Rusinowo. The Symbolic Culture of Foragers in the Late Palaeolithic
and the Early Mesolithic. T. Płonka, K. Kowalski (eds.) Wrocław 2017, p. 147–161
DOI 10.23734/22.18.107

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3.3.2. The residue filling the lines of the ornament

Abstract: Surfaces of Palaeolithic objects made of flint, bone and antler are sometimes covered by irregular stains from organic substances: resins, wood tar, waxes, etc. Some of these substances result from deliberate action, others are traces of deposition in ashes of a hearth. The most likely to be affected in this way are depressed features on the surface of an object. The surface of the artefact from Rusinowo is covered by intentionally executed patterns, filled by a dark grey and a black substance partly, and in an irregular manner. This black and grey substance was sampled from the grooves and studied via FTIR, μFTIR (Fourier Transform Infrared Spectroscopy and micro-Fourier Transform Infrared Spectroscopy respectively) and SEM/EDS (Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy). FTIR was used to make a comparative study of reference substances: charcoal, soot, burnt spruce needles and raw antler of modern elk. The black colour in the grooves of the Rusinowo find is caused by the presence of a residue of ash from a hearth, or hearths, presumably in a natural mixture with fulvic acids. To a minor extent, the black colour may be attributed to the presence of a Fe-S phase. No evidence was found to validate a deliberate origin of the staining.

Keywords: FTIR, μFTIR, SEM/EDS, bioapatite, collagen, black substance, elk antler, Late Palaeolithic, archaeology

Introduction

The ornament grooves on the Late Palaeolithic artefact from Rusinowo are partly and in an irregular manner filled with a black substance. The aim of the present study was identifying their origin and nature – whether some form of an organic (eg, wood tar or soot) or inorganic colouring agent (eg, bone char), trace of some intentional activity other than painting (practices concerned with the artefact's surface) or the result of diagenetic processes.

Traces of black organic substances in the form of irregular, usually very fine clusters, have been detected on the surface of Palaeolithic objects, including Late Palaeolithic ones. Spectroscopic studies have disclosed the presence of a mixture of resins and wood tars (Vahur *et al.* 2011; Trąbska *et al.* 2016), used mostly as adhesive, although the array of uses, at least during younger ages, is wider (Pietrzak 2010). On the other hand, the studies of the origin of the black stains on the surface of the artefact from Rusinowo (cf. section 3.3.1., in this sub-chapter) have disclosed the presence mostly of FeS_2 phases, chiefly pyrite, most likely having a natural origin.

The material and methods

The black substance subjected to the studies was extracted with a sterile needle from three neighbouring grooves (AVf22, AVg23 and h23). It was investigated via the method of scanning electron microscopy with x-ray microanalysis (SEM/EDS). The instrument used was a FEI Nano Nova scanning electron microscope coupled with an Oxford Link ISIS x-ray detector. Samples were analysed in a low vacuum technique, in two stages: first, without

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coating with graphite, next, with the surface coated to obtain high-quality images.

Phase analysis of samples from the artefact was made with the analytical technique of reflected micro-infrared spectroscopy (µFTIR). The instrument used was FTS 40 Pro f-y Lab coupled with a UMA 500 Digilab microscope. The spectra were collected by M. Pomianowska of the Institute of Forensic Research in Cracow, whom the authors wish to thank for her contribution. Sample 1 represents what macroscopically is a whitish-grey substance, sample 2 – a grey substance, sample 3 – a black substance.

The original depositional environment of the artefact is unknown, and it is unclear by what substances it had been surrounded. Given the presence on the surface of the object of dark grey, irregular staining, one of the possible identification of the substance inside the grooves was ash and/or peat. Therefore, the decision was taken to report in the present study on a series of infrared spectra collected from selected black substances associated with hearths, and on black components of peat. Reference substances include the black component of ashes excavated from the archaeological site Targowisko near Cracow (sampled during motorway construction led fieldwork when the chronology was still only approximate), black ash from a modern fire, a black cluster from the Neumarkt peatbog (Germany), soot particles lifted from the surface of a vessel where they had developed over an open fire, and spruce needles burnt in a modern fire. Another reference was a FTIR spectrum collected from modern raw antler of elk.

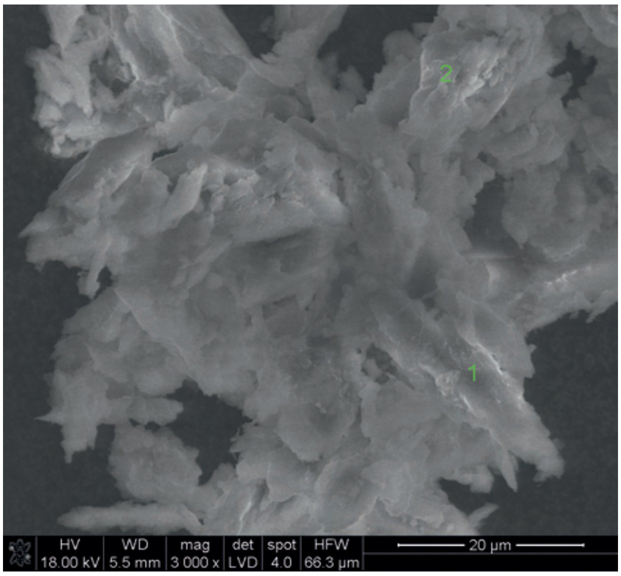

Fig. 1. Rusinowo. General view of sample extracted from the ornament groove showing oblong crystals of bioapatite. EDS analysis was made for points 1 and 2

For the reference substances infrared spectra were obtained by M. Jakus on a Bruker Equinox 55 spectrometer using the KBr pellet transmission technique and W. Góralik on a Thermo Scientific Nicolet IR-200 spectrometer using the attenuated total reflectance technique (ATR), both at the Faculty of Chemistry of the Jagiellonian University; we are very grateful for their assistance. The spectra were interpreted with reference to the RRUFF database (http://WWW.rruff.com) and data published in the cited literature.

SEM/EDS study results

Samples of the dark grey and the black substance reveal the presence of needle-like clusters consisting mainly of calcium phosphate(s) and, in a smaller quantity, of silica. There are subsidiary amounts of sodium, potassium, sulphur and iron (Figs. 1, 2). However, it is notable also that iron concentrates in specific clusters with sulphur and silicon. In the SEM image, these clusters appear amorphous (Figs. 3, 4), or take the form of oval clusters, with discernible crystalline walls. All clusters concentrating iron and sulphur are very small and isolated (Figs. 5, 6).

