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


The lower Frasnian (transitans Zone with Ancyrodella priamosica = MN 4 Zone) rhythmic basin succession of marly limestones and shales (upper Szydłowiek 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), bichuioline 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 Szydłowiek Beds, distinguished by the Styliolina coquina interbedded between limestone-biodetrital 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.

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-Lysogóry 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 Szydłowiek 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-
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, approximately 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. Gągol, 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).

Table 1

<table>
<thead>
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<th></th>
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<tbody>
<tr>
<td>euxinic (euxinic)</td>
<td>no pyritic fossils; finely disseminated framboids only</td>
<td>small (&lt; 5 μm), abundant with narrow size range (standard deviation &lt; 2)</td>
<td>finely laminated II 1</td>
<td>&lt; 1 (carb) &lt; 3 (shales)</td>
</tr>
<tr>
<td>lower dysoxic (lower dysaerobic)</td>
<td>no pyritic fossils; finely disseminated framboids only</td>
<td>small (&lt; 5 μm), abundant, but with rare, larger framboids</td>
<td>&lt; 1 (carb) &lt; 3 (shales)</td>
<td></td>
</tr>
<tr>
<td>upper dysoxic (upper dysaerobic)</td>
<td>pyritic fossils, nodular, tubular and crustose pyrite cavity lining pyrite druse, sparse nodular pyrite</td>
<td>moderately common to rare, broad range of sizes, with only a small proportion &lt; 5 μm diameter</td>
<td>microburrow-wed, bioturbation may partly obscure finely laminated fabric II 2</td>
<td>&gt; 1 (carb) &gt; 3 (shales)</td>
</tr>
<tr>
<td>oxic (aerobic)</td>
<td>no pyrite concentration</td>
<td>no framboids, very rare pyrite crystals</td>
<td>burrowed/massive, no fine lamination II 3–5</td>
<td>&gt;&gt; 1 (carb) &gt;&gt; 3 (shales)</td>
</tr>
</tbody>
</table>

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.
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 Szyd³ówek Beds up to 100 m thick (Malec, 2003). They are overlying Middle Devonian dolomites and biostromal-marly Laskowa Góra Beds, and underly- ing Upper Devonian detrital limestones of the Kostom³oty Beds (Szulczewski, 1981). The lower and uppermost parts of 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 Szyd³ówek Beds are well exposed in the Kostom³oty quarries, and the highest part was studied in two outcrops (Fig. 2A): 1 — primarily at the Ma³e Górki = Kostom³oty 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 Mogi³ki = Kostom³oty V (Kt-V) quarry in eastern Kostom³oty Hill, 2 km to E (see Figs. 3–5 and 8). In both exposures, the monotonous middle Szyd³ówek 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 Phlogoniderhynchus 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 Szyd³ówek Beds (Racki, 1985). Higher in the section, within the basal Frasnian part of the Szyd³ówek Beds, a transition to overlying Kostom³oty 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 Szyd³ówek Beds. The first occurrence of this conodont species marks the base of the punctata Zone and the boundary between the lower and middle Frasnian substages (Ziegler and Sandberg, 2001; see http://sds.uta.edu/sds18/page0042.htm).
MATERIALS AND ANALYTICAL METHODS

The upper Szydłowiek 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-IIE 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 frambooid populations. To better establish the character of oxygen-depleted regimes in the Szydłowiek to Kostomłoty Beds 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...
obtained by dissolution of micrite and/or (sporadically) brachiopod shell material in 100% H$_3$PO$_4$ 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 δ$^{13}$C and ± 0.04‰ for δ$^{18}$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 SZYDŁÓWEK BEDS

The 4.7 m thick, dark to black upper Szydłówek Beds at the Kt-IIE section (Fig. 4) represent a series of thin-bedded, homogeneous, 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 Philogoiderhynchus 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 micropetectolites; 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
graphic interval of the Szydłówek Beds (Fig. 6D). The pyrite content increases in places above 20% (although it is mostly between 1 to 2%; Gol, 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-IIJ section (Fig. 7), and towards 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 Male Górki (Fig. 8). The distinctively black-coloured Styliolina Horizon is 4 to 10 cm thick (Fig. 4B), and is well expressed both at the Kt-IIJ section and traced 2 km to E (Mogilki site; Fig. 6E). This horizon occurs as a graded styliolinid-brachiopod coquinite parting within detrital layers of the Kt-IIJ 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 amphioporoids, 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 (Wiązik, 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-IIJ, 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.

