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Geochemical and ecological aspects of lower Frasnian pyrite-ammonoid level at Kostomłoty (Holy Cross Mountains, Poland)

Grzegorz RACKI, Agnieszka PIECHOTA, David BOND and Paul B. WIGNALL



Racki G., Piechota A., Bond D. and Wignall P. B. (2004) — Geochemical and ecological aspects of lower Frasnian pyrite-goniatite level at Kostomłoty (Holy Cross Mountains, Central Poland). *Geol. Quart.*, 48 (3): 267–282. Warszawa.

The lower Frasnian (*transitans* Zone with *Ancyrodella priamosica* = MN 4 Zone) rhythmic basin succession of marly limestones and shales (upper Szydłówek Beds) at Kostomłoty, western Holy Cross Mts., Central Poland, contains a record of the transgressive-hypoxic Timan Event in this drowned part of southern Laurussian shelf. The unique facies consists of organic-rich marly shales and a distinctive pyritic, goniatite level, 1.6 m thick. The faunal assemblage is dominated by pyritized shells of diminutive mollusks with cephalopods (including goniatites *Epitornoceras* and *Acanthoclymenia*), buchioline bivalves (*Glyptohallicardia*) and styliolinids. This interval is marked by moderately low Th/U ratios and pyrite framboid size distributions suggestive of dysoxic rather than permanent euxinic conditions. The scarcity of infauna and bioturbation resulted in finely laminated sedimentary fabrics, as well as the low diversity of the presumed pioneer benthos (mostly brachiopods). In the topmost part of the Szydłówek Beds, distinguished by the *Styliolina* coquina interbedded between limestone-bioturbated layers, the above geochemical proxies and C-isotope positive shift indicate a tendency to somewhat increased bottom oxygen deficiency and higher carbon burial rate linked with a bloom of pelagic biota during high-productivity pulse. The geochemical and community changes are a complex regional record of the initial phase of a major perturbation in the earth-ocean system during a phase of intermittently rising sea level in the early to middle Frasnian, and associated with the highest positive C-isotope ratios of the Devonian.

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Key words: Holy Cross Mountains, Frasnian, pyritic fossils, geochemical proxies, anoxia, Timan Event.

INTRODUCTION

A number of Devonian biotic events have been identified; these are usually associated with fluctuating anoxia and/or nutrient dynamics in a punctuated greenhouse climatic setting (e.g. House, 1985, 2002; Walliser, 1985, 1996; Becker, 1993; Streel *et al.*, 2000; Copper, 2002; House, 2002; Sageman *et al.*, 2003; Bond *et al.*, 2004). Of these, the environmental change at the Frasnian-Famennian (F-F) boundary, and associated biotic crisis, is the best studied whereas several other Devonian biospheric perturbations remain rather poorly known. House (2002) emphasized an overvalued significance of terminal Frasnian events, however, and urged that study of other events was required to adequately place the F-F mass extinction in its Devonian context.

The relatively continuous carbonate sequence in the Holy Cross Mountains, which represents the South Polish part of the

Laurussian shelf (Fig. 1), contains well studied F-F boundary sections (e.g. Narkiewicz and Hoffman, 1989; Casier *et al.*, 2000; Joachimski *et al.*, 2001; Dzik, 2002; Racki *et al.*, 2002; Bond and Zatoń, 2003; Bond *et al.*, 2004). This article presents first results of an interdisciplinary project on the preceding early to middle Frasnian biotic succession and events, inspired by results of previous Belgian-Polish geochemical study presented in Yans *et al.* (in press). An initial stage of the project focuses on the generally deeper-water, northern Kostomłoty-Łysogóry facies region (Fig. 1B) that remains crudely recognized, mostly due to poorer exposure (Racki, 1993; Szulczewski, 1995). The goal of this study is to provide a documentation of the geochemical and depositional signatures of distinctive lower Frasnian pyritized-fossiliferous level in the Szydłówek Beds, well exposed at Kostomłoty, north of Kielce (Szulczewski, 1981; Racki *et al.*, 1985; Racki and Bultynck, 1993). The data are combined with overall palaeontological-ecological characteristics, derived mostly from unpublished master theses (Więzik, 1984; Niemczyk, 2003). Tentative interpretation in terms of main pro-

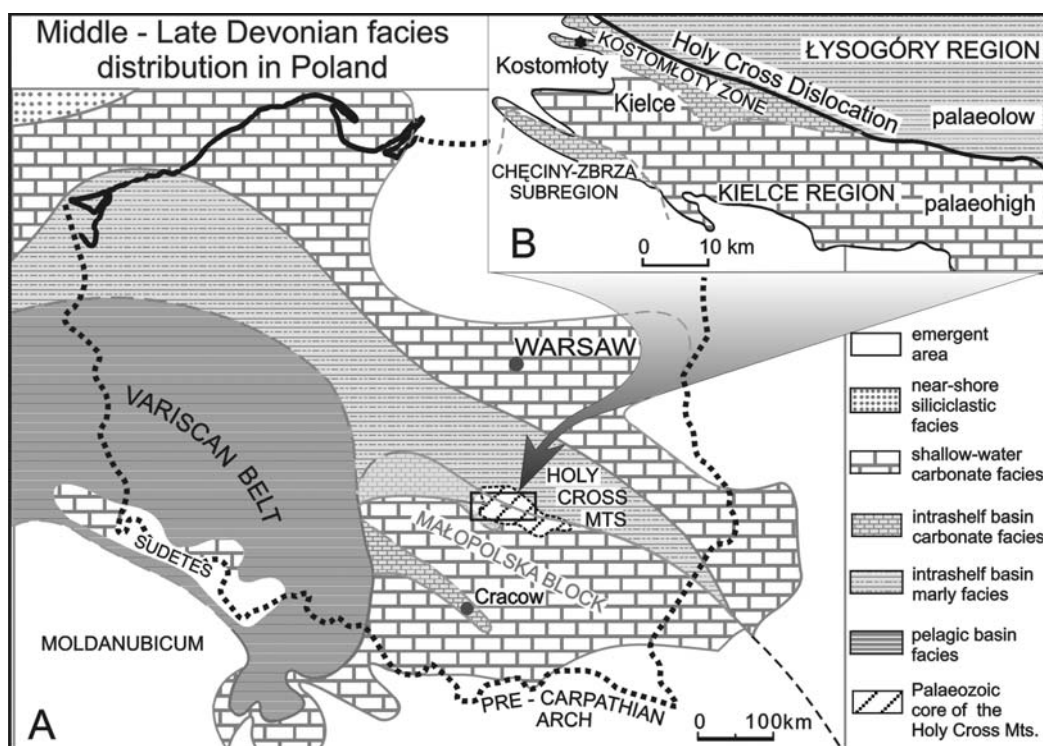


Fig. 1. A — location of Holy Cross Mountains against the palaeogeographic framework of the Devonian in Poland (modified after Racki, 1993, fig. 1); B — palaeogeographic pattern of the Givetian to Frasnian of Holy Cross Mountains (based on Racki 1993, fig. 2), with a location of the Kostomłoty site

Table 1

Diagnostic characteristics of oxygen-controlled facies (modified from Bond *et al.*, 2004, table 1)

Conditions (facies)	Pyrite taphofacies (Brett <i>et al.</i> , 1991)	Framboidal populations	Sedimentary fabric/Ichnofabric Index (II) (Droser and Bottjer, 1986)	Th/U ratio
euxinic (euxinic)	no pyritic fossils; finely disseminated framboids only	small (< 5 m), abundant with narrow size range (standard deviation < 2)	finely laminated II 1	< 1 (carb) < 3 (shales)
lower dysoxic (lower dysaerobic)		small (< 5 m), abundant, but with rare, larger framboids		< 1 (carb) < 3 (shales)
upper dysoxic (upper dysaerobic)	pyritic fossils, nodular, tubular and crustose pyrite ↓ cavity lining pyrite druse, sparse nodular pyrite	moderately common to rare, broad range of sizes, with only a small proportion < 5 m diameter	microburrowed, bioturbation may partly obscure finely laminated fabric II 2	> 1 (carb) > 3 (shales)
oxic (aerobic)	no pyrite concentration	no framboids, very rare pyrite crystals	burrowed/massive, no fine lamination II 3–5	>> 1 (carb) >> 3 (shales)

cesses responsible for the deposition (oxygenation levels vs. productivity and sedimentation rate; *cf.* Brett *et al.*, 1991; Table 1) is presented, in connection with the record of global transgressive-anoxic events (House and Kirchgasser, 1993; Becker and House, 1997; House *et al.*, 2000), as well as a record of profound perturbation of global carbon cycling in the described fragment of Laurussian shelf (Yans *et al.*, in press).

GEOLOGICAL SETTING

Kostomłoty Hills represent the westernmost outcrops of the Devonian system in the Holy Cross Mountains, approxi-

mately 3 km NNE of Kielce (Fig. 2A). This lithologically diverse sequence (Fig. 2B) is exposed in the southern limb of the Miedziana Góra Syncline, which is a subordinate unit of the complex central (Kielce–Łagów) synclinorium of the Holy Cross Mountains. The sediments are intensively disharmonically folded due to contrasting lithology; they are also faulted in places (e.g. Gagol, 1981, fig. 31; Lamarche *et al.*, 1999, fig. 6; Figs. 3 and 5A), and display syn-fold cleavage, related to the intensive polyphase Variscan tectonics *sensu lato* (Lamarche *et al.*, 1999). Several exposures of Middle to Upper Devonian carbonate rocks, including active quarries, have been studied since the nineteenth century (see review in Szulczewski, 1971 and Racki *et al.*, 1985).

