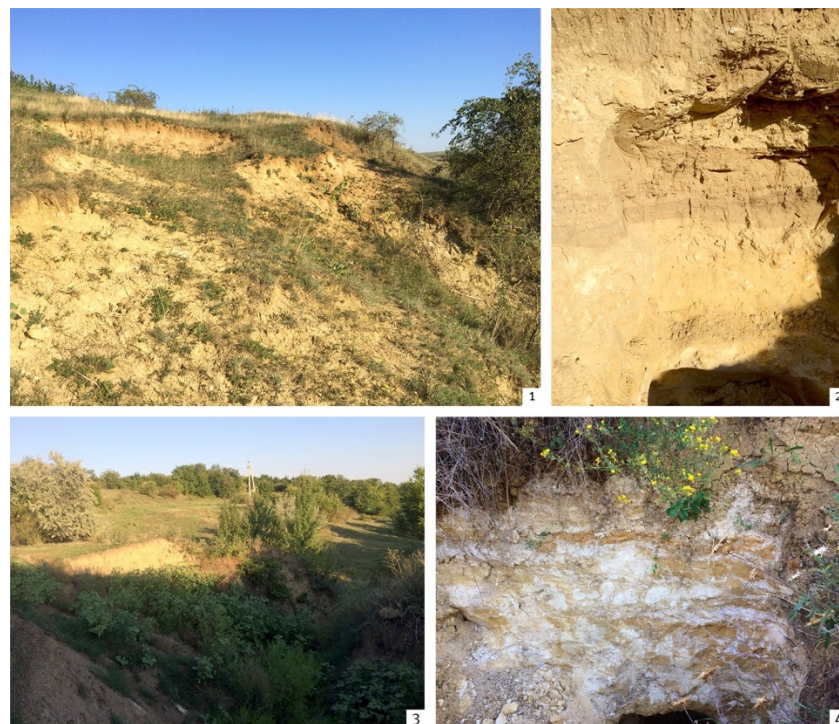


Figure 5. Glinjeni II-La Şanţ. Clay outcrops in the vicinity of “Glinjeni II-La Şanţ. Samples 9 (1, 2) and 10 (3, 4) are shown. Photos by Maria N. Vetrova.

The following strategy for ceramic sampling has been adopted: (1) the ceramic sherds were taken from the complex of the earlier Cozia-Saharna culture, the later Basarabi-Şoldăneşti culture and so-called mixed complexes; (2) sherds were taken from different types of ware: non-polish vessels (so-called kitchenware) and polish high-quality vessels (so-called tableware); (3) archaeometry investigations were carried out in “blind”, that is, the special markers denoting a cultural type of vessels were removed; (4) clay samples that could be used for ceramic making were collected from outcrops near the Glinjeni II-La Şanţ site (Figures 4 and 5).

Clay of the samples 9 and 10 was selected from two clay outcrops on the territory of the modern village Glinjeni, where the local people use clay for modern pottery making (Figure 5 (1,2)). The coordinates of the outcrop location are 47.827892 N, 28.871603 E. No clay outcrop was found in the vicinity of the fortified settlement of Glinjeni II-La Şanţ. There are outcrops of limestones. Other samples of clay were selected from other outcrops located in the Dniester valley (Figure 4).

2.2. Methods

The compositions of ceramic paste of 20 pottery sherds were studied in the thin sections with the help of the polarizing microscope Leica PS. The petrographic analysis of pottery was applied for determinations of mineral composition of clay paste, their structure, and optical characteristics, which allow to reconstruct the technological features of pottery making and indicate possible raw material sources. Through thin section analysis of pottery, the following features of ceramic pastes can be determined [24]:

1. Nature and characteristics of non-plastic inclusions: mineral compositions, percent, size, shape and distribution of separate particles.
2. Textural and optical characteristics of clay matrix (birefringence, color).
3. Shape, amount and orientation of voids.
4. Particulars of surface treatment and decoration.
5. Mineral composition of ceramic matrix.

In most cases, it is possible to determine if non-plastic inclusions are natural or they were added as a temper [25,26]. These petrographic characteristics allow determining the character of temper material. The addition of such materials as sand, crushed rocks, or grog into clay prevents wares from cracking in the process of drying and firing. Charcoal, ash, and cinder were used for improving the firing process and increasing the temperature [24]. The firing temperature and atmospheric conditions were determined on the basis of the color of the sherd inner part. The red or red-orange color of the inner part indicates oxidizing conditions formed in excess oxygen, while dark-brown, dark-red-black and black (black-gray) colors evidence a decrease in oxygen inside the oven and prevailing of restorative conditions [27].

Therefore, the ceramic groups differed on the basis of their petrographic characteristics, which provides information regarding the recipe of ceramic paste and partly reflects their geochemical composition, which can be changed because of the different mineralogical composition of clay and temper. On the basis of thin section analysis, some groups of paste recipes were divided.

The bulk chemical composition of ceramic sherds and clay samples was determined by the XRF-WD method using a SPECTROSCAN MAX GV spectrometer (Table 2). The specimens were prepared using the standard procedure of powder sample pressing on a boric acid substrate [28,29]. Previously powdered samples were fired at the temperature 950 °C to determine the loss on ignition (LOI) [30]. The clay samples for the XRF-WD analysis were pretreated with the help of the quartering method to make the material more homogeneous. After that, the samples were prepared according to the standard method similar to the preparation of the ceramic samples. Chemical composition data of all samples were processed by the principal-component factoring analysis and correlation analysis (Statistica 10.0) (Figure 6).

Table 2. XRF-WD analysis of ceramics sherds from the Glinjeni II-La Şanţ site.

