

# Palaeoceanographic linkage of geochemical and graptolite events across the Silurian–Devonian boundary in Bardzkie Mountains (Southwest Poland)

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## Abstract

The Silurian–Devonian (S–D) transition in the Bardzkie Mountains is developed as deep-water, graptolitic black shales. The highest Silurian *transgrediens* Zone and the first Devonian *uniformis* Zone are separated by a thin (30 cm) interval of a linograptid ‘interregnum’. Thirteen samples from the S–D transition have been analysed for major and minor elements. Si/Al, Si/Al/TOC, Ga/Al<sub>2</sub>O<sub>3</sub>, V/V + Ni ratios and TOC, Mn, Zr, Ti, Re, Mo, Cd, Cu and REE have been found to correlate with the habitat replacement of the graptolite assemblages. The linograptid burst, accompanied by changing sediment geochemistry across the S–D boundary, are attributed to short-term shallowing of the upwelling system which introduced specific nutrient-rich waters into the mixed layer. © 1997 Elsevier Science B.V.

**Keywords:** black shales; geochemical event; graptolite event; palaeoceanography; Silurian–Devonian boundary; Poland

## 1. Introduction

The Silurian–Devonian transition has long attracted the attention of geoscientists as a model example of the ‘golden spike’ application in redefining chronostratigraphic boundaries (McLaren, 1977). In reconstructing the Earth’s history in terms of an event scenario, this transition has not so far been related to any distinct event. Boucot (1990) noted minor bio-events which are not synchronous with the systems’ boundary and are difficult to tie to any particular causative physical factors.

The focus is here on the Silurian–Devonian

transition recorded in an oceanic pelagic sequence of the Bardzkie Mountains (Sudetes) in southwestern Poland. The succession of graptolite assemblages (EP) has been compared with geochemical data (ZS) to propose a possible model of palaeoceanic events.

## 2. Regional setting

The Palaeozoic succession of the Bardzkie Mountains (West Sudetes) is conventionally assigned to the Saxothuringian domain of the European Variscides (Fig. 1). The succession reveals fragments of an accretionary prism, including the uppermost Ordovician to Lower

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Fig. 1. Map showing the location of the section studied (arrowed) within the main tectono-facies zones of the European Variscides (modified from Bard et al., 1980).

Carboniferous sequences, believed to be deposited on the ocean floor in trench and volcanic arc settings (Wajsbrych, 1986; Franke et al., 1993). The original spatial configuration and geotectonic significance of the West Sudetes remain poorly constrained. In palaeogeographic reconstructions of the Silurian world (Scotese and McKerrrow, 1990; Moore and Hayashida, 1993), the West Sudetes can be placed within an area of Gondwana-derived continental to microplate-sized islands and island arcs, located in the southern part of the warm, tropical to subtropical Rheic ocean (Fig. 2).

### 3. Local stratigraphic setting

The best, most complete section of the Lower Palaeozoic in the Bardzkie Mountains is known

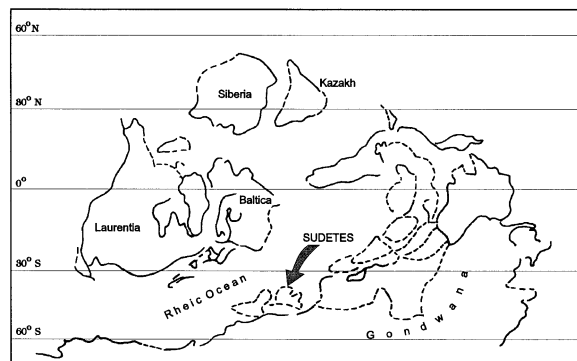


Fig. 2. Late Silurian palaeogeography showing the present-day continental outlines (modified from Scotese and McKerrrow, 1990).

from Zdanów (Fig. 3). The section begins with the Ashgill Jodłownik Beds, which are shaly deposits laid down in oxygenated bottom conditions. The shales are interbedded upwards with thin silt turbidites and possibly tractionites. Upwards, the shales become increasingly interbedded with light-coloured radiolarian cherts (Porębska, 1982; Wyżga, 1987).

Silurian and Lower Devonian strata, ca. 70 m thick, are highly condensed stratigraphically and show a distinct tri-partition, with two levels of black graptolitic shales separated by grey-greenish shales. In the informal lithostratigraphic nomenclature these are known as the Lower and Upper Graptolitic Shales and the Green Shales, respectively, all showing continental extents (Jaeger, 1976). The lithology is typified by radiolarian bedded cherts, siliceous shales and clayey shales containing phosphate nodules and thin tuff layers. All these shaly sediments show a variety of pervasive subtle laminations, lacking any disruption by bioturbation. Faunal remains comprise only planktonic elements, including abundant graptolites, rare conodonts and radiolarians. Deposition is inferred to have taken place on a distal basin plain in a fully pelagic setting far from any recognizable land influence, and was accompanied by anoxic bottom conditions (Wyżga, 1987). The biostratigraphy and chronostratigraphy of the Zdanów section are based on graptolites (Malinowska, 1955; Porębska, 1982; Fig. 3).

The Silurian–Devonian boundary interval at Zdanów (Fig. 4, Table 1) consists of black, laminated, non-bioturbated, clayey and siliceous shales. The highest Silurian *transgrediens* Zone (1.8 m thick) and the first Devonian *uniformis* Zone (3.2 m thick) are separated by a 30 cm thick interval: the so-called linograptid ‘interregnum’. The Silurian–Devonian boundary has been assigned to the base of the *uniformis* Zone (Porębska, 1982).

