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THE OCCURRENCE OF GAGATE IN SOŁTYKÓW (THE HOLY CROSS MTS.)

Abstract. The gagate studied occurs in the inanimate nature reserve "Gagates of Sołtyków", where it accompanies brown coals of the Zagaje Series in Lower Jurassic sediments. It represents banded fossil coal with jet-black colour, composed of collotelinite and gelinite. Reflectivity of collotelinite ranges from 0.37 to 0.43%. Infrared spectroscopy has revealed low condensation of aromatic components of the gagate, while chemical analyses have shown its low degree of coalification. It can be classified as the bright variety of hard brown coal. The H/C and O/C atomic ratios indicate the position of the Sołtyków gagate to be of mixed, terrestrial-marine type of organic matter. Elevated content of hydrogen ($H^{daf} = 5.87\%$) and low reflectivity of collotelinite (0.37– 0.43%) point to bituminization of original wood tissue (lignine). It is possible that the gagate was enriched in aliphatic hydrocarbons within a water layer of a moderate reductivity.

Key-words: gagate, collotelinite, gelinite, IR, chemical analysis, Sołtyków

INTRODUCTION

Gagate (jet) is a gem with black or dark brown colour. Its occurrence within coaly sediments indicates the terrestrial origin of their organic matter. According to Taylor et al. (1998), jet is bituminized driftwood, an example of assimilation of lipoid or bituminous material within coaly matter, commonly known in Europe from Liassic, Jurassic and Cretaceous sediments. It represents former wood that has been secondarily impregnated with bitumen from surrounding organic matter and deposited in the environment of stagnant water. Jet also appears to be the product of diagenetic changes different from those occurring in coal.

Gagate was used as a gem already some 10,000 years ago. The most famous specimen comes from Whitby (Yorkshire, United Kingdom). Gagate can be found in almost all parts of the world, but its high-quality varieties for gem making are rare. Main localities where gagates are mined include India, northern France, Spain, Portugal, Germany, Austria, United Kingdom (Whitby), Turkey and USA (Utah).

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The authors give here mineralogical and petrographical characteristics of the gagate-bearing rocks from Sołtyków near Opoczno (Poland), express an opinion on their genesis and, additionally, assess the gagate quality for gem making.

GEOLOGICAL SETTING OF THE OPOCZNO AREA

In Poland gagates occur near Kielce, in Lower Jurassic sediments, and accompany brown coals of the Zagaje Series. Being also accompanied with brown coal beds, they appear in the Ore-bearing Series. Up to now the exploited gagates belonged to the Zagaje Series.

The specimens investigated were collected in Sołtyków near Odrowąż (Stąporków district, Końskie administrative region, Świętokrzyskie Voivodeship; 20°38'E, 51°08'N; Fig. 1). They occur in the inanimate nature reserve "Gagates of Sołtyków", where besides the gagates also footprints of dinosaurs can be observed in the Lower Jurassic strata 208 mln years old. The geological profile of the Sołtyków area is as follows:

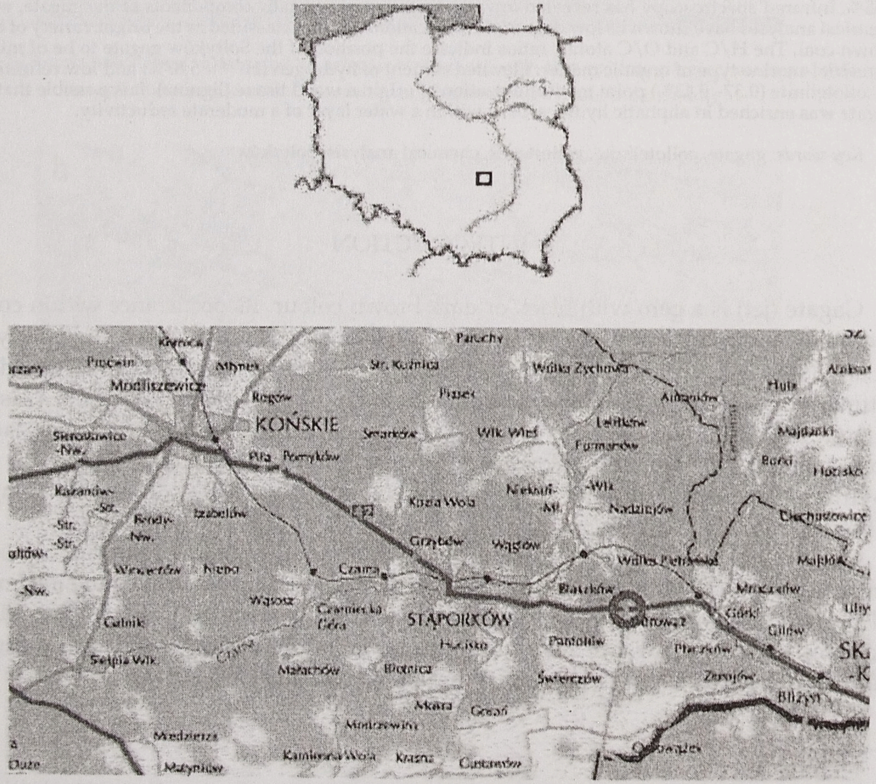


Fig. 1. Location map of the Sołtyków area

- ➢ Triassic — Upper Keuper, represented by variegated clays, limestones and breccias;
- ➢ Jurassic — Rhaetian and Liassic, represented by clays, sandstones, gravels and conglomerates of the Zagaje Series.

MACRO- AND MICROSCOPIC OBSERVATIONS

The gagates studied are a fossil coal with jet-black colour and banded structure. (Phot. 1). Alternating dull and vitreous coal bands are relatively thin (15 or so millimetres) and contain numerous pyrite grains, developed as framboids with diameters from some μm to slightly less than 20 μm. Surfaces of the layers and of fracture zones are covered by thin, canary-yellow efflorescences. The efflorescences are probably products of alteration of iron sulphides and resemble the minerals of the jarosite group.

Microscopic investigations were carried out both in transmitting and reflected light; in the latter immersion optics was used. Two macerals: collotelinite and gelinite, belonging to the vitrinite group, have been found among petrographic constituents of the gagates. Collotelinite reveals a variable degree of preservation of its cellular structure, and the cells are usually weakly visible (Phot. 2) and filled with gelinite, sometimes resinite or bituminous substance. The mean reflectivity coefficient of the collotelinite (R_o) is variable and ranges between 0.37 and 0.43%. The reflectogramme is unimodal with a standard deviation of 0.028. In the vicinity of impregnation zones, where the cellular structure is better visible and the cells are filled with resinite or bituminous substance, the R_o value significantly decreases. In blue light the resinite impregnations are fluorescent in brown-yellow and orange colours. The gelinite is light grey, in some places this colour turns to dark grey. Discrete colour changes are revealed among the bands, what was observed by Kosmowska-Ceranowicz and Migaszewski (1988) and described as a "spotted collinite". They use the term "collinite", following the older ICCP nomenclature (ICCP 1971). The current name is gelinite.

The observations have revealed few small fragments of fusinite and semifusinite. Numerous are pyrite grains with the framboidal development, characteristic of the syngenetic iron sulphides. The epigenetic pyrite fills in small fractures in collotelinite and gelinite (Phot. 3)

X-ray analyses have confirmed the components of the gagates investigated to be fully amorphous.

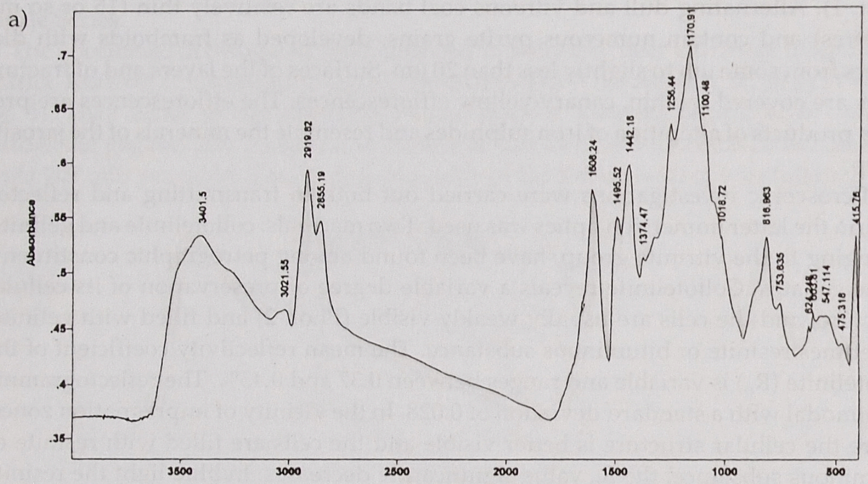
INFRARED INVESTIGATIONS

Infrared investigations were carried out on two gagate samples. Their interpretation is presented below:

- ➢ wide band at 3400 cm^{-1} — stretching bands of the OH group;

