

ARTICLES

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**TRANSCARPATHIAN INFLUENCES
IN THE EARLY NEOLITHIC OF POLAND.
A CASE STUDY OF KOWALEWKO AND RUDNA WIELKA SITES**

ABSTRACT

J. Kabaciński, I. Sobkowiak-Tabaka, Zs. Kasztovszky, S. Pietrzak, J. J. Langer, K. T. Biró, B. Maróti 2015. *Transcarpathian influences in the Early Neolithic of Poland. A case study of Kowalewko and Rudna Wielka sites*, AAC 50: 5–32.

The aim of the paper is to present and discuss traces of a long-distance contacts of the Early Neolithic Linear Band Pottery Culture registered at two sites, of which one is located in the Polish Lowland and second in the uplands of the southern Poland. They are manifested by the presence of obsidian finds and application the wood-tar substances, both of which being considered as a Transcarpathian phenomenon.

The paper focuses on determination of characteristic chemical elements of obsidian artefacts from the two Polish Early Neolithic localities using non-invasive Prompt Gamma Activation Analysis (PGAA) as well as on a physicochemical analyses of composite organic-mineral substances found on pottery. The results of the analyses allow a discussion on the relationships between the Early Danubian societies inhabiting territories located on both sides of the Carpathians.

Key words: Early Neolithic; Poland; Carpathian Basin; obsidian; wood tar

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INTRODUCTION

Identification of traces of a long-distance contacts of prehistoric societies is one of the most intriguing issues in the archaeological research. On one hand, it provides the evidence for the existence of internal ties between related societies

inhabiting large territories. On the other, they enable us to discuss the dynamic of a cultural system and its potential for external expansion¹.

From the end of the Last Glacial and the down of the Holocene (ca. 9550 cal BC) most of Europe witnessed an intensive development of the Mesolithic hunter-gatherer-fisher societies that for next few thousand years created a stable socio-economic systems based on advanced subsistence strategies. In Central Europe that picture changed about the mid 5th millennium cal BC, when vast areas south and north of the Sudety Mountains and Carpathians were relatively quickly settled by the first farming communities of the Danubian origin. On the territory of the present day Poland that first farming groups, called the Linear Band Pottery Culture (LBK) formed a stable settlement centres in the southern loess uplands and in the fertile areas of heavy soils of the Kuyavia and Pырzyce regions. Then, 100–200 years later they reached as far north as the Baltic coasts. In this way the territory covered by the early farming societies stretched approximately 1000 km along the S-N axis. Obviously, it created a problem in maintaining continuous contacts between such distant areas, additionally separated by not so easy-to-cross mountain chains.

One of the most characteristic feature of the Linear Band Pottery Culture is its striking uniformity of material culture, settlement structures and burial customs. It considerably limits the possibilities of direct detection of long-distance exchange and contacts. However, the research on the distribution of exotic raw materials and particular, unique ways of pottery decoration may help to tackle that problem. We are referring here to obsidian and wood-tar.

Obsidian is a rock of volcanic origin knapped by different prehistoric groups in the areas of volcanic activity. Its distinctive appearance makes it easy to identify it within stone inventories even if detailed analyses are necessary to identify its exact sources. The best known outcrops of obsidian are from eastern Slovakia and northern Hungary. In Poland the earliest utilization of obsidian is confirmed already in the Lower Palaeolithic at Rusko (Pawlikowski 1994), and it is present in the Upper Palaeolithic inventories of southern Poland, Slovakia and Hungary (Moutsiou 2014) as well as at the Late Palaeolithic and the Mesolithic sites (Szeliga 2002). Intensive inflow of the Carpathian obsidian is registered both in the early and the late Linear Cultures between 2nd half of the 6th and circa mid 4th millennium cal BC (Szeliga 2009), wherein in the post-linear cultures (i.e. the late Malice Culture) a decreasing tendency was observed (Szeliga 2007).

¹ PGGa analysis of obsidian artefacts was supported by the European Commission under the 7th Framework Programme through the Key Action: Cultural Heritage Advanced Research Infrastructures: Synergy for a Multidisciplinary Approach to Conservation/Restoration, Grant Agreement N 228330 — CHARISMA. Investigations at site Rudna Wielka were supported by Generalna Dyrekcja Dróg Krajowych i Autostrad, Oddział w Rzeszowie (Agreement No. 2814/36/2011). We are grateful to Dr. M. Szeliga for the sample from Tominy; Mr. R. Pietrzak for the information concerning site in Kowalewko and Mr. P. Pachulski for providing data about the obsidian from Rudna Wielka site.

At the Linear Band Pottery Culture sites obsidian occurs from the beginning of the “Notenkopf phase” (Kaczanowska 1971, 12; Szeliga 2009). In the late phases obsidian artefacts sometimes appear together with imports of the Eastern Linear Pottery Culture or the Bükk Culture (Kaczanowska 2003, 6–9; Kozłowski *et al.* 2014).

There is ca. 70 LBK sites in Poland where obsidian items were registered (Szeliga 2009, 289). Most of them concentrate in the south-eastern part, i.e. in the vicinity of Rzeszów and Sandomierz (middle Wisłok and San river), the Lublin Upland and the area of Kraków–Miechów Loess region (Kadrow 1990; Kulczycka-Leciejewiczowa 1979). In limited number they are also known from the Lower Silesia (Wojciechowski 1988, 47) and Kuyavia (Kabaciński 2010, 104). More over, extremely rare examples were found in Pырzyce Land (Kulczycka-Leciejewiczowa 1980).

Generally speaking, wood tar is a substance extracted during the process of destructive birch wood and bark dry distillation through flameless combustion in the absence of air. Initially, wood and bark were subjected to thermal decomposition in simple pits dug into the ground. Later on, a one- and two-vessel method was favoured. The production of wood tar is the first technological-chemical process in the history of mankind. It was widely known already in the Mesolithic almost across the entire Europe. Six basic technological groups of tar and bituminous substances as well as composite materials have been distinguished so far. Technological groups I–IV encompass wood-tar substances of different degree of thermal degradation. Group V comprises bituminous substances while the last group (VI) covers composite materials — wood-tar derivatives (Pietrzak 2012, 84–96).

However wood-tars played a significant role in the Early and Middle Neolithic. Linear pottery with remains of wood-tar substances was registered at over a dozen archaeological sites located mainly in the Vistula basin, i.e. the Rzeszów Region, the Polish Lowland — Kuyavia and Chełmno Land (Fig. 1; Pietrzak 2012).

THE SITES

In the present paper materials from two sites, namely Kowalewko, site No. 14 and Rudna Wielka, Site No. 5 were subjected to analyses. The first one is located north of Poznań, on the Szamotuły Plain (Fig. 1). During rescue excavations along the Yamal-Europe pipe-line carried out in 1997 by R. Pietrzak and T. Skorupka on the behalf of the Poznań Prehistoric Society a small settlement of the “late Notenkopf phase” of the Linear Band Pottery Culture (several features and over 1 thousand of sherds) was discovered. The flint inventory belonging to the LBK consisted of 52 pieces made of erratic Cretaceous Baltic flint, chocolate flint and Jurassic flint, and one obsidian blade (Kabaciński 2010; *cf.* Fig. 2:1). That blade was studied by PGAA method (see below).