### 4. Succession of graptolitic events across the Silurian–Devonian boundary in Zdanów

In the interval under discussion, the replacement of graptolitic biotas is abrupt (Fig. 4). It forms a

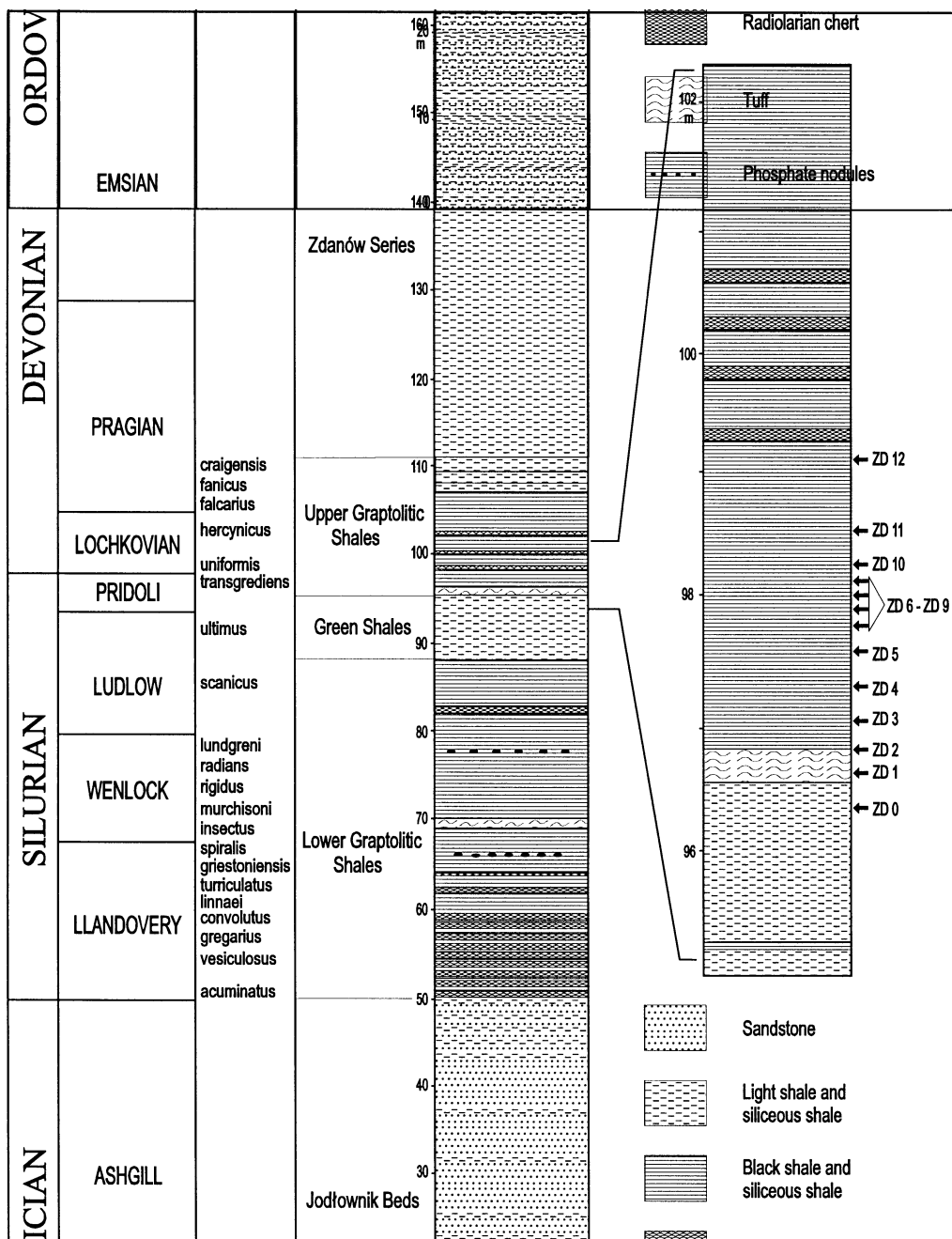


Fig. 3. Stratigraphic succession of the Zdanów section and sample locations.

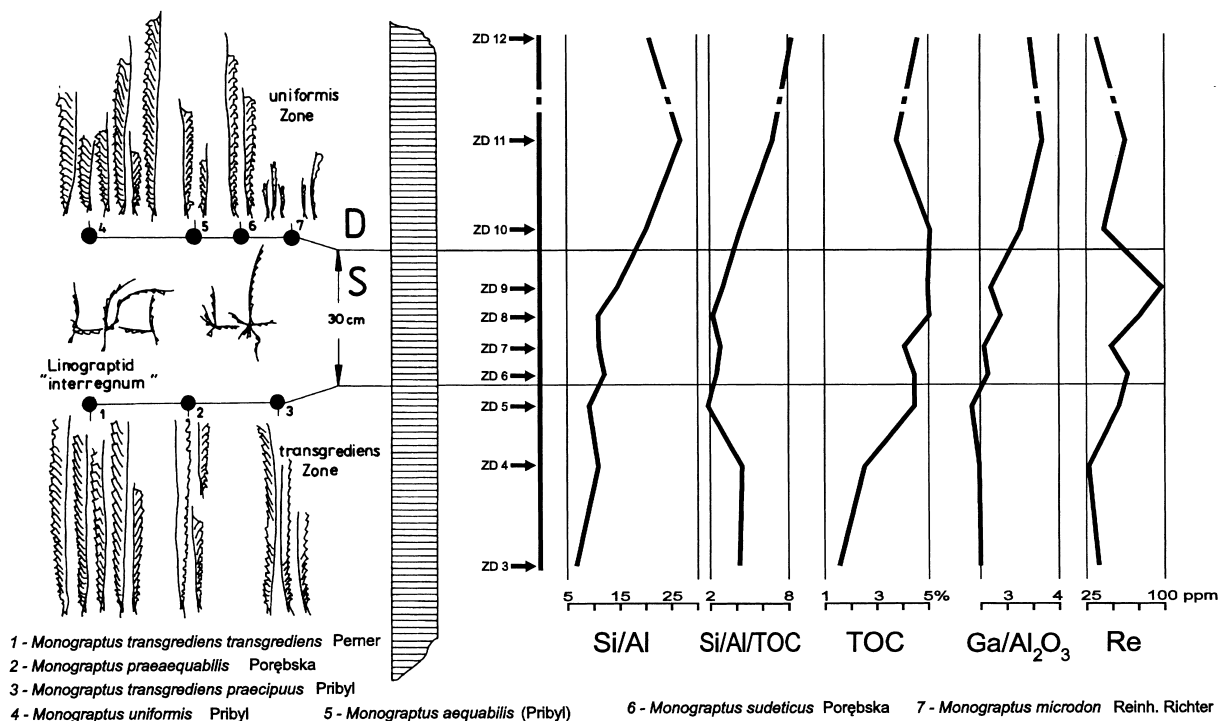


Fig. 4. Graptolite succession and geochemical patterns across the Silurian/Devonian boundary in the Zdanów section.

