The article discusses the results of interdisciplinary studies of a Romanesque stone head of high-quality artistry. It was discovered in 2017 during excavations at Nowy Targ (New Market) Square in the city of Wroclaw (Lower Silesia, Poland). The sculpture originally came from one of the Romanesque sacred buildings of Wroclaw, none of which have survived to this day. Although it had been made in the mid-12th century, it was found in the remains of a wooden residential building burnt down in the 14th century. The results of petrographic analyses indicate that the stone head was made of fine-grained sandstone classified as lithic wacke. The raw material was most likely a Devonian-Carboniferous sandstone from the Opava Mountains. However, similar sandstones also occurred in several medieval mines located in Upper Silesia. According to a popular belief, medieval aesthetics required such sculptures to be polychromed. The non-destructive analyses conducted with the microscopic XRF, XRD, and FTIR methods demonstrated that a clean stone surface was also acceptable.

KEY WORDS: Romanesque, XRF, XRD, FTIR, medieval Poland, polychrome

1.1. INTRODUCTION

Polychrome Romanesque sculptures have been subjected to several studies, but it is only recently that expert laboratory techniques have been employed in these investigations. The applicable methods include i.a., microscopic petrographic analysis, XRD analysis, and identification of chemical compounds (with XRF, EMPA and other tools; Calza et al. 2015; de Souza Felix et al. 2015; Gasanova et al. 2018, 83-90). The results obtained across the world have confirmed the well-established opinion (Dodwell 1993, 23-55) that polychrome medieval stone and wooden sculptures were a widespread phenomenon.
The well-studied examples from the cathedrals in Meißen (Donath 2001, 10-34) and Freiberg (Hütter 1963, 238-240) in nearby Saxony are particularly noteworthy. The only polychrome Romanesque sculptures in Silesia to have received more scholarly attention were those in the Cistercian abbey of Trzebnica. The paints were based on chalk (white), and white or red lead (Poksińska 1992; 1993; 1994, 345-351).

In Western Europe, the widespread practice of painting architectural sculptures resulted in the development of a specialized class of painters. Presumably, most of the artisans decorating church interiors were itinerant craftsmen carrying out their commissions (Dodwell 1993, 37-39). No later than in the second half of the 12th century, guild rules were introduced to regulate their profession (Boileau 1873, 157; Crawford 2013, 7). According to these rules, the same group of craftsmen decorated sculptures of stone, wood, and other materials.

In this paper we discuss a Romanesque sculpture found during excavations in the Old Town of Wroclaw, Lower Silesia’s capital. The sculpture was a secondary deposit. The main purpose of this study was to find out whether the coloured deposits on the sculpture’s surface were remains of paint and, if so, whether there is any connection between the petrographic features of the rock material and the type of paint. We also tried to identify the pigments. Since the artefact is of high artistic and display value, we utilized analytical techniques affecting it only minimally. Petrographic analysis of the rock material used for the sculpture was also essential, as it can provide crucial information on how the Romanesque construction industry in Wroclaw was organized.
1.2. ARCHAEOLOGICAL CONTEXT

The excavation area was situated in the eastern part of medieval Wrocław, historically the main city of Silesia. It extended over a square between the present Nowy Targ (New Market) Square, Św. Katarzyna (St Catherine) Street, Wit Stwosz/Św. Wojciech (Veit Stoss/St Adalbert) Street, and Św. Wit (St Vitus) Street (Fig. 1). Before World War II, this area had been fully built up. However, the buildings were destroyed in the final weeks of the war.

One of the most intriguing finds recorded during the excavations was a fragment of a sandstone figural sculpture – a head. Most probably, it originally decorated one of Wroclaw’s Romanesque ecclesiastical buildings. Since none of them is fully preserved to the present day, and therefore archaeology is the only available source of information.

