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Extent and duration of marine anoxia during the Frasnian– Famennian (Late Devonian) mass extinction in Poland, Germany, Austria and France

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Abstract – The intensity and extent of anoxia during the two Kellwasser anoxic events has been investigated in a range of European localities using a multidisciplinary approach (pyrite framboid assay, gamma-ray spectrometry and sediment fabric analysis). The results reveal that the development of the Lower Kellwasser Horizon in the early Late *rhenana* Zone (Frasnian Stage) in German type sections does not always coincide with anoxic events elsewhere in Europe and, in some locations, seafloor oxygenation improves during this interval. Thus, this anoxic event is not universally developed. In contrast, the Upper Kellwasser Horizon, developed in the Late *linguiformis* Zone (Frasnian Stage) in Germany correlates with a European-wide anoxic event that is manifest as an intensification of anoxia in basinal locations to the point that stable euxinic conditions were developed (for example, in the basins of the Holy Cross Mountains, Poland). The interval also saw the spread of dysoxic waters into very shallow water (for instance, reefal) locations, and it seems reasonable to link the contemporaneous demise of many marine taxa to this phase of intense and widespread anoxia. In basinal locations, euxinic conditions persisted into the earliest Famennian with little change of depositional conditions. Only in the continental margin location of Austria was anoxia not developed at any time in the Late Devonian. Consequently it appears that the Upper Kellwasser anoxic event was an epicontinental seaway phenomenon, caused by the upward expansion of anoxia from deep basinal locales rather than an 'oceanic' anoxic event that has spilled laterally into epicontinental settings.

Keywords: Frasnian, Fammenian, Kellwasser, mass extinction, anoxia.

1. Introduction

Marine anoxia is widely thought to have played a role in the end-Frasnian (Late Devonian) mass extinction. In particular, the close correspondence between extinctions and the development of two discrete anoxic events provides evidence for a causal link (House, 1985; Casier, 1987; Walliser *et al.* 1989; Goodfellow *et al.* 1989; Buggisch, 1991; Becker, 1993). In Germany the anoxic events are manifest as two, decimetre-thick, bituminous limestones known as the Lower and Upper Kellwasser horizons developed in the Late *rhenana* and Late *linguiformis* conodont zones, respectively (Buggisch, 1972; Schindler, 1990; Walliser, 1996). Age-equivalent anoxic facies are also known over a wide area from Morocco to the Subpolar Urals (Fig. 1; Wendt & Belka, 1991; Racki *et al.* 2002; Yudina *et al.* 2002), and they are postulated to be of global extent (Engel, Franke & Langenstrassen, 1983).

Despite the clear evidence for anoxia presented by the Kellwasser facies, the anoxic kill mechanism has been subject to considerable criticism (e.g. McGhee, 1996; Copper, 1998). Arguments against the hypo-

thesis, some more tenable than others, take several stances: (a) Anoxic events are common throughout the Frasnian (and earlier Devonian) but only the Lower and Upper Kellwasser horizons are associated with extinctions (Claeys, Kyte & Casier, 1994; McGhee, 1996, p. 157). In fact, this claim is incorrect; earlier anoxic events are also associated with extinction events (Becker & House, 1994; Brett & Baird, 1995, p. 309; House *et al.* 2000, p. 173), although they are not of the same magnitude (House, 2002). (b) Anoxia is not developed in shallow-water locations and therefore cannot be responsible for the demise of shallow-water taxa, particularly reef inhabitants (Sandberg *et al.* 1988; House *et al.* 2000; Casier *et al.* 2002; House, 2002). As our data below show, this assertion may not be correct. (c) According to Copper (1998), dysaerobic brachiopods were amongst the victims of the extinction when in fact their ability to withstand low oxygen levels should have enhanced their survival chances. However, the dysaerobic rhynchonellids did indeed preferentially survive the crisis (Sartenaer, Racki & Szulczewski, 1998; Baliński, 2002). (d) The Kellwasser anoxic events were not developed globally (Becker *et al.* 1991; Bratton, Berry & Morrow, 1999; House, 2002).

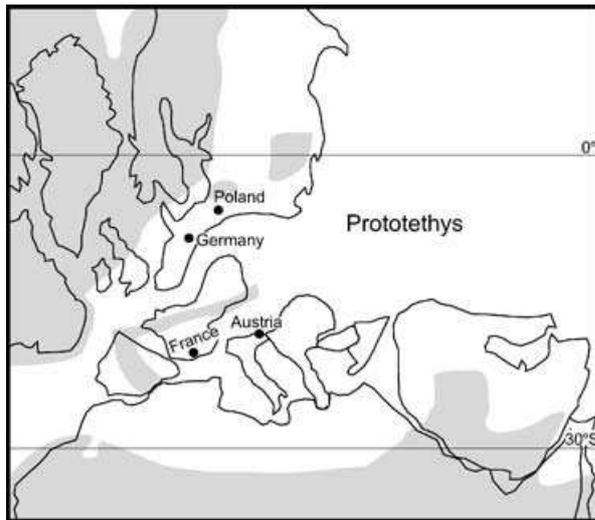† Author for correspondence: wignall@earth.leeds.ac.uk

Figure 1. Late Devonian palaeogeography of the European region showing study areas, after Joachimski & Buggisch (1993). Shaded areas show position of land during Late Devonian times.

A final point that may be made against the anoxia-extinction hypothesis is the detailed timing of the extinctions, particularly of pelagic taxa. Many benthic taxa go extinct at the base of the Upper Kellwasser Horizon, notably ostracods (Casier, 1987) and trilobites (Schindler, 1993; Feist & Schindler, 1994; Chlupác, Feist & Morzadec, 2000), together with the presumed-pelagic entomozoacean ostracods (Olempska, 2002). However, other pelagic groups, in particular goniatites and homoctenids, go extinct either during or at the termination of Upper Kellwasser Horizon deposition (Walliser *et al.* 1989; Schindler, 1990; Becker & House, 1994) when water column oxygen levels ostensibly improved during a major, eustatic sea-level fall (Buggisch, 1991; Joachmiski & Buggisch, 1993; McGhee, 1996, p. 157). However, the debate on the role of anoxia is hindered by a lack of knowledge of the spatiotemporal development of anoxia throughout the Frasnian–Famennian crisis interval. Only a few studies, focused on single locations, have investigated redox changes from before the mass extinction interval until the recovery phase in the Famennian Stage, and their results have shown considerable variation from site to site. Thus, Joachimski *et al.* (2001) suggested oxygen-restricted deposition was prevalent for the entire interval from the Early *rhenana* to the Late *triangularis* conodont zones of the basinal Kowala section in Poland (but see the somewhat different history of Racki *et al.* 2002). For the same interval, the Syv'yu River section (Subpolar Urals) recorded persistent dysoxic conditions punctuated by a euxinic pulse in the Late *linguiformis* Zone (Yudina *et al.* 2002).

In this study we document the late Frasnian–early Famennian oxygenation history of the European region using a combination of sedimentary fabric and pyrite petrographic data, supplemented with a gamma-ray spectrometry study, from widely distributed locations (Poland, France, Germany and Austria). We hope to determine how widespread the anoxic Kellwasser facies were and if they were unusual in the context of the Late Devonian seas, and thus ultimately to address the question of whether anoxia was implicated in the Late Devonian mass extinction.

2. Study areas

2.a. Germany

The classic Devonian outcrops of the Rhine Slate Mountains and Harz Mountains contain the type locality for the Kellwasser horizons. The region records the drowning of carbonate platforms in the Frasnian with the establishment of a basin-and-swell topography (Buggisch, 1972; Krebs, 1979). The Kellwasser horizons are seen on submarine swells where 'Cephalopodenkalk' facies (condensed limestones rich in cephalopods) are developed. Steinbruch Benner, an abandoned quarry near the village of Bicken in the Rhine Slate Mountains (Fig. 2a), provides a typical section through a Frasnian–Famennian swell succession, and was chosen for study. Just over 9 m of section were logged, spanning the Early *rhenana* to Late *triangularis* zones, and 56 discrete beds were identified.

2.b. Poland

The Holy Cross Mountains of central Poland provide extensive outcrops of a Late Devonian carbonate platform and basin system that formed part of a large, equatorial carbonate shelf, 600 km wide (Szulczewski, 1995; Racki & Baliński, 1998; Racki *et al.* 2002). As in Germany, the Polish Frasnian interval records the gradual drowning of reef facies, although some reefs persisted locally until the end of the Frasnian Stage. Study was concentrated in the area around Kielce where a Frasnian reef complex (the Dyminy Reef) is flanked by two intrashelf basins, the Chęciny–Zbrza Basin in the south and the Łysorgóry Basin in the north. The three study sites span this considerable range of palaeobathymetries: Kowala Quarry, an expanded base of slope to basinal succession from the southern basin; Psie Górki, an abandoned quarry in the suburbs of Kielce that exposes very shallow water facies from a forereef setting; Płucki, a trench section within the Łysorgóry–Kostomłoty Basin (Fig. 2b).

