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AMBER FROM THE UPPER CRETACEOUS DEPOSITS OF SW POLAND

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Abstract. Abundant small grains and aggregates of amber have been found in the Upper Cretaceous sediments of the North-Sudetic basin. They occur in a thin brown-coal seam within the Santonian coal-bearing formation. Amber was investigated using optical methods and IR absorption spectroscopy. IR spectra have revealed that amber from Bolesławiec is made up of aromatic rings with aliphatic branches consisting of carboxyl, phenol, alcohol and ester groups.

INTRODUCTION

According to the ICCP lexycon (Stach 1975), the name of amber is given to fossil resin forming independent concentrations in sedimentary rocks of the geological formations of different age. In Poland fossil resins have been reported from the Upper Carboniferous coals, the Palaeogene flysch sediments of the Outer Carpathians, the Miocene sediments of the Carpathian Fore-deep and from the Tertiary formations occurring in the northern and central parts of the country (Niedźwiedzki 1908; Czeczott 1962; Zalewska 1964, 1974; Woźny 1966; Urbański *et al.* 1971). They have been described under different names such as succinite, rumanite, delatynite or gedanite. The occurrences of amber in Cretaceous deposits have reported mainly from America (Langenheim, Beck 1965; Langenheim 1969): the United States (Maryland, South Carolina) and Canada (Manitoba). Fossil resins from the Upper Cretaceous of Czechoslovakia (Moravska Třebova,

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Boskovice), referred to as neudorfite and walchowite, were described by Ratajczak (1968). A new locality with amber has been found in the Upper Cretaceous coal-bearing formation in the North-Sudetic basin (SW Poland).

GEOLOGICAL POSITION OF AMBER

The Upper Cretaceous deposits in the North-Sudetic basin formed in the period between the Cenomanian and Santonian. They attain a thickness of about 1000 m, outcropping in several localities, e.g. near Bolesławiec and Lwówek. Complete profiles of those sediments were obtained from the data yielded by numerous boreholes drilled both in the marginal and central parts of the basin. The sequence of beds, their lithology and fauna were studied by several authors (Milewicz 1956, 1970; Mazur, Milewicz 1958; Alexandrowicz 1971, 1976). On the basis of their investigations, the following lithostratigraphic units can be distnguished (Fig. 1):

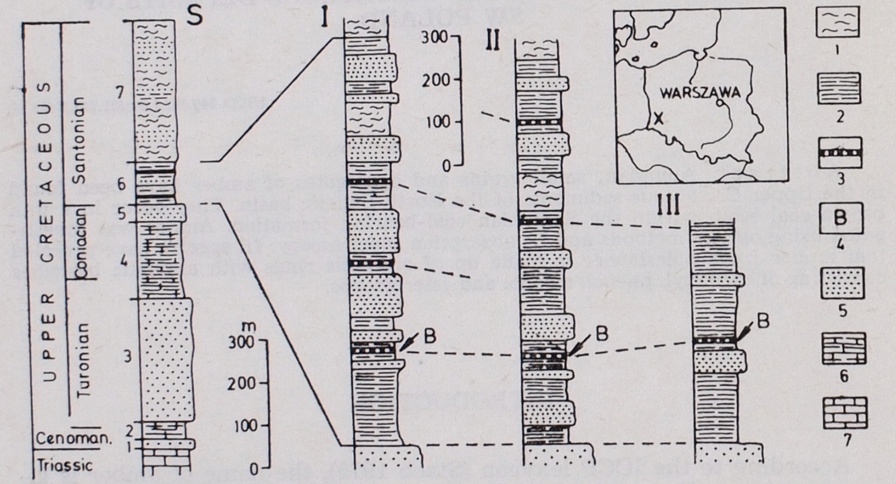

Fig. 1. Locality and stratigraphical position of Upper Cretaceous amber from SW Poland

S — profil of upper Cretaceous in North Sudetic basin, *1—7* — lithostratigraphical units described in text; *I, II, III* — lithological profiles of brown coal formation in three selected boreholes, *1* — clays, white and red kaolins, *2* — grey clays and claystones, *3* — seams of brown coal, *4* — occurrence of amber, *5* — sandstones, *6* — marls and marly shales, *7* — triassic limestones

1 — medium- and coarse-grained sandstones, assigned to the Cenomanian,

2 — marl and calcareous mudstones with *Actinocamax plenus Bl.*, *Inoceramus labiatus Schloth.* and *Rotalipora cushmani* (Morrow), representing the uppermost part of the Cenomanian and the Lower Turonian,