Table 1

Description of samples from the Zdanów S–D boundary section

Sample	Macroscopic description	Mineralogical composition
ZD0	Green shale, laminated, detrital quartz grains	I, Q (F)
ZD1	Pyroclastics, laminated	I, Q (Z, F)
ZD2	Black–brown shale, laminated	I, Q (F)
ZD3	Black shale, laminated	I (Q, F)
ZD4	Black shale, laminated	I (Q, F)
ZD5	Black shale, laminated	I (Q, F)
ZD6	Black shale, laminated	I (Q, F)
ZD7	Black shale, laminated	I (Q, F)
ZD8	Black shale, laminated	I (Q, F)
ZD9	Black shale, laminated	I, Q (F)
ZD10	Siliceous black shale, laminated	Q, I (F)
ZD11	Siliceous black shale, laminated	Q (I)
ZD12	Siliceous black shale, laminated	Q (I)

Q = quartz, I = illite, F = feldspars, Z = zeolites, () = subordinate amounts.

characteristic pattern composed of a succession of three taxonomically different assemblages:

(1) The latest Silurian fauna, further referred to as *transgrediens* fauna, consists of relatively common specimens of *Monograptus trans-*

*grediens transgrediens* Perner, *Monograptus transgrediens praecipuus* Pribyl, *Monograptus praeaequabilis* Porebska and rare *Linograptus posthumus* (Reinh. Richter).

(2) A successive, younger assemblage represents

an exceptionally high population of the long-range (early Ludfordian–Lochkovian) *L. posthumus*. Besides its abundant occurrence, this species stands out by its, as yet unprecedented, strong morphologic variability, expressed in branching patterns (Porębska, 1982).

- (3) The *uniformis* fauna, which is diagnostic of the Devonian, tends to appear suddenly, though not in a large quantity. This fauna is represented by *Monograptus uniformis uniformis* Pribyl, *Monograptus uniformis angustidens* Pribyl, *M. uniformis parangustidens* Jackson and Lenz, *M. microdon* Reinh. Richter and *Monograptus sudeticus* Porębska. The frequency of *L. posthumus* decreases drastically attaining a level similar to that found in the *transgrediens* Zone.

The succession of the most important graptolitic bioevents recognized in the interval studied can be summarized as follows: (1) the extinction or rapid emigration of the Silurian *transgrediens* fauna; (2) the population burst of *L. posthumus*; and (3) the rapid immigration of the Devonian *uniformis* fauna. This succession of graptolitic faunas was most likely a habitat displacement. Thus, the key issue is graptolite ecology. As yet, there is no agreement on some of the fundamental questions regarding graptolite behaviour (compare Underwood, 1993; Rigby, 1991, 1992), but competition must have meant that forms as different as multi-branched linograptids, on one hand, and uni-branched Silurian and Devonian monograptids, on the other, were suited to different ecological niches. Rigby (1991, 1992) developed a theoretical relationship between food availability and the graptoloid morphology. Berry et al. (1987) and Wilde et al. (1990) suggested that the graptolitic ecology was closely linked to changes in the depth and thickness of the denitrification zone. In the Early Palaeozoic ocean this zone was likely to have been a global transition redox layer between the oxygen-rich mixed surface layer and more anoxic (euxinic) waters at depth (Wilde et al., 1991).

Thus, from the aforementioned studies it can be suggested that the uniserial, straight monograptid colonies (*uniformis* and *transgrediens plexus*) were

probably high-intensity feeders adapted to conditions at the base of the mixed layer, or near the top of the denitrification zone. Large, multiramous linograptid colonies were likely to be low-intensity feeders living higher in the mixed layer. The short-term expansion of the *Linograptus* population above normal background levels may be a response to a rise in the anoxic pycnocline, favouring the proliferation of the *Linograptus* population but at the same time lethal for *transgrediens plexus* forms. The diversity of the *Linograptus* branching patterns in the linograptid interregnum probably records maximum food efficiency of this species. A sinking of the pycnocline with the onset of the Devonian caused a decline in the linograptid fauna, and re-established living conditions favourable for uniserial *uniformis*-type graptolites.

## 5. Sample location and geochemical methods

Samples for geochemistry were collected from a 4.5 m thick section extending from the top of the Green Shales (D0 — middle Pridoli) to the middle part of the Upper Graptolitic Shales (D12 — middle Lochkovian). Distances between sampling sites were chosen to properly document the graptolite zonation. Samples of black and siliceous shales (ZD3–ZD12) represent a succession of macroscopically monotonous lithologies. The sample locations are shown in Fig. 2. The macroscopical and mineralogical description of the samples studied is given in Table 1.

Mineralogy was determined using the XRD method and microscopical observations. Most of the major and minor elements were determined from glass beads using a Philips XRF spectrometer. Sulphur and carbon were determined coulometrically on a Coulomat 702 (Stroehlein). Solutions were prepared using acid attack HF–HNO<sub>3</sub>–HClO<sub>4</sub> in a teflon bomb and measured by the AAS method (Cd, Bi and Tl) on a Perkin-Elmer 4000 spectrophotometer and by the ICP/MS method (REE) on a Perkin-Elmer ELAN SCIEX 250 spectrometer.

## 6. Mineralogy

Green (ZD0) and black shales (ZD2–ZD8) are composed principally of quartz, illite, and minor amounts of feldspar (albite). Pyroclastic rock (ZD1) contains additionally small amounts of zeolites. Siliceous black shales (ZD9–ZD12) contain mainly quartz and minor amounts of illite. Samples of the lower (ZD0–ZD4) and upper (ZD11–ZD12) parts of the section reveal macroscopically visible lamination (spacing: 0.1–0.5 mm). Samples ZD5–ZD10 display finer lamination visible only under a microscope. Samples ZD0 and ZD10–ZD12 contain minor amounts of quartz grains (0.02 mm in diameter), probably recrystallized radiolarians. In sample ZD10 relatively well preserved spherical radiolarians (0.05 mm in size) are observed occasionally.

## 7. Geochemical results

Detailed results of the geochemical investigation of the section are published elsewhere (Sawłowicz, in prep.). Here, only the most pertinent data for an environmental study are presented (Table 2).

