

Joanna Trąbska

DOI: 10.15584/anarres.2020.15.2

Institute of Archaeology, Rzeszów University, Moniuszki 10, 35-015 Rzeszów, Poland;
e-mail: joanna.trabska@archeologia.rzeszow.pl; ORCID: 0000-0003-2160-6629

Graphite in an archaeological context comparing to other black substances – research problems and prospects

Abstract

Trąbska J. 2020. Graphite in an archaeological context comparing to other black substances – research problems and prospects. *Analecta Archaeologica Ressoiviensia* 15, 17–29

In the archaeological context, substances with a black color have been extensively used in many ancient communities, in the form of items and layers, with the use of biogenic and mineral substances, and requiring a separate methodological approach. Each of them behaves differently in technological and postdepositional processes. The potential degree of the complexity of intentionally applied layers (e.g. paints or cosmetics) and the overlap of secondary substances and crusts, increases difficulties in obtaining unambiguous results and their interpretation. Graphite plays an important role among them. Several areas of the current use of graphite are, or at least could be, commonly shared in the present and in the past, and thus their analysis could be inspiring for archaeology and archaeometry. Graphite fingerprint and potential fingerprints are discussed in terms of their variability. The problem of graphitization as a potential source of misleading interpretation is discussed.

Key words: black substances, black layers, graphite, archaeology, fingerprints

Received: 30.06.2020; **Revised:** 22.11.2020; **Accepted:** 02.12.2020

Introduction

Ancient and modern people alike have willingly used black substances for many purposes, for example applying them on various surfaces and manufacturing objects. The identification of these substances is the subject of archaeometric research and allows us to obtain information on technological processes and the exchange of raw materials. It is also a part of the analysis of the symbolic meaning of the color. A considerable body of work has been devoted to the study of black substances in the context of use and origin.

The aim of this article is to emphasize the diversity of black substances, including graphite-like ones, the problems that are hidden in their research, the potential for the appearance of secondary phases whose presence may be misleading in interpretations, and the complexity of the systems in which they occur, especially in paints. The attention will be focused on graphite,

the types of its fingerprints and the numerous factors affecting the uncertainty of their interpretation.

Black substances known from the archaeological context

In the archaeological context, substances with a black color have been extensively used in many ancient communities. These can be items (e.g. the spectacular Caergwrle Bowl; Smith 2005, further literature there), medicines, cosmetics, binders (e.g. Trąbska *et al.* 2014), residues used on dishes (e.g. Craig *et al.* 2013), magic items (Baczyńska and Lityńska-Zajac 2005), fuel (Klíma 1956; Smith 2005), ceramic inclusions (e.g. Kwiecińska *et al.* 1970; Druc 2001) and layers (Gediga *et al.* 2019), including those resulting from previous conservation activities (Wiłkojć 2018). The literature cited above serve as examples, and there are of course many more sources.

The blacks are biogenic and mineral substances. Depending on the method of use, they were produced or processed to obtain a fine fraction or a monolith. Biogenic substances include the ones obtained from solid and liquid caustobio-lites: peat, brown coal (including jet and sapropelite considered by some researchers to be a variety of brown coal), hard coal, anthracite, shungite, asphalt, bituminous shale and other bitumens. All the mentioned rocks occur in many varieties (e.g. Bothe 2007; Gjostein Resi 2005; Smith 2005; Teichmüller 1992; Waleńczak 1987). The biogenic black group also includes soot resulting from incomplete combustion of plant debris: bark, branches, stones, fruit of trees, herbaceous plants and even fungi, e.g. birch, oak, beech, cherry, plum, date, almond, coconut, Italian nut, vine, yeast. Blacks were also obtained from the combustion of other biological substances: bone, ivory, bistre, gelatin, paper, and papyrus (Eastaugh *et al.* 2005). Also, wood tar and tar were used for sealing, impregnating, decorating, healing, and as magical substances. Fine biogenic black fractions were obtained in a variety of ways: by simple grinding and sieving, but also by depositing soot from the flame on a cool medium or in furnaces, these are called lamp blacks. Charring processes were also carried out in closed crucibles and with temperature control to avoid tar formation on the one hand, and destruction of the raw material on the other (Witruwicz 2000; Winter and West FitzHugh 2007). It should be emphasized that different starting and variously prepared substances provided products of different shades as well as different microstructural features.

Black mineral substances identified as raw materials for making objects and layers are also numerous. Antimony and its compounds (Chaundri and Jain 2009), manganese and its compounds (Chalmin *et al.* 2007), manganese and iron compounds (Trąbska *et al.* 2003), black iron compounds (Kotowiecki 2004), chromite (Groot *et al.* 2006), black lead compounds (Chaundri and Jain 2009), and finally black rocks, e.g. black shales (Smith 2005).

Different forms of inorganic and carbonaceous matter vary in their specific characteristics, and therefore also in terms of their fingerprints. Each of them requires a separate analysis and methodology and each behaves differently in technological and post-depositional processes, a phenomenon that can be used in researching artefacts.

Black pigments and dyes currently available for sale illustrate the multitude of these substances and the variety of their shades. These include, for example, black from vines, ivory black, dried blister soot, sepia

– dried cuttlefish dye, ground charcoal, and among inorganic substances, e.g. iron bluish black – intense or dark (original names of pigments and dyes from various companies have been preserved). This variety must have been known earlier as it was documented at least in historical paints (Winter and West FitzHugh 2007).

Graphite, a common substance used in the past, is an inorganic form of carbon. Nevertheless, there are numerous forms: semi-graphite (Kwiecińska and Petersen 2004), chaoite (hexagonal impact mineral), brown lonsdaleite, tetragonal fullerite (black, tetragonal mineral present in trace amounts in the Karelia shungites and in the basalt chimney in the Viloyati region, Tajikistan; www.mindat.org), cliffonite (pseudomorphosis of graphite after kamacite, also known from some iron meteorites) or chiemsite – impact carbon glass with microfossils (www.mindat.org, www.chiemgau-impact.com). Many of these rare substances were listed as pigments (Eastaugh *et al.* 2005), however, they certainly were mentioned as a casual admixture, clearly indicating geological provenance and even location.

Problems of black layers research

When considering painting layers (neglecting a variety of a substrate) we are dealing with complex systems, which include color-modifying substances or fluxes. For example, in black sintered or vitrified surfaces of Etruscan ceramics (bucchero nero) and Attic ceramics, the raw material was illite clay mixed with iron compounds and it was the type of the latter that determined the shade of black. The shine-modifying components were feldspar and quartz with the alkali and probably also boron fluxes (Gliozzo *et al.* 2004). Conclusively, a painting layer cannot be studied as composed of only pigments. Studies of layers demand a specific approach compared to “3D” objects, although many elements remain in common. The surfaces that are the result of human activities are intentionally covered for decorative purposes (paintings, intentional patina, black and similar decorations – black inlaid, inc. niello; in some cases also as cosmetics; Colombini and Modugno 2009; Demakapoulou *et al.* 1995; Tapsoba *et al.* 2010; Winter and WestFitzHugh 2007), informational purposes (characters and also the forms mentioned earlier), protective purposes (varnishes, intentional patina, impregnates, Aucouturier *et al.* 2010; Connan 1999; Harrel and Lewan 2002).

In the area of environmental sciences, research on layers and crusts is a dynamically developing branch of geochemistry (Schindley and Dorn 2017).

