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LITHOLOGICAL AND GEOCHEMICAL FEATURES OF TURONIAN CARBONATES WITH STYLOLITES IN POKUTTYA–BUKOVYNA (UKRAINIAN CARPATHIANS)

CECHY LITOLOGICZNE I GEOCHEMICZNE TUROŃSKICH OSADÓW WĘGLANOWYCH ZE STYLOLITAMI KARPAT POKUCKO-BUKOWIŃSKICH

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Abstract. Chemical analysis of carbonates with stylolites from the autochthon of the Pokuttya–Bukovyna Carpathians showed that the $CaCO_3$ content in the rocks ranges between 68 and 92%, insoluble residue makes 8–32%. Investigation of clayey limestones using the polarizing microscopy allowed to establish that the 0.02–1 mm sized organic debris (foraminifera, gastropods, brachiopods and inocerams) makes 40–55% of the rock. The rest is the matrix represented by pelitomorphic calcite. X-ray diffractometry showed that insoluble residue of the organic-rich clay from stylolites is represented by the hydromicaceous mineral – illite with admixture of organic matter. Results of quantitative spectral analysis revealed the increased iron and strontium (>10 times) content in both limestones and organic-rich clays. Infrared spectrometry of chloroform bitumen extracted from the organic-rich clay from stylolites showed that the dispersed organic matter by its origin consists mainly of planktonogenic (autochthonous) microcomponents and underwent significant postsedimentary transformations: polymerization and oxidation.

Key words: Turonian limestones, stylolites, material composition, Carpathian autochthon.

Abstrakt. Badania składu materialnego węglanów ze stylolitami w Karpatach pokucko-bukowińskich wykazały, że zawartość $CaCO_3$ w skałach waha się od 68 do 92%, a pozostałości nierozpuszczalnej od 8 do 32. Szczątki organiczne wielkości od 0,02 do 1 mm (otwornice, ślimaki, ramienionogi i inoceramy) stanowią 40–55% skały, a reszta to kalcyt pelitomorficzny. Części nierozpuszczalne materiału stylolitów to na ogół minerał hydromikowy – illit oraz materia organiczna, cechująca się zwiększoną zawartością żelaza i strontu (>10 razy). Spektoskopia infraczerwona bituminu chloroformowego zawartego w stylolitach wykazała, że materia organiczna powstała głównie z mikroskładników planktonicznych (autochtonicznych) i uległa istotnym zmianom postsedymentacyjnym: polimeryzacji oraz utleniania.

Słowa kluczowe: wapienie turonu, stylolity, skład mineralny, autochton karpacki.

INTRODUCTION

The Turonian deposits in the autochthon of the Pokuttya–Bukovyna Carpathians have been drilled by deep boreholes. Significant scientific and applied interest to the platform deposits of this region appeared after the discovery of the Lopushna field in 1984, with oil accumulations in the Jurassic, Cretaceous and Paleogene formations. The thickness of Turonian strata within the territory under study varies from 25 to 150 m, average 100 m. The Turonian deposits contain many stylolites filled with organic-rich clay.

Turonian strata with numerous streaks of black clays, which fill the stylolites, are found not only in the Carpathian autochthon, but are widespread within the Volhyno–Podillya Platform, where they are represented by the chalk-like *Pithonella* limestones, 20 to 100 m thick (Gavrilishyn *et al.*,

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1991; Dubicka, Peryt, 2012), comprising a few millimetres to three centimetres thick stylolites.

The existence of "hard ground" fabric in epicontinental Turonian limestones with the streaks of black clays, which fill the stylolites, indicates certain paleoceanographic environments, which resulted in accumulation and fossilization of organic matter on the background of carbonate deposition. Namely, we consider that the streaks of black clays in the sediments of the oxic facies (limestones), are the evidence of short-term sub-phases of the Cenomanian/Turonian oceanic anoxic event. Cretaceous marine organic-rich sediments, whose deposition resulted from global oceanic anoxic events, are known worldwide (e.g. Lancelot *et al.*, 1972; Paul *et al.*, 1974; Schlanger *et al.*, 1973; Schlanger, Jenkyns, 1976), including also SE Poland (Peryt, Wyrwicka, 1993; Peryt *et al.*, 1994). The aim of this study is the investigation of stylolite-bearing Turonian carbonate deposits.