Sample ZD0 represents the uppermost part of the Green Shales in the section. In comparison to black shales in the section, it is characterized by the lowest contents of silica and TOC, the highest contents of alumina,  $\text{TiO}_2$ ,  $\text{P}_2\text{O}_5$ , MnO, Ce and REE, and the lowest ratios of  $\text{V}/(\text{V}+\text{Ni})$ ,  $\text{Ga}/\text{Al}_2\text{O}_3$  and  $\text{Si}/\text{Al}$ . The tuffaceous sample ZD1 is characterized by the lowest contents of silica, and the highest contents of  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , Cu, Cd, Cr, Ni, V, W, Y, Tl. Sample ZD2, taken from shale just above a tuff layer, is composed of laminae of black shale and pyroclastic material. Except for a higher content of TOC and S, it is geochemically similar to the underlying green shale, although it carries some admixture of a pyroclastic material typified by high contents of  $\text{Fe}_2\text{O}_3$ , Cd, V and Tl.

Samples ZD3–ZD5 belong to the *transgrediens* Zone. Samples ZD6–ZD9 were taken from the linograptid interregnum, and samples ZD10–ZD12 from the *uniformis* Zone. Higher samples in the *transgrediens* Zone are characterized by increasing

contents of  $\text{SiO}_2$  and TOC, and decreasing contents of  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{P}_2\text{O}_5$ , MnO, and REE. The first sample of this zone (ZD 3) is enriched in both REE and P. The major element geochemistry of the linograptid interregnum is uniform and characterized by the lowest  $\text{Si}/\text{Al}/\text{TOC}$  ratio. Some of the minor elements of the interregnum are very variable. The first sample of the linograptid interregnum (ZD6) contains an unusually high content of Cu, and the next sample ZD7 contains unusually high contents of Mo, Co and Cd, in comparison to other samples of the section. The uppermost sample (ZD9) is characterized by the highest Re and REE contents. Geochemically, the *uniformis* Zone is significantly different from the preceding zones, and is characterized by the highest contents of silica,  $\text{Ga}/\text{Al}_2\text{O}_3$ , and  $\text{Si}/\text{Al}$  ratios, and the lowest contents of  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , Ce, and Zr. The uppermost sample of this zone (ZD12) is abnormally enriched both in REE and P.

### 7.1. Interpretation

The unusual concentrations of Cu, Mo and Cd in the linograptid interregnum could be explained by bioenrichment (Degens and Ittekkot, 1982). Glikson et al. (1985) found that, in Australian oil shales, Cu was occasionally concentrated in bacterial cell walls and Mo concentrated by nitrogen-fixing cyanobacteria. Moreover, high contents of these elements may be due to a very low sedimentation rate (see Brumsack, 1986). The uppermost sample (ZD9) of the linograptid interregnum is characterized by the highest Re and REE content and may reflect the strongest anoxic conditions and the lowest sedimentation rate. Under strongly reducing conditions Re is removed and precipitated as an insoluble sulphide or oxide (Goldberg, 1987).

A  $\text{Si}/\text{Al}$  ratio of about 3 is considered to be an average ratio for terrigenous sediments (Garrels and MacKenzie, 1971). Thus, the values of  $\text{Si}/\text{Al}$  ratio above 3 reflect biogenic silica (radiolarian) production. This ratio initially increases in the *transgrediens* Zone, then stabilizes and suddenly jumps at the linograptid interregnum/*uniformis* boundary, and thereafter stabilizes in the *uniformis* Zone (Fig. 3).  $\text{Si}/\text{Al}/\text{TOC}$  is suggested here as a

Table 2  
Geochemistry of the Zdanów S–D boundary section

Sample	SiO <sub>2</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	CaO (%)	MgO (%)	Na <sub>2</sub> O (%)	K <sub>2</sub> O (%)	TiO <sub>2</sub> (%)	P <sub>2</sub> O <sub>5</sub> (%)	S (%)	C <sub>carb.</sub> (%)	TOC (%)
ZD0	70.1	13.7	3.3	0.17	1.46	0.5	3.42	0.66	0.06	0.19	0.05	0.27
ZD1	50.3	15.7	9.8	0.24	1.01	0.61	2.49	0.50	0.54	0.50	0.46	3.56
ZD2	68.5	11.1	5.3	0.17	1.01	0.34	2.80	0.56	0.10	0.80	0.04	1.28
ZD3	76.4	9.7	2.1	0.21	0.91	0.70	2.29	0.45	0.09	0.15	0.07	1.64
ZD4	81.4	6.4	1.9	0.21	0.58	0.32	1.57	0.30	0.05	0.21	0.22	2.49
ZD5	77.4	7.9	1.2	0.20	0.73	0.34	2.00	0.39	0.03	0.17	0.20	4.56
ZD6	81.2	6.0	1.1	0.18	0.54	0.30	1.48	0.29	0.02	0.14	0.16	4.56
ZD7	81.5	6.1	1.0	0.16	0.54	0.33	1.53	0.31	0.02	0.16	0.02	4.05
ZD8	79.3	6.3	1.1	0.22	0.59	0.29	1.59	0.31	0.03	0.16	0.01	4.96
ZD9	80.9	5.6	1.0	0.16	0.51	0.25	1.40	0.29	0.02	0.09	0.08	4.94
ZD10	83.6	3.7	1.1	0.11	0.32	0.19	1.01	0.22	0.02	0.21	0.03	5.09
ZD11	86.9	3.2	0.7	0.09	0.26	0.17	0.86	0.21	<0.01	0.23	0.10	3.78
ZD12	87.2	3.8	0.9	0.11	0.31	0.10	0.93	0.21	0.15	0.07	0.06	4.56

