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# Novel method of ancient pottery analysis based on radioactive isotope ratios: a pilot study

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## Abstract

The proposed method has been applied to a multi-phased settlement complex and pottery manufacturing centre in Ostrowite in northern Poland. In this study the radioactive isotope ratios method has been applied to a set of ceramic pottery specimens from the same multi-layered archaeological site and probably produced from local raw material. The pilot radiometric research was based on: 24 Neolithic (5200–5000 BCE), 21 Early Iron Age (800–600 BCE), 4 Roman Period (100–400 CE), and 13 Middle Ages (1030–1320 CE) pottery fragments, and also 8 samples of local clay (glacial till) and 3 burned clay samples. The method shows the similarities within the ceramic material used to manufacture the pottery. The variations in the quantitative and qualitative compositions of the basic products (clay, silt, loam, sand, ash and organic admixtures) used in the preparation of the ceramic paste change the isotopic composition and activity ratios. Pottery from each ceramic manufacturing centre, based on the specific composition of the raw materials, have characteristic isotope ratios. Radioactive isotope ratios as fingerprints of ancient ceramic manufacturing centres have not yet been applied as an archaeometric method. In this study two isotope ratios have been selected and applied:  $^{40}\text{K}/^{228}\text{Ac}$  and  $^{226}\text{Ra}/^{208}\text{Tl}$ . All analysis have been done using gamma spectrometry system, with quality and quantity analysis of the spectrums. Low-background passive shield was used for obtain improvement of results quality. The pilot study confirms the grouping of isotope ratio results for each sample type, even in terms of similarities with the base clay material collected in this region.

**Keywords:** Neolithic, Middle Ages, Pottery, Radionuclides, Isotope ratios, Prehistoric ceramic, XRF, Gamma spectrometry

## Introduction

Ancient ceramics are among the most common finds during archaeological work for the time span between the Neolithic and the Modern Period. Ceramic, mostly locally, production was a complex process including: using suitable clay, removal of impurities and preliminary clay preparation, construction (modelling) of pottery vessel, drying, decoration and firing. However, fine (thin-walled) and thick walled ceramics vessels were prepared in a different manner. For fine ceramic production fine-grained masses, mostly sorted, and well mixed was

applied. For thick-walled version nonhomogeneous material was applied. For temper of this ceramic mass organic material was added [1].

In many cases ceramics are the sole remains, hence is used as a primary factor in establishing the chronology for sites and complexes [2]. That is why, even in the early days of the discipline, archaeology has continued to develop methods of examining ceramic finds based on a typology of shape and decoration, macroscopic observations of the production techniques, raw materials and the supposed functions of certain forms. Contemporary research into archaeological pottery includes several scientific methods in order to trace the raw material sources for pottery production, as this is extremely important in reconstructing the economy, manufacturing methods, organization and social dimensions of ceramic

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production [3, 4]. The other aspect is to trace the dispersion of pottery over certain areas for given periods of time, identification of production centres as well as the trade and transport networks. To answer these questions a multidisciplinary project was undertaken based on a few techniques developed in recent years. The latter has involved close cooperation with geologists and geomorphologists to develop techniques to try to identify the sources of the raw materials, petrographic methods of analysis for pottery finds, and a range of microscope type methods and devices [5]. There are several archaeometric techniques that can be used to reliably identify the origin of prehistoric ceramics: particle-induced X-ray emission (PIXE) [6], X-ray diffraction (XRD) [7], X-ray fluorescence spectrometry (XRF) [8–11], Mössbauer spectroscopy (EM) [12], laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [13], neutron activated analysis (NAA) [14], Sr/Nd/Pb isotope analysis [15], electron microprobe [16] and many others [4]. Our aim was to apply a new method based on the analysis of radioactive isotope ratios to examine pottery samples from a single archaeological settlement complex that probably used the same local sources of raw materials but dating from different time periods and manufactured using different techniques.

Each geological material constituting the base material or additions (e.g. sand, organic material, ash, fire clay, calcium carbonate and bone) has its own characteristic content of individual isotopes, which in juxtaposition constitute a set of markers characteristic for the material—with a strictly characteristic composition based on the  $^{238}\text{U}/^{226}\text{Ra}$ , or  $^{232}\text{Th}/^{228}\text{Th}$  radioactive series and  $^{40}\text{K}$ , etc. The content of U, Th, and K elements in rocks and sediments is closely related to the mineral composition. Potassium is derived from potassium feldspar, mica and clay minerals. Thorium occurs in clay minerals and heavy minerals, while elevated uranium contents are found in rocks containing phosphates, aluminosilicates or even organic substances [17]. The relationships between mineral composition and the content of radioactive elements allowed the development of model measurements for the natural radioactivity and the mineral composition in ceramics [18, 19] and natural geological structures [20], which confirm the usefulness of this new method of archaeometric research.

The ceramic is composed of differing composition of raw materials, where isotope concentrations may fluctuate, depending on the final ceramic mixture, but the isotope ratios are unique for a given material composition for a specific region and raw material source. The selection of appropriate pairs of radioactive isotopes to constitute a characteristic fingerprint is not a trivial task, but the use of many independent isotopes from various

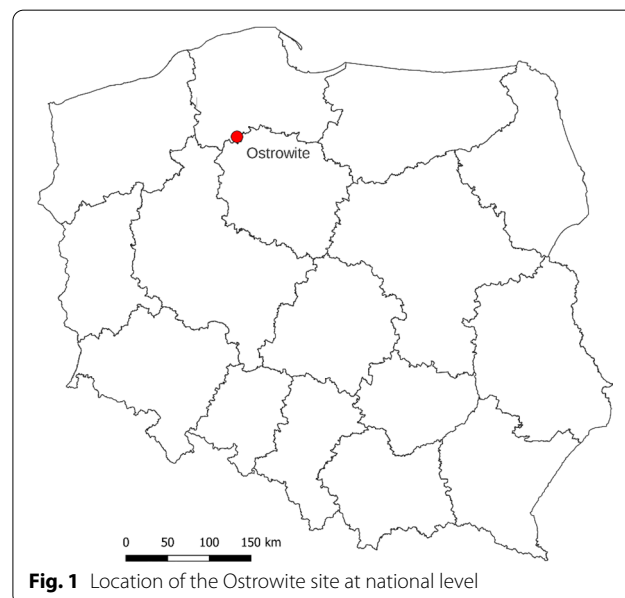
radioactive series and  $^{40}\text{K}$  enables a more precise assessment of the potential relationships between ceramic samples and their origins. It is assumed that a local settler used material from local resources, such as daub in the construction of buildings, while finished ceramic vessels were more widely used in a given region.

The radioactive isotope ratios method applied in ancient ceramics has not been well studied, which gives our method a pioneering nature. The method aims to help identify the similarities and differences between fragments of tableware and other pottery. The method uses natural radioactive isotopes as markers and features a number of advantages, such as avoiding the need for calibration or the destruction of the samples, which is extremely important in the case of pottery fragments from museums or other collections. This methodological approach was developed based on the field of chemometric and radiometric research, as well as archaeological and ceramic research [21–24].

In this study two different instrumental analysis, based on radioanalytical (isotopic ratio) and chemical composition (of selected elements) of the ceramic will be applied for comparison.