The sculpted head was discovered within the heavily damaged remains of the rear of the building designated as stratigraphic unit 62. According to the cadastral plan made before 1945, the building was situated in the back of a plot marked as Nowy Targ (New Market) Square 10. The discovered traces clearly indicate that the structure was destroyed by fire (Fig. 2). During the research it was not possible to determine the extent of the building and to reconstruct its plan, as it was largely destroyed by foundation trenches in the Renaissance era. Only fragments of the hard earthen floor of the building in the form of a burnt concave and a layer of debris consisting mainly of lumps of orange and red pugging clay, charcoal, and ash were recorded. This rubble indicates that the walls of the building were of half-timber construction. Under the layer of rubble, the sculpture of the head was exposed (116.75 m above sea level), in the immediate vicinity of which there were weaving spindles of various sizes, and a round shield made of slate rock. A hole was made in its center, while the surface on both sides was provided with incisions, occasionally arranged in small crosses and grids. Apart from this, the find was surrounded by burnt organic material consisting mainly of plant debris, charred remains of hair, and small fragments of fabric. Both in the rubble and directly on the usable surface of the building there were also fragments of ceramics, which can be dated broadly to the 14th century. This dating was also confirmed by the stratigraphic relationship of the level at which the remains were discovered with respect to the lower and higher layers. The head itself, made of sandstone, bore clear signs of fire damage, and the cuts on the right side were probably made with a metal tool. These traces indicate that the head was forcibly separated from the rest of the figure. Based

Fig. 2. Sculpture in situ. Photo by P. Duma
Fig. 3. View of the Romanesque head. Photo by P. Duma

Fig. 4. Wrocław, city map showing sculpture’s deposition place. Developed by N. Lenkow
on stylistic analogies from both Wroclaw and other parts of Europe, it is believed that the sculpture was created close to the middle of the 12th century, i.e., its deposition took place nearly 200 years after its creation. It is possible that it came from the furnishings of one of the city’s churches.

The burnt organic material found in the immediate vicinity of the head and spindle whorls was subjected to botanical analysis\(^1\). The collected sample contained fibre fragments, burnt straw or hay, wood fragments, and diaspore. Macroscopic analysis made it possible to identify the remains of many plant species. In the first place was cabbage (Brassica rapa), black mustard (Brassica nigra), cabbage (Brassica sp.), and common rye (Secale cereale). Traces of poppy seeds (Papaver sp.), knotweed (Polygonum sp.), common pea (Pisum sativum), cornflower (Centaurea cyanus), stinking nightshade (Hyoscyamus niger) and corn spurry (Spergula arvensis) were also found. It seems that most of these plants were left over from the food supply of the people living in the building.

\(^1\) The analysis was performed by Agata Sady.
These plants may have been introduced accidentally and were common in the vicinity of crops. It is possible, however, that they were also used for pharmacological purposes. This applies, inter alia, to stinking nightshade. Since antiquity, it has been used as an ingredient of potions with various properties: as a plant that induces sleep, calms, relieves pain (including toothache) (Musiał 2017, 61). In larger quantities, it could have hallucinogenic properties, or was even poisonous to both humans and animals (Bartnik 2017, 104).

The head is only slightly smaller than a natural human head. It was made of sandstone and bears clear traces of burning. On its left side, traces of hammering and cutting, most probably made with a metal tool, were identified. They indicate that the figure was mechanically decomposed, and the head purposefully separated. The head’s depth was 16.5 cm, its width 9 cm, and its height 26.5 cm.

The head seems to be abnormally elongated, the ball-shaped eyes are situated deep in the skull and framed with almond-shaped eye-openings. The hair and the beard are fairly compact, adhering to the body, and covered with dense grooves. The individual streaks of hair are barely separated from one another (Fig. 3).

Such style was typical of Romanesque figural sculpture between ca. 1100 and the beginning of the second half of the 12th century in southern France (Schapiro, Finn 1985, 23-40). Similar works might be found e.g., in the Benedictine abbey in Moissac. The stonemasons educated in this abbey worked at construction sites in the whole of Europe, thereby spreading their specific style of stone carving (Aubert 1965, 530). The most evident Silesian example of this artistic manner is the “Biestrzyków Prophet”, a high-relief bust attached to a flat background plate. It was most probably part of a full-figure sculpture integrated into a group of similar figures (Świechowski 2004, 220). The Prophet dates back to the fifth or sixth decade of the 12th century. It likely originated in the Benedictine abbey church founded in the Olbin district in Wrocław by Piotr Włostowic. Włostowic was a voivode appointed by the Polish High Duke Władysław II Wygnaniec (the Exile). The sculpture might have been part of the decorations framing the main portal (Świechowski 1955; 1961, 249-253; Morelowski 1955, 10-35; Kmiecik, Szwed 2018, 79-82).