MATERIAL AND METHODS

In order to study the material composition of Turonian deposits and organic matter from stylolites of these rocks, drill core samples have been taken from the following wells: Sviatoslav 3 (1479–1487 m), Lopushna 4 (4166–4174 m), Chornoguzy 3 (1204–1210 m), Chornoguzy 14 (1170–1177 m) and Ispas 7 (897–904 m) (Fig. 1). Twenty-two samples have been studied. Chemical analysis was used to study the carbonate rocks (laboratory of the Department of Sedimentology of IGGCM NAC of Ukraine). Organic-rich clay was taken from stylolites to extract bitumen using the cold extraction method (Korchagina, Chetverikova, 1976). At first, the sample was extracted by chloroform bitumen A and by benzene-ethanol bitumen A. After extraction of bitumen A and treatment of the residue by 10% HCl, bitumen C was extracted by benzene-ethanol. X-ray diffractomentry was used to investigate the insoluble residue of organic-rich clay from stylolites. X-ray investigations were made (laboratory of the Department of Geochemistry of Sedimentary Sequences of IGGCM of NAS of Ukraine, analyst Y. Yaremchuk) using the ADP-2 diffractometer (Fe-anticathode, Mn-filter, 32 kV, 12 mA, counter rate 1 degree/min) on initial samples (fraction <0.01 mm). Infrared spectrophotometry was used to study the chloroform bitumen of organic matter from stylolites, whose structural-group composition, genetic type and extent of transformation were established. Shooting of spectra was made using the UR-20 instrument in a frequency range from 4000 to 700 cm^{-1} (prism NaCl).