2.c. France

The basinal Frasnian–Famennian carbonate facies of the Montagne Noire region of southern France are
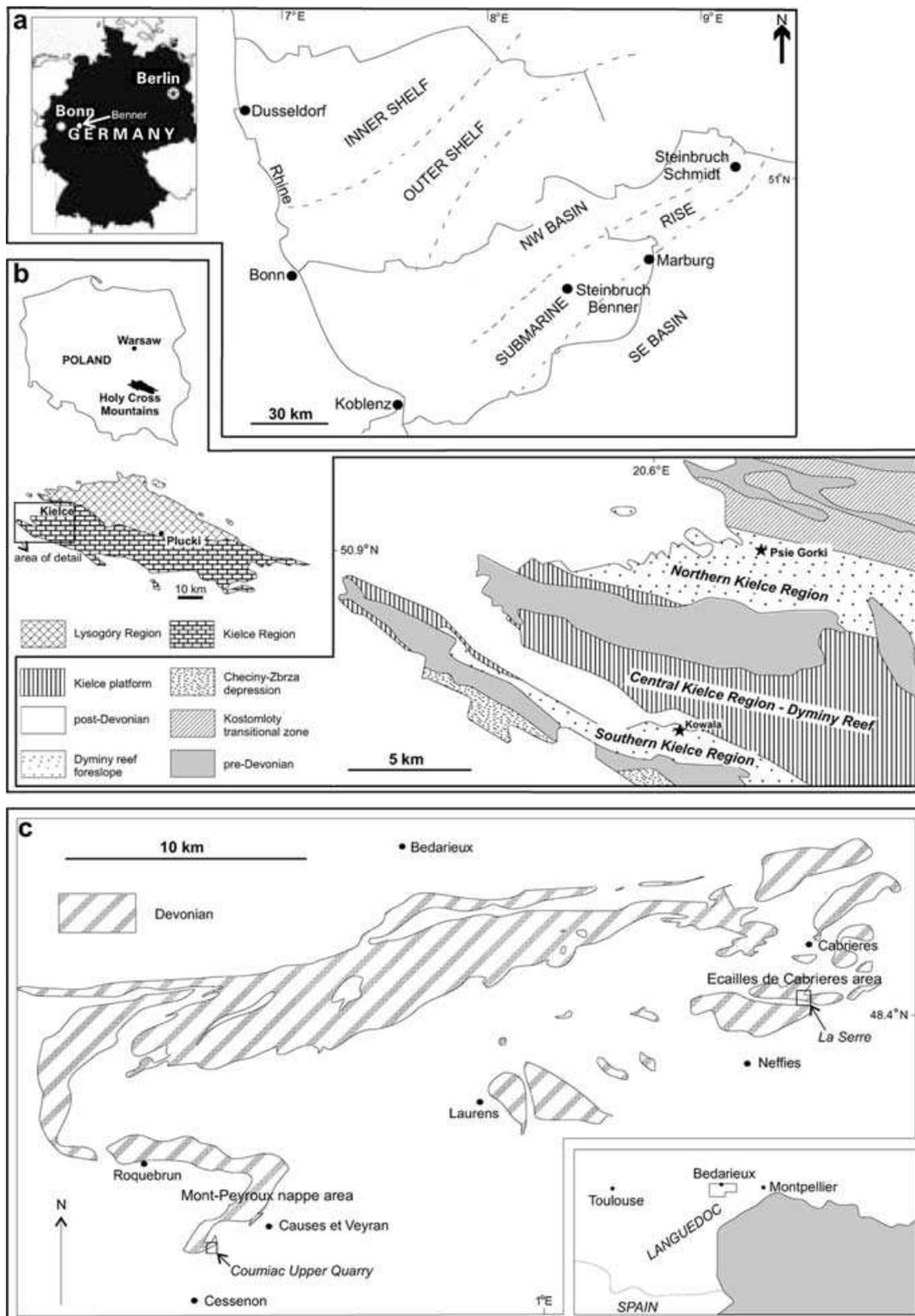
Figure 2. Locality maps of the study sites. (a) Steinbruch Benner, northern Germany. (b) Holy Cross Mountain area, central Poland. (c) Montagne Noire region, SW France.

well known and they provide the global stratotype for the stage boundary at Coumiac (Klapper *et al.* 1993), an abandoned quarry near Cessenon (Fig. 2c). This section was studied, together with the trench section at

La Serre, near Cabrières. The trench was excavated to provide a global stratotype for the F–F and Devonian–Carboniferous boundaries (Feist, 1985; Paproth, Feist & Flajs, 1991).

Table 1. Summary of characteristics used to define oxygen-related depositional conditions and facies

Conditions (Facies)	Framboidal populations	Sedimentary fabric	Th/U ratio
Euxinic (Euxinic)	Small ($< 5\ \mu$m), abundant with narrow size range	Finely laminated	< 1.0
Lower dysoxic (Lower dysaerobic)	Small ($< 5\ \mu$m), abundant but with rare, larger framboids	Finely laminated	< 1.0
Upper dysoxic (Upper dysaerobic)	Moderately common to rare, broad range of sizes, with only a small proportion $< 5\ \mu$m diameter	Microburrowed, bioturbation may partly obscure finely laminated fabric	> 1.0
Oxic (Aerobic)	No framboids, very rare pyrite crystals	Burrowed/massive, no fine lamination	$\gg 1.0$

2.d. Austria

The Frasnian–Famennian boundary is exposed in a 20 m high cliff section at Lake Wolayer in the Carnic Alps of southernmost Austria. This carbonate platform section ranges from the Emsian to the basal Famennian stages (Joachimski, Buggisch & Anders, 1994) and the highest strata are penetrated by sediment-filled, extensional fissures that formed during the break-up and drowning of the platform (Schönlaub & Histon, 1999).

3. Analytical procedure and rationale

Oxygenation levels recorded in the Frasnian–Famennian boundary sections were assessed using three independent criteria: sediment fabric (that is, presence of lamination), pyrite framboid size populations and authigenic uranium values. Thus, all sections were logged in detail with care taken to identify the presence (or absence) of fine lamination/bioturbation features. Field determinations were supplemented by petrographic analysis of thin sections. In addition, polished blocks were examined under backscatter SEM to determine the pyrite content and, where present, the size distribution of pyrite framboid populations.

Framboids form as an aggregate of iron monosulphide microcrysts at the redox boundary and they cease to grow in the more intensely anoxic conditions of the underlying sulphate-reduction zone (Wilkin & Barnes, 1997), where more slowly growing crystalline pyrite may form. If bottom waters become anoxic (that is, if euxinic conditions develop), then framboids develop in the water column but are unable to achieve diameters much larger than 5 μm before they sink below the Fe-reduction zone and cease to grow (Wilkin, Barnes & Brantley, 1996). Thus, euxinicity produces populations of tiny framboids with a narrow size range. In contrast, in dysoxic environments, where anoxic conditions only extend up into surficial sediments, size is largely governed by the local availability of reactants and the framboids are larger and more variable in size (Wilkin, Barnes & Brantley, 1996). Studies of ancient sediments reveal pyrite framboid analyses can additionally provide a subtle indicator of environmental stability.

Many lower dysaerobic biofacies record variable oxygenation regimes in which long-term euxinicity is punctuated by brief seafloor oxygenation events that allowed colonization by a benthic pioneer fauna (Hallam, 1980; Wignall & Myers, 1988). Thus, there is often a dichotomy between geochemical evidence from lower dysaerobic facies which records long-term (average) depositional conditions and palaeoecological evidence which can record shorter-term (atypical) events (Raiswell, Newton & Wignall, 2001). Such facies have a distinctive pyrite framboid size signature dominated by small, syngenetic populations formed in euxinic conditions but with the addition of rare, larger ($> 5\ \mu$m diameter) framboids formed within the sediment during brief intervals of seafloor oxygenation (Wignall & Newton, 1998; Table 1).

Most sections were also analysed using a field portable gamma-ray spectrometer which assays concentrations of K, Th and U. This provides a measure of redox conditions because of the enrichment of U in anoxic conditions (Wignall & Myers, 1988). Thus, the U content of sediments is a combination of authigenic and detrital components whereas the Th content is entirely detrital. As a result, Th/U ratios of anoxic strata are characteristically low. However, lithological variation can also affect the ratio; detrital sediments generally have higher Th contents than carbonates with the result that the Th/U ratio of anoxic shales is less than 3 (Myers & Wignall, 1987), but for carbonates the ratio is typically lower than 1 (Table 1).