#### The site

The multi-phase settlement complex in Ostrowite (53°38'49"N 17°39'11"E) is situated in northern Poland, in the Pomorskie voivodeship (province), within the Chojnice district (Fig. 1.). It is situated in the recently glaciated area of the Pomeranian Lakeland, on an undulating moraine plateau formed by glacial till [24]. The complex has been known to archaeologists and antiquaries since



**Fig. 1** Location of the Ostrowite site at national level

the last quarter of the nineteenth century, with modern archaeological research beginning in the 1990s conducted by archaeologists from the universities in Łódź and Toruń.

The current phase of research has been ongoing since 2000 as a field school for students from the Institute of Archaeology University of Łódź. The archaeological complex is situated about 1.5 km northeast of the contemporary village of Ostrowite on the shore of Ostrowite Lake (also known as Leśne/Waldsee Lake) and about 9 km southeast of Chojnice town. One result of the intense archaeological research is that the subsequent settlement phase at the site has been examined:

- (1) Early Neolithic settlement—clay pits attributed to the Linear Pottery Culture (LPC), dated to 5200–5000 BCE [25];
- (2) Early Iron Age—settlement features and a small cremation cemetery of the Wielka Wieś Phase of the Pomeranian Culture, dated to about 800–600 BCE [24];
- (3) Roman Period—settlement features with relics of long houses, granaries, pits, hearths, lime production kilns and a single (so far) inhumation grave, dated to period between the first and fourth centuries CE and attributed to the Wielbark Culture [24];
- (4) Middle Ages—settlement features, relics of a defensive structure (moat or ditch), two phases of a timber bridge (approx. 1160 CE and 1300 CE) and an inhumation cemetery dated to the mid-11th to the beginning of the fourteenth centuries CE [22–25].

The specific situation of several phases of occupation and pottery production in Ostrowite, without any proven continuity between the subsequent settlement phase, and thus between pottery production traditions and techniques, gives a unique possibility to test a new method. The proposed verification of the isotope concentration method was firstly verified and compared on fragments of the Early Neolithic LPC, Early Iron Age, Roman Period and medieval pottery found in Ostrowite. The detailed archaeological recognition of the site, along with an analysis of the surficial geology of the region, carried out over many years, provide valuable material for research purposes.

As a comparative material we used several pottery samples from two other sites: in Leśno [26n] (Walenta 2009), and in Odry [27n, 28n] (Grabarczyk 1997, 2007). Both are dated to Roman Period (first-second century CE) and attributed to the same Wielbark culture as Roman Period pottery from Ostrowite, which implies relatively similar production techniques used for making those vessels. Both sites are situated about 31–35 km from Ostrowite

in basically the same geohistorical region of Eastern Pomerania.

The oldest ceramics in Central Europe, connected with the Linear Pottery Culture, appear at the Vistula River tributary around 7500 years ago [25–28], which gives an opportunity to study the distribution of ceramics and trace long distance trade in the Early Neolithic. In the last few years, several new finds of LPC materials and settlements have been documented outside traditional areas like Kuyavia or the Chełmno Lakelands [25, 28] where archaeologists had identified the sites of this culture previously [29–31]. The unexpected discovery of LPC pits with large amounts of materials like pottery fragments, flints, bones and other artefacts and ecofacts in Ostrowite [22] outside the traditional LPC centres like Kuyavia, Lesser Poland (Małopolska), Sandomierz Upland and Great Poland (Wielkopolska) extends the known area of occupation of this Early Neolithic communities. It also raises questions about long-distance contacts between Ostrowite and those “traditional” centres evoked by the finds of flints in southern Poland.

In this study, the Early Neolithic pottery characteristics will be compared to finds from later periods. The Early Iron Age (Hallstatt C Period) was a crucial step in the development of settlements and technology in large areas of central, eastern and northern Europe, a period experiencing the adaptation of metallurgical innovations from the southern part of the continent and the transition between the Bronze Age and the Iron Age. A relatively small rural settlement together with a cremation cemetery existed in Ostrowite in this period. It gives us an opportunity not only to search for short and long-distance connections between local communities, but also to examine the differences between the everyday utilitarian pottery and funerary urns used in cremation rituals. The Roman Period settlement assemblages from Ostrowite are characteristic for the large cultural area occupied by communities of the Wielbark Culture, which is connected by most archaeologists with the Goths, known from late Roman written sources. The Roman Period settlement complex in Ostrowite is relatively large, with a fairly established chronology, based on radiocarbon analyses as well as on traditional studies of specific groups of finds [23]. In this time, we can expect to find traces of long-distance trade in some ceramic types and the use of ceramic vessels as containers for loose or liquid goods. Trade connections in this period reached even the territory of the Roman Empire via the “Amber Route”.

In the Medieval Period, Ostrowite become a local trade centre, located on the border between the Kingdom of Poland and the Pomeranian Principalities [23]. This gives an opportunity to study interactions between different groups of people. It was also a period of major

changes in ceramic production techniques, with the popularisation of the potter's wheel and the use of more advanced firing techniques. Ceramic production can be divided into two streams: private household production and more specialised, craft production. In all cases we suspect the local production for most of the assemblage with the addition of imported examples, which are almost impossible to determine with traditional methods based on classification and taxonomy since pottery production is highly standardised across all the North-West Slavic areas. Throughout all these periods the production techniques should be different but based on the same raw material. This region is rich in deposits of good quality clay (glacial till composed mostly of clayey silts and silty clays) that has been used extensively. Some evidence of use clay resources have been investigated and analysed by geomorphologist (Additional file 1: Figure S1).

## Materials and methods

### Sample collecting

The pilot radiometric research and methodological development were each based on a set of 13 different medieval vessels, 4 Roman Period, 21 Early Iron Age, 24 fragments of Neolithic pottery and a set of 8 clay samples collected locally. The samples were collected during the regular archaeological excavation conducted since 2000 as an element of the field school for archaeology students. All the potsherds were acquired from well-defined archaeological contexts, in most cases the backfills of settlement pits, cultural layers and, in the case of two samples from the Early Iron Age, from cremation graves (Fig. 2).

The pottery fragments were washed, air-dried, and organised in a professional manner by the archaeologists. The 62 fragments of pottery, as well as the 3 burned clay and 8 raw clay materials from various pits, were packed in plastic pots. All the samples are listed and described in Table 1.

The samples of possible raw material for pottery production were collected within the site area and in the closest vicinity from eight locations. The postglacial region is rich in high-quality clay material, which has potentially determinate an extensive pottery production in various prehistorical and historical periods. Geomorphological research confirmed the more intensively exploitation of clay resources in some points around the lake. Therefore, in this study the samples of clay material from specific depth layers have been analysed (Table 2). Samples were taken from the walls of archaeological outcrops or with the use of hand auger from depths of 0.6–1.2 m b.s.l.