The results of FTIR study of the substance from the grooves and reference substances

Substances identified in spectra collected from the whitish-grey sample (Fig. 7) include: apatite and/or bioapatite (bands 606, 964, 1053 and 1050 cm^{-1}), collagen (bands at 1230, 1645–55 cm^{-1}), calcite (bands at 875, 1425–31 and 1796 cm^{-1}, band at 2510 cm^{-1} – vibrations from components of limewater), organic compounds other than collagen (1594, 2853 and 2925 cm^{-1}); additionally, a band was attributed to vibrations from OH groups (at around 3400 cm^{-1}). Not to be discounted is the presence of calcium sulphate minerals (most likely, gypsum), suggested by the

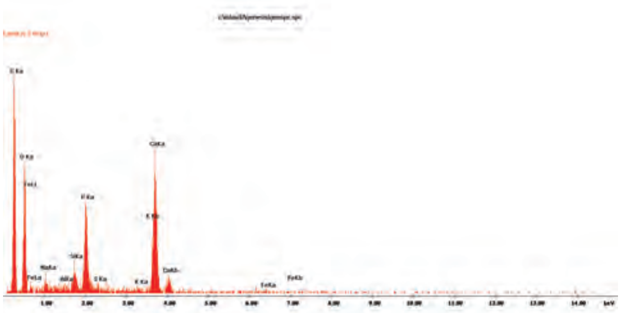

Fig. 2. Rusinowo. EDS spectrum identifying the chemical composition of areas sampled from points 1 and 2. Next to calcium phosphate, an organic substance was detected, and negligible amounts of silica, aluminium, sodium, sulphur, potassium and iron

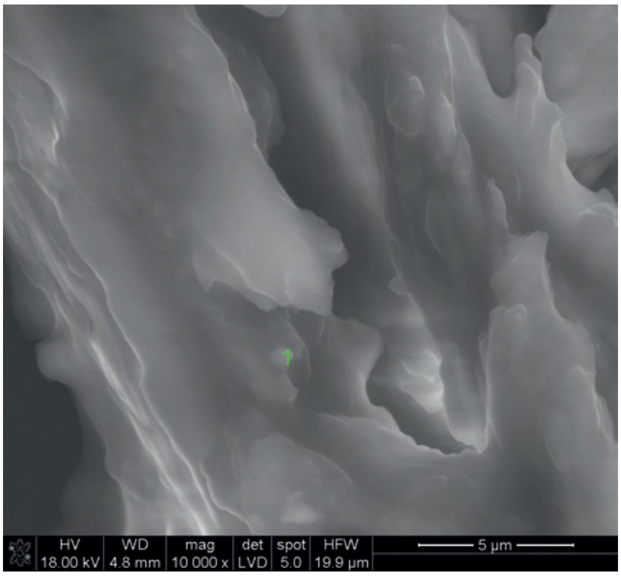

Fig. 3. Rusinowo. Antler fragment. The small cluster marked with a number and its immediate vicinity represents a concentration of iron, sulphur and silica

band at 680 cm^{-1} and the thickening of the band around 1100 cm^{-1}). The collagen spectrum is depleted: there are no bands at 1550 cm^{-1} from the vibrations of amide II. As a result of the presence of carbonate phases (mainly calcite) it is not possible to indicate bands from the vibrations of CO$_3$ groups built into the structure of the apatite (both type A: bands at 880, 1450 and 1545 cm^{-1} and type B: bands at 875, 1410 and 1544 cm^{-1}) which according to some researchers assist identification of thermal alteration of the mineral (Moencke 1963-66; Jones *et al.* 1995; Böke *et al.* 2004; Belbachir *et al.* 2009; Chadefaux *et al.* 2009; Berzina-Cimdina, Borodajenko 2012; Thompson *et al.* 2013; Tables 2 and 3).

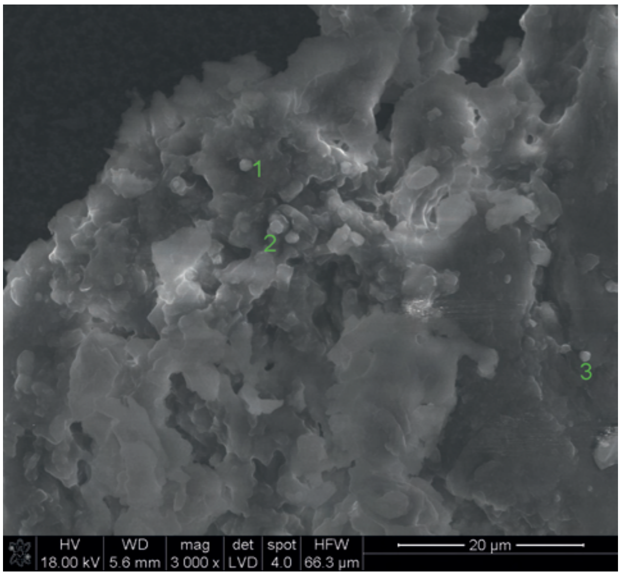

Fig. 5. Rusinowo. Globular clusters found in points 1, 2, 3 are concentrations of iron and sulphur

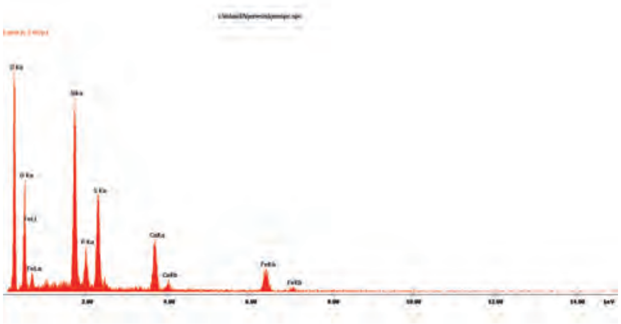

Fig. 4. Rusinowo. EDS spectrum representing the chemical composition of cluster marked as 1 (Fig. 3). Next to iron and sulphur there is a high concentration of silica

The FTIR spectra collected from the grey substance filling the grooves of the zigzag ornament revealed the presence of several substances (Figs. 8–11). The presence of bioapatite, possibly also of mineral apatite, is suggested by bands at 1099–1111, 1080, 1057–1062, 1041–1050, 950–964 and 606 cm^{-1} (Moencke 1963-66; Berzina-Cimdina, Borodajenko 2012; Thompson *et al.* 2013; Table 2).

An evident component in the grey samples is calcite with a dissimilar level of crystallization. In the investigated samples it is manifested by the presence of bands at 1780–1799, 1734–1750, 1422–1450, 875–878, 713–730 and 690–694 cm^{-1} (Figs. 7–11, possibly, also Fig. 12). The broad range of the wavenumber values may result from the co-occurrence of different Ca-CO$_3$ phases, differing in the size of crystallites. The most diagnostic for detection of calcium carbonate in the spectra collected from the investigated samples is a narrow band at 875–878 and an intensive band at around 1430 cm^{-1}. In some spectra (Fig. 9, to a smaller extent Fig. 7), which by their shape indicate the presence of calcium carbonate in the form of crystalline calcite, appears to be the band at 2513–2517 cm^{-1}, recorded by one of the authors (JT) on the spectrum collected from limewater (Moencke 1963-66).