In addition to investigating the nature of oxygen restriction in our sections, we also undertook a carbon isotope analysis of the Psie Górki section in Poland to provide a means of correlation. Eight samples from Psie Górki were analysed at the Laboratory of Stable Isotopes of the Polish Academy of Sciences in Warsaw. The analyses were carried out on CO_2 obtained by sample reaction with 100 % H_3PO_4 at 25 °C for 24 hours. The measurements were made on a Finnegan MAT Delta plus mass spectrometer equipped with Isodat 6.0 software. The results are expressed relative to the PDB standard using an NBS-19 reference sample. Carbon isotope results for other sections are already available in the literature. The trace element concentrations of the redox sensitive elements U, V and Zn at Psie Górki were also assayed by XRF at the Central Chemical Laboratory, Polish Geological Institute, Warsaw.

4. Germany

4.a. Steinbruch Benner

Just over 9 m of section, spanning the Early *rhenana* to Late *triangularis* zones, were studied at Steinbruch Benner. Light grey, well-bioturbated micrites and wackestones (biomicrites) dominate the succession and they contain a diverse assemblage including brachiopods, cephalopods and trilobites together with homoctenids (Schindler, 1990). This last group is only abundant up to the end of the Frasnian Stage (Fig. 4a, b), although a single specimen was also encountered in the basal Famennian strata (Fig. 4c). The lithological monotony is interrupted by the development of two horizons of finely laminated, black biomicrites and thin black shales (Fig. 3). These are the celebrated Lower and Upper Kellwasser horizons whose fossil content is dominated by homoctenids and to a lesser extent cephalopods (Fig. 4a).

Pyrite, in the form of blebs and rarer crystals, is common throughout much of the Steinbruch Benner section, but framboids are only encountered in the Kellwasser horizons and the basal bed of the Famennian Stage (bed 47, Fig. 4d). Size analysis of the framboids revealed the populations to be typical of lower dysaerobic facies, as defined above (mean diameter 4–6 μm, standard deviation 1.6–2.4 μm) with persistent euxinicity developed in the middle of the Upper Kellwasser Horizon. For technical reasons, it did not prove possible to use the gamma-ray spectrometer at Steinbruch Benner.

4.a.1. Interpretation

The sediment fabric and framboid analysis at Steinbruch Benner confirms the long-established view that the Kellwasser horizons record discrete anoxic depositional phases in an otherwise well-oxygenated Late Devonian submarine swell locality (Buggisch, 1972). However, the second phase of oxygen-poor deposition lasted for slightly longer than the interval recorded by the Upper Kellwasser Horizon as indicated by the presence of framboid populations in the earliest Famennian strata (Fig. 3). The presence of non-framboidal pyrite at other levels indicates anoxic conditions developed during diagenesis, but the bioturbation and diverse fauna indicate essentially normal seafloor oxygenation.

Studies of other German sections add some different information to the redox history of the Kellwasser horizons. At Steinbruch Schmidt the variable ostracod content of the Upper Kellwasser Horizon suggests large fluctuations from aerobic to anaerobic facies (Casier & Lethiers, 1998), although reported enrichments in chalcophile trace metals from this section indicate persistent euxinicity (Goodfellow *et al.* 1989). The aerobic ostracod assemblages may be allochthonous. In their detailed microfacies study of the same

section, Devleeschouwer, Herbosch & Préat (2002) reported (but did not illustrate) a change, in the topmost Upper Kellwasser Horizon, from dark, laminated mudstones and packstones to bioturbated mudstone and wackestone facies that persist until the Late *triangularis* Zone (cf. fig. 3 of Devleeschouwer, Herbosch & Préat, 2002). This facies change is attributed to major sea-level fall and sequence boundary formation at the F–F boundary. No evidence is found for sea-level fall at Steinbruch Benner; instead, pyrite framboid evidence indicates that oxygen levels were gradually (rather than abruptly) improving across the stage boundary. The Steinbruch Benner section may be a deeper water locality than Steinbruch Schmidt, thereby accounting for the somewhat longer history of oxygen restriction at this former locality, but the Steinbruch Schmidt section requires a detailed assessment of its redox history for true comparison.

5. Poland

5.a. Kowala

Over 200 m of Late Devonian carbonates from the Chęciny–Zbrza Basin are exposed in the active Kowala Quarry. In this study we focused on 143 m of section from the centre of the quarry that span the uppermost *jamiae* to *rhomboidea* conodont zones (Fig. 5). Micrites dominate the succession but thin beds of calcareous, dark grey shales and calcarenites (pelbiosparites, grainstones) also occur; the last lithology frequently contains an allochthonous reef fauna derived from Dyminy Reef (Racki *et al.* 2002). The branching stromatoporoid *Amphipora* is present in all the carbonate lithologies in the Frasnian portion of the succession and its broad facies distribution suggests it was able to float post-mortem. A total of 11 lithological units were distinguished (Fig. 5), which roughly equate with units H-1 to H-4 in the scheme devised by Szulczewski (1971, 1996), Racki & Baliński (1998) and Racki *et al.* (2002), and used by others (e.g. Joachimski *et al.* 2001; Girard & Lécuyer, 2002).

Units 1 and 2 are dominated by medium-dark grey micrites, with either a massive or finely laminated fabric, interbedded with thin (< 10 cm) calcarenites and dark grey, fissile, calcareous shales. The calcarenites contain an allochthonous fauna that includes rugose corals, crinoids and brachiopods. Unit 3 lacks the thin calcarenite horizons in all but the basal 1.5 m and is distinguished by the dominance of pale grey, nodular, micrite beds. A metre-thick limestone in the upper part of unit 3, of Late *rhenana* Zone age, is distinctive both because of its dark grey colour and fine lamination. This bed is bounded by two thin, dark grey, laminated shales. After a short unexposed interval, corresponding to the Early *linguiformis* Zone, the section resumes with the finely laminated micrites (with
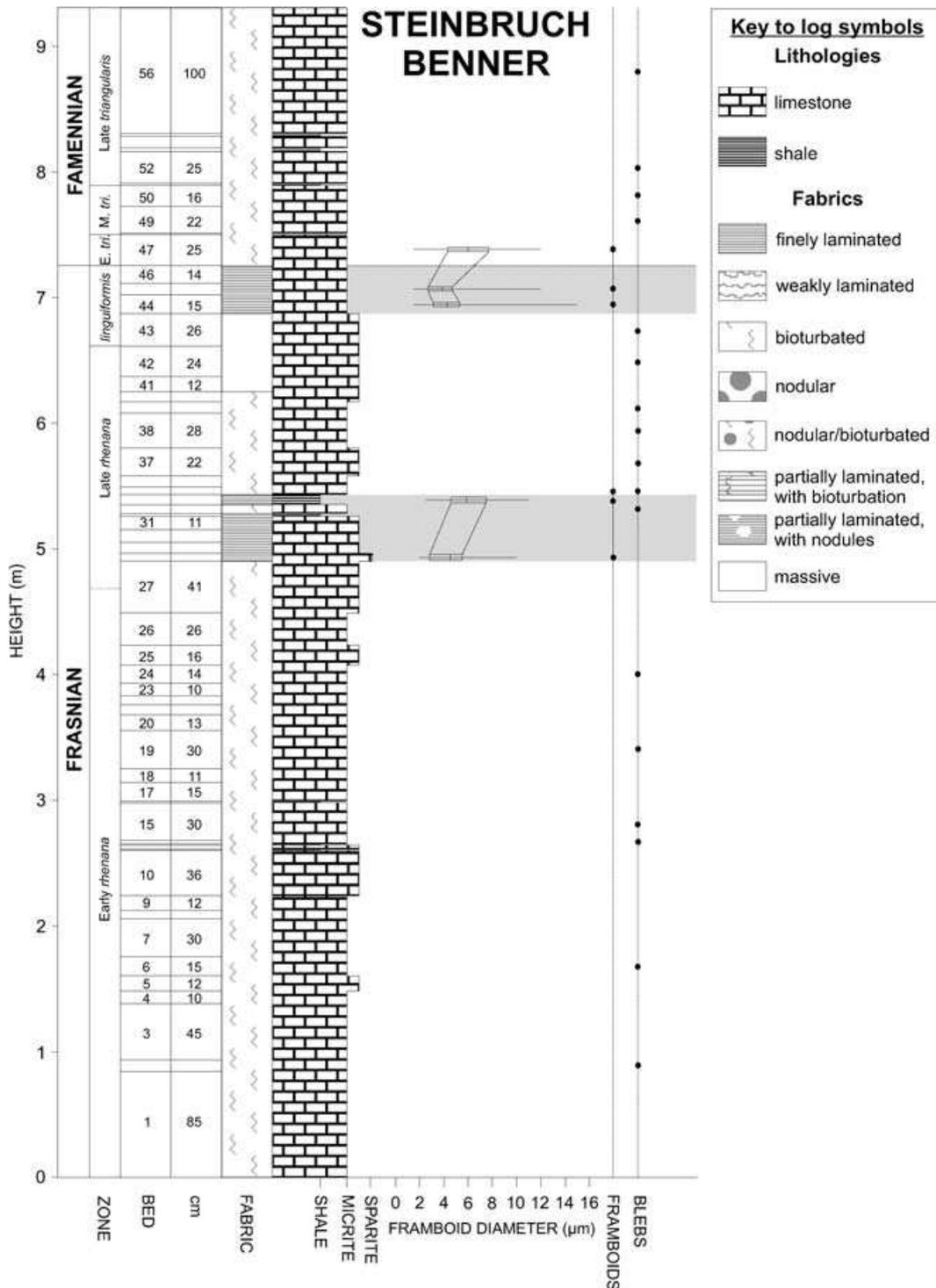
Figure 3. Graphic log of Steinbruch Benner section showing box-and-whisker plots of framboid diameters (the 'whiskers' depict minimum and maximum diameters, the 'box' depicts the 25th and 75th percentile and the central line the median average). Conodont zonation based on Schindler (1990).