| Sample | (%) SiO ₂ | TiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | MnO | MgO | CaO | Na ₂ O | K ₂ O | P ₂ O ₅ | | | |
|----------------------|----------------------|------------------|--------------------------------|--------------------------------|------|------|-------|-------------------|------------------|-------------------------------|-----|-----|----|
| Hligeni | | | | | | | | | | | | | |
| 1 | 62.73 | 0.762 | 14.12 | 5.01 | 0.10 | 2.01 | 8.87 | 0.38 | 2.96 | 0.41 | | | |
| 2 | 61.24 | 0.777 | 14.44 | 5.38 | 0.09 | 2.03 | 8.15 | 0.30 | 2.90 | 0.25 | | | |
| 3 | 67.55 | 0.832 | 14.10 | 5.85 | 0.08 | 1.75 | 1.94 | 0.38 | 2.87 | 0.17 | | | |
| 4 | 71.14 | 0.752 | 13.19 | 5.32 | 0.10 | 1.51 | 3.00 | 0.50 | 2.74 | 0.30 | | | |
| 5 | 72.01 | 0.783 | 12.95 | 5.28 | 0.09 | 1.64 | 2.90 | 0.45 | 2.69 | 0.53 | | | |
| 6 | 65.36 | 0.795 | 15.27 | 5.64 | 0.09 | 1.96 | 6.76 | 0.32 | 3.08 | 0.50 | | | |
| 7 | 64.25 | 0.786 | 13.21 | 5.17 | 0.08 | 1.62 | 2.93 | 0.43 | 3.13 | 0.40 | | | |
| 8 | 62.54 | 0.741 | 14.79 | 5.33 | 0.07 | 2.48 | 6.60 | 0.35 | 3.84 | 0.30 | | | |
| 9 | 64.52 | 0.848 | 15.33 | 6.13 | 0.06 | 2.22 | 2.64 | 0.35 | 3.14 | 0.26 | | | |
| 10 | 62.41 | 0.871 | 17.47 | 6.05 | 0.09 | 2.08 | 4.31 | 0.75 | 2.82 | 0.55 | | | |
| 11 | 64.23 | 0.834 | 15.86 | 6.18 | 0.09 | 2.15 | 1.26 | 0.40 | 3.87 | 0.62 | | | |
| 12 | 66.90 | 0.811 | 14.31 | 5.83 | 0.09 | 1.84 | 5.80 | 0.40 | 2.98 | 0.38 | | | |
| 13 | 62.34 | 0.823 | 14.82 | 5.39 | 0.06 | 1.88 | 3.16 | 0.50 | 3.32 | 0.37 | | | |
| 14 | 65.36 | 0.763 | 15.01 | 6.21 | 0.11 | 1.93 | 2.89 | 0.40 | 3.69 | 0.47 | | | |
| 15 | 64.47 | 0.820 | 14.73 | 5.79 | 0.08 | 2.12 | 4.86 | 0.30 | 3.34 | 0.34 | | | |
| 16 | 65.35 | 0.766 | 15.45 | 5.29 | 0.07 | 2.15 | 4.17 | 0.45 | 3.57 | 0.21 | | | |
| 17 | 64.49 | 0.816 | 14.02 | 5.85 | 0.10 | 1.57 | 3.20 | 0.40 | 2.76 | 0.26 | | | |
| 18 | 67.28 | 0.875 | 14.84 | 6.47 | 0.10 | 2.27 | 3.05 | 0.36 | 3.45 | 0.50 | | | |
| 19 | 63.98 | 0.816 | 14.69 | 5.49 | 0.07 | 1.84 | 3.49 | 0.50 | 3.31 | 0.51 | | | |
| 20 | 66.08 | 0.802 | 14.55 | 5.79 | 0.06 | 1.84 | 3.18 | 0.50 | 3.30 | 0.27 | | | |
| Clay_Dniester | | | | | | | | | | | | | |
| 1-Clay | 72.54 | 0.975 | 14.38 | 3.66 | 0.09 | 1.88 | 1.85 | 0.90 | 2.13 | 0.18 | | | |
| 2-Clay | 73.80 | 0.931 | 14.27 | 3.42 | 0.10 | 1.87 | 1.05 | 0.84 | 2.11 | 0.17 | | | |
| 3-Clay | 61.60 | 0.793 | 10.60 | 2.45 | 0.12 | 2.49 | 15.42 | 2.02 | 2.50 | 1.01 | | | |
| 4-Clay | 73.29 | 0.866 | 14.34 | 3.38 | 0.07 | 1.84 | 1.58 | 0.74 | 2.15 | 0.23 | | | |
| 5-Clay | 72.88 | 0.928 | 14.82 | 3.48 | 0.09 | 1.80 | 1.72 | 0.48 | 2.13 | 0.19 | | | |
| 6-Clay | 64.99 | 1.406 | 13.90 | 5.32 | 0.16 | 3.58 | 6.72 | 0.29 | 2.49 | 0.08 | | | |
| 7-Clay | 68.68 | 0.970 | 12.67 | 3.27 | 0.08 | 2.36 | 6.66 | 1.87 | 2.12 | 0.20 | | | |
| 8-Clay | 67.97 | 0.941 | 14.70 | 3.72 | 0.10 | 2.31 | 6.17 | 0.57 | 2.21 | 0.18 | | | |
| 9-Clay | 64.53 | 1.102 | 16.35 | 5.47 | 0.07 | 2.56 | 5.24 | 0.71 | 3.08 | 0.08 | | | |
| 10-Clay | 64.92 | 1.208 | 16.20 | 5.25 | 0.08 | 2.38 | 6.89 | 0.75 | 3.05 | 0.10 | | | |
| Sample | ppm V | Cr | Ni | Cu | Zn | Rb | Sr | Y | Zr | Nb | Ba | (La | Pb |
| Hligeni | | | | | | | | | | | | | |
| 1 | 108 | 106 | 51 | 25 | 99 | 108 | 243 | 36 | 193 | 17 | 649 | 32 | 20 |
| 2 | 125 | 125 | 52 | 24 | 96 | 106 | 177 | 30 | 188 | 17 | 718 | 15 | 25 |
| 3 | 111 | 114 | 48 | 20 | 101 | 106 | 132 | 34 | 230 | 16 | 701 | 20 | 17 |
| 4 | 101 | 116 | 61 | 21 | 88 | 100 | 128 | 32 | 278 | 18 | 697 | 43 | 20 |
| 5 | 115 | 110 | 44 | 24 | 96 | 109 | 181 | 37 | 249 | 16 | 777 | 40 | 20 |
| 6 | 135 | 124 | 57 | 25 | 102 | 123 | 204 | 31 | 219 | 17 | 732 | 43 | 18 |
| 7 | 104 | 125 | 54 | 26 | 96 | 103 | 190 | 32 | 208 | 16 | 959 | 41 | 18 |
| 8 | 95 | 95 | 51 | 25 | 97 | 108 | 198 | 28 | 179 | 15 | 722 | 39 | 21 |
| 9 | 120 | 117 | 61 | 26 | 107 | 129 | 144 | 26 | 192 | 16 | 633 | 27 | 18 |
| 10 | 125 | 168 | 75 | 29 | 122 | 115 | 260 | 33 | 192 | 18 | 823 | 44 | 25 |
| 11 | 155 | 123 | 58 | 37 | 115 | 126 | 165 | 32 | 167 | 17 | 733 | 33 | 21 |
| 12 | 129 | 170 | 60 | 36 | 150 | 105 | 164 | 29 | 233 | 18 | 716 | 46 | 27 |
| 13 | 130 | 131 | 47 | 37 | 115 | 105 | 198 | 25 | 215 | 17 | 696 | 45 | 22 |
| 14 | 128 | 130 | 59 | 28 | 109 | 128 | 173 | 34 | 199 | 16 | 688 | 41 | 22 |
| 15 | 131 | 108 | 53 | 28 | 119 | 118 | 195 | 37 | 200 | 17 | 830 | 32 | 19 |
| 16 | 121 | 123 | 55 | 24 | 94 | 120 | 167 | 31 | 220 | 16 | 460 | 32 | 22 |
| 17 | 132 | 112 | 52 | 26 | 99 | 124 | 166 | 33 | 195 | 12 | 694 | 44 | 24 |
| 18 | 152 | 145 | 64 | 29 | 104 | 115 | 170 | 34 | 254 | 21 | 837 | 47 | 23 |
| 19 | 128 | 124 | 49 | 27 | 100 | 103 | 205 | 34 | 246 | 18 | 500 | 31 | 18 |
| 20 | 127 | 125 | 57 | 23 | 98 | 114 | 141 | 32 | 265 | 17 | 456 | 33 | 18 |
| Clay_Dniester | | | | | | | | | | | | | |
| 1-Clay | 79 | 111 | 39 | 38 | 70 | 105 | 130 | 30 | 355 | 15 | 515 | 51 | 21 |
| 2-Clay | 95 | 80 | 42 | 28 | 77 | 97 | 123 | 32 | 350 | 16 | 482 | 52 | 19 |

| | | | | | | | | | | | | | |
|---------|-----|-----|----|-----|-----|-----|-----|----|-----|----|-----|----|----|
| 3-Clay | 32 | 66 | 33 | 27 | 96 | 69 | 240 | 25 | 264 | 12 | 495 | 16 | 13 |
| 4-Clay | 100 | 80 | 35 | 31 | 69 | 87 | 121 | 28 | 359 | 13 | 448 | 44 | 21 |
| 5-Clay | 71 | 79 | 39 | 28 | 69 | 89 | 111 | 27 | 291 | 14 | 517 | 15 | 20 |
| 6-Clay | 126 | 98 | 53 | 120 | 52 | 117 | 222 | 37 | 348 | 8 | 673 | 96 | 24 |
| 7-Clay | 76 | 88 | 35 | 36 | 65 | 93 | 257 | 30 | 309 | 13 | 593 | 70 | 17 |
| 8-Clay | 92 | 96 | 41 | 28 | 70 | 93 | 127 | 28 | 223 | 12 | 478 | 38 | 13 |
| 9-Clay | 122 | 123 | 66 | 56 | 101 | 146 | 224 | 29 | 150 | 12 | 449 | 44 | 21 |
| 10-Clay | 115 | 119 | 65 | 65 | 112 | 153 | 240 | 22 | 181 | 14 | 420 | 51 | 18 |