The stone head discovered in Nowy Targ (New Market) square was an architectural ornament of a church, and there were very few venues in Wrocław...
which might have featured it. Those were: the Cathedral of St John the Baptist in Ostrów Tumski, St Martin’s church (situated within the princely fort/seat on the cathedral island), St Peter’s church, and the abbey church of Holy Virgin Mary. St Vincent’s church in the Olbin area (close to the cathedral island), which belonged to Piotr Włostowic is also possible. Furthermore, one other church – namely, that of Canons Regular of the Lateran/St Augustine on Piasek Island (Sand Island, Insula Arena) in Wroclaw, might be considered (Fig. 4).

1.3. MATERIALS AND STUDY METHODS

For the petrographic analysis we collected a small piece of stone from the inner part of the sculpture.

Fig. 7. SEM-EDS analysis of the rock material used for carving the head. XRF energy spectrum of the rock material.

Developed by B. Miazga
It was examined in transmitted light using a Nikon Pol 200 polarizing microscope. The assessment of the modal composition and grain size was carried out with the JMicrolVision software. It utilizes the point counting method performed on digital microscopic images of thin rock slices. The sandstone’s granulometry was defined by using the equivalent diameter of the grains intersected with lines traversing the raster and spaced 1.0 mm from one another. The cement was examined with a Siemens 5005 diffractometer (with Ni-filtered CoKα radiation) at the Institute of Geological Sciences, University of Wroclaw. Powder method at scattering angles (2θ) ranging from 6 to 89° was applied.

Fragments of the sculpture’s polychromy were investigated with a HIROX RH 2000 digital microscope at the Institute of Archaeology, University of Wroclaw. Representative samples of rock material and their white, yellow, and red coatings were observed at the Faculty of Chemistry, University of Wroclaw, with a Hitachi S-3400N scanning electron microscope equipped with a Thermo Scientific Energy Dispersive Spectrometer. The acceleration voltage was 30.0kV. We collected BSE photos of the analyzed samples made at 65-200x powers of magnification, as well as quantitative and semi-quantitative EDS data.

For the energy-dispersive XRF measurements, a tabletop Spectro Midex spectrometer with an X-ray tube with molybdenum anode and a Peltier-cooled, semiconductor Si Drift Detector (SSD) was used. It operated with a voltage of 46 kV and an amperage of 0.4 mA. The XRF examination was fully non-invasive and did not include sampling, as the device’s measurement chamber was large enough to room the whole preserved sculpture fragment.

Studies of the phase composition of the deposit samples and rock material were conducted by the Crystal Structure Oriented Powder Diffractometry Group, Faculty of Chemistry, Jagiellonian University. The experiments with X-ray powder diffractometry utilized CuKα radiation and a Panalytical X’pert pro

Fig. 8. Rock material observed with a light microscope (160-200x magnification). Developed by B. Miazga
MPD diffractometer. It operated in Bragg-Brentano geometry at the angle range of 8.0-70.0° 2θ and a measurement step of 0.013°. The analysis of the obtained diffraction images was made with X’pert HighScore software utilizing the PDF-4+ 2017 database of diffraction data. The FT-IR analyses utilized the Thermo Nicolet 380 spectrometer operating at a 4000-400 cm⁻¹ range. Powder method was applied. The deposit sample was mixed with spectrally pure KBr and the spectrum was captured in the absorbance mode. The spectral analysis used the HR Inorganica and US Geological Survey databases.

Fig. 9. Infrared spectrum of the analyzed sample and calcite (*) and quartz (•), identified in the sample. Diffraction image of the rock material sample. Quartz (red line), calcite (blue) and microcline (green line)* detected.

* While analyzing the XRD results, it is important to bear in mind that the samples featured a significant quartz content that might impair the identification of other mineral components. Our interpretation selected substances which best matched the sample’s diffraction image. Developed by B. Miazga
1.4. PETROGRAPHIC FEATURES AND ORIGIN OF THE ROCK MATERIAL

The excavations conducted at Nowy Targ (New Market) square between 2010 and 2017 yielded a significant number of stone artefacts of various types. The assemblage included mostly miscellaneous stone tools used e.g., as knife sharpeners or pads, as well as small fragments of architectural elements. Detailed characteristics of their petrographic features, quantitative analysis of the lithological types, and remarks on the places of origin of the rock material are available elsewhere (Gunia 2018, 1060-1070).