### Research methods

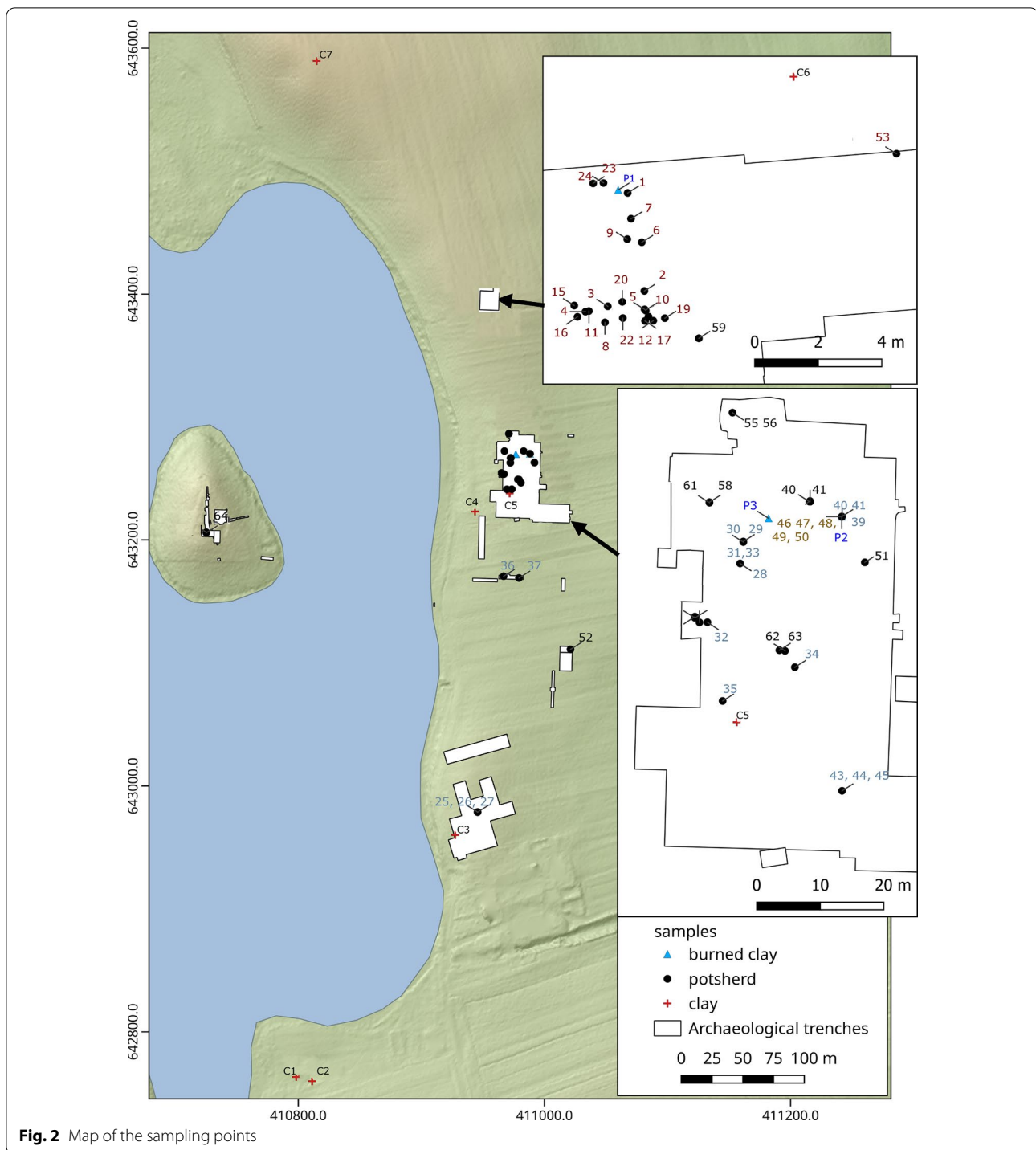
The pottery specimens were weighed and, in assumption of new method based on isotopic ratio, measured without destruction. The mass of the samples fluctuated between approx. 5 and 139 g. The raw material samples were dried at room temperature per several days and remains of sediments were mechanically removed from the ceramic fragments with a soft bristle brush. In this form samples were used for radiometric analysis using gamma spectrometry system (Additional file 2: Figure S2).

Directly for XRF analysis (as comparative method) some small part of the samples were destroyed. Subsequently, samples of several grams were cut from each fragment using a Secotom 15 geological saw, manufactured by Stuers, using the "wet" method, for further detailed analysis. The precise cutting of the sample also allowed to obtain a relatively smooth cross-sectional surface. Smaller fragments of ceramics were used to measure the volumetric density. These measurements were made with a digital analytical balance PS1000 with a set designed for measuring the density of solids and liquids in at least 99.5% isopropyl alcohol, at the temperature of 20 °C, during 3 min. The value of bulk density was read directly from the balance after previously entering the measurement parameters. The obtained results of the volume density measurements are presented in Table 1. Raw material has been summarized in Table 2. Petrographic features and the nature of the impurities were observed using the Leica M125 stereoscope. The results of these observations are summarized in Appendix Table 3. Some photos have been added as examples (Appendix, photos).

### Radioactive isotopic method

All measurements were based on the low-level gamma spectrometry system located at the Institute of Applied Radiation Chemistry, Lodz University of Technology [32, 33]. For background reduction, a unique passive system based on 20 mm of steel, 100 mm of 'spectrometric' lead, additionally padded with 5 mm of low activity <6 Bq/kg of  $^{210}\text{Pb}$  layer (Plombum, Poland), and 5 mm of high purity electrolytic copper. All measurements were taken in the continuously ventilated laboratory room for  $^{222}\text{Rn}$  and its progeny concentration reduction [17, 32, 33].

AGX3020 HPGe (Canberra) detector model with a relative efficiency of 30%, combined with a 2002CLS (Canberra) an offset preamplifier, was used as a basic detector. The system was equipped with a 9-inch NaI(Tl) crystal as an additional guard detector (Scionix). The Compton Suppression system can also be used in anticoincidence and coincidence modes. A Gamma spectrometry system (Canberra) with an active



**Fig. 2** Map of the sampling points

shield can be used for small samples with a mass lower than about 5 g. However, background has been monitored and subtract from measurements each individual samples. In most environmental analysis the primary HPGe detector was enough to provide good quality analyses [32–35].

The high resolution of the HPGe detector and 80,000 s measurement time ensure good statistics for the natural radionuclide analysis in ceramic fragments. Uncertainty of a single measurement was determined at the level of  $1\sigma$  for single energy peak. In practice, this ensured specific error for each of the isotope below