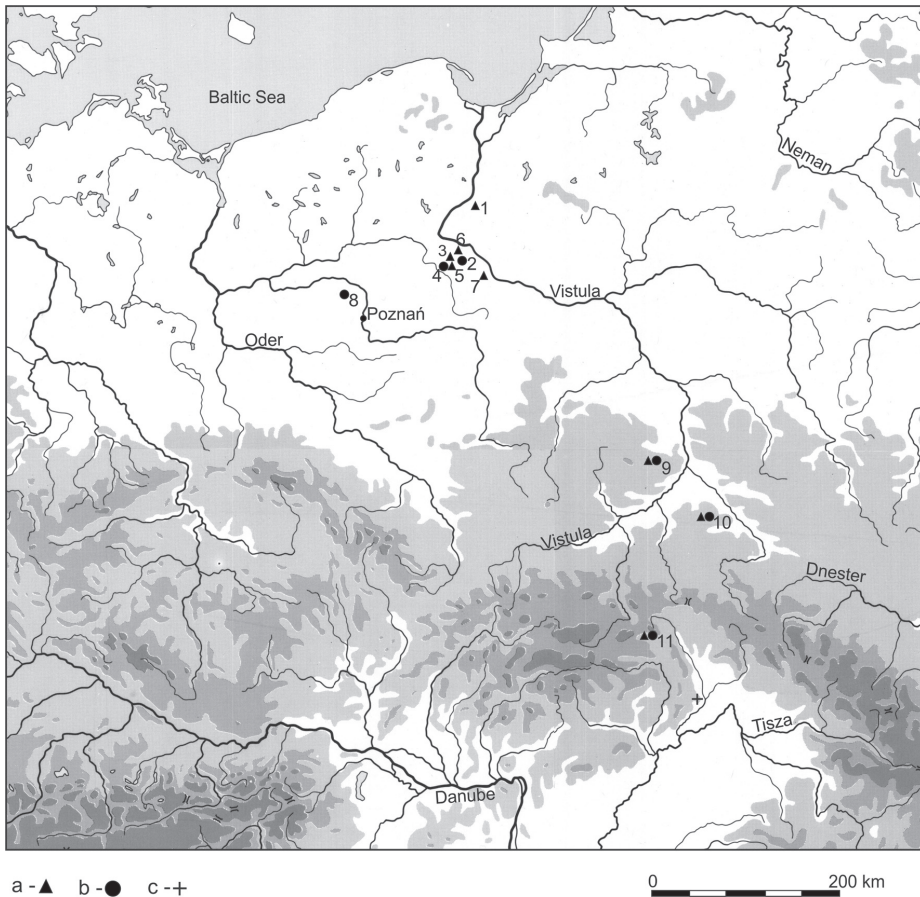


Fig. 1. Location of Linear Pottery sampled sites
(a — pottery with wood-tar residues; b — obsidian artefacts; c — Slovakian obsidian outcrops;
p — powiat; w — województwo); drawn by A. Tabaka.

1 — Ryńsk, p. Wąbrzeźno, w. kujawsko-pomorskie, site No. 42; 2 — Zagajewice, p. Radziejów, w. kujawsko-pomorskie, site No. 1; 3 — Chełmiczki, p. Inowrocław, w. kujawsko-pomorskie, site No. 10; 4 — Chabsko, p. Mogilno, w. kujawsko-pomorskie, site No. 40; 5 — Roźniaty, p. Inowrocław, w. kujawsko-pomorskie, site No. 2; 6 — Siniarzewo, p. Aleksandrów Kujawski, w. kujawsko-pomorskie, site No. 1; 7 — Nakonowo Stare, p. Włocławek, w. kujawsko-pomorskie, site No. 2; 8 — Kowalewko, p. Oborniki, w. wielkopolskie, site No. 14; 9 — Tominy, pow. Opatów, w. świętokrzyskie, site No. 6; 10 — Rudna Wielka, p. Rzeszów, w. podkarpackie, site No. 5; 11 — Šarišské Michaľany, okres Sabinov, Slovakia.

The site No. 5 in Rudna is located in the southern part of the Sandomierz Basin (Fig. 1). As a result of rescue excavations carried out by the Institute of Archaeology and Ethnology of the Polish Academy of Sciences in 2010², 46 features (2 long houses and several pits), ca. 2.4 thousand of sherds, as well as flint and stone assemblage related to the Linear Band Pottery Cultu-

² Site No. 5 was excavated several times by different companies in connection with the construction of a motorway (Przybytek 2010; Sobkowiak-Tabaka [ed.] 2012).

re were discovered. Out of 21 artefacts made of obsidian, seven pieces, were investigated by PGAA method (see below); they had been unearthed by IAE PAS — 4 flakes, 2 blades and one truncated piece (Fig. 2).

The LBK settlement existed in the end of the “Notenkopf phase” and in the beginning of “Želiezovce phase” (Witczak 2012). On surface of several sherds residues of wood-tar substances were registered (Pietrzak, Langer 2012). Five samples of wood-tar substances were analysed in detail.



Fig. 2. Obsidian artefacts analysed; Photo by P. Szejnoga.

1 — Kowalewko, powiat Oborniki, województwo wielkopolskie, site No. 14; 2–8 Rudna Wielka, powiat Rzeszów, województwo podkarpackie, site No. 5.

THE METHODS

For the analysis of obsidian finds Prompt Gamma Activation Analysis was applied. That is a non-invasive method to determine elemental composition of obsidian artefacts. The method was developed and the experiments were performed on an external horizontal beam of cold neutrons at the Budapest Research Reactor (Révay, Belgya 2004). The method enables to determine the “bulk” major geochemical components and some characteristic trace elements for the irradiated volume. The experimental station is described by L. Szentmiklósi, Z. Révay, Z. Kis (2010), the principles of determination of elemental concentrations are discussed by Z. Révay (2009). As it is shown

by Zs. Kasztovszky *et al.* (2008) and by I. Sobkowiak-Tabaka *et al.* (2015) — the major components of alkalines (Na_2O and K_2O), TiO_2 , Fe_2O_3 , as well as trace elements, such as B and Cl are easy to measure and they are perfect fingerprints of various raw material sources. With the help of their concentrations, one can identify the provenance of the archaeological finds with high level of confidence.

Samples of wood-tar were subject of initial physicochemical analysis according to the procedures used by the Archeometry Laboratory of Faculty of Chemistry, Adam Mickiewicz University, located in Śrem (Langer, Pietrzak 2000; 2004a; 2004b; Langer, Pietrzak, Wieczorek 2002; Pietrzak 2012). The basic methods of the analysis were: infrared spectrophotometry (FTIR) and electron paramagnetic resonance using EPR spectrometer PDP Radiopan SE / X 2547 (Krzyminiewski, Langer, Kośko 1998).

The samples were also researched by thin layer chromatography (TLC, SiO_2 , Merck, carbon tetrachloride, hexane-5: 1, 3:1 cyclohexane-chloroform 10:1 chloroform-methanol 10:1 to 5:1 and 3:1), measurements of the melting point (polarizing microscope Boetius Wagemma model PHMK 05, operating at the temperature range from 20°C to 300°C), microscopic observations in visible and ultraviolet light (CB polarizing optical microscope) and scanning electron microscope Philips SEM 515 (Kośko, Langer 1986; Langer 1989; Pollard, Heron 1996; Langer, Kośko 1999).

RESULTS OF THE ANALYSES

Prompt gamma activation analysis of obsidian implements

When we compared the PGAA results of samples from Kowalewko and Rudna Wielka with the data on other geological and archaeological obsidians, we found out that all of the investigated pieces from Poland show the composition typical for “Carpathian 1 (C1)” type of obsidian (Table 1). This high quality black or translucent grey obsidian can be found in the northern Tokaj Mountains, Slovakia; the most significant quarries are Vinicky, Cejkov, Kasov, Velka Bara and Mala Bara (Biró 2014; Kasztovszky, Biró 2014). Although according to the composition determined by the PGAA, it is difficult to distinguish between the materials from the various C1 sources, the investigated pieces from Poland seem to be the most similar in composition to the Cejkov or the Kasov ones (Fig. 3).

Physicochemical analysis of wood-tar substances

Five samples of wood-tar substances residues found both on the internal (Sr 812) and external (Sr 813-1, Sr 813-2, Sr 814, Sr 815) surface of sherds were analysed in detail.

Table 1

Concentrations of major and some trace components for the investigated artefacts as determined by PGAA.

The values of major oxides are in mass%, while the trace elements in $\mu\text{g/g}$.

The last digit of the given values represents the precision of the method; prepared by Zs. Kasztovszky.