3 — thick-bedded, medium- and coarse-grained sandstones with local inserts of shales and mudstones,

4 — marls and shales with intercalations of calcareous mudstones, containing a fairly rich fauna which points to Upper Turonian and Coniacian age (*Placenticeras orbignyanum* Geinitz, *Inoceramus latus* Sow., *Globotruncana coronata* Bolli),

5 — white fine- and medium-grained sandstone with a poor Coniacian fauna,

6 — dark-grey clay shales with pelecypodal fauna (*Cyrena cretacea* Dresch.), containing mudstone and sandstone intercalations and a few thin brown-coal seams (Santonian),

7 — clays and white, grey and red kaolins with numerous intercalations of medium- and coarse-grained kaolin sandstones (Santonian).

The above complex of sediments consists of two distinctive parts (Fig. 1). Its lower members (*1—5*) are represented by marine deposits regarded to be of Cenomanian, Turonian and Coniacian age whereas the upper members (*6, 7*) formed on the continent, after the regression of the Cretaceous sea. The regression took place about the end of the Coniacian, after the deposition of white sandstones (member *5*), giving rise in the area of the North-Sudetic basin to a flat, marshy land bordering from the south a sea bay which covered the area of Żary pericline and North Lusatia (Alexandrowicz 1976). The warm climate of the Santonian promoted the prolific growth of vegetation, and the conditions were suitable for intense accumulation of organic matter, as well as for the formation of vast swamps. The nearby sea-shore was favourable to periodic marine ingressions, due to which inserts with brackish fauna can be encountered among the continental deposits (Chmura 1956, Milewicz 1970, Alexandrowicz 1976). Such conditions gave rise to a paralic coal-bearing formation of inconsiderable thickness (50—100 m) and limited extent, confined only to the North-Sudetic basin.

In the lower part of the stratigraphic profile of the Santonian coal-bearing formation, very characteristic sediments have been found. These are grey and dark-grey, somewhat marly clays and claystones, showing distinct parallel lamination, with laminae of quartzose silts and scarce intercalations of arkosic sandstones. The clays contain carbonized plant remains and a fairly abundant pelecypodal (*Cyrena*, *Cardium*) and foraminiferal (*Verneuillinoides*, *Ammobaculites*) fauna. The member in question attains a thickness of 20—30 m, and a brown-coal seam 10—30 cm thic appears in its upper part, 15—25 m above the bottom of the Santonian sediments (Fig. 1, *I—III*). The presence of the seam has been confirmed by several boreholes in the northern and central parts of the North-Sudetic basin. Core samples obtained from three boreholes have revealed the presence of fairly numerous small amber grains, randomly disseminated through the seam (Fig. 1 — *B*).

A higher stratigraphic position in the profile is occupied by grey clays with inserts of arkosic sandstones and ashen-grey or green claystones. The clays and claystones contain abundant remains of carbonized plants whereas fauna is scarce or absent altogether. The brown coal intercalations are of variable thickness (2—20 cm), pinching out among clays with flora detritus (Fig. 1). Despite persistent investigation, no amber has been found in this member.

In the lower brown-coal seam discussed in the preceding section (Fig. 1 — *B*), amber appears in the form of grains and lenses. Amber grains are spherical, oval or irregular in shape, up to several mm in size, grains of 1—3 mm in diameter being the most common. They have low specific gravity (1.0—1.1 G/cm^3) and hardness ranging 2.0—3.0 in Mohs scale. The amber is usually yellow in colour with different tinges: cream-yellow, honey yellow, orange or brown. It has an intensive glassy lustre and conchoidal fracture, uneven and rough on larger surfaces. Its transparency is nearly perfect. The amber grains are embedded in the carbonaceous shale groundmass, occasionally contacting with vitrite and fusite. On the bedding planes fragments of fusinized plant tissue are visible, revealing the organic structure of wood.

Microscopic examinations in transmitted light of powder preparations have shown that the amber is optically isotropic. Very weak optical anisotropy has been noticed on larger fragments exhibiting a distinct conchoidal fracture; yet, in the authors' opinion, in is to attributed to internal strains. Neither seeds or spores nor any remains of organic structures have been detected in the microscopic preparations though they could be expected considering the process of formation of amber. Only mineral admixtures appearing as grains of quartz or clay and carbonate minerals have been found.

Refractive index was measured by Becke's method, using a solution of bromoform and kerosene as the immersion liquid. The liquid refractive index was measured with Abbe's refractometer with an accuracy ±0.001. Refractive indices (n) for amber vary from 1.489 to 1.507.