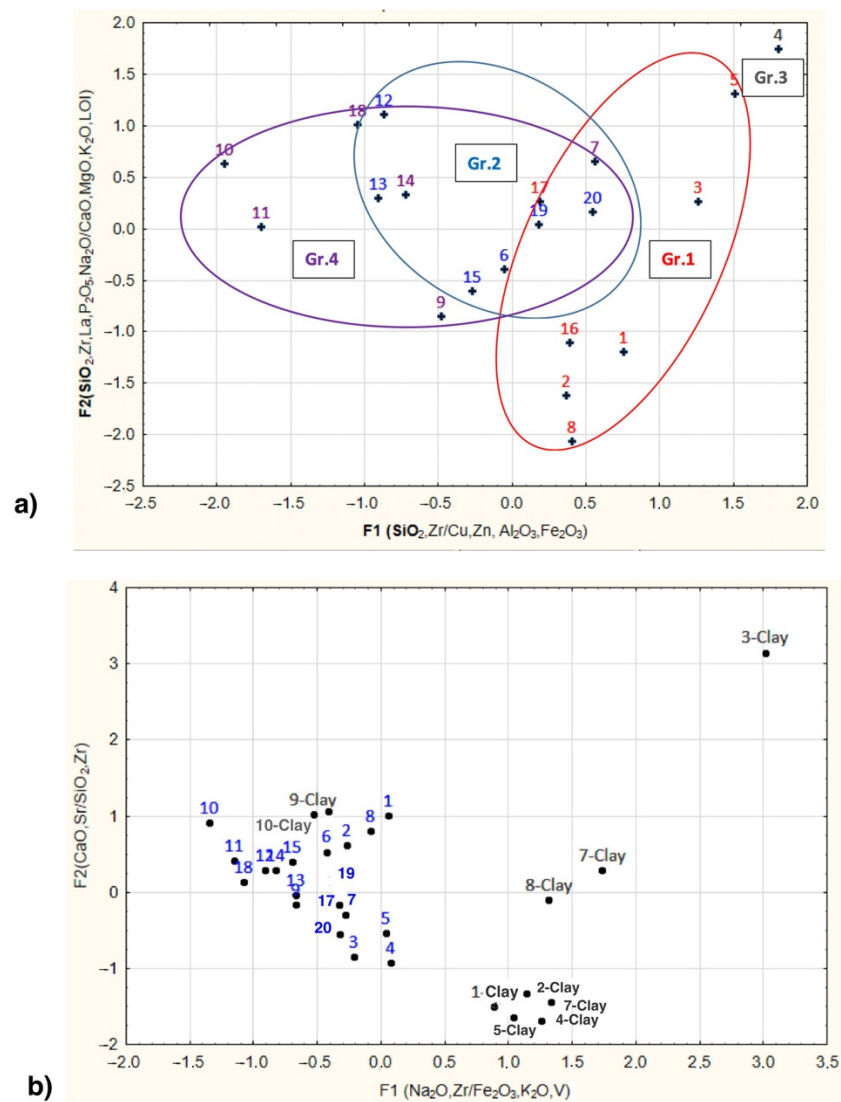


Figure 6. Glinjeni II-La Şanç site. The graphics of the principal-component factoring analysis on the basis of XRF-WD results: (a) groups on ceramics composition; (b) compositions of ceramic sherds and clay samples.

At first, all chemical analysis data were calculated in decimal logarithms. The first factor explains 24.7% of the total variance and the second is 15.0% from the sum of the four calculated factors. The first two factors were chosen for an explanation of the distribution of geochemical compositions of samples. Factor (F1) and Factor (F2) account for 39.7% of the total variance.

The factor F1 is characterized by the formula $(\text{SiO}_2, \text{Zr}/\text{Cu}, \text{Zn}, \text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3)$. Such components as Al_2O_3 , Fe_2O_3 are the main chemical components of clay minerals and iron oolite inclusions. The chemical components $(\text{SiO}_2, \text{Zr}, \text{Na}_2\text{O})$ are included in minerals such

as quartz, feldspar, and zircon, etc. The factor F2 is characterized by the formula (P_2O_5 , La, Nb, MnO, Ba, Y, Cu, Zn/ CaO, MgO, K_2O , LOI), which is the antagonism between components of apatite, manganese minerals and carbonates.

The SEM-EDX analysis was performed using a Scanning Electron Microscopy Hitachi S-3400N in combination with a microanalyzer EDX, which allows performing qualitative/quantitative chemical analyses of elements (Figure 7).

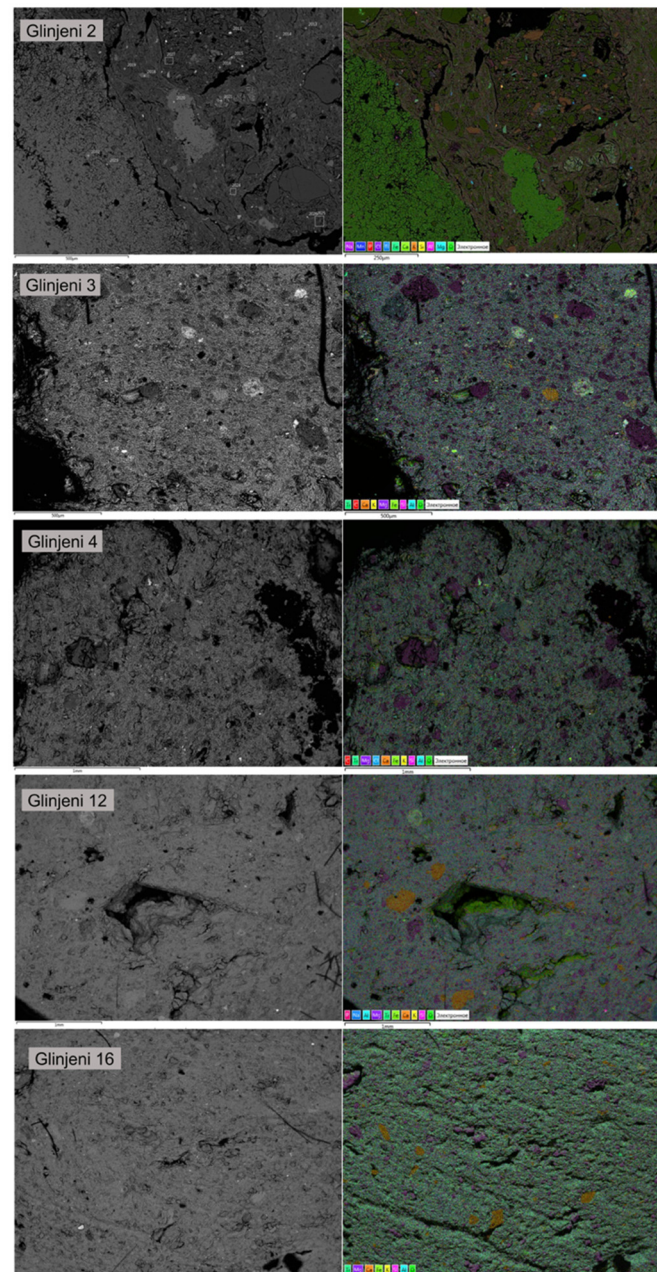


Figure 7. Geochemical maps of ceramics on the basis of SEM-EDX from the Glinjeni II-La Şanţ site.

Characteristics of the SEM-EDX system are: microscope resolution up to 3 nm (30 kV accelerating voltage, SE); accelerating voltage from 300 V to 30 kV; spectrometer Oxford Instruments X-Max 20 for Energy-dispersion analysis (EDX) has the active crystal area of 20 mm²; provides a stable result with count rate to 100,000 pulses per second; guaranteed resolution: the Mn $K\alpha$ line 127 eV at the C $K\alpha$ line 56 eV; the accuracy of the analysis—1 wt %. For identification of minerals, the calculation formula “SEM Petrology Atlas” [31] was used.