**Table 1** Ceramic sample list

Id	Code	Chronology	Mass [g]	Density [g/cm <sup>3</sup> ]	Thickness [mm] (max)
1	X87	Neolith	85.1	2.045	9/13
2	Y70	Neolith	34.0	2.187	6.4/86
3	Y95	Neolith	99.3	1.986	13.2
4	Y133	Neolith	42.1	2.055	8.1
5	Y231	Neolith	59.9	2.008	10.3
6	Y236	Neolith	34.2	2.023	7.8
7	Y270	Neolith	81.3	1.870	8.2
8	Z38	Neolith	46.9	2.111	8.9
9	Z109	Neolith	37.9	2.041	7.5
10	Z143	Neolith	20.3	2.100	11.7
11	Z262	Neolith	19.7	1.996	8.4
12	Z302	Neolith	21.4	2.062	10.7
13	Z330	Neolith	33.1	2.119	6.5
14	Z341	Neolith	9.34	1.933	6.2
15	Z358	Neolith	27.1	1.963	6.3
16	Z374	Neolith	8.85	1.989	5.7
17	Z388	Neolith	46.1	2.051	13.5
18	Z434	Neolith	60.1	2.109	8.9
19	Z438	Neolith	50.3	2.153	4.5
20	Z489	Neolith	39.5	2.063	12.3
21	Z499	Neolith	66.5	2.085	14.2
22	Z509	Neolith	22.6	1.968	9.1
23	Z632	Neolith	13.0	2.098	5.1
24	Z647	Neolith	13.9	2.114	5.7
25	Os/583/04	Iron age	81.6	2.206	15.5
26	Os/611/04	Iron age	40.7	2.283	10.8
27	Os/611/04	Iron age	72.2	2.189	8.2
28	Os/2209a/14	Iron age	101.5	2.138	8.7
29	Os/2234/14	Iron age	38.7	2.313	10.3
30	Os/2234/14	Iron age	72.9	2.129	9.7
31	Os/2279/14	Iron age	36.0	2.184	7.8
32	Os/2873/17	Iron age	57.8	2.219	13.3
33	Os/3115/18	Iron age	63.1	2.126	9.8
34	Os/3194/18	Iron age	139.5	2.133	12.1
35	Os/997/08	Iron age	127.8	2.167	11.8
36	Os/1870/12	Iron age	139.0	2.101	14.4
37	Os/1892/12	Iron age	79.4	2.024	10.0
38	Os/1960/12	Iron age	52.7	2.108	8.6
39	Os/2419/15	Iron age	35.1	1.645	11.8
40	Os/2442/15	Iron age	51.8	2.212	8.8
41	Os/2475/15	Iron age	61.8	2.363	11.5
42	Os/3030/17	Iron age	43.0	2.177	9.3
43	1282a	Iron age	18.5	2.048	6.3
44	1282b	Iron age	10.3	1.975	10.6
45	1282c	Iron age	13.0	2.202	9.7
46	1691/16	Romanian period	20.9	1.538	8.2
47	1692/19	Romanian period	7.9	2.189	5.8
48	2419	Romanian period	31.0	2.080	12.0

**Table 1** (continued)

Id	Code	Chronology	Mass [g]	Density [g/cm <sup>3</sup> ]	Thickness [mm] (max)
49	2209	Romanian period	5.15	2.046	8.9
50	Os/2189/14	Middle age	32.7	2.208	6.3
51	Os/2551/16	Middle age	38.9	2.254	8.3
52	Os/2583/16	Middle age	25.9	2.222	7.1
53	Os/2614/16	Middle age	48.9	2.092	10.5
54	Os/2614/16	Middle age	33.4	2.110	8.5
55	Os/2988/17	Middle age	39.5	2.100	7.2
56	Os/2988/17	Middle age	49.4	2.139	6.2
57	Os/3007/17	Middle age	77.5	2.268	7.7
58	Os/3443/19	Middle age	64.7	2.087	11.32
59	Os/2988/17	Middle age	115.0	2.011	11.2
60	Os/3007/17	Middle age	19.7	2.246	8.8
61	Os/3115/18/3	Middle age	65.1	2.109	5.3
62	St. 1 w-wa 8	Middle age	106.0	2.114	12.0
P1	P1	Neolith	100.0	–	–
P2	P2	Romanian period	117	–	–
P3	P3	Middle Age	37.0	–	–

**Table 2** Raw material sample list

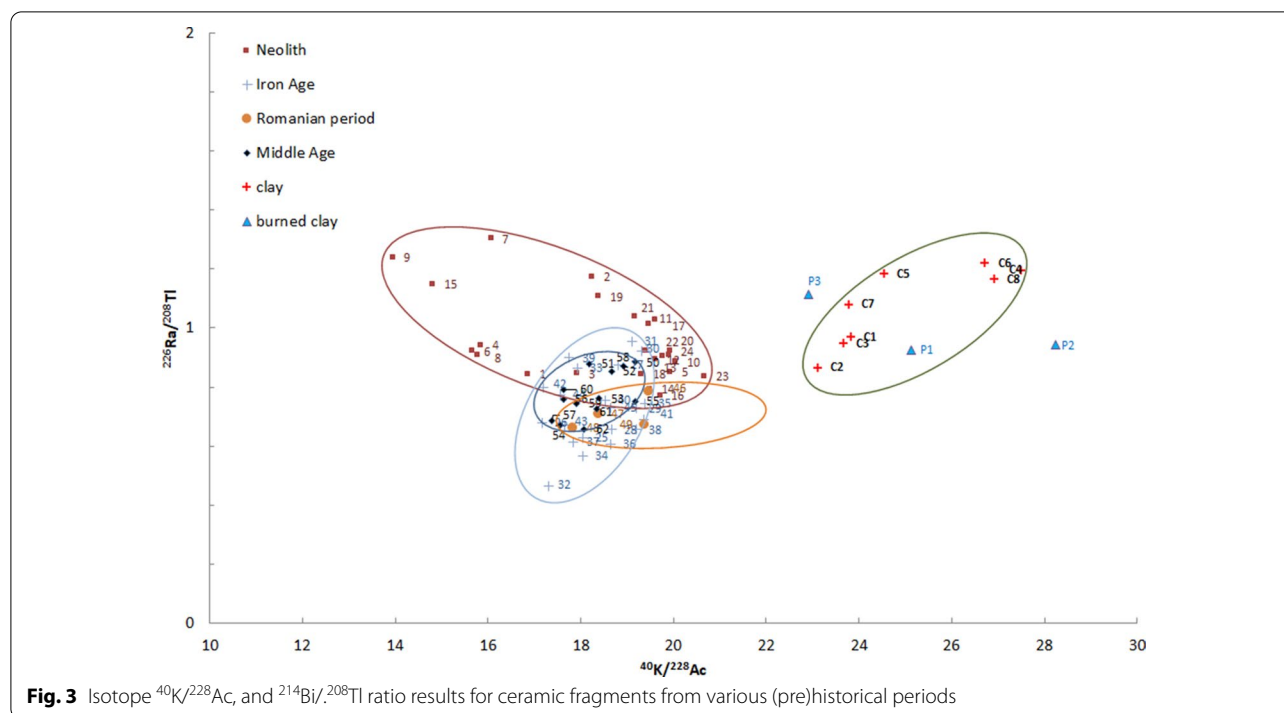
Id	Archeological code	Mass (g)	Type of material
C1	PT1 65–75 cm	46.2	Raw material—glacial till
C2	PT2 80–100 cm	48.3	Raw material- glacial till
C3	PT3 60–70 cm	49.1	Raw material- glacial till
C4	PT4 60–70 cm	47.8	Raw material- glacial silty sand
C5	PT5a 60–70 cm	49.5	Raw material- glacial till
C6	PT5b 100–110 cm	50.0	Raw material- glacial till
C7	PT6 110–120 cm	50.0	Raw material- glacial till
C8	PT7 60–70 cm	50.2	Raw material—lacustrine (or glaciolacustrine) silt

7%. Despite mass fluctuation, relatively long measurement time over 22 h ensure acceptable error level lower than 10% for activity ratio of two isotopes. For sample Id 9 (Z109) activity ratios were analysed 5 times for control of values fluctuation. In practice for this sample  $^{40}\text{K}/^{228}\text{Ac}$  and  $^{226}\text{Ra}/^{208}\text{Tl}$  activity ratios were controlled and equal to:  $13.95 \pm 0.32$  and  $1.24 \pm 0.037$ , respectively.

Samples were collected several years (3–6 years) before all measurements, therefore secular equilibrium was ensured for all investigated isotopes. The share of bone in the ceramic mixture in one case (st.1, w-wa8) could slightly change the isotope concentration levels, but it did not affect the isotope ratios. Samples before analysis were clean and dry in room temperature. All of them were analysed in original geometry, without

crushing. Non-destructive analysis is highly recommended for museum or collector's items.

