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# ENVIRONMENTAL CHANGES DURING THE CENOMANIAN–TURONIAN BOUNDARY EVENT IN THE OUTER CARPATHIAN BASINS: A SYNTHESIS OF DATA FROM VARIOUS TECTONIC-FACIES UNITS

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**Abstract:** The paper summarizes the results of author's studies on the environmental changes around the Cenomanian–Turonian Boundary Event (CTBE) in the Outer Carpathian basins located close to the northern margin of the Western Tethys, whose sea floor was situated below the calcite compensation depth. The sedimentary, biotic and chemical records allowed to recognize the successions related to the oceanic anoxic event (OAE-2) and trace changes around this event sediments within the frame of the stable carbon isotope excursion and biostratigraphic datum events. The changes so traced included changes in: type of deep-water sedimentation, accumulation rate, productivity, oxygenation of bottom water and benthic foraminiferal assemblages.

Correlation of the palaeoenvironmental changes with the carbon isotope curve and biostratigraphic datum events allowed the comparisons between the various sedimentary areas in the Outer Carpathians, and with other areas of the Western Tethys. Most of the interpreted events around the CTBE were synchronous in the northern branch of the Western Tethys that extended to the Umbria–Marche and Sicily carbonate platforms. These events included: (1) an increase in productivity before the interval with the highest shift in $\delta^{13}C$ values, (2) the main interval of organic-rich sedimentation (Bonarelli level), (3) a rapid change to oxygenated sediments near the Cenomanian–Turonian (C–T) boundary and continued during the Early Turonian, (4) fluctuations in oxygen content in bottom waters with short intervals of anoxia during the earliest Turonian, (5) deposition of a thick bentonite layer, near the start of the $\delta^{13}C$ excursion, roughly synchronous with the phase of a positive shift in Pb isotopic compositions in the silicate sediment fraction in one of the Umbria–Marche sections, (6) an interval of extremely low hemipelagic sedimentation with hiatuses near the base of the C–T boundary and during the earliest Turonian, correlated with the maximum rise of the sea level.

The presented data from the Outer Carpathians suggest that the OAE-2 could be triggered by enhanced productivity; however, subaerial volcanic eruptions, accompanied by hydrothermal activity and formation of large igneous provinces could also be a factor which enriched the ocean-atmosphere system in $CO_2$. Sluggish deep-water circulation, probably deteriorating through the Late Cenomanian, favoured preservation of organic matter during the latest Cenomanian. The mechanism of rapid oxygenation of bottom waters near the C–T boundary was related to recurrent inflows of (?)saline warm and oxygenated waters.

**Key words:** Cenomanian–Turonian boundary event, stratigraphy, palaeoenvironment, Late Cretaceous, Outer Carpathians, Poland.

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## INTRODUCTION

The widespread accumulation of organic carbon-rich sediment accompanied by a positive $\delta^{13}C$ excursion in marine carbonates and organic matter across the Cenomanian–Turonian boundary (Late Cretaceous) is one of the most prominent episodes of the Mesozoic, described as the Oceanic Anoxic Event (OAE-2) by Schlanger and Jenkyns (1976) or as the "Cenomanian–Turonian Boundary Event" (CTBE) by Thurow and Kuhnt (1986). This event represents period during which oceanic bottom waters became depleted in oxygen for a long time and it involved disturbances in various groups of organisms (e.g., Kaiho, 1994; Hallam & Wignall, 1997; Peryt, 2004). The CTBE was also

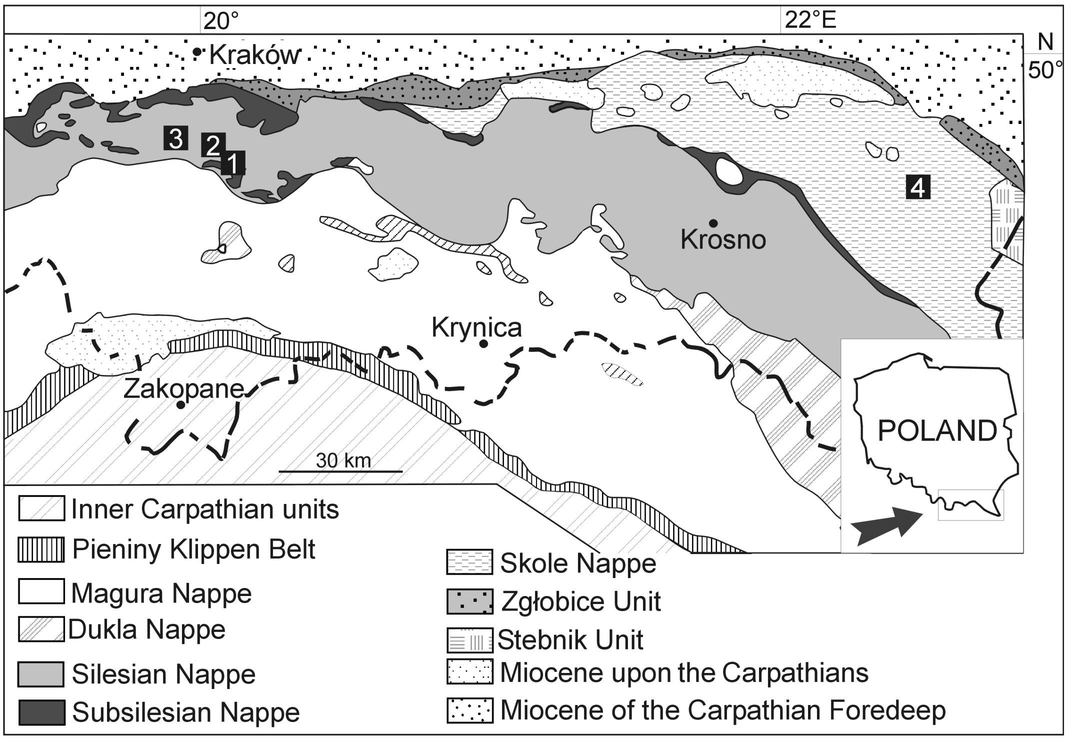


**Fig. 1.** Geological sketch-map of the Polish Carpathians (after Żytko, 1999) with location of the studied sections: 1 – Zasań, 2 – Trzemeśnia, 3 – Barnasiówka-Ostra Góra and Barnasiówka-Jasienica, 4 – Spława

time of climate perturbation on a global scale, linked with changes of oceanic water temperature (Arthur *et al.*, 1988; Norris & Wilson, 1998; Norris *et al.*, 2002; Voigt *et al.*, 2003; Gustafsson *et al.*, 2003) related to changes in atmospheric $CO_2$-partial pressure (e.g., Barron *et al.*, 1995; Huber *et al.*, 1995; Bice & Norris, 2002). Various triggering mechanisms have been proposed so far for OAE-2: (1) increased oceanic $CO_2$ derived from activity of large igneous provinces (e.g., Sinton & Duncan, 1997; Kerr, 1998) involving subaerial volcanism (Kuroda *et al.*, 2007) and hydrothermal activity (Snow *et al.*, 2005), (2) increased productivity (e.g., Larson & Erba, 1999; Kuhnt *et al.*, 2005; Mort *et al.*, 2007), and (3) increased potential for organic matter preservation due to water-column stratification and low bottom-water circulation (e.g., Bralower & Thierstein, 1984; Sinninghe Damsté & Köster, 1998).

The CTBE was recorded mostly from epicontinental seas, marginal shelves, and carbonate platforms of the Tethyan and Atlantic oceans (e.g., Jenkyns, 1980; Arthur & Premoli-Silva, 1982; Herbin *et al.*, 1986; Kuhnt *et al.*, 1990; Luciani & Cobianchi, 1999; Strasser *et al.*, 2001; Lüning *et al.*, 2004; Scopelliti *et al.*, 2004; Erbacher *et al.*, 2005; Kolonic *et al.*, 2005; Bąk K. *et al.*, 2005; Wójcik-Tabol, 2006). Scarce data are known about this event in deep-water environments below the calcium compensation depth (CCD). Most of them are related to the North and Central Atlantic, where sections are strongly condensed (e.g., Kuhnt *et al.*, 1990) or, most frequently, hiatuses are present (e.g., Graciansky *et al.*, 1987). Deep-basin sediments are also known from other parts of the Western Tethys (Herbin *et al.*, 1986; Thurow *et al.*, 1988; Kuhnt *et al.*, 1990), but only black shales from these successions have been studied so far, for organic matter content and type of kerogene. The sedimentary and biostratigraphic studies carried out in the Outer Carpathians (Bąk K. *et al.*, 2001) allowed to recognize those parts of the deep-water sedimentary successions which represent the CTBE from an environment close to the northern margin of the Western Tethys. The later studies were carried out by the author (Bąk K., 2006, 2007a, b, in press) in selected sections in three tectonic-facies units of the Polish Outer Carpathians (Fig. 1) that correspond to two marginal basins and a submerdged ridge. The studies were focused on interpretation of palaeoenvironmental changes around the CTBE. This paper summarizes the sedimentary, biotic and chemical records across the C–T boundary (CTB) in the Outer Carpathians and shows the correlation of the environmental changes at that time with the orbital time scale, based on the stable carbon-isotope and biostratigraphical data.

## FACIES SUCCESSION AROUND THE CENOMANIAN–TURONIAN BOUNDARY IN THE OUTER CARPATHIANS

All the sections in the Outer Carpathians around the CTB display a similar facies succession that includes a series of organic-rich shales, followed by ferromanganese sediments. The CTB sediments in this area were included into the Barnasiówka Radiolarian Shale Formation (BRSF;

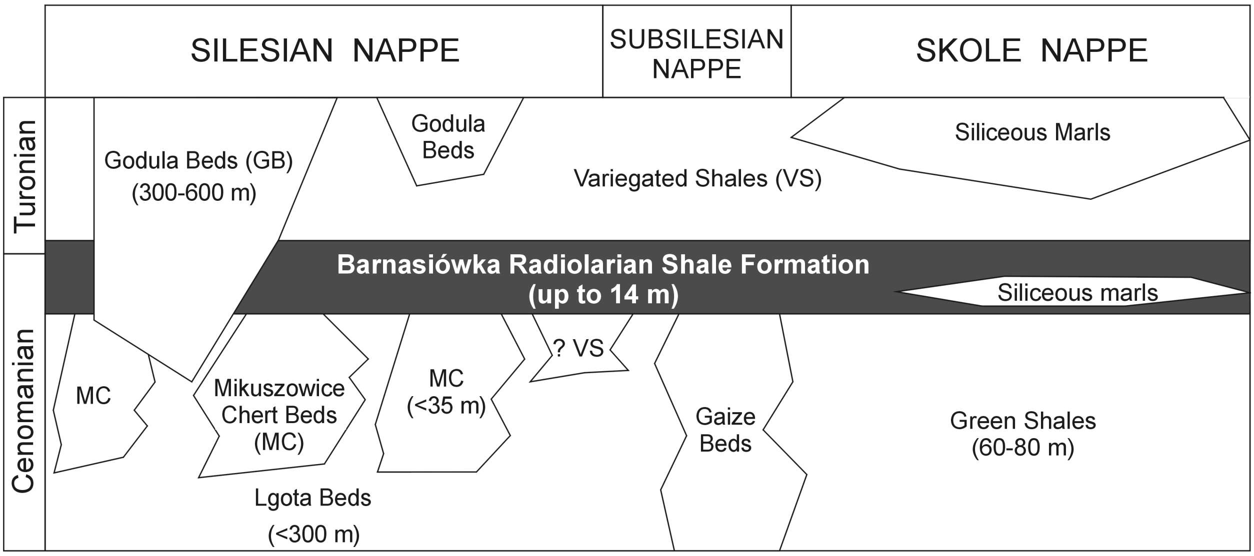


**Fig. 2.** Lithostratigraphy of the Cenomanian–Turonian sediments in the Polish part of the Outer Carpathians (after Koszarski & Ślączka, 1973; Kotlarczyk, 1978; Gucik, 1987; Gucik *et al.*, 1991; Bąk K. *et al.*, 2001

Bąk K. *et al.*, 2001). This unit was recorded in three of the four nappes in the Polish part of the Outer Carpathians (the Skole, Subsilesian and Silesian nappes; Fig. 2). It probably occurs also in another major tectonic unit, the Magura Nappe, but strongly tectonically sheared sections from this nappe (Oszczypko *et al.*, 2004) preclude such correlation.