Sample	MnO (ppm)	Ce (ppm)	Cu (ppm)	Mo (ppm)	Re (ppm)	Zr (ppm)	Cd (ppb)	REE (ppm)	V/V + Ni	Ga/Al <sub>2</sub> O <sub>3</sub>	Si/Al	Si/Al/TOC
ZD0	130	95	89	8	19	105	335	168	0.72	1.60	4.5	16.90
ZD1	120	57	170	15	38	88	1730	174	0.69	1.46	2.8	0.80
ZD2	90	53	88	18	30	105	1020	161	0.95	2.16	5.5	4.29
ZD3	70	52	59	11	40	66	345	107	0.71	2.47	7.0	4.27
ZD4	60	46	43	21	30	53	290	94	0.88	2.50	11.3	4.55
ZD5	60	44	27	15	62	62	305	61	0.92	2.27	8.7	1.91
ZD6	50	32	140	8	70	49	265	70	0.86	2.67	12.0	2.75
ZD7	50	36	23	50	53	51	700	95	0.89	2.62	11.9	2.94
ZD8	60	54	24	16	75	53	230	86	0.91	2.86	11.2	2.26
ZD9	60	53	38	12	100	53	190	121	0.91	2.68	14.4	2.92
ZD10	50	21	19	11	42	36	175	83	0.89	3.24	20.1	4.43
ZD11	50	24	<10	8	65	33	115	72	0.89	3.68	27.1	7.17
ZD12	60	25	40	12	34	36	275	90	0.93	3.44	20.4	8.04

ratio reflecting the relative contribution of organic matter from siliceous and non-siliceous plankton. This ratio is around 4.4 in the *transgrediens* Zone decreases to 2.3–2.9 in the linograptid interregnum and again increases in the *uniformis* Zone from 4.4 to 8.0. A decrease of this ratio and an increase in TOC content begin in the uppermost sample of the *transgrediens* Zone.

Vanadium accumulates relative to nickel in strongly reducing environments (Lewan, 1984). Anoxic sediments are also characterized by low contents of Mn (Quinby-Hunt and Wilde, 1994). The green shale (ZD0) has 130 ppm MnO and a V/V + Ni ratio of 0.7, suggesting moderate anoxic conditions. The relatively uniform and low contents of MnO (around 60 ppm) and the high

ratios of V/V + Ni (around 0.9) in samples ZD2 to ZD12 reflect strongly anoxic conditions at the sea bottom. For comparison, Hatch and Leventhal (1992) put the boundary between dysoxic/anoxic and anoxic bottom waters at a V/V + Ni ratio between 0.7 and 0.8 in the Upper Pennsylvanian shales in Kansas.

Shaw (1957) showed that Ga is depleted relative to Al during weathering. The Ga/Al<sub>2</sub>O<sub>3</sub> ratio is the lowest in the Green Shales, slowly increases upsection in the *transgrediens* Zone and linograptid interregnum, and strongly increases in the *uniformis* Zone. This may reflect a decrease in continental weathering. The similar behaviour of TiO<sub>2</sub> and Zr (decreasing contents upwards in the section) suggests an increasing distance from the land. The

decrease in REE contents through the *transgrediens* and *uniformis* Zones may reflect both above-mentioned processes, which resulted in a decreasing detrital influx to the sediment. In the linograptid interregnum this general trend could be overprinted by other processes as well. The here observed significant increase in the REE content can be explained either by a lower sedimentation rate, which would result in a more efficient scavenging of REE from seawater, by upwelling of deep water rich in REE (Elderfield and Greaves, 1982), or by different adsorption processes on non-siliceous planktonic matter.

The content of sulphur in the Zdanów section is very low in comparison to other black shales, and is comparable to that of average shale with a low organic carbon content. Typically, sulphur in black shales is bound in sulphides formed by bacterial sulphate reduction. A low content of sulphides can result from a limited supply of iron, organic matter or sulphates. In the present instance, the availability of iron seems to be a crucial limiting factor. Another possible explanation is provided by Wilde et al. (1989) who suggested that, at a certain level of anoxicity, easily soluble ammonia complexes of iron may impede the precipitation of iron sulphides. A very low content of metals may be related to a scarcity of sulphides, which are one of the main metal carriers in black shales and, moreover, it reflects a large distance from land and/or moderate weathering.

The relatively uniform and low contents of MnO (around 60 ppm) in the black shales (ZD3 to ZD12), coupled with high V/V + Ni ratios, reflect strongly anoxic conditions at the sea bottom. The green shale (ZD0) has 130 ppm MnO and low V/V + Ni ratio, suggesting moderate anoxic conditions. The very low content of Mn in comparison with other black shales may be due to a very low content of carbonates, which in some anoxic sediments can precipitate manganese.

The average content of phosphorus in the Zdanów section is lower than in the 'average' shale and 'average' black shale. Only the highest sample in the *uniformis* Zone has a higher P<sub>2</sub>O<sub>5</sub> content. This may reflect either an increased upwelling, or syndepositional redistribution of phosphorus; sev-

eral beds enriched in phosphate nodules are observed in the black shale sequence.

## 8. Discussion

In many ways, the Silurian Period represents a unique situation not comparable with Cenozoic and Mesozoic environments. The graptolite-bearing black-shale lithotype appears to represent a peculiar record of the Silurian hydrosphere, atmosphere and biosphere — a unique system which probably did not reappear later during Earth's history. The depositional environment of graptolitic black shales favoured a preservation of organic matter, with deep-water anoxia being the most crucial environment (compare Wilde and Berry, 1982).

The graptolitic black shales in the Zdanów section can be considered to represent a bioproductite whose lithology reflects subtle variations in the primary productivity of the main Silurian organic carbon producers — cyanobacteria and phytoplankton (Wellman and Richardson, 1993) as well as radiolarians. This productivity record appears to have been diluted only to an insignificant degree by terrigenous influx. The very fine-grained, illitic shales were probable derived from distant sources and deposited mainly as eolian dust. The abundance and vertical stacking of siliceous oozes in pelagic sections are believed to reflect mainly periodic variations in the productivity of siliceous plankton (Lisitzin, 1985). The effects of pre-diagenetic opal dissolution and burial diagenesis are thought to be insufficient to distort the primary productivity signal (compare Decker, 1991). Fluctuations in TOC content are not always simply related to the intensity of organic productivity. However, a slow and nearly constant sedimentation rate, very low terrigenous input, and evidence of permanent anoxia observed in the Zdanów section, all indicate that the preserved TOC is a strong productivity signal (compare Demaison and Moore, 1980).