Phenomena of this kind are on the one hand burdensome, e.g. as unwanted patina on the surfaces of monuments and as places releasing pollution, but on the other hand they are collectors of information on environmental parameters in stratigraphic and temporal cross-sections. Microcomponents of cultural layers and speleothems, both plant and resin debris, as well as inorganic ashes, are important carriers of information about ancient and modern processes; it is difficult to omit them in these considerations.

Cross-sectional studies of speleothems from South Korean caves have revealed the presence of carbon from burned fuels. It had a spherulite and a spherulite-chain habit characteristic of high-temperature clusters of this element, (Jeong *et al.* 2003), in mineralogical terms it was poorly ordered graphite. Black lamines in the speleothems of the Kraków area caves (Prądnik Valley) are evidence of human habitation in the Neolithic, Bronze Age and later (Gradziński *et al.* 2003). Gray, sometimes reddish sediment surrounding the remains of the shaman at the Upper Paleolithic site of Dolní Věstonice I contained a large amount of black bone ash, used during a funeral ceremony (Trąbska *et al.* 2016). Charcoals, which are indicators of the use of fire, have been subjected to research aimed at identifying the manner and degree of its degradation at archaeological sites, which is important in identifying the oldest manifestations of fire use (Cohen-Ofri *et al.* 2006).

Layers formed unintentionally are traces of thermal influence, of a contact with an organic matter, crusts resulting from the precipitation of environmental components (e.g. manganese compounds, metal sulfides, also from ancient metal emissions; Caplete and Schindler 2018), urban and industrial crusts. They may resemble deliberate layers (Trąbska and Trybalska 2014). During the research of the decorated final-Paleolithic object from an antler from the Rusinowo site (NE Poland), it was necessary to solve the problem of the origin of black fillings and stains: were black paints applied in the grooves of the ornament? Were the stains the result of storing the item in an organic container or case? It turned out that all the colors are of natural origin, and they emerged due to framboid pyrite (Trąbska *et al.* 2017). A similar problem was encountered when examining black tiny points on a surface of a flint Magdalenian object from the Klementowice site (E Poland) where very few clusters of organic matter (resin glue) were masked by natural manganese compounds (Trąbska *et al.* 2014). Scanning microscopy (SEM / EDS), Raman spectroscopy and laser ablation – gas chromatography – mass

spectrometry (LA-GC-MS) are the main (but not only) methods used for examining layers and crusts (Caplete and Schindler 2018); the use of other types of couplings in the case of the last of mentioned method is also possible.

Due to the possible degree of complexity of intentionally applied layers (including cosmetics, see Chaundri and Jain 2009) and the overlap of secondary substances, the following systems can be found in research work. Objects or layers may have been made of (i) original and simple raw material that has not undergone any changes, (ii) simple raw material that has undergone environmental or deliberately introduced transformations, (iii) intentionally complex material (e.g. paints or cosmetics) that were not influenced by the environmental factors, (iv) intentionally complex material that has undergone changes, (v) all of the above-mentioned materials obscured by the presence of secondary micro-sediments and crusts. Assemblies can be organic-organic, organic-inorganic and inorganic-inorganic. In addition, in all versions we may be dealing with deliberate treatments that could have led to the processing of the raw material, resulting in changes in the composition or specific characteristics of the ingredients (e.g. the size of crystallites). Natural clusters can be mistaken with intentional clusters. In addition, we may be dealing with imitation of raw material A by raw material B. The specific metallic gloss characteristic of graphite-coated ceramics could be obtained in the same way as the medieval Africans in Congo did it (see below). Demetrykiewicz describing the black surface of the urns from SE Poland reports that “they were blackened only by means of hot, thick smoke”, having anointed the vessel with fat and smoothed it, and the effect was similar to graphite vessels (1897). The problem of distinguishing between “real” and “fake” graphitized surfaces is therefore not new, but in recent years research regarding that issue has moved forward thanks to the development of research methods and experiments (Ablamowicz and Karwowski 2009; Kreiter *et al.* 2014; Łaciak and Stoksik 2010; Łaciak *et al.* 2019).

It may be difficult to distinguish between deliberately used and secondary carbon in artefacts though the use of both was documented (e.g. Łaciak *et al.* 2019). There has been no research conducted to date regarding this issue. Amorphous carbon occurring with graphite in archaeological objects, esp. pottery, may not necessarily have been introduced deliberately. It can arise as a result of the Boudouard reaction of disproportionation of carbon monoxide originating from the thermal transformation of various carbon-

ceous substances ($\text{CO} = \text{C} + \text{CO}_2$) under conditions possible to attain in the systems typical for old technological processes, i.e. at a temperature of about 800°C and higher. Currently, this reaction is of interest due to the possibility of reducing the effects of greenhouse gas emissions (Lahijani *et al.* 2015).

Medieval Congo ceramics, decorated in a sophisticated way with vegetable pastes and palm oil applied on the hot surfaces of dishes by dipping in paints, is an example of the complexity of the composition of black surface colors. Charcoal dust was rubbed into grooves on dishes and the surface was often covered with waxes and resins, and to obtain the black mirror effect a mixture of earth pigments, metallic iron powder, bone black and charcoal were applied; the latter also acted as a plasticity modifier (Hexter and Hopwood 1992). Gedl and Malinowski wrote about painting the graphited surface with a non-graphitic black (soot is likely to be mentioned) (Łaciak 2010; Łaciak *et al.* 2017); thus, we also deal with a combination of several types of black substance. Black paints composed of inorganic (iron and manganese oxides) and organic components were identified in geometric ornaments in rock paintings in NW Argentina (Vázquez *et al.* 2008).

Graphite in an archaeological and modern context

Soft and easily abraded graphite items are characterized by their rather small dimensions, for example the Neolithic pendant from the Brzezie site (Małopolskie voivodship) (Trąbska and Wesełucha-Birczyńska 2014). They are not numerous, and more often graphite can be found as inclusions in graphite ceramics or on the surface of objects, e.g. graphite-coated pottery, produced in different places around the world, e.g. in South Africa (Pikirayi 2007), not only in the Hallstatt or Celtic communities (e.g. Abłamowicz and Karwowski 2009; Poleska 2006). While graphite objects are relatively easy to study in terms of raw material composition, ceramic surfaces and other paint or impregnation layers are not, for the reasons discussed above. Graphite-coated surfaces were developed by applying graphite powder, rubbing, and polishing the graphite surface before or after firing (Abłamowicz and Karwowski 2009; Kreiter *et al.* 2014; Łaciak *et al.* 2019). A review of prehistoric ceramics in which graphite was used to develop the surface and as a filler can be found in the same works.

Graphite as a filler in ceramics of various types plays an important functional role; it increases the ther-

mal conductivity of vessels and resistance to chemicals (as evidenced by studies of alchemical crucibles from the workshop in Oberstockhall near Vienna, Martínón-Torres *et al.* 2003). The foundry crucible and casting molds made of clay with “high graphite content” were identified at Celtic sites of the Tyniec group near Kraków. Also, objects interpreted as whetstones (fragments of graphite vessels with strong surface smoothing) were identified there (Poleska 2006, further literature there). About 30% of the graphite admixture was identified in the mint form of Zakrzów (Lesser Poland Voivodeship) (<http://naukawpolsce.pap.pl>).