The sections of the CTB sediments come from two basinal settings: the Skole Basin (Spława section; Bąk K., 2007b, in press), the Silesian Basin (Barnasiówka-Jasienica, Barnasiówka-Ostra Góra and Trzemeśnia sections; Bąk K., 2007a), and the the Subsilesian submarine ridge (Zasań section; Bąk, K., 2006) (Fig. 3). In all these sections, the Upper Cenomanian successions consist of thin-bedded turbidites which contain mainly biogenic material, rich in sponge spicules, radiolarians, calcareous benthic foraminifers, non-keeled planktonic foraminifers and calcareous nannoplankton. Siliciclastic grains include mainly quartz and glauconite. The turbidites were laid down in deep-water conditions, on a sea floor below the CCD. The hemipelagic sediments that alternate with the turbidites are non-calcareous radiolarian-rich green shales. This succession includes also thin layers of black organic-rich shales, whose number increases significantly up the sections.

There is a gradual passage from the turbidite (or calciturbidite) to the organic-rich facies, which is 2–3 m thick. This facies contains organic-rich shales with TOC values attaining 8%, intercalated with green radiolarian shales and bentonites. This facies is correlated with the Bonarelli level of the Umbria–Marche area, Italy (Arthur & Premoli Silva, 1982).

In all the studied sections, the organic-rich sediments are followed by a Fe-Mn layer with macronodules, up to 9 cm thick. The nodules are built of Ca-rhodochrosite crystals in their cores, and of Fe-Mn oxides-hydroxides, as pseudomorphs after Mn carbonates, in their outer black rims. These Fe-Mn sediments are followed by red and green parallel- laminated shales (40–90 cm) which include Fe and Fe-Mn incrustations and micronodules, followed in turn by orga- nic-rich shale and the second Fe-Mn layer with macronodules at the top. The overlying succession of Variegated Shales consists of hemipelagic red and green non-calcareous shales and of turbidites with sponge spicules and siliciclastic material, with sporadic intercalations of organic-rich shales.

**Table 1**

Number of samples used in various micropalaeontological and geochemical studies (Bąk, 2006, 2007a, b, in press)

| | Microfossil analyses from extracted samples | Microfacies analyses from thin sections | $\delta^{13}C$ analyses | Pyrolitic analyses and TOC measurements | Bulk chemical analyses | XRD analyses |
|---|---|---|---|---|---|---|
| Trzemeśnia - Barnasiówka composite section | 77 | 106 | 30 | 46 | 59 | 4 |
| Spława section | 47 | 46 | 18 | 13 | 45 | 6 |
| Zasań section | 28 | 15 | 23 | 6 | 6 | 16 |

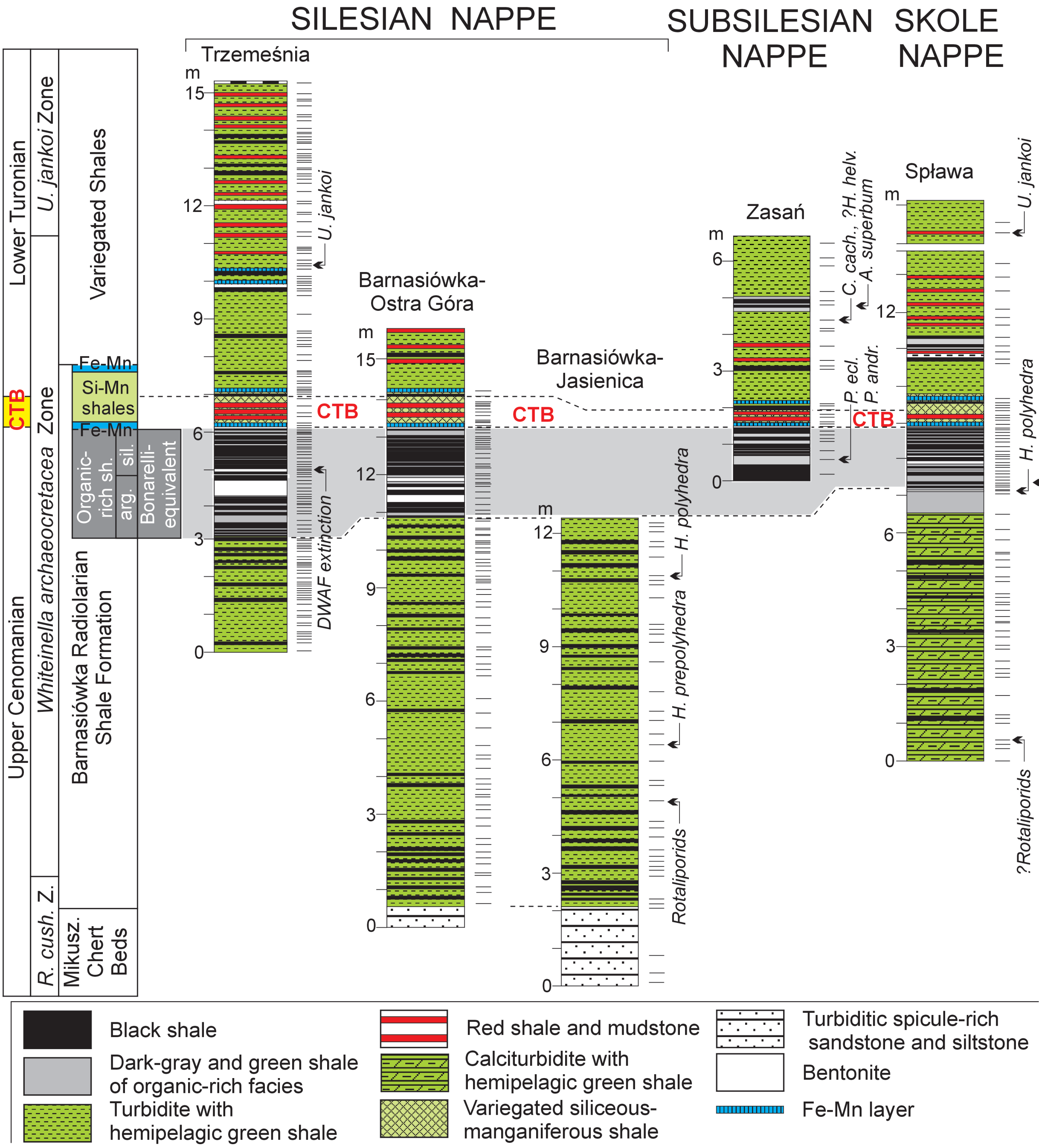


**Fig. 3.** Correlation of the studied Upper Cenomanian–Lower Turonian sections in the Polish Outer Carpathians with foraminiferal and radiolarian datum events; arg – argillaceous, *C. cach.* – *Crucella cachensis*, CTB – Cenomanian–Turonian boundary interval, DWAF – deep-water agglutinated foraminifers, *H. helv.* – *Helvetoglobotruncana helvetica*, Mikusz. – Mikuszowice, *P. andr.* – *Patellula andrusovi*, *P. ecl.* – *Patellula ecliptica*, *R. cush*. Z. – *Rotalipora cushmani* Zone, sil – siliceous, Si-Mn – siliceous – manganiferous. Note that the CTB is placed here basing on the chemostratigraphic data (for details – see Fig. 6). Horizontal lines along the sections point to the samples position (for numbering – see Bąk K., 2006, 2007a, in press)

## MATERIAL AND METHODS

This synthesis is based on various micropalaeontological and geochemical studies in four sections (Table 1). Microfossils (foraminifers and radiolarians) were extracted from 152 samples. Microfacies were analysed in 167 thin sections. Carbon isotope analyses of organic carbon were performed on 71 samples. Rock-Eval analyses were performed on 65 samples to obtain total organic carbon (TOC) content and pyrolitic indices. Bulk chemical composition of sediments was measured in 110 samples and supplemented by point chemical analyses using EDS. Mineral composition of 26 samples was determined by X-ray diffraction analysis (XRD).

## STRATIGRAPHY OF THE C–T BOUNDARY INTERVAL IN THE OUTER CARPATHIANS

### Biostratigraphy

Biostratigraphy of the CTB interval in the Outer Carpathians is based on foraminiferal and radiolarian datum events (Fig. 3). The turbidite succession at the base of the studied sections and the overlying organic-rich facies (Bonarelli-equivalent level) represent the time period after extinction of *Rotalipora* morphotypes, corresponding to the lower part of foraminiferal *Whiteinella archaeocretacea* Zone (Upper Cenomanian). Five radiolarian species appear successively in this succession (Bąk M., 1999, 2000, 2004; Bąk K. *et al.*, 2001; Bąk K. *et al.*, 2005; Bąk M. *et al.*, 2005), including *Hemicryptocapsa prepolyhedra*, *H. polyhedra*, *Pseudodictyomitra tiara*, *Patellula andrusovi* and *P. ecliptica*. Both *Patellula* species appear near the base of the siliceous part of the organic-rich facies (see below). These radiolarian datum events, characteristic also of sections from Umbria–Marche, the North Atlantic Ocean and the Pacific Ocean (e.g., Foreman, 1975; Pessagno, 1976; Taketani, 1982; Thurow, 1988; Marcucci-Passerini *et al.*, 1991; O'Dogherty, 1994; Musavu-Moussavou & Danelian, 2006), correspond to the Upper Cenomanian (summary in Bąk M., 2000, 2004).

The base of the Turonian could not be here unequivocally located because of the rare occurrence of microfossils and their poor state of preservation. The Cenomanian–Turonian boundary lies within a 3–5 m thick succession (Fig. 3) as shown by the datum events of foraminiferal species, such as the extinction of deep-water agglutinated foraminifers and the first occurrences (FOs) of *Uvigerinammina jankoi* and *Helvetoglobotruncana helvetica*. The FO of radiolarian species such as *Crucella cachensis* and *Alievum superbum*, regarded as the markers of the Lower Turonian (Pessagno, 1976; Schaaf, 1985; Thurow, 1988; O'Dogherty, 1994; Erbacher & Thurow, 1997; Bąk M. & Bąk K., 1999; Bąk M., 2000, 2004), confirm the position of the CTB within this interval; it is located in the interval between the top of the organic-rich facies and somewhere in the lowermost part of the Variegated Shales.