Samples of the grey residue filling the grooves of the artefact may contain a minor quantity of sulphate

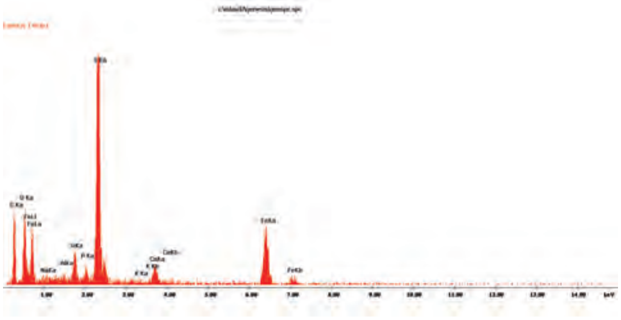

Fig. 6. Rusinowo. EDS spectrum identifying the chemical composition in points 1 – 3 (Fig. 5)

Table 1. Rusinowo. Infrared vibrations from samples of black substance extracted from grooves of the ornament. Assignement and interpretation is based on source data cited in Tables 2 and 3

Whitish-gray samples (Fig. 7)	Gray sample (Fig. 8)	Gray sample (Fig. 9)	Gray sample (Fig. 10)	Gray sample (Fig. 11)	Black sample (Fig. 12)	Assignement/ Interpretation
3380	3340	3340	3340	3340	3340	Vibrations from OH group
2960	2960	2960	–	2960	2960	Vibrations from C–H group
2925	2923	2921	2922	2923	2939	
–	–	–	–	–	2874	
2853	2852	2853	2853	2852	–	
–	–	2517	–	2517	–	Limewater
–	–	–	1880	–	–	Vibration from C=O groups
1785	–	1797	1790	1790	–	Calcite Aragonite Limewater
1740	–	1740	1740	–	1737	Calcite
1645–1655	1680	1680	–	–	1680	Vibrations from C–O groups Collagen – Amide I
1594	1601	1590	1610	1585	1570	Vibrations from C–O groups
–	–	–	–	–	–	Collagen – Amide II
–	–	1500	–	–	–	Vibrations from rings of aromatic compounds
1425 –1431	1430	1431	1426+1450	1439	1450	Vibrations from C–O groups: Limewater Calcite Poorly crystallized apatite Collagen – Amide II
1280–1310	–	–	–	–	1310	Vibrations from C=O, C=N, C=C groups
–	–	–	1200+1250	1280	1244	Collagen – Amide III
–	–	–	–	–	1164	Calcite
–	–	1111	–	1099	–	Poorly crystallized apatite
1080	1080	–	–	–	–	Vibrations from sulphate groups
–	–	–	1062	–	1057	Poorly crystallized apatite Vibrations from C–O groups in alcohols Limewater
1035	1049	1041	1041	1043	–	Vibrations from C–O groups in alcohols, from C–N groups in amines
964	960	–	950	–	–	Apatite
875	875	877	878	876	876	Calcite Limewater
800	800	800	773+800	800 780	–	Quartz
–	–	713	–	713	–	Calcite
–	–	–	694	–	–	Limewater Calcite Quartz Apatite
–	–	–	680	–	–	Gypsum
–	606	–	–	–	–	Gypsum Albite

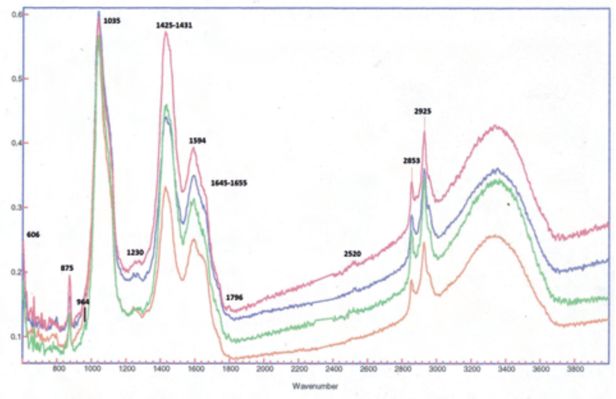

Fig. 7. Rusinowo. Infrared spectrum of whitish-gray substance sampled from ornament grooves. On the horizontal axis – wavenumber value expressed in cm^{-1}, on the vertical axis – absorption

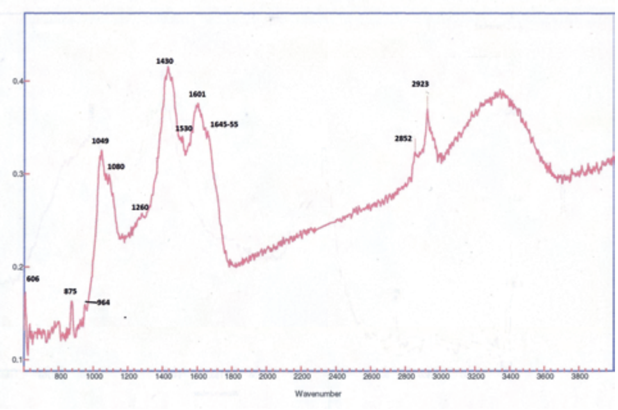

Fig. 8. Rusinowo. Infrared spectrum of whitish-gray substance sampled from ornament grooves. On the horizontal axis – wavenumber value expressed in cm^{-1}, on the vertical axis – absorption

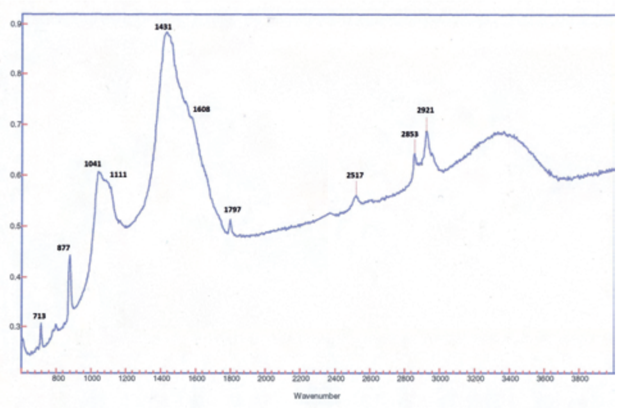

Fig. 9. Rusinowo. Infrared spectrum of gray substance sampled from ornament grooves. On the horizontal axis – wavenumber value expressed in cm^{-1}, on the vertical axis – absorption

Fig. 10. Rusinowo. Infrared spectrum of gray substance sampled from ornament grooves. On the horizontal axis – wavenumber value expressed in cm^{-1}, on the vertical axis – absorption