Site	Inven- tory no.	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	CaO	Na ₂ O	K ₂ O	H ₂ O	Cl	B	Sm	Gd	B/SiO ₂	TiO ₂ / SiO ₂
Kowalewko		76.5	0.045	12.9	1.00	0.056	0.80	3.60	4.82	0.22	565	43.7	3.1	4.0	0.57	0.00059
Rudna Wielka	A64 I	76.5	0.039	12.8	0.82	0.060	0.72	3.86	4.84	0.27	553	45.5	3.0	3.8	0.59	0.00051
Rudna Wielka	A64 II	76.2	0.043	12.9	0.85	0.060	0.74	3.92	4.83	0.38	549	44.8	3.0	4.0	0.59	0.00056
Rudna Wielka	A7	76.2	0.046	13.0	0.96	0.059	0.77	3.71	4.76	0.41	568	43.3	3.0	3.8	0.57	0.00060
Rudna Wielka	A73	76.0	0.039	13.1	0.94	0.056	0.84	3.95	4.85	0.21	543	45.5	2.9	4.2	0.60	0.00051
Rudna Wielka	A70	76.2	0.042	13.2	1.00	0.058	0.81	3.53	4.80	0.17	494	43.5	2.9	3.7	0.57	0.00055
Rudna Wielka	A43 I	76.5	0.035	13.0	0.96	0.058	0.76	3.71	4.80	0.15	537	45.2	3.0	3.8	0.59	0.00046
Rudna Wielka	A43 II	76.3	0.042	12.9	0.94	0.063	0.86	3.73	4.90	0.19	544	45.9	3.0	3.9	0.60	0.00055
Archaeological Poland	Average (8)	76.3	0.041	13.0	0.93	0.059	0.79	3.75	4.80	0.25	544	44.7	3.0	3.9	0.59	0.00054
Comparative material	Pieces	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	CaO	Na ₂ O	K ₂ O	H ₂ O	Cl	B	Sm	Gd	B/SiO ₂	TiO ₂ / SiO ₂
Type/Location																
C1/Vinicky	Average (6)	76.2	0.065	13.1	1.00	0.051	0.92	3.59	4.61	0.32	588	36.7	3.1	3.9	0.48	0.00085
C1/Cejkov	(1)	76.2	0.046	13.1	1.02	0.054	0.79	3.57	4.88	0.17	597	43.9	3.2	4.1	0.58	0.00061
C1/Mala Bara	Average (2)	75.8	0.051	13.1	0.75	0.068	0.93	3.84	5.06	0.27	608	45.0	3.5	4.9	0.59	0.00067
C1/Velka Bara	Average (4)	73.9	0.017	14.0	0.84	0.051	1.26	3.76	4.61	1.40	694	61.3	3.0	3.5	0.83	0.00023
C1/Kasov	(1)	75.9	0.043	13.0	1.10	0.053	1.21	3.95	4.59	0.14	541	47.8	3.0	3.6	0.63	0.00057

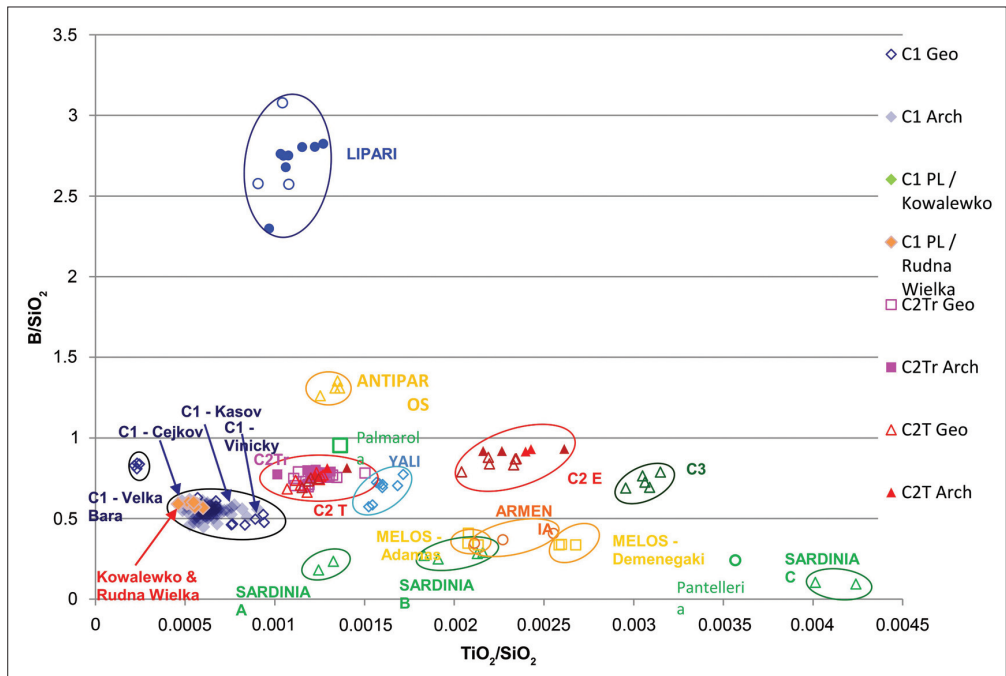


Fig. 3. A possible classification of raw material for Polish archaeological objects, based on their boron- and titanium-oxide content; computer designed by Z. Kasztovszky.

Samples Sr 812, Sr 814 and Sr 815 were extracted from the production remains (on both surfaces of vessels), whereas samples Sr 813-1 and Sr 813-2 were taken from ornamentation present exclusively on external surface of vessels having the form of a very fine colouring layers (Fig. 4:2–3).

SAMPLES SR 813-1, SR 813-2

Both samples come from a black colouring layer less than 1 mm thick present only on the external surface of ceramic vessels (Fig. 4:2a; 4:2b; 4:3; Fig. 5:2–3). The analysed organic materials were applied on the ceramic body while they were liquid, as evidenced by the way the layers of the pigment are bound with the walls of the vessels.

Samples Sr 813-1 i Sr 813-2 are middle fractions of wood tar, as indicated by the partial solubility in organic solvents (Tab. 3): chloroform (CHCl_3), tetrahydrofuran ($\text{C}_4\text{H}_8\text{O}$), methylene chloride (CH_2Cl_2), carbon tetrachloride (CCl_4) and benzene (C_6H_6) as well as the range of melting temperatures (161–173°C) and the softening point (148–158°C; see Tab. 2).

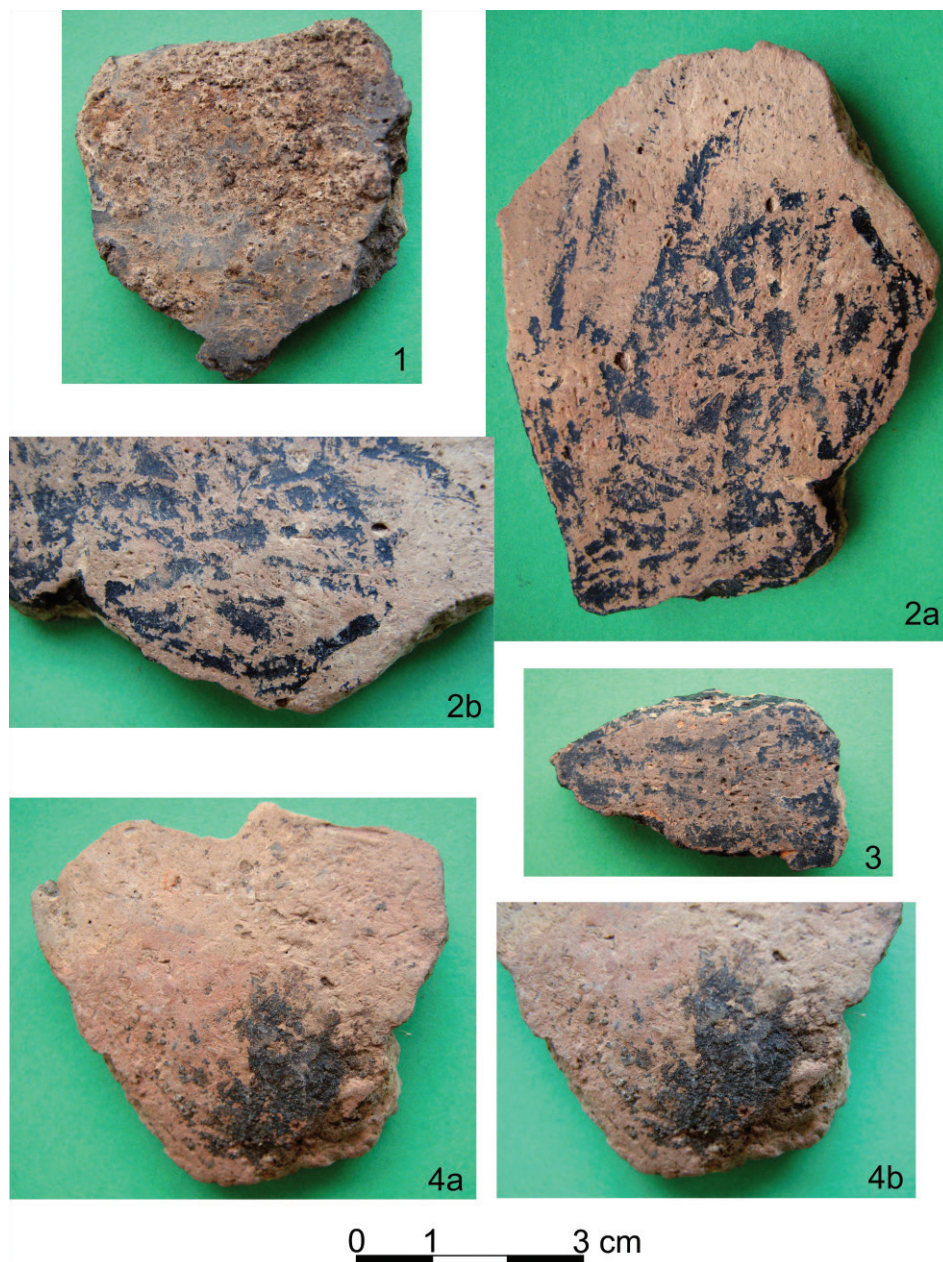


Fig. 4. Rudna Wielka, powiat Rzeszów, województwo podkarpackie, site No. 5.