Analysis of pottery by means of X-ray micro-Computer Tomography was applied for assessment of technological features of the inner structure. A 3D visualization of voids of the inner structure allowed for reconstruction the character of burned organic inclusions and assessment of the distribution of particles of different density [32] (See Supplementary Materials). The samples of ceramics were scanned using the SkyScan 1172 device with a beam energy of 100 kV, a flux of 80 μ A and aluminum filter with a resolution of 4–6 μ m, performing a 180-degree rotation with a step size of 0.4 degrees. CTvox and CTAn have been used for the visualization and calculation of cavities. Analysis and 3D visualization of porosity with pore sizes more than 5 μ m allows to determine their origin. These pores can be a result of thermal shock, fractures from mineral inclusions, and burnout of organic remains, etc. The ratio between open and closed porosity relates to fractures in ceramics and is the technological parameter that characterizes the quality of pottery manufacture. It can be calculated as the coefficient of pore sphericity. The ceramic sherds of 2 \AA –2 \AA –15 mm of size were used for m-CT-tomography. The scanning volume resolution is 6.9 μ m/voxel. Open and closed porosity was calculated from total volume of the ceramic fragment. The pore sphericity was assessed in virtual volume by CTAn software. After scanning of a sample in the virtual program, the Volume Of Interest (VOI) with sizes of 7 \AA –7 \AA –7 mm was selected in the central part of the sample. Geometrical parameters (linear dimension, volume, sphericity) of all pores from volume were analyzed by operation of the Individual object analysis (CTAn) [33].

Furthermore, sample 10 was also studied by DTA-TG and XRD analysis. The Setsys Evolution 16 (Setaram, France) equipment was used for DTA-TG analysis. XRD analysis was provided with the application of Rigaku «Ultima IV» Diffractometer with Co K α emission, at a rate of 2°/min, in 2 Θ 5–70° (Table 2).

According to scholars [34,35] and DTA and TG diagrams there are three main stage of weight loss during the heating of ancient ceramics: dehydration (20–100 °C), decomposition of hydroxides and organics (380–500 °C), decompositions of carbonates—mainly calcite (700–800 °C). The powder sample was heated from room temperature until 1100 °C in an oxygen atmosphere (80%O₂ 20% N₂) at a rate of 10°/min. Mass loss in sample 10 at dehydration of clay and hydroxides as well as burning of organics (400–600 °C) consists of 2.46%, decomposition of carbonates (600–800 °C): 1.23%, decomposition of clay and removal of constitutional water (higher 850 °C): 0.61%. Total mass loss is 8.19% (25–1100 °C) (Figure 8).

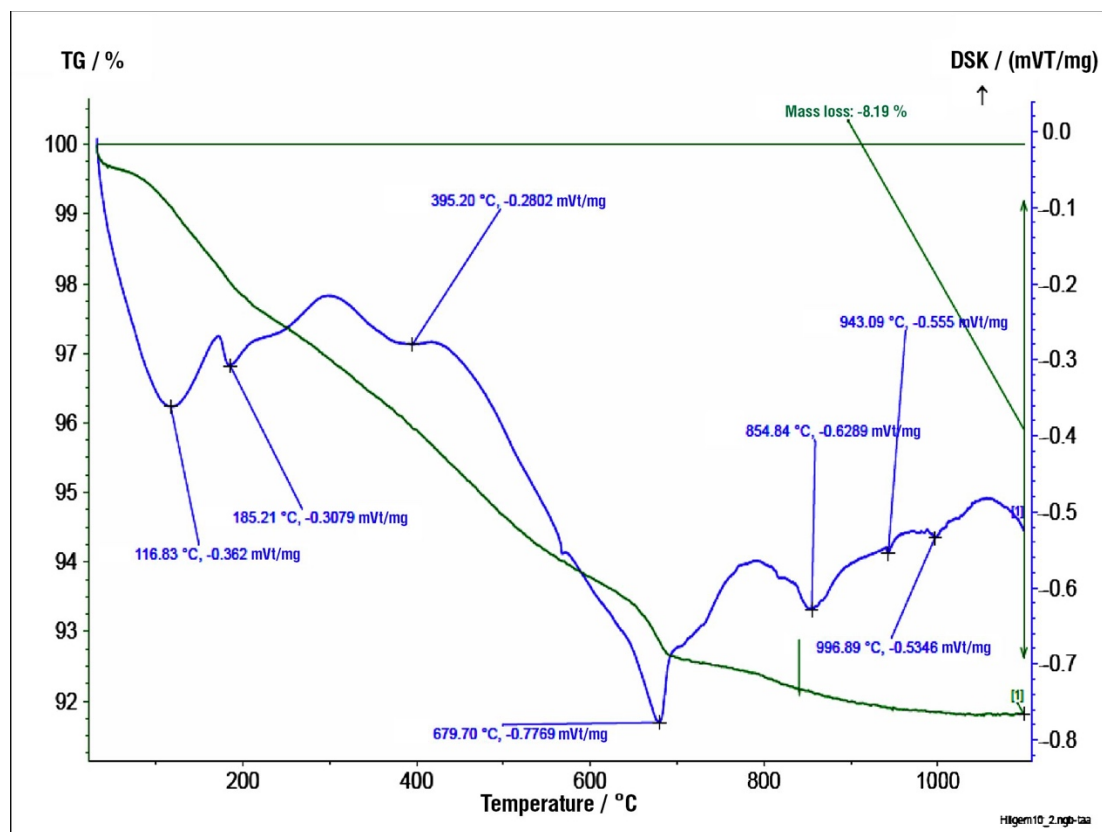


Figure 8. Diagram of DTA-TG of ceramic sample 10 from the Glinjeni II-La Şantı site.

The analyses were held at the “RDMI” Research Centrum of Saint-Petersburg University and the research Centrum of “Geology and Geoecology” of the Herzen State University.

3. Results

Chemical composition data of sherds obtained with XRF-WD (Table 3) were projected into the factors representing clay, clastic material, and temper composition (Figure 6). The variations in the chemical composition of samples depend on the clay, clastic material, and temper composition. The comparison with the chemical composition of local raw sources (samples clay 9, 10) confirmed the use of local clay, sand, and carbonate rocks for pottery manufacture. The results of SEM-EDX are presented in Table 3 and Figure 7. According to DTA-TG analysis, the firing temperature of ceramic sample 10 did not exceed 650–700 °C (Figure 8). The same is correct for other ceramic samples, judging from their mineralogical compositions.

Table 3. Mineral composition of ceramics on the basis of SEM-EDX and XRD analysis from the Glinjeni II-La Şantı site.

| Sample | SEM-EDX | XRD |
|--------|--|--|
| #2 | smectite, illite, glauconite, calcite, quartz, microcline, zircon (Hf), titanomagnetite, apatite (Ce,Nb), rutile. | No data |
| #3 | smectite, illite, glauconite, calcite, quartz, titanomagnetite, rutile, chromite, celsian barite | No data |
| #4 | smectite, glauconite, calcite, quartz, titanomagnetite, rutile + magnetite, chromite, celsian barite, apatite, zircon (Sc, Y, Hf), monazite. | No data |
| #10 | smectite, glauconite, chlorite, titanomagnetite, zircon, kaolinite, phlogopite, gadolinite, monazite | quartz (54%), mica/illite (26%), albite (11%), calcite (7%), |

| | | |
|-----|---|---|
| | | microcline (1%), amphibole (less than 1%) |
| #12 | smectite, glauconite, quartz, calcite, zircon, titanomagnetite, magnetite, rutile | No data |
| #16 | smectite, glauconite, calcite, rutile, microcline, zircon (Hf) | No data |

Four ceramic groups have been divided based on the results obtained using archaeometry analysis (chemical composition, firing temperature, and type of fractures).

Group 1. Ceramic paste of smectite-carbonate clay with many clastic inclusions. The temper is grog (25%) + sand (8–10%) (Figure 9). Samples: 1, 2, 3, 5, 8, 16, 17.