- 3037–3021 cm^{-1} band — stretching bands of the aromatic C–H groups;
- band with two distinct "peaks" at around 2920 and 2850 cm^{-1} — associated with aliphatic groups (methylene CH_2 groups);
- band around 1610 cm^{-1} — interpreted usually as the –C=C– framework vibrations of aromatic rings. The band may also be associated with asymmetric vibrations of the $–COO^-$ groups (in carboxylic groups) and hydroxyl-chinone vibrations of the C=O groups. The C=O bond is characteristic of the carboxyl groups of organic acids (humic acids) as indicated in numerous papers, among others by Wagner (1982, 1992) and Wagner et al. (1983);

a)



b)

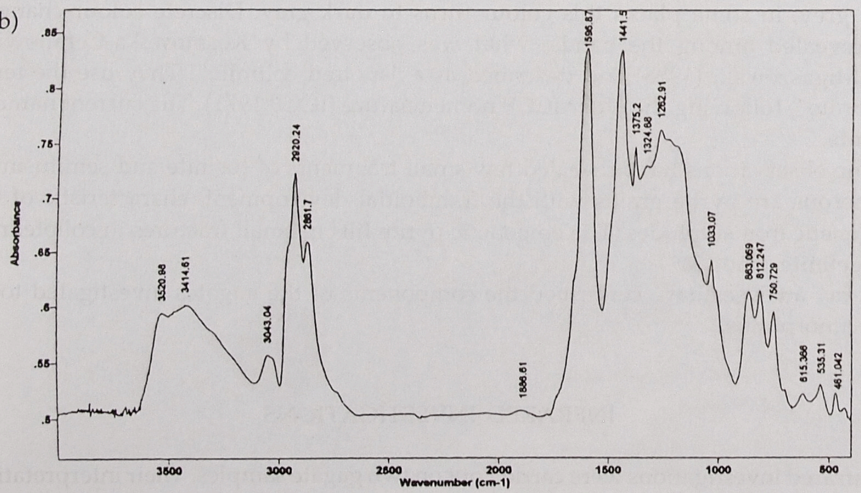


Fig. 2. IR spectra of gagate (a) and vitrain (b)

- 1450 cm^{-1} band — records vibrations of the CH_2 aliphatic groups;
- intensive band at 1440 cm^{-1} — associated with vibrations of the metoxyl OCH_3 groups;
- absorption in the 1300–1100 cm^{-1} region — attributed to the stretching C–O and bending O–H vibrations in oxidized functional groups of various aliphatic and aromatic structures. Most probably they represent carbonyl and hydroxyl groups of carboxyl acids, whose presence is indicated by the sharp band at 1170 cm^{-1};
- band around 820 cm^{-1} — associated with the C–H bonds in aromatic rings (benzene derivatives).

Infrared bands of the gagates of Sołtyków were compared (Fig. 2) with a spectrum of the Carboniferous vitrinite from the No. 404 seam (the Morcinek mine in the Upper Silesian Coal Basin). Higher intensity of bands at 1600 and 1440 cm^{-1} in the spectrum of the Morcinek vitrinite and additional bands at 1375 and 1325 cm^{-1} prove a higher degree of condensation of its aromatic groups. This conclusion is supported by the presence of the band at 750 cm^{-1}, attributable to aromatic rings (Van der Marel, Beutelspacher 1976), absent in the spectra of the gagates. Weaker absorption of the bands around 1600 and 1440 cm^{-1} in the gagates indicates the presence of oxygen groups.

From the results of infrared analyses it can be concluded that the gagates studied should be interpreted as a caustobiolite with a complex, humic-sapropelic character. This corresponds well with the statements of Gabzdyl (1984) that the position of gagates in the systematic of solid caustobiolites is uncertain and of Kosmowska-Ceranowicz and Migaszewski (1988) that the genesis of gagates is ambiguous. The latter authors compared the infrared spectra of the gagate of Sołtyków with those of fossil resins and did not detect the 1700 cm^{-1} band in the spectra of the former. Despite this band being characteristic of the carbonyl group present in resins, they considered the gagate a resin-bearing variety of brown humic coal.

Considerable differences in absorption of the band around 1600 cm^{-1} (C=C benzene rings) were observed in gagates and vitrain from the Balkan Coal Basin in Bulgaria by Petrova et al. (1985). As the number of benzene rings in the gagates was several times lower than that in the vitrain from hard coal, they concluded that the coal molecules of the gagate are highly undeveloped in their aromatization and condensation.

CHEMICAL ANALYSIS

The results of chemical analysis (Table 1) suggest that the gagate of Sołtyków is a caustobiolite of a low rank. According to the ASTM classification of coals (Stach et al. 1982; Taylor et al. 1998), gagates (jets) fall within the subbituminous B/C group. Therefore, the gagate studied should be interpreted as a caustobiolite belonging to the bright varieties of hard brown coal.