Fragments of pottery with traces of black wood tar; Photo by S. Pietrzak.

1 — Feature A 100 — vessel 180 — sample Sr 812 (inner surface); 2a — Feature A 45 — vessel 664 — sample Sr 813-1 (external surface); 2b — Feature A 45 — vessel 664 — sample Sr 813-1 (external surface — section); 3 — Feature A 45 — vessel 664 — sample Sr 813-2 (external surface); 4a — Feature A 66 — vessel 428 — sample Sr 814 (external surface); 4b — Feature A 66 — vessel 428 — sample Sr 814 (external surface — section).

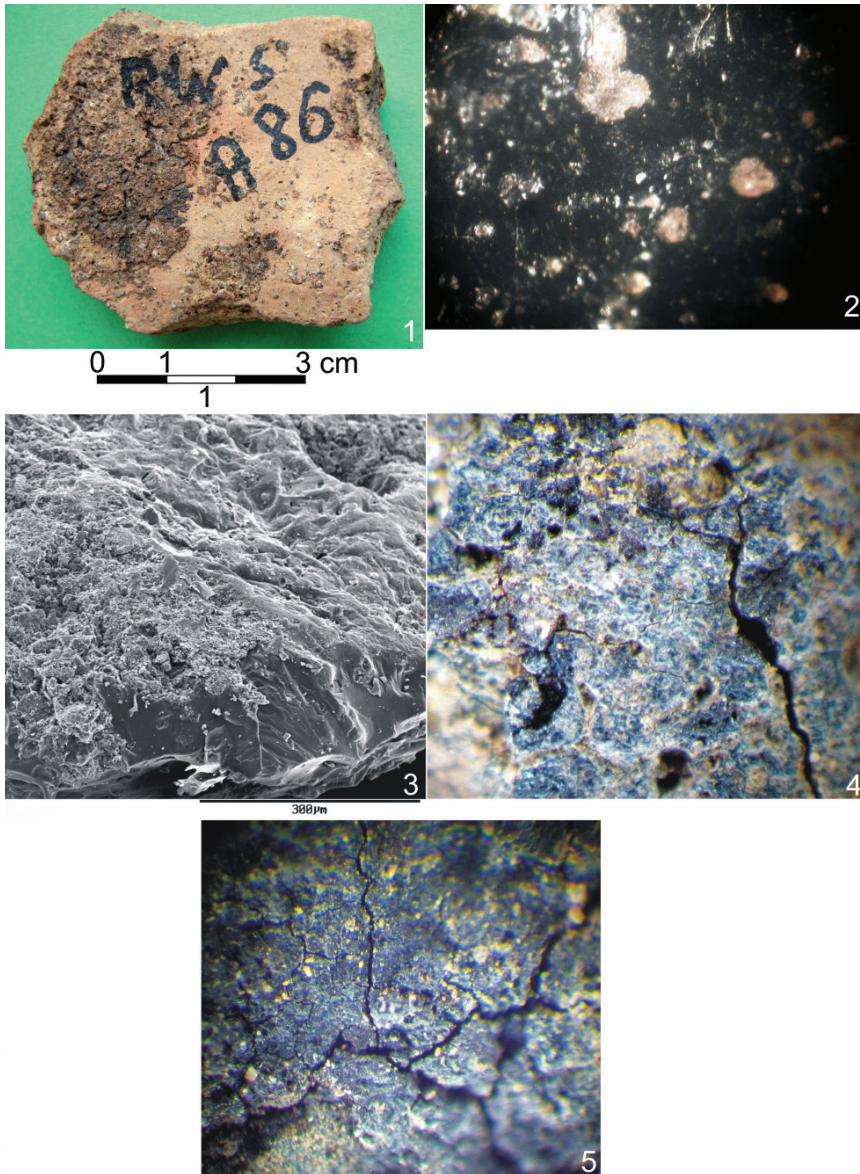


Fig. 5. Rudna Wielka, powiat Rzeszów, województwo podkarpackie, site No. 5.
Fragment of pottery with traces of pigment and results of electron microscope SEM analysis;
Photo by S. Pietrzak.

1 — Feature. A 100 — vessel 164 — sample Sr 815 (external surface); 2 — Even distribution of a thin layer of a pigment (composite material) on the wall of a ceramic vessel with deliberate mineral admixture — Sr 170 (PZO polarized light optical microscope, magnification 120 ×); 3 — Image of the organic surface with an admixture of minerals components showing the composite nature of the analysed archaeological sample — sample Sr 813-2 (the scanning electron microscope [SEM], magnification 500 ×); 4 — Highly thermally degraded surface of organic substance — sample Sr 814 (polarized light optical microscope [PZO], magnification 120 ×); 5 — Polymer structure of wood-tar with clearly visible surface cracks — sample Sr 812 (polarized light optical microscope [PZO], magnification 120 ×).

The observed high content of mineral admixtures in the analysed organic samples, with an even, directional arrangement, as confirmed by microscopic observations (Fig. 5:2–3), confirms a composite (organic and mineral) nature of the examined materials. Such modified materials were characterised by increased mechanical strength (abrasion resistant layers).

Table 2

Rudna Wielka, powiat Rzeszów, województwo podkarpackie, site No. 5. Range of temperatures for temperature of softening and melting points of archaeological preparations; prepared by S. Pietrzak.

Sample code	Temperature of softening point [°C]	Temperature of melting temperatures [°C]	Comments
Sr 812	136–146	150–158	internal surface
Sr 813-1	150–158	165–173	external surface
Sr 813-2	148–156	161–172	external surface
Sr 814	234	—	external surface
Sr 815	138–148	158–165	external surface

SAMPLES SR 812, SR 814 I SR 815

Wood tar substances Sr 812 (Fig. 4:1), Sr 814 (Fig. 4:3a; 4:3b) and Sr 815 (Fig. 5:1) were identified on internal and external surfaces of the vessels in the form of relatively thick (2–3 mm) layers of black tar. Sample Sr 814 represents a heavy tar fraction insoluble in organic solvents, marked by heavy thermal degradation, confirmed by the presence of a microporous structure formed during the preparation or processing of tar, in the process of rapid decomposition of volatile substances (Fig. 5:4).

In contrast, the analysis of the surface of organic samples Sr 812 and Sr 815 revealed the presence, though less intensive than in the case of sample Sr 814, of structures resulting from the rapid decomposition during the preparation of tar under elevated temperatures (Fig. 5:5). The analysed tar samples are the middle fraction of tar with the softening point of 136–148°C and the range of melting temperatures of 150–165°C (Tab. 2). These observations are consistent with the recorded partial solubility of both samples, i.e. Sr 812 and Sr 815, in methylene chloride (CH_2Cl_2), chloroform (CHCl_3), acetone ($\text{C}_3\text{H}_6\text{O}$) and tetrahydrofuran ($\text{C}_4\text{H}_8\text{O}$; see Tab. 3).

Both samples showed a weak, yet positive reaction with ammonium thiocyanate NH_4SCN , which confirms the presence of a small amount of iron compounds (Fe), which are the result of contamination of the analysed substance with the soil material (Tab. 3). Such a reaction indicates a small amount of accidental admixture of mineral components in the organic material under examination.

Table 3

Rudna Wielka, powiat Rzeszów, województwo podkarpackie, site No. 5.
Results of solubility of archaeological preparations; prepared by S. Pietrzak.