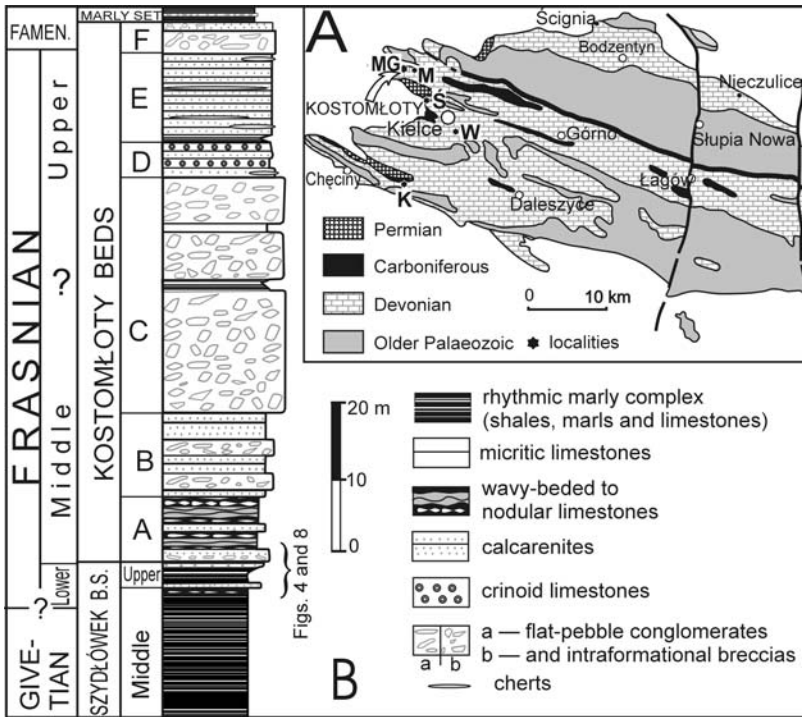


Fig. 2. A — generalized composite lithological section of the Givetian to Famennian strata exposed on Kostomłoty Hills (based on Szulczewski, 1981; Więzik, 1984; Racki *et al.*, in prep.); B — location of the studied Kostomłoty quarries (MG — Małe Górki; M — Mogiłki) against the geological map of western Holy Cross Mts.; other localities: W — Wietrzna, Ś — Śluchowice, K — Kowala

1985). Higher in the section, within the basal Frasnian part of the Szydłówek Beds, a transition to overlying Kostomłoty limestones is marked by the appearance of various, mostly fine-grained, limestone layers (see Fig. 4). The top of the unit is defined by the lowest thick (> 0.5 m) intraclastic bed (Racki *et al.*, 1985; Racki and Bultynck, 1993, fig. 4).

Abundant conodonts prove the *Ancyrodella pramosica*–*A. africana* level of the *transitans* Zone (Racki and Bultynck, 1993; Klapper, 1997), whilst the index *Palmatolepis punctata* was found in the topmost breccia layer of the Szydłówek Beds. The first occurrence of this conodont species marks the base of the *punctata* Zone and the boundary between the lower and middle Frasnian

(Ziegler and Sandberg, 2001; see <http://sds.uta.edu/sds18/page0042.htm>).

The Givetian to Frasnian boundary interval (Fig. 2B; see details in Racki *et al.*, 1985 and Racki and Bultynck, 1993) consists of dark-coloured marls defined as Szydłówek Beds up to 100 m thick (Malec, 2003). They are overlying Middle Devonian dolomites and biostromal-marly Laskowa Góra Beds, and underlying Upper Devonian detrital limestones of the Kostomłoty Beds (Szulczewski, 1981). The lower and uppermost parts the unit comprise micritic and partly bioclastic limestone layers, and this lithological succession is the basis for a three-fold subdivision of the succession (Racki *et al.*, 1985; Racki and Bultynck, 1993), which can be attributed to a shelf-basin system.

The lowermost and upper portions of the Szydłówek Beds are well exposed in the Kostomłoty quarries, and the highest part was studied in two outcrops (Fig. 2A): 1 — primarily at the Małe Górki = Kostomłoty II (Kt-II) active quarry in western hill, where three sections have been logged in different years since 1984, as well as in 2 — the abandoned Mogiłki = Kostomłoty V (Kt-V) quarry in eastern Kostomłoty Hill, 2 km to E (see Figs. 3–5 and 8). In both exposures, the monotonous middle Szydłówek suite is characterized by an interlayering of marly shales (to marls) and marly limestones, with septarian nodule horizons and shelly pavements of the large rhynchonellid *Phlogoderhynchus polonicus* (Roemer) (Biernat and Szulczewski, 1975; Sartenaer and Racki, 1992). The position of the Middle-Upper Devonian boundary has been approximated within the upper part of the conodont-poor middle Szydłówek Beds (Racki,

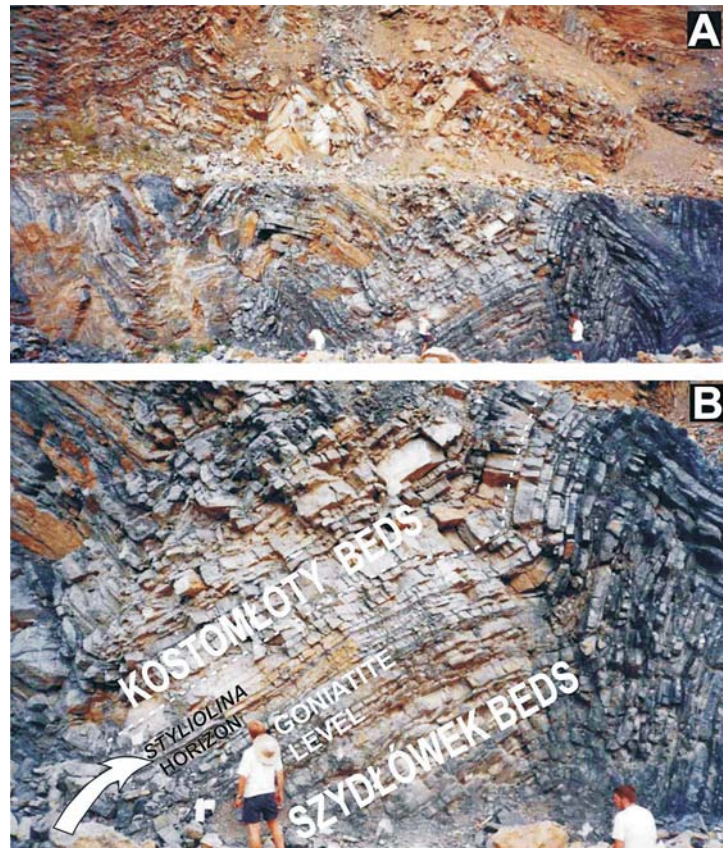


Fig. 3. A — overall view of folded Upper Devonian strata exposed in the northeastern wall of the Małe Górki quarry (lower exploitation level) in July 2000, section Kt-II-E; B — close-up of the wall, showing transition from Szydłówek to Kostomłoty beds (Fig. 4)

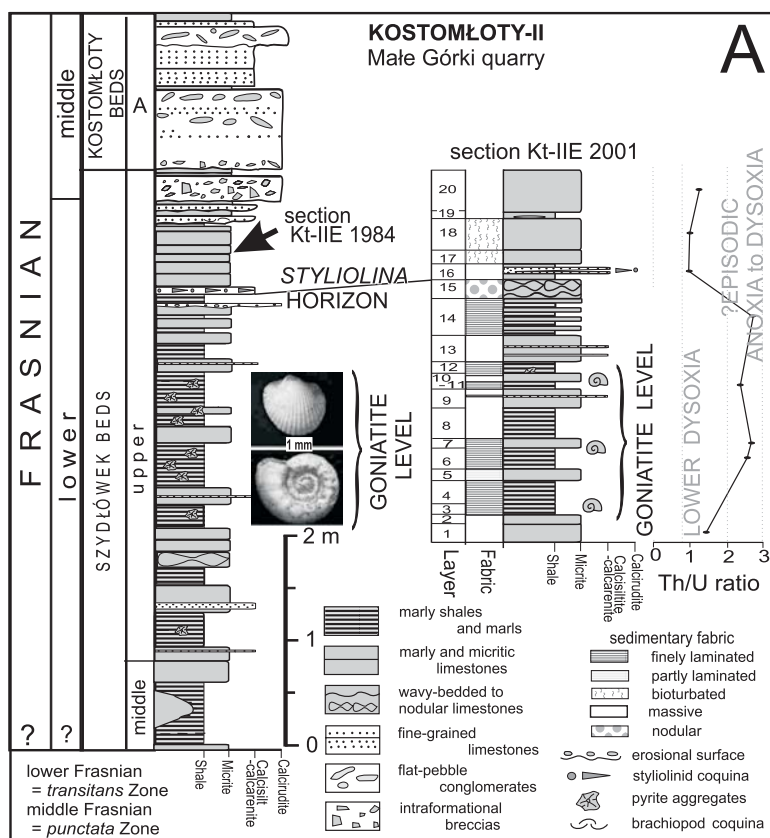


Fig. 4. A — results of gamma-ray spectrometry analysis across upper Szydłówek Beds in the Małe Górki section exposed in July 2001 (see Figs. 3 and 4B), and its correlation with the reference section described by Racki (1985) and Racki *et al.* (1985); interpretation of benthic oxygenation regimes based on multiproxy data. Two main moluscan fossil groups (pyritized goniatite and *Buchiolina* bivalve) from the Goniatite Level are shown. Frasnian substages after Ziegler and Sandberg (2001); B — close-up of the logged succession from Figure 4A, with well visible black *Styliolina* coquina in the top-most Szydłówek Beds (Fig. 3B), probably recording the most oxygen-depleted regimes; note the arrowed coin (5 zł) as a scale; 16, 18 — number of layer

MATERIALS AND ANALYTICAL METHODS

The upper Szydłówek Beds at the Małe Górki quarry have been logged in detail and assayed with a field portable gamma-ray spectrometer *Envispec GR 320* in 2001 in the eastern wall (section Kt-IIIE in Figure 3). This part of the active quarry is now covered, and only the western wall has been accessible since 2002 (Kt-IIW in Figures 5 and 8; Niemczyk, 2003).