common stylolites) of unit 4. The F–F boundary has been located within this unit (Joachimski *et al.* 2001; Racki *et al.* 2002) at a level marked by the development of two thin chert beds and several thin beds of crinoidal debris (Fig. 6). A detailed description of these boundary beds is in Racki *et al.* (2002). Much of the central part

of unit 4 is a pale grey-pink. This colour appears to be the result of intense oxidation by ground waters because the zone of 'bleaching' is discordant with bedding and varies in thickness, and unoxidized dark grey patches remain (Fig. 6). The overlying Famennian units are dominated by interbedded horizons of dark
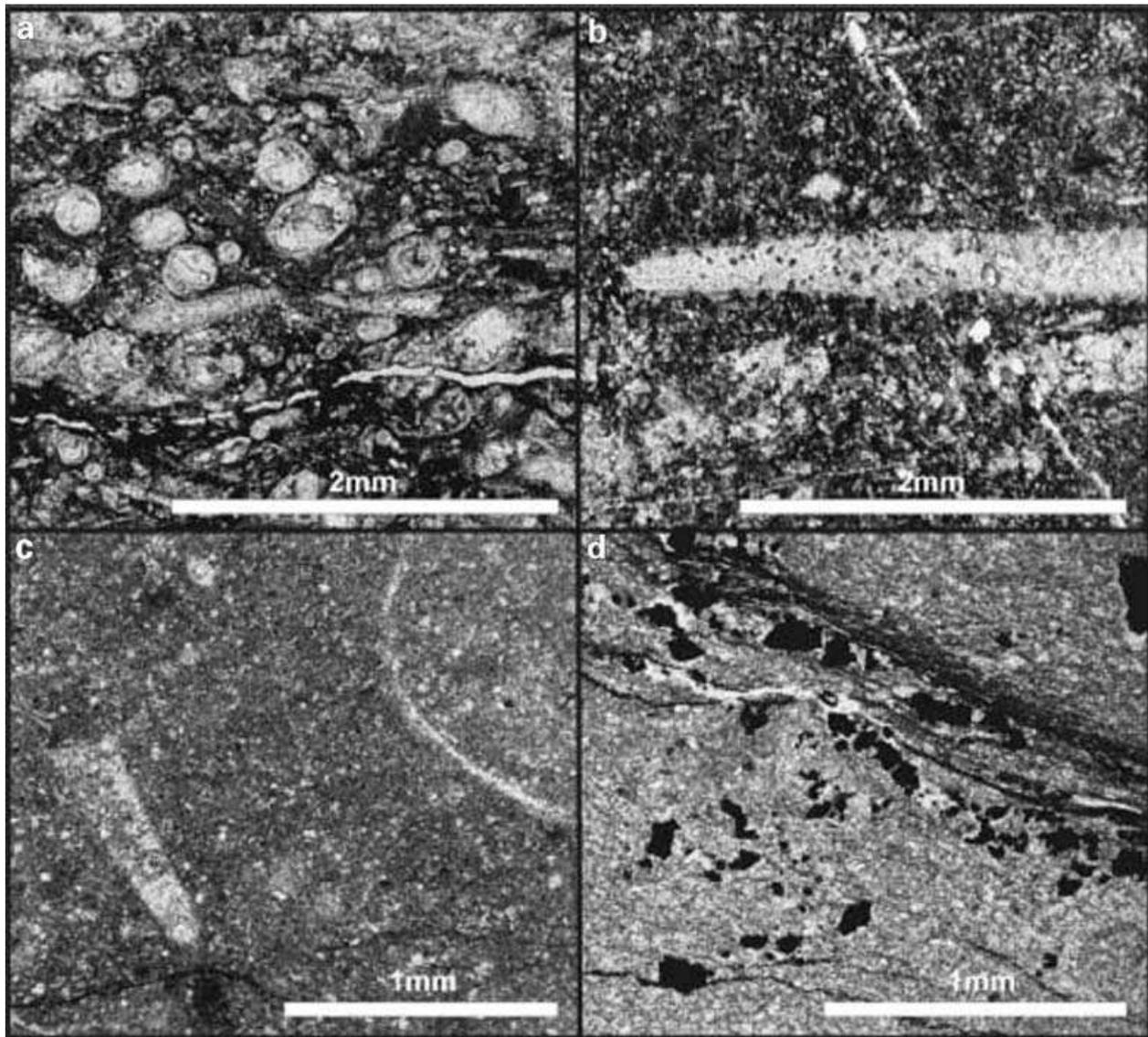
Figure 4. Photomicrographs of rocks from Steinbruch Benner. (a) Bed 44 showing densely packed homoctenids. (b) Bed 45 showing a large homoctenid in a wackestone from the centre of the Upper Kellwasser Horizon. (c) Bed 47 showing a single homoctenid (?) from the base of the Famennian. (d) Further view of bed 47 strata showing the abundance of pyrite (opaque lumps) at this level.

grey, pyritic marl and micrite. Bioturbation becomes progressively more important higher in the section. The lowest burrowed horizon occurs at the base of unit 5 where 2 m of micrite contain microburrows less than 1 mm in diameter. Bioturbation reappears in the base of unit 6 (latest *triangularis* Zone) in the form of larger, wispy burrows, but thin interbedded shale horizons (≤ 2 cm thick) are not disrupted, indicating that burrow depths were limited to only a centimetre or so. Not until unit 9 does bioturbation become sufficiently pervasive to disrupt thinner beds, although substantial, finely laminated intervals continue to occur up to unit 11 (Fig. 5).

The Th/U ratios measured at Kowala show a gradual upward increase from the base of the section that coincides with a gradual increase of clastic content (the dominant micrite beds of the Frasnian are gradually replaced by marls in the Famennian). This trend is temporarily reversed in the latest *rhenana*–earliest *triangularis* interval where ratios decline, culminating in low values (<1.0) around the F–F boundary (Fig. 5).