Solvent	Sample code				
	Sr 812	Sr 813-1	Sr 813-2	Sr 814	Sr 815
Hexane (C ₆ H ₁₄)	–	–		–	–
Cyklohexane (C ₆ H ₁₂)	–	–	–	–	–
Carbon tetrachloride (CCl ₄)	–	+	+	–	–
Methylene dichloride (CH ₂ Cl ₂)	++	++	++	–	++
Chloroform (CHCl ₃)	+++	++	++	–	+++
Ethyl acetate (C ₄ H ₈ O ₂)	–	–	–	–	–
Methanol (CH ₃ OH)	–	–	–	–	–
Acetone (C ₃ H ₆ O)	+	–	–	–	+
Tetrahydrofuran (C ₄ H ₈ O)	+++	+++	+++	–	+++
Toluene (C ₇ H ₈)	–	–	–	–	–
Benzene (C ₆ H ₆)	–	+	+	–	–
Water (H ₃ O ⁺)	–	–	–	–	–
Hydrochloric acid (HCl)	–	–	–	–	+
Sodium hydroxide (NaOH)	–	–	–	+	–
Ammonium thiocyanate (NH ₄ SCN)	+	+++	+++	++	+

[+++] very good solubility, [++] good solubility, [+] poor solubility, [–] lack of solubility

TECHNOLOGICAL CHARACTERISTICS OF ORGANIC SUBSTANCES

Four out of five samples, namely Sr 812, Sr 813-1, Sr 813-2 and Sr 815, were subject to TLC analysis due to good solubility in certain organic solvents (Tab. 3) Prepared chloroform solutions were subject to chromatographic separation (TLC) on silica gel (Merck, 0.25 mm) and the results of the analysis were compared to modern reference samples of birch and pine tar. TLC analyses revealed that certain substances noticeable in modern wood tars are absent in the archaeological samples (Tab. 4), perhaps as a result of their rapid volatilization during the process of formation or secondary heat treatment. The observed peculiarity can also be caused by the influence of post-depositional factors over the time. It is clearly evident that the samples share common features with a reference sample of birch tar, as illustrated by the results of a fraction of higher polarity, using a chloroform/methanol solvent in the ratio 10:1 or 5:1 (Tab. 4).

Table 4

Rudna Wielka, powiat Rzeszów, województwo podkarpackie, site No. 5.
 Results of chromatography analysis (TLC) in development phase of hexane:
 carbon tetrachloride 3:1 represented by the coefficients R_f ; prepared by S. Pietrzak.

Sample code	Db	* Sr 812	* Sr 813-1	* Sr 813-2	* Sr 815	Ds
Coefficient R_f	0.94 a					0.80 a
	0.68 a					0.68 a
	0.46 a					0.46 a, f
	0.32 f					0.32 f
	0.26 f	0.26 f	0.26 f	0.26 f	0.26 f	
	0.00 a	0.00 a	0.00 a	0.00 a	0.00 a	0.00 a

Db — birch wood tar; Ds. — pine wood tar; f — fluorescence; a — absorption

For the infrared spectrophotometry of the archaeological samples basic infrared region was used, comprising a reciprocal centimetre range of 4000–400 cm^{-1} , which corresponds to a wavelength of 2.5–25 μm (MIR — Mid Infrared), typical of vibrations and rotations of the majority of molecules and characteristic groups of atoms (functional groups) they are built of.

A FTIR spectrum of the analysed substance is considered to be a “fingerprint”, characteristic and unique for a given compound. Hence, the matching of the spectra produced under identical conditions is deemed a proof of the identity of compounds. Therefore, it was possible to compare archaeological materials with modern reference samples of wood tars in order to determine the structure of the examined compounds by the meticulous analysis of the spectra (Kośko, Langer 1986; Regert, Vacher 2001; Regert, Rolando 2002).

The analyses revealed that two (Sr 812, Sr 815) of the five examined samples represent a technological group I of wood tar substances. The spectra of these two samples are a good match for the reference spectrum of modern birch tar (Fig. 6; Tab. 5).

Results of the FTIR analysis performed on two archaeological samples, namely Sr 812 and Sr 815, revealed that they are derivatives of tar produced from wood, as shown by an increased share of fraction of carboxylic acid esters (absorption around 1733 cm^{-1}), in relation to their acids (absorption around 1710 cm^{-1}). Cellulose present in wood is of a different composition and a higher molecular weight and its higher content in wood, as compared to bark, increases the ester content in the products of thermal decomposition (Surmiński 1996). The absorption around 884 cm^{-1} and 730 cm^{-1} evidence the use of birch bark for the production of the examined archaeological sample, whilst lack of absorption at about 860 cm^{-1} eliminates pine wood or bark as a source of the

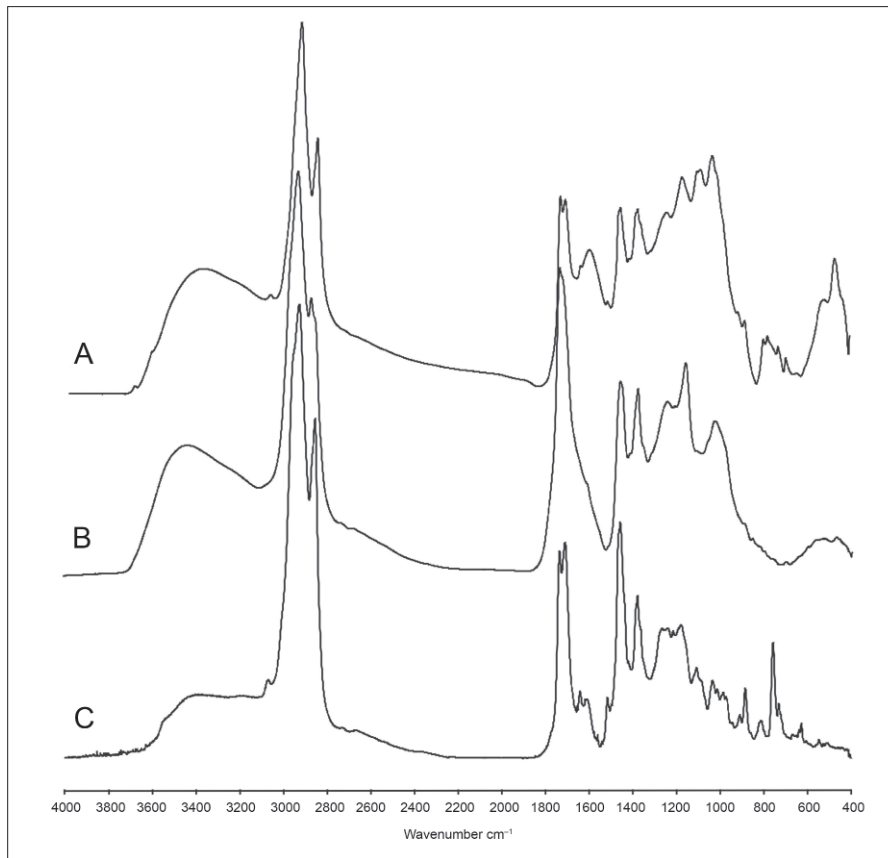


Fig. 6. FTIR spectra of wood tar from Rudna Wielka, powiat Rzeszów, województwo podkarpackie, site No. 5; computer design by S. Pietrzak.

A — from a fragment of a vessel — sample Sr 812 (technological group I); B — from a fragment of a vessel — sample Sr 815 (technological group I); C — reference spectrum of modern birch tar — wood tar.

organic matter used for the production of the analysed substances (Regert, Vacher 2001; Ruthenberg, Weiner 1997; Regert, Rolando 2002). Such interpretation of the spectra of both archaeological samples (Sr 812 and Sr 815) is confirmed by the analysis of reference spectra for modern birch tar (Fig. 6:A–B).

Another sample (Sr 814) represents technological group IV of organic substances (Langer, Pietrzak 2000; Pietrzak 2012). Results of the FTIR analysis showed that the sample is a highly thermally degraded organic material (Fig. 8; Tab. 2–3), as evidenced by the absence of ester groups and a substantial content of carboxyl groups in the FTIR spectra. The majority of the mineral content observed in the FTIR spectrum, correlated with microscopic observations (Fig. 5:4) and the melting point (Tab. 2) as well as solubility analysis (Tab. 3) confirm accidental contamination of the sample with soil material.