Considering the relationships between graptolitic events and geochemical signatures recognized in the Zdanów section, the following sequence of



palaeoceanographic events can be proposed for latest Silurian—earliest Devonian times (Fig. 5):

### 8.1. Middle Ludlow—middle Pridoli

The Green Shales appear to record an anoxic ocean with a pronounced thermohaline stratification, with the mixed layer and nitrate-reduction zone below. Restricted deep-water circulation led to decreasing upwelling conditions. This lowered the overall supply of nutrients to the upper water column and had a particularly negative effect on the productivity of cyanobacteria and phytoplankton (TOC content about 0.3%). The lack of graptolites may be due to limiting anoxic levels. The relatively low V/V+Ni ratio and the high Mn content suggest a dysaerobic/anaerobic water column. Thus, the Green Shales can be interpreted as anoxic deposits reflecting a low primary bioproductivity. They may record an ocean state comparable to a starved ocean basin (*sensu* Berger et al., 1989), a stagnant basin (Bralower and Thierstein, 1984), and to some extent comparable to the 'secundo episode' of an ocean-climate evolution (Jeppsson, 1990).

Various oceanic–climatic–biotic feedback systems have been postulated for such ocean conditions (Brasier, 1992), but their discussion is beyond

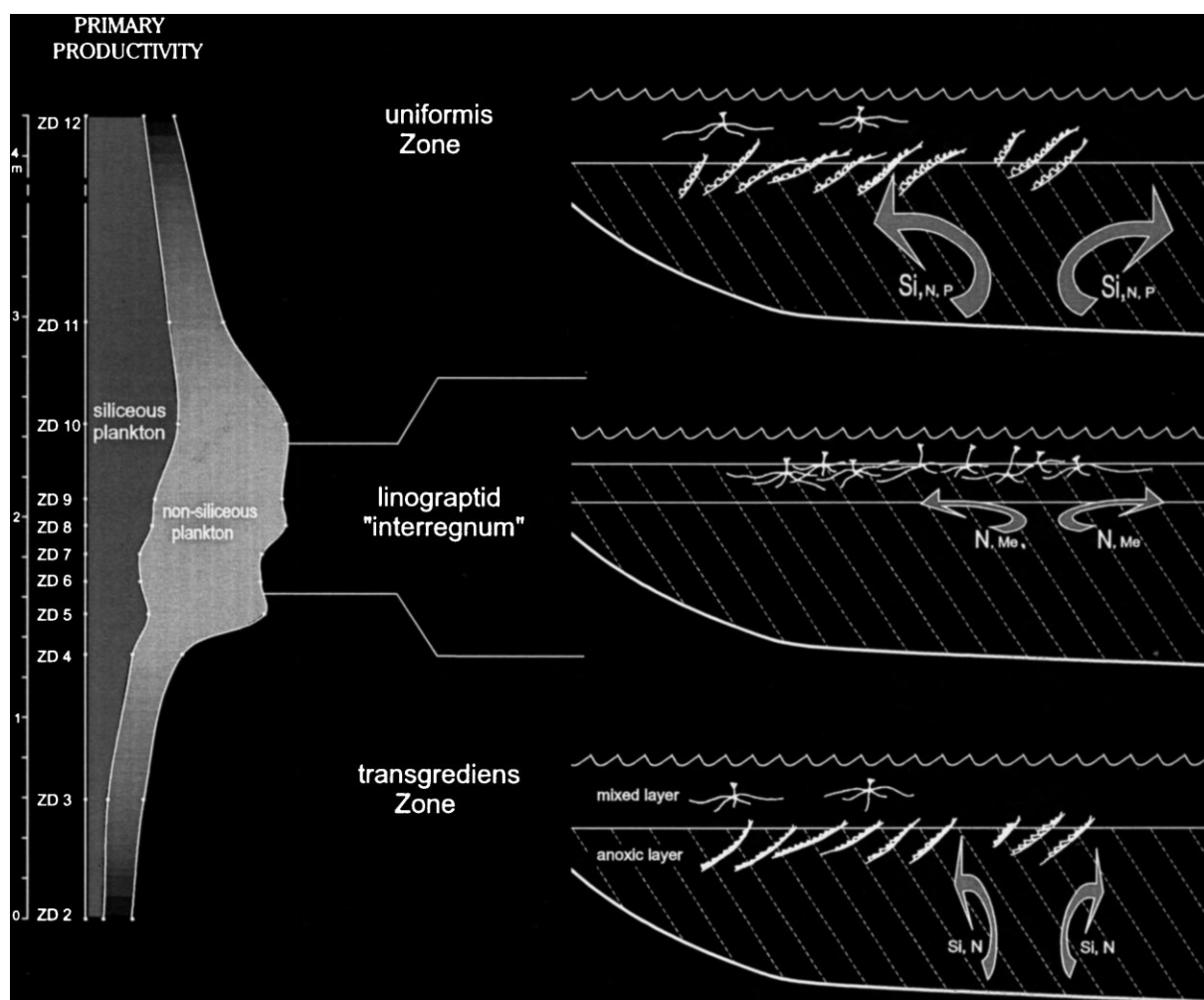


Fig. 5. Scenario of palaeoceanographic events during the latest Silurian and earliest Devonian.

the scope of the present paper. However, it is noteworthy that the deposition of the Green Shales was coincident with the warmest climatic conditions during the Silurian (compare Frakes, 1979), and by a global stillstand of sea-level (Schenk, 1991). The high Zr and  $\text{TiO}_2$  contents and the low Ga/ $\text{Al}_2\text{O}_3$  ratio point to a more intense weathering, and possibly smaller distances to land-masses, compared with succeeding periods.

### 8.2. *Late Pridoli (transgrediens Zone)*

The rapid onset of a black-shale facies marks a new stage in the evolution of the Silurian anoxic ocean. This event was interregional in extent, as it has been recorded at numerous coeval sections across the northern periphery of Gondwana, such as Bavaria, Thuringia, the Carnic Alps, Sardinia, and northern Africa (Jaeger, 1976). Therefore, it is very likely that this event was related to global cooling, postulated at the end of the Silurian and at the beginning of the Devonian. This climatic change must have influenced continental weathering and may be documented by lower contents of Zr,  $\text{TiO}_2$ , REE and a higher Ga/ $\text{Al}_2\text{O}_3$  ratio in the Zdanów section. Such cooling would result in a renewal of oceanic circulation, leading to nutrient enrichment of surficial waters (Fig. 5). Moreover, this enrichment could have been locally enhanced by volcanic activity, as observed in the Zdanów section. Intensive upwelling promoted the primary bioproductivity (increase of Si/Al ratio and TOC content) and led to an increased anoxia (higher V/V + Ni ratio), in turn enhancing the preservation of organic matter in the bottom sediment.