Seven samples from Kostomłoty were examined under backscatter SEM to determine the size distribution of pyrite framboid populations. To better establish the character of oxygen-depleted regimes in the Szydłówek to Kostomłoty Beds passage interval, 35 bulk sediment samples from Małe Górki (Kt-IIW section) and Mogiłki (Kt-V) were investigated for carbon and oxygen isotopes at the Laboratory of Stable Isotopes of Polish Academy of Sciences in Warsaw (Table 2). The analyses were carried out on CO₂

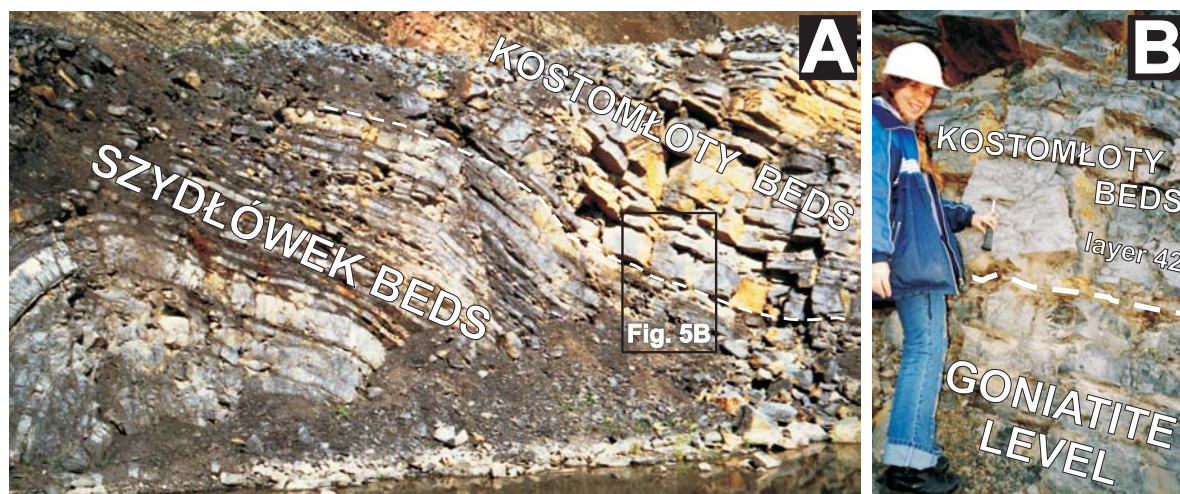


Fig. 5. A — transition from Szydłówek to Kostomłoty Beds in the western part of the Małe Górki quarry (lower exploitation level) in April 2002; B — close-up of the wall in October 2003, showing the Goniatite Level and basal Kostomłoty Beds (section Kt-IIW see Fig. 8)

obtained by dissolution of micrite and/or (sporadically) brachiopod shell material in 100% H_3PO_4 at 25°C for 24 hours. The measurements were made on a *Finnigan MAT Delta plus* mass-spectrometer. The results are expressed in ‰ relative to the PDB standard, using a NBS-19 reference sample. The accuracy of measurements approximates ± 0.02 for $\delta^{13}C$ and $\pm 0.04\text{‰}$ for $\delta^{18}O$. In addition, the total organic carbon (TOC) content in four samples was determined using a non-automatic *Leco CR-12* analyser.

GONIATITE LEVEL IN THE UPPER SZYDLÓWEK BEDS

The 4.7 m thick, dark to black upper Szydłówek Beds at the Kt-III section (Fig. 4) represent a series of thin-bedded, homo-

geneous, micritic limestones interbedded, in the middle part, with several shaly-marly partings, up to 0.4 m thick, with common styliolinids and rarer *Amphipora* branches. This 1.6 m thick clay- and pyrite-rich interval was distinguished as the Goniatite Level by Racki *et al.* (1985), and is limited in geographical extent to the Małe Górki site. In Mogiłki, neither pyritization nor ammonoid faunas are recognized in coeval, partly clayey interval. A few fossil-poor calcarenites are notable, locally with *Phlogoiderhynchus polonicus* (small-sized variety of Sartenaer and Racki, 1992) that can also occur in dispersed shelly accumulations which contain many allochthonous, lagoonal microbiotic indicators (calcispheroids and other microproblematics; *cf.* Racki, 1993) (Fig. 6A–C). In addition to abundant pyritized minute fossils (see Figs. 4A and 6B), other forms of pyrite, including centimeter-sized pyrite crusts flattened parallel to bedding occur over a broader strati-

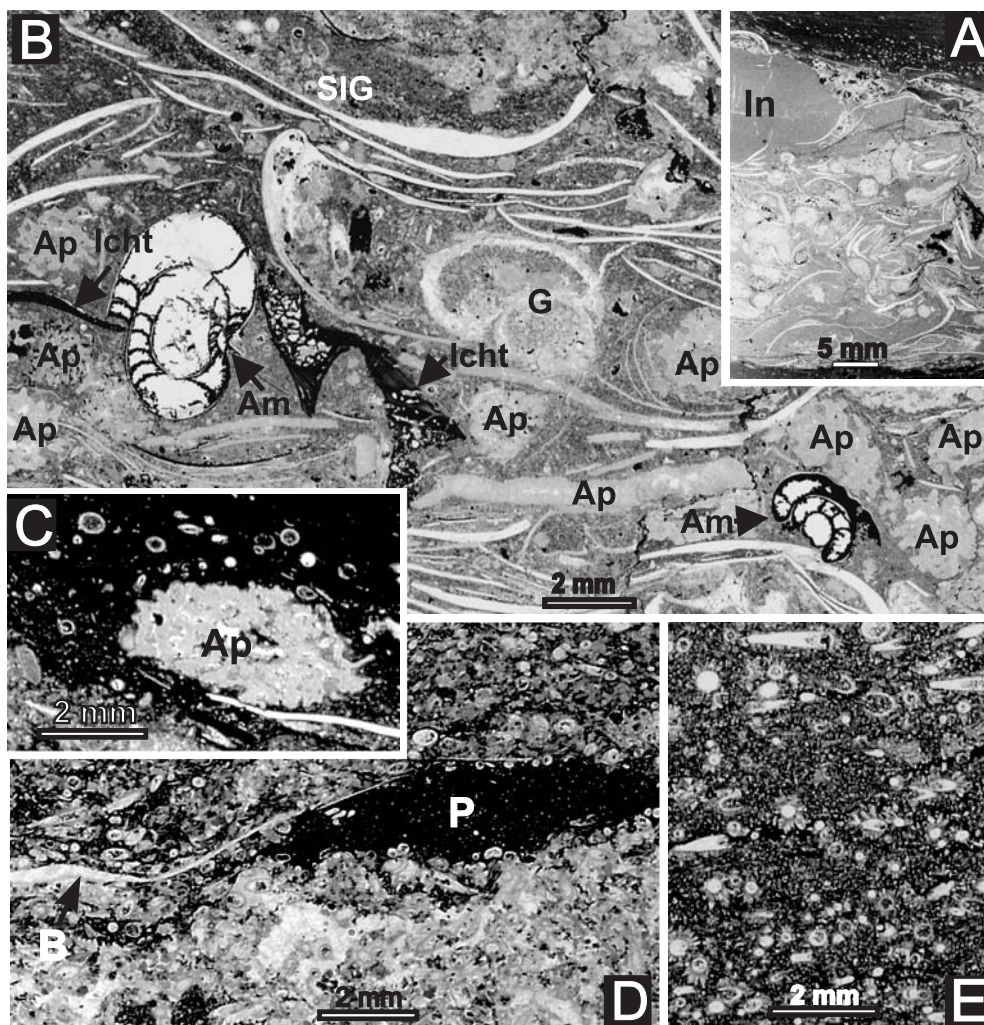


Fig. 6. Photomicrographs of lower Frasnian limestones from western Kostomłoty (A–D) and Mogiłki (E) sections (Fig. 8)

A–C — overall character (A) and details (B–C) of the brachiopod-*Amphipora* intraclastic grainstone/packstone lenticle (bed 37 in Fig. 8) bounded by shales with *Styliolina*-rich laminae. Note co-occurrence of numerous *Amphipora* branches (Ap) and broken brachiopod valves, and pyritized ammonoids (Am), ichthyoliths (Icht) and gastropods (G), as well as presence of cm-sized micritic clasts (In in 6A), and graded styliolinid-intraclastic grainstone (SIG in 6B) capped by *Amphipora*-*Styliolina* shale (6C); D — *Styliolina* grainstone with several brachiopod valves (B; lower half) overlaid by packed *Styliolina* shale, with a larger pyrite nodule in a central part (P); bed 43 in Figure 8; E — *Styliolina* packstone with common syntaxial overgrowths on the shells (see Tucker and Kendall, 1973, and Figure 3P in Hajłasz, 1993); bed 41 in Figure 8