Table 5

Rudna Wielka, powiat Rzeszów, województwo podkarpackie, site No. 5.
Infrared spectrophotometry results of archaeological samples (FTIR); prepared by S. Pietrzak

Sample code	Db	Sr 812	Sr 813-1	Sr 813-2	Sr 814	Sr 815	Ds
Wavenumber [cm ⁻¹]	3371	3388	3412	3394	3390	3397	3351
	3069	3071	3071	3068			3057
	2927	2926	2926	2925	2924	2926	2958
	2854	2854	2853	2854	2852	2853	2869
	1734	1733	1733	1731		1733	1726
	1709	1710	1711	1710	1700	1710	1694
	1653	1640	1640	1638	1623	1640	
	1608	1600	1616	1614		1604	1602
	1539						1514
	1456	1456	1457	1456	1433	1456	1461
	1377	1376	1376	1374	1376	1376	1383
	1239	1244	1240	1237		1241	1270
	1178	1173	1164	1161	1163	1173	1175
	1107	1104	1084	1082	1080	1087	1108
	1034	1034	1033	1034	1033	1033	1037
							886
	884	884	885	884		884	857
		797	798	798	797	797	821
	757	778	779	777	778	779	755
	730	730	729	730		730	
	694	694	694	694	694		
668	647	648	647	647	647	668	
	519	514	516	515	513		
	469	468	471	467	465		

Db — birch wood tar; Ds — pine wood tar; 884, 730 cm⁻¹ — main peak for birch wood tar; 857 cm⁻¹ — main peak for pine wood tar

The presence of such a large amount of mineral components in the structure of the organic material may evidence a contact of still liquid tarry substance with the ground e.g., as an outcome of a damage (crack) of a ceramic vessel for the tar production or reprocessing. The spectrum in question evidences that the sample was subject to high temperature which caused the thermal degradation and removal of most of the functional groups of the molecule. As

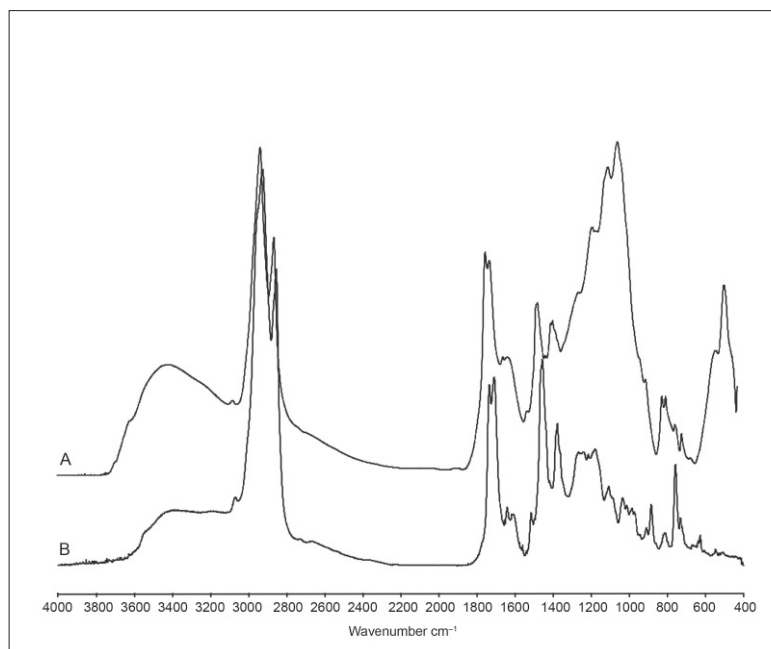


Fig. 7. FTIR spectra of wood tar from Rudna Wielka, powiat Rzeszów, województwo podkarpackie, site No. 5; computer design by S. Pietrzak.

A — from a fragment of a vessel — sample Sr 813-1 (technological group VI);
B — reference spectrum of modern birch tar — wood tar.

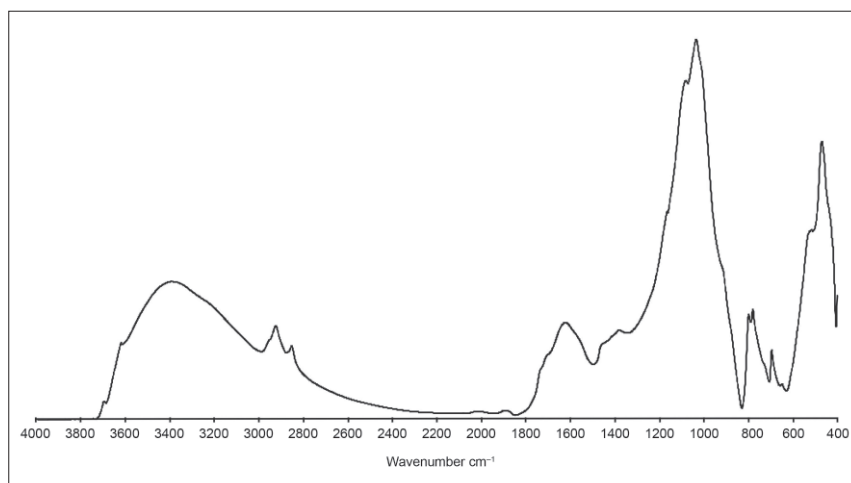


Fig. 8. FTIR spectrum of wood tar from Rudna Wielka, powiat Rzeszów, województwo podkarpackie, site No. 5. A fragment of a vessel sample Sr 814 (technological group IV); computer design by S. Pietrzak.

a result, we do not observe the characteristic vibration frequency in the spectrum or a considerable reduction in the intensity of the respective peaks. Hence, at this stage of the research the type of raw material used for the production of the examined tar sample cannot be determined.

Due to its unique organic-mineral (composite) nature, a group of organic pigments designated as Sr 813-1 and Sr 813-2, which were identified as representing a technological group VI of composite materials, should be discussed separately (Langer, Pietrzak 2008; Pietrzak 2010). The FTIR spectra of the analysed samples (Tab. 5; Fig. 7) are first of all characterised by the predominant content of purposefully added mineral components (FTIR: $\sim 1084\text{ cm}^{-1}$, 1034 cm^{-1}) as compared to the much smaller amounts of saturated compounds of hydrocarbon substituents consisting mainly of groups CH₂ and CH₃ (FTIR: 2926 cm^{-1} , 2854 cm^{-1} , 1457 cm^{-1} , 1376 cm^{-1}) and salts of carboxylic acids (RCOO-, FTIR: $\sim 1600\text{ cm}^{-1}$). Wood tar substance was added in this case as an organic binder, while the mineral components were used as the filling material. These modifications produced an externally homogeneous material, yet with macroscopically visible boundaries between the components of this technologically advanced conglomerate. The FTIR spectra of the two analysed samples revealed the presence of diagnostic bands which indicate the type of raw material from which the examined substances were procured. These samples are certain to have been made from birch, as evidenced by the absorption of about 884 cm^{-1} and 730 cm^{-1} (Regert, Vacher 2001; Ruthenberg, Weiner 1997; Regert, Rolando 2002). As was the case with samples of technological group I of tar substances (Sr 812, Sr 815), samples Sr 813-1 and Sr 813-2 were procured from birch wood, as indicated by the predominate position of the ester content (from 1733 to 1731 cm^{-1}) in relation to their acids (1711 – 1710 cm^{-1}) (Tab. 5, Fig. 6–7).

SPECTRAL ANALYSIS

Similarly, the EPR spectra of all analysed tar samples are proved to consist thin resonance lines of spectral parameters attributed to organic radicals: g of about 2.0027 – 2.0023 and ΔH of about 0.58 – 0.55 mT (Tab. 6; Fig. 9). Noticeable, broad lines (ΔH of about 124.53 – 112.03 mT) reflect the presence of paramagnetic substances (iron compounds), present in the mineral admixture contained in the organic material (Tab. 7; Fig. 10).

The comparability of conditions of the tar production process along with the similarity of the thermal history of the materials forming the analysed layers are confirmed by the similar intensity, position and width of the EPR lines. They correspond to carbon radicals present in the organic layer. A noticeable similarity of paramagnetic mineral substances contained in two analysed samples (Sr 813-1, Sr 813-2) in the form of the EPR signals possibly evidence the intentional usage of admixture in tar (composite materials).

Table 6

Rudna Wielka, powiat Rzeszów, województwo podkarpackie, site No. 5.
EPR spectrum characteristics of organic radical signals occurring in representative samples;
prepared by S. Pietrzak.