### Chemostratigraphy

More precise stratigraphy of the CTB interval in the Outer Carpathians is enabled by stable carbon isotope data. This is related to the worldwide carbon excursion which took place in the latest Cenomanian (e.g., Scholle & Arthur, 1980; Arthur *et al.*, 1988; Peryt & Wyrwicka, 1991, 1993; Gale *et al.*, 1993; Jenkyns *et al.*, 1994; Paul *et al.*, 1999; Voigt, 2000; Stoll & Schrag, 2000; Keller *et al.*, 2001, 2004; Bowman & Bralower, 2005; Erbacher *et al.*, 2005; Fischer *et al.*, 2005; Gale *et al.*, 2005; Kuhnt *et al.*, 2005; Sageman *et al.*, 2006; Voigt *et al.*, 2007). The structure of this curve, recorded at the GSSP section at Pueblo (Colorado, USA; Sageman *et al.*, 2006) and in the reference key sections of this boundary at Wadi Bahlul, Tunisia (Caron *et al.*, 2006) and Eastbourne, England (Gale *et al.*, 2005), enables correlation of these geochemical data with the FO of the ammonite *Watinoceras devonense*, a biomarker of the CTB (Bengston, 1996; Kennedy *et al.*, 2005; Gradstein *et al.*, 2004). This boundary lies close to the maximum peak of $\delta^{13}C$ that terminates $\delta^{13}C$ high values in this section (plateau interval *sensu* Pratt, 1985). A correlation of the organic carbon curves from the Outer Carpathians with the high resolution data from the Pueblo (Sageman *et al.*, 2006), Wadi Bahlul (Caron *et al.*, 2006), Gubbio (Tsikos *et al.*, 2004) and Calabianca (Scopelliti *et al.*, 2004) sections was presented by Bąk K. (2007a, in press). The CTB lies within the 0.5–0.9 m thick interval in the Outer Carpathian sections, between the base of the first Fe-Mn layer and the base of the first organic-rich shale, which directly underlies the second Fe-Mn layer (Fig. 4).

## ENVIRONMENTAL CHANGES DURING THE C–T BOUNDARY EVENT IN THE OUTER CARPATHIAN BASINS

### Organic-rich sedimentation

Black organic-rich shales and mudstones are the most characteristic lithologies in the CTB sections (Fig. 5). The thickest interval with the black shales, 1.8–2.4 m thick, lies between the turbidite (or calciturbidite) succession and the first Fe-Mn layer in all Outer Carpathian nappes (its higher thickness – 3.1 m – in the Trzemeśnia section is due to tectonic repetition). This facies, corresponding to the Bonarelli level in the Umbria–Marche (Appeninnes), contains a dozen or so black shale (mudstone) layers, intercalated with green shales (mudstones, partly bentonites). The microfacies of the green shales (Bąk K, 2006, 2007a, b, in press) display features characteristic of hemipelagic sediments (enriched in radiolarians). However, thin laminae in these shales may have resulted from diluted gravity flows or from action of bottom currents. Black shales are parallel-laminated and less rich in radiolarians. In all sections, two parts of organic-rich facies could be distinguished in relation to the silica content, which increases by about 20% in its higher part (up to 77% in the Barnasiówka-Ostra Góra section). The lower part includes thick bentonite layers, which are practically absent in the upper part.

#### *Timing of the main phase of organic-rich sedimentation with respect to OAE-2 in the Outer Carpathians*

The duration of anoxic conditions and black shale sedimentation during the C–T transition varied from basin to basin, due to differences in regional relief, water depth, cir-

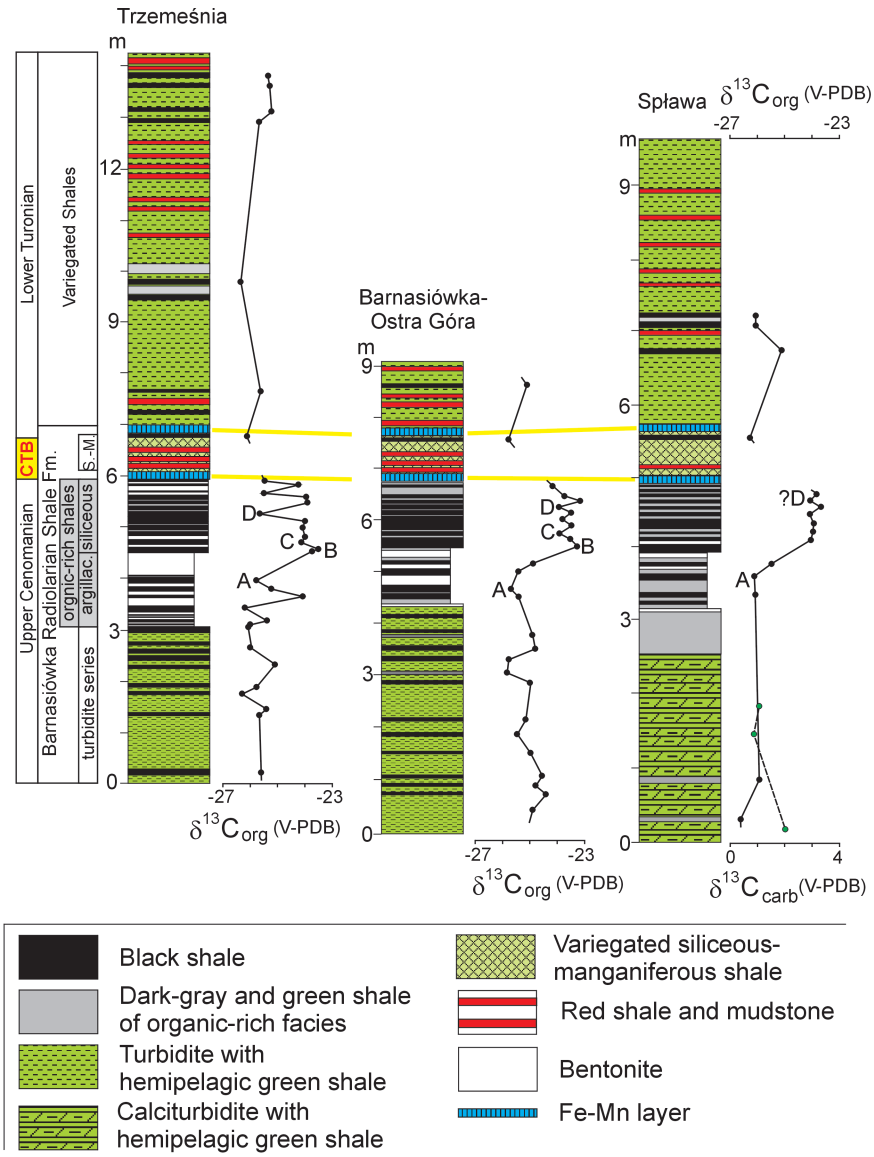


**Fig. 4.** Correlation of carbon isotope data around the Cenomanian–Turonian boundary interval (CTB) in the Polish Outer Carpathians (Bąk K., 2007a, in press). A, B, C, D – chemostratigraphic points used for this correlation

culation and surface productivity (as in shelf basins and slopes across North Africa and deep-sea basins of the adjacent oceans; Lüning *et al.*, 2004). Consequently, there is a question about the relation of the organic-rich strata from the Outer Carpathian basins to the OAE-2, whose definition is based not on the "black shale event" (Herbin *et al.*, 1986) but on the positive carbon-isotope excursion and its complex structure. Recently, two definitions of the OAE-2 were presented in literature. In both the lower boundary is defined similarly, at the beginning of the $\delta^{13}$C excursion (e.g., Kuhnt *et al.*, 2005). The differences concern the end of the OAE-2. In a conservative estimate (Kuypers *et al.*, 2002), the OAE-2 extends up to the end of the "plateau interval" of Pratt (1994) that corresponds to the lower part of the *W. devonense* Zone (Sageman *et al.*, 2006). In the second definition (Sageman *et al.*, 2006), the end of the OAE-2 is placed at the base of the interval with higher $\delta^{13}$C values within the post-plateau isotope interval.

The correlation of the carbon isotope profiles from the Outer Carpathians with other CTB sections (Bąk K., 2007a, in press) shows that deposition of the organic-rich facies is an expression of OAE-2 and it represents the main phase of this event (Fig. 6). The base of the OAE-2 lies within the uppermost part of the turbidite succession (1–1.5 m below its top). Similar position of the base is also recorded from the Bonarelli level in the Umbria–Marche sections (cf. Tsikos *et al.*, 2004). The termination of this event was not recognized here, because of the lack of organic carbon stable isotope data from the oxidized series that overlies the organic-rich facies, and because of the presence of hiatuses re-

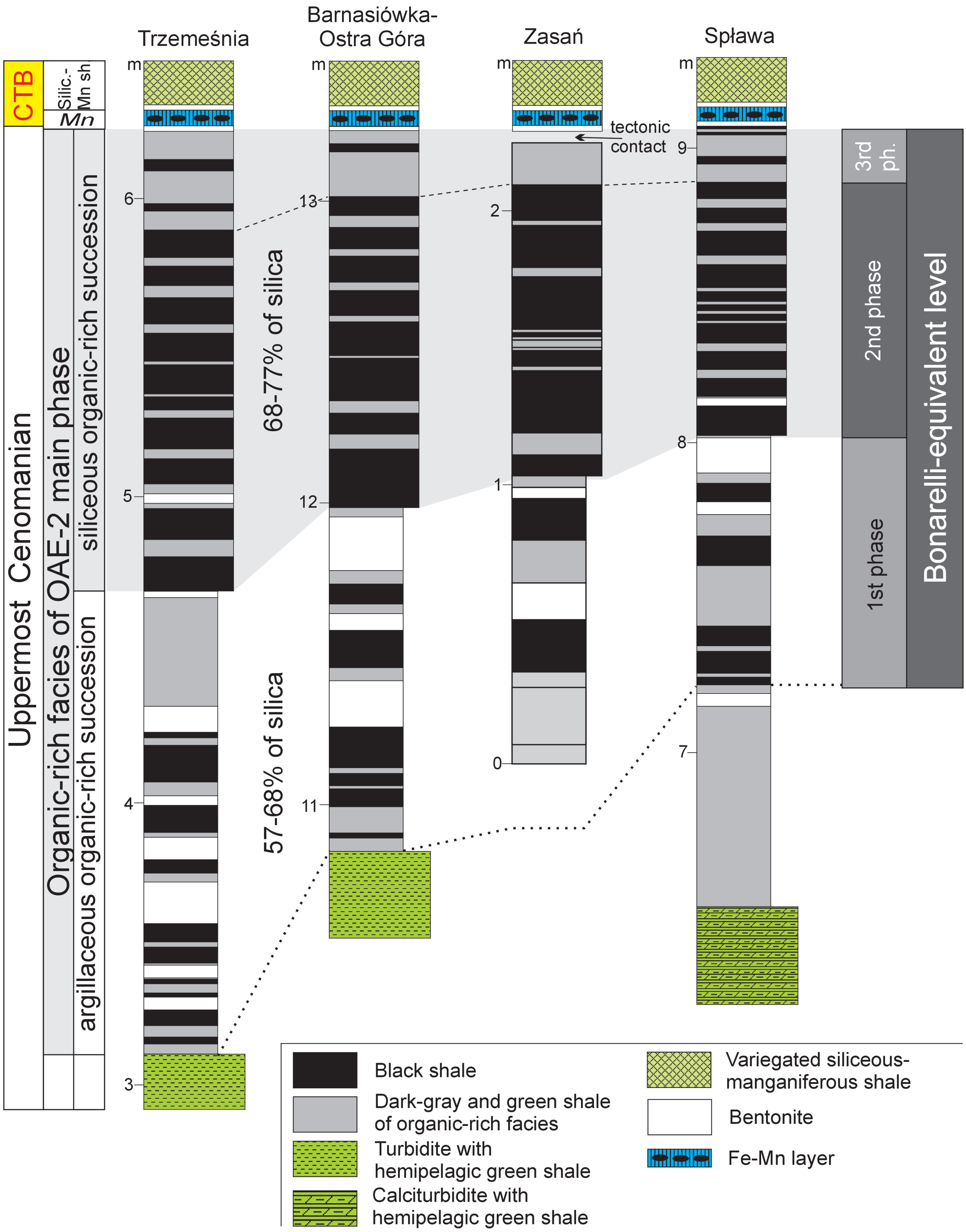


**Fig. 5.** Correlation of the Upper Cenomanian organic-rich facies (Bonarelli-equivalent level) in the Polish Outer Carpathians. Note that the OAE-2 organic-rich sediments at the Zasań section are presented on the basis of new field studies in 2006

flected, among others, by the Fe-Mn layer. The correlation of the carbon curve structure and lithological successions in the Prealpes (Strasser *et al.*, 2001), Umbria–Marche (Tsikos *et al.*, 2004) and Sicily (Scopelliti *et al.*, 2004) sections shows that the main phase of organic rich sedimentation was nearly synchronous in the Western Tethys. It corresponds to the youngest 400–500 kyr of the Late Cenomanian.