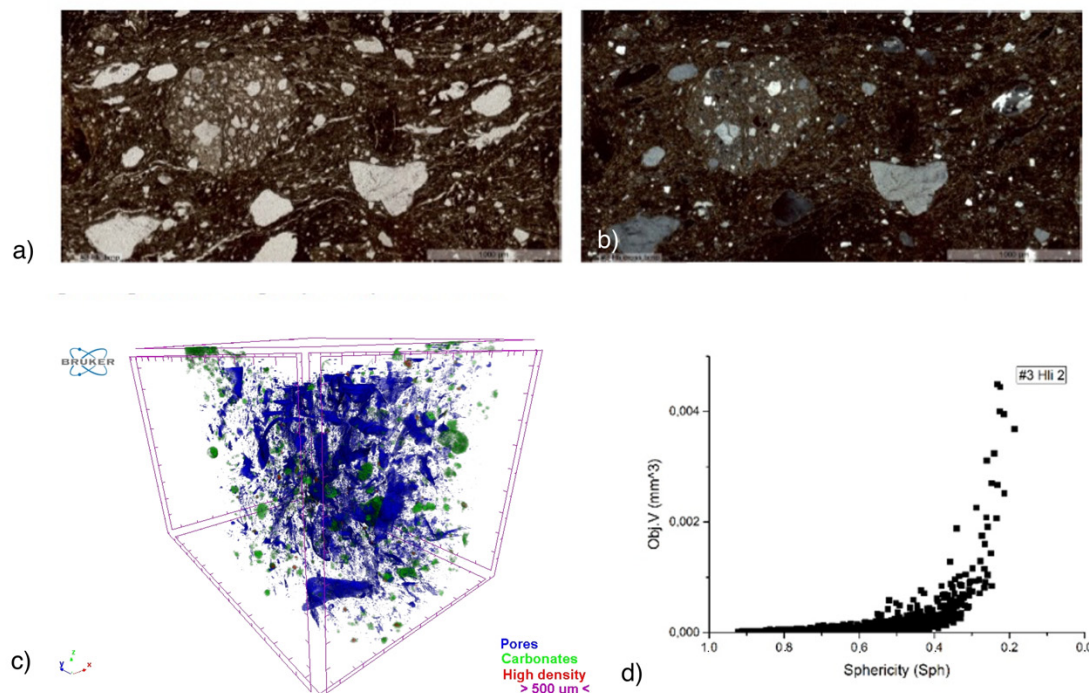


Figure 9. Group 1; Glinjeni II-La Şanţ site. Thin section of sample #3: (a) plan polarized light, field of view 1 mm; (b) cross-polarized light, field of view 1 mm; (c) m-CT 3D visualization of inner structure of sample; (d) diagram of sphericity on the basis of m-CT.

The ceramic paste consists of smectite-carbonate clay with 50% of clastic inclusions. Temper: 1. Sand (8–10%), grain sizes of 0.2–1.0 mm, middle roundness. Mineral composition: feldspar, chalk with fossils, gneiss, quartz. 2. Grog—crushed pottery of the same as a sherd composition (25%)—samples 1, 2, 8, 16, 17 and others with ceramic matrix composition with kaolinitic grog—samples 3, 5. Particle sizes are 0.4–2.0 mm, porosity is about 7%. The artificial admixture of sand was identified on the basis of particle size distribution and mineral composition. The sand added is characterized by well-sorting, more large grain sizes and has another mineral composition in comparison to the clastic material of clay.

These samples are characterized by high concentrations of SiO₂, Zr elements that connect with sand additives. Samples 1, 2, 8, 16, 17 are enriched by carbonate admixture, which is a part of clay. Some difference in the chemical and mineral compositions was found for samples 3, 5. They have less carbonate concentration and higher content of SiO₂, Zr. According to SEM-EDX analysis (Table 3), the ceramic matrix of sample 3 contains such minerals as celsian-barite, chromite and kaolinite in grog particles.

The firing temperatures did not exceed 650–700 °C in the reduction atmosphere. The ceramics have a high degree of fracture. The fracture parameter is the coefficient of

sphericity according to m-CT analysis, which in this case is between 0.5 and 0.2 (with an average of 0.3) and denotes the middle quality of the ceramics (Figure 9d).

Group 2. Ceramic paste of smectite clay with many clastic inclusions. The temper is grog (25%) + crushed carbonate rocks (10%) (Figure 10). Samples: 6, 12, 13, 15, 19, 20.

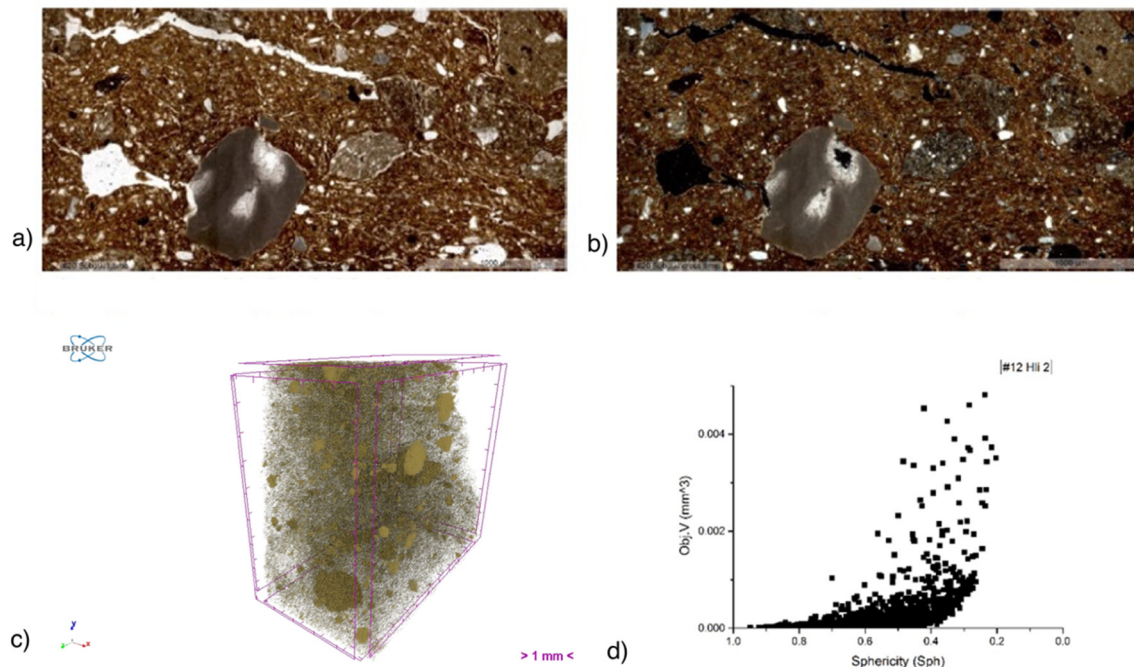


Figure 10. Group 2; Glinjeni II-La Şanţ site. Thin section of sample #12: (a) plan polarized light, field of view 1 mm; (b) cross-polarized light, field of view 1 mm; (c) m-CT 3D visualization of inner structure of sample with carbonate inclusions; (d) diagram of sphericity on the basis of m-CT.

Ceramic paste consists of smectite composition with 50% of clastic inclusions. Temper: 1. Crushed carbonate rocks (10%) enriched by microfossils (foraminifers), particle sizes of 0.5–1.5 mm. 2. Grog—crushed pottery (25%) other than ceramic matrix composition, particle sizes are 0.4–2.0 mm, porosity is about 7%.

These samples are characterized by high concentrations of carbonates (CaO, LOI) and medium levels of SiO₂, Zr, Al₂O₃, Fe₂O₃ content. Such composition is connected with the presence of many crushed carbonate rocks and grog. The mineral composition of this type of ceramics based on SEM-EDX (Table 3) is smectite clay, chlorite, calcite with accessories as quartz, zircon, titanomagnetite, magnetite, and rutile.