### Table 2

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

<table>
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<tr>
<th>Samples</th>
<th>δ¹³C</th>
<th>δ¹⁸O</th>
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<td>Kostomłoty–Małe Górki (Kt-IIW)</td>
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<tr>
<td>18</td>
<td>0.018</td>
<td>–4.447</td>
</tr>
<tr>
<td>19</td>
<td>0.711</td>
<td>–4.763</td>
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<tr>
<td>20</td>
<td>2.100</td>
<td>–4.517</td>
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<tr>
<td>25</td>
<td>2.509</td>
<td>–4.396</td>
</tr>
<tr>
<td>26</td>
<td>3.072</td>
<td>–3.946</td>
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<tr>
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<tr>
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<tr>
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<td>–3.692</td>
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<td>48</td>
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<td>Kostomłoty–Mogilki (Kt-V)</td>
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<tr>
<td>80</td>
<td>2.008</td>
<td>–4.124</td>
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* — 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 calcisphereids in clasts.
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 Opisthocoelus and Buchiola. Brachiopods are represented by small-sized biernatelids and larger (up to 3 cm) leiorhynchid rhynchonellids, probably mostly P. polonicus, supplemented by sporadic inarticulates (cf. Wiêzik, 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 association). Rock-forming styliolinids include widespread Styliolina ex. gr. nucleata Karpinsky, and S. domanicense Lyashenko (Haj³asz, 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. frambooid size populations (Table 1). Interpretation of the oxygen-depleted environments (Byers, 1977; Wignall, 1994)
was reinforced by microfacies analysis of limestone layers, as well as carbon isotope secular trends.

**GAMMA-RAY SPECTROMETRY VS. SEDIMENTARY FABRIC**

Gamma-ray spectrometry (GRS) of the 3.4 metres thick section of the upper Szydlówka Beds at Małe Górkki 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 Szydlówka 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 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-
tions thus adding an authigenic component to the detrital sedi-
ment 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 con-
tents: detrital sediments generally have higher Th contents than
carbonates with the result that the Th/U ratio of shales is typi-
cally greater than 3, but for pure carbonates the ratio is typically
lower than 1 (Myers and Wignall, 1987). At Ma³e 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 de-
posits (Myers and Wignall, 1987; Fig. 4A) suggesting oxy-
gen-restriction during deposition of the pyritic level.

PYRITE TAPHOFACIES VS. FRAMBROID SIZE POPULATIONS

Framboidal pyrite is common in the western Kostomloty
samples from the upper Szyd³ówek Beds, including the finely
laminated Goniatite Level. Four shaly samples are all domi-
nated by syngenetic populations with most framboids being
5–10 \( \mu \text{m} \), but with rarer larger forms supplemented by some
pyrite macrocrysts (Fig. 9A–B).

Sparse, and on average smaller and less variably sized, py-
rite framboids are found locally in the stylolinite sample (Fig.
9C–D). In contrast, sample Kt-IIW/47 from the overlying
fine-grained variety of Kostomloty 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 framboïds develop in the sulfidic
water column but are unable to achieve diameters much larger
than 5 \( \mu \text{m} \) before they sink below the Fe-reduction zone and
cease growth (Wilkin et al., 1996). Thus, euxinicity produces
populations of tiny framboids with a narrow size range. In con-
trast, 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 euxinicity is punctuated by brief sea-floor
oxygenation (see Bond et al., 2004).

Framboidal pyrite from the upper Szyd³ówek Beds has a
size distribution indicative of dysoxic conditions. The presence
of pyritic fossils paired with nodular and crustose pyrite aggre-
gates 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
Kostomloty 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 \( \delta^{13} \)C excursions in the transitans
Zone (Szyd³ówek Beds) and the transitional transits-punctata zonal interval (Kostomloty Beds). The first shift is ob-
served mostly below the Goniatite Level, where values of \( \delta^{13} \)C
increase from 0 to 3‰. The gradual decrease in \( \delta^{13} \)C is regis-
tered near the top of the Szyd³ówek Beds with a 0.8‰ mini-
imum within the upper Goniatite Level. The upper less distinct-
ive positive excursion in \( \delta^{13} \)C is affirmed higher in this succe-
sion. The increase in \( \delta^{13} \)C culminates up to ca. 3.1‰ above the
Styliolina Horizon.