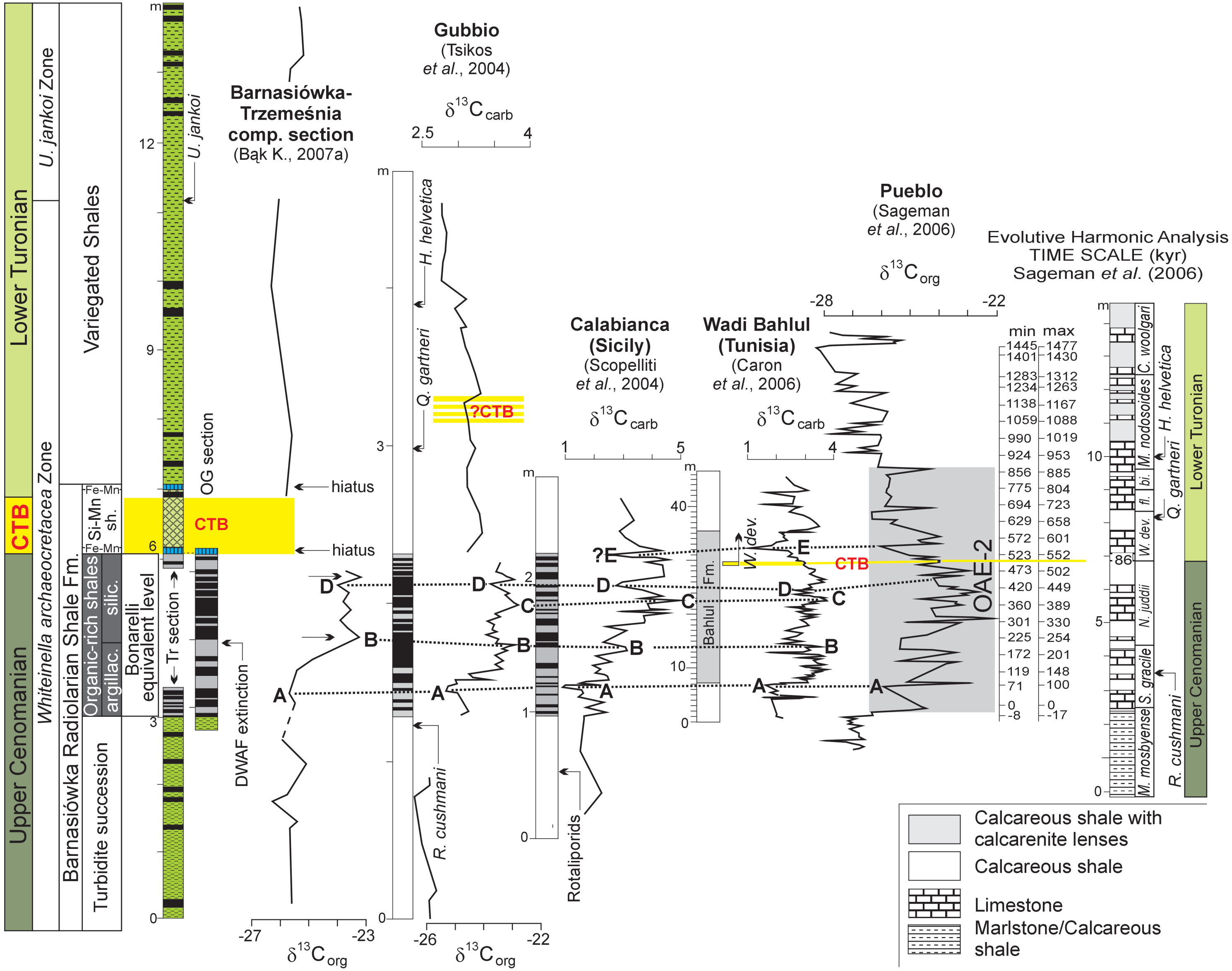


**Fig. 6.** Correlation of the studied CTB sections (Tr – Trzemeśnia, OG – Barnasiówka-Ostra Góra) in the Polish Outer Carpathians (Bąk K., 2007a, in press) with sections from carbonate platforms of the Western Tethys (Gubbio and Calabianca), African epicontinental sea (Wadi Bahlul) and stratotype section at Pueblo; logs with position of organic-rich sediments, selected biostratigraphic datum events and chemostratigraphic events (A, B, C, D); Si-Mn sh. – siliceous-manganiferous shales. For explanations of the Outer Carpathian stratigraphical log – see Fig. 3

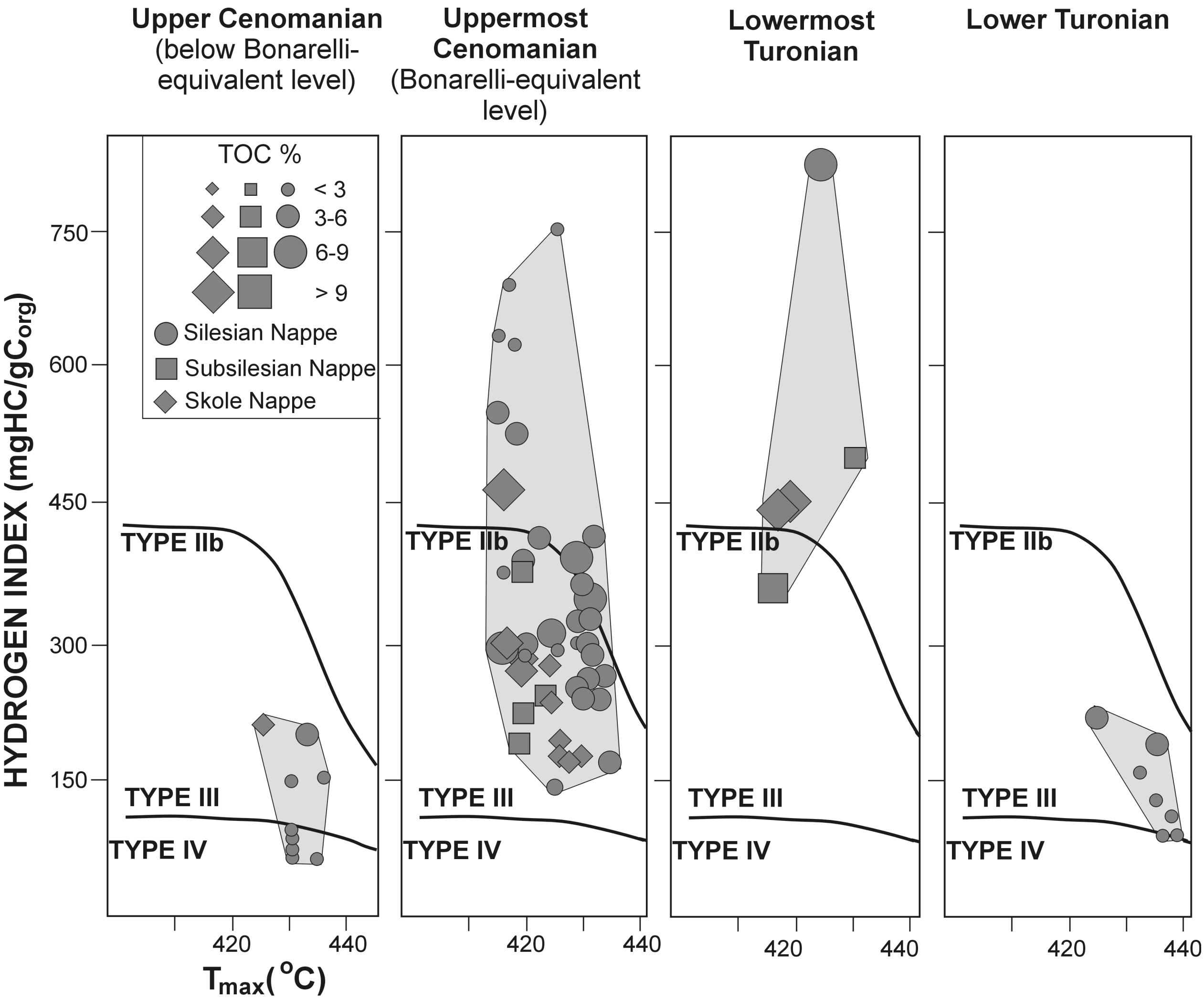


**Fig. 7.** Rock-Eval hydrogen index versus temperature of maximum hydrocarbon evolution of Upper Cenomanian–Lower Turonian organic-rich shales in the Polish Outer Carpathians; type IIb, III, and type IV indicate approximate evolution for different end-member types of sedimentary organic matter as defined by Tissot and Welte (1985)

***Correlation of organic-rich shales in the Outer Carpathian CTBE sections***

Correlation of the organic-rich shales between the Outer Carpathian sections is not possible in the Upper Cenomanian turbidite successions because of the local sea floor relief. Even in the neighbouring sections at the Barnasiówka Ridge (Ostra Góra is 2 km away from the Jasienica section), the number and thickness of black shale layers varies in this succession. The same is true for the organic-rich facies of the Bonarelli-equivalent level. However, in this case, three parts have been distinguished in the black shale interval, basing on changing silica content and thickness of the green shales (Fig. 5). The best correlative black shale horizon occurs at the base of the second Fe-Mn layer, near the top of the BRSF (Fig. 4). It is well recognizable in all studied sections. Most probably this horizon may be correlated with the organic-rich shale in the post-Bonarelli facies, found in the Rotter Satel section of the Prealps (Strasser *et al.*, 2001), and the Rottergraben section of the Helvetic Zone (Wagreich *et al.*, in press) sections. This horizon records decrease in oxygen content during the earliest Turonian high sea level stand. In the Variegated Shales, the number and thicknesses of the black organic-rich shales vary from section to section, being dependent on the size and frequency of turbidity currents.