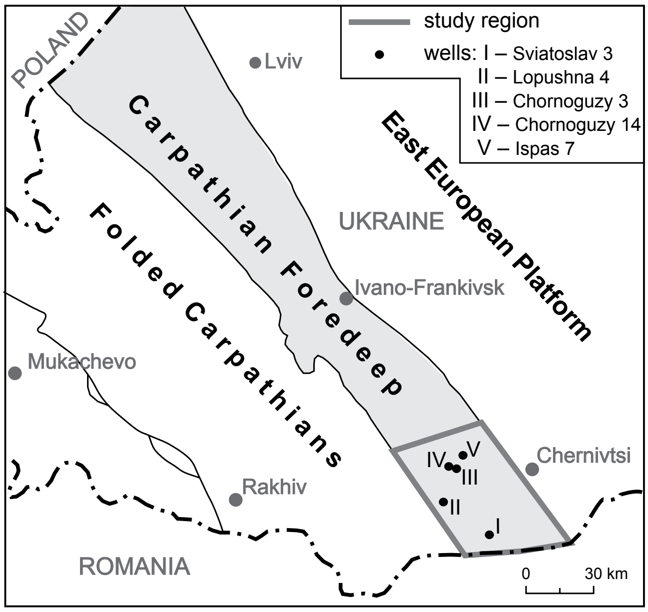

Fig. 1. Sketch map of the study region

RESULTS

MINERALOGICAL PETROGRAPHIC INVESTIGATIONS

Chemical analysis showed that the $CaCO_3$ content in Turonian carbonate rocks ranges between 68 and 92%, insoluble residue makes 8–32%. Clayey limestones are organogenic-detrital, light-grey, non-stratified, massive and stylolitized. The microscopic investigations allowed establishing that the proportion of organic debris in the rock is 40–55%. Rarely, whole carbonate shells are observed, but mainly bioclasts (foraminifera, gastropods, brachiopods, prismatic layer of inocerams), from 0.02 to 1 mm in size, and spheres are present. The matrix of the rock is composed of pelitomorphic calcite (<0.01 mm) within which bioclasts are evenly distributed. Locally, calcite (7–10%) is observed in a shape of tabular grains with dimensions of 0.1–0.2, occasionally 1.2 mm. In limestones, rounded and semi-rounded grains of pale-green authigenic glauconite (1–5%, 0.02–0.2 mm in size) are found. Glauconite fills foraminiferal shells and carbonate spheres. Accessory minerals found in the rock include zircon (up to 0.5%). Ore minerals are represented by pyrite (1–2%), which is evenly distributed in the carbonate matrix.

Stylolites of the Turonian clayey limestones are represented mainly by horizontal toothed stylolitic sutures, 1–5 mm thick; sometimes the stylolites show nodulous fabric. Stylolites are fully filled with organic-rich clay with admixture of pyrite (Fig. 2A, B).

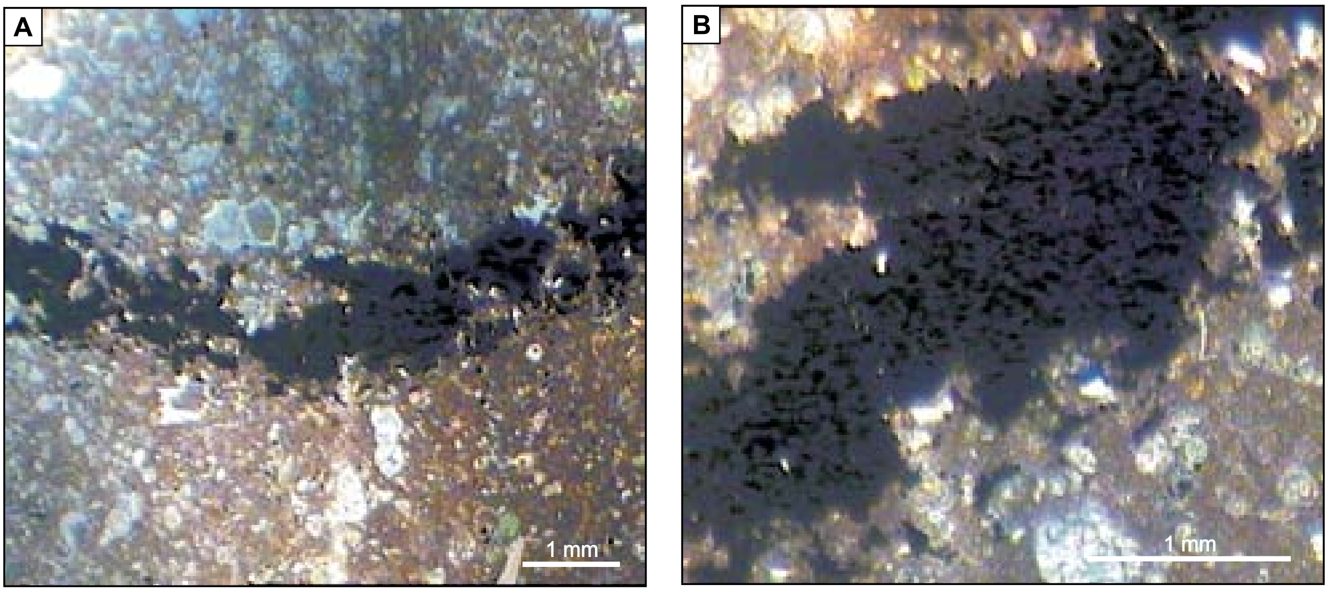

Fig. 2. Horizontal stylolite filled with organic-rich clay with admixture of pyrite

Clayey limestone, Turonian, well Lopushna 4, depth 4166–4174 m. Thin section, without analyser

GEOCHEMICAL INVESTIGATIONS

Organic-rich clay was collected from stylolites to extract bitumen using the method of cold extraction. The following component composition was obtained: chloroform bitumen A – 9–12%, benzene-ethanol bitumen A – 3–4%, benzene-ethanol bitumen C – 1–2%, insoluble residue – 82–85%.