Pyrite framboid size analysis from 19 horizons revealed a broad spectrum of size-frequency distributions in the Kowala sediments (Figs 5, 7). Tiny framboid populations with little size variation only occur in the uppermost *linguiformis* Zone and basal Famennian. The 'bleached' F–F boundary strata proved to have neither framboids nor other forms of pyrite, but careful sampling of the rare, unoxidized remnants revealed abundant, tiny ($< 6 \mu$m diameter) pyrite framboids at this level. Pyrite populations from the other laminated
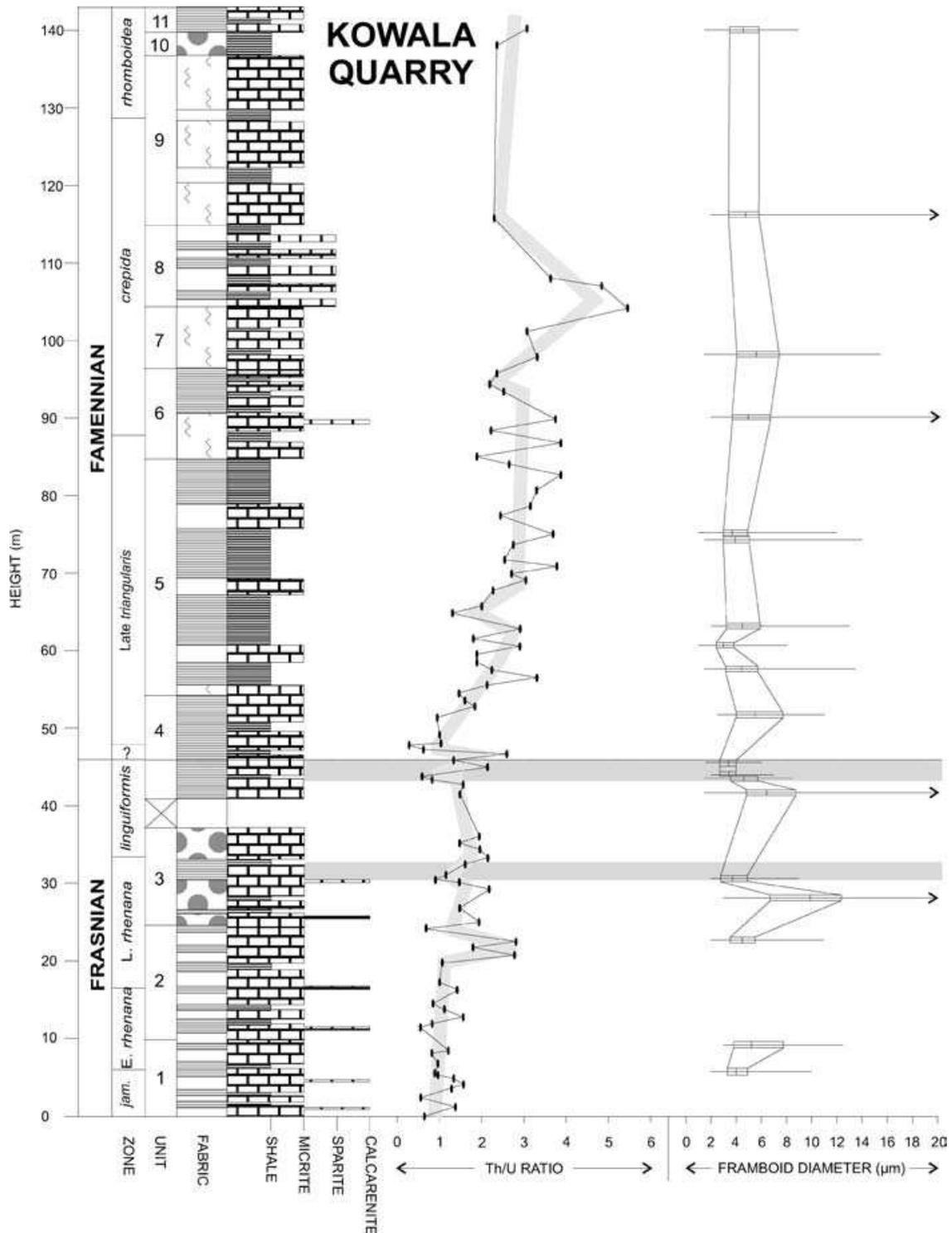
Figure 5. Graphic log of the F–F boundary beds at Kowala, showing box-and-whisker plots of framboid diameters, and Th/U ratios derived from gamma-ray spectrometry data. Conodont zonal boundaries are from Szulczewski (1996) and Racki & Baliński (1998). For legend see Figure 3.

horizons at Kowala proved to have a similar dominance of tiny framboids but with the addition of rare, larger framboids. The largest populations, in terms of both their mean and standard deviation, came from burrowed horizons (Fig. 5).

5.a.1. Interpretation

The dominance of finely laminated, pyrite framboid-rich strata in the study interval at Kowala indicates that oxygen-restricted deposition occurred for much of the
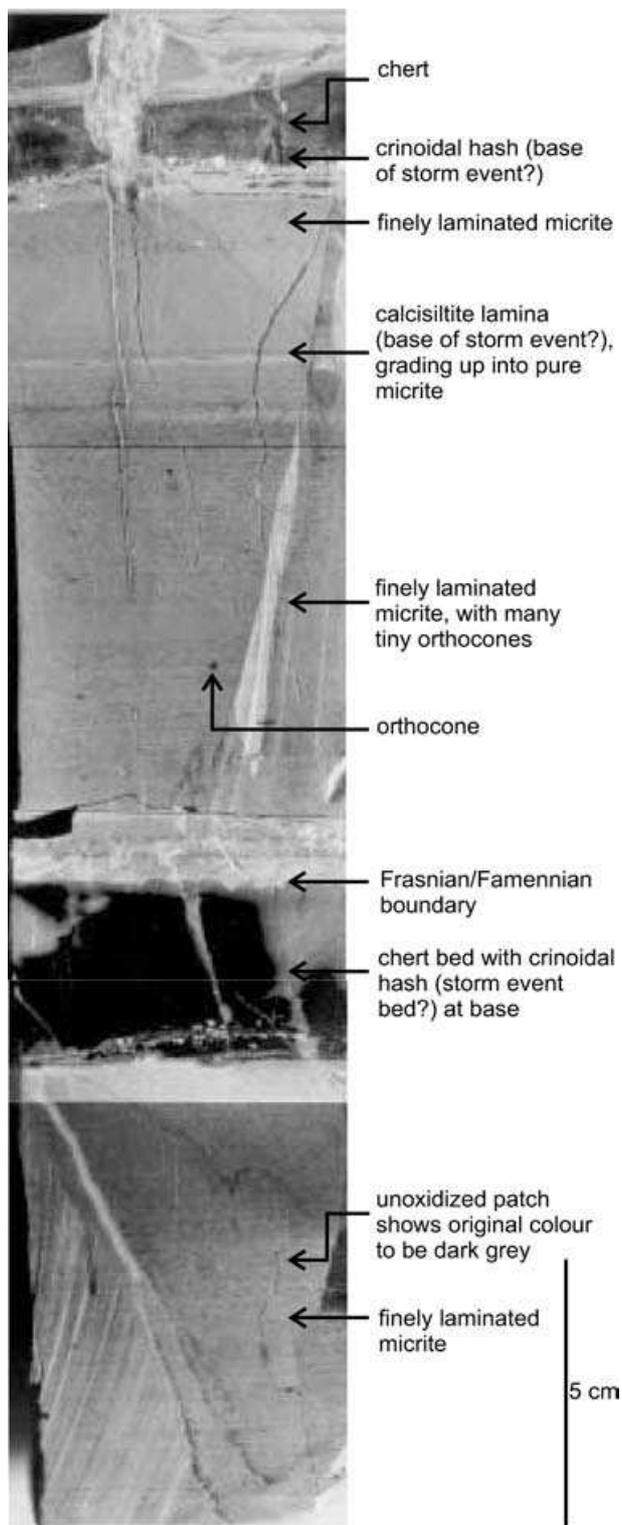
Figure 6. Composite photograph of a polished slab of the Frasnian–Famennian boundary bed at Kowala Quarry, Poland, showing finely laminated fabric and presence of dark beds of chert. The rock is a pale grey colour except for a dark unoxidized patch in the lower right part of the field of view that yielded abundant pyrite framboids with a size-frequency distribution characteristic of euxinic deposition.
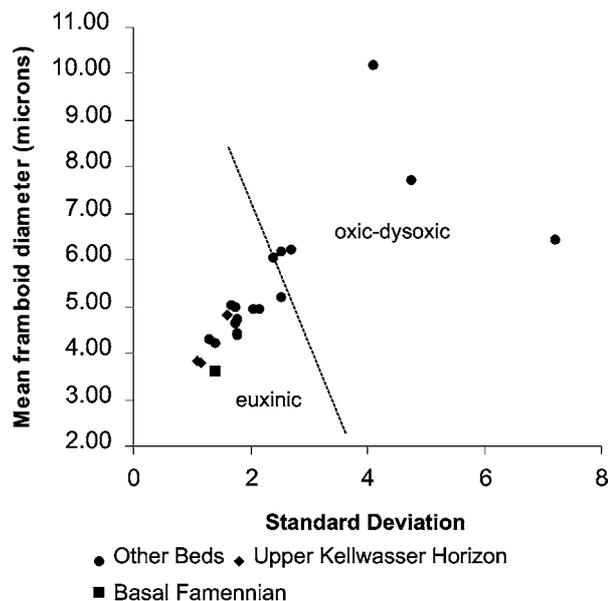

Figure 7. Mean versus standard deviation of pyrite populations from Kowala showing the most intensely anoxic samples (smallest mean and standard deviation) from the Upper Kellwasser anoxic interval and a bed in the basal Famennian.