Sample code	Spectroscopic coefficient g of separation	Extent of gradient [mT]	Comments
Sr 812	2.0024	0.55	Internal layer
Sr 813-1	2.0027	0.56	External layer
Sr 813-2	2.0026	0.55	External layer
Sr 814	2.0025	0.55	External layer
Sr 815	2.0023	0.58	External layer

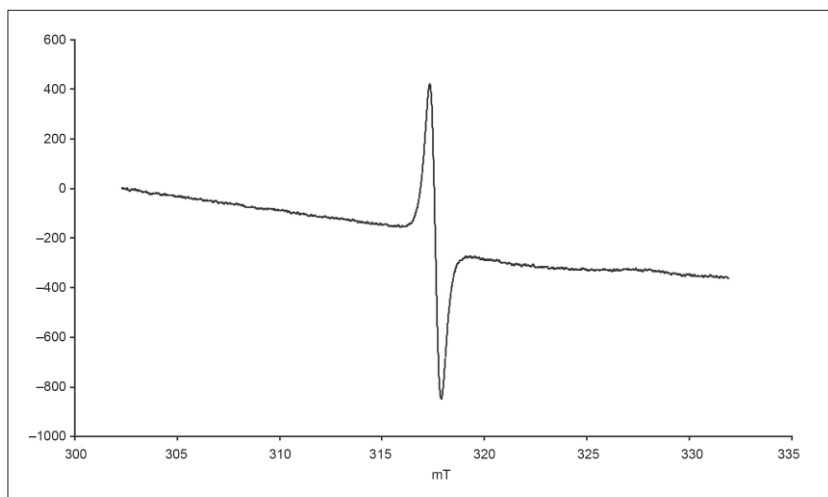


Fig. 9. EPR spectrum of organic radicals of wood tar from Rudna Wielka, powiat Rzeszów, województwo podkarpackie, site No. 5. Sample Sr 813-1; computer design by S. Pietrzak.

The advantage of the EPR method lies in the possibility of studying composite materials consisting of an organic constituent as an organic binder and of mineral constituent of a larger volume, used as a filler, as well as very thin layers of organic material (below 1 mm), heavily contaminated with inorganic substances from a ceramic base (e.g., organic pigments on the external surfaces of vessels; see Bensimon *et al.* 2000; Józwiak, Langer, Pietrzak 2001; Pietrzak 2012).

Table 7

Rudna Wielka, powiat Rzeszów, województwo podkarpackie, site No 5.
EPR spectrum characteristics of mineral components occurring in representative samples;
prepared by S. Pietrzak.

Sample code	Spectroscopic coefficient g of separation	Extent of gradient [mT]	Comments
Sr 812	2.2973	124.53	Internal layer
Sr 813-1	2.3009	116.87	External layer
Sr 813-2	2.3175	118.47	External layer
Sr 814	2.2709	112.03	External layer
Sr 815	2.2132	115.39	External layer

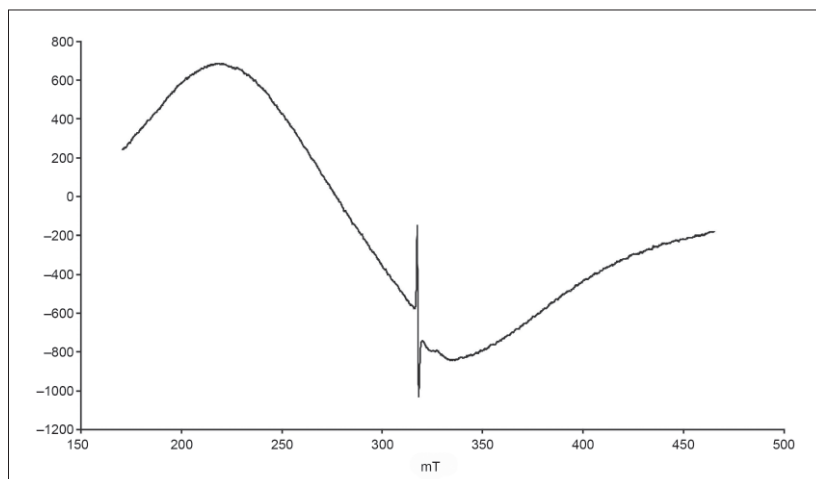


Fig. 10. EPR spectrum of mineral components of wood tar from Rudna Wielka, powiat Rzeszów, województwo podkarpackie, site No. 5. Sample Sr 813-1; computer design by S. Pietrzak.

The advanced method of tar production in terms of technology is suggested by the absence of residual raw material, unobservable even with the help of the electron microscope SEM (Fig. 5:2–5). This demonstrates the considerable knowledge and skills of producers who were able to separate the raw material (wood or bark) from the final product (tar) in a two-chamber production vessel.

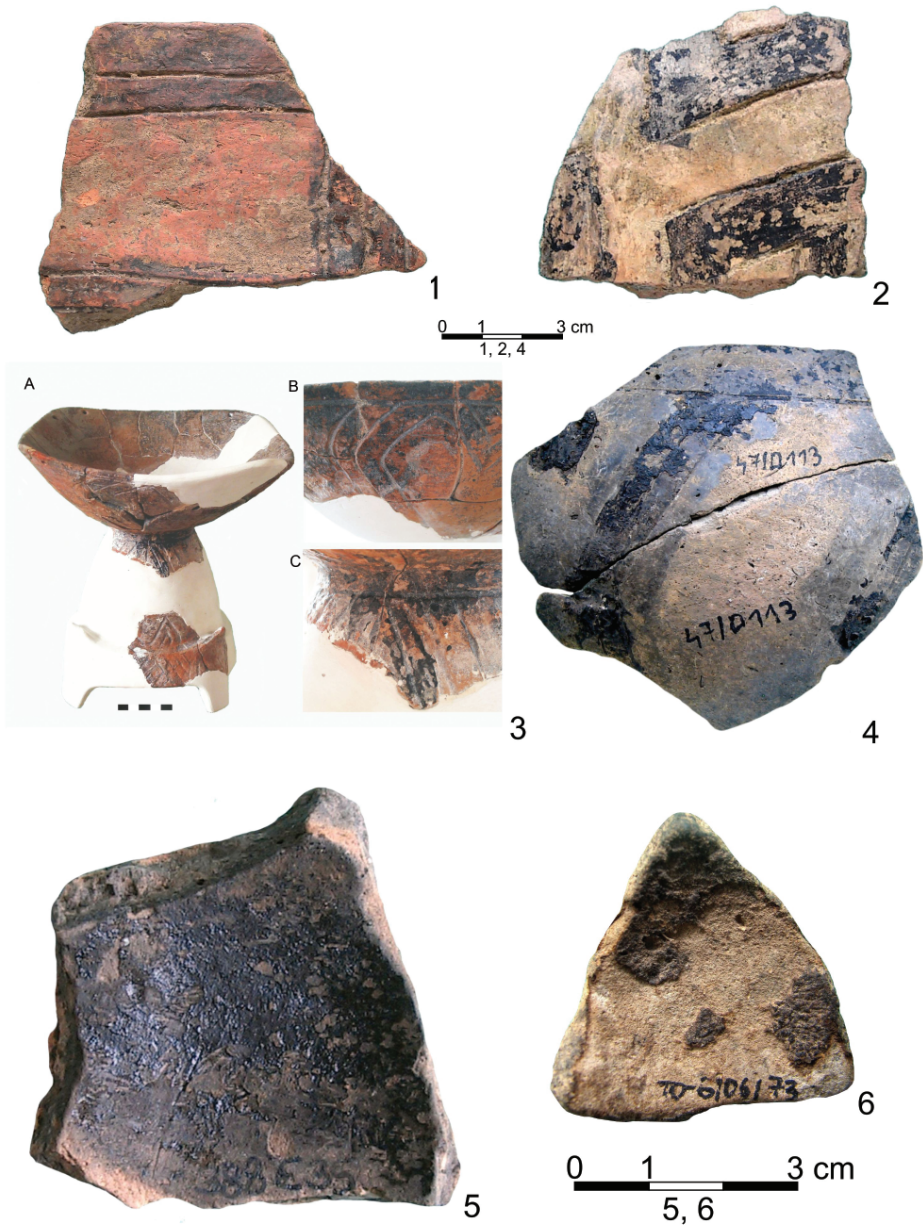


Fig. 11. Fragments of vessels with residues of wood tar; Photo by S. Pietrzak.

1 — Šarišské Michaľany, okres Sabinov, Slovakia (Tiszadob group) — sample Sr 10 (technological group VI);
 2 — Šarišské Michaľany, okres Sabinov, Slovakia (Bükk Culture) — sample Sr 151 (technological group VI);
 3 — Ryńsk, powiat Radziejów, województwo kujawsko-pomorskie, site No. 42 — sample Sr 438 (technological group VI);
 4 — Chełmiczki, powiat Inowrocław, województwo kujawsko-pomorskie, site No. 10 — sample Sr 632, 638; 5 — Roźniaty, powiat Inowrocław, województwo kujawsko-pomorskie, site No. 2 (GAZ 388) — sample Sr 83 (technological group I); 6 — Tominy, powiat Opatów, województwo świętokrzyskie, site No. 6 — Sr 648 (technological group I).