The atomic H/C (0.99) and O/C (0.13) ratios place the gagate of Sołtyków in van Krevelen diagram within the mixed, terrestrial-marine type organic matter (Fig. 3).

TABLE 1

Chemical analysis of a gagate from of Sołtyków [wt.%]

C^{daf}	H^{daf}	N^{daf}	S^{daf}	O^{daf}	Moisture	Ash	V^{daf}	H/C	O/C	C/N
70.65	5.87	0.83	10.75	11.88	3.6	10.4	48.95	0.99	0.13	98

daf — dry ash free, V — volatile matter.

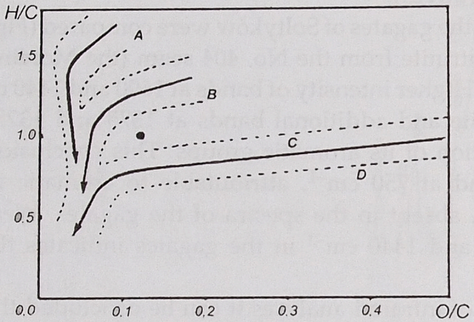


Fig. 3. Types of organic matter after van Krevelen

A — marine type of organic matter, B — transitional, marine/terrestrial type of organic matter, C — terrestrial type of organic matter, D — residual type of organic matter

The C/N index after Tyson (1995) differentiate terrestrial and marine sediments as it ranges in the former between 12 and 1,340 and in the latter between 11 and 70. Being equal to 98 for the gagate studied, the index confirms the gagate of Sołtyków to be formed of the terrestrial plant material.

GENESIS OF THE GAGATES FROM SOŁTYKÓW

Araucaria trees, strongly resembling currently growing *Araucaria araucana* or Chilean pine, were one of dominant plant species in Middle Jurassic. Their fragments, washed into a basin by rivers transporting significant amounts of sediments, were gradually soaked with water and permeated with numerous microelements. Transported farther onto the basin floor, they were deposited within a thick layer of sediments. A considerable pressure of a still growing pile of the sediments dispersed partly decomposed tree fragments, leaving *in situ* their more resistant parts that were eventually altered into gagates. Hemingway (1933) described "gagatization" of the Araucaria tress. According to him, the weight of accumulated mud and water imparted a considerable pressure that flattened single trees into narrow organic beds. Overlaying sediments completely sealed up the wood layers, which were next fossilized without

the access of oxygen. The process proceeded from outside the trunks and along tree rings. This explains why some gagates possess a very hard central core: their centres must have been silicified prior to gagatization.

Investigations carried out in the "Sołtyków gagates" reserve (Gierliński et al. 2000) revealed that the gagate-bearing muds and clays were deposited in shallow lakes and swamps. These sediments are intersected by sandy deposits of old river channels. Well-preserved tree trunks and branches prove a proximity of forests. The shores of the lakes and swamps as well as the banks of the rivers were strengthen by low growing plant assemblages, composed mainly of horsetails. With the passage of geologic time, newly formed rivers changed their channels, meandering onto already deposited sediments. During succeeding inundations, rising waters deposited sand, mud and tree trunks on flood plains, forming eventually crevasse splays.

Recently, Bechtel et al. (2001) described Upper Cretaceous (Turonian) jet from Styria (Austria). Considering it to be a bituminous driftwood (collotelinite), they confirmed its origin as terrestrial organic matter derived from the trees of Coniferales. They considered two possibilities: the bitumen impregnations of driftwood may be derived externally, i.e. from surrounding rocks (Stach et al. 1982; Suarez-Ruiz et al. 1994), or internally, i.e. from the resin-impregnated driftwood itself within which hydrocarbons were generated during maturation. In the results of geochemical studies Bechtel et al. (2001) rather excluded the possibility an external origin of the bituminous matter characteristic for jet. They accepted an internal source of bitumen in the jet samples due to resin impregnation of the wood tissue before its deposition in the sediment. According to them, the most probable origin of the hydrogen-rich vitrain (jet) is the incorporation of microbial-derived lipids into the organic matter.

It is supposed that the gagates of Sołtyków must have additionally been bituminized, the conclusion being inferred from their elevated hydrogen content (almost 6 wt.%). Bituminization that developed within the humic matter (lignine) may have involved chemical alteration of vitrinite that was enriched in aliphatic hydrocarbons within a water layer with a moderate redox potential. Similar phenomena were observed by Wagner (1992) in the coals occurring within the flysch sediments of the Carpathians.