The methodology of radiometric studies of ancient ceramics is based on low-background and high-resolution gamma radiation spectrometry [17, 32–35]. The basic element of the method is the use of the natural radionuclides occurring in geological materials, including clays. Each geological component of the material, as well as tempering or aesthetic additives, or technological impurities, has its own characteristic content of individual isotopes, which in combination constitute a set of markers characteristic for the material—a fingerprint with a strictly characteristic composition of the isotopes  $^{40}\text{K}$ ,  $^{226}\text{Ra}$  ( $^{214}\text{Bi}$ ), or  $^{232}\text{Th}$  ( $^{228}\text{Ac}$  and  $^{208}\text{Tl}$ ) (Fig. 3), etc. The concentration of isotopes can fluctuate depending on the composition of the material, in result isotope ratios have form a unique fingerprint for any given material composition collected in a region. The selection of appropriate pairs of radioactive isotopes constituting a characteristic fingerprint is not a trivial task. Same isotopes activity concentration ( $^{222}\text{Rn}$ , and  $^{220}\text{Rn}$  decay progenies, eg.  $^{208}\text{Tl}$ ) correlates with physico-chemical properties of each group of the ceramic samples (porosity, density of the material). Activity concentration of  $^{226}\text{Ra}$  is mostly correlated with contribution of illitic material + kaolinite and organic matter in geological material [36]. The illite/smectite and kaolinite are natural sorbents for Ra and  $^{210}\text{Pb}$  isotopes. Radioactive  $^{40}\text{K}$  in range from 473– to 1001 Bq/kg was measured on feldspar, mica and clay



**Fig. 3** Isotope  $^{40}\text{K}/^{228}\text{Ac}$ , and  $^{214}\text{Bi}/^{208}\text{Tl}$  ratio results for ceramic fragments from various (pre)historical periods

layers provided from other geological structure erosion eg. granite weathering [36]. The use of many various isotopes from different radioactive series and  $^{40}\text{K}$  allow a more precise assessment of the possible relationships between the ceramic samples and, possibly, their raw material and origin. Local manufacture used rather local material resources, and the finished ceramic products were widely used in a given region. The close availability of good quality clay potentially contributed to the cultivation of the ceramic tradition in this region for many historical periods and to wholesale production and possibly further distribution. This is more important for the daub used in constructing the buildings within the site area.

The selection of radioactive isotopes  $^{40}\text{K}$ ,  $^{226}\text{Ra}$  (based on the  $^{214}\text{Bi}$ ) and  $^{232}\text{Th}$  ( $^{228}\text{Ac}$  and  $^{208}\text{Tl}$ ) is highly important due to:

1. the use of a standard method, without the need for efficiency calibration (isotope ratios eliminate the need for the efficiency parameter), where as a result each sample may have its own mass and geometry (Because of the analysis activity ratios isotopes emitted photon with similar energies ( $^{40}\text{K}/^{228}\text{Ac}$ , mean-1460 keV/911 keV), and ( $^{226}\text{Ra}/^{214}\text{Bi}$ )/ $^{208}\text{Tl}$ - 609 keV/583 keV), we obtain abbreviation of the coefficients correlated with detection

efficiency, depended on density, size, geometry, mass, for the same sample.);

2. the natural long-lived isotopes, which are present in each sample in some concentration, are characteristic for it (clustering).

The  $^{40}\text{K}$  radionuclide concentration has been analysed directly on the base of 1460 keV peak energy line. The  $^{226}\text{Ra}$  isotope concentration was analysed on a base of  $^{214}\text{Bi}$  isotope (609 keV peak energy line,  $T_{1/2}=19.9$  min) from  $^{238}\text{U}$  series, while  $^{232}\text{Th}$  was analysed on the base of two different progenies,  $^{228}\text{Ac}$  (911 keV peak energy line,  $T_{1/2}=6.15$  h) and  $^{208}\text{Tl}$  (583 keV peak energy line,  $T_{1/2}=3.05$  min) isotopes (direct products of the  $^{228}\text{Ra}$  and  $^{212}\text{Po}$  isotope decay from thorium series). All analyses were carried out after 30 days from enclosing of the samples, required to obtain secular equilibrium between the parent isotope and its progenies. Two isotope ratios, with similar energy of the photos  $^{40}\text{K}/^{228}\text{Ac}$ , and  $^{214}\text{Bi}/^{208}\text{Tl}$  were used to test and verify the proposed method.

Similar energies of isotope reduce problem of spectrometry calibration for each geometry of ceramic sample.

From other hand calculation of activity ratio allow for investigation of variability of ceramic produced in each historical period.

### XRF analysis

In the next stage of the research, efforts were made to obtain information on the chemical composition of the ceramic fragments. Due to the potential influence of many factors, both related to the technology of ceramics production, use and subsequent deposition in various environments, it was decided to make measurements on each surface of the ceramic fragment. A handheld energy dispersion X-ray fluorescence spectrometer (pXRF) by Olympus model Vanta VMR was used for geochemical analyses [9, 10, 37]. This spectrometer enables quick and precise identification and analysis of elements from Mg to U. This model is equipped with a tube with a rhodium anode (Rh) and power of 4 W. Thanks to it, the measuring range of 5–200  $\mu$ A currents and 8–50 keV voltage can be obtained. The spectrometer has a large-area SDD detector with filtration of the primary beam with one permanent filter [8–11, 37]. The study of ceramics was carried out using the 3-beam Geochem3 measurement method. The first beam at a voltage of 40 keV and an exposure time of 10 s, the following elements were excited: Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Ba, W, Hg, Pb, Bi, Tu, U (counts of remaining unassigned peaks). The second beam with a voltage of 10 keV and time of 20 s was excited by: Mg, Al, Si, P, S, K, Ca, Ti, Mn. The third beam with a voltage of 50 keV during 20 s, Ag, Cd, Sn, Sb, Ba, La, Ce, Pr, Nd, LE were applied.

Last calibration for the Geochem 3 measurement program was carried out just before the analysis of ceramic series of samples at the Olympus service, and the contents of the measured elements was certified based on various geological reference materials.

### PCA analysis

For the results of XRF chemical composition interpretation, the hierarchical Principal Component Analysis (PCA) grouping methods were applied. PCA method has been applied for provides a representation of chosen variables: Mg, Al, Si, K, Ti, Fe, Zn, Rb, Zr and Ba. which allows finding variables that are characteristic of prehistoric ceramic groups [38, 39].

### Results

The scatter plot of isotope ratios showed the scale of similarity (Fig. 3). The similarity between each pair of isotope ratios indicated which of the tested objects had the same material composition based on the regional resources. Each group of results represented the manufacturing technologies and historical age.

However, the method of isotope ratios proved to be more accurate and clearly indicated the grouping of the results.