Table 2

Results of carbon and oxygen isotopic analyses for two Kostomłoty sections (Fig. 8)

Samples	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
Kostomłoty–Małe Górkki (Kt-IIW)		
18	0.018	-4.447
19	0.711	-4.763
20	2.100	-4.517
25	2.509	-4.396
26	3.072	-3.946
32	1.737	-4.463
35	2.044	-4.200
37	0.799	-5.049
39	0.877	-5.559
40	1.058	-5.261
41	1.465	-4.812
42	1.885	-4.428
43	2.197	-3.740
46	3.075	-4.424
47	1.761	-3.692
48	1.363	-4.583
Kostomłoty–Mogiłki (Kt-V)		
7	0.702	-4.229
12	1.854	-4.226
17	0.902	-4.867
20	0.805	-4.863
23	1.896	-3.941
25	2.389	-4.015
29	1.383	-4.104
32	1.188	-4.410
37	1.955	-3.621
40	2.413	-4.159
42	3.338	-3.753
47	3.273	-3.674
53	1.785	-4.663
66*	1.407	-4.247
68	0.012	-4.181
70	0.758	-4.613
71	0.916	-4.553
74	2.145	-4.050
80	2.008	-4.124

* — for breccia the values refer to the matrix

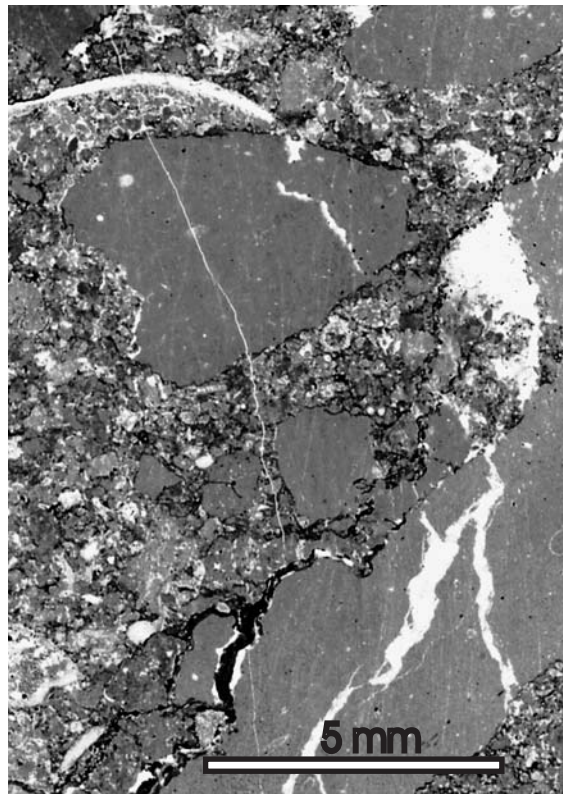


Fig. 7. Photomicrograph of the basal middle Frasnian breccia (the top of the Szydłówek Beds), to show large angular clasts of *Styliolina* wackestone in fine lithoclastic-skeletal matrix with crinoid and brachiopod debris, as well as with abundant calcispheroids in clasts

graphic interval of the Szydłówek Beds (Fig. 6D). The pyrite content increases in places above 20% (although it is mostly between 1 to 2%; Gagol, 1981, table 13). The fissility of the Goniatite Level and underlying layers varies according to the carbonate content (mostly above 25%), whilst the organic carbon content is close to 1% regardless of lithology, with the maximum TOC value 1.78% in the Kt-IIW/31 sample.

A single breccia layer forms the top of the Szydłówek Beds at Kt-IIIE section (Fig. 7), and toward the west the coarse-grained varieties are more frequent; in fact, the diachronous nature of the bottom of Kostomłoty

Beds becomes clear from the correlation of the nearby sections at Małe Górkki (Fig. 8). The distinctively black-coloured *Styliolina* Horizon is 4 to 10 cm thick (Fig. 4B), and is well expressed both at the Kt-IIIE section and traced 2 km to E (Mogiłki site; Fig. 6E). This horizon occurs as a graded styliolinid-brachiopod coquinoid parting within detrital layers of the Kt-IIW section (bed 43 in Figs. 6D and 8) that are characterized by overall higher skeletal content, especially fine crinoid debris.

FAUNAL ASSEMBLAGE

The collection of fossils (more than 2700 specimens exceeding 0.25 mm in size), studied by Niemczyk (2003), has been obtained from the shaly samples mostly by boiling in Glauber salt and washing, or by dissolving in a weak acetic acid. With exception of most brachiopods and amphiporoids, the macrofossils are preserved as pyritized steinkerns (see Racki, 1985; Dzik, 2002; Fig. 4A), with sporadic pyrite overgrowth.

As well as styliolinids, molluscs dominate the pyritized diminutive fauna of the Goniatite Level. Specimens, below 1 cm in size and with an average size of 3–4 mm (Fig. 4A), are mostly identifiable only to higher taxonomic levels. Cephalopods (orthocone nautiloids, ammonoids) and bivalves dominate (ca. 80–90% recovered specimens), together with rare gastropods and brachiopods, as well as amphiporoid and sporadic tabulate coral branches (Więzik, 1984; Niemczyk, 2003). Strongly fragmented nautiloid shells preclude their taxonomic identification, as well as a more precise analysis of the faunal composition and dynamics in the lower Frasnian interval. However, in the western site Kt-IIW, brachiopods are certainly the most numerous component (58% of the collection), followed by ammonoids (20%; Niemczyk, 2003). Only the ammonoid fauna was studied by Dzik (2002), but partly erroneously referred to the adjacent Laskowa quarry section. The association is dominated (cf. Niemczyk, 2003) by *Epitornoceras mithracoides* (Frech) and *Acanthoclymenia genundewa* (Clarke), supplemented by *Koenenites lamellosus* (Sandberger and Sandberger) and *Linguatornoceras compressum* (Clarke). Occurrence of true *Manticoceras* (Dzik in Racki, 1985) is not confirmed in this study. However, according to Becker (e-mail comm., 2004), some of the taxonomy in Dzik (2002) is debatable, and a juvenile *Manticoceras* is certainly present in the material: in particular, all or a part of the specimens linked with the genus *Koenenites* probably belongs to the *Manticoceras lamed* Group.

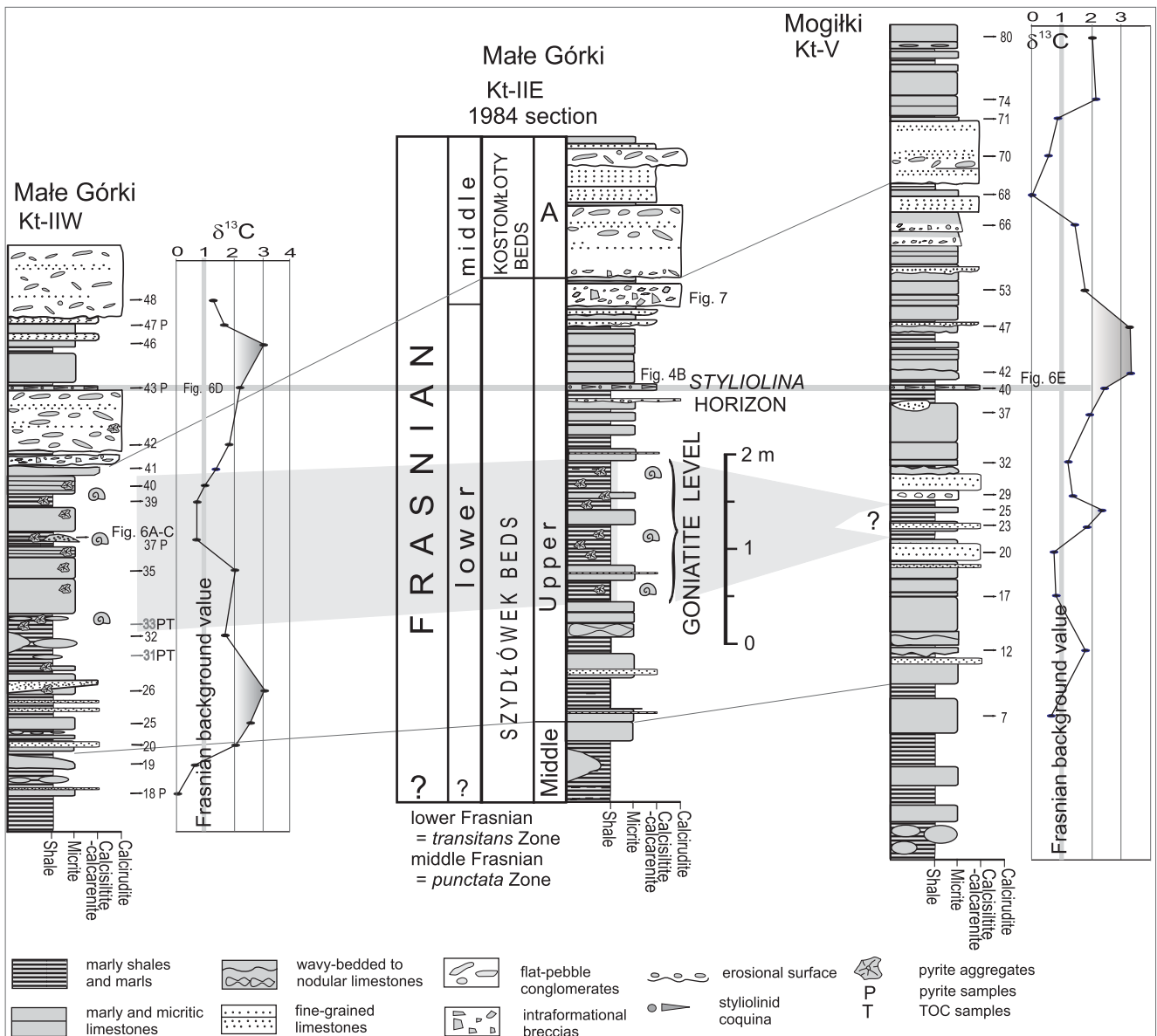


Fig. 8. Stable carbon isotope geochemistry for the lower to middle Frasnian strata in Kostomłoty sections (Fig. 2A), correlated with the reference 1984 section described by Racki (1985) and Racki *et al.* (1985). Note the time marker styliolinite horizon and a rapid facies transition over a distance of ca. 100 m recorded in the diachronous bottom part of Kostomłoty Beds at Małe Górki (Kt-II). The lower-middle Frasnian “background” $\delta^{13}\text{C}$ value of ca. 1‰ is taken from the regional (Fig. 10) and broadly supra-regional data (Yans *et al.*, in press)