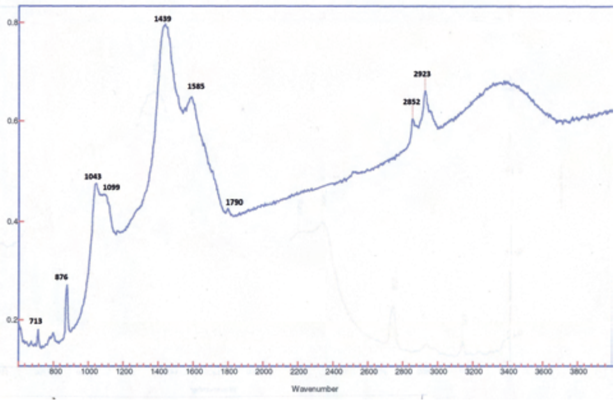

Fig. 11. Rusinowo. Infrared spectrum of gray substance sampled from ornament grooves. On the horizontal axis – wavenumber value expressed in cm^{-1}, on the vertical axis – absorption

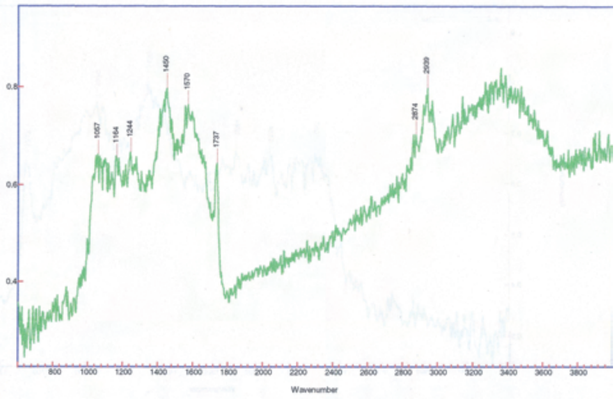

Fig. 12. Rusinowo. Infrared spectrum of black substance sampled from ornament grooves. On the horizontal axis – wavenumber value expressed in cm^{-1}, on the vertical axis – absorption

Table 2. Bands from vibrations generated by apatite, calcite and limewater, gypsum, pyrite, mackinawite and of bovine and human collagen in cm^{-1}. Band intensity: “s” (strong), “m” (medium), “w” (weak).

Modern elk antler (current research)	Modern bovine bone (Chadefaux *et al.* 2009)	Collagen I from human tissue (Jackson *et al.* 1995)	Collagen I from human tissue (Belbachir *et al.* 2009)	Bioapatite (Thompson *et al.* 2013)	Calcite (Moencke 1963–6)	Limewater (unpublished individual research)	Gypsum (Boke *et al.* 2004)	Pyrite (www.rruff; ID R0500190)	Pyrite (www.rruff; ID R050070)	Mackinawite (Lennie *et al.* 1995)
–	–	–	–	–	–	–	3580 m	–	–	–
–	–	–	–	–	–	3400 m	3430 m	–	–	–
3281 m	–	–	–	–	–	–	–	–	–	–
3073 w	–	–	–	–	–	–	–	–	–	–
2965 w	–	–	–	–	–	–	–	–	–	–
2920 w	–	–	–	–	–	2920 w	–	–	–	–
–	–	–	–	–	–	2800 w	–	–	–	–
–	–	–	–	–	–	2500 w	–	–	–	–
–	–	–	–	–	–	–	–	2160 w	2180	–
–	–	–	–	–	–	–	–	1980 w	1980	–
–	–	–	–	–	1795 w	1780 w	–	–	–	–
–	1680 s	–	–	–	–	–	–	–	–	–
–	1660 s	1661 s	1659 s	–	–	–	–	–	–	–
1641 m	1640 s	1636 s	–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	1690 w	–	–	–
–	–	–	–	–	–	–	1610 w	–	–	–
–	1550 m	1557 s	1555 s	–	1545	–	–	–	–	–
–	1500 w	–	–	–	–	–	–	–	–	–
1531 m	–	–	–	–	–	–	–	–	–	–
–	1470 m	–	–	–	–	–	–	–	–	–
–	–	1456 m	1454 w	1455	–	–	–	–	–	–
1444 m	1450 m	–	–	1450	–	–	–	–	–	–
1413 m	1420 s	–	–	–	1435 s	1435 s	–	–	–	–

–	–	1405 m	1403 w	1410	–	–	–	–	–	–
–	1340 w	1337 w	1340 w	–	–	–	–	–	–	–
–	1270 w	1282 w	–	–	–	–	–	–	–	–
1235 w	1240 w	1236 m	–	–	–	–	–	1230 m	1210	
–	–	1204 w	1203 w	–	–	–	–	–	–	–
–	–	1174 w	1160 w	–	–	–	–	–	–	–
–	–	–	–	–	–	–	1146 s	–	1150	–
–	–	–	–	–	–	–	1116 s	–	–	–
–	–	–	–	–	–	–	–	–	–	–
–	–	–	–	–	–	1040 w	–	–	–	–
–	–	1082 w	1079 w	–	–	–	–	–	–	–
–	–	1081 w	–	–	–	–	–	–	–	–
–	–	1031 w	1035 w	1028–1100	–	–	–	–	–	–
1018 s	–	–	–	–	–	–	–	–	–	–
958 m	–	–	–	960	–	–	–	–	–	–
–	–	–	–	880	–	–	–	880 m	–	–
872 w	–	–	–	875	877 m	865 m	–	–	–	–
–	–	–	–	–	–	–	–	–	830	–
–	–	–	–	–	–	–	–	–	–	790 m
–	–	–	–	–	712 m	700 w	–	–	–	–
–	–	–	–	–	–	–	669 m	–	680	–
–	–	–	–	632–650	–	–		–	–	–
600 m	–	–	–	605	–	–	602 m	–	–	–
–	–	–	–	–	–	–	–	–	570	560 m
560 m	–	–	–	565	–	–	–	–	–	–
–	–	–	–	–	–	–	–	470 s	–	–
–	–	–	–	–	–	–	–	–	450	–
–	–	–	–	–	–	–	–	–	–	300 s

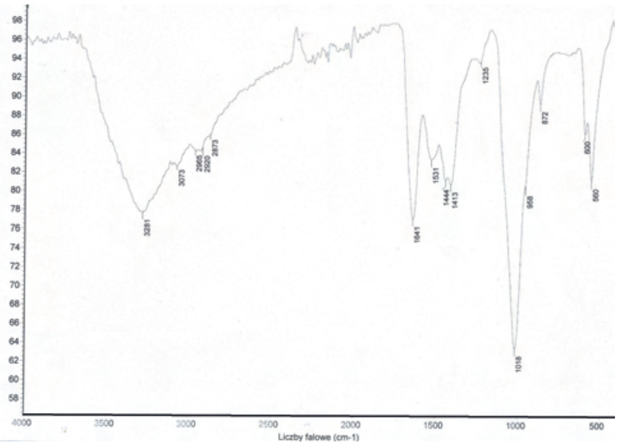

Fig. 13. Infrared spectrum of modern elk antler. On the horizontal axis – wavenumber value expressed in cm^{-1}, on the vertical axis – transmittance