The analyzed sample was taken from the inside of the stone head. The rock was fine-grained, with plain, non-laminated structure, cream grey, locally

Fig. 10. Microscopic image of the white deposit from the head’s surface, 20x magnification (a, c), 100x magnification (b, d). Stratigraphy of the white deposit on the stone sculpture. The rock, black, the burnt “underlay” and the white substance on the top are visible in the pictures. Developed by B. Miazga
covered with dark grey patina. The macroscopically visible features indicate that the material was a clastic, cream-grey rock with psammite structure, evenly-sized grains, without any visible sedimentary lamina-
tion. The microscopic observations showed a compact lithic framework consisting predominantly of 0.2-0.4 mm clasts displaying a low degree of rounding. The rock featured a low maturity of the primary sediment, moderately sorted grains (mostly isometric clasts) and low porosity reaching ca. 3.5% of the volume. The cementation was of a mixed porous-contact type with the cement consisting mostly of clay and in some places of iron and clay (Fig. 5).

The framework grains included quartz, feldspars, lithic fragments, and accessory minerals such as chlorite, zircon, rutile, and non-transparent iron oxides.

Most prevalent among the framework grains is quartz. Quartz grains are usually isometric (less often slightly elongated). Oblong specimens are relatively rare. The framework grains were most often moderately, and sometimes only slightly rounded. Most of the clasts might be categorized as sub-rounded or sub-angular, less often angular. Their maximum size reached 0.7 mm. Some of the discussed quartz grains were monocrystalline. Polycrystalline quartz, however, was also frequent and present most probably in

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Fig. 11. XRF energy spectrum of the white deposit. SEM-EDS analysis of the white deposit. Developed by B. Miazga
rock fragments (quartzites?). Here, the quartz grains were moderately rounded: most of them were sub-rounded or sub-angular. The grains observed through a single nicol appeared as colourless, non-pleochroic, not displaying visible cleavage and with relatively low relief. In polarized light, their interference colours were low to medium, most often grey and yellowish-grey. While the quartz did not contain inclusions of
other minerals, submicroscopic fluid inclusions were visible. The latter sometimes caused the opacity of the surrounding quartz background.

Moderately rounded, almost isometric (less often slightly elongated) feldspar fragments were also present. Their grains reached as much as 0.6-0.7 mm. In many cases, they were severely weathered and replaced with secondary aggregates of rusty-orange small blades consisting of feldspar decomposition products. Based on these pseudomorphs, it is neither possible to reliably identify the original optical properties of feldspar nor classify it typologically. At the same time, weakly weathered grains of alkalic feldspars were rare. They sometimes weakly developed perthite overgrowths formed through exsolution. Grains with characteristic cross-hatch, twinning intergrowths classified as microcline also occurred. Most of them exhibited optical properties similar to quartz grains. At the same time, they displayed characteristic opaque spots on the surface, as well as narrow concentrations of silty weathering products arranged predominantly along the cleavage direction.

Lithic ingredients constituted a significant part of the grain framework in the discussed rock. Their largest, moderately rounded fragments reached 0.6-0.7 mm. Most of them, however, were no larger than 0.5 mm. The rock fragments included many aggregates with grains of polycrystalline quartz consisting of a few quartz minerals grown together. Grains including both quartz and feldspar blades were also frequent, as well as intergrowths of randomly oriented crystals of these two minerals. In most cases, the feldspars were moderate to heavily weathered or replaced with orange-brownish, secondary aggregates of decomposition products arranged in fine blades. Occurring very rarely were grains consisting of very fine quartz crystals, fine muscovite blades in the form of sericite and including small amounts of feldspar. In such grains, the muscovite blades were arranged in parallel to one another.

The microscopically visible structural and textual features of these fragments might indicate that there were several lithological types of lithic ingredients. They represent most probably pieces of igneous rocks (acidic), and some of them (with regularly arranged grains) metamorphic crystalline slates. It is important to bear in mind that some of the polycrystalline quartz aggregates discussed above might have been formed through the crushing of fine-grained quartz-arenite sandstones. This might be indirectly indicated by the lack of traces of recrystallization (blastosic) of the original quartz in the grain framework.

Among the less prevalent (accessory) rock ingredients, chlorite is particularly noteworthy. It usually forms up to 0.35 mm blades which sometimes make parallel concentrations consisting of a few specimens. Microscopic observation showed that their colour was greenish, only slightly pleochroic, and that they had unidirectional cleavage and relatively high relief. When observed under crossed nicols, they displayed low, grey (first order) or subnormal, violet-blue interference colours. Interstitial chlorites occurred incidentally in the grain framework.