In order to determine the mineral composition of the insoluble residue, the X-ray diffractometry method was used. On the diffractometric curve (Fig. 3) we observe series of basal reflexes 1.0; 0.44; 0.33 nm, which are characteristic of the dioctahedron variety of hydromica of illite type (Drits, Saharov, 1976). Apart from illite, the admixtures of fine quartz, which was diagnosed on reflexes 0.42; 0.334 nm, feldspar (0.324 nm), and organic matter, which is evidenced by a halo of small intensity in the range of angles 22–32°, are observed. Hence, the insoluble residue is represented by hydromica mineral of illite and organic matter.

The trace elements composition of organic-rich clay from stylolites of Turonian carbonate rocks was determined based on the quantitative spectral analysis (laboratory of the Department of Oil and Gas Hydrogeology, Geochemistry and Hydrosphere Protection of IGGCM of NAS of Ukraine, analyst R. Kozak). The following average content of trace elements in the samples of organic-rich clays were determined (in %): Pb – $9x10^{-3}$; Mn – $2x10^{-2}$; Fe – 2.42; Ti – 0.13; Cr – $2x10^{-3}$; Cu – $9x10^{-3}$; Be – $2x10^{-4}$; Co – $3x10^{-3}$; Zn – $1x10^{-2}$; Ni – $6.5x10^{-3}$; V – $6x10^{-3}$; Mo – $6x10^{-5}$; Sr – 0.23; Ba – 1,4x 10^{-2}; Cd – $5.6x10^{-3}$.

Similar investigation of trace elements composition based on the quantitative spectral analysis was made for the carbonate substance of the rock. The established average content of trace elements in the samples of carbonate matter did not differ essentially from the average content of trace

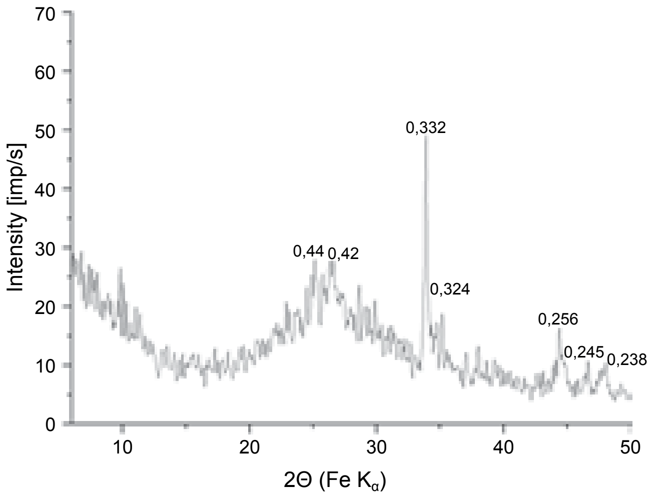

Fig. 3. X-ray diffractogram of the clayey fraction <0.01 mm

Well Sviatoslav 5, depth 1576–1578 m: It – hydromica (illite), Fs – feldspar, Q – quartz; halo of small intensity in the range of angles 22–32° indicates the presence of organic matter in the sample

elements of the organic-rich clay (in %): Pb – $2x10^{-3}$; Mn – $3x10^{-2}$; Fe – 2; Ti – 0.2; Cr – $2x10^{-3}$; Cu – $5x10^{-4}$; Be – $3x10^{-4}$; Co – $8x10^{-4}$; Zn – $1x10^{-2}$; Ni – $1.5x10^{-3}$; V – $2x10^{-3}$; Mo – $6x10^{-4}$; Sr – 0.2; Ba – $5x10^{-2}$; Cd – $4.3x10^{-3}$.