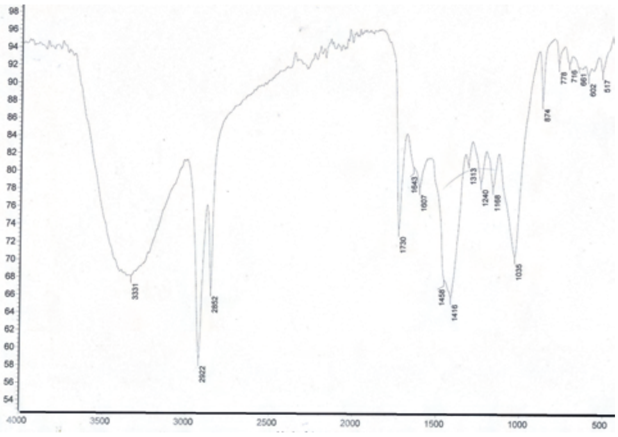

Fig. 14. Infrared spectrum of a reference substance – burnt spruce needles. On the horizontal axis – wavenumber value expressed in cm^{-1}, on the vertical axis – transmittance

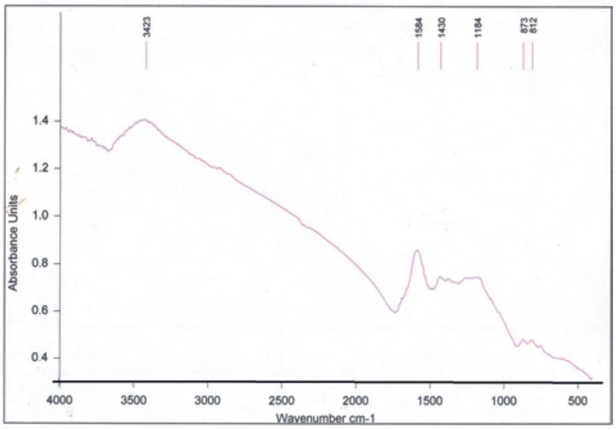

Fig. 15. Infrared spectrum of a reference substance – black ash (charcoal) from a modern fire. On the horizontal axis – wavenumber value expressed in cm^{-1}, on the vertical axis – absorption

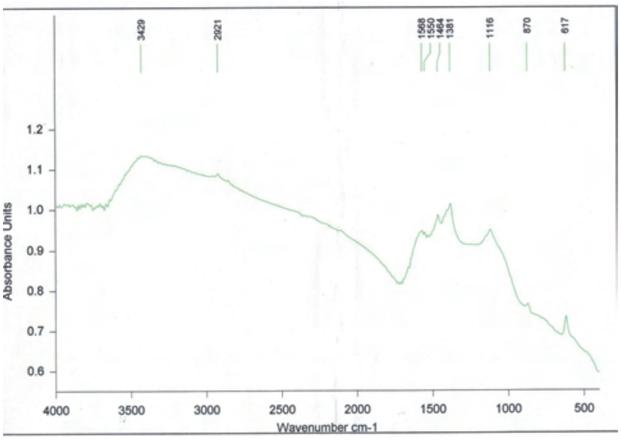

Fig. 16. Infrared spectrum of a reference substance – black ash (charcoal) from a prehistoric fire from archaeological site Targowisko. On the horizontal axis – wavenumber value expressed in cm^{-1}, on the vertical axis – absorption

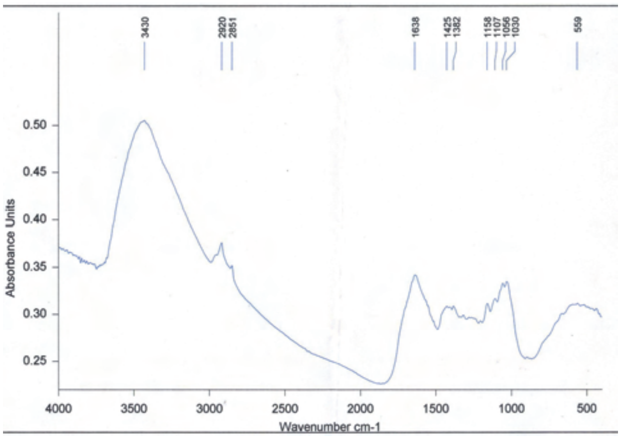

Fig. 17. Infrared spectrum of a reference substance – soot collected from the surface of a sooty vessel. On the horizontal axis – wavenumber value expressed in cm^{-1}, on the vertical axis – absorption

Table 3. Infrared vibrations originating from reference substances and interpretation/assignement of vibrations from organic and inorganic compounds.

Ash from Neolithic firepit (Fig. 16)	Ash from modern „tourist" campfire (Fig. 15)	Peat from site at Neumarkt	Soot from a vessel surface (modern) (Fig. 17)	Burnt spruce needles (Fig. 14)	Prehistoric charcoal from Kebara (Cohen–Ofri *et al.* 2006)	Modern charcoal, incompletely combusted (Guo, Bustin 1998)	Modern charcoal, completely combusted (Guo, Bustin 1998)	Experimental birch wood tar (Pietrzak 2010)	Vibrations from organic compounds (Kęcki 2016)	Vibrations from organic compounds (McMurry 2007)	Vibrations from inorganic compounds (Moencke 1963–6; Ewing 1985; Błaszczak *et al.* 1993)
1	2	3	4	5	6	7	8	9	10	11	12
–	–	3698	–	–	–	–	–	–	Vibrations from O–H groups	–	–
–	–	3621	–	–	–	–	–	–	Vibrations from O–H groups in alcohols, phenols, carboxylic acids	Vibrations from O–H groups in alcohols Vibrations from N–H groups in amines	–
3429	3429	3455	3430	–	–	3400	–	–	Vibrations from O–H groups	–	–
–	–	–	–	3331	–	–	–	3371	Vibrations from C–H groups in alkenes	Vibrations from N–H groups in amines	–
–	–	–	–	–	–	–	–	3069	Vibrations from C–H in vinyl and aryl groups	Vibrations from =C–H, C=C, O–H groups (carboxylic acids)	–
2921	2934	2922	2920	2922	–	2920	–	2927	Vibrations from C–H groups	–	–
2885	2890	–	–	–	–	–	–	–		–	–
–	–	2852	2851	2852	–	2850	–	2854		–	–
–	–	–	–	1730	–	–	–	1734	Vibrations from C=O– groups	Vibrations from C=C and C–C groups in aromatic compound Vibrations from C=O groups in esters, aldehydes, ketones, carboxylic acids Vibrations from C=C groups in alkenes	–
–	–	–	–	–	1719	–	–	–	–	Aromatic esters	–
–	–	–	–	–	–	1708	–	1709	–		–
–	–	–	–	–	–	–	–	1653	Vibrations from C=C, O–H groups	–	–
–	–	1631	1638	1634	–	–	1650	1640	Vibrations from N–H groups	–	Vibrations from O–H groups
–	–	–	–	1607	–	–	1600	1608	Vibrations from C=C groups in alkenes	–	–
–	1584	–	–	–	1593	–	–	–			
1568	–	–	–	–	–	–	–	–	Vibrations from aromatic rings	–	–