Because of the small amounts of amber available for investigations (a dozen or so grains), the aromaticity index could not be determined by X-ray diffraction method. Therefore, infrared absorption spectroscopy was employed to obtain further data.

Infrared spectra were recorded in a C. Zeiss UR-10 spectrometer between 700 and 3800 cm^{-1} ($\lambda = 14.3 - 2.6$ µm). The samples were prepared in KBr discs (1 mg of substance and 300 mg of KBr). The spectra obtained (Fig. 2) were interpreted basing on the papers of Czerski, Czuchajowski (1962), Gadsden (1975), Murchison (1966), Silverstein (1970), Ratajczak (1968), Urbański *et al.* (1971).

It has been found that the spectra of light (yellow) and dark (brown) ambers show close similarity in the position and intensity of the bands. The only differences noted are due to the presence of mineral admixtures — quartz, kaolinite and calcite, which have been already detected by microscopic examinations. To obtain the comparative data, spectroscopic analyses were also carried out on a present-day pine resin derived from the Baltic coast and on resin occurring in bituminous coal (the coal-bearing Carboniferous formation, Upper Silesia).

In the spectra of ambers from Bolesławiec the following absorption bands are present: 740—840, 920—980, 1040, 1090, 1120—1180, 1210—1230, 1265, 1320—1350, 1380, 1410, 1450—1470, 1510—1560, 1650, 1694, 1730, 2850—2870, 2930 cm^{-1}. Besides, a band 2320—2370 cm^{-1} has been recorded, which is due to absorbed CO$_2$.

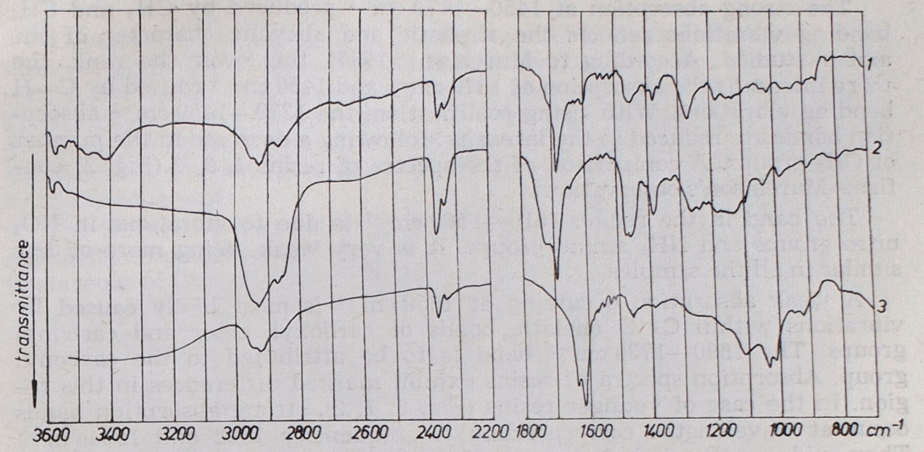

Fig. 2. IR spectra of
1 — resin from present-day pine tree derived from the Baltic coats, *2* — amber from Bolesławiec (Cretaceous), *3* — resinite from bitumineous coal (upper Carboniferous)

Bands in the region between 740 and 890 cm^{-1} with peaks at 820, 860, 880 cm^{-1} are caused by C—H groups in the polycyclic aromatic compounds. They also appear in the spectra of Baltic pine resin and resinite. The band at 920—980 cm^{-1} is attributed to CH=CH$_2$ and CH=CH vibrations and to vibrations in the COOH carboxyl groups. The absorption between 1010 and 1030 cm^{-1} is produced by vibrations in the CH=CH$_2$ or alcohol groups. It is interesting to note that in all the three spectra (Fig. 2) there appears a peak (1030 cm^{-1}) in that region owing to the presence of kaolinite; it coincides with the actual absorption band of organic compounds. The clearest spectrum is yielded by the present-day resin.

The absorption centered close to 1080—1090 cm^{-1} arises from SO$_3$H sulpho groups. It is weak in the spectra of younger resins and absent in the spectrum of resinite.

The band in the region between 1120 and 1180 cm^{-1} is produced by C=O bonds in phenol groups and aromatic ethers. The intensity and shape of this absorption are variable. It is most pronounced in the spectrum of present-day resin (peaks at 1125, 1155, 1180 cm^{-1}). The same observations have been made for the bands occurring at 1210—1230 cm^{-1}, which correspond to bending vibrations of OH phenol groups. These absorptions are not pronounced, being absent altogether in the spectrum of the Carboniferous resinite.