jamiae–rhomboidea interval. Previously reported trace metal data from the shorter *rhenana–triangularis* time interval similarly indicate 'persistent anoxia' (Joachimski *et al.* 2001, p. 120). However, in detail there is considerable, albeit subtle, variability. Thus, lower dysaerobic biofacies (cf. Table 1) predominate. However, in unit 3 the occurrence of microburrows and larger pyrite framboids indicates substantially improved seafloor ventilation during the Late *rhenana* Zone, as does the improved benthic fossil diversity recorded at this level (Racki & Baliński, 1998; Sartenaer, Racki & Szulczewski, 1998; Racki *et al.* 2002). Within this interval, though, there is a return to euxinic-dominated deposition in the form of a dark grey, finely laminated micrite bed bounded by dark grey, laminated shales. These distinct beds appear to correspond to a peak of total organic carbon (TOC) values in the dataset of Joachimski *et al.* (2001), and these authors correlated this level with the Lower Kellwasser Horizon of Germany. However, the conodont zonation at Kowala suggests that this level is probably within the late Late *rhenana* Zone (Racki *et al.* 2002; Fig. 5), whereas the Lower Kellwasser Horizon of Germany occurs in the early Late *rhenana* Zone. The correlation made by Joachimski *et al.* (2001) is supported by their carbon isotope data that shows a weak, positive $\delta^{13}C_{carb.}$ spike at the level of TOC enrichment, but it only has a magnitude of less than 1‰ (Joachmiski *et al.* 2001, fig. 8). This is less then half the excursion magnitude recorded for the Lower Kellwasser Horizon in Germany (Joachimski & Buggisch, 1993) and the excursion is not marked by an accompanying isotope excursion in organic carbon data (Joachimski *et al.* 2001, fig. 8).

The presence of the Lower Kellwasser event at Kowala is therefore equivocal but, in contrast, an equivalent of the Upper Kellwasser Horizon is more clearly represented at Kowala. This is in the form of euxinic facies: finely laminated micrites from the top of the *linguiformis* Zone, with diagnostic framboid populations (Fig. 5). The low point of Th/U ratios around this level probably reflects authigenic U enrichment during this peak intensity of anoxia, but for the most part Th/U fluctuations are most clearly related to carbonate/clastic variations. Framboids from the basal metre of the Famennian strata indicate that this peak persisted across the F–F boundary as does the conodont Ce anomaly data of Girard & Lécuyer (2002) and the V/Cr data of Racki *et al.* (2002).

5.b. Płucki

It was only possible to examine the immediate F–F boundary interval (*linguiformis*–Early *triangularis* zones) in the Płucki trench section (Fig. 8). Older levels, including one exposing a bed of Cephalopodenkalk facies (cf. Dzik, 2002, pp. 625–6), were exposed in other trenches in close proximity (Racki *et al.* 2002), and a sample of this facies was included in this study. Finely laminated alternations of dark grey shales and medium grey micrites, with common pelagic fossils (entomozoaceans, homoctenids and orthocones) dominate the basal 2 m of the Płucki trench. These are capped by a 35 cm thick bed of massive, dark grey–black packstone with abundant fossils (aff. *Buchiola*, orthocones, entomozoaceans and homoctenids in the lower part but predominantly orthocones in the upper part). This bed is an example of 'Cephalopodenkalk'-style facies which characterizes the Upper Kellwasser Horizon in Germany, and this Polish example is essentially the same age, although the uppermost orthocone-dominated portion is somewhat younger, being of basal Famennian age (Olempska, 2002; Racki *et al.* 2002; Dzik, 2002). The younger Famennian strata consist of medium-grey micrites, with less discernible lamination, that occasionally show a nodular fabric, and contain a fauna dominated by aff. *Buchiola* and orthocones.

Framboidal pyrite is common in all the Płucki samples, including the *ex situ* sample of Cephalopodenkalk facies, and they are all dominated by small populations with mean diameters around 4.0 μm, but with a 'tail' of rare larger forms (Fig. 8). Gamma-ray spectrometry revealed that Th/U ratios varied somewhat more than the rather uniform lithologies might predict. Lowest values were from the F–F boundary with highest values at the base of the measured section (Fig. 8).

5.b.1. Interpretation

The basinal Płucki section clearly records persistent anoxic deposition in the *linguiformis–triangularis*

interval with pyrite populations indicative of euxinic deposition, although the rare, larger framboids probably grew within the sediment during brief intervals of seafloor oxygenation. The less distinct lamination in the *triangularis* sediments and higher Th/U values at the base of the section could indicate better oxygenation at these levels, but there is no corresponding change in the pyrite framboid data. Interestingly, the V/Cr index suggests an increasing intensity of anoxia in the basal Famennian at Płucki (Racki *et al.* 2002, fig. 9). Although somewhat conflicting, all data are generally in accord in indicating oxygen-restricted deposition throughout the F–F boundary interval at Płucki.

Unlike the section at Kowala, where the equivalent of the Upper Kellwasser Horizon is identifiable by an increase in intensity of anoxia, the Płucki section records anoxia throughout deposition and the Upper Kellwasser event is identified by an increase in pelagic fossil content. House (2002, p. 20) suggested that such enrichments generally record mass mortality of water column dwellers during crisis intervals. This seems unlikely because, after all, all organisms living in the water column will ultimately die and sink to the seabed regardless of whether they die in a mass mortality or individually. More likely, the bioclast concentration reflects the extreme condensation seen at this level and/or population blooming (Racki *et al.* 2002).

5.c. Psie Górki

The forereef facies of the Psie Górki section have been studied in detail by previous workers (Racki, 1990; Casier *et al.* 2002). These have revealed latest Frasnian (*linguiformis* Zone) strata to consist of packstones/biomicrites composed of reef debris (mostly stromatoporoid, coral and dascycladacean clasts). At the F–F boundary these are sharply succeeded by grainstones/calcarenites composed of crinoids (in the lower part) and algal mat intraclasts, but none of the Frasnian reef fauna (Casier *et al.* 2002). An 8 cm thick bed of laminated micrite separates these two principal lithologies (Fig. 9). This is level H-1a in Racki's (1990) study and, in thin section, it is seen to be a finely laminated micropelsparite with a few thin beds of sharp-based calcarenites and a few homoctenids. No pyrite was seen in this 'boundary bed' during SEM investigation. XRF determination of the redox-sensitive trace metals U, V and Zn, normalized to Al, revealed their enrichment from a level just beneath the F–F boundary (Fig. 9). Note that for several samples the Al content was below the detection limit. The carbon isotope study revealed a major positive excursion just beneath the boundary bed with values remaining heavy in the lower Famennian strata (Fig. 9), a similar pattern to that seen in contemporaneous strata at Kowala (Joachimski *et al.* 2001, fig. 8).
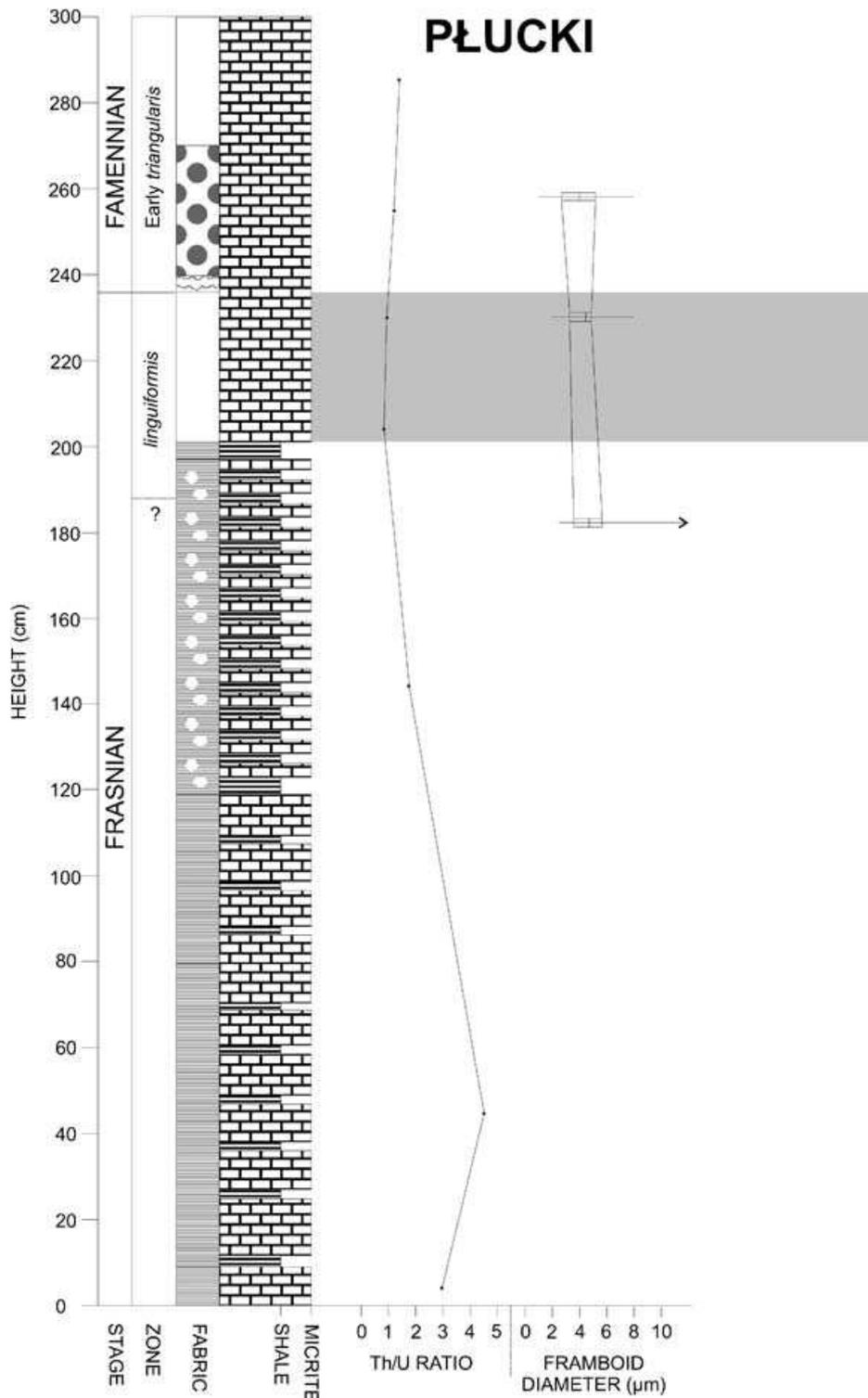
Figure 8. Graphic log of the F–F boundary beds at Płucki, showing box-and-whisker plots of framboid diameters, and Th/U ratios derived from gamma-ray spectrometry data. Conodont zonal boundaries are from Olempska (2002). For legend see Figure 3.