DISCUSSION

In the southern and south-eastern part of Poland the inflow of the Carpathian obsidian in the form of nodules both in the “Notenkopf” and “Želiezovce” phase was registered (Kaczanowska 1985; Szeliga 2007). It can be inferred that at the sites located in this area the entire process of working obsidian took place only once (Szeliga 2009). On the contrary obsidian distribution in the area located further to the north and west, i.e. the Lower Silesia, Kuyavia, Greater Poland and Pырzyce Land included flake or blade blanks, and sporadically tools (Kabaciński 2010, 106; Szeliga 2009).

In the Polish Lowland (Greater Poland, Kuyavia) in the early period of the LBK presence the communities based their production on chocolate or Jurassic flint supplemented by a local raw material — erratic Baltic Cretaceous flint (Kabaciński 2010). From this area only 3 sites with obsidian artefacts are known, namely Zagajewice, site 1 (Grygiel 2004), Chabsko, site 40 and Kowalewko, site 14 (Kabaciński 2010, 104). At the settlement in Zagajewice (“Notenkopf phase” of the LBP) 4 pieces were found (crested blade, flake, blade and burin). In Chabsko and Kowalewko (“late Notenkopf phase” of the LBK) only single items were discovered (Kabaciński 2010, 104). In contrast to the Lowland flint production in the Lesser Poland was based mostly on good quality local raw material, namely Jurassic flint. In the Sandomierz Upland a diversity in raw material utilization was observed — chocolate flint, Świeciechów flint and also imported Jurassic flint were used. The greatest raw material diversity was noted in the vicinity of Rzeszów loess region which is due to the location between outcrops of different kinds of raw materials, i.e. Jurassic, Volhynian, chocolate and Świeciechów flints, radiolarite and obsidian (Balcer 1983). The presence of the latter material in the whole structure of the inventory at sites in Rzeszów (i.e. Rzeszów–Piastów) exceeds even 20% (Kadrow 1990). According to M. Szeliga (2009, 205) the LBK societies inhabiting Rzeszów and Przemyśl area were direct importers of obsidian from the Carpathian outcrops. Moreover, they controlled further distribution of this raw material.

Very intensive inflow of Carpathian obsidian confirms interregional contacts between linear societies from southern Poland and the East Linear Pottery communities from eastern Slovakia and north-eastern Hungary. We are referring here especially to Kapušany-Tiszadob group of LBP Culture and the Bükk Culture exploring and widely distributing obsidian (Kaczanowska 1985, 47–48; Kaczanowska, Kozłowski, Šiška 1993). On the other side, in the chipped stone industries of the Bükk Culture different kinds of “northern” flints were observed, i.e. chocolate, Jurassic and Dniester flint. Even though they did not play a major role in the flint production, their presence confirms the existence of contacts and trade. According to M. Kaczanowska, J. K. Kozłowski, S. Šiška (1993) it proves rather the exchange of prestige goods than the economic meaning of this raw materials.

These Transcarpathian influences are clearly visible also thanks to the imports of vessels registered at many sites in the southern Poland (Czekaj-Zastawny 2014; Furmanek 2010; Godłowska 1982; Godłowska, Kaczanowska 2009; Kamińska 1964; Kulczycka-Leciejewiczowa 1980) and also in Kuyavia (Grygiel 2001; Pyzel 2009). They are almost always accompanied by obsidian artefacts (Godłowska, Kaczanowska 2009; Wilczyński 2014), whose wider dispersion is connected with the classic stage of the LBK development (Kulczycka-Leciejewiczowa 1979; Szeliga 2009, Fig. 2).

At all sites that yielded pottery with remains of wood-tar pigment, excavations yielded silica raw materials of southern origin, mostly chocolate flint and/or obsidian (Kabaciński 2010; Szeliga 2008, 2009; Szeliga, Zakoscielna 2009).

Samples: Sr 238 from Ryńsk, site 42; Sr 638 from Chełmiczki, site 10; Sr 10 from Šarišské Michalany (Tiszadob group) and Sr 151 from Šariške Michalany (Bükk Culture) represent a category of organic-mineral composite pigments. A black pigment is present on vessels in the form of a relatively thin (less than 1 mm), matt, evenly distributed and slightly cracked layer filling in a geometric engraved ornament. On external surfaces of vessels we noticed traces of a red mineral substrate (iron oxides), from 0.1 to 0.3 mm thick, onto which a thin layer of black colouring material was applied. Colouring layers were distributed in liquid form over a fired base, and hence, they heavily adhered to walls of the vessels. The use of mineral substrate was to even the surface and aid the adhesion of the organic material to the surface of the ceramic vessels. Microscopic observations revealed the presence of a substantial quantity of mineral impurities (sand grains), which was an outcome of an intentional modifications of tar properties, as indicated by uniform distribution of the grains and the fact that some grains fused into the observed surface. The admixture of mineral components improved the adhesion and durability of the pigment layer on a ceramic base, and greatly increased the abrasion resistance. A deliberate addition of a considerable amount of mineral substances resulted in the production of a mixed (organic-mineral) composite material.

The same technology of composite material preparation was identified in Roźniaty, site 2 (sample Sr 83), and Siniarzewo, site 1 (samples Sr 88-2, Sr 95, Sr 96) in order to caulk the inner surfaces of the vessels (Pietrzak 2012). In contrast, samples Sr 808-1 and Sr 808-2 from Nakonowo Stare, site 2, and Sr 648 from Tominy, site 6 provided examples of the application of organic-mineral composite materials used as a binder for the repair of fractured vessels. In this case, tar fulfilled a function of an organic binder, while mineral components were used as a filling material. The producers' intention was to thermally fix the analysed substance on the surface of vessels and to increase its resistance to external agents (abrasion) by adding mineral components. This is demonstrated by the results of the melting point measurement: no melting point up

to 300°C. Furthermore, the analysed sample shows a significant reduction in the solubility in organic solvents, which is in accordance with the foregoing observations and proves its substantial thermal degradation. The image of the surface revealed the presence of micro-porous structures, characteristic of vigorous reactions of excreting gases and volatile vapours of substances due to high temperatures. The advanced method of wood tar production, using a two-chamber production system with a container for catching the product is evidenced by the high purity of the analysed substances devoid of residues of unprocessed wood or bark, as revealed by microscopic observations.

FINAL REMARKS

Well organized system of distribution of chocolate flint on the Polish Lowland from the Świętokrzyskie Mountains area was not only of economic meaning, but also could have been a significant element of connection with *homeland* (Kabaciński 2010). This could also refer to the distribution of obsidian and application of organic pigment by the Lowland communities of the LBK culture as an integral part of the LBK cultural package and an element of their cultural identity, alongside the flint production technology, long houses and so on. The very first usages of black wood-tar pigments appeared in upper Tisza Region (i.e. Šarišske Michalany) from where this idea (innovation) extended *via* the Vistula river to the north (Koško *et al.* 2006).

The non-utilitarian meaning of obsidian distribution is indirectly supported by the experimental observations done by M. Szeliga. In contrast to flint tools, obsidian implements, in spite of sharp edges, were less resistant and effective at work (Szeliga 2009). In this case the intensification of interregional contacts, information exchange and alliance-making should be taken into consideration (Whallon 2006). That phenomenon of long-distance contacts of a rather symbolic nature is documented for a slightly later times by the discovery of the Hungarian Bodrogkeresztur vessels at a late Mesolithic settlement in Dąbki, located on the southern Baltic coast and dated to later 5th millennium cal BC (Czekaj-Zastawny, Kabaciński, Terberger 2011; Czekaj-Zastawny *et al.* 2013).

Production of organic pigment prepared as a composite material is known from Kuyavia (the Central Polish Lowland). Microscopic observation proves that application of an additional mineral layer allowed to even the surface of the substrate and facilitated better binding of the organic-mineral composite material with the clayish surface of a vessel. It is possible that the *know-how* on how to make and use composite materials was received by Kuyavian LBK societies from the south, as a result of interregional interactions. Application of composite substances based on wood tar is observed not only with respect to pigments but also as a mean for waterproofing vessels (Pietrzak 2012).

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