Graphite in cast iron is tested as an important element of its classification based on the morphology, quantity and distribution of the mineral (Cvikel *et al.* 2013). A discovery of artefacts originating in Greece (Messemvria site) allowed to make the supposition of early (i.e. 5th century BC) production of cast iron on the European continent (Kostoglou and Navasaitis 2006). The research problem ‘with the participation’ of graphite regarding the reconstruction of Hannibal’s route across the Alps (218 BC) was interestingly formulated. The surfaces of hornblende shales were searched for signs of burning by fire, currently manifested in the presence of poorly ordered graphite (Mahaney *et al.* 2008). Finally, graphite was used as a writing and sketching substance, for example the 17th century Dutch pencil in a brass holder, found in Gdańsk (Trawicka and Ceynowa 2011). Fragments of graphite with smoothed surfaces identified at Zagórze 2 (Poland, Małopolska voivodeship; Dulęba *et al.* 2012) could be used as styli but also as a substance for the surface treatment of ceramics, though it was experimentally proved that this method of ornamenting is less efficient than rubbing with a powder (Abłamowicz and Karwowski 2009).

Graphite and other more or less common forms of carbon, including semi-graphite, graphene, fullerenes and carbonaceous matter with different levels of ordering and origin are treated in mineralogical aspects as indicators of interpretation of natural processes (Pasteris and Wopenka 1991; Touzain *et al.* 2010). The interpretation of the origin of substance C in one of the oldest rocks on Earth, the meta-sediments of West Greenland, is a good example (Ohtomo *et al.* 2013).

Much attention is paid to the current use of graphite and its similar phases (Mukhopadhyay and Gupta 2013). Several areas of use of graphite are or could be commonly used in the present and in the past. Some of them could be an inspiration for archaeology and archaeometry. Suggested areas of research are former glass production: graphite in glasses can

be both a strong reducing agent enabling obtaining black products and a glass degassing aid. Graphite is now part of high temperature coatings due to its oxidation resistance of up to several hundred degrees Celsius. Carbon-based coatings are difficult to wet with metal or slag. The use of graphite as a surface protective coating also increases the abrasion resistance of the object. Graphite is an excellent lubricant in binders made of mineral oils, kerosene, alcohol and even water with various additives, which is due to its outstanding cleavage and flexibility. Exceptional thermal conductivity in a direction perpendicular to the crystallographic axis *c* allows removal of excess heat from an object covered with a graphite coating. These properties allowed it to be used in graphite glass vessels and in ceramic vessels with graphite filler in alchemical, chemical, and pharmaceutical laboratories of different periods (Tamashausky 2003).

We know that graphite mined in the late nineteenth and early twentieth century in Zakrzów near Niemcza (Poland, Dolnośląskie Voivodeship) was used as a lubricant and in the production of foundry molds (Lis and Sylwestrzak 1986). In modern metallurgy, graphite is used in welding, forging, casting, and the production of wires as well as in powder metallurgy. The potential to use graphite in the archaeological context in this area was suggested long ago (Kwiecińska *et al.* 1970). In combination with rubbers and resins, graphite gives the opportunity to create light, flexible and easy to mold – and above all heat-conducting forms. Modern sculptures can be a potential analogy – graphite powder casts (<https://www.silesiakultura.pl>). Conduction, of course, is possible when the graphite particles are in contact with each other, which occurs due to their fragmentation or the use of naturally fine dust. At this point it is worth noting that the particle size also regulates the viscosity of the system: 10% of particles of 5 microns size significantly increase this viscosity, while 10% of 100-micron particles have no effect on it. Graphite is used as a soft polishing powder (Tamashausky 2003). A few studies have revealed the antibacterial effects of graphite and graphene (Liu *et al.* 2011). Graphite is inert in an oxidizing atmosphere up to 450°C and up to over 3000°C in a reducing atmosphere, thus being one of the more refractory substances. This inertness means that graphite dust, even with a size of 3 microns, is not explosive, which has facilitated its transport and storage (Tamashausky 2003).

Instead of graphite, coal was found as a filler in the La Tène pottery from the Thunau am Kamp site (Lower Austria) (Pawlikowski and Karwowski 2017).

Using black substances other than graphite in ceramic pastes, e.g. soot or brown coal, is an old research problem. Currently, the distinction of these components is possible due to relatively simple and fast Raman spectroscopy studies.

Criteria for distinguishing graphite of different origin (fingerprints)

Fingerprints are features or sets of features characteristic of a strictly defined type of raw material and the object made from it. They must be measurable in the raw material as well as in the artefact; they also must have a small variability, that allows the unequivocal assignment of a specific artefact to the type of deposit (genetic provenance) or a specific location. Fingerprints must be stable under conditions of technological processes and postdepositional conditions; if we intend to study artefacts of this nature (e.g. graphite in fired ceramics), their behavior should be well known.

Graphite occurs in deposits of various genesis, which means that it is diverse in many respects. However, this diversity is not unequivocal. The origin of substance C in graphite parent rocks is different, e.g. from igneous fluids, volatile phase from the Earth's mantle, liquids of basites and ultrabasites of the asthenosphere, lithosphere and gases derived therefrom, diamonds, biogenic carbon, and abiotic carbon. The temperature and pressure to which the carbonaceous substance was subjected varies, as well as various host rocks and associated minerals (e.g. Pasteris and Wopenka 1991; Smirnov 1986; Touzain *et al.* 2010). All these phenomena influence the specific parameters of a graphite, thus resulting in the ambiguity of the interpretation of provenance studies.

Graphite fingerprints are as follows: crystal morphology including grain shape and size, degree of crystallinity, presence of rhombohedral phase, presence of 3D intermediate phase (towards diamond formation), graphite isotope composition, C/H ratio, type and amount of trace elements, presence and type associated minerals and their specific characteristics, e.g. isomorphic substitutions and (very rarely) microfossils. The best result can be achieved by studying several features at the same time. The range of specific features of graphite may be extended.

Attempts to indicate the features that differentiate graphites have long been undertaken in the studies of the relationship of the conditions of the mineral formation and its specific characteristics. Kwiecińska and Szpunar (1970) studied graphite from the Male

Vrbno deposit (Czech Republic), regionally and contact-metamorphosed, and from the Pinerolo deposit in Piedmont (Italy), contact-metamorphosed. Clear differences can be seen in C/H values, in crystallite sizes and micromorphology. Natural carbon and graphite pigment in siliceous rocks formed at different times and in different conditions differs in the size of crystallites observed in the image of HRTEM (High Resolution Transmission Electron Microscopy), in the characteristics of Raman spectra and the C:H ratio measured by NMR (Nuclear Magnetic Resonance) spectroscopy (Delarue *et al.* 2016).

Morphology is the most commonly used parameter when describing graphite. Numerous studies indicate that the spectrum of the mineral form, even in one deposit, is much broader than the general descriptions would indicate. In the graphite of Sri Lanka (well-known deposits, from which graphites often used for comparative studies come from), derived from the fluid phase, different forms of the mineral are present (fibrous, flake, spherulite, semi-spherulite, fine crystalline and recrystallized fine graphite) (Touzain *et al.* 2010). Spherical aggregates, hollow channel structures, coatings on other minerals, whiskers, barrel forms, spheres, cones and triskelions have been observed among Khibiny alkaline pegmatite graphites (Kola Peninsula, Russia) (Jaszczak *et al.* 2007). Therefore, one should pay attention to the presence of many forms in one deposit, although usually (but not always) only one form prevails. The scaly form of graphite is attributed to early-magmatic alkaline rocks. Extremely high pure graphite, usually needle-like, usually comes from vein deposits (Luque *et al.* 1998; Smirnov 1986; Tamashauský 2003). It is known from experimental studies that the type of precursor also affects the form of graphite microstructures, e.g. flakes, microspheres and aggregates are obtained from anthracite heated in 2000 and 2500°C; their proportion depends on the initial amount of anthracite (Rodríguez *et al.* 2011). Information on this feature is obtained through microscopic observations; the scanning microscopy image provides the most comprehensive results, but polarized microscopy in reflected light can also be useful.