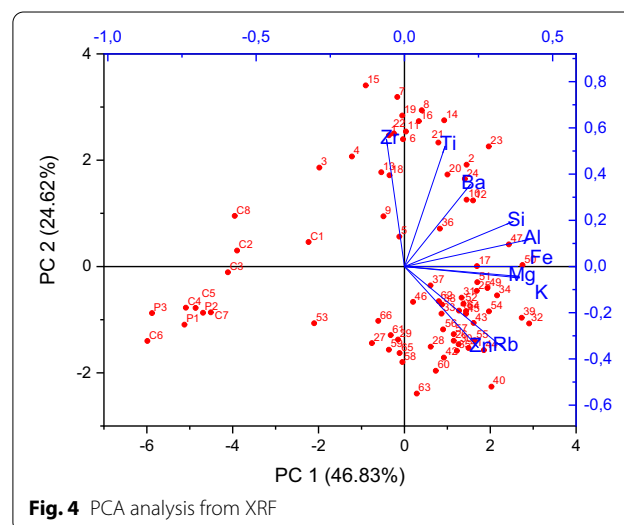
The t-test was applied for  $^{40}\text{K}/^{228}\text{Ac}$  and  $^{226}\text{Ra}/^{208}\text{Tl}$  to confirm the statistical significance of the grouping. Each test confirmed the statistical significance of the difference with  $p < 0.0035$  (meeting the criterion  $< 0.05$ ) between the types of pottery origin from various prehistorical and historical periods. Single sample with the Id 9 (code Z109) did not conform with that typical for the group  $^{40}\text{K}/^{228}\text{Ac}$  and  $^{226}\text{Ra}/^{208}\text{Tl}$  results. This suggested that this vessel may have been imported from another manufacturing region.

The average value for  $^{40}\text{K}/^{228}\text{Ac}$  and  $^{226}\text{Ra}/^{208}\text{Tl}$  in each group of the analysed samples were different:

- For Early Neolithic ceramic  $^{40}\text{K}/^{228}\text{Ac}$  ratio was  $18.3 \pm 2.0$ , and  $^{226}\text{Ra}/^{208}\text{Tl}$  activity ratio was  $0.959 \pm 0.142$ .
- Early Iron Age ceramic  $^{40}\text{K}/^{228}\text{Ac}$  ratio was  $18.3 \pm 0.8$ , and  $^{226}\text{Ra}/^{208}\text{Tl}$  activity ratio was  $0.727 \pm 0.125$ .
- Roman Period ceramic  $^{40}\text{K}/^{228}\text{Ac}$  ratio was  $19.8 \pm 0.8$ , and  $^{226}\text{Ra}/^{208}\text{Tl}$  activity ratio was  $0.683 \pm 0.072$ .
- Middle Age ceramic  $^{40}\text{K}/^{228}\text{Ac}$  ratio was  $18.2 \pm 0.6$ , and  $^{226}\text{Ra}/^{208}\text{Tl}$  activity ratio was  $0.771 \pm 0.079$ .
- Clay-raw material  $^{40}\text{K}/^{228}\text{Ac}$  ratio was  $25.7 \pm 1.7$ , and  $^{226}\text{Ra}/^{208}\text{Tl}$  activity ratio was  $1.103 \pm 0.145$ .

The activity of the  $^{40}\text{K}/^{228}\text{Ac}$  and  $^{226}\text{Ra}/^{208}\text{Tl}$  ratio results obtained in this study were tested by hierarchical analysis method.

The developed method of isotope ratios was compared with the XRF method based on the relationships between the elements in the natural sediments or clays (Fig. 4). The content of certain aluminium silicates containing Al, Si and P was correlated with the concentrations of  $^{238}\text{U}$  and  $^{226}\text{Ra}$ . The content of Th ( $^{232}\text{Th}$ ) correlated with heavy minerals, represented by Ti, V or Cr [34]. In this



**Fig. 4** PCA analysis from XRF

study PCA analysis was applied for chosen representative element Mg, Al, Si, K, Ti, Fe, Zn, Rb, Zr and Ba. Two significant principal components were identified—PC1 (46.83%) and PC2 (24.62%), which fully describe about 71% of the total variation.

In the ceramic and raw material, various individual clusters were indicated on clustering. Specimen Id 9 (Z109) was grouped with the Neolithic ceramics, but this result had the largest distance from centroid of the Neolithic samples group. The low similarity of this individual vessel to the Neolithic ceramics collected at Ostrowite indicates a different raw material composition [39–46], a different origin of this material or even a different manufacturing technology, therefore it has been identified as an imported vessel (Fig. 3).

Hierarchical clustering analysis does not need an indication of the number of clusters, and can be applied to relatively small groups of observations. Both the hierarchical clustering approaches indicated an additional grouping of the results, and helped in the interpretation of the subgroups.

The Neolithic and medieval ceramic specimens were classified as different groups even if they were produced in the region, based on local geological resources [45, 46]. Ceramic vessels from Iron age and Romanian Period had rather more diversified material compositions and some fragments were more varied. In practice such types of fragments generated additional subgroups in the hierarchical approach.

## Discussion

The radioactive isotope content of any geological sample (lithic rock, sand, silt or clay) is characteristic for a specific type of geological material. The use of the isotope ratio method allows each sample to be distinguished in terms of source. Ostrowite has been a settlement centre for at least seven thousand years, for communities from many archaeological cultures located on several intersecting routes in at least four chronological phases. The earliest pottery to be manufactured in Ostrowite dates to 5200–5000 BCE, during the existence of the Early Neolithic settlement. Subsequent settlement phases and pottery production horizons are dated to the Early Iron Age (approx. 800–600 BCE), the Roman Period (First to fourth centuries CE) and the Middle Ages (Eleventh to fourteenth centuries CE). The site has a long tradition of experience in ceramic production [40–43].

Ceramics from different periods and for different purposes deserve special attention. The local transport and distribution of utility and table ceramics was practiced on a routine basis. In the history of excavations, there have been specimens found of ceramics from other cultures, sometimes located thousands of kilometres away. The

question for archaeologists is whether the pottery found in the settlement region is a local product or an import. The answer to this question carries a lot of information about settlement migration or the scale of distribution of liquids (wines, oil or other) and loose goods (grain and other agricultural products), where ceramics acted as a storage and transport container. Thus, the fragments of ceramics found in the Ostrowite region, catalogued, archived, and constantly supplemented with new finds, constitute a valuable database of ceramic materials, one where the method has been checked and tested in terms of its usefulness for further archaeometric research. The research revealed differences between samples from various historical ages.

Early Iron Age pottery seems to be similar to those from the Roman Period and the Medieval Period. Significant differences occurred only in samples 2198, 2209 and 1282. The first two were fragments of cinerary urns from the small cremation cemetery. They appear to be quite similar to the Neolithic pottery as well as Roman Period samples 2419 and 1692–16. In all these cases microscopic analysis revealed the presence of plant remains as additives to clay. The plant contribution has rather negligible effect on the isotope ratios, due to low mass and burnout effect during firing.

Roman Period ceramics generally seem to be similar in terms of the radioactive isotope ratio to Medieval assemblages. This may mean that the earlier population used similar sources of raw materials and additives as the later Slavic groups. The results of the excavations seem to prove this observation. The only excavated clay pit from the Roman Period so far was located relatively closely to features interpreted as Medieval clay pits. Significant and important technological changes in pottery production, such as the wide introduction of the potter's wheel, changes in the organization of pottery workshops and the supposed use of more advanced kilns, which took place during the Early Medieval Period (in the tenth and eleventh centuries CE) did not affect the isotopic characteristics of the ceramics.

This study involved the application of a new method of ceramic analysis. The selection and variety of the samples collected in the Ostrowite region made it possible to evaluate the usefulness of this method as an archaeometric method. The method of isotope ratios proved to be more accurate and therefore more reliable than traditional methods. The method therefore has the potential to further improve the analysis of the distribution of ceramics over a wider spectrum of ceramic variability. It allows the grouping of pottery derived from common sources of clay and similar additives, and therefore forms an unambiguous indicator of common origin.