The 1265 cm^{-1} (amber from Bolesławiec) and 1280 cm^{-1} (present resin) bands arising from C—O stretching vibrations and OH bending vibrations in COOH carboxyl groups show a different behaviour. In the present-day resin these bands increase in intensity while their absence in resinite testifies to a decrease in the amount of the substance containing carboxyl groups.

The absorption in the region 1320—1385 cm^{-1} is caused by C—CH$_3$ vibrations. It is the most intense and pronounced in amber from Bolesławiec.

The strong absorption at 1450—1470 cm^{-1} produced by CH_2 and CH_3 bending vibrations reflects the aliphatic and alicyclic character of the amber studied. According to Murchison (1966), the lower the rank, the more intense is the absorption at 1370 cm^{-1} and 1450 cm^{-1} caused by C—H bending vibrations. With rising coalification, the 1370—1450 cm^{-1} absorption bands are reduced in the intensity, following a decrease in the number of CH_3 groups. A comparison of the spectra of resins *1, 2, 3* (Fig. 2) confirms Murchison's observations.

The band in the region 1510—1560 cm^{-1} is due to vibrations in NO_2 nitro groups and NH_3 amino groups. It is very weak, being more or less similar in all the samples.

A weak absorption occurring at 1650 cm^{-1} is most likely caused by vibrations within C=O chelatic bonds of carboxyl, ester and carbonyl groups. The 1690—1730 cm^{-1} band is to be attributed to the carbonyl group. Absorption spectra of resins exhibit marked differences in this region. In the case of younger resins (Fig. 2, *1, 2*), strong absorption bands occur at wavelengths corresponding to frequencies 1692 and 1694 cm^{-1}. They evidence the aliphatic nature of the resins studied. A high content of acid and ester groups is, according to Murchison (1966), characteristic of the lowest rank resins, which display strong absorption at 1694—1702 cm^{-1}. Similar effects in the range of wave numbers 1700—1715 cm^{-1} have been recorded by Ratajczak (1968) for walchowite and neudorfite from Czechoslovakia and by Urbański *et al.* (1971) for succinite and gedanite (Baltic ambers).

A different spectrum in the region discussed is yield by the Carboniferous resinite which displays absorption at 1620 cm^{-1}. A shift of the band assigned to the carboxyl group to a frequency close to 1600 cm^{-1} reflects some structural changes occurring in the Carboniferous resins. It is feasible that carboxyl groups decrease in number, which provides evidence of advanced *aging* of the resin due to the rising rank. This involves internal estrification — the process of formation of ester (CO) carbonyl groups. Simultaneously, C—C vibrations in the benzene ring have been noted, suggesting some aromatization of organic compounds.

The adsorption appearing in the spectrum of amber from Bolesławiec at 1730 cm^{-1} is caused by C=O stretching vibrations in aliphatic aldehydes.

The 2850, 2870 and 2920—2950 cm^{-1} bands are produced by stretching vibrations in aliphatic CH_2 and CH_3 groups. Those sharp absorptions are overlapped by a very broad and diffuse band between 2400—3600 cm^{-1}. It is regarded as arising from OH groups present within the carboxyl groups engaged in inter- and extramolecular hydrogen bonds.

Infrared spectra have revealed that amber from Bolesławiec is made up of aromatic rings with aliphatic branches consisting of carboxyl, phenol, alcohol and ester groups. Moreover, sulpho groups and an insignificant amount of amino compounds have been ascertained. Worth noting are very intense absorption bands attributed to C=O vibrations in carboxyl groups and aromatic esters, testifying to a high content of acid and ester groups in this amber. This fact suggests that the amber studied is of low rank, which has also been confirmed by chemical analysis made on vitrite occurring in its closest vicinity. The contents of carbon and hydrogen presented on a dry ash-free basis are 74.6% and 6.3%, respectively.

A comparison of the spectra yielded by amber from Bolesławiec with those of present-day resin and Carboniferous resinite has also revealed certain characteristic relationship. It has been found that an increase in the intensity of the bands associated with C=O vibrations in carboxyl groups and aromatic esters is attended by an increase in the intensity of the bands corresponding to C—O stretching vibrations and bending vibrations in acid groups.

The infrared spectrum of amber from Bolesławiec shows the closest similarity in pattern to the spectra of neudorfite and walchowite from the Cretaceous of Czechoslovakia (Ratajczak 1968).