Among other fossil groups, provisionally surveyed by Niemczyk (2003), common buchioline bivalves dominantly belong to *Glyptohallicardia ferruginea* (Holzapfel), with rare *Planocardia tennicosta* (Sandberger and Sandberger) and unidentified species of *Opisthocoeilus* and *Buchiola*. Brachiopods are represented by small-sized biernatellids and larger (up to 3 cm) leiorhynchid rhynchonellids, probably mostly *P. polonicus*, supplemented by sporadic inarticulates (*cf.* Więzik, 1984). Relatively diverse microgastropods, with maximum size 7 mm, include indeterminable subulitids and *Palaeozygopleura (Rhenozyga)*, and *Naticopsis kayseri* (Holzapfel), but *Lahnaspira taeniata* (Sandberger) is by far the most numerous of the gastropods (> 80% of the associa-

tion). Rock-forming styliolinids include widespread *Styliolina ex. gr. nucleata* Karpinsky, and *S. domanicense* Lyashenko (Hajłasz, 1993).

GEOCHEMISTRY AND FRAMBOIDAL PYRITE

Oxygenation levels were interpreted in the Kostomłoty succession using three independent criteria: sediment fabric (i.e. presence of fine lamination/bioturbation features), authigenic uranium values (*cf.* Bond *et al.*, 2004) and pyrite taphofacies vs. framboid size populations (Table 1). Interpretation of the oxygen-depleted environments (Byers, 1977; Wignall, 1994)

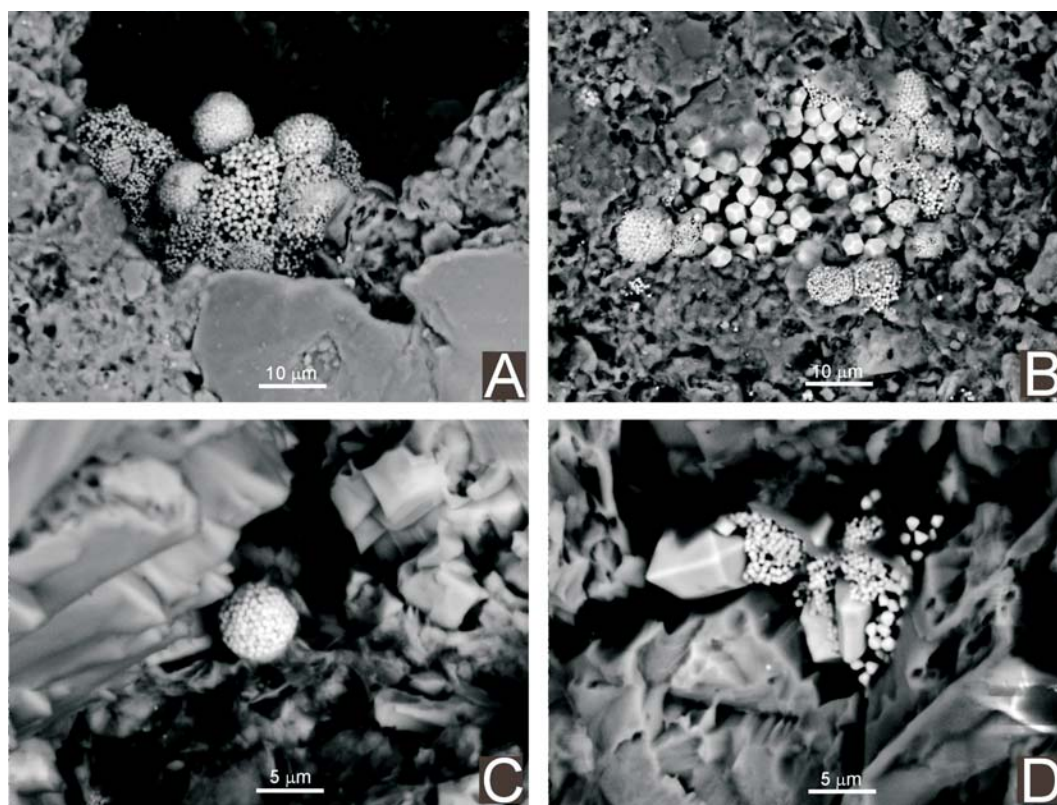


Fig. 9. SEM photos of framboidal pyrites from the Goniatite Level at Kt-IIW section (Fig. 8), to present several smaller framboids, accompanied by a few large ones, and also some pyrite macrocrystals, the typical signature of dominantly dysoxic settings; sample Kt-IIW/37 (A–B) and Kt-IIW/43 (C–D)

was reinforced by microfacies analysis of limestone layers, as well as carbon isotope secular trends.

anoxic conditions often measured as either authigenic U enrichment or a decline in Th/U ratios (Wignall and Myers, 1988; Allison *et al.*, 1995). Uranium is precipitated in anoxic condi-

GAMMA-RAY SPECTROMETRY VS. SEDIMENTARY FABRIC

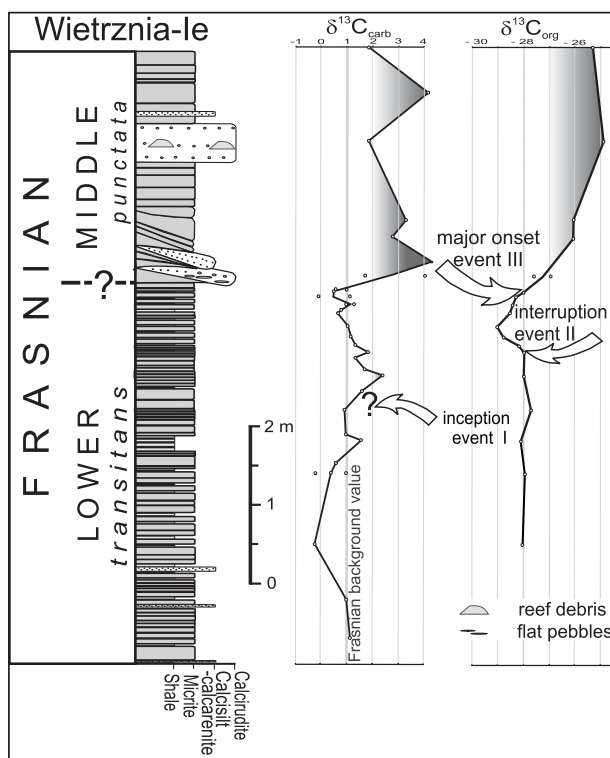
Gamma-ray spectrometry (GRS) of the 3.4 metres thick section of the upper Szydłówek Beds at Małe Górki was measured, and the laminated shaly interval (the Goniatite Level) revealed Th/U ratios of 2–2.5 (Fig. 4A). Between beds 16 and 18, near the top of Szydłówek Beds, the Th/U ratio approaches 1.0. The fabric of the more carbonate-rich layers is less laminated, and essentially nodular to massive (i.e. bioturbated).

INTERPRETATION

Field portable gamma ray spectrometer can provide a measure of redox conditions because of the enrichment of U under



Fig. 10. Stable carbon isotope geochemistry for the lower to middle Frasnian strata at Wietrznia (reference section Ie in Racki and Bultynck, 1993) in Kielce (Piechota and Małkowski, in prep.). Note a general similarity of the carbonate C-isotopic trend to the Kostomłoty curves (Fig. 8). The conclusive proof of the distinctive positive $\delta^{13}\text{C}$ excursion, but initially interrupted by fall in the upper *transitans* Zone, is provided by organic matter data. A diagenetic bias of the carbonate record is visible in far more varying $\delta^{13}\text{C}$ values (circles in rows exhibit different values measured in a sample from one bed). In the lower *transitans* Zone, four $\delta^{13}\text{C}$ values for brachiopod calcite from Wietrznia cluster around 1‰ (from 0.45 to 1.41‰; Yans *et al.*, in press); for other explanations see Figure 8