The discussed sandstones only exceptionally included zircon as an accessory ingredient, and only a few crystals were identified. The minerals usually have a fine, columnar habit and feature relatively well-preserved automorphic crystals reaching up to 0.2 mm. As far as its optical features are concerned, zircon has a high positive relief. It is colourless, non-pleochroic and lacking visible cleavage. Under crossed nicols, it displays high, third order, red-violet interference colours. Apart from zircon, isolated opaque, oval or irregularly shaped iron oxides were identified. Their size usually did not exceed 0.15 mm.

The cement consisted predominantly of clay minerals in the form of a silty, rusty-brown mass – similar to the filling of feldspar pseudomorphs. Therefore, deciding whether concentrations of clay minerals are part of the cement or a secondary product of weathering may prove challenging. Sometimes clay minerals in the form of small concentrations of blades arranged in parallel or radially can be observed between larger framework grains. Their colour is similar but their arrangement indicates that they are part of the cement (or clay matrix). They occurred in the form of micro-blades or micro-scales situated between the framework grains. The cement was, thus, of a porous-contact type. The locally visible rusty-orange inclusions among the clay ingredients might indicate the presence of dispersed quantities of iron hydroxides (goethite?, lepidocrocite?) in the background.

The analysis of the modal composition of the discussed rock showed that it consisted mostly of quartz (42.0% of the volume), feldspars (with clay pseudomorphs; 33.0% of the volume), and lithic components – 16.5%. The cement made 4% of the rock’s volume, pores 3.5%, and other components (including accessory minerals) – 1%.

The analysis of the framework grains demonstrated that fractions with different grain sizes constituted
a significant part of the sample’s volume. Such a composition reflects the poor sorting of the primary sediment. The maximum grain size did not exceed 0.7 mm but many of them fell within the 0.4-0.5 mm range.

As the granulometric measurements showed, the sample consisted mostly of 0.2-0.3 and 0.3-0.4 mm grains which constituted respectively 25% and 23% of the framework grains. The 0.1-0.2 mm, 0.5-0.5 mm and

Fig. 14. SEM-EDS analyses of black substance samples: 1, 2 – top part; 3, 4 – bottom part. Developed by B. Miazga

Fig. 15. Diffraction image of the black sample. Quartz (red line), kaolinite (dark blue line) and galena (green line). Developed by B. Miazga
0.5-0.7 mm fractions made 16%, 18% and 14% of the volume respectively. Grains falling in the ranges of 0.05-1 mm and below 0.05 mm constituted only a few per cent of the analyzed grains.

The fine-grained clastic rock used for the sculpture has features typical of arkose. According to the system by Pettijohn et al. (1972, 12-34), it may be classified as a lithic wacke. The petrographically similar, middle Turonian Cretaceous sandstones – identified in the formations of the Intra-Sudetic Synclinorium (Kozłowski 1986) – had many applications in the architecture. The Radków sandstone also belongs to this group and includes feldspars and lithic ingredients of similar character – apart from quartz. These sandstones, however, are typically yellowish (Dziedzic ed. 1979, 20-44). Moreover, carving stones from this group usually feature distinctively well-preserved feldspar plates, which makes them different from the discussed sample.

Similar rocks, matching the characteristics of greywacke or arkose, might be found in the Opawskie Mountains. They occur as small deposits of Devonian-Carboniferous clastic rocks. Greywacke from these deposits was quarried in the Braciszów area, while arkose occurred in the Zubrzycy area. The material might have also originated on the Czech side of the Opava Mountains. The clastic rocks of the Opavas are described as grey sandstones, yellowish when weathered, consisting mostly of poorly rounded quartz, well-preserved feldspars and clasts of metamorphic, volcanic and sedimentary rocks (Sawicki 1979). Blades of various accessory minerals might also be identified, including post-biotite chlorite. However, their grain framework does not include severely weathered feldspars.

The petrographic characteristics of the analyzed sandstone match in some respects the Carboniferous greywacke found with illitic shales in the vicinity of Toszek, near Pyskowice (Zieliński 1964). This source of raw material, however, is rather improbable since the model composition of the Toszek arkose does not include potassium feldspars which were identified in the analyzed sample. The source of the raw material might have also been located outside of the present area of Poland. To identify them, field investigations and examination of samples from medieval stone quarries in Germany, Bohemia, Slovakia and Austria will be necessary.