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BURSZTYN Z OSADÓW GÓRNEJ KREDY POŁUDNIOWO-ZACHODNIEJ POLSKI

Streszczenie

Utwory górnej kredy niecki północnosudeckiej są wykształcone jako piaskowce z wkładkami łupków marglistych i margli z fauną morską (cenoman-turon-koniak) oraz jako iły, łupki ilaste i piaskowce ze szczątkami flory (santon). Bezpośrednio po regresji morza kredowego, w dolnym santonie osadziła się paraliczna formacja węglonośna o miąższości 50—100 m, w obrębie której występuje kilka cienkich wkładek węgla brunatnego (fig. 1).

W dolnym pokładzie węgla w próbkach rdzeniowych pochodzących z kilku otworów wiertniczych, znaleziono nagromadzenia małych ziaren i grudek bursztynu. Podano jego charakterystykę makro i mikroskopową oraz przeprowadzono badania metodą spektroskopii absorpcyjnej w podczerwieni. Dla porównania wykonano badania spektroskopowe współczesnej żywicy z sosny rosnącej na wybrzeżu Bałtyku oraz rezynitu występującego w karbońskim węglu kamiennym (fig. 2). Analiza widm absorpcyjnych wykazała, że bursztyn z Bolesławca jest zbudowany z układów pierścieni aromatycznych z alifatycznymi odgałęzieniami, w skład których wchodzą grupy karboksylowe, fenolowe, alkoholowe i estrowe. Porównując widma bursztynu Bolesławca z widmami innych żywic stwierdzono najsilniejsze podobieństwo do neudorfitu i walchowitu z formacji kredowej Czechosłowacji.

OBJAŚNIENIA FIGUR

Fig. 1. Lokalizacja i pozycja stratygraficzna bursztynów górnokredowych w południowo-zachodniej Polsce

S — syntetyczny profil górnej kredy w niecce północnosudeckiej, *1—7* — ogniwa litostratygraficzne opisane w tekście, *I, II, III* — profile litologiczne formacji węgla brunatnego w trzech wybranych wierceniach, *1* — iły i glinki białe i czerwone, *2* — szare iły i iłowce, *3* — pokłady węgla brunatnego, *4* — występowanie bursztynu, *5* — piaskowce, *6* — margle i łupki margliste, *7* — wapienie triasowe

Fig. 2. Widma absorpcyjne w podczerwieni

1 — żywicy współczesnej pochodzącej z sosny wybrzeży Bałtyku, *2* — bursztynu z Bolesławca (kreda), *3* — rezynitu z węgla kamiennego (górny karbon)

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ЯНТАРЬ ИЗ ОСАДОЧНЫХ ПОРОД ВЕРХНЕГО МЕЛА В ЮГО-ЗАПАДНОЙ ПОЛЬШЕ

Резюме

Породы верхнего мела в северо-судетском бассейне представлены светлыми песчанниками с включениями мергелистых сланцев и мергелей содержащих останки морской фауны (ценоман — турон — коньяк) и глинами, глинистыми сланцами и песчанниками с останками растительности (сантон). Непосредственно после регрессии мелового моря в нижнем сантоне отложились паралические угленосные породы толщиной в 50—100 м, в которых содержится несколько тонких слоёв бурого угля (фиг. 1).

В нижнем слое угля в образцах из буренных скважин были обнаружены скопления мелких зёрнышек и обломков янтаря. Была представлена его макро- и микроскопическая характеристика и были проведены исследования методом абсорбионной ИК-спектроскопии. Для сравнения были проведены спектроскопические исследования современной сосновой смолы из деревьев растущих на побережьях Балтийского моря и резинита, который был обнаружен в каменном угле каменноугольного периода (фиг. 2). Анализ спектров поглощания показал, что янтарь из Болеславца построен из системы ароматических колец с алифатическими разветвлениями, в состав которых входят карбоксиловые, феноловые, алкогольные и эфирные группы. Сравнивая спектры янтаря из Болеславца со спектрами других смол было установлено самое большое сходство с нейдорфитом и вальховитом из меловых отложений Чехословакии.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Локализация и стратиграфическое положение верхнемелового янтара в юго-западной Польше

S — Синтетический профиль верхнего мела в северо-судетском бассейне, *1—7* — литостратиграфические звена описанные в статье, *I, II, III* — литостратиграфические профили формации бурого угля в трёх избранных скважинах, *1* — глины и белые и красные глинки, *2* — серые глины и глинистые породы, *3* — залежи бурого угля, *4* — местонахождения янтаря, *5* — песчанники, *6* — мергели и мергелистые сланцы, *7* — триасовые известняки

Фиг 2. Инфракрасные спектры поглощения

1 — современной смолы из сосны растущей на берегах Балтийского моря, *2* — янтаря из Болеславца (меловой период), *3* — резинита из каменного угля (верхний каменноугольный период)