The degree of crystallinity reflects the size of an area with the same structure order (perfectly ordered crystals are extremely rare in nature). This area is known as a crystallite. The size of a crystallite depends on the conditions of mineral formation, i.e. the energy supplied and the ability to organize the structure of the starting substance. Crystallites are small areas and their characteristics can be researched with the use of

HRTEM, XRD and Raman spectroscopy. Unlike crystallites, grains are visible under polarizing and scanning microscopes.

The graphite of the Silesia-Moravia zone (NE Czech Republic) is considered to have lower crystallinity than the graphite of the Moldanubikum zone (among others SW Czech Republic). Nevertheless, in the latter there is not only highly ordered graphite, but also so-called amorphous graphite (actually cryptocrystalline), and mixed graphite. A similarly ambiguous situation also applies to carbonaceous matter in the metasediments of the Eastern Alps (Teichmüller and Teichmüller 1982) and many other occurrences. In graphite from Borrowdale deposits (Cumbria, Great Britain) the co-occurrence of colomorphitic and high-crystalline graphite was evidenced using Raman spectroscopy (Barrenechea *et al.* 2009). In summary, graphite from a given location may be characterized by different degrees of crystallinity, and organic matter may have different levels of graphitization. Despite many sources of uncertainty, this parameter allows, in general, to relate graphites to the type of deposit (Luque *et al.* 1998).

The study of the size of the crystallites of graphite in a pendant from the Neolithic site of Brzezie (Poland, Małopolska Voivodeship) allowed the mineral to be defined as moderately ordered. Unfortunately, it was impossible to assign it to a specific deposit due to the lack of a reference database (Trąbska and Wesełucha-Birczyńska 2014). Raman spectroscopy is commonly used to define this parameter in order to characterize even poorly ordered carbonaceous material and graphite based on the spectra bands, their presence, location, shape (half width) and mutual relationship (Beyssac *et al.* 2002; Pasteris and Wopenka 1991; Reich and Thomsen 2004; Rodríguez *et al.* 2013). Carefully collected, the shape and location of Raman bands can be used as a geothermometer, allowing the determination of the temperature of formation of the graphite or graphitized substance with an accuracy of up to 50°C (Beyssac *et al.* 2002). This feature was used to estimate the temperature of alleged fires on Hannibal's route across the Alps (Mahaney *et al.* 2008).

Unfortunately, the energy of the laser used affects the shape and location of these bands (Pimenta *et al.* 2007). When preparing the sample for testing, grinding and milling should be avoided – all such activities, again, affect the location of Raman bands (Rantitsch *et al.* 2016, more literature therein). For example, graphite with a sharp band of 1581 cm⁻¹, milled in a ball mill for 25–50 hours, was characterized by the appearance of an additional 1353 cm⁻¹ band (Pasteris

and Wopenka 1991). These generated structure disorders may adversely affect the conclusions of the study. This will not apply to “3D” objects that have hardly been subjected to such treatment. Structure disorders can, however, appear in graphites applied on surfaces of pottery, possibly also graphite in ceramic mass (see Kreiter *et al.* 2014).

Another method for defining the degree of crystallinity is HRTEM (High Resolution Transmission Electron Microscopy). It is less frequently used due to the labor-intensive process of sample preparation, but it nonetheless provides information on the extent of order structures, on the presence of ring structures and their polygonization, and the evolution of precursor micropores towards lamellar forms (Rantitsch *et al.* 2016).

The study of the size of graphite crystallites can also be carried out by X-ray diffraction analysis by identifying the ordering of structures relative to the crystallographic axes *a* and *c*, based on the analysis of full width at half maximum (002) and (110), respectively. It is also possible to measure the number of aromatic layers in a carbonaceous substance, whose presence makes the carbonaceous substance susceptible to graphitization (Laggoun-Defarge 1994; Rodriguez 2011, further literature there). The presence of quartz may obscure the interpretation of the relevant diffractogram.

Measurement of the C/H ratio in the tested black substance also helps to define the degree of crystallinity, because the amount of hydrogen decreases with the increasing maturity of the carbonaceous substance (Delarue *et al.* 2016; Kwiecińska and Szpunar 1970). Measurement by NMR spectroscopy supplements the results obtained by HRTEM and Raman spectroscopy methods.

Graphite crystallizes in a hexagonal system, but sometimes it has a rhombohedral component. In special geological conditions, its quantity may be relatively high, which could allow the use of this feature as a fingerprint. In graphites from Sri Lanka, it appears in the amount of 13 to 32%, in other graphites (e.g. from Bavaria) its amount was estimated at about 14% (Lipson, Stokes 1942). The presence of this phase is influenced by shear pressure and shear deformations (Touzain *et al.* 2010). In experimental studies, the rhombohedral phase appears after a few hours in hexagonal graphite under the influence of both hydrostatic and directional pressure, albeit in a very small amount. It undergoes transformation into a hexagonal phase after several hours of heating at a temperature above about 1300°C (Laves and Baskin 1956).

Prolonged grinding or milling of hexagonal graphite significantly increases the amount of rhombohedral phase (Bacon 1952, Wilhelm *et al.* 2007). This phenomenon, in favorable research conditions, would reveal the fact of graphite processing (milling, grinding) and thus identify the semi-raw material. Most likely, however, it would not make sense to use this feature as a fingerprint for graphitized ceramics. This type of graphite has also been identified in ‘kish’ graphite formed in cast steel (Lipson and Stokes 1942).

The identification of rhombohedral phase is mainly achieved by the Raman spectroscopy method and X-ray diffraction analysis, as well as XPS (X-ray Photoelectron Spectroscopy) to a lesser extent. Mathematical processing of parameters obtained by means of these methods is useful in identifying the arrangement of rhombohedral elements in a hexagonal structure (which depends on the type of raw material and the conditions of its processing and as such, it can also be a component of fingerprints) (Parthasaradhy *et al.* 2006; Wilhelm *et al.* 2007). No information about rhombohedral phase identification was provided in the context of archaeological artefacts.

The 3D phase appears in the graphite that evolves towards diamond formation, and therefore in very high-pressure zones (Fayos 1999; Sekine and Sato 1993). Identification of this phase can be carried out by X-ray diffraction and electron microscopy. Undoubtedly, its presence in graphite from artefacts would be a “strong” fingerprint.

The isotope composition of graphite, in particular the $\delta^{13}\text{C}$ value, but also other isotopes, e.g. oxygen, hydrogen or nitrogen for a weakly graphitized substance, carries information about the primary carbon origin (Hahn-Weinheimer and Hirner 1981) which can be biotic or abiotic; it can come from various sources and undergo various transport and precipitation processes. Biogenic genesis of graphite found in Greenland’s metasediments, which are about 3.7 billion years old, was evidenced thanks to isotope analyzes (Ohtomo *et al.* 2013). Isotope analyzes allowed the differentiation of graphite separated from Celtic vessels from different Transdanubia sites and to further determine its genetic provenance (Havancsák *et al.* 2011).