The firing temperatures did not exceed 650–700 °C in the reduction atmosphere, during a short time period. The ceramics have a very high degree of fracture because of many carbonate inclusions. The fracture parameter is the coefficient of sphericity according to m-CT analysis, which in this case is between 0.7 and 0.2 (with an average of 0.5) and denotes the bad quality of the ceramics.

Group 3. Ceramic paste of smectite clay with many clastic inclusions. The temper is grog (25%) + crushed carbonate rocks (10%) + sand (8–10%) (Figure 11). Sample 4.

Ceramic paste consists of smectite composition with 50% of clastic inclusions. Temper: 1. Crushed carbonate rocks (10%) enriched by microfossils (foraminifers), particle sizes of 0.5–1.5 mm. 2. Grog—crushed pottery (25%) of the same as a ceramic matrix composition, particle sizes are 0.4–2.0 mm. 3. Sand (8–10%), grain sizes of 0.2–1.0 mm, middle roundness. Mineral composition: feldspar, chalk. Porosity is about 8%. Samples: 4.

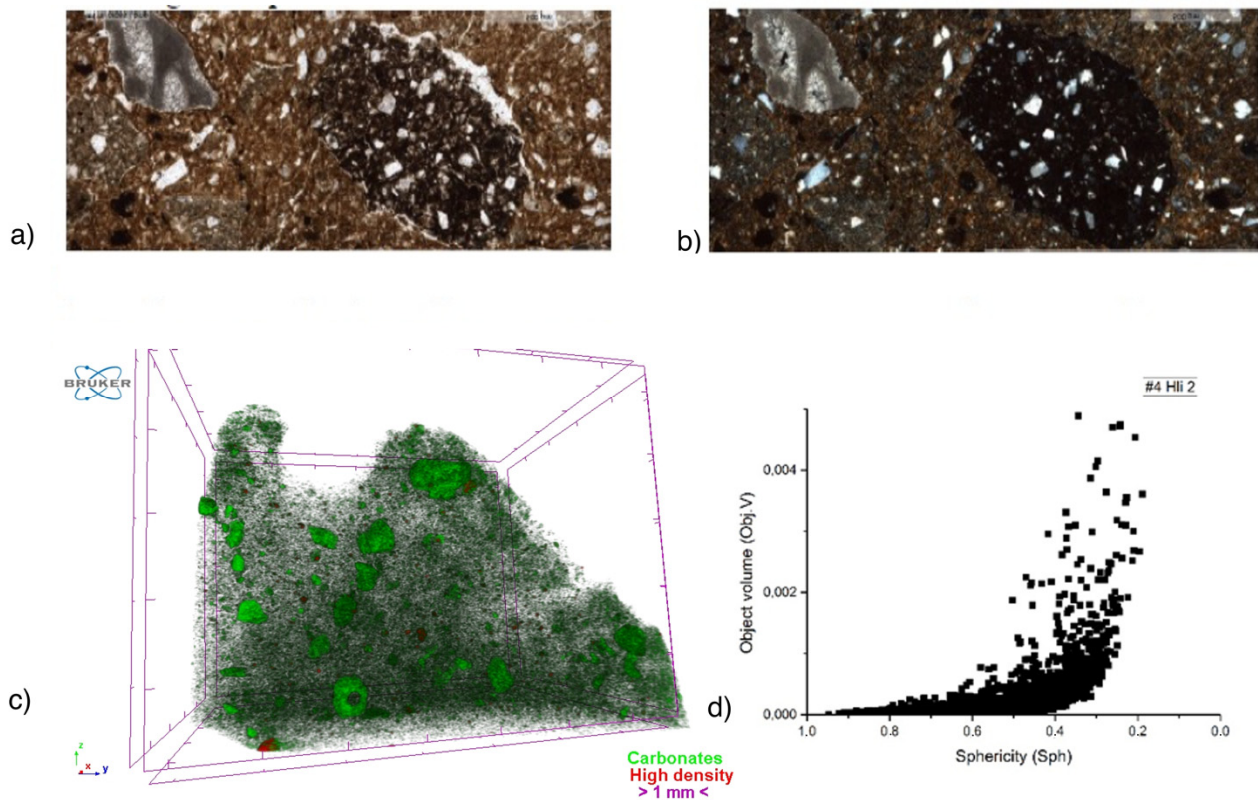


Figure 11. Group 3; Glinjeni II-La Şaŋt site. Thin section of sample #4: (a) plan polarized light, field of view 0.5 mm; (b) cross-polarized light, field of view 0.5 mm; (c) m-CT 3D visualization of inner structure of sample with carbonate inclusions; (d) diagram of sphericity on base of m-CT.

The sample is characterized by high concentrations of elements (SiO_2 , Zr) and medium levels of CaO, MgO, Sr elements in comparison with samples of group 2, which consisted of carbonate clay tempered by crushed carbonates. Such composition is connected with the presence of significant sand and grog. The mineral composition of this sample based on SEM-EDX (Table 3) is smectite, glauconite, calcite with accessories such as quartz, titanomagnetite, magnetite, rutile, celsian-barite, chromite, apatite, zircon (Sc, Y, Hf), and monazite.

The firing temperatures did not exceed 650–700 °C in the reduction atmosphere, during a short time period. The ceramics have a very high degree of fracture. The fracture parameter according to m-CT analysis, which in this case is between 0.7 and 0.2 (with an average of 0.5) and denotes the bad quality of ceramics.

Group 4. Ceramic paste of smectite clay with many clastic inclusions. The temper is grog (25%) (Figure 12). Samples: 9, 11, 14, 10, 7, 18.

Ceramic paste consists of smectite composition with 40–50% of clastic inclusions. Temper: 1. Grog—crushed pottery (25%) of the different composition, particle sizes are 0.5–5.0 mm. Porosity is from 7 to 15%.

There are some differences in geochemical and mineralogical composition of these samples. The ceramics of 10 and 11 are characterized by high concentrations of elements (Al_2O_3 , Fe_2O_3 , Na_2O , Zr, P_2O_5). This can be dependent on the chemical composition of grog. The presence of apatite was determined as an accessory mineral. The clay is characterized by a high content of iron oxides. The samples 14 and 9 have lower concentrations of Al_2O_3 , Fe_2O_3 elements.