5.c.1. Interpretation

Interpreting the environmental change at Psie Górki is somewhat problematic. The apparently abrupt reef extinction in the terminal *linguiformis* Zone may be due to the presence of an omission surface at the top of the packstones (Racki, 1990). Casier *et al.* (2002) report meteoric diagenesis developed downwards from this level. However, the overlying laminated bed indicates a cessation of bioturbation and therefore provides tentative evidence for reef termination by anoxic deposition in this shallow-water setting. The
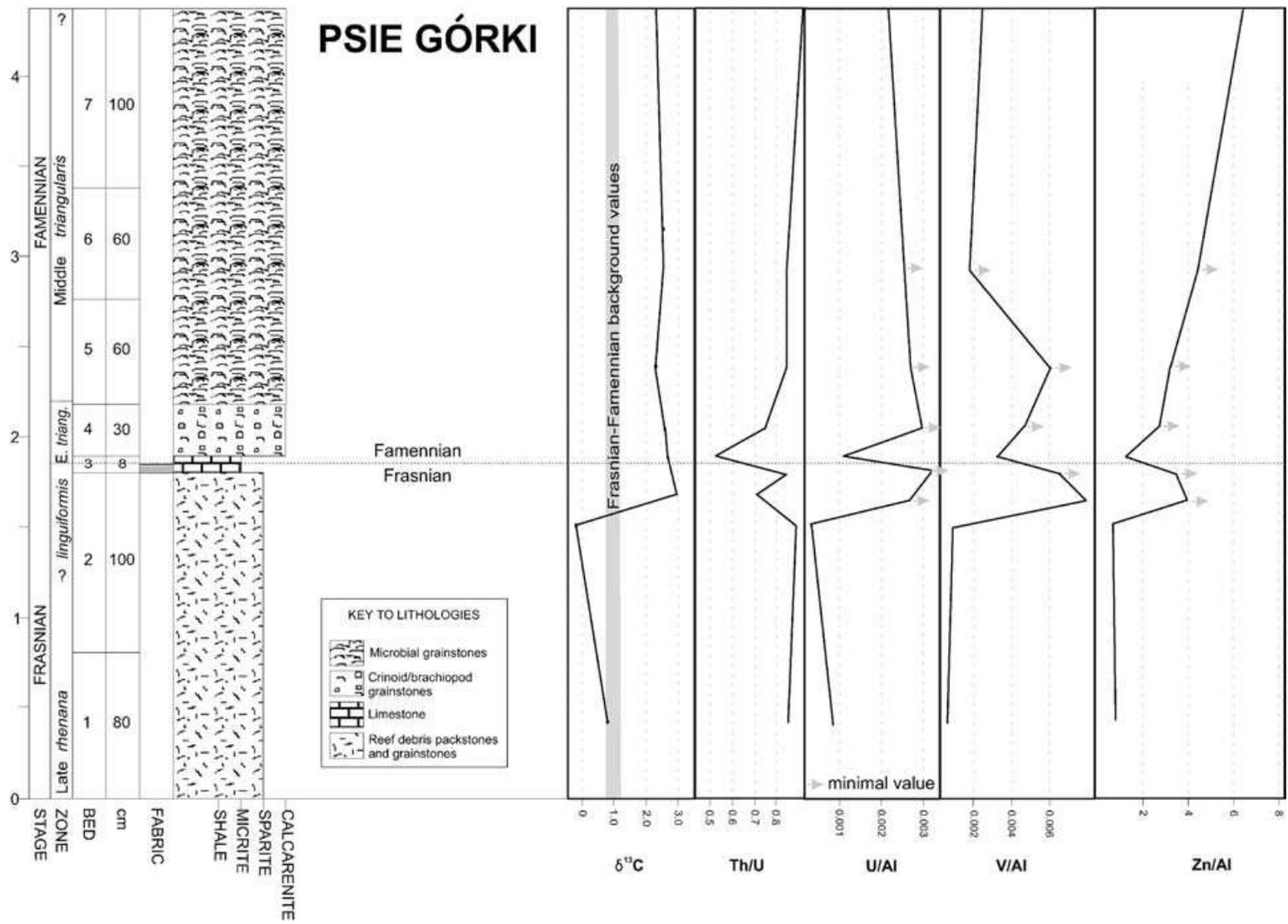
Figure 9. Graphic log of the F–F boundary beds from the forereef location of Psie Górki, Kielce, showing associated fluctuations in C isotopes and redox-sensitive trace element ratios, showing a change to oxygen-restricted deposition in the Late *linguiformis* Zone.

absence of framboids may reflect weathering at this long-abandoned quarry, or an original absence due to the development of dysoxic waters without the requisite deeper, euxinic water column necessary for Fe fixation. The considerable elevation of U/Al, V/Al and Zn/Al, and decline of Th/U ratios in the latest *linguiformis* to Middle *triangularis* interval all provide unequivocal evidence for oxygen-restricted deposition in this forereef locality: testimony to the development of extremely shallow-water dysoxia.

5.d. Summary of Polish redox record

The Holy Cross Mountain basinal locations reveal that oxygen-poor deposition typified much of the later Frasnian and early Famennian interval. Nevertheless, the Upper Kellwasser anoxic event is still manifest as an intensification of anoxia (in the Chęciny–Zbrza Basin), or as a decline in sedimentation rates to produce Cephalopodenkalk facies within a continuous record of anoxic deposition (Łysogóry Basin). Concentration of pelagic bioclasts is not seen in the Chęciny–Zbrza Basin, although small orthocones and aff. *Buchiola* become common in the Late *linguiformis* Zone (Fig. 6), as well as scattered goniatite coquinas (Dzik, 2002; Racki *et al.* 2002, fig. 16c). Remarkably, during the peak intensity of anoxia within the basins, oxygen-poor water even spread into shallow forereef settings. The stability of the euxinic water column during the Late *linguiformis* Zone, as evidenced by its pyrite framboid population, suggests that a considerable volume of the lower water column was probably sulphidic and therefore relatively immune to transient seafloor oxygenation events. The Lower Kellwasser event is not clearly manifest in the Polish record with an intensification of anoxia in the Kowala record being too young to correlate with the Lower Kellwasser Horizon.

6. France

6.a. Coumiac

The Frasnian portion of the Coumiac section is dominated by massive, diffusely bioturbated, pink to red micrites that locally contain abundant bivalves and tentaculitoids. Above this, Famennian strata consist of micrite beds with a nodular appearance known as the 'griotte' facies (Fig. 10). Two thin, medium-dark grey beds are developed within this otherwise uniform succession (beds 24a and 31g of the Becker *et al.* (1989) numbering scheme). Bed 24a is 18 cm thick, finely laminated micrite of the same age as the Lower Kellwasser Horizon (Late *rhenana* Zone) and bed 31g is a 7 cm thick, homoctenid–ostracod packstone (Fig. 11) of the same age as the Upper Kellwasser Horizon (latest *linguiformis* Zone). The highest levels of the Coumiac section consist of the bright red nodular limestones of the Lower Griotte Formation that succeed

the Upper Coumiac Formation in the Late *triangularis* Zone.