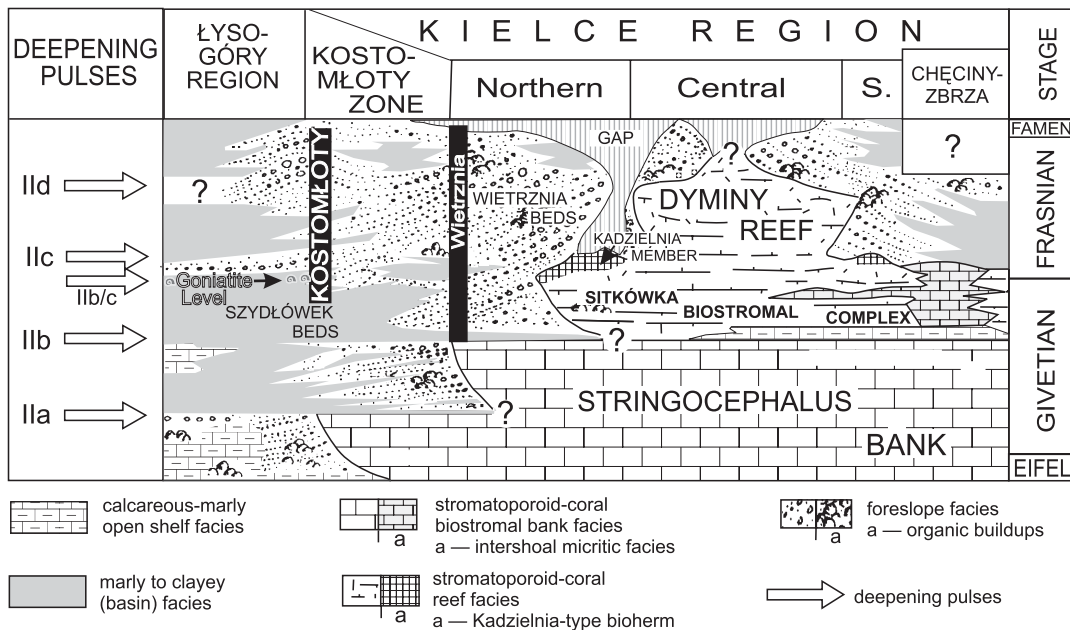


Fig. 11. Position of the Kostomłoty sections under study (Fig. 1B) against developmental stages of the Middle to Late Devonian bank-to-reef complex of the Holy Cross Mountains; stratigraphic-facies cross-section (after Racki 1993, fig. 3, changed) is shown to emphasise eustatic rhythmic control of the depositional pattern; Ila–IId — transgressive-regressive cycles modified from Johnson *et al.* (1985)

tions thus adding an authigenic component to the detrital sediment component. In contrast sediment Th content is entirely terrigenous in origin. However, the carbonate to clastic ratio of sediments also exerts a fundamental control on Th and U contents: detrital sediments generally have higher Th contents than carbonates with the result that the Th/U ratio of shales is typically greater than 3, but for pure carbonates the ratio is typically lower than 1 (Myers and Wignall, 1987). At Małe Górki the fluctuations of the Th/U ratio can be seen to primarily reflect the lithological variations. Thus, the marly layers display higher Th/U values, between 2 and 3, than the purer carbonate layers. However, these values are typical of dysoxic clastic deposits (Myers and Wignall, 1987; Fig. 4A) suggesting oxygen-restriction during deposition of the pyritic level.

PYRITE TAPHOFACIES VS. FRAMBOID SIZE POPULATIONS

Framboidal pyrite is common in the western Kostomłoty samples from the upper Szydłówek Beds, including the finely laminated Goniatite Level. Four shaly samples are all dominated by syngenetic populations with most framboids being 5–10 μm, but with rarer larger forms supplemented by some pyrite macrocrysts (Fig. 9A–B).

Sparse, and on average smaller and less variably sized, pyrite framboids are found locally in the styliolinite sample (Fig. 9C–D). In contrast, sample Kt-IIW/47 from the overlying fine-grained variety of Kostomłoty Beds does not contain framboids but merely blebs of pyrite.

INTERPRETATION

Studies of recent and ancient sediments reveal that, where secondary pyrite growth is limited, framboid size distribution may be reliably used to indicate redox conditions. If bottom

waters become euxinic, then framboids develop in the sulfidic water column but are unable to achieve diameters much larger than 5 μm before they sink below the Fe-reduction zone and cease growth (Wilkin *et al.*, 1996). Thus, euxinic conditions produce populations of tiny framboids with a narrow size range. In contrast, in dysoxic settings, where anoxic conditions are restricted to the surficial sediments, size is largely governed by the local availability of reactants; thus, the framboids are larger and more variable in dimension (Wilkin *et al.*, 1996), especially when a long-term euxinic condition is punctuated by brief sea-floor oxygenation (see Bond *et al.*, 2004).

Framboidal pyrite from the upper Szydłówek Beds has a size distribution indicative of dysoxic conditions. The presence of pyritic fossils paired with nodular and crustose pyrite aggregates is characteristic of upper dysoxic facies (Brett *et al.*, 1991; see Table 1). In the *Styliolina* Horizon, episodes of anoxic conditions are suggested, whilst limited pyrite data from Kostomłoty Beds are indicative of far better oxygenation.

CARBON ISOTOPES

The C isotope record, based on the Kt-IIW section (Fig. 8; Table 2), shows two positive δ¹³C excursions in the *transitans* Zone (Szydłówek Beds) and the transitional *transitans-punctata* zonal interval (Kostomłoty Beds). The first shift is observed mostly below the Goniatite Level, where values of δ¹³C increase from 0 to 3‰. The gradual decrease in δ¹³C is registered near the top of the Szydłówek Beds with a 0.8‰ minimum within the upper Goniatite Level. The upper less distinctive positive excursion in δ¹³C is affirmed higher in this succession. The increase in δ¹³C culminates up to ca. 3.1‰ above the *Styliolina* Horizon.

This latter isotopic trend is reproduced by preliminary data from the more extended Mogiłki succession. Like in the

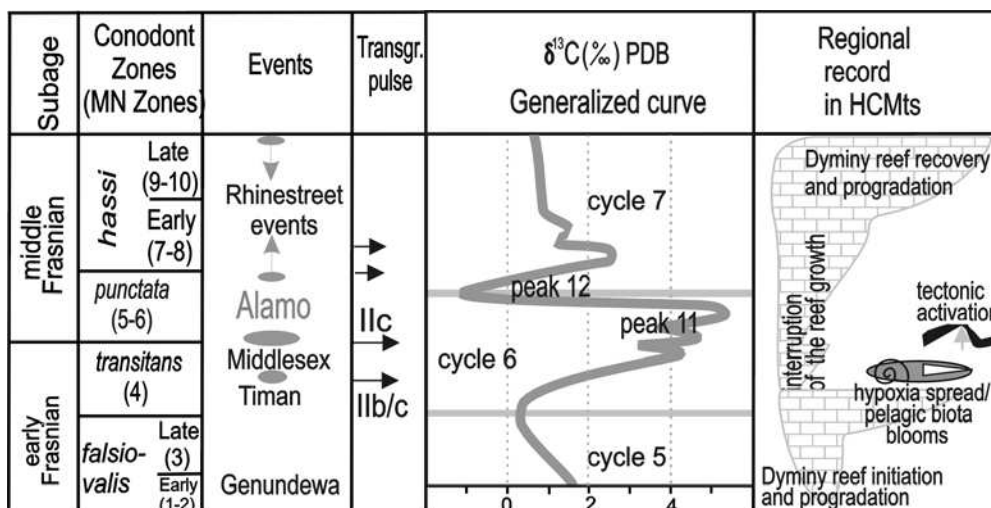


Fig. 12. Early to middle Frasnian event stratigraphy scheme to show relationships between eustatic/biotic events (based mostly on fig. 1 in House, 2002; Racki, 1993), presumed global carbon-isotopic cyclicity (inorganic record only from Ardennes; modified from fig. 3 in Yans *et al.*, in press), and their manifestation the western Holy Cross Mountains (based on Kostomłoty, Ścignia, Wietrzna, Śluchowice and Kowala sections, Racki, 1993 and references cited; see Figs. 2A and 11). Long-lasting Rhinstreet “Event” encompasses several deepening pulses from the *punctata* to at least *jamieae* Zones (= MN6 to MN11 Zones; Klapper and Becker, 1999)

Kt-IIW section, the uppermost Szydłówek Beds are marked by the significant $\delta^{13}\text{C}$ shift from 1.4‰ to above 3.3‰, with a peak located also just above the guide styliolinite intercalation (Fig. 8). However, the lower positive excursion is obscured by highly fluctuating values, with a 2.4‰ maximum in a level approximately corresponding to the Goniatite Level. In addition, a gradual increase in $\delta^{13}\text{C}$ values (from 0 to 2.1‰) is recorded in the basal Kostomłoty Beds in the *punctata* Zone.

INTERPRETATION

Diagenetic alteration of carbonates frequently obscures the primary carbon and oxygen isotope pattern, but brachiopod shells and micritic matrix may retain its general features through time (e.g. Azmy *et al.*, 1998; Stanton *et al.*, 2002; Brand *et al.*, 2004). Values of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ from the mostly organic-rich micrites of upper Szydłówek Beds at Małe Górki (Table 2) show a moderate level of covariance ($r = 0.57$ for 16 samples) suggestive of some post-sedimentary modification but, as discussed by Marshall (1992), not definitely; therefore, only more reliable carbon isotopic data (as summarized in Brand, 2004; see also Joachimski *et al.*, 2004) are interpreted below.

Positive $\delta^{13}\text{C}$ excursions, established at the Kostomłoty sections, are of the similar range in absolute values, and up to 2.3‰ above the assumed lower-middle Frasnian “background” $\delta^{13}\text{C}$ value of ca. 1‰ (Fig. 10). These signals could be most simply explained as a global pulse of elevated organic carbon production (e.g. Azmy *et al.*, 1998; Caplan and Bustin, 1999), although other factors are possibly involved as well (Kump and Arthur, 1999; Saltzman, 2002; Sageman *et al.*, 2003; see below). An increase in $\delta^{13}\text{C}$ may serve as indicator of enhanced burial of organic matter that is expected to reduce the concen-

tration of oceanic dissolved carbon dioxide (Brasier, 1995; Caplan and Bustin, 1999; Joachimski *et al.*, 2002).