### 1.5. ARCHAEOMETRIC RESULTS

Sample 1: A cream-grey sample was taken from a minor chip on the top of the head of the analyzed sculpture. It served as a model for comparing the phase and chemical composition of the rock and the

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Fig. 16. Diffraction image of the yellow sample. Quartz (red line), biotite (grey line), kaolinite (brown line), orthoclase (light blue line). Developed by B. Miazga
coloured deposits. The microscopic observation suggested a significant quartz content in the analyzed surface (Fig. 7). The EDS spectrum contained peaks of silicon, aluminium and oxygen (ca. 25, 10 and 50% wt respectively), as well as reflections showing small quantities of carbon, potassium, iron (all of them ca. 3% wt) and calcium (ca. 4% wt). Trace quantities of sodium, magnesium, phosphorus and sulphur (below
The XRF analysis detected also low signals of lead, iron, manganese, rubidium and strontium (Fig. 8b). The FTIR spectral analysis identified quartz and calcite as the main components of the rock used for the sculpture (Fig. 9a), while diffraclometry also detected potassium feldspar (microcline; Fig. 9b).

The results obtained for sample no. 1 indicate that it contained typical sandstone components, such as quartz, feldspars and carbonates in the cement.

Sample 2: The sample was taken from the white deposit covering part of the man’s hair (Fig. 6). Microscopic observations at a low power of magnification showed that this – rather soft – deposit was located mostly in the surface concavities and covered an earlier, black layer resembling burnt organic substance (Fig. 10a).

The obtained EDS results demonstrated that sample no. 2 included mostly oxygen (ca. 45% wt), silicone (ca. 16% wt), calcium (ca. 13% wt) and aluminium (ca. 9% wt). The sample also contained small quantities of other elements, such as potassium (ca. 3% wt), iron (ca. 3% wt), carbon (ca. 2% wt), magnesium (ca. 1%) and a small addition of manganese (ca. 0.2% wt). Elements associated with environmental contamination and human activities, such as phosphorus (ca. 6% wt), sulphur (ca. 0.8 % wt) and chlorine (ca. 0.5% wt; Fig. 10b), were also present.

The diffraction analysis detected the presence of quartz and kaolinite. The infrared spectroscopy provided the same results, confirming the presence of aluminosilicate minerals. It also detected a slight amount of an organic substance (identified through weak C-H stretching of methyl and methylene groups in alkanes).

The presence of feldspar weathering products and the composition of the sculpture’s raw material are reflected by the secondary kaolinite and higher contents of aluminium and silicon dioxide in the sample. The occurrence of phosphorus, chlorine, and sulphur indicates the significant impact of environmental deterioration on the sculpture. This indirectly suggests that the Romanesque sculpture was originally placed outside of a sacral building.

The analyzed sample lacks intensive lead signals which would indicate that the medieval artisans utilized the most popular white pigment of their time – that is, white lead paint (Clark 2002). The phosphorus, calcium, and iron concentrations might suggest that the sample was contaminated with anthropogenic products. Thus, the examined substance was likely a calcium residue contaminated with layers of soil (Fig. 11a).

Sample 3. The sample is a fragment of black, solid deposit, in some places with a matte patina. The microscopic view of the surface revealed local networks of cracks resembling those found in materials vitrified in high temperature (Fig. 13). Both the top and bottom surfaces of the black substance were examined, as shown in Fig. 14.

The SEM-EDS data analysis of the outer part of the sample showed that in the examined micro-areas, carbon (more than 40% wt), oxygen (ca. 30% wt), nitrogen (ca. 5% wt) and calcium (ca. 4% wt)
dominated. Other elements, such as sodium, magnesium, aluminium, silicon, sulphur, chlorine, potassium, iron, copper, and zinc (below 1% wt) occurred in small quantities. The analyses of the bottom part of the glassy deposit indicate a higher frequency of components with the ordered internal arrangement (minerals). Apart from the 30% oxygen content, significant quantities of calcium (more than 20% wt) and ca. 10% of phosphorus and aluminium were detected. Iron and carbon constituted ca. 5% wt each.

The XRF analyses of sample no. 3 detected trace quantities of potassium, calcium, manganese, iron, lead, rubidium, and strontium, as well as copper and zinc. Nevertheless, these metals did not make more than 4% of the analyzed deposit.