1	2	3	4	5	6	7	8	9	10	11	12
1550	–	–	–	–	–	–	–	–	Vibrations from N–H groups in amide II		Vibrations from carbonate groups
–	–	–	–	–	–	–	–	1539	Vibrations from N–H groups	Vibrations from NO_2 groups	–
–	–	–	–	–	1511	1508	–	1515	Vibrations from rings of aromatic compounds	–	–
1464	–	–	–	1458	–	–	–	1456	Vibrations from C–C groups in aliphatic compounds	–	Vibrations from carbonate groups
–	1430	–	1425	–	1430	1430	–	–		–	Vibrations from carbonate groups
–	–	–	–	1416	–	–	–	–		–	–
–	–	–	–	–	1400	–	–	–		–	–
1381	1381	–	1382	–	–	–	–	1377	Vibrations from C–H groups in aliphatic compounds	–	Vibrations from nitrate groups
–	–	–	1317	1313	1317	–	–	–	Vibrations from C–N groups	–	
–	–	–	1280	–	–	–	–	–	Vibrations from C–N and C–O groups	Vibrations from C–C groups in alkanes	Vibrations from PO_2 groups
–	–	–	–	–	1252	–	–	–	Vibrations from C–C, C–H groups in aliphatic and aromatic compounds	–	–
–	–	–	–	1240	–	–	–	1239		–	–
–	–	–	1204	–	–	–	–	–	Vibrations from C–O groups	Vibrations from C–N groups in amines	–
–	1184	–	–	–	–	–	–	1178	Vibrations from C–O groups and from C–H in aromatic hydrocarbon Vibrations from O–H groups in alcohols	–	Vibrations from sulphate groups
–	–	–	–	1168	–	–	–	–	Vibrations from O–H groups in alcohols	–	–
–	–	–	1158	–	–	–	–	–		Vibrations from O–H groups in alcohols Vibrations from C–N groups in amines	Vibrations from sulphate groups
1116	–	–	–	–	–	–	–	–		–	Vibrations from sulphate groups
1100	–	–	1107	–	–	–	–	1107		–	Vibrations from sulphate groups Vibrations from phosphate groups
–	–	–	–	–	1088	–	–	–		–	Quartz
–	–	–	1056	–	–	–	–	–		–	Apatite Albite
–	–	1032	1030	1035	–	–	–	1034		Vibrations from C–N groups in amines	Vibrations from phosphate groups

1	2	3	4	5	6	7	8	9	10	11	12
–	–	–	897	–	–	–	–	–	Vibrations from C–H groups in alkenes and aromatic compounds	–	Vibrations from carbonate group
870	873	–	–	874	–	–	–	884		Vibrations from C–H groups in alkenes	Vibrations from carbonate groups
–	812	–	–	–	–	–	–	–		Vibrations from C–H groups in aromatic compounds	Smectite
–	–	796	–	–	796	–	–	–		–	Quartz
–	–	777	–	778	–	780	700–900	–		Vibrations from C–H groups in aromatic compounds	Albite
–	751	–	–	–	–	–	–	757		–	–
–	–	–	–	–	–	–	–	730		–	–
–	–	–	–	716	–	–	–	–		–	–
–	–	693	–	–	–	–	–	–		–	Quartz
–	–	–	–	661	–	–	–	668	–	–	Vibrations from sulphate groups
617	–	–	–	602	–	–	–	–	–	–	Vibrations from phosphate groups Quartz
–	–	–	559	–	–	–	–	564	–	–	Vibrations from phosphate groups Pyrite
–	–	529	–	–	–	–	–	–	–	–	Smectite
–	–	–	–	517	–	–	–	–	Vibrations from C–C groups in aromatic compounds	–	–
–	–	467	–	–	–	–	–	–	–	–	Quartz
–	–	428	–	–	–	–	–	–	–	Vibrations from sulphate groups in pyrite	–

minerals. Most likely, this is gypsum, but the bands that may be ascribed to this mineral are characterized by a weak intensity and it is hard to say which of the Ca-SO_4 phases is found here. The presence of gypsum is suspected from the presence of bands at 1150, 1111, 680 and 606 cm^{-1}. It is likely that there is some coincidence of bands originating from different substances (Figs. 8, 9, Table 2). In one sample (Fig. 10) quartz was detected, also likely is the presence of feldspar (albite) (bands at 694, 773 and expansion of the band at 1062 cm^{-1}) (Moencke 1963-66; Table 2). The amount of these phases is very small.

An organic substance identifiable on the infrared spectra collected from the whitish-grey and grey samples is collagen, a component of antler. In spectra collected from samples submitted for analysis, collagen may be attributed to bands from the range of 1641-1680, 1531-1557 and 1236-1250 cm^{-1}. The quite broad range of the wavenumber is given here to illustrate the existence of evident differences in the structure of collagen from different organisms (cf. Table 3). Furthermore, these differences intensify depending on temperature (Thompson *et al.* 2013) and diagenetic processes (Chadefaux *et al.* 2009). Bands originating from vibrations of pure bioapatite and collagen in the antler of elk are visible also in the reference spectrum (Fig. 13). In the whitish-grey and grey samples, the shape of the collagen spectrum diverges somewhat from the curve of the reference collagen spectrum.

In the spectra under discussion there are identifiable bands from the vibrations of an organic substance other than collagen. These are bands at 1585–1610 cm^{-1}, and bands at 2852–2925 cm^{-1}. In the spectrum shown in Fig. 10 there is a band at 1880 cm^{-1}, and bands at 2852 and 2925 cm^{-1} have an observably smaller intensity (McMurry 2007; Kęcki 2016).

The spectrum from the black sample is characterized by the presence of bands which may be ascribed to vibrations from functional groups of organic compounds (1057, 1164, 1244, 1450, 1570, 1737, 2874 and 2939 cm^{-1}), although some of them may coincide with bands representing apatite (1057 cm^{-1}), clay minerals (1164 cm^{-1}) and carbonate minerals (1450 cm^{-1}) (McMurry 2007; Kęcki 2016).

In the reference spectrum collected from modern elk antler (Fig. 13) there are discernible bands originating from bioapatite (560, 600, 872, 958, 1018, 1413 and 1444 cm^{-1}) and collagen (1235 cm^{-1} – amide III, 1531 cm^{-1} – amide II, 1641 cm^{-1} – amide I), and a group of bands of a low intensity associated with the vibrations of groups CH_2 and CH_3 (2873, 2920, 2965, 3073 and 3281 cm^{-1}). The spectrum reveals the presence of CO_3 groups built into the structure of the apatite (bands at 872, 1413 and 1444 cm^{-1}) (Chadefaux *et al.* 2009; Thompson *et al.* 2013).