***Origin, contents and accumulation rate of organic matter***

Pyrolitic analyses of organic-rich shales (Bąk K., 2006, 2007a, in press) demonstrate changes in origin of organic matter supplied to the sea floor during the Late Cenomanian–Early Turonian (Fig. 7). The black shales in the Upper Cenomanian turbidite (or calciturbidite) succession contain relatively small amount of organic matter (TOC values between 1 and 3.5%) of mixed land and marine origin (mainly III type of kerogen). Content of organic matter of marine origin (II type of kerogen) is significantly higher in the black shales of the Bonarelli-equivalent level (TOC values between 3 and 8%). The same type of organic matter occurs in thin black shale layers that directly underlie the second Fe-Mn layer (the top of the BRSF) and in the lowermost part of the Variegated Shales corresponding to the lowermost Turonian. The TOC content in these sediments is the highest in the whole CTB interval, reaching even 18%. The younger, but still Early Turonian, black shales contain less organic matter (TOC between 1 and 3%), and most of them are land-derived.

The presented changes in the type of organic matter in hemipelagic sediments, coincident with fluctuations of accumulation rate, are related to sea level changes around the CTBE and to low tectonic activity in the surrounding areas. Eustatic sea level rise during this event, with its maximum in the earliest Turonian (cf. Jarvis *et al.*, 2006), caused a decrease in supply of siliciclastic material to the Tethyan marginal basins and could promote increased nutrient supply to surface waters that would have supported increased productivity in epicontinental seas and marginal deep basins.

During the Bonarelli-equivalent interval, the calculated mean accumulation rate of organic matter for the black shales was 0.5 g/m$^2$/year in the Silesian and Skole nappes (details in Bąk K., in press). This is slightly higher than in other marginal basins of the Western Tethys (cf. Kuhnt *et al.*, 1990) suggesting enhanced productivity in surface waters.

### Records of primary productivity

Palaeoproductivity around the CTBE in the Outer Carpathians was discussed in details by Bąk K. (2007a, b). According to this discussion, increased productivity during the OAE-2 is well supported by data. The significant increase in surface productivity took place in the interval of the largest positive carbon-isotope shift (interval between points ‘A’ and ‘B’ in Fig. 3). In this interval, the silica and barium indices (Ba/Al and Si/Al ratios), regarded as proxies of primary productivity, show increases of nearly 40% and 20%, respectively. The shift of these values is related to the beginning of the largest eustatic sea level rise (even 40 m during the OAE-2; Jarvis *et al.*, 2006), which favoured organic and siliceous plankton production in the epicontinental seas and marginal basins.

The increase in productivity near the base of the $\delta^{13}C$ positive excursion interval could be nearly synchronous in the Tethyan basins as shown by Mort *et al.* (2007), who analyzed accumulation rates of phosphorus, organic matter, and authigenic phosphate. The rates were rising and arrived at a distinct maximum at the onset of the OAE-2.

A high enrichment in barium, a proxy of productivity, occurs also in the first Fe-Mn layer, lying directly above the Bonarelli-equivalent level at the Spława section, the Skole Nappe. This enrichment is three times higher than that reported from the Pacific and Atlantic oceans (Dymond *et al.*, 1992) and similar to that in well-oxygenated sediments in the Arabian Sea, an area of high primary productivity (Schenau *et al.*, 2001). This supports the suggestion that the increased productivity, at least in the Skole Basin lasted also after the OAE-2, during the earliest Turonian.

The occurrence of numerous radiolarian-rich layers in the whole CTB interval, dominated by small opportunistic specimens of the genus *Holocryptocanium* may reflect an increase in upwelling. However, a comparison of the contents of productivity-sensitive elements in the deep-water sections of the Western Tethys seems to show that primary productivity in the Outer Carpathian basins was lower than in the Umbria–Marche and Sicily basins. These differences could be related to differences in palaeogeographic situations of these areas, namely the more distal position of the Outer Carpathian basin floor in relation to the marginal shelves of the European Platform, which could be areas of high surface productivity. The Upper Cenomanian sediments with abundant radiolarians and coprolites drilled in the Zagórzyce-6 well (Moryc, 1997) may confirm the existence of coastal upwelling with highly productive surface water during this time on the shelf of the European Platform.

### Oxygenation of bottom water

The changes in oxygen content at the sea floor have been interpreted on the basis of deep-water agglutinated foraminiferal (DWAF) assemblages, chemical indices, microfacies and organic matter content in the sediment. Generally, three intervals of various state of oxygenation could be distinguished around the CTBE of the Outer Carpathian basins (see Fig. 8): the first one, characteristic for sedimentation of the Upper Cenomanian turbidite (or calciturbidite) succession, the second one, typical of the latest Cenomanian organic-rich sedimentation, and the third one, characteristic of the earliest Turonian.

During the first interval, Eh fluctuated at the sea floor from oxic to anoxic values. Light-green hemipelagic shales including relatively well diversified DWAF assemblages with infaunal forms record oxic-dysoxic conditions. The moderate-low values of redox indices, such as U/Th and V/(V+Ni), and occurrence of abundant bioturbation of structures confirm this interpretation. On the other hand, the black organic-rich shales (TOC: 1–3.5%) devoid of benthic foraminifers or containing rare and poorly diverse assemblages of Biofacies B *sensu* Kuhnt and Kaminski (1989), with very small silica-cemented forms, are characteristic of oxygen-depleted conditions. High values of chemical redox indices suggest in this case even anoxic conditions. This disagreement with the biotic signal about the Eh values is here interpreted as the long-termed anoxia which caused the organic-rich sedimentation, alternating with short intervals of better oxygenation, probably induced by bottom current activity, which enabled colonization of benthic foraminifers. During the late phase of this interval, temporary disappearance of DWAF is noted; some taxa also became extinct. The abundance and diversity of DWAF gradually decreases (from 15–19 species to 5–7 species).

This Late Cenomanian interval of generally oxygen-depleted conditions could be related to enhanced (?fluctuating) productivity with fluxes of organic matter to the sediments from one side, and to a relatively high potential of oxidation in bottom waters from the other side, which resulted in dysoxic conditions at the sea floor (similar fluctuations of phosphorous contents are described by Mort *et al.*, 2007).

During the main phase of the OAE-2, recorded by the main phase of organic-rich sedimentation (Bonarelli-equivalent level), the number and timing of anoxic (euxinic) periods increased. Taking into account the biotic and chemical redox indices (Bąk K., 2007a, b), this interval could be divided into three subintervals. Firstly, anoxia has been interrupted by longer periods with better oxygenation, marked by deposition of green shales. The dysoxic conditions, probably short-termed, occurred also during the sedimentation of black organic-rich shales (TOC up to 3%), as shown by the occurrence of *Pseudobolivina*-dominated assemblages in this sediment. Such biofacies could be related to the Cretaceous *Gabonita*-biofacies (e.g., Holbourn *et al.*, 1999) and to modern buliminid-bolivinid assemblages in oxygen-depleted areas with enhanced supply of organic matter (e.g., Schumacher *et al.*, 2007). Green shales in the first subinterval of OAE-2 represent periods of low oxygen levels at the sea floor as indicated by the presence of low oxygen tolerant benthic foraminifers of the Biofacies B. The second subinterval with longest lasting anoxic (euxinic) conditions is reflected by a dozen or so thick layers of parallel-laminated black organic-rich shales (TOC: 3–8%), devoid of DWAF. This subinterval begun at the level of the highest shift in $\delta^{13}C$. Anoxia was interrupted by short-termed (?)dysoxic conditions, reflected by dark-green shales. Chemical indices point to slightly better oxygenation during sedimentation of the green shales, though no benthic foraminifers have been found in this sediment. Rare opportunistic DWAF (Biofacies B) appeared during the third, shortest subinterval of OAE-2; they have been found in the thick green shales. The duration of anoxia in this subinterval was shorter, as marked by the thin black shales with a high TOC content (above 5%).

A distinct change in oxygenation is reflected by the earliest Turonian siliceous-manganiferous shale succession that includes the two Fe-Mn layers. This change is marked by the beginning of the Fe-Mn precipitation (for details – see chapter below). The first Fe-Mn layer is overlain by the first red shale layers. Numerous small infaunal DWAF are present at the base of this first red shale, indicating that sea floor was then well oxidized. This DWAF assemblage may be correlated with the initial phase of recovery interval (for data from neritic–bathyal sections see Peryt & Wyrwicka, 1991, 1993). Distinct negative shift in values of redox chemical indices at the base of this succession confirms well oxygenated uppermost part of the sea floor sediment. Surprisingly, the benthic foraminifers disappeared above the mentioned interval, and only a single bed with poorly preserved (?redeposited) specimens is present in the overlying succession of the green and red shales. The chemical redox indices point to decrease in Eh near the sediment surface, which could have influenced the benthic communities. Other factors such as high temperature of bottom water (cf. Gustafsson *et al.*, 2003) and soft substrate (soupground) could be also unfavourable for the DWAF colonization. Short-termed periods of anoxia, marked by thin organic-rich black shales (TOC up to 18%) appeared again in this interval. The well-oxygenated conditions which enabled colonization of diversified DWAF assemblages (late phase of recovery interval) appeared later, during the ?Early–Middle Turonian.

## Sources and origin of detritic material

### *Turbidites and calciturbidites*

Most of the siliciclastic and biotic grains in the arenite, siltite and lutite fractions of the CTB interval successions occur in thin turbidite layers. This detritic material was supplied by diluted and slow suspension flows, as shown by the predominance of parallel lamination and by rare cross lamination in the siltstone and sandstone layers. The thickness and number of the turbidites are highest in the Silesian Nappe, changing from section to section, probably due to various sources of clastic supply and to uneven relief of the Silesian Basin bottom and its surrounding slopes. Composition of the redeposited material and proportion of arenite and siltite to lutite fractions in turbidites changes in the studied CTB interval successions. The Middle–Upper Cenomanian spicule-rich turbidites in the Silesian and Subsilesian nappes (Mikuszowice Chert Beds) are gradually replaced by quartz-glauconitic sandstones rich in silica and biomicrites with numerous planktonic and calcareous benthic foraminifers, radiolarians and some admixture of sponge spicules (Bąk K., 2007a). The similar facies change takes place in the Middle–Upper Cenomanian of the Skole Nappe, where fine-grained and thin-bedded turbidites are replaced by calciturbidites (siliceous marls) built of quartz, calcite, glauconite and fragmented foraminiferal tests, and sponge spicules (Bąk K., 2007b). Lutite fraction of turbidites increases in the Upper Cenomanian successions in all studied sections; marly shales dominate over sandstone (or siltstone) in most turbidite couplets. Biogenic particles are the main components of the turbidites and calciturbidites in the Upper Cenomanian, dominated by non-keeled planktonic foraminifers and associated by calcareous benthic foraminifers, sponge spicules and radiolarians. The number of radiolarians increases upwards in the studied sections, probably reflecting the expansion of oxygen minimum zone at the neritic depths, which resulted in dissolution of calcareous grains in the outer shelf–upper slope environment.

The turbidite sedimentation ceased during the OAE-2 and the earliest Turonian. Only extremely rare currents (?bottom currents) transporting glauconite, quartz and sponge spicules in siltite fraction are recorded in the organic-rich facies and the overlying lowermost part of the Variegated Shales. In the Bonarelli-equivalent level, increased values of chemical indices such as Al/(Al+Fe+Mn) ratio and Rb/Al and good correlation between $Al_2O_3$ and $SiO_2$ have been found in green shales, suggesting times of increased terrigenous supply to the basin floor or increased velocity of bottom currents (Bąk K., 2007a, b).