This latter isotopic trend is reproduced by preliminary data
from the more extended Mogi³ki succession. Like in the

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**Fig. 11.** Position of the Kostomloty sections under study (Fig. 1B) against developmental stages of the Middle to Late Devo-
nian 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–IIIa — transgressive-regressive cycles modi-
fied from Johnson et al. (1985)
Kt-IIW section, the uppermost Szydłówek Beds are marked by the significant δ13C shift from 1.4‰ to above 3.3‰, with a peak located just above the guide stylolinite 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 δ13C 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 δ13C and δ18O 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 definitively; therefore, only more reliable carbon isotopic data (as summarized in Brand, 2004; see also Joachimski et al., 2004) are interpreted below.

Positive δ13C 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” δ13C 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 δ13C may serve as indicator of enhanced burial of organic matter that is expected to reduce the concentration of oceanic dissolved carbon dioxide (Brasier, 1995; Caplan and Bustin, 1999; Joachimski et al., 2002).

On the contrary, the noticeable drop in δ13C characterizes black-shale facies (especially the upper Goniatite Level). A diagenetic signal, with proportionally more 12C-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 Wietrznia succession at Kielce, located in the same sedimentary basin (see Figs. 2A and 11), reveal the δ13C “low” in the uppermost transitans Zone (Piechota and Małkowski, in prep.). Thus, regionally primary character of the lower Frasnian negative δ13C 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 δ13C 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 δ13C 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 bioclines from regional and global viewpoints.
DEPOSITIONAL ENVIRONMENT AND BIOTA

The Kostomłoty-Lysogóry 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 Szydlówka 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 Lysogóry 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 Acanthocylnenia 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 Scignia near Bodzentyn in this region (Fig. 2A).

Laminated sedimentary fabric and the dominantly pelagic biota of the Goniatite Level (stylolinitids, cephalopods) suggest benthic anoxia (Oxygen Restricted Biofacies, ORB 2 of Wignall, 1994; Allison et al., 1995). However, Th/U ratios and pyrite framoid 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 northern slope of the Dymny Reef by the onset of the storm-affected hemipelagic deposition found in the middle Wietrzna 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 Stylolina acme producing a coquina resembling recent pteropod oozes (Tucker and Kendall, 1973). This marker horizon (Fig. 8) certainly records an interval of increased biotic productivity, reflected in the positive δ13C 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), synsedimentary tectonic pulses probably caused large-scale resedimentation phenomena and coarse-detrital deposition (see Fig. 6) during the basal middle Frasnian sea level rise (Ilc cycle of Johnson et al., 1985; Racki, 1993).

In ecological terms, the typical goniatite “Buchiola” dark shales carry a pyritized dimmutive 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 Lukender, 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 Phlegoiderhynchus Level in Holy Cross Mts. (Sartenaer and Racki, 1992; Racki, 1993). Moreover, biernatellid athyroids successfully settled the Kostomłoty basin during deposition of middle Szydlówka Beds (Balinski, 1995). For the Buchiolinae, in contrast to traditional view of these minute, ribbed, carinothid bivalves as an epiphanckton (Thayer, 1974; House, 1975), Grimmm (1998) suggested exclusively benthic mode of life (as did Allison et al., 1995). On the other hand, allochthonous amphioporoids (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 Dymny 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 Lysogóry Basin (sensu lato) developed throughout early Frasnian eustatic rise of the Ihb/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-Frasnian transition time interval, a global bio-event. The reference Genundewa Limestone of New York is considered as a transgressive anoxic facies marked by pelagic stylolinites with a meagre benthos (House and Kirchgasser, 1993; Thayer, 1974). In general terms, the early Frasnian biotic turnover...
Klapper and Becker, 1999; Over et al. 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 transits 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., 2000) 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 Kielce region (for a location see Fig. 2A), as well as from the OMZ zone to –1.20‰ (cycle 6 in Fig. 12). This carbonate “heavy carbon” interval, that commenced during the early to middle Frasnian rising sea level stands (Yans et al., 2003, 2004), where maximum anoxia is developed distinctly prior to the Kostomłoty succession (Walliser, 1996). 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 13C due to augmented carbonate weathering may have also enhanced a positive 13C 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 δ13C 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 13C-depleted water masses effectively mixed with isotopically dissimilar 13C-enriched oceanic waters (Immenhauser et al., 2003). This positive δ13C 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 Szydlówka 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 stylolinitids. 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.

The topmost part of the Szydlówka Beds, distinguished by the Styliolina coquina intertwined between limestone-biodetrital 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.

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