Analysis of the reference samples for black, burnt substances (Figs. 14–17) revealed the presence of mostly organic substances, with a smaller number corresponding to inorganic substances. In the latter, we identified sulphate minerals (probably, gypsum), carbonate minerals, and possibly, phosphate minerals, quartz, albite and smectite. Quartz (as the spectra show – well crystallized) is of detrital origin, similarly as albite and smectite. The sulphate and the phosphate minerals identified in the samples are most likely to be contaminations from plant ash. The amount of the latter in the investigated samples is minor. This is nothing to wonder at – after all, the study was made of black charcoal, that is, a variously carbonized organic substance. The peat sample (despite its macroscopically black colour) is dominated by inorganic compounds (smectite, quartz and albite) (Table 3).

An organic substance detected on the spectra collected from modern charcoal from an open fire and from an archaeological site (Figs. 15, 16) is structurally similar to charcoal burnt at low temperatures (around 300°C – charcoal from a modern open fire) and at a slightly higher temperature (around 400°C – charcoal from the site Targowisko). The evidently burnt condition of the tested reference samples is indicated by the depleted structure of OH groups (the flattening of the spectrum at approximately 3000–4000 cm^{-1}) and the decided domination of aromatic components over aliphatic ones (the shape of the spectrum at approximately 500-1800 cm^{-1}). In the soot sample (Fig. 17) there is a slightly greater amount of aliphatic components, as indicated by the presence of distinct bands at 2851 and 2920 cm^{-1}. Experimental data suggest that the duration of exposure to high heat has an impact on the shape of spectra (Guo, Bustin 1998). Not to be discounted either is a certain variation which results from the use of different tree species and their different elements. However, we are unable to isolate the effect of particular components of the process on the shape of the obtained spectra. The spectrum shown in Fig. 14 represents carbonized spruce needles which have not completely lost their shape. They had been exposed to the heat of an open fire by being placed close to the central embers and left there for about 3 hours. The obtained spectrum displays a sharp band at 1730 cm^{-1} and a band at 1607 cm^{-1}. Some bands (eg, at 1240 cm^{-1}) coincide with bands in the spectrum collected from the antler of elk (eg, 1236 cm^{-1}), which may obstruct interpretation.

Discussion

The ornament grooves in the ancient antler object retain a residue of whitish-grey, grey and black substances. All of them were investigated. The first is the result of the presence in the sample of the components of the antler – bioapatite and collagen, the occurrence of inorganic compounds, formed on the surface of the object as a result of diagenetic processes or settled on it as a result of contamination from lake chalk and detrital minerals (quartz, feldspar, clay minerals). On spectra collected from the whitish-grey samples extracted from the grooves, next to bands originating from bioapatite and collagen, there are also bands resulting from the presence of an organic substances other than collagen. These are bands at 1594–1608 cm^{-1} and bands at 2853–2925 cm^{-1}. The first group appears in the reference spectra collected from charcoal (particularly the low-temperature charcoal, Fig. 15) and burnt spruce needles (Fig. 14). The bands from the range of 2853–2925 cm^{-1}, also present in the reference spectrum collected from spruce needles, correspond to the presence of CH_3 and CH_2 groups associated with open-chain organic compounds. This suggests exposure to low-impact, ie, low-value temperatures, (below ca. 300°C) and/or the brief duration of this impact.

On the spectrum collected from the grey substance (Fig. 10), next to calcite, bioapatite and quartz there is a band at 1426 cm^{-1} and the earlier mentioned band at 1610 cm^{-1}. The band at 1426 cm^{-1} could result both from the presence of organic compounds (cf. Fig. 14) and from the occurrence of carbonate minerals originating from the ashes. The band at 1880 cm^{-1} is most likely to correspond to the presence of overtones. The low intensity of bands originating from CH_3 andCH_2 groups, and from OH groups (in the range 2800–3600 cm^{-1}) indicates the impact of temperature higher than in the case of other samples. Nevertheless, it need not have exceeded 400°C (Guo, Bustin 1998).

Special interest is raised by the black substance, because it may have been applied intentionally inside the grooves as a pigment, or represents a trace of some other type of sort deliberate treatment. The questions to be answered are whether the origin of the substance is inorganic (carbonized bioapatite), organic (collagen) or mixed? Its presence on the artefact, is it the result of deliberate action, or does it represent a residue from its depositional environment? Was it subjected to thermal transformation? Did it originate from the ashes of an open fire?

The SEM image of the grey and the black substance disclosed the presence, among the oblong crystals of bioapatite (Figs. 1, 2) of very fine, isolated clusters combining iron, sulphur and silicon (Figs. 3, 4), or globular clusters concentrating iron and sulphur (Figs. 5, 6). There is a striking similarity to the composition of Fe-S phases, chiefly pyrite which has been identified in the dark areas on the antler outside the grooves (cf. section 3.3.1., in this sub-chapter). However, some differences are visible. Here, the clusters of iron sulphide are quite scattered and much smaller. The reasons for this may be of two types: "technical", due to the much smaller volume of the extracted sample, or – natural. Perhaps, the substance which contributed to the formation of the Fe-S phases penetrated into the grooves to a much smaller extent than on the more exposed surface.

On the spectrum collected from the black substance filling the grooves on the antler object (Fig. 12) there is a distinct band at 1570 cm^{-1} originating from the vibrations of aromatic compounds. This band is characteristic for charcoal, which contains these compounds in quantity (Francioso *et al.* 2011). Also distinct are bands at 1450 cm^{-1} and 1730 cm^{-1}, respectively, from the vibrations of aromatic rings and carbonyl groups of ester compounds (McMurry 2007). Although these bands originate from vibrations of C=O groups of organic compounds, they may be related at least partly to C=O groups vibrating in limewater (Trąbska 1995). The spectrum resembles, at the same time, the spectra collected from charcoal and burnt spruce needles (Figs. 14–16). Furthermore, it is similar to spectra collected from "mature" fulvic acids extracted from fluvial sediments (De Paolis, Kukkonen 1997). The shape of spectra collected from samples removed from the grooves in the antler artefact is divergent from spectra collected from natural, thermally unmodified lignins (Bykov 2008). Furthermore, the investigated spectrum is similar to some spectra collected from wood tar (Pietrzak 2010). However, we are definitely inclined to interpret the black substance not as wood tar, deliberately obtained and introduced into the grooves, but as a mixture of ashes naturally resulting from a fire, perhaps as an element of a natural mixture with fulvic acids. This is suggested mainly by the irregular arrangement of the black and dark grey stains on the surface of the artefact, and by the lack of traces of continuous blackening of the residue filling the grooves.