The deposition of diluted gravity flows returned during the Early–Middle? Turonian. Very fine-grained turbidites include mostly quartz and glauconite; some layers are spiculites; calcareous biogenic particles are absent.

The share of land-derived siliciclastic material was fairly constant during the CTB interval as is shown by the nearly constant values of Rb/Al and Ti/Al ratios along the sections and the strong correlation of $Al_2O_3$ and $TiO_2$ (Bąk K., 2007a, b).

The siliciclastic and biogenic particles were supplied to the Outer Carpathian basins from at least two different sources during the CTB interval. Biogenic particles with admixture of detrital quartz and glauconite grains were transported from the northern margin of the Silesian and Skole basins. The redeposited calcareous benthic foraminifers, consisting mainly of gavelinellids were supplied from neritic-upper bathyal zones (Bąk K., 2007a, b). The source area of this material was the shelf of the marginal part of the European Platform, as inferred from flute cast orientations and from the published data on the transport directions from the neighbouring area (Książkiewicz, 1962). Glauconite-rich sandstones devoid of any biotic components, the second most frequent type of redeposited sediments, may have come from the Silesian Ridge, which was the main source area of this material in younger Turonian through Santonian times. These turbidite layers are here a precursor of the Godula Beds, a thick formation (300–600 m in the studied area) of turbidite glauconitic sandstones and grey-greenish shales deposited in a shifting system of submarine fans, interfingered with non-channelized aprons (Słomka, 1995). Probably, a third source area of redeposited material was an (?)isolated plateau (mound), with floor rising above the CCD. The turbidite layers built of planktonic foraminiferal wackestones may have come from such areas.

***Volcanoclastic material***

Thin layers of bentonite (blue-green argillaceous shale) occur in all studied sections of the CTB interval. Their number and thickness rise in the lower part of the Bonarelli-equivalent level (Fig. 3). The number of bentonite layers in this succession varies in the studied sections and their correlation is not clear. Some of these horizons in the Trzemeśnia section are tectonically duplicated. The only correlative horizons of bentonite occur directly below and above the first Fe-Mn layer (Bąk K. *et al.*, 2001). Petrography of the bentonites in the CTB interval successions have been studied by Koszarski *et al.* (1962), Gucwa (1966), Burtan and Turnau-Morawska (1978) and by Bąk K. (2006). According to Wieser (in Koszarski *et al.*, 1962), all the bentonites have similar mineralogical compositions and come from the same group of volcanics.

The thick bentonite layer in the lowermost part of the Bonarelli-equivalent level could be correlated with a negative shift near the base of the $\delta^{13}C$ positive excursion interval (Fig. 4). This is consistent with a short-termed negative shift in organic carbon at the base of the Bonarelli level in Umbria–Marche that is associated with shifts in Pb isotopic compositions of the silicate fraction (Kuroda *et al.*, 2007). According to Kuroda *et al.* (2007), both shifts can be explained by abrupt increase in relative supply of volcanogenic silicate minerals and $CO_2$ from massive subaerial volcanism, associated with formation of large igneous provinces.

**Accumulation rate**

The calculation of accumulation rate for the Upper Cenomanian turbidite and calciturbidite succession is difficult because of scarce of biostratigraphic and chemostratigraphic data in the Outer Carpathian sections. However, taking into account the assumption that this succession represents most of the Upper Cenomanian and at least the upper part of the Middle Cenomanian (cf. Bąk M. *et al.*, 2005), the accumulation rate could be estimated as ca. 5–7 mm/kyr on the basis of revised Mesozoic chronology (Gradstein *et al.*, 2004). Because the total thickness of turbidite layers is more than 90% in this succession, the estimated value shows that the accumulation rate of hemipelagic sediments during this time was extremely low, not exceeding 1 mm/kyr.

The precise calculation of the accumulation rate is possible for the organic-rich facies (Bonarelli-equivalent level), basing on the correlation of the $\delta^{13}C$ data with the carbon isotope curve and orbital time scale at Pueblo (Sageman *et al.*, 2006; see detailes in Bąk K., 2007a, in press). Using this correlation and taking into account that the present thickness was farther reduced after the early diagenesis, the mean accumulation rate of these sediments may be calculated at *ca*. 3–4 mm/kyr in the Skole Basin and 5–6 mm/kyr in the Silesian Basin. These results show that the accumulation rate increased a few times during the OAE-2 in comparison to the Middle–Upper Cenomanian hemipelagic sediments. The calculated values for the OAE-2 sediments are comparable with other deep-water sections in the Western Tethys (cf. Scopelliti *et al.*, 2004; Kuroda *et al.*, 2005) and much lower than in outer shelf environments, such as Demerara Rise (equatorial North Atlantic; Erbacher *et al.*, 2005), Tarfaya (Morocco shelf; Kuhnt *et al.*, 2005) and shelves in North Africa (Lüning *et al.*, 2004), where accumulation rate was one order of magnitude higher during the latest Cenomanian.

The siliceous variegated shales with the two Fe-Mn layers represent an interval of much lower accumulation rate than the underlying organic-rich facies. The precipitation of Fe-Mn layers with nodules and the occurrence of the Fe-Mn hardgrounds in this succession (Bąk, K., 2007a, in press) prove the presence of hiatuses during the latest Cenomanian and the earliest Turonian. Duration of the hiatuses related to the formation rhodochrosite layers (nodules) may be estimated as at least one hundred thousand years, by comparison with the growth time of rhodochrosite nodules in deep pelagic sediments on the Galapagos Ridge (Morad & Al-Aasm, 1997). This growth time was relatively short comparing to precipitation of Mn oxide-hydroxide in deep-sea nodules and crusts.

The calculation of the accumulation rate for the studied part of the Turonian Variegated Shales is impossible due to the lack of bio- and chronostratigraphic markers. It seems likely that this rate was lower than during the Middle–Late Cenomanian and slightly higher than during the earliest Turonian, taking into account the microfacies observed in this succession, dominated by hemipelagic sediments (Bąk K., 2006, 2007a, b, in press). The accumulation rate gradually increased up section as a consequence of more frequent gravity flows.

### Ferromanganese sediments *vs* CTBE

The characteristic lithological elements in the CTB section of the Outer Carpathians are ferromanganese layers with nodules. Two of them occur in the same stratigraphic position in all studied sections, directly above the top of the Bonarelli-equivalent level, and are separated by a thin (0.5–1.0 m thick) succession of variegated siliceous-manganiferous shales.

The mineralogic and chemical composition of these two layers with nodules, their sedimentary structures and their stratigraphic position in relation to the underlying oxidized sediments (Bąk K., 2006, 2007a, in press) suggest that their present form is mainly due to diagenesis, but their origin was related to changes in sea floor environment. Both Fe-Mn horizons precipitated as the Ca-rhodochrosite (partly siderite) layers. The mechanism of their formation (for details see Bąk K., 2006) was related to the initial stage of bottom water oxygenation in the Outer Carpathian basins, in the terminal interval of the OAE-2. Initially, recurrent inflows of warm, saline oxic water caused precipitation of the Fe-Mn oxy-hydroxides directly above the manganese reduction zone in sediment (or at the sediment/water interface), and the recurrent anoxia caused reduction of the oxides in the high alkalinity environment, facilitating rhodochrosite precipitation at the sediment surface.

The Ca-rhodochrosite layers could be later diagenetically altered to Fe-Mn and Ba-Mn oxides-hydroxides (even recently within the supergene zone) or precipitation of these oxide-hydroxides could be superimposed on chemogenic carbonate precipitation, as is documented for the modern metalliferous crusts in the Kebrit Deep in the Red Sea (Dekov *et al.*, 2007). In such case, the alteration of Mn carbonates to Mn oxide-hydroxides could be related to long-termed oxygenation of bottom and pore-water, due to increase in deep-water circulation. This suggestion is presented on the basis of the occurrence of variegated clays with numerous small infaunal benthic foraminifers in sediments directly above the first Fe-Mn layer. These are the first red shale (oxidized) laminae above the organic-rich facies, and the first appearance of benthic foraminifers in the post-OAE-2 interval. The presented data may reflect significant changes in bottom water hydrodynamics in the Outer Carpathian basins, probably linked with the reorganization of the Western Tethyan palaeogeography, which resulted in extremely low sedimentation rate or even hiatuses, postulated also for the condensed Turonian successions on the European Platform (e.g., Marcinowski & Szulczewski, 1972; Marcinowski, 1974; Jasionowski, 1995; Krajewski *et al.*, 2000). These changes in bottom water activity could be synchronous in the Western Tethys and in the adjacent areas, as is shown by the correlation of manganese maxima around the CTBE that correspond to the end of the carbon-isotope excursion (Bąk K., 2006).

#### *Hydrothermal activity during the CTBE*

Some chemical indices of the Fe-Mn layers, studied in detail in the Zasań and Spława sections, display features typical of hydrothermal origin of Mn, Fe and other metals. However, an unambiguous answer on the existence of such source of metals is not possible because of masking by the prolonged hydrogenous and diagenetic influences. These changes are especially visible when the two layers in the Spława section are compared: the first displays features of hydrogenous to diagenetic sediment, while the second one has features of hydrothermal deposit, similarly as the first Fe-Mn horizon in the Zasań section (Bąk K., 2007 in press).

The proportions of Mn, Fe and (Ni+Cu+Co) place these two Fe-Mn layers in the domain of hydrothermal Fe-Mn nodules and shallow-water diagenetic concretions in the triangular diagram of Bonatti *et al.*, 1972, 1976). A relatively low content of Co, Cu and Zn in the studied Fe-Mn layers is characteristic of hydrothermal crusts (Glasby, 2000). The low value of Co/Zn ratio resembles that of hydrothermal sediments. The low Rare Earth Elements content and a low positive europium (Eu) anomaly with respect to the upper continental crust may also suggest a contribution of a hydrothermal source. On the other hand, the Fe/Mn ratio is lower than in Mn crusts and nodules of the present-day oceans (Glasby, 2000). The studied Fe-Mn layers do not display a distinct negative cerium (Ce) anomaly, and the positive Eu anomaly is not as large as in the modern nodules and crusts of hydrothermal origin. Concluding, some geochemical features may suggest hydrothermal activity around the CTBE. Such activity could have begun during the Albian and lasted through the Turonian, if we take into account the data from various sections in the Outer Carpathians (Gucwa, 1966; Wieser, 1982a, b; Geroch *et al.*, 1985). Hydrothermal activity during the CTBE interval, with maximum near the end of the carbon isotope excursion, was described from the Pacific and Atlantic oceans and also from epicontinental seas (summary in Bąk K., 2006). Most authors linked these hydrothermal vents with rapid formation of the Caribbean igneous province and with activity on mid-oceanic ridges. In the studied area, hydrothermal activity could be facilitated by the maximum rate of the continental crust extension under the Carpathian basins (e.g., Oszczypko, 2004), probably generated by a hot spot, which according to Golonka (2004), now generates volcanism in western Turkey and northern Aegean.