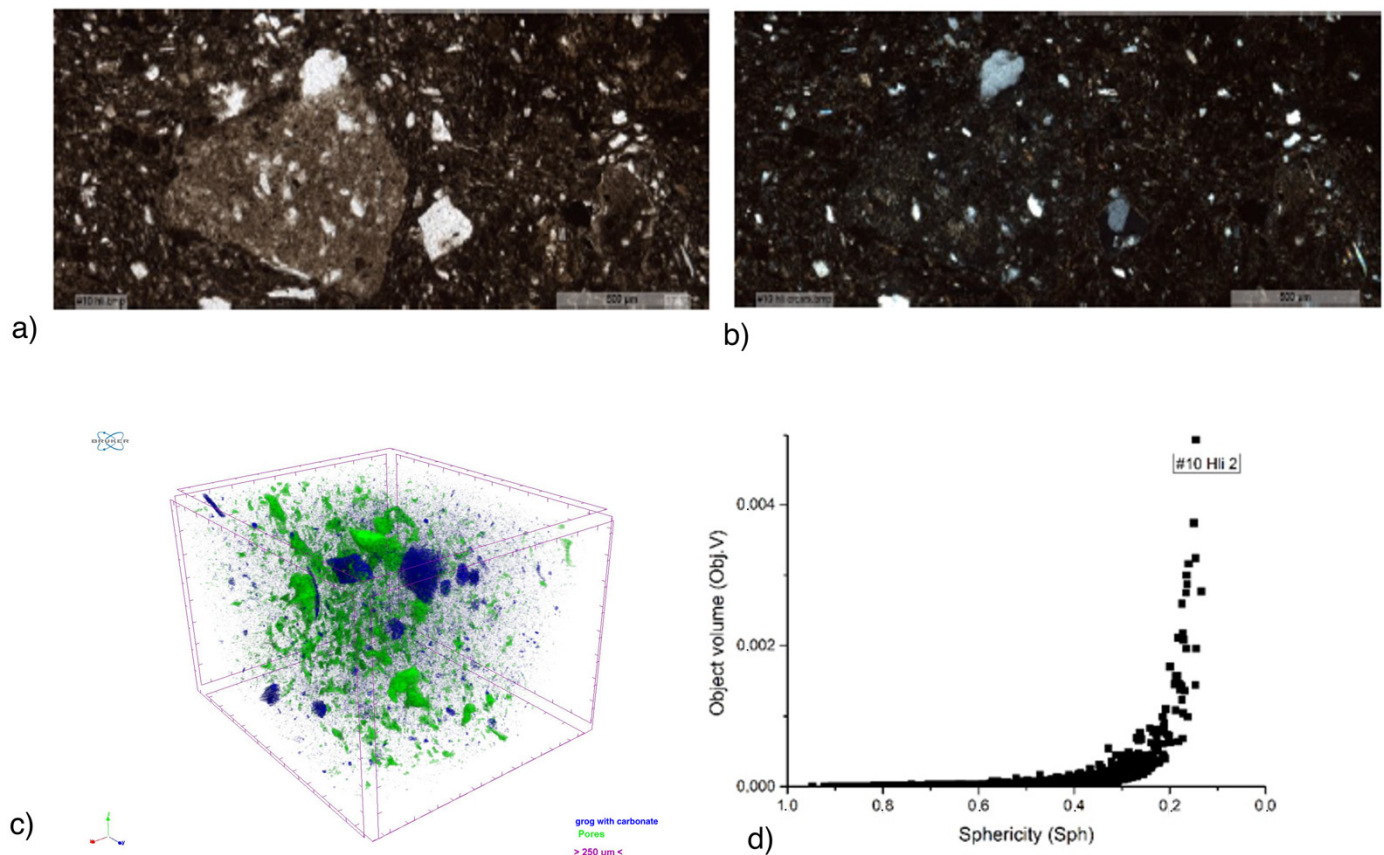


Figure 12. Group 4; Glinjeni II-La Şanţ site. Thin section of sample #10: (a) plan polarized light, field of view 0.5 mm; (b) cross-polarized light, field of view 0.5 mm; (c) m-CT 3D visualization of inner structure of sample with grog inclusions; (d) diagram of sphericity on base of m-CT.

Mineralogical composition of sample 10 includes smectite, glauconite, chlorite, kaolinite, phlogopite, titanomagnetite, magnetite, monazite, zircon, gadolinite.

The firing temperatures did not exceed 650–700 °C in the reduction atmosphere, during a short time period, excluding sample 7, which was fired in an oxidizing atmosphere. The ceramics have a very low degree of fracture. The fracture parameter according to m-CT analysis, which in this case is between 0.5 and 0.1 (with an average of 0.3), denotes the good quality of the ceramics. Sample 10 has especially good quality, which is characterized by low porosity (7%).

4. Discussion

Archaeological investigations have estimated that the Glinjeni II-La Şanţ site in the period of 10th–beginning of 7th cc. BC was occupied by people continuously and ceramic production had been developed. Although remains of oven constructions have not been recovered, as on the Saharna Mare site [8], special tools for the decoration of pottery have been found [19]. Such kinds of tools for pottery decoration were discovered on each of the excavated sites with the Cozia-Saharna artifacts in this region [16,20]. The local character of pottery production in the Glinjeni II-La Şanţ site is demonstrated by mineralogical and geochemical investigations of ceramics and raw clay sources. Most of the Glinjeni II-La Şanţ ceramic samples were made of smectite clay from local deposit outcrops located near the site. Such local production of pottery lasted for a long time, namely from the 10th–beginning of the 7th cc. BC. Detailed examination of technological features, morphology, and typology of studied ceramics allowed us to establish differences in composition and technology associated with cultural and chronological periodization.

Technological group 1 consists of the pottery samples made of a ceramic paste of smectite-carbonate clay tempered by grog and sand. The first subgroup according to geochemical composition includes the samples of pottery (1, 2, 8, 16, 17) that were referred to the earlier Cozia-Saharna culture. The second subgroup of ceramics (3, 5) belongs to the Basarabi-Şoldăneşti culture. The samples 3 and 5 are characterized by some differences in mineral and geochemical composition that could be evidence of other raw material sources, which were collected outside the Glinjeni II-La Şanţ site. Such accessory minerals as celsian-barite, chromite in clay matrix and kaolinite in grog particles in their composition are not typical for this geological province. They have some similarities with pottery from the Saharna Mare and Şoldăneşti sites. In the late period, this tradition was wide spread on the other sites.

Technological group 2 connects sherds from vessels of different cultural traditions and chronological stages: the samples 6, 12, 15 belong to the Cozia-Saharna culture, but samples 13, 19, 20 are from wares of the Basarabi-Şoldăneşti culture. The pottery is made of smectite clay tempered by grog and crushed carbonate rocks. This technological tradition was preserved and adopted by bearers of later cultural traditions. All of this is evidence of the transfer of this ceramic technology from one culture to another.

Interestingly, technological group 3, including one of sample 4, which belongs to the Cozia-Saharna culture, has a complex ceramic recipe composed of smectite clay tempered by grog, crushed carbonates, and sand. In its mineral composition, such accessory minerals as celsian-barite, chromite, zircon (Sc, Y, Hf), and monazite were registered. The chemical composition has significant differences from other samples from this site. However, apparently, this sherd was imported from other site, for instance, from the Saharna Mare site, where this tradition had spread to [8]. The ceramics of this paste recipe were found on the Solonceni-Hlinaia site also. According to archaeological excavations [20,36,37], these sites are the earliest settlements because the layers of the Cozia-Saharna culture also contain the complexes and materials of the Holercani-Hansca culture, dated to the second half of 12th–11th cc. BC. The artifacts of the Holercani-Hansca culture have not been discovered on the Glinjeni II-La Şanţ site [38]. Therefore, the complex pottery technology with additions of grog, carbonates, and sand had not been accepted on this site. However, an imported vessel in the materials of the Glinjeni II-La Şanţ site indicates the direct contact and exchange of items or technological ideas and skills between habitants of the inner area of the Middle Dniester basin.

The materials of a later cultural horizon of the Basarabi-Şoldăneşti culture were discovered on the Glinjeni II-La Şanţ site. For several ceramic samples of this culture, non-local raw material sources were used, for instance, for samples 3 and 5. According to the principal-component factoring analysis, it can be concluded that all studied samples correspond in their chemical composition to the composition of clay samples (# 9, 10). Thus, ceramic samples are expected to be made of the local clay sources. However, based on the SEM-EDX analysis, some ceramic sample (# 10, 3, 4) content contains specific accessory minerals that could not occur in the compositions of other sherds. In addition, there are differences in concentrations of some chemical elements in samples (# 3, 4, 5, 10). This allows suggesting a non-local character of raw material sources used for manufacturing of these samples. The clay deposits from other microregions had most likely been used, but for such conclusions, more detailed geological and geochemical investigations should be undertaken in the Dniester region. It is also worth noting that the typological and morphological features of vessels of these samples are typical for import technologies.

Notably, sample 10 differs from other ceramics, both in mineral and geochemical compositions as well as some technological characteristics. The ceramic matrix contains such minerals as phlogopite, amphibole, gadolinite as accessory minerals. The manufacturing technology differs by sherds of high quality with low inner fractures. The chemical composition of the sherd as well the mineral and geochemical composition of white paste used for inlay indicate its imported products [5]. The appearance of innovations in the

technological pottery process started to emerge on the Glinjeni II-La Şanţ site with such other ceramic types as sample 10.