### 8.3. *Latest Pridoli (linograptid interregnum)*

The linograptid interregnum is characterized by expanding cyanobacterial and algal microplankton and by a population burst of *Linograptus* (Fig. 5). The first event is marked by an increasing TOC content and by a decreasing Si/Al/TOC ratio. Bloom-forming cyanobacteria fix nitrogen, and are very sensitive to copper, cadmium and molybdenum (note the unusually high contents of these elements in some beds of the Zdanów section) under anaerobic conditions. A high productivity

of cyanobacteria would deplete oxygen levels in the upper mixed layer and, consequently, an expanding anoxic layer promoted the explosive expansion of multi-branched *Linograptus* colonies. The highest anoxic bottom conditions probably existed at the end of this interval (reflected by the highest Re content). These bioevents could have been caused by an increase in nutrient supply related to upwelling of anoxic waters into the mixed layer, comparable perhaps to modern upwelling off the Peru coast (Dugdale, 1983), which has led to an increased nitrate/silicate ratio, resulting in cyanobacterial blooms. This process was probably stabilized for an interval of 0.2–0.5 m.y. (stable content of Si, Al, Fe, P, TOC and many minor elements). The changing upwelling regime postulated for the linograptid interregnum may be related to a short duration drop in sea-level (see the eustatic curve for the latest Silurian (Schenk, 1991).

The linograptid interregnum has not been recognized in coeval sediments of the East European Platform (Porebska, in press). The succession of graptolite events is different, apparently reflecting the different geotectonic, palaeogeographic (Baltica) and climatic regimes of this epicontinental platform. The first appearance of *M. uniformis* took place in the Silurian (the stratigraphic ranges of *M. transgrediens* and *M. uniformis* are overlapping), the frequency of *Linograptus* colonies is constant, and geochemical features of the sediment do not vary significantly.

Linograptid interregna, known from the Pridoli of the East European Platform (Teller, 1964) have not yet received an adequate environmental explanation. However, they demonstrate a particular ecological sensitivity of this long-lived, opportunistic and recurrent species. Hence, it is important to note that the ecological burst of *L. posthumus*, recorded in the Zdanów section, does not represent an exceptional event. The unique significance of this burst stems from its stratigraphic position within the succession of other unique graptolite events and, perhaps, from its association with cyanobacterial and algal bloom.

The linograptid event was not global. Its possible interregional extent, controlled by a changing upwelling regime, can be traced in the S–D bound-

ary strata attributed to the southern parts of the Rheic ocean (southern Germany, Carnic Alps, Sardinia and northern Africa).

#### 8.4. *Early Lochkovian (uniformis Zone)*

With the beginning of the Devonian, the lino-graptid stage of the Silurian ocean was rapidly replaced by a new dynamic state characterized by more vigorous circulation, different nutrient levels, and a sinking pycnocline (Fig. 5). Conditions changed, favouring the spread of siliceous plankton, as reflected by a sudden increase in the Si/Al ratio. This points to a further strengthening of oceanic circulation and to a concomitant advection of waters enriched in dissolved silica and phosphorous. A more distal position of the Zdanów section with respect to the continental source is suggested by a significant increase in the Ga/Al<sub>2</sub>O<sub>3</sub> ratio.

### 9. Summary and conclusions

The facies development, graptolite succession and geochemistry in the uppermost Silurian and lowest Devonian strata of the Bardzkie Mountains were controlled mainly by palaeoceanic circulation. The Green Shales and Upper Graptolitic Shales record two different stages of an anoxic palaeocean. The first stage was characterized by a moderately anoxic water column and thermohaline stratification; the latter by a strongly anoxic water column and intense circulation. Distinct features of the S–D boundary are the linograptid burst and a non-siliceous plankton bloom, accompanied by significant fluctuations of some major and minor elements contents. These events are attributed to short-term shallowing of the upwelling system which introduced nutrient-rich waters into the mixed layer.

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### References

- Bard, J.P., Burg, J.P., Matte, P., Ribeiro, F.B., 1980. La chaîne hercynienne d'Europe occidentale en termes de tectoniques des plaques. 26th Int. Geol. Cong. Paris, 1980. Mem. Bur. Rech. Geol. Min. 108, 233–246.
- Berger, W.H., Smetacek, V.S., Wefer, G., 1989. Ocean productivity and palaeoproductivity — an overview. In: Berger, W.H., Smetacek, V.S., Wefer, G. (Eds.), *Productivity of the Ocean: Present and Past*. Dahlem Konferenzen, Wiley, Chichester, pp. 1–34.
- Berry, W.B.N., Wilde, P., Quinby-Hunt, M.S., 1987. The oceanic oxygen minimum zone: a habitat for graptolites. *Bull. Geol. Soc. Denmark* 35, 103–114.
- Boucot, A.J., 1990. Silurian and pre-Upper Devonian bioevents. In: Kauffman, E.G., Walliser, O.H. (Eds.), *Extinctions Events in Earth History*. Springer, Berlin, pp. 126–131.
- Bralower, T.J., Thierstein, H.R., 1984. Low productivity and slow deep-water circulation in mid Cretaceous oceans. *Geology* 12, 614–618.
- Brasier, M.D., 1992. Nutrient-enriched waters and the early skeletal fossil record. *J. Geol. Soc. London* 149, 621–629.
- Brumsack, H.J., 1986. Trace metal accumulation in black shales from the Cenomanian/Turonian Boundary Event. In: Walliser, O. (Ed.), *Global Bio-Events*. Springer, Berlin, pp. 337–343.
- Decker, K., 1991. Rhythmic bedding in siliceous sediments — an overview. In: Einsele, G., Ricken, W., Seilacher, A. (Eds.), *Cycles and Events in Stratigraphy*. Springer, Berlin, pp. 464–479.
- Degens, E.T., Ittekkot, V., 1982. In situ metal-staining of biological membranes in sediments. *Nature* 298, 262–268.
- Demaison, G.Y., Moore, G.T., 1980. Anoxic environments and oil source bed genesis. *Am. Assoc. Petrol. Geol. Bull.* 64, 1179–1209.
- Dugdale, R.C., 1983. Effects of source nutrient concentrations and nutrient regeneration on production of organic matter in coastal upwelling centers. In: Thiede, J., Suess, E. (Eds.), *Coastal Upwelling — Its Sedimentary Record*. NATO Conf. Ser. 4: Marine Science 10. Plenum, New York, pp. 175–180.
- Elderfield, H., Greaves, M.J., 1982. Rare earth elements in seawater. *Nature* 296, 214–219.
- Frakes, L.A., 1979. *Climates Through Geologic Time*. Elsevier, Amsterdam, 310 pp.
- Franke, W., Żelaźniewicz, A., Porebski, S.J., Wajsprych, B., 1993. Saxothuringian Zone in Germany and Poland: differences and common features. *Geol. Rundsch.* 82, 583–599.
- Garrels, R.M., MacKenzie, F.T., 1971. *Evolution of Sedimentary Rocks*. Norton, New York, 395 pp.
- Glikson, M., Chappell, B.W., Freeman, R.S., Webber, E., 1985. Trace elements in oil shales, their source and organic associa-