## CONCLUSIONS

The sedimentary, biotic and chemical records across the CTB in the Outer Carpathian basins allowed to distinguish the successions correlated to the OAE-2, and point to the

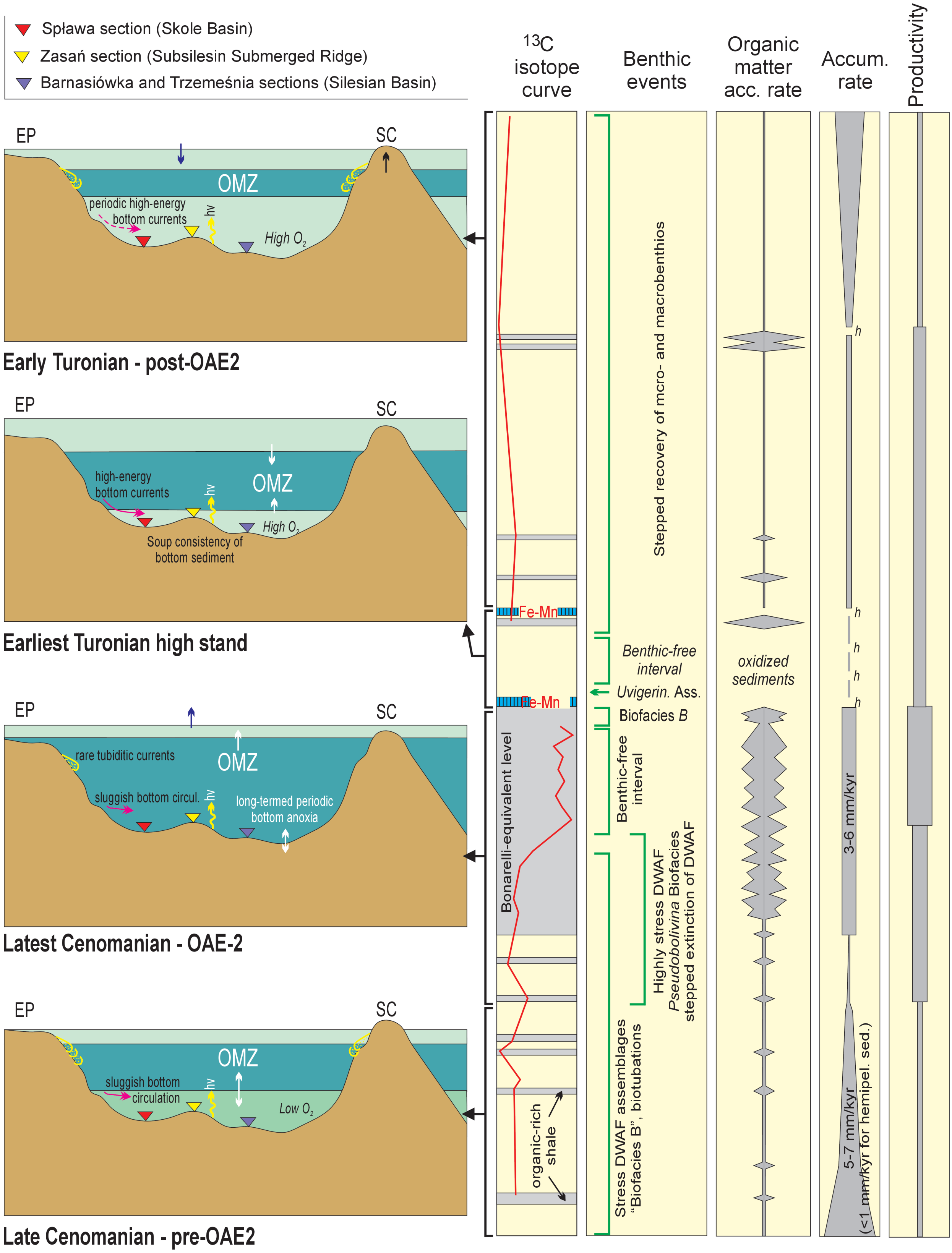


**Fig. 8.** Schematic model to explain biogeochemical observations around the CTB interval in the Outer Carpathian basins. EP – shelves of European Platform, hv – hydrothermal vents, OMZ – oxygen minimum zone, SC – Silesian Cordilliera; h – hiatus

following changes in palaeoenvironment around this event (Fig. 8):

– changes in type of sedimentation, from siliceous hemipelagic sedimentation with rare turbidite (and calciturbidite) events during the Late Cenomanian, through hemipelagic organic-rich sedimentation during the latest Cenomanian, corresponding to the interval of $\delta^{13}C$ positive excursion, to hemipelagic siliceous sedimentation in the Early Turonian;

– changes in accumulation rate, which was generally very low but increased a few times during the latest Cenomanian organic-rich sedimentation up to 3–5 mm/kyr, and decreased (with numerous hiatuses) directly above the CTB;

– changes in productivity, which increased significantly in the Late Cenomanian (0.5 g/m$^2$/year) near the base of the carbon isotope excursion, and remained high also in the earliest Turonian;

– changes in Eh at the sea floor, from low to moderate during the Late Cenomanian with tendency to lowering, including a prolonged phase of anoxia and short-lasting dysoxia at the base of $\delta^{13}C$ excursion interval; rapid oxygenation took place directly above the CTB and continued through younger Turonian times with short anoxic intervals;

– changes in benthic foraminiferal assemblages which followed the changes in oxygenation of the sea floor, with interval of temporary disappearance, which begun near the base of the largest shift in $\delta^{13}C$ and finished within the plateau of the $\delta^{13}C$ excursion, during the latest Cenomanian.

The comparison of the mentioned above palaeoenvironmental changes with the carbon isotope curve and biostratigraphic datum events allowed correlation between various sedimentary areas in the Outer Carpathians, and with other areas of the Western Tethys:

– an increase in productivity before the interval with the highest shift in $\delta^{13}C$ values could be nearly synchronous in the Western Tethyan basins;

– an interval of the main organic-rich sedimentation (Bonarelli level) was also synchronous, at least in the northern branch of the Western Tethys, as far as the Umbria–Marche and Sicily carbonate platforms;

– a phase of oxygenation which began near the C–T boundary and continued during the Early Turonian was also synchronous in the northern branch of the Western Tethys. The fluctuations of oxygen in bottom waters with short intervals of anoxia during the earliest Turonian could occur in the same time;

– a thick bentonite layer near the base of the $\delta^{13}C$ excursion (2$^{nd}$ order negative shift) can be roughly correlated with the phase of a positive shift in Pb isotopic compositions in the silicate sediment fraction in one of the Umbria–Marche sections (Kuroda *et al.*, 2007). This shift was interpreted by these authors as a signal of substantial increase in the supply of silicate minerals from massive subaerial volcanism associated with large igneous provinces in the Pacific and Indian oceans.

– an extremely low accumulation rate with hiatuses near the base of the CTB and during the earliest Turonian post-excursion interval of $\delta^{13}C$ values, reflected by precipitation of Fe-Mn sediments, is correlated with the maximum rise of the sea level, interpreted from epicontinental sections.

Concluding, the presented data from the Outer Carpathians suggest that the OAE-2 could be triggered by enhanced productivity, but sluggish deep-water circulation, probably decelerating through the Late Cenomanian, favoured preservation of organic matter during the latest Cenomanian. It is also possible that subaerial volcanic eruptions associated with hydrothermal activity and formation of large igneous provinces, recorded near the base of the $\delta^{13}C$ excursion, caused massive $CO_2$ degassing, which would have prevented or slowed the formation of deep water, resulting in ocean stratification, as suggested by Kuroda *et al.* (2007).

The mechanism of rapid oxygenation of bottom waters near the CTB was related to recurrent inflows of ?saline warm oxygen-rich waters, coming probably from marginal epicontinental seas, taking into account the mechanism of Fe-Mn layers precipitation.

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## Streszczenie

### ZMIANY W ŚRODOWISKU BASENÓW KARPAT ZEWNĘTRZNYCH W CZASIE GLOBALNEGO ZDARZENIA OCEANICZNEGO NA GRANICY CENOMANU I TURONU; SYNTEZA WYNIKÓW BADAŃ Z RÓŻNYCH JEDNOSTEK TEKTONICZNO-FACJALNYCH

*Krzysztof Bąk*

Rozprzestrzeniona globalnie sedymentacja osadów organicznych w basenach morskich w pobliżu granicy cenomanu i turonu (kreda), której towarzyszyły zaburzenia w zawartości izotopów trwałych węgla w morskich węglanach i materii organicznej były jednym z wyjątkowych epizodów w czasie mezozoiku, które opisano w literaturze jako oceaniczne zdarzenie beztlenowe (OAE-2; Schlanger & Jenkyns, 1976) lub jako zdarzenie na granicy cenomanu i turonu (CTBE; Thurow & Kuhnt, 1986). W literaturze obszaru medyterańskiego jest również ono znane jako zdarzenie Bonarelli (Bonarelli Event). Ten długotrwały epizod niedotlenienia wód dennych, trwający kilkaset tysięcy lat był między innymi przyczyną zaburzeń świata organicznego, zarówno planktonu jak i bentosu morskiego (Kaiho, 1994; Hallam & Wignall, 1997; Peryt, 2004). Był to jednocześnie okres najwyższego poziomu oceanu światowego w historii fanerozoiku oraz okres dużych zmian klimatycznych w skali globalnej, związany z perturbacjami w zawartości $CO_2$ w atmosferze i oceanie (Barron *et al.*, 1995; Huber *et al.*, 1995; Bice & Norris, 2002), prowadzący do dużego wzrostu temperatury wód powierzchniowych i dennych w basenach oceanicznych (Arthur *et al.*, 1988; Norris & Wilson, 1998; Norris *et al.*, 2002; Voigt *et al.,* 2003; Gustafsson *et al.*, 2003). Inny niż obecnie typ cyrkulacji głębokowodnej w tym czasie był przyczyną niskiego gradientu temperatur wód oceanicznych, zarówno w przekroju pionowym jak i w rozciągłości geograficznej.

Przyczyny zaistnienia zdarzenia beztlenowego na granicy cenomanu i turonu są kontrowersyjne i niejednoznaczne. Jako pierwotną przyczynę najczęściej wymienia się wzrost $CO_2$ związany z aktywnością magmową i hydrotermalną w obrębie tak zwanych dużych oceanicznych prowincji magmowych, aktywnością wulkanizmu subpowierzchniowego czy też aktywnością na grzbietach śródoceanicznych (e.g., Sinton & Duncan, 1997; Kerr, 1998; Snow *et al.*, 2005; Kuroda *et al.*, 2007). Niezależnie od przyczyny pierwotnej, kontrowersyjne jest pochodzenie i zachowanie w osadach dużej ilości materii organicznej. Jako przyczynę tego zjawiska wskazuje się tutaj na wzrost produktywności w wodach powierzchniowych oceanu światowego (Larson & Erba, 1999; Kuhnt *et al.*, 2005; Mort *et al.*, 2007) ale i również na wzrost potencjału zachowania materii organicznej w kolumnie wody, związany z jej stratyfikacją i ograniczoną cyrkulacją głębokowodną (Bralower & Thierstein, 1984; Sinninghe Damsté & Köster, 1998).