Two kinds of samples, organic-rich clay from stylolites and surrounding carbonate rock, have been compared by the average content of trace elements in the whole, in carbonate rocks, in clay and in organic matter. It was established that the average content of trace elements in the sample does not exceed the average content of trace elements (Vinogradov, 1962) for clayey and carbonate rocks and dispersed organic matter, apart from Fe and Sr. The increased content of iron can be explained by the presence of pyrite in the rock. The content of strontium significantly (>10 times) exceeds the average values for carbonate rocks. It has been established (Yudovich *et al*., 1980) that the Sr content for carbonate deposits has a direct dependence on the content of carbonate (skeletal) matter. If aragonite is prevailing, then the rocks contain a significant amount of strontium, while with a decrease of aragonite, the strontium content is decreasing.

Since stylolites are filled up with organic-rich clay, the chloroform bitumen, which is the most informative, because it is represented by the hydrocarbon compounds, was studied using the method of infrared spectrophotometry. Investigations of the infrared spectra showed the structural and hydrocarbon type content of chloroform bitumen, its genetic type and extent of transformation. Investigations of chloroform bitumen A showed that, in terms of its hydrocarbon type content, it is mainly single-type (Fig. 4). The bitumen contains a great amount of oxygen compounds, which is indicated by an intense absorption band in the range of 1760 cm^{-1}, caused by the stretching vibrations of C = O groups of aliphatic aldehydes, carboxylic acids and aliphatic ethers.