The type of trace elements in graphite also allows the determination of the origin of carbonaceous matter. Increased vanadium content is observed in the graphites of some metamorphogenic deposits, e.g. graphitic quartzites in Moravia (Czech Republic; Houzar and Šrein 2000). A comparison of rare earth elements (REE) of graphite and adjacent black shales

allows the establishment of a genetic relationship between them (Schrauder *et al.* 1993). Investigations of trace elements have enabled the identification of different origins of graphite in ceramic pastes of graphitic pottery from the Bavarian (Kropfmühl deposits) and Czech La Tène sites (Gebhard *et al.* 2004). NAA (Neutron Activation Analysis) and Mössbauer spectroscopy were used here.

Accompanying minerals characterize a graphite parent rock, and they can be different. For example, graphite of vein origin, genetically associated with pegmatites and arising in hydrothermal processes, is accompanied by minerals typical for these occurrences. The most abundant mineral impurities occur with so-called amorphous graphite, which results from the conditions for the formation of such rocks. Residual graphite, similarly contaminated with minerals, is concentrated in the weathering zones of parent graphite-bearing rocks (Luque *et al.* 1998; Smirnov 1986). Graphite waste at the Olomouc-Neředín site in Latern was considered to have originated from South-Czech graphite-muscovite shale from the vicinity of Svinov-Mohelnice (Hlava 2008). So that it is possible to collect evidences of provenance on the ground of minerals accompanying graphite in filler grains in ceramics but it must be remembered that technological processes (e.g. firing) can lead to changes in the original minerals.

Information from accompanying minerals is obtained not only based on their type, but also on the basis of their specific characteristics, e.g. chemical composition. As an example, let us consider vanadium substitution in the muscovite crystal lattice accompanying graphite in the Moravian quartzites of Moldanubikum (Houzar and Šrein 2000). The methods by which these issues can be studied are the classic methods of mineralogical research, ranging from polarizing microscope to XRD, Raman, infrared spectroscopy and others, depending on the amount and type of material. Microfossils traces in graphite are very rare (Hamilton *et al.* 1970); it is undoubtedly a very “strong” fingerprint.

The problem of graphitization

Graphite can be present in artefacts from its application, but it may also appear because of the graphitization of a carbonaceous matter. This process occurs to varying degrees or not at all. The results of experimental studies on ceramic pastes into which hard coal crumbs were introduced, after which the whole mixture was fired at a temperature of 700°C in

a reducing atmosphere, are an example of the latter situation. Coal has not been graphitized (Pawlikowski and Karwowski 2017). We know that tar begins to organize its structure after 10 minutes of exposure to 600°C at normal pressure but only to a very small extent (Trąbska *et al.* 2011). Graphitization was used in the aforementioned work on the reconstruction of Hannibal’s route across the Alps. It was this phenomenon that allowed the effect of high temperature on hornblende shales to be traced (Mahaney *et al.* 2008).

The analogy flowing from the analysis of modern processes for the preparation of graphite, for example in the presence of quartz and oxides of some metals (Acheson reaction), indicates that organic substances may undergo rapid graphitization, i.e. lasting only hours or days, but technological processes taking place at 1700°C were rarely achievable for ancient communities. The formation of very small, several dozen-degree clusters of secondary graphite is then observed (Lee *et al.* 2015). Graphitization not only depends on the conditions of the process, but also to a large extent on the type of starting substances, the so-called precursors. These are substances with specific structure features, including the presence of planarly arranged aromatic rings, which can therefore easily be graphitized, e.g. anthracite. Depending on the precursor structure, the degree of the graphitization of the secondary graphite varies. Generally, it is very difficult to distinguish primary from secondary graphite (Rodriguez *et al.* 2013). The scope of the graphitization process in graphite, graphitic ceramics and in graphite objects that have been affected by temperature is poorly recognized. In the area of archaeometric research, no attempt has been made to identify primary graphite and to distinguish between primary and secondary graphite.

The graphitization of carbonaceous matter occurs in natural processes under the influence of temperature, depends on its duration, host-rock lithology, type of starting substance and shear stress, especially in low P-T conditions. Graphitization may begin already at 750°C, but the time factor plays a role here. At high pressure, it already starts at 500°C. It was noticed that some types of carbonaceous substances are reluctant to graphitize, which results in, among others, the presence of low crystallinity graphite in rocks subjected to a high degree of metamorphism. Graphite appears in natural conditions, not only as a result of graphitization of a carbonaceous matter, but also in the process of the direct precipitation from carbon-bearing fluids, i.e. containing CO, CO₂, CH₄ and other substances (Delarue *et al.* 2016; Luque *et al.* 1998; Tamashausky 2006).

According to some researchers, the transformation of graphite into less ordered phases is possible. A small amount of alkali (about 1%) is needed and a temperature of about 1100°C. Then, large alkali ions diffuse into the graphite network and destroy it. Coke was used in the experiments during which this phenomenon was observed (Bhattacharya *et al.* 2015). In postdepositional conditions at archaeological sites, the destruction of a graphite component within charcoal was observed. This is an important finding in research on the beginning of the use of fire which is based on an analysis of the composition of the ash (Cohen-Ofri *et al.* 2006). Other researchers believe that the effects of the graphitization processes are irreversible (e.g. Teichmüller and Teichmüller 1982), which makes it possible to use a graphitized carbonaceous substance and graphite as a source of information on the origin of the starting substance and conditions of the technological processes. It should be stressed that further investigations in this area are required. Results of interesting experiments of a half-year deterioration of graphite-coated pottery did not reveal any macroscopic changes but, unfortunately, they were not followed by instrumental analyses (Abłamowicz and Karwowski 2009). As can be seen, graphitization processes are less clear-cut than one might think and require careful observation.

Summary

The identification of the black components of items and layers allows the reconstruction of technological habits and methods of obtaining raw material. However, an interpretation of the research results is not a simple matter. Black substances that entirely or only partly make up objects found in the archaeological context can have an overly complex composition. Many processes of the formation and disappearance of components of black layers in artefacts are not yet known and require experimental research. On the other hand, graphite has attracted great interest in many branches of research and industry in recent years; new data are constantly appearing. A broad look at the presence of black components, including graphite in various ancient technological aspects, may attract the interest of scientists representing numerous other fields. The interdisciplinary exchange of experience is highly desirable in this area. Provenance studies based on the use of only one fingerprint may provide equivocal results, as well as neglecting their variability.