Zapis oceanicznego zdarzenia beztlenowego na granicy cenomanu i turonu jest znany głównie z osadów mórz epikontynentalnych i obszarów oceanicznych z sedymentacją węglanową (Jenkyns, 1980; Arthur & Premoli-Silva, 1982; Herbin *et al.*, 1986; Kuhnt *et al.*, 1990; Luciani & Cobianchi, 1999; Strasser *et al.*, 2001; Lüning *et al.*, 2004; Scopelliti *et al.*, 2004; Erbacher *et al.*, 2005; Kolonic *et al.*, 2005; Bąk *et al.*, 2005a; Wójcik-Tabol, 2006). O wiele mniej wiadomo jest na temat natury tego zdarzenia w głębokich basenach, z dnem poniżej strefy kompensacji węglanowej, głównie z powodu niewielu odsłoniętych profili osadów lub też kondensacji stratygraficznej i erozji podmorskiej, jakie miały miejsce w tym czasie (Herbin *et al.*, 1986; Graciansky *et al.*, 1987; Thurow *et al.*, 1988; Kuhnt *et al.,* 1990).

Badania terenowe wespół z badaniami biostratygraficznymi prowadzone na obszarze polskiej części Karpat Zewnętrznych (Fig. 1) pozwoliły rozpoznać sukcesję osadów z zapisem zdarzenia z granicy cenomanu i turonu z głębokich środowisk oceanicznych (Bąk K. *et al.*, 2001). Sukcesywne studia wybranych profili osadów z różnych jednostek tektoniczno-facjalnych tego obszaru (Bąk K., 2006, 2007a, b, in press) dały możliwość interpretacji zapisu tego zdarzenia w kontekście zmian środowiska i jego przyczyn, jakie miały miejsce w różnych częściach głębokich basenów, położonych w północnej części Zachodniej Tetydy. Badania te stworzyły ponadto możliwość korelacji zmian w różnych środowiskach głębokowodnych w oparciu o porównanie danych bio- i chemostratygraficznych (Fig. 2). Niniejsza praca stanowi syntezę tych badań.

Profile osadów wokół granicy cenomanu i turonu wykazują bardzo duże podobieństwa we wszystkich badanych jednostkach tektoniczno-facjalnych Karpat Zewnętrznych, odpowiadających trzem strefom sedymentacji w karpackiej części Zachodniej Tetydy, to jest w basenie śląskim, skolskim i na podmorskim grzbiecie podśląskim (Fig. 3, 4). Prawdopodobnie, podobny typ sedymentacji charakteryzował również basen magurski, ale silnie stektonizowane osady jednostki magurskiej (Oszczypko *et al.*, 2004) nie pozwalają na jednoznaczną ich korelację z innymi obszarami Karpat Zewnętrznych.

Szczegółowe badania osadów z zapisem zdarzenia z granicy cenomanu i turonu prowadzono w profilach: Zasań (jednostka podśląska; Bąk K., 2006), Barnasiówka-Ostra Góra, Barnasiówka-Jasienica, Trzemeśnia (jednostka śląska; Bąk K., 2007a) i Spława (jednostka skolska; Bąk K., 2007b, in press). Zestawienie rodzaju analiz oraz ich rozdzielczości przedstawiają Tabela 1 i Fig. 3.

We wszystkich profilach najbardziej charakterystyczną sukcesją litologiczną jest seria czarnych łupków organicznych z przeławicającymi je zielonymi łupkami radiolariowymi (ok. 2 m miąższości), odpowiadająca poziomowi Bonarelii w profilach "środkowej" kredy z pelagicznych platform węglanowych Zachodniej Tetydy. Sukcesja ta reprezentuje maksimum intensywności sedymentacji organicznej w basenach karpackich w czasie zdarzenia oceanicznego na granicy cenomanu i turonu; zawartość materii organicznej sięga tam do 8% (Fig. 5). Innym charakterystycznym elementem wszystkich badanych profili są dwa poziomy Fe-Mn (z konkrecjami) w serii silnie krzemionkowych pstrych łupków (0,5–1 m miąższości), których powstanie miało miejsce bezpośrednio po zakończeniu sedymentacji organicznej. Te dwie charakterystyczne sukcesje osadów leżą w obrębie serii turbidytowych górnego cenomanu–dolnego turonu, zawierających hemipelagiczne łupki radiolariowe (zielone w górnym cenomanie i pstre w dolnym turonie) oraz cienkie horyzonty łupków organicznych.

Stratygrafia osadów górnego cenomanu–dolnego turonu (Fig. 3) jest oparta na zasięgach gatunków wskaźnikowych otwornic (Bąk K., 2006, 2007a, in press) i promienic (Bąk M., 2000, 2004; Bąk K. *et al.*, 2001; 2005b; Bąk M. *et al.*, 2005) oraz na analizie krzywej izotopowej $\delta^{13}$C (Fig. 4; Bąk K., 2007a, in press). Badania chemostratygraficzne dały większą rozdzielczość stratygraficzną dzięki korelacji uzyskanych krzywych z krzywymi $\delta^{13}$C w innych profilach morskich (Fig. 6), w tym z profilem stratotypowym granicy cenomanu i turonu (GSSP) w Pueblo (Sageman *et al.*, 2006). Na tej podstawie powstała możliwość określenia pozycji granicy cenomanu i turonu w profilach karpackich; znajduje się ona w serii pstrych łupków krzemionkowo-manganowych (0,5–0,9 m miąższości), bezpośrednio powyżej serii osadów organicznych. Porównanie krzywych izotopowych z orbitalną skalą czasu opracowaną dla profilu GSSP w Pueblo (Sageman *et al.*, 2006) pozwoliło na oszacowanie czasu sedymentacji organicznej odpowiadającej zdarzeniu anoksycznemu, na ok. 400–450 tys. lat.

Interpretacja struktur sedymentacyjnych, mikrofacji, składu chemicznego i mineralnego osadów, skorelowana z danymi bio- i chemostratygraficznymi wskazuje na liczne zmiany, jakie zaszły w środowisku głębokowodnych basenów Karpat Zewnętrznych w czasie i wokół zdarzenia oceanicznego na granicy cenomanu i turonu (Fig. 8). Są to:

– zmiany w typie sedymentacji; od sedymentacji hemipelagicznej z rzadkimi spływami rozcieńczonych prądów zawiesinowych zawierających bogaty materiał biogeniczny w czasie późnego cenomanu, poprzez sedymentację organiczną (odpowiadającą okresowi wzrostu $\delta^{13}$C) do krzemionkowej sedymentacji hemipelagicznej w czasie wczesnego turonu. Charakter tych zmian jest podkreślony przez różne pochodzenie materii organicznej dostarczanej na dno basenów karpackich (Fig. 7);

– zmiany w tempie akumulacji osadów, które było generalnie bardzo niskie w późnym cenomanie, wzrosło kilkakrotnie w czasie najmłodszego cenomanu (okres wzrostu $\delta^{13}$C) do 3–5 mm/tys. lat i obniżyło się znacząco (z przerwami w sedymentacji) we wczesnym turonie;

– zmiany w produktywności wód powierzchniowych basenów karpackich, ze wzrostem w czasie najmłodszego cenomanu (do ok. 0.5 g/m$^2$/rok), który rozpoczął się na początku okresu z najwyższymi wartościami $\delta^{13}$C i trwał przynajmniej do wczesnego turonu;

– zmiany w natlenieniu wody dennej, od warunków dysoksycznych (z krótkotrwałymi epizodami anoksycznymi) w późnym cenomanie, poprzez długotrwałe okresy anoksyczne z krótkimi interwałami lepszego natlenienia w najmłodszym cenomanie (okres sedymentacji facji organicznych), do warunków dobrego natlenienia dna we wczesnym turonie (z krótkotrwałymi epizodami warunków beztlenowych);

– zmiany w zespołach bentosu otwornicowego, które były pochodną zmian natlenienia wód dennych. Okresy maksimum niedotlenienia dna w czasie interwału z najwyższymi wartościami $\delta^{13}$C (najmłodszy cenoman) wiązały się z zanikiem mikrofauny bentosowej. W czasie wczesnego turonu, warunki stresowe jak wysoka temperatura wód i niesprzyjająca zasiedleniu wodnista konsystencja osadu pomimo dobrych warunków natlenienia dna ograniczały możliwość zasiedlenia dna przez bentos otwornicowy.

Porównanie zmian w środowisku basenów karpackich w czasie i wokół zdarzenia oceanicznego z krzywą izotopową $\delta^{13}$C i danymi biostratygraficznymi pozwoliło na korelację zdarzeń w różnych basenach Zachodniej Tetydy. Wynika z niej, że kilka ze zdarzeń w basenach Zachodniej Tetydy (przynajmniej w jej północnej, karpacko-alpejskiej "gałęzi") było równoczasowych; dotyczy to: (1) wzrostu produktywności w najmłodszym cenomanie (tuż przed okresem wysokich wartości $\delta^{13}$C), (2) okresu maksimum sedymentacji organicznej (poziom Bonarelli), (3) okresu wzrostu natlenienia wód dennych w najmłodszym turonie i krótkotrwałych okresów anoksycznych na dnie w czasie wczesnego turonu. Obecność grubej warstwy bentonitu w najniższej części osadów organicznych (w pobliżu poziomu z najwyższymi wartościami $\delta^{13}$C) może być korelowana ze wzrostem zawartości izotopów ołowiu w krzemianowych minerałach pochodzenia wulkanicznego występujących w poziomie Bonarelli w Północnych Apeninach (Kuroda *et al.*, 2007), co może potwierdzać sugestie o dużym wpływie wulkanizmu powierzchniowego, jako pierwotnej przyczyny, która wywołała perturbacje w zawartości $CO_2$ w późnym cenomanie. Bardzo niskie tempo sedymentacji (z przerwami w sedymentacji) w pobliżu granicy cenomanu i turonu oraz w czasie najstarszej części turonu, które w osadach odzwierciedla obecność serii pstrych łupków krzemionkowo-manganowych z dwoma poziomami warstw Fe-Mn jest korelowane z najwyższym poziomem morza w czasie maksymalnej fazy transgresji.

Prezentowana synteza badań w profilach górnego cenomanu–dolnego turonu w polskiej części Karpat Zewnętrznych wskazuje, że akumulacja dużej ilości materii organicznej w czasie zdarzenia oceanicznego OAE-2 mogła wynikać z podwyższonej produktywności wód powierzchniowych, aczkolwiek słaba cyrkulacja głębokowodna sprzyjała zachowaniu materii organicznej. Powierzchniowy wulkanizm oraz równoczasowa działalność hydrotermalna (również w basenach karpackich) a także wzrost aktywności w obrębie dużych oceanicznych prowincji magmowych, jakie miały miejsce w najmłodszym cenomanie (w okresie poprzedzającym wystąpienie wysokich wartości $\delta^{13}C$ w osadach morskich) mogły być pierwotną przyczyną wzrostu $CO_2$ w oceanie i atmosferze, który z kolei wpływał na zmiany temperatur wód (obniżenie gradientu pomiędzy niskimi i wysokimi szerokościami geograficznymi), prowadząc do zmian w cyrkulacji głębokowodnej, w tym do ich stratyfikacji (por. Kuroda *et al.*, 2007). Mechanizm nagłej zmiany w natlenieniu wód głębinowych w pobliżu granicy cenomanu i turonu, interpretowany tutaj w oparciu o mechanizm powstawania rodochrozytowych warstw manganowych był związany z powtarzającymi się spływami prądów gorącej, zasolonej i natlenionej wody, pochodzących najprawdopodobniej z otaczających mórz epikontynentalnych.