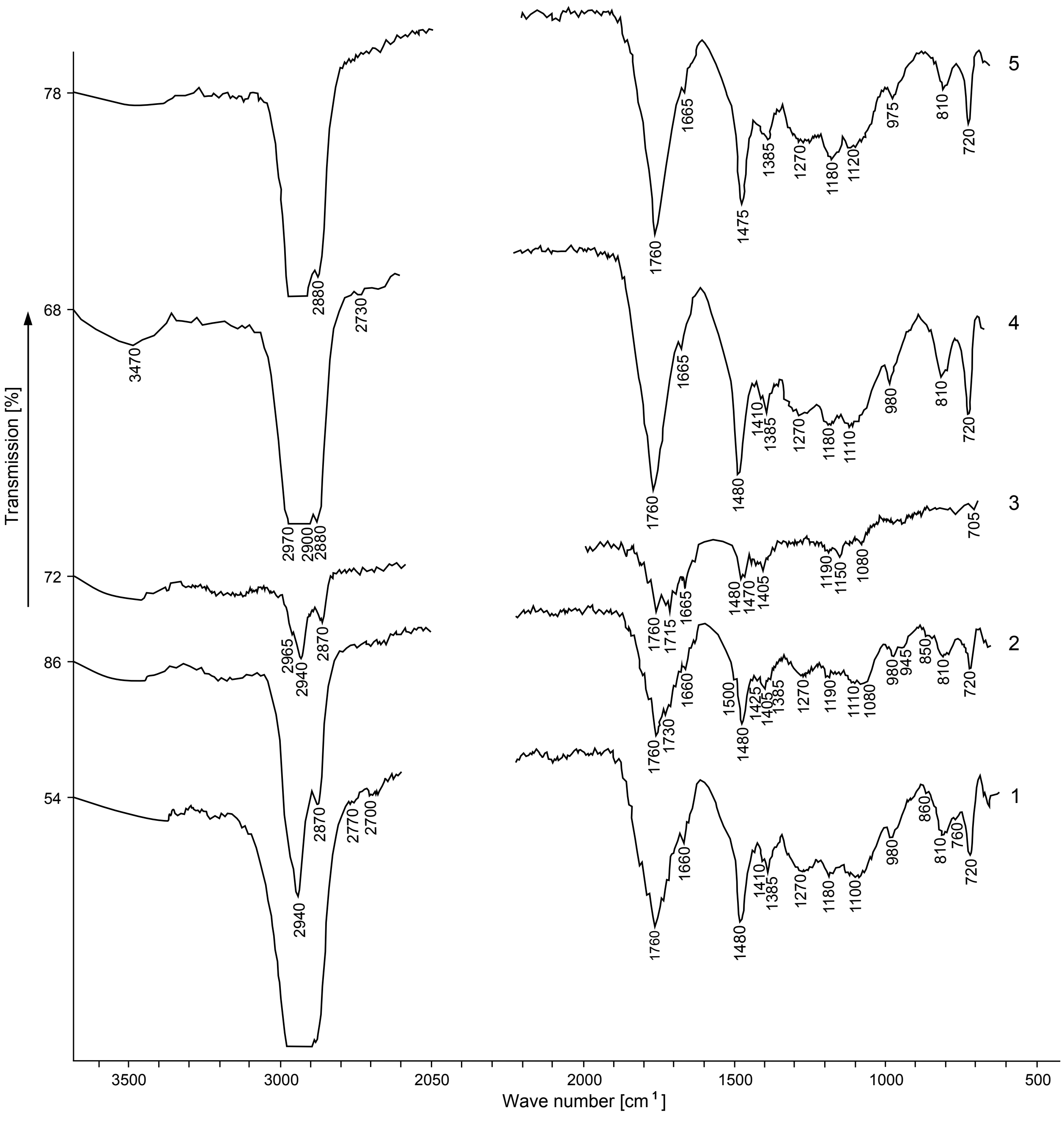

Fig. 4. IR-absorption spectra of the chloroform bitumen A, extracted from stylolites of Turonian clayey limestones

Wells: 1 – Ispas 7 (897–904 m); 2 – Lopushna 4 (4166–4174 m); 3 – Sviatoslav 3 (1479–1487 m); 4 – Chornoguzy 3 (1204–1210 m); 5 – Chornoguzy 14 (1170–1177 m)

Absorption bands of the skeleton of these organic compounds, that is bonds C–C and C–O, are fixed in a range of 1270–1110 cm^{-1}. A wide absorption band of small intensity at 3550 cm^{-1} corresponds to vibrations of the bound OH-hydroxyl group. Absorption bands at 1660 cm^{-1} also confirm the presence of OH groups. Saturated hydrocarbons are characterized by absorption bands in a range of 2900–2800 cm^{-1}, stretching vibrations of aliphatic compounds and deformational vibrations in methane CH_2 and methyl groups CH_3 (1390–1375 cm^{-1}; 1495–1480 cm^{-1}). The characteristic absorption of double-stranded alkanes $(CH_2)_{n\geq4}$ is observed at 725–720 cm^{-1}. Absorption bands at 980 cm^{-1} and 1175 cm^{-1} show the presence of substituted naphthenes – isoalkanes, as well as groups of C–O acids and ethers. All the spectra of these samples indicate the aliphatic nature of the molecules of ether, carboxylic acids and aldehydes. It should be mentioned that in the analyzed IR-spectra, the main absorption bands of the benzene ring of aromatic compounds (3000–3100 cm^{-1} and 1450–1600 cm^{-1}) are lacking. No clear aromatic triplet in a range of 900–700 cm^{-1} is fixed. However, in all the analyzed IR-spectra, a clear absorption band 810 cm^{-1} is present, confirming in this case the bounds of C–H aliphatic class.

Using the reference line method, the optical densities of the absorption bands were calculated. Since bitumen represents a mixture of many compounds and their absorption bands in IR-spectra are complex, one reference line was used for all absorption bands in the frequency range from 700 cm^{-1} to 1800 cm^{-1} (Tab. 1).

For semiquantitative analysis of IR-spectra, a range of spectral ratios were determined for the functional groups, which give the information on the structure of alkane (K_1), quantity of oxygen-containing compounds (K_2), correlation of CH_2 and CH_3 in the paraffin chains (C_3).