Thus, the development of ceramic technology on the Glinjeni II-La Şanţ site in the early stage (10th–9th cc. BC) is marked by using different recipes of ceramic pastes. The most common ceramic technology is a paste recipe using clay tempered by grog and reducing firing to temperatures of about 600–750 °C (technological group of ceramics 4). Pottery differs by high quality and low fractures. The second group of ceramics developed in this period was made from clay tempered by grog and crushed carbonates (technological group 2). These ceramics are worse with respect to their technological qualities. It has high inner fractures. However, the pottery of this technology was met in the ceramic collection of the Basarabi-Şoldăneşti cultural tradition (8th–beginning of 7th cc. BC). On the Glinjeni II-La Şanţ site, this pottery was made using local raw material sources. The third technological tradition is the addition of grog and sand (the technological recipe 1) had developed parallel to other sites at the same time. The roots of this tradition can be found in the Cozia-Saharna culture on both the Saharna Mare and the Glinjeni II-La Şanţ sites. The pottery is characterized by medium quality.

Investigations of ceramic pastes and the raw clay sources suggest that some vessels of Early Hallstattian (Carpathian-Danubian) type were made from local raw sources. Probably, such pottery types were produced by local potters as an imitation of the Hallstattian vessels. Such tradition was also considered for the pottery manufacturing on the settlements of the Northern Hungary [39]. This situation can be explained not only by trading connections and people migrations but also exchange of skills, experience, and technological innovations between carriers of the Hallstattian cultures and the local societies of Eastern and South-Eastern Europe.

5. Conclusions

The results of archaeometry investigations of ceramics from the Glinjeni II-La Şanţ site reveal two important points. On the one hand, continuity of technology of ceramic manufacture was traced, but on the other hand, there are some differences in ceramic technology between earlier Cozia-Saharna and later Basarabi-Şoldăneşti cultural traditions. This is a marker of chronological differences in pottery technologies. It is also worth noting that on the Glinjeni II-La Şanţ sites, potters applied technological operations that were developed earlier elsewhere, for example, on the Saharna Mare site. In the period of 10th–9th cc. BC, several different ceramic technologies were applied: with additions such as a temper (1) grog; (2) grog and carbonates; (3) beginning of grog and sand usage.

There is one imported sample of a very early cultural tradition that used a paste recipe with additives of grog, sand, crushed carbonates, and this was probably brought from the Saharna Mare site onto the Glinjeni II-La Şanţ site. The materials of the Holercani-Hansca culture connected with the earlier stage of the Cozia-Saharna culture had not been found on the Glinjeni II-La Şanţ site.

Later, during 8th–beginning of 7th cc. BC, the ceramic technologies using local raw material sources and paste recipes with additives of grog and sand were developing. Several vessels made from this technology were brought from other settlements.

Correlation of archaeological and archaeometry data of ceramics from the Glinjeni II-La Şanţ site gives us the possibility to differ earlier and later chronological markers in the paste recipes of pottery of 10th–beginning of 7th cc. BC in the region of the Middle Dniester basin. The presence of crushed carbonates in the paste recipe is an earlier chronological marker (the end of the Bronze Age to the beginning of the Early Iron Age), whereas ceramic pastes with kaolinite in clay matrix and grog indicate the period of 8th–beginning of 7th cc. BC. Some innovations in the ceramic technology on this territory were connected with migrations of mobile societies in the North-Western Pontic Sea region in these periods. The appearance of these cultural traditions on the territory of the Dniester basin initiated the development of new pottery technologies. Such process could be a result of the transmission of ideas, skills, and experience as reflected in the emergence on the

settlement of both import vessels and pottery that had been made of local raw material sources using imported technologies.

Supplementary Materials: The following are available online at www.mdpi.com/article/10.3390/heritage4040160/s1, 3D visualization of inner voids in ceramic sample #6 by means of m-CT.

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Appendix A

The description of Glinjeni II-La Șanț fortified settlement and the samples.

Appendix A.1. Glinjeni II-La Șanț Fortified Ssettlement

Glinjeni II-La Șanț site (Resina district, Republic of Moldova; 47.48'54" N; 28.52'29" E) is situated in the southwestern forest steppe, in the river basin of the Dniester, in the southwestern periphery of the modern village Glinjeni, Republic of Moldova. The site is located at an altitude of 184 m above sea level. It was built on the upper terrace of the left bank of the deep and narrow river valley of the Chorna, a right tributary of the Dniester River and stretches over a length of 42 km, with approximately west–east orientation (Figure 1).

Size. The monument consists of a fortified part and an adjacent contemporaneous open settlement. The fortified part has the shape of an elongated triangle. The settlement is protected by a steep slope from two sides. From the side of the open settlement, there is a rampart (height 3–3.5 m), in front of which the outer staircase ditch is dug up to 4 m deep. The total area of the settlement is more than 12 ha. The trapezoidal site with an area of about 6 ha is bounded on the north-east, south and southwest by the steep slopes of the headland and on the north-west—by an imposing defensive system. It consists of a rampart with a length of about 320 m, width at the base of about 20–25 m and height of about 3.0–3.5 m. In front of it is a ditch about 10–15 m wide and about 3 m deep. At a distance of about 100 m from the western edge of the promontory, the rampart and the ditch are interrupted for a width of about 4 m, probably forming a passage to the fortress. On this particular segment, a section of the road paved with stone pieces was discovered [19]. In

the north-east of the gate is a mound with a diameter of about 25 m and about 3 m high, surrounded by a small ditch, which can be interpreted as the remains of a “bastion” or a guard tower [23].

Excavations. Until now ca. 2000–2300 quer. m (of about 12 ha) has been excavated. The monument was discovered by the famous Moldovan archaeologist Vsevolod I. Markevich in 1954 who failed to identify its correct chronological range. In the late 1960s, Georgiy B. Fedorov from Moscow and the Moldovan archaeologist Georgiy F. Chebotarenco conducted excavations in the vicinity of the village Glinjeni and reinvestigated a number of open settlements that were classified as Slavic monuments. The open settlement was named Glingen V. In 1979, the Russian researcher Anna I. Meluykova and the Moldavian scientist Nataliya V. Goltseva conducted small excavations at the open settlement Glinjeni V and studied mainly the layer of the Early Iron Age. In 1989–1990, Goltseva carried out very large excavations on the fortified part of the monument [19] (pp. 3–40). After these investigations, it became clear that all the chronologically different settlements located in the vicinity belonged to one monument, which was named Glinjeni II-La Șanț. In 2015–2016, Aurel Zănochi, Ion Niculiță and Mihai Băț conducted large-scale exploration surveys along the river Chorna and identified 36 partly previously unknown monuments of the Early Iron Age [23] (pp. 38–43, Figures 2–4; diagr. 1–2).

Chronology. The Glinjeni II-La Șanț is a multilayer fortified settlement (Late Paleolithic to Early Medieval, with interruption) without traceable vertical stratigraphy. All findings from different stages were found in the general cultural layer with a thickness of 0.6 to 1.2 m. A horizontal stratigraphy with features (dwellings, pits, ditches) of different chronology was applied. As a result of the archaeological investigations carried out on the headland area, several layers were discovered: Cucuteni-Tripolie, Cozia-Saharna, Basarabi-Șoldănești, Thracian-Getic (the 7th/6th–5th cc. BC), Getic (the 4th–3rd cc. BC), of Etulia type (the 3rd–5th cc. AD), and the medieval (the 8th–10th/11th cc. AD). To denote the existence of different periods, the term “cultural and chronological horizon” was used in case the findings were correlated with each other, assigned to a specific time period, and their cultural attribution was made [19]. Several cultural and chronological horizons are attributed to the Early Iron Age.

Appendix A.2. Glinjeni II-La Șanț, Sampled Ceramics

Sampled ceramics. For the purposes of this study, two cultural-historic horizons of the Early Iron Age in Glinjeni II-La Șanț: the Cozia-Saharna culture and the Basarabi-Șoldănești culture are of interest (Figures 2 and 3; Table 1): Nos. 1; 2; 4; 6–9; 11; 12; 14–18 (Cozia-Saharna culture); Nos. 3; 5; 10; 13; 19; 20 (Basarabi-Șoldănești culture).

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