The study confirmed that the production technology influences the macroscopic differentiation (appearance) in a negligible way and it rather affects the content of radioactive elements and their ratios. However, differences in appearance may indicate that the vessel comes from a different region and is therefore a preliminary indicator of imports. The variability of the content of radioactive isotopes and the isotope ratios specific for each group are the result of the characteristic mineral composition of the raw material.

A high K content indicates a high proportion of clay in the semi-finished product [36]. U correlates with aluminosilicates or organic components [17, 47], while Th is an index of metal-rich heavy minerals [48]. Using these relationships, it is possible to assess possible groupings of results through the ratios of the content of elements. The method of ratios of the radioactive isotopes, the emitted gamma photons having similar energy, allows the reduction of the influence of mass differentiation or the geometry of the ceramic samples, which significantly improves the quality of analyses. The method of isotope relations gives repeatable results with low measurement uncertainty, which is an important factor for the assessment of possible cases of imported ceramics, indicative of migration or trade relations between settlement groups living in the region.

The firing temperature has rather secondary importance for the content of relatively volatile elements such as K (boiling point 760 °C) due to its solid physical form and the presence of K in the form of various compounds [49]. However, this will be analysed in a future set of experiments.

Summarizing, to the advantages of the new, radiometric method of ceramics and raw material analysis belong:

- Non-destructive (non-invasive) approach for unique ceramic fragments,
- The measurable-method based on the isotopic ratios of radioactive isotopes commonly present in ceramic and geological material doesn't need certify reference material for quantity calibration of spectrometer or any improvement for ceramic analysis.
- The method is independent from other analytical processing (doesn't require chemical preparation or additional devices)
- Due to using HPGe detector, the method is highly selective and specific,

- The method can be applied for various types of the ceramic samples and raw materials,
- Disadvantages
  - Minimum one measurement day for each single ceramic sample or raw material. Thus, the method should be considered as unappropriated for research on large pottery collections and could be applied on selected samples chosen from larger sets in order to answer certain questions regarding raw materials and provenance.

## Conclusions

Collections of variety of ceramics from Ostrowite archaeological site were used for verification purposes and confirmed the usefulness of the new method of archaeometric research. High historical value implies the importance of the non-invasive nature of the research method.

The ratios of radioactive isotopes are determined by a number of factors characterizing the ceramic product:

- (1) Type of raw material, clay or loam, used in the production process,
- (2) Type and number of additives for different vessel uses.

A new non-invasive archaeometric method based on natural radionuclides were developed and tested. The applied methods allowed the grouping of the raw material, whether found in Neolithic or medieval ceramics, Roman or Iron Age vessels. In this study both types of pottery and raw material analysis were based on low-background gamma radiation spectrometry measured by HPGe detector. The basic element of the method is the use of natural radionuclides occurring in geological material. The specific fingerprint of each was based on two radioactive isotope ratios  $^{40}\text{K}/^{228}\text{Ac}$  and  $^{226}\text{Ra}/^{208}\text{Tl}$ .

The application of a non-invasive methodology that does not require reference material gives great analytical possibilities and can provide a number of answers as to the origin of the samples, directions of ceramic distribution or production technology. Appropriately selected isotope ratios were used as markers and the methodology proposed in the work has the features of a chemometric analysis.

The use of a large scale radioanalytical study in the future should allow a detailed analysis to establish the provenance of ancient pottery, trades routes and interactions between human groups in the past.

**Table 3** Petrographic characteristic of the samples

Sample	determination density [g/cm <sup>3</sup> ]	The color of the cross-section of ceramics and clay fields		Petrographic nature								
		Crumb or sandy sprinkles	"Pseudoengob" Blackened	Textural features of lytic components			Textural features of empty spaces					
				Homogeneous with clay mass texture	Equigranular texture	Variegated texture	Porphyritic texture	Lack of empty spaces	Chaotic texture	Parallel texture		
1	2.0	0	0	0	1	0	0	0	0	1	0	0
2	2.2	0	0	0	1	0	0	0	0	1	0	0
3	2.0	0	0	0	1	0	0	0	0	1	0	0
4	2.1	0	1	0	1	0	0	0	0	1	0	0
5	2.0	0	1	0	0	0	1	0	0	0	1	0
6	2.0	0	1	0	1	0	0	0	0	1	0	0
7	1.9	0	1	0	1	0	0	0	0	1	0	0
8	2.1	0	0	0	1	0	0	0	0	0	0	0
9	2.0	0	0	0	0	0	1	0	0	0	1	0
10	2.1	0	1	0	1	0	0	0	0	0	1	0
11	2.0	0	0	0	1	0	0	0	0	1	0	0
12	2.1	0	0	0	1	0	0	0	0	1	0	0
13	2.1	0	0	0	1	0	0	0	0	1	0	0
14	1.9	0	0	0	1	0	0	0	0	1	0	0
15	2.0	0	1	0	1	0	0	0	0	1	0	0
16	2.0	0	1	0	1	0	0	0	0	1	0	0
17	2.1	0	0	0	1	0	0	0	0	1	0	0
18	2.1	0	1	0	1	0	0	0	0	1	0	0
19	2.2	0	0	1	1	0	0	0	0	1	0	0
20	2.1	0	0	0	1	0	0	0	0	1	0	0
21	2.1	0	0	0	1	0	0	0	0	1	0	0
22	2.0	0	0	0	1	0	0	0	0	1	0	0
23	2.1	0	1	0	1	0	0	0	0	1	0	0
24	2.1	0	0	0	1	0	0	0	0	1	0	0
25	2.2	0	0	0	0	0	0	0	1	0	1	0
26	2.3	1	0	0	0	0	0	0	1	0	1	0
27	2.2	1	0	0	0	0	0	0	1	0	1	0
28	2.1	0	0	0	0	1	0	0	0	0	1	0
29	2.3	1	0	0	0	0	0	0	1	0	1	0
30	2.1	0	0	0	0	0	0	0	1	0	1	0
31	2.2	1	0	0	0	0	1	1	0	1	1	0

**Table 3** (continued)

Sample determination	Volume density [g/cm <sup>3</sup> ]	The color of the cross-section of ceramics and clay fields		Petrographic nature			
		Crumb or sandy sprinkles	"Pseudoengob" Blackened	Textural features of lytic components		Textural features of empty spaces	
				Homogeneous Equigranular with clay mass texture	Variegated texture	Lack of empty spaces	Chaotic texture
32	2.2	0	0	0	1	0	1
33	2.1	0	0	0	1	0	0
34	2.1	0	0	0	1	0	0
35	2.2	1	0	0	1	0	0
38	2.1	0	0	0	0	1	0
37	2.0	0	0	0	1	0	0
38	2.1	0	0	0	1	0	0
39	1.6	1	0	0	1	0	1
40	2.2	0	0	0	1	0	0
41	2.4	0	0	0	1	0	1
42	2.2	0	0	0	0	0	0
43	2.0	0	0	0	0	1	0
44	2.0	1	0	0	1	0	0
45	2.2	0	0	0	0	1	0
46	2.1	0	1	0	1	0	1
47	1.5	0	0	0	1	0	1
48	2.2	0	0	0	1	0	0
49	2.1	0	0	0	1	0	0
50	2.2	0	0	0	0	0	1
51	2.3	0	0	0	1	0	0
52	2.2	0	0	0	0	0	0
53	2.1	0	0	0	0	1	0
54	2.1	0	0	0	1	0	0
55	2.1	0	0	0	1	0	0
56	2.1	0	0	0	1	0	0
57	2.3	0	0	0	0	1	0
58	2.1	0	0	0	0	1	0
59	2.0	0	0	0	1	0	0
60	2.2	0	0	0	0	1	0