References

- Abłamowicz D. and Karwowski Ł., 2009. Production of graphite vessels by the Lusatian Culture population (in Polish, with English summary). In L. Domańska, P. Kittel and J. Forysiak (eds.), *Środowiskowe uwarunkowania lokalizacji osadnictwa* (= *Środowisko – Człowiek – Cywilizacja* 2). Poznań: Bogucki Wydawnictwo Naukowe, 377–387.
- Aucouturier M., Mathis F., Robcis D., Castaing J., Salomon J., Pichon L., Delange E. and Descamps S. 2010. Intentional patina on metal archaeological artefacts: non-destructive investigation of Egyptian and Roman museum treasures. *Corrosion, Engineering and Science Technology* 45(5), 314–321.
- Bacon G.E. 1952. The reduction of the crystalline perfection of graphite by grinding. *Acta Crystallographica* 5, 392.
- Baczyńska B. and Lityńska-Zajac M., 2005. Application of *Lithospermum officinale* L. in early Bronze Age medicine. *Vegetation History and Archaeobotany* 14, 77–80.
- Barrenechea J.F., Luque F.J., Millward D., Ortega L., Beyssac O. and Rodas M., 2009. Graphite morphologies from the Borrowdale deposit (NW England, UK): Raman and SIMS data. *Contributions to Mineralogy and Petrology* 158(1), 37–51.
- Beyssac, Goffe, Chopin and Rouzaud. 2002. Raman spectra of carbonaceous material in metasediments. *Journal of Metamorphic Geology* 20, 859–871.
- Bhattacharyya A., Schenk J., Rantitsch G., Thaler C. and Stocker H. 2015. Effect of alkaline elements on the reactivity, strength and structural properties of blast furnace cokes. *Metalurgija* 54, 503–506.
- Bothe C. I. 2007. Asphalt. In B.H. Berrie (ed.), *Artist's Pigments. A Handbook of Their History and Characteristics* 4. London: Washington and Archetype Publications, 1–38.
- Caplete J.N. and Schindler M. 2018. Black rock-coatings in trial, British Columbia. Canada: Records of past emissions of lead, zinc, antimony, arsenic, tellurium, tin, selenium, silver, bismuth and indium-bearing atmospheric contaminants. *Canadian Mineralogist* 56, 113–127.
- Chalmin E., Farges F., Vignaud C., Susini J., Menu M. and Brown Jr. G.E. 2007. Discovery of Unusual Minerals in Paleolithic Black Pigments from Lascaux (France) and Ekain (Spain). *American Institute of Physics Conference Proceedings*, 220–222.
- Chaundri S.K. and Jain N.K. 2009. History of cosmetics. *Asian Journal of Pharmaceutics* 3(3), 164–167.
- Cohen-Ofri I., Weiner L., Boaretto E., Mintz G. and Weiner S. 2006. Modern and fossil charcoal: aspects of structure and diagenesis. *Journal of Archaeological Science* 33, 428–439.

- Colombini M.P. and Modugno F. 2009. Organic Materials in Art and Archaeology. In M.P. Colombini and F. Modugno (eds.), *Organic Mass Spectrometry in Art and Archaeology*. Oxford: Wiley&Sons, 36.
- Connan J. 1999. Use and trade of bitumen in antiquity and prehistory: molecular archaeology reveals secrets of past civilisations. *Philosophical Transactions of the Royal Society B* 354, 33–50.
- Craig, O., Saul, H., Lucquin, A., Nishida Y., Taché K., Clarke L., Thompson A., Altoft D.T., Uchiyama J., Ajimoto M., Gibbs K., Isaksson S., Heron C.P. and Jorgan P. 2013. Earliest evidence for the use of pottery. *Nature* 496, 351–354.
- Cvikel D., Mentovich E.D., Ashkenazi D., and Kahanov Y., 2013. Casting techniques of cannonballs from the Akko 1 shipwreck: Archaeometallurgical investigations. *Journal of Mining and Metallurgy. Section B: Metallurgy* 49(1), 107–119.
- Delarue F., Rouzaud J-N., Derenne S., Bourbin M., Westall F., Kremer B., Sugitani K., Deldicque D. and Robert F. 2016. The Raman-Derived Carbonization Continuum: A Tool to Select the Best Preserved Molecular Structures in Archaean Kerogens. *Astrobiology* 16(6), 407–417.
- Demakopoulou K., Mangou E., Jones R.E. and Photos-Jones E. 1995. Mycenaean black inlaid metalware in the National Archaeological Museum Athens: a technical examination. *Annual of the British School at Athens* 90, 137–153.
- Demetrykiewicz W., 1897. Cmentarzyska i osady przedhistoryczne w okolicy Tarnobrzega i Rozwadowa nad Sanem/Cemeteries and prehistoric settlements in the area of Tarnobrzeg and Rozwadów on the San. Kraków: Akademia Umiejętności.
- Druc I. 2001. Soil sources for ceramic production in the Andes. In I. Druc (ed.), *Archaeology and Clays (= British Archaeological Reports. International Series 942)*. Oxford: Archaeopress, 1–12.
- Dulęba P., Okoński J., Przybyła M. M. and Suchorska-Rola M. 2012. Ostatnie sezony badań na terenie kompleksu stanowisk Zagórze 2 – Staniątki 26, gm. Niepołomice, woj. małopolskie/Last seasons of research in the Zagórze 2 site complex – Staniątki 26, commune Niepołomice, voivodeship Lesser. In S. Kadrow (ed.), *Raport 2007–2008 1*. Warszawa: Narodowy Instytut Dziedzictwa, 321–342.
- Eastaugh N., Walsch V., Chaplin T. and Siddal R. 2005. *Pigment Compendium. A Dictionary of Historical Pigments*. Amsterdam: Elsevier.
- Fayos J. 1999. Possible 3D carbon structures as progressive intermediates in graphite to diamond. *Journal of Solid State Chemistry* 148(2), 278–285.
- Gebhard R., Bott R., Distler N., Michalek J., Riederer J., Wagner F.E. and Wagner U., 2004. Ceramics from the Celtic oppidum of Manching and its influence in Central Europe. *Hyperfine Interactions* 154, 199–241.
- Gjostein-Resi H. 2005. Archaeological Finds of Jet from Norway. Signs of continuous contacts westwards in the Viking and Medieval Periods? *Collegium Mediaevale* 18 (ojs.novus.no).
- Gliozzo E., Kirkman I.W., Pantos E., M. and Memmi Turbanti I. 2004. Black gloss pottery. Production sites and technology in northern Etruria 2: Gloss technology. *Archaeometry* 46(2), 227–246.
- Gradziński M., Górny A., Pazdur A. and Pazdur M.F. 2003. Origin of black coloured laminae in speleothems in the Kraków–Wieluń Upland, Poland. *Boreas* 32, 532–542.
- Groot N.C.F., Dik J., Van der Kooij P., Alkemade P.F.A., Sivel V.G.M. and Tichelaar F.G. 2006. Dark and shiny: The discovery of chromite in Bronze Age faience. *Archaeometry* 48(2), 229–236.
- Hahn-Weinheimer P. and Hirner A. 1981. Isotopic evidence for the origin of graphite. *Geochemical Journal* 15, 9–15.
- Hamilton L.H., Ramsden A.R. and Stephens F.J. 1970. Fossiliferous graphite from Undercliff, New South Wales. *Journal of the Geological Society of Australia* 17(1), 31–37.
- Harrel J.A. and Lewan M.D., 2002. Sources of mummy bitumen in ancient Egypt and Palestine *Archaeometry* 44 (2), 285–293.
- Havancsák I., Fekete J. and Bajnóczi B. 2011. Carbon isotope study on Celtic-graphite tempered archaeological ceramics from the South Transdanubian region (Hungary). *Central European Geology* 54 (1–2), 75–79.
- Hexter M.R. and Hopwood W.R. 1992. Investigation of decorative coating on Kongo ceramics Using UV Light and FTIR analysis. *Materials issues in art and archaeology 3: symposium held in April 27-May 1, 1992, San Francisco, California, U.S.A.*, 291–307.
- Hlava M. 2008. Grafit v době laténské na Moravě/Graphite in the La Tène period in Moravia. *Památky Archeologické* 99, 189–258.
- Houzar S. and Šrein V., 2000. Variation in chemical composition of V-bearing muscovite during metamorphic evolution of graphitic quartzites in the Moravian Moldanubicum. *Journal of the Czech Geological Society* 45, 143–148.
- Jaszczak J.A., Dimovski S., Hackney S.A., Robinson G.W., Bosio P. and Gogotsi Y. 2007. Micro- and nanoscale graphite cones and tubes from Hackman Valley, Kola Peninsula, Russia. *Canadian Mineralogist* 45, 379–389.