The powder diffraction X-ray analysis of the substance confirmed its almost amorphous character. The identified reflections indicated the presence of quartz, kaolinite, and a small amount of galena (Fig. 15). The characteristic “hump” on the sample’s diffractogram at the scanning angles 2θ: 25-28° and 35-40° also testified the significant content of non-crystalline (amorphous) substances. Apart from the mineral substances (mostly various silicon and aluminium oxides, including quartz), the FTIR analysis detected noteworthy quantities of phosphorus compounds and organic substances.

These results therefore indicate that the black deposit containing large quantities of carbon compounds was probably a combustion product of organic substances. The glassy surface adjacent to the sandstone developed due to high temperature. It might have been a fire, as the field investigations suggest.

The notable phosphorus content in the sample might derive from the combustion of organic matter (e.g., connective tissue, and specifically bone tissue), deterioration associated with the formation of secondary apatite, or phase transitions which occurred when the artefact was covered by the deposits.

Sample 4. The sample is a fragment of yellow, mineral deposit taken from the eye area in the sculpture’s face.

The results of the EDS analyses showed that the examined sample consisted mostly of compounds of oxygen and light metals. The oxygen content often exceeded 45% wt, and the silicon and aluminium contents amounted respectively to 24% and 10% wt. Carbon, calcium and iron occurred in significantly smaller quantities (2-3% for C; ca. 4% for Ca and Fe; Fig. 16).
The X-ray fluorescence analyses indicated that the percentage of manganese and iron was higher in the sample than in the sculpture’s rock material (Fig. 17a). The same applies to lead, rubidium, and strontium. Silicone, aluminium, and oxygen in the examined deposit originated from quartz and aluminosilicates (feldspars).

The X-ray investigations confirmed the presence of these elements in various minerals. Reflections of quartz, biotite, kaolinite, and orthoclase were identified (Fig. 16). Besides the mineral substances (mostly quartz), the FTIR examination detected organic compounds (characteristic signals of CH₂ and CH₃ groups in the range 2950-2850, 1450-1380 cm⁻¹).

The archaeometric investigations demonstrated that the analyzed sample contained mostly ingredients connected to rock weathering. The yellowish colour results most probably from the presence of decomposed iron hydroxides (goethite?) with dusty and amorphous texture (ochre?). The contaminations containing phosphorus, sulphur, and chlorine might be either deterioration products from the surface of the sculpture exposed to weather conditions or products of post-depositional mineral transformations.

1.6. CONCLUDING REMARKS

The examined stone artefact is part of a sculpture which decorated one of the Romanesque buildings of Wroclaw. It may be dated to the 12th century but it was deposited in a wooden building in the backyard of a city plot no sooner than in the 14th century. It was carved from a stone well-suited for the purpose. The rock material was a fine-grained, cream-grey arkose sandstone originating in the Sudetes. The stone quarry was probably distant, likely situated in the mountains in the southern Opole region of Silesia. The Romanesque churches of Wroclaw typically featured massive granite walls, as well as architectural details and sculptural decorations of sandstone (Świechowski 1955, 11-44; Lasota, Piekalski, 1990/1991, 118-130).

The archaeometric analyses of the deposits sampled from the surface of the Romanesque sculpture excluded the possibility that it had been painted, particularly as concerns the use of white pigment. Not only does this conclusion result from microscopic observations, but also the outcome of advanced mineralogical and micro-area chemical composition analyses. The samples did not yield any traces of lead pigment, so characteristic of medieval art. The pigment occurred both in white paints and as a lightening ingredient in other paints (de Souza Felix et al. 2015; Gasanova et al. 2018). Moreover, the analyses did not detect thermal decomposition products of white lead (Ball, Casson 1977, 1949-1950) as would be formed in a fire.

Nevertheless, the studies of the deposits covering the sculpture yielded exciting information. First, the presence of amorphous carbon in the black deposit sample confirmed that the artefact had been exposed to high temperature (i.e., fire). Second, the phosphorus traces in the deposits document the anthropogenic factor in the object’s production and usage stages or post-depositional weather deterioration.

Although painting sculptural decorations was a common practice in Christian Europe (recorded also in the nearby Cistercian church in Trzebnica), the discussed artefact seems to have remained unpainted. Both the microscopic and spectroscopic analyses aimed at identifying pigment traces on the sculpture’s surface gave negative results. Thus, painting Romanesque stone sculptures did not have to be extensively practiced in 12th-century Silesia. The aesthetic principles determining the look of local sacral buildings might have differed from Western European patterns.

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