On the contrary, the noticeable drop in $\delta^{13}\text{C}$ characterizes black-shale facies (especially the upper Goniatite Level). A diagenetic signal, with proportionally more ^{12}C -enriched carbonate coming from the sulphate-reduction zone during deposition of the clay-rich goniatite interval, is very likely but remains undetermined. Organic carbon isotopic data from the reference fore-reef Wietrzna succession at Kielce, located in the same sedimentary basin (see Figs. 2A and 10–11), reveal the $\delta^{13}\text{C}$ “low” in the uppermost *transitans* Zone (Piechota and Małkowski, in prep.). Thus, regionally primary character of the lower Frasnian negative $\delta^{13}\text{C}$ excursion is unquestioned and may record a reduction in primary productivity as well as a decreased oceanic mixing and/or a sea level fall during their deposition (e.g. Caplan and Bustin, 1999; Immenhauser *et al.*, 2003). Nonetheless, a pronounced inter-locality variation within the $\delta^{13}\text{C}$ shifts in the *transitans* Zone, registered only in the certainly diagenetically-biased carbonate samples (initial event I in Fig. 10), remains a puzzle for further chemostratigraphical research. It is notable as well that coeval $\delta^{13}\text{C}$ values for a brachiopod calcite from Ardennes indicate a distinctly higher increase to values around 4.4‰ (Fig. 12; Yans *et al.*, in press).

DISCUSSION

Above appraisal of different proxies for oxygen-deficient environments, studied in the Szydłówek Beds to Kostomłoty Beds transition, provides a starting point for the elucidation of the evolving habitats and biofacies from regional and global viewpoints.

DEPOSITIONAL ENVIRONMENT AND BIOTA

The Kostomłoty-Łysogóry basin represents a submerged, small ("tongue"-like) part of the Laurussian shelf (Fig. 1), formed during the latest Eifelian deepening pulse (Fig. 11; Racki, 1993). The Szydłówek Beds are an example of the rhythmic Givetian to Frasnian hemipelagic deposition in the oxygen-depleted basin of the Kostomłoty transitional zone, occasionally affected by bioclastic-debris supplied from adjacent shoals, especially from vast lagoonal areas of the evolving Kielce carbonate platform (Racki and Bultynck, 1993). Northward, in the Łysogóry area, a comparable deeper-water facies is thicker (ca. 300–400 m, Nieczulice Beds; Czarnocki, 1950; Turnau and Racki, 1999; Malec, 2003). A similar ammonoid fauna with *Epitornoceras mithracoides* and *Acanthoclymenia genundewa*, but probably somewhat more advanced phylogenetically, was described by Dzik (2002) from lower Frasnian (*priamosica-africana* fauna; Racki, unpub.) black marly shales and limestones at Ścignia near Bodzentyn in this region (Fig. 2A).

Laminated sedimentary fabric and the dominantly pelagic biota of the Goniatite Level (styliolinids, cephalopods) suggest benthic anoxia (Oxygen Restricted Biofacies, ORB 2 of Wignall, 1994; Allison *et al.*, 1995). However, Th/U ratios and pyrite framboid sizes imply only dysoxic conditions. Very intensive early skeletal pyritization is evident from non-compacted shelly fossils, which additionally supports the dysaerobic facies assignment (Table 2; Brett *et al.*, 1991). Among shelly benthos (see below), numerous leiorhynchid brachiopods occur in places in the bottom part of shaly layers with the pyritized fossils (Krawczyński, pers. comm., 2004), suggesting perhaps transient colonization of atypical lower dysaerobic-type habitat (ORB 4). Nonetheless, the preservation of fine lamination indicates that a soft-bodied bioturbating community was mostly excluded, and presence of bacterial mats, restricting seawater recharge, could be an explanation for a sharp gradient in redox potential at the sediment-water interface (Powell *et al.*, 2003). Moreover, a key role of microbial biofilm in fossil pyritization processes has recently been emphasized by Borkow and Babcock (2003).

These unusual low-oxygen environments are part of hemipelagic settings that developed during early Frasnian deepening pulse (Fig. 11) under conditions of decreased carbonate productivity (an important factor in fossil pyritization; Brett *et al.*, 1991). This sea level rise is manifested also in the fore-reef environment over the northern slope of the Dyminy Reef by the onset of the storm-affected hemipelagic deposition found in the middle Wietrznia Beds (Szulczewski, 1971; Racki 1993; Racki and Bultynck, 1993). Basinal oxygen-deficiency probably increased near the close of the early Frasnian and was associated with a *Styliolina* acme producing a coquina resembling recent pteropod ooze (Tucker and Kendall, 1973). This marker horizon (Fig. 8) certainly records an interval of increased biotic productivity, reflected in the positive $\delta^{13}\text{C}$ excursion. The spectacular bloom of a suspension-feeding macroplankton (Thayer, 1974) was probably an immediate biotic response to enhanced nutrient supply. On the other hand, Kostomłoty basin was somewhat susceptible to transient oxygenation episodes and variable redox regimes (see examples in

Raiswell *et al.*, 2001 and Racki *et al.*, 2002), and progressive bioturbation of bottom muds in the early to middle Frasnian transition timespan is revealed by sedimentary fabric data (Fig. 4A). This changing level of bottom-water oxygenation permitted colonization by a pioneer soft-bodied infaunal biota, perhaps similar to high-density, symbiont-bearing annelid faunas encountered in modern dysoxic settings (Levin *et al.*, 2003).

The stagnant depositional phase in the Kostomłoty basin was followed by high-energy events recorded in the basal Kostomłoty Beds. As discussed by Racki and Narkiewicz (2000), syndimentary tectonic pulses probably caused large-scale resedimentation phenomena and coarse-detrital deposition (see Fig. 6) during the basal middle Frasnian sea level rise (IIc cycle of Johnson *et al.*, 1985; Racki, 1993).

In ecological terms, the typical goniatite/"*Buchiola*" dark shales carry a pyritized diminutive fauna, suggestive of a hypothetical site of ammonoid breeding (House, 1975, p. 482). It is somewhat uncertain whether the minute individuals are mostly juveniles or dwarfed adults (e.g. opportunistic species; see a comparable Cretaceous community in Lukeneder, 2003). Nonetheless, an increased juvenile mortality was a prominent biotic character of many hypoxic habitats, exemplified by low-diversity gastropod association described from a Carboniferous black shale by Nützel and Mapes (2001). Episodic pioneer colonization by specialized shelly faunas occurred as benthic oxygenation, and probably gradual shallowing, occurred westward in the Kostomłoty area (see Fig. 8). In fact, leiorhynchid and lingulid brachiopods are well-known dwellers of muddy low-oxygen habitats (Wignall, 1994; Allison *et al.*, 1995), exemplified in the early to middle Frasnian *Phlogoiderhynchus* Level in Holy Cross Mts. (Sartenaer and Racki, 1992; Racki, 1993). Moreover, biernatellid athyroids successfully settled the Kostomłoty basin during deposition of middle Szydłówek Beds (Baliński, 1995). For the Buchiolinae, in contrast to traditional view of these minute, ribbed, cardiolid bivalves as an epiplankton (Thayer, 1974; House, 1975), Grimm (1998) suggested exclusively benthic mode of life (as did Allison *et al.*, 1995). On the other hand, allochthonous amphiporoids (also calcispheroids and enclosing intraclasts; see Figs. 6A–C and 7), as well as crinoid detritus and some reef-dwelling gastropods (palaeozygopleurids; Krawczyński, 2002), are distal signatures of basinward transport of skeletal-muddy material from the Dyminy Reef during severe storm episodes (Racki and Bultynck, 1993).

RECORD OF THE GLOBAL DEEPENING-ANOXIC EVENT

The peculiar hypoxic regimes of the Goniatite Level are a typical example of the starved deeper-water regimes of the Łysogóry Basin (*sensu lato*) developed throughout early Frasnian eustatic rise of the IIb/c Subcycle (Figs. 11–12), as discussed by Racki (1993, p. 156–157) and Narkiewicz (1988). The diminutive ammonoid fauna from Kostomłoty is interpreted by Dzik (2002) as related to the Genundewa-Frasne deepening interval, a global bio-event. The reference Genundewa Limestone of New York is considered as a transgressive anoxic facies marked by pelagic styliolinids with a meagre benthos (House and Kirchgasser, 1993; Thayer, 1974). In general terms, the early Frasnian biotic turnover

(called also *Manticoceras* Event; Walliser, 1985, Racki, 1993), is regarded as a stepwise evolutionary change promoted by intermittent pulsatory transgression (House, 2002). Dzik (2002) recorded *Acanthoclymenia genundewa* that suggested correlation between the Goniatite Level and the Genundewa Limestone together with the overlying West River Shale of New York State (see House and Kirchgasser, 1993). However, the Genundewa Event has been dated as the upper part of the MN 2 Zone of Klapper (1997; see House and Kirchgasser, 1993; Becker and House, 1997; House *et al.*, 2000). Thus, this event predates the Kostomłoty hypoxic and eutrophic episode, and the conodont data (*cf.* Over *et al.*, 2003) point to time-equivalency of the Goniatite Level and the West River Shale. This implies delayed migration of the goniatite community toward this part of Laurussian shelf, as noted also for coeval conodonts by Racki and Bultynck (1993).