- tion with particular reference to Australian deposits. *Chem. Geol.* 53, 155–174.
- Goldberg, E.D., 1987. Comparative chemistry of platinum and other heavy metals in the marine environment. *Pure Appl. Chem.* 59, 565–571.
- Hatch, J.R., Leventhal, J.S., 1992. Relationship between inferred redox potential of the depositional environment and geochemistry of the Upper Pennsylvanian (Missourian) Stark Shale Member of the Dennis Limestone, Wabaunsee County, Kansas, U.S.A. *Chem. Geol.* 99, 65–82.
- Jaeger, H., 1976. Das Silur und Unterdevon vom Thüringischen Typ in Sardinien und seine regionale geologische Bedeutung. *Nova Acta Leopold. N.F.* 45 (224), 263–299.
- Jeppsson, L., 1990. An oceanic model for lithological and faunal changes tested on the Silurian record. *J. Geol. Soc. London* 147, 663–674.
- Lewan, M.D., 1984. Factors controlling the proportionality of vanadium to nickel in crude oils. *Geochim. Cosmochim. Acta* 48, 2231–2238.
- Lisitzin, A.P., 1985. The silica cycle during the last ice age. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 50, 241–270.
- Malinowska, L., 1955. *Stratygrafia gotlandu Gór Bardzkich*. Biul. Inst. Geol. 95, 5–81.
- McLaren, D.J., 1977. The Silurian–Devonian Boundary Committee: a final report. In: Martinsson, A. (Ed.), *The Silurian–Devonian Boundary*. IUGS Ser. A, No. 5, Stuttgart, pp. 1–34.
- Moore, G.T., Hayashida, D.N., 1993. Late Early Silurian (Wenlockian) general circulation model-generated upwelling, graptolitic shales and organic-rich source rocks — an accident of plate tectonics? *Geology* 21, 17–20.
- Porebska, E., 1982. Latest Silurian and Early Devonian graptolites from Zdanów section, Bardo Mts (Sudetes). *Ann. Soc. Geol. Polon.* 52, 89–200.
- Quinby-Hunt, M.S., Wilde, P., 1994. Thermodynamic zonation in the black shale facies based on iron–manganese–vanadium content. *Chem. Geol.* 113, 297–317.
- Rigby, S., 1991. Feeding strategies in graptoloids. *Palaeontology* 34, 797–813.
- Rigby, S., 1992. Graptoloid feeding efficiency, rotation and astogeny. *Lethaia* 25, 52–68.
- Schenk, P.E., 1991. Events and sea-level changes on Gondwana's margin; the Meguma Zone (Cambrian to Devonian) of Nova Scotia, Canada. *Geol. Soc. Am. Bull.* 103, 512–521.
- Scotese, C.R., McKerrow, W.S., 1990. Revised World maps and introduction. In: McKerrow, W.S., Scotese, C.R. (Eds.), *Palaeozoic Palaeogeography and Biogeography*. *Geol. Soc. London Mem.* 12, 1–12.
- Shaw, D.M., 1957. The geochemistry of gallium, indium and thallium. In: Ahrens, L.H., Press, F., Runcorn, S.K., Urey, H.C. (Eds.), *Physics and Chemistry of the Earth*, vol. 1. Pergamon, Oxford, pp. 164–211.
- Teller, L., 1964. Graptolite fauna and stratigraphy of the Ludlovian deposits of the Chełm borehole, eastern Poland. *Stud. Geol. Polon.* 13, 1–88.
- Underwood, Ch.J., 1993. The position of graptolites within Lower Palaeozoic planktic ecosystems. *Lethaia* 26, 189–202.
- Wajsbrych, B., 1986. Sedimentary record of tectonic activity on a Devonian–Carboniferous continental margin Sudetes. In: Teisseyre, A.K. (Ed.), *IAS 7th Regional Meet.*, 23–25 May 1986, Excursion Guidebook, Ossolineum, Wrocław, pp. 141–162.
- Wellman, C.H., Richardson, J.B., 1993. Terrestrial plant microfossils from Silurian inliers of the Midland Valley of Scotland. *Palaeontology* 36, 155–193.
- Wilde, P., Berry, W.B.N., 1982. Progressive ventilation of the ocean-potential for return to anoxic conditions in the post-Palaeozoic. In: Schlanger, S.O., Cita, M.B. (Eds.), *Nature and Origin of Cretaceous Organic Carbon-Rich Facies*. Academic Press, London, pp. 209–224.
- Wilde, P., Quinby-Hunt, M.S., Berry, W.B.N., Orth, C.J., 1989. Palaeo-oceanography and biogeography in the Tremadoc (Ordovician) Iapetus Ocean and the origin of the chemostratigraphy of *Dictyonema flabelliforme* black shales. *Geol. Mag.* 126, 19–27.
- Wilde, P., Quinby-Hunt, M.S., Berry, W.B.N., 1990. Vertical advection from oxic and anoxic water from the main pycnocline as a cause of rapid extinction or rapid radiation. In: Kauffman, E.G., Walliser, O.H. (Eds.), *Extinction Events in Earth History*. Springer, Berlin, pp. 85–98.
- Wilde, P., Berry, W.B.N., Quinby-Hunt, M.S., 1991. Silurian oceanic and atmospheric circulation and chemistry. *Spec. Pap. Palaeontol.* 44, 123–143.
- Wyżga, B., 1987. Lower Palaeozoic of Bardo Mountains (Sudetes): a sequence of deep sea pelagic sediments. *Geol. Sudetica* 22, 119–145.