**Table 3** (continued)

Sample determination	Volume density [g/cm <sup>3</sup> ]	The color of the cross-section of ceramics and clay fields		Petrographic nature									
		Crumb or sandy sprinkles	"Pseudoengob" Blackened	Textural features of lytic components				Textural features of empty spaces					
				Homogeneous Equigranular with clay mass texture		Variegated texture	Porphyritic texture	Lack of empty spaces	Chaotic texture	Parallel texture			
61	2.1	0	0	0	0	1	0	0	0	0	0	1	
62	2.1	0	0	0	0	1	0	0	1	0	0	1	
Sample determination	Petrographic nature	Characteristic features of the clay mass											Crumbs of older ceramics and lumps of dried clay
		Textural features of empty spaces					Characteristic mineral and rock components						
		Cavern texture	Bubble texture	Spongy texture	Fluid texture	Vegetable texture	Smudges	Noodles	Feldspars	Lithodlastic crystalline rocks	Concretions Fe		
1		0	0	0	0	1	0	0	0	0	1	0	
2		1	0	0	0	1	0	0	0	0	0	0	
3		1	0	0	0	1	0	1	0	0	1	0	
4		1	0	0	0	1	1	0	0	0	1	1	
5		0	0	0	0	1	0	0	0	0	0	1	
6		0	0	0	0	1	0	0	0	1	1	1	
7		1	0	0	0	1	0	0	0	0	0	0	
8		0	0	0	0	0	0	1	0	0	1	1	
9		0	0	0	0	1	0	1	1	1	1	1	
10		1	0	0	0	1	1	0	0	0	1	0	
11		1	0	0	0	1	0	0	0	0	1	1	
12		0	0	0	0	1	1	0	0	0	1	0	
13		1	0	0	0	1	0	0	0	0	0	0	
14		0	0	0	0	1	0	0	0	0	0	0	
15		0	1	0	0	1	0	1	0	0	0	1	
16		0	1	0	0	1	0	1	0	0	0	1	
17		1	1	0	0	1	0	0	0	0	1	0	
18		0	1	0	0	1	0	0	0	0	0	1	
19		1	0	0	0	0	0	0	0	0	1	0	
20		1	1	0	0	1	0	0	0	0	1	1	
21		1	1	0	0	0	1	0	0	1	1	1	

**Table 3** (continued)

Sample determination	Petrographic nature		Characteristic features of the clay mass										Characteristic mineral and rock components				Crumbs of older ceramics and lumps of dried clay
	Textural features of empty spaces																
	Cavern texture	Bubble texture	Spongy texture	Fluid texture	Vegetable texture	Smudges	Noodles	Feldspars	Lithoclastic crystalline rocks	Concretions Fe							
22	0	0	0	0	1	0	0	0	0	0	0	0	0	0			
23	0	1	0	0	1	0	0	0	0	0	0	0	1	1			
24	1	0	0	0	1	0	0	0	0	0	0	0	1	0			
25	0	0	0	1	1	1	0	1	1	1	1	1	1	0			
26	0	0	0	1	0	1	0	1	1	1	1	1	1	0			
27	0	0	0	1	0	1	0	1	1	1	1	1	1	0			
28	0	0	0	1	1	0	0	1	1	1	1	1	1	0			
29	0	0	0	1	1	0	1	1	1	1	1	1	1	0			
30	0	0	0	1	1	1	1	1	1	1	1	1	1	1			
31	1	0	0	1	0	0	0	1	1	1	1	1	1	0			
32	1	0	0	1	0	0	0	1	1	1	1	1	1	1			
33	1	0	0	1	0	1	0	1	1	1	1	1	1	0			
34	1	0	0	1	1	0	0	1	1	1	1	1	1	0			
35	1	1	0	1	1	1	1	1	1	1	1	1	0	0			
38	0	0	0	1	1	1	1	1	1	1	1	1	1	0			
37	0	0	0	1	0	0	0	1	1	1	1	1	0	0			
38	0	0	0	1	0	0	1	1	1	1	1	1	1	0			
39	0	1	1	1	0	0	0	1	1	1	1	1	0	0			
40	0	0	0	1	1	1	0	1	1	1	1	1	0	0			
41	0	0	0	1	0	0	0	1	1	1	1	1	0	0			
42	0	0	0	1	1	0	1	1	1	1	1	1	1	0			
43	0	1	0	0	1	0	0	1	1	1	1	1	1	0			
44	0	1	0	1	0	1	0	1	1	1	1	1	1	0			
45	0	0	0	1	1	0	0	1	1	1	1	1	1	0			
46	0	1	0	0	1	0	0	1	1	1	1	1	1	0			
47	0	0	1	1	0	0	0	1	1	1	1	1	0	0			
48	1	0	0	1	0	0	0	1	1	1	1	1	1	0			
49	1	1	0	1	1	0	0	1	1	1	1	1	1	0			
50	0	1	0	0	0	0	0	1	1	1	1	1	1	1			
51	0	0	0	1	0	1	1	1	1	1	1	1	1	0			

**Table 3** (continued)

Sample determination	Petrographic nature		Characteristic features of the clay mass						Characteristic mineral and rock components				Crumbs of older ceramics and lumps of dried clay		
	Textural features of empty spaces														
	Cavern texture	Bubble texture	Spongy texture	Fluid texture	Vegetable texture	Smudges	Noodles	Feldspars	Lithodlastic crystalline rocks	Concretions Fe					
52	0	0	0	1	0	0	0	0	1	1	0	0			
53	1	1	0	1	0	0	0	0	1	1	1	1			
54	0	1	0	1	0	0	0	0	1	1	1	1			
55	0	1	0	1	0	0	0	0	1	1	0	0			
56	0	1	0	1	0	0	0	0	1	1	1	1			
57	0	0	0	1	0	0	0	0	1	1	1	0			
58	0	0	0	1	0	0	0	0	1	1	1	0			
59	1	0	0	1	0	0	0	0	1	1	0	0			
60	0	0	0	1	0	0	0	0	1	1	0	0			
61	0	1	0	1	0	0	0	0	1	1	1	1			
62	1	0	1	0	1	0	0	0	1	1	1	1			

## Appendix

### Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s40494-022-00745-y>.

**Additional file 1.** The cross-section of the ceramic sample with glacial till.

**Additional file 2.** Ceramic sample prepared for instrumental analysis.

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### Author contributions

MDL: wrote the main manuscript text, applied chemometric methods, conduct measurements, elaborate the results. JS: field works, collecting research material, correction of the manuscript text. MK: chemical composition analysis, chemometric analysis. DP: elaboration of pottery, manuscript correction. PK: field works, collecting research material, manuscript correction. All authors read and approved the final manuscript.

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### Availability of data and materials

Data available within the article or its supplementary materials.

### Declarations

### Competing interests

The authors declare no competing interests.

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