- Jeong G.Y., Kim S.J. and Chang S.J. 2003. Black carbon pollution of speleothems by fine urban aerosols in tourists caves. *American Mineralogist* 88, 1872–1878.
- Klíma B. 1956. Coal in the Ice Age: The Excavation of a Palaeolithic Settlement at Ostrava-Petřkovice in Silesia. *Antiquity* 20, 118, 98–101.
- Kostoglou M. and Navasaitis J. 2006. Cast iron in ancient Greece: myth or fact? *Mediterranean Archeology and Archaeometry* 6, 2, 55–58.
- Kotowiecki A. 2004. Artefacts in Polish collections made of meteoritic iron. *Meteoritics and Planetary Science* 39, Supplement 8, A151–A156.
- Kreiter A., Szabolcs C., Bendő Z., Imre J.E., Pánczél P. and Váci G. 2014. Shine like metal: an experimental approach to understand prehistoric graphite coated pottery technology. *Journal of Archaeological Science* 52, 129–142.
- Kwiecińska B. and Petersen H.I., 2004. Graphite, semi-graphite, natural coke, and natural char classification – ICCP system. *Coal Geology* 57, 99–116.
- Kwiecińska B. and Szpunar J., 1970. Badania tekstury grafitów metodą dyfrakcji neutronów. *Mineralogia Polonica* 1, 61–72.
- Kwiecińska B., Wirska-Parachoniak M. and Parachoniak W., 1970. Zastosowanie transmisyjnej mikroskopii elektronowej w badaniach nad tzw. grafitową ceramiką celtycką/The use of transmission electron microscopy in research on the so-called graphite Celtic ceramics. *Ochrona Zabytków* 23(4), 315–320.
- Lahijani P., Zainal Z.A., Mohammadi M. and Mohamed A.R. 2015. Conversion of the greenhouse gas CO₂ to the fuel gas CO via the Boudouard reaction: A review. *Renewable and Sustainable Energy Reviews* 41, 615–632.
- Laves F. and Baskin Y. 1956. On the formation of the rhomboedral graphite modification. *Zeitschrift für Kristallographie* 107, 337–356.
- Lee S-M., Kang D-S and Roh J-S. 2015. Bulk graphite: materials and manufacturing process. *Carbon Letters* 16(3), 135–146.
- Lipson H.S. and Stokes A.R. 1942. The Structure of Graphite. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences* 181, 101–105.
- Lis J. and Sylwestrzak H. 1986. *Minerały Dolnego Śląska/Minerals of the Lower Silesia*. Warszawa: Wydawnictwa Geologiczne.
- Liu S., Zeng T.H., Hofmann M., Burcombe E., Wei J., Jiang R., Kong J. and Chen Y. 2011. Antibacterial Activity of Graphite, Graphite Oxide and Reduced Graphite Oxide: Membrane and Oxidative Stress. *American Chemical Society* 5(9), 6971–6970.
- Luque F.J., Pasteris J.D., Wopenka B., Rodas M. and Barrenechea J.F. 1998. Natural fluid-deposited graphite: mineralogical characteristics and mechanism of formation. *American Journal of Science* 298, 471–498.
- Łaciak D. and Stoksik H. 2010. Problematyka ceramiki malowanej i „grafitowanej” z wczesnej epoki żelaza w świetle badań fizykochemicznych/The problems of painted and “graphited” ceramics from the early Iron Age in the light of physicochemical research. *Przegląd Archeologiczny* 58, 105–146.
- Łaciak D., Markiewicz M., Łydźba-Kopczyńska B., Gediga B., August C., Hojniak M., Rusek G. and Miazga B. 2017. Rekonstruowanie procesu wytwórczego ceramiki – badania nad halstacką ceramiką malowaną z cementarzysta w Domasławiu, stan. 10/11/12, pow. wrocławski. In S. Siemianowska, P. Rzeźnik and K. Chrzan (eds.), *Ceramika i szkło w archeologii i konserwacji*, Wrocław: Instytut Archeologii i Etnologii Polskiej Akademii Nauk, Ośrodek Badań nad Kulturą Późnego Antyku i Wczesnego Średniowiecza, 179–208.
- Łaciak D., Borowski M., Łydźba-Kopczyńska B., Baron J. and Furmanek M. 2019. Archaeometric characterisation and origin of black coatings on prehistoric pottery. *Geochemistry* 79(3), 453–466. <https://doi.org/10.1016/j.chemer.2019.07.004>.
- Mahaney W., Kalm V., Dirszovsky R., Milner M., Sodhi R., Beukens R., Dorn R., Tricart P., Schwartz S. and Chamorro-Perez E. 2008. Hannibal’s trek across the Alps: Geomorphological analysis of sites of geoarchaeological interests. *Mediterranean Archaeology and Archaeometry* 8(2), 39–54.
- Martinón-Torres M., Rehren T. and Osten S. 2003. A 16th century lab in a 21th century lab: archaeometric study of the laboratory equipment from Oberstockstall (Kirchberg am Wagram, Austria). *Antiquity* 77, 298, 1–9.
- Mukhopadhyay P. and Gupta R.K. 2013. *Graphite, graphene and their polymer nanocomposites*. Boca Raton, FL: CRC Press.
- Ohtomo Y., Kakegawa T., Ishida A., Nagase T. and Rosing M.T. 2013. Evidence for biogenic graphite in early Archaean Isua metasedimentary rocks. *Nature Geoscience* 7, 25–28 DOI:10.1038/NGEO2025, 1–4.
- Parthasaradhy G., Sreedhar B. and Chetty T.R.K. 2007. Spectroscopic and X-ray diffraction studies on fluid deposited rhomboedral graphite from the Eastern Ghats Mobile Belt, India. *Current Science* 90(7), 995–1000.
- Pasteris J.D. and Wopenka B. 1991. Raman spectra of graphite as indicators of metamorphism. *Canadian Mineralogist* 29 (1), 1–9.
- Pawlikowski M. and Karwowski M. 2017. Mineralogical examination of graphite (?) pottery. Example – valley settlement in Thunau am Kamp, Lower Austria. *Aux-*