The data, given in Table 2, allowed establishing that the proportion of CH_2-groups is higher or equal to the proportion of CH_3-groups, which means that the structures are insignificantly branched (K_1 = 0.49–0.54) and the length of the paraffin chains is sufficiently great (C_3 = 0.65–0.81). K_2 (1.03–1.39) shows a significant amount of carboxylic acids and aliphatic ethers (Bolshakov *et al.*, 1967; Glebovskaya, 1971).

Analysis of the oxygen-containing functional groups showed that in these groups the carboxylic oxygen is predominant, which is included into the structural fragment of fatty acids. This allows concluding that the studied organic matter belongs to the sapropelic type, that is made up of planktonic (autochthonous) microcomponents (Kontorovich, 1976).

Table 1

Normalized optical densities of the main absorption bands of chloroform bitumen, extracted from organic-rich clay, taken from stylolites of Turonian deposits of the autochthon of the Pokuttya–Bukovyna Carpathians

Well	Depth interval [m]	Normalized optical densities for wave numbers						
		1760	1660	1475	1385	975	810	720
Lopushna 4	4166–4174	1.20	0.45	1	0.60	0.30	0.25	0.35
Chornoguzy 3	1204–1210	1.28	0.23	1	0.52	0.31	0.25	0.42
Chornoguzy 14	1170–1177	1.39	0.28	1	0.54	0.24	0.17	0.35
Ispas 7	897–904	1.08	0.33	1	0.49	0.27	0.24	0.33

Table 2

Spectral ratios of chloroform bitumen, extracted from organic-rich clay, taken from stylolites of Turonian deposits of the autochthon of the Pokuttya–Bukovyna Carpathians

Well	Depth interval [m]	Coefficients of relative intensities of bands		
		K_1	K_2	C_3
Lopushna 4	4166–4174	0.49	1.08	0.67
Chornoguzy 3	1204–1210	0.52	1.23	0.81
Chornoguzy 14	1170–1177	0.54	1.39	0.65
Ispas 7	897–904	0.49	1.03	0.67

CONCLUSIONS

The $CaCO_3$ content in the investigated Turonian clayey limestones ranges between 68 and 92%, insoluble residue makes 10–20%. Stylolites in these rocks are represented mainly by horizontal 1–5-mm thick toothed sutures and sometimes by nodulous fabrics. Stylolites are fully filled with organic-rich clay with admixture of pyrite. Bitumen, yield from the organic-rich clay taken from stylolites of the Turonian deposits, is 15–18%, insoluble residue – 82–85%. The insoluble residue of the organic-rich clay is represented mainly by the hydromicaceous mineral of illite and admixture of organic matter. The investigated trace element content in the samples does not differ much between the carbonate rocks and the organic-rich clay and does not exceed the average content established for the trace elements in dispersed organic matter as well as in clayey and carbonate rocks. The increased iron content reflects a significant amount of pyrite in the rock. The strontium content (in %), significantly exceeding (>10 times) the average values for carbonate rocks, is the evidence of the significant role of aragonite in the carbonate (skeletal) material.

The analysis of IR-spectra of the chloroform bitumen A showed that organic matter in stylolites by its origin is composed mainly of planktonogenic (autochthonous) microcomponents. This organic matter underwent essential post-sedimentary transformation: polymerization and oxidation, which is evidenced by a significant amount of oxygen compounds and lack of main absorption bands of the benzene ring of aromatic structures. Benzene compounds are very stable and are broken in the hydrocarbon compounds by the latter. Aniline chains and naphthene rings primarily undergo oxidation, resulting in the formation of oxygen-containing functional groups. Later on, destructive oxidation of the structural links extends towards the opening of the aromatic compounds until the formation of aliphatic dicarboxylic acids and aliphatic ethers, and this is proved by the studied IR-spectra.

The lithological and geochemical investigations of Turonian stylolitized carbonate rocks of the autochthon of the Pokuttya–Bukovyna Carpathians suggest that their formation most likely resulted from the periodical short-term occurrence of anoxia within the Pokuttya–Bukovyna shelf of the sedimentary basin.

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