Utilization of the gagates of Sołtyków as gems is limited. First of all, their occurrences are uneconomic because the amount of the gagates is subordinate. However, it seems possible that other gagate occurrences may be found along the outcrops of the lowermost Lower Jurassic strata within the northern limb of the Mesozoic cover of the Holy Cross Mountains, i.e. along the Kamienna river valley between Ostrowiec Świętokrzyski and Skarżysko Kamienna and next between Skarżysko and Końskie, branching toward Opoczno (Heflik 1989). This area may be thus considered perspective for gagates.

Another problem to be addressed is the quality of the gagates of Sołtyków. The quality of gagate ornaments is controlled by the following:

- colour; the colour of the gagates in question is jet-black, pure (deep?) and uniform, improving considerable their appearance;
- impurities; unfortunately, the gagates studied contain considerable amounts of pyrite inclusions that lower their gem-making properties;

- amount and character of fractures; the gagate-bearing rocks are relatively strongly fractured and the fractures are filled with pyrite;
- luster; the gagates of Sołtyków are characterized by the most prized type, i.e. vitreous lustre.

Summarizing, the gagates of Sołtyków are ornamental rocks of rather good quality and can be utilized as gemmological raw materials, if only their mining in the perspective areas is possible.

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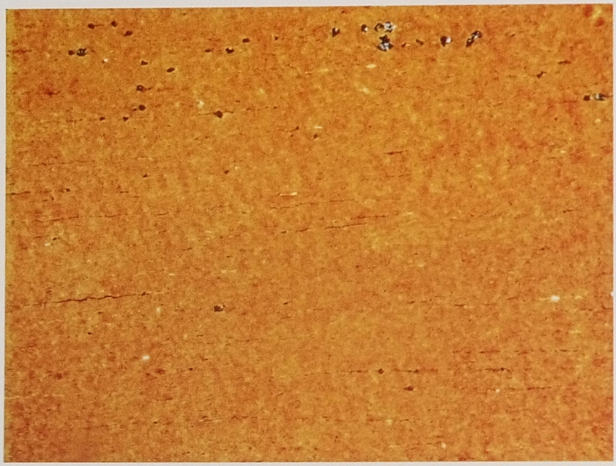
WYSTĘPOWANIE GAGATU W SOŁTYKOWIE (GÓRY ŚWIĘTOKRZYSKIE)

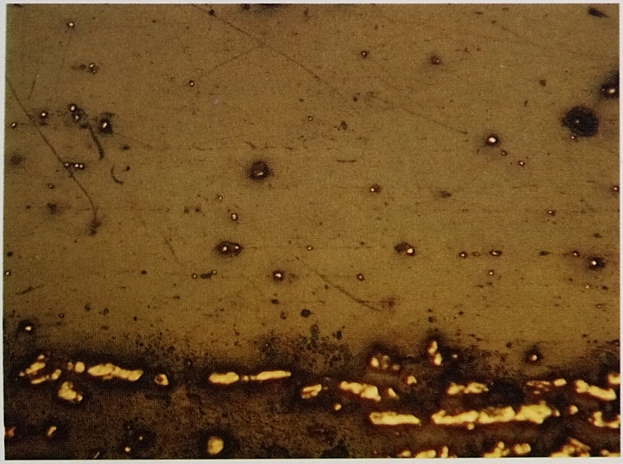
Streszczenie

Próbki gagatu zostały pobrane z odsłonięć w rezerwacie przyrody nieożywionej "Gagaty Sołtykowskie" w okolicy Opoczna. Gagat występuje tu w osadach dolnej jury i towarzyszy węglom brunatnym serii zagajskiej. Makroskopowo przedstawia węgiel kopalny o barwie smołowo-czarnej i teksturze warstwowanej. Badania mikroskopowe wykazały obecność kolotelinitu i żelinitu. Refleksyjność kolotelinitu waha się od 0,37 do 0,43%. Analiza widm absorpcyjnych w podczerwieni gagatu i witrytu pochodzącego z GZW (karbon) ujawniła w tym ostatnim wyższy stopień kondensacji układów aromatycznych. Wyniki analizy chemicznej wskazują na niski stopień uwęglenia gagatu. Można go uznać za błyszczącą odmianę twardego węgla brunatnego. Podwyższona zawartość wodoru i obniżona wartość refleksyjności kolotelinitu świadczą o zbituminizowaniu tkanki drzewnej (ligninowej).

Phot. 1. Gagate from Sołtyków with banded structure contains numerous pyrite grains. Natural size



Phot. 2. Collotelinite with pyrite grains. Transmitted light, 100×



Phot. 3. Gelinite with syngenetic and epigenetic pyrite. Reflected light, 230×