- iliary sciences in archaeology, preservation of relics and environmental engineering 23, 1–10.
- Pikirayi I. 2007. Ceramics and group identities. Towards a social archaeology in southern African Iron Age ceramic studies. *Journal of Social Archaeology* 7 (3), 286–301.
- Pimenta M. A., Dresselhaus G., Dresselhaus M.S., Cancado L.G., Jorio A. and Saito R. 2007. Studying disorder in graphite-based systems by Raman spectroscopy. *Physical Chemistry Chemical Physics* 9, 1276–1291.
- Poleska P. 2006. *Celtycki mikroregion osadniczy w rejonie podkrakowskim (= Biblioteka Muzeum Archeologicznego w Krakowie 2)*. Kraków: Muzeum Archeologiczne w Krakowie.
- Rantitsch G., Lämmerer W., Fisslthaler E., Mitschke S. and Kaltenböck H. 2016. On the discrimination of graphite and semi-graphite by Raman spectroscopy. *Journal of Coal Geology* 159, 48–56.
- Reich S. and Thomsen C. 2004. Raman spectroscopy of graphite. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* 362, 2271–2288.
- Rodriguez S., Marques M., Suárez-Ruiz I., Camean I., Flores D. and Kwiecińska B. 2013. Microstructural investigations of natural and synthetic graphites and semi-graphites. *International Journal of Coal Geology* 111, 67–79.
- Rodriguez S., Suárez-Ruiz I., Marques M., Flores D., Camean I. and Garcia A.B. 2011. Development of graphite-like particles from the high temperature treatment of carbonized anthracites. *International Journal of Coal Geology* 85, 219–226.
- Schindler M. and Dorn R.I. 2017. Coatings on Rocks and Minerals: The Interface Between the Litosphere and the Biosphere, Hydrosphere and Atmosphere. Elements. *An International Magazine of Mineralogy, Geochemistry and Petrology* 13 (3), 155–158.
- Schrauder M., Beran A., Hoernes S. and Richter W. 1993. Constraints on the Origin and the Genesis of Graphite-Bearing Rocks From the Variegated Sequence of the Bohemian Massive (Austria). *Mineralogy and Petrology* 49, 175–188.
- Sekine T. and Sato T. 1993. Shock induced mechanism of phase transformation from rhomboidal BN to cubic BN. *Journal of Applied Physics* 74, 2440–2444.
- Smirnov W. I. 1986. *Geologia złóż kopalin użytecznych*. Warszawa: Wydawnictwa Geologiczne.
- Smith A.H.V. 2005. Coal microscopy in the service of archaeology. *Coal Geology* 62, 49–59.
- Tamashauskay A.V. 2006. *An Introduction to Synthetic Graphite*. Available from: <https://asbury.com>.
- Tamashauskay A.V. 2003. *Graphite: a multifunctional additive for paint and coatings*. Available from: <https://asbury.com>.
- Tapsoba I., Arbault S., Walter P. and Armatore C. 2010. Finding Out Egyptian Gods' Secret Using Analytical Chemistry: Biomedical Properties of Egyptian Black Makeup Revealed by Amperometry at Single Cells. *Analytical Chemistry* 82, 2, 457–460.
- Teichmüller M. 1992. Organic petrology in the service of archaeology. *International Journal of Coal Geology* 20 (1–2), 1–21.
- Teichmüller R. and Teichmüller M. 1986. Relations between coalification and palaeogeothermics in Variscan and Alpidic foredeeps of western Europe. *Paleogeothermics* 5, 53–78.
- Touzain P., Balasooriya N., Bandaranayake K. and Descolas-Gros C., 2010. Vein graphite from the Bogala and Kolongaha mines – Sri Lanka: A possible origin. *Canadian Mineralogist* 48, 1373–1384.
- Trawicka E. and Ceynowa B. 2011. *Gdańsk w Europie, Europa w Gdańsku. Kontakty handlowe i kulturowe Gdańska w świetle wykopalisk archeologicznych. Katalog wystawy*. Gdańsk: Muzeum Archeologiczne w Gdańsku.
- Trąbska J., Weselucha-Birczyńska A., Trybalska B. and Gawel A. 2017. The surface of the artefact. In T. Płonka and K. Kowalski (eds.): *Rusinowo. The Symbolic Culture of Foragers in the Late Palaeolithic and the Early Mesolithic*. Wrocław: University of Wrocław. Institute of Archaeology, 119–146.
- Trąbska J., Oliva M., Gawel A. and Trybalska B. 2016. Dolní Věstonice I female grave. Red colourants and other components of the burial fill and grave floor. *Studia Praehistorica Belgica* 8. *Anthropologica et Praehistorica* 126, 161–178.
- Trąbska J., Trybalska B. 2014. True and fake red layers on the objects from archaeological and historical context: microscopic observations. *Geology, Geophysics and Environment* 40(2), 241–254.
- Trąbska J., Weselucha-Birczyńska A. and Trybalska B. 2014. Black crust on the surface of a flint artefact from Klementowice. In T. Wiśniewski (ed.), *Klementowice. A Magdalenian site in Eastern Poland*, Lublin: Wydawnictwo UMCS, 336–342.
- Trąbska J. and Weselucha-Birczyńska A. 2014. Badania fazowe i strukturalne grafitowej zawieszki ze stanowiska Brzezcie 17, gm. Kłaj/Phase and structural studies of the graphite pendant from Brzezcie 17, commune Kłaj. In A. Czekań-Zastawny (ed.), *Brzezcie 17, osada kultury ceramiki wstęgowej rytej (= Via Archaeologica. Źródła z badań wykopaliskowych na trasie autostrady A4 w Małopolsce)*. Kraków: Krakowski Zespół do Badań Autostrad, 491–498.

- Trąbska J., Weselucha-Birczyńska A., Zięba-Palus J. and Runge M.T. 2011. Black painted pottery, Kildehuse II, Odense County, Denmark. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 79 (4), 824–830.
- Trąbska J., Trybalska B., Gawel A. and Bytnar K. 2003. I. Pigmenty i warstwy malarskie ceramiki neolitycznej kultury trypolskiej (Bilcze Złote) II. Zabytki kamienne z Bilcza Złotego. *Materiały Archeologiczne* 34, 179–194.
- Vázquez C., Maier M.S., Parera S.D., Yacobaccio H. and Solá P. 2008. Combining TXRF, FT-IR and GC-MS information for identification of inorganic and organic components in black pigments of rock art from Alero Hornillos 2 (Jujuy, Argentina). *Analytical and Bioanalytical Chemistry* 391, 1381–1387.
- Waleńczak Z. 1987. *Geochemia organiczna*. Warszawa : Wydawnictwa Geologiczne.
- Wilhelm H.A., Croset B. and Medjahdi G. 2007. Proportion and dispersion of rhomboedral sequences in the hexagonal structures in graphite powders. *Carbon* 45, 2356–2364.
- Wiłkojć E. 2018. Konserwacja obrazów wielkoformatowych w Zamku Królewskim na Wawelu. In J. Ziętkiewicz-Kotz (ed.), *Sztuka konserwacji – konserwacja sztuki. Katalog wystawy*. Kraków: Drukarnia Pasaż, 39–48.
- Winter J. and West FitzHugh E. 2007. Pigments Based on Carbon. In Berrie B.H. (ed.). *Artistst' Pigments. A Handbook of Their History and Characteristics* 4. London: Washington and Archetype Publications.
- Witruwiusz 2000. *O architekturze ksiąg dziesięć/De Architectura Libri Decem*. Przekład: K. Kumaniecki. Warszawa: Prószyński i S-ka.

Web sources

- <https://asbury.com> (access 10.06.2020)
- www.chiemgau-impact.com (access 15.05.2019)
- www.mindat.org (access 15.05.2020)
- <http://naukawpolsce.pap.pl/aktualnosci/news%2C408318%2Cceltyccy-mincerze-w-krakowie.html> (access 15.05.2020)
- <https://www.silesiakultura.pl/r/miasta/zabrze/zabrze/wystawa-rzezby-w-weglu-i-graficie-symbol-gorniczego-trudu> (access 15.05.2020)