Table 4. Rusinowo. Bands from vibrations generated by amide groups of collagen from samples taken from the grooves of the ornament and from a reference sample (Fig. 13). Band intensity: "s" (strong), "m" (medium), "w", "v.w." (weak, very weak).

Sample	Amide I	Amide II	Amide III
White sample (Fig. 7)	1645–1655 m	Very weak shoulder of adjacent band	Ca. 1255 v.w.
Gray sample (Fig. 8)	1645–1655 m	1530 m	Ca. 1260 w
Gray sample (Fig. 9)	–	Very weak shoulder of adjacent band	–
Gray sample (Fig. 10)	1641 w	Very weak shoulder of adjacent band	1230–1260 v.w.
Gray sample (Fig. 11)	–	–	Ca. 1260 v.w.
Black sample (Fig. 12)	1640, shoulder of adjacent band, m	1550–1570 s	1244 w
Elk antler (Fig. 13)	1641 s	1531 m	1235 w

The presence of pyrite is suggested by bands at 2180, 1980, 1210–1230, 1150, 790, 830, 680 and 560–570, and most of all, the most intensive bands at 450 and 300 cm^{-1} (http://www.rruff.com). Unfortunately, the main band does not appear in the recorded spectra. Another "suspect", mackinawite, is very poorly marked on the infrared spectrum, in an area around 300, 600 and 780 cm^{-1} (Lennie *et al.* 1995). Therefore, its presence cannot be confirmed either. In sum, the phases predominantly consisting of iron and sulphur are not visible in the recorded spectra. This is due both to their weak signal in infrared spectroscopy and their minuscule quantity (Figs. 1–6).

There have been numerous attempts to apply the analysis of the shape of spectra collected from bioapatite to evaluate anthropogenic and diagenetic alteration of substances. Analysis has been made of the crystallinity of the apatite based on the width and intensity ratios of the bands, making a study of carbonate group substitutions, thought to indicate exposure of bone to high heat (Chadefaux *et al.* 2009; Thompson *et al.* 2013, with further literature). In our case analysis of this sort is unfeasible, owing to the multiple-phase character of the studied samples, and the presence of a high concentration of calcium carbonate. Nevertheless, it is possible to note the evident difference in the position of bands from bioapatite in antler of modern elk in relation to the position of the bands from apatite in samples subjected to analysis (Figs. 7–11 vs. Fig. 13). The shift towards a higher wavenumber of the main band collected from apatite in the substance sampled from the ornament grooves of the Rusinowo artefact (1018 vs. 1041–1049 cm^{-1}) would be the result of the presence of secondary apatite, or of other secondary phosphate phases.

Three main bands from collagen corresponding to vibrations from amide groups I, II and III are clearly visible in the reference spectrum (respectively: 1641, 1531 and 1235 cm^{-1}, Fig. 13). The distinct appearance of these bands in a similar position in relation to collagen of a different origin has been observed in other studies (eg, Sionkowska *et al.* 2004; Chadefaux *et al.* 2009). However, the collagen is a protein susceptible to diagenetic and thermal alteration, presumably induced by anthropogenic factors. The direction of these alterations is not unambiguous and makes it impossible to construct a model (Chadefaux *et al.* 2009). Bands from collagen change intensity and position when exposed to moisture (Zhang *et al.* 2004) and, obviously, temperature. In an oxidising atmosphere their intensity is decreased, they increase in width and finally disappear (Thompson *et al.* 2013). Table 4 presents the collected data on the behaviour of bands from collagen in samples from the artefact and in the reference sample.

In relation to the reference sample, the bands have shifted in the direction of higher wavenumber value, their intensity has changed, and some have disappeared. However, the reasons for these changes are hard to specify. They do not seem to be associated with the colouring of the samples. The field of diagenetic and thermal alterations of collagen is still insufficiently studied.

The question arises whether the blackening of the grooves could result from the presence of black bone ash. Ash of this sort is easily obtainable, as may be seen from analyses of bone materials excavated from hearth features on Palaeolithic sites (Schiegl *et al.* 2003), it is also easy to observe in microscopic studies of sediments. On the other hand, it is harder to identify the burning of bone materials or antler using FTIR, with its much smaller intrusion into the analysed object. As noted earlier, the diagnostic parameters proposed for some time now (Chadefaux *et al.* 2008; Thompson *et al.* 2013), despite their outward simplicity, are not unambiguous and are dependent on many factors. Moreover, they have been applied to "pure" osseous material, faunal or human. Consequently, in our case, we have to resort to the analysis of the microstructure of bioapatite from antler as seen in the SEM image, and this does not indicate any processes of burning. This becomes apparent once we compare the spectra collected from samples removed from the artefact with spectra from the modern antler of elk (Figs. 7, 8, 9, 11 vs. Fig. 13).

The difference between the spectra from the substance extracted from grooves in the artefact and reference spectra from ash consists in the presence of secondary carbonate and sulphate minerals in the former. In the modern black ash they are not present. Calcium carbonates in the reference samples are from plant ash, they are present also in samples removed from the grooves in the artefact, where they also may be interpreted as a residue of plant ashes, but alternately, also as the effect of diagenetic processes. There are more of them here than in the modern ashes, they form a richer group in terms of their phase composition. The presence of hydrocarbon phases suggests the effect of modern-period processes of dissolution and crystallization of $CaCO_3$. Most likely, these were promoted by the acidic environment generated by the oxidising pyrite.

Gypsum (or other calcium sulphate minerals) is present in the samples from the grooves in a small amount. It has taken form at the cost of the weathering of iron sulphides in the presence of carbonate ions.

Apatite occurs only in samples from the artefact and is most likely a "relic" of the antler surface. Although it could be a component of plant ash (in particular, from burnt oak or beech, Trąbska 1995) it did not occur in the reference samples. The shape of the spectrum obtained from the modern antler of elk displays a similarity with spectra obtained from the white and whitish-grey samples taken from the grooves.

Quartz and feldspar (most likely, albite) are presumably detrital minerals, a small amount contaminating the material filling the grooves. Authigenic quartz is also possible here, it would have taken form as a result of diagenetic processes.

Conclusions

The black substance filling the grooves of the antler artefact from Rusinowo comes from burnt, black plant ash. It found its way into the grooves when the object was placed in ashes of a hearth or hearths. This substance is composed of charcoal, other burnt remains (eg, conifer needles) and isolated, small clusters of Fe-S phases, also imparting a black colour. No evidence was found to prove that wood tar, soot or bone char had been applied deliberately to the interior of the grooves to colour them. It is important to note that on the surface of the object, outside the grooves, the presence of similar substances was not detected (cf., section 3.3.1., in this sub-chapter). They could be the result of a temporary contact of the artefact with ashes of a hearth, and subsequent cleaning of its surface from accretions. These accretions had a chance to survive only in the depressed features of the antler object.