On the other hand, the timing of the Goniatite Level (i.e. *transitans* Zone with *Ancyrodella priamosica* = MN 4 Zone; Klapper and Becker, 1999; Over *et al.*, 2003) points to its link with the Timan Event of Becker and House (1997) (Fig. 12), even if the guide genus *Timanites* has not yet been found; the absence of this genus in Poland is typical for the western Palaeotethys (Becker, 2000, p. 391, fig. 2). The main styliolinite depositional phase of North Africa lies in the *transitans* Zone (Wendt and Belka, 1991: “Lower Kellwasser Beds”; Becker and House, 2000), and has been used jointly with Australian (Becker and House, 1997) and Timan evidence (House *et al.*, 2002) to define the global Timan Event. Notably, according to Becker and House (1997), this deepening pulse was characterized by a diversity of oxygenation regimes.

In general terms, however, organic-enriched deposition, with common styliolinid coquinas, is a remarkable supra-regional feature during early Frasnian spreading of oxygen-depleted waters onto the shelves, interpreted as evidence for an ongoing rise of the oxygen minimum zone (OMZ) triggered by transgressive pulses (Lüning *et al.*, 2003, 2004). Remarkably, this characteristic facies is described also from the basal middle Frasnian in the submerged Silesia-Cracow part of the southern Polish Devonian shelf (see Fig. 1A; Narkiewicz, 1978; Sobstel, 2003), and is also typical of the celebrated middle Frasnian Domanik suite of Eastern Laurussia (Maksimova, 1970; Kuzmin *et al.*, 1997). This depositional phase is especially well recorded in black organic-rich strata (TOC up to 14%) of the North Gondwanan shelf (Walliser, 1985, p. 404; Wendt and Belka, 1991; Becker and House, 1997, p. 135; Lüning *et al.*, 2003, 2004), where maximum anoxia is developed distinctly earlier, in MN 1-2 corresponding to the earliest Frasnian (Lüning *et al.*, 2004).

The oxygen-poor denitrified waters could indeed be attractive for biota due to increased chemical availability of nutrients occurring as reduced nitrogen compounds (anoxitropic biotope of Berry *et al.*, 1989). This still poorly-known niche (Levin *et al.*, 2003) was occupied by Palaeozoic plankton and nekton, such as styliolinids, thin-shelled bivalves and brachiopods, small orthocone nautiloids, and early ammonoids (e.g. Thayer, 1974), and was widespread across the oxygen-deficient shelves during sea level highstand in greenhouse climates (Berry *et al.*, 1989). Blooming of the specially adapted

biota during some anoxic events, exemplified by the Late Famennian *annulata* Event, is well known (Becker, 1992; Walliser, 1996).

REGIONAL RESPONSE TO THE MAJOR BIOGEOCHEMICAL PERTURBATION

The recent high-resolution carbon isotopic data of Yans *et al.* (in press) from lower to middle Frasnian brachiopod calcites of Belgium (Ardennes) reveal the most significant Devonian positive $\delta^{13}\text{C}$ shift to 5.85‰, followed by the abrupt negative excursion in the *punctata* Zone to -1.20‰ (cycle 6 in Fig. 12). This carbonate “heavy carbon” interval, that commenced during deepening pulse in the late *transitans* Zone and lasted ca. 0.5 m.y., is generally supported by isotopic data from Holy Cross Mts., including one brachiopod measurement ($\delta^{13}\text{C}$ = 4.32‰) from the *punctata* Zone at Kostomłoty–Mała Górki. Although a global extent of this isotope anomaly still awaits detailed study it is nevertheless strongly suggested by similar biogeochemical signals reported from the lower to middle Frasnian passage strata of Moravia and South China (Yans *et al.*, in press; see also van Geldern and Joachimski, 2001; Geršl and Hladil, 2004).

The advanced study of the Frasnian localities of Holy Cross Mts. (Piechota and Małkowski, in prep.) has confirmed and refined this overall positive-to-negative pattern. The somewhat fluctuating positive carbonate $\delta^{13}\text{C}$ excursion up to 4.5‰ is especially well-proved in bulk micrite samples from Kowala in the southern Kielce region (for a location see Fig. 2A), as well as in organic matter from Wietrzna (Fig. 10). Comparison with the $\delta^{13}\text{C}$ curves from the Kostomłoty sections (Fig. 8) shows that the Goniatite Level and *Styliolina* Horizon likely correspond to the variously recorded initial phase of this $\delta^{13}\text{C}_{\text{carb}}$ rise (event I), better developed in the Kostomłoty successions. Thus, the above discussed high-productivity styliolinid acme in progressively more hypoxic conditions was a conspicuous regional feature closely preceding the major worldwide perturbation in a carbon cycling (Fig. 12).

The highly positive C-isotope ratios are a signature of exceedingly enhanced bioproductivity and organic matter burial during the early to middle Frasnian rising sea level stands (Yans *et al.*, in press). An extraordinary acceleration of plant-mediated chemical weathering, promoted by a land-derived nutrient input, is usually assumed to be a crucial control on the generally elevated Frasnian marine bioproductivity (Algeo *et al.*, 1995; Joachimski *et al.*, 2001, 2002). Furthermore, influx of heavy carbon ^{13}C due to augmented carbonate weathering may have also enhanced a positive $\delta^{13}\text{C}$ signal (Kump and Arthur, 1999; Saltzman, 2002). The weathering biogeochemical impact would be especially significant only when linked to an accelerated water cycle during intensified greenhouse conditions (Ormiston and Oglesby, 1995; Saltzman, 2003); nevertheless, a prominent increase in surface water temperature is observed later in the middle Frasnian, with calculated ocean-surface water temperatures rising to 32°C during the late Frasnian (Joachimski *et al.*, 2004). Potentially important in the climatic-weathering context, Frasnian volcanism in the nearby Pripyat Trough (Belarus) associated with a development of a large-scale intraplate rifting, was

also essentially younger (see Aizberg *et al.*, 2001) than the worldwide biogeochemical perturbation under discussion.

More importantly, if nutrients were supplied exclusively from weathering of continental rocks, the nearshore domains (and not the distal pelagic areas) should show extensive evidence of eutrophication. However, the reverse is mostly true, what supports a marine nutrient recycling and/or upwelling as a main fertilization source for open carbonate shelves (Becker, e-mail comm., 2004; *cf.* also Racki *et al.*, 2002; Hiatt and Budd, 2003; Sageman *et al.*, 2003). In fact, the Frasnian sea level rises are seen as a key stimulus for organic matter burial (e.g. Lüning *et al.*, 2003, 2004; Sageman *et al.*, 2003), and the model of transgression-promoted migrating OMZ may be generally applied for the Kostomłoty intrashelf basin because the positive $\delta^{13}\text{C}$ shift is observed in intermittent, two-step eustatic sea level rise across the early to middle Frasnian transition (Racki, 1993; Fig. 12). In addition, the geochemical impact of meteoric fluids is diminished during sea level rise, and thus ^{13}C -depleted water masses effectively mixed with isotopically dissimilar ^{13}C -enriched oceanic waters (Immenhauser *et al.*, 2003). This positive $\delta^{13}\text{C}$ trend was temporarily reversed in its initial phase at least in the described part of the Laurussian shelf (Fig. 10). Nevertheless, an origin and maybe supra-regional extent of this signal (Fig. 12) requires additional investigation. An intricate intra-regional record of the major biogeochemical perturbation in the Devonian earth-ocean system (appearing conspicuous even when compared with the F-F boundary event; Yans *et al.*, in press) is especially noteworthy.

CONCLUSIONS

In the lower Frasnian (*transitans* Zone) rhythmic basin succession of upper Szydłówek Beds at Kostomłoty (western Holy Cross Mts.) includes a distinctive horizon named the

Goniatite Level. It is 1.6 m thick, highly fossiliferous, and pyrite- and organic-rich (Racki *et al.*, 1985). The mostly pelagic assemblage is dominated by diminutive (?mostly juvenile) molluscs including goniatites (Dzik, 2002), bivalves and styliolinids. This shaly-dominated interval is marked by a Th/U ratio and pyrite-framboid size-signature suggestive of dysoxic environments. The scarcity of infauna and bioturbation, resulting in laminated fabrics, as well as a low diversity of the presumed benthos (mostly brachiopods), suggest a stressful benthic habitat under conditions of reduced carbonate productivity and overall sediment starvation.

In the topmost part of the Szydłówek Beds, distinguished by the *Styliolina coquina* intertwined between limestone-bioturbated layers, the above geochemical proxies indicate a tendency to somewhat increased (?fluctuating) bottom oxygen deficiency and higher carbon burial rate linked with a bloom of pelagic biota during high-productivity episode. The specialized biota and distinctive environments were paired with invasion of oxygen-depleted waters during the transgressive Timan Event (*cf.* Becker and House, 1997) in the drowned part of southern Laurussian shelf that was free, however, of a sulfidic lower water column in the Kostomłoty basin.

Acknowledgments. This work has been supported by the State Committee for Scientific Research (KBN grant 3 P04D 040 22 for G. Racki). The British Council funded the Polish fieldwork for English co-authors as an element of the Academic Research Collaboration (ARC) scheme. Anonymous journal reviewer and T. Becker are kindly acknowledged for thoughtful examination of a draft and many constructive suggestions for improving the manuscript. Several workers and students of the Silesian University, particularly Dr. W. Krawczyński, Dr. M. Racka, M. Lewandowski, M. Rakociński, I. Jabłeka and A. Witek, assisted in the field and laboratory works. Drs. M. Sobstel, K. Małkowski and L. Marynowski kindly provided conodont, isotopic and TOC data, respectively.

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