Except for the F–F boundary interval, Th/U ratios of the Coumiac section are high. At the boundary there is a dramatic decline due to a tenfold increase in U concentrations which reach values of up to 5 ppm (Fig. 10). Diligent searching for framboidal pyrite revealed that it was only present in bed 31g where the mean diameter was 6 μm, but with a 'tail' of larger examples up to diameters of 16 μm. No framboids were found in bed 24a.

6.a.1. Interpretation

The Kellwasser anoxic events clearly punctuated the prolonged history of very well-oxygenated deposition at Coumiac, although their expression was distinctly different. The Lower Kellwasser Horizon equivalent is finely laminated, but poorly fossiliferous, whereas the Upper Kellwasser event is recorded by a poorly laminated bed with abundant pelagic fossils. Pyrite framboid sizes suggest a lower dysaerobic facies for the latter event, but the absence of framboids from the lower horizon is curious; it may be due to weathering. The entire F–F boundary interval appears enriched in authigenic U, but this is probably due to the averaging effect of gamma-ray spectrometry surveys. When held to a face of vertical strata, as at Coumiac, spectrometers measure the average value of radionuclides over around 1.5 m of vertical section and therefore can include both U-rich and U-poor horizons (Myers & Wignall, 1987). The true U enrichment in the thin Kellwasser horizons may be substantially more than that measured.

6.b. La Serre

The lower levels of the Lower Serre section consist of beds of coarse dolomite spar that are replaced by micrites from bed 8, in the Early *rhenana* Zone (Fig. 12). The 2 m thickness of limestone that straddles the Early–Late *rhenana* zonal boundary is a darker grey colour and consists of massive homoctenid packstones grading up into wackestones. These are succeeded by just over 1 m thickness of well-bioturbated micrites, with common pyrite blebs, which are capped by an alternating succession of dark grey, laminated shales and limestones (Fig. 12). This succession ranges in age from latest Late *rhenana* Zone to at least the *crepida* Zone and shows little lithological change; all the limestone beds consist of dark grey, partly dolomitized micrites. The basal Famennian bed is noteworthy due to the prolific abundance of chitinozoans (cf. Paris *et al.* 1996). In the La Serre area the higher levels of the Famennian strata consist of grey, nodular limestones (Griotte facies) that begin in the *rhomboidea* Zone (Becker, 1993).

Framboidal pyrite is present in all the dark grey beds of shales and limestones at La Serre, although
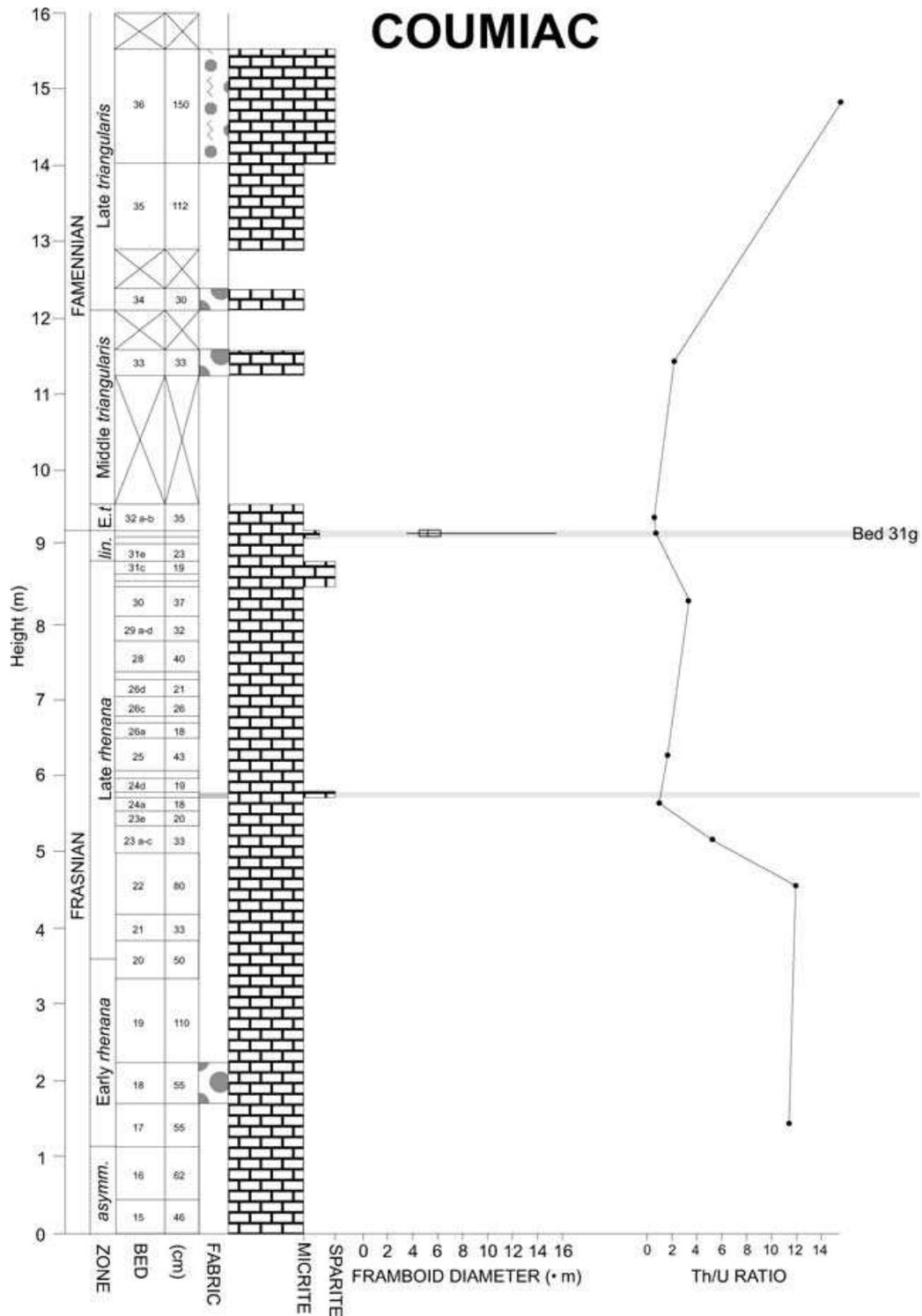
Figure 10. Graphic log of the F–F boundary beds at Coumiac, pyrite framboid diameter data and Th/U ratios. Conodont zonal boundaries are from Becker *et al.* (1989). Only bed 31g yielded pyrite framboids in this section. For legend see Figure 3. Note there are several unexposed intervals in the Famennian section.

intense weathering of many shale beds sometimes precluded framboid size assay. Framboid size ranges were generally similar in all the beds examined with little to distinguish the populations formed during the Upper Kellwasser event from other populations (Fig. 12).

6.b.1. Interpretation

The initial phase of anoxic deposition at La Serre is recorded by the development of dysaerobic limestones straddling the Early/Late *rhenana* zonal boundaries, an interval that coincides with well-oxygenated deposition
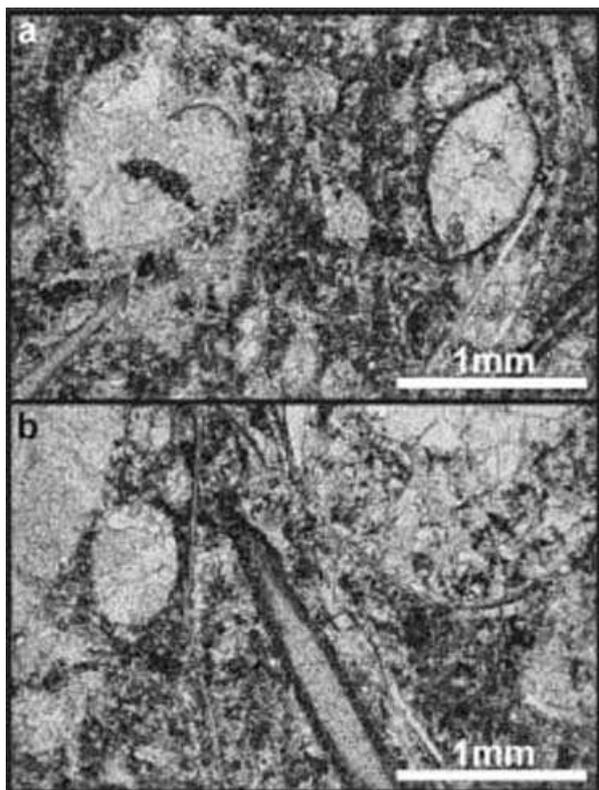
Figure 11. (a, b) Photomicrographs of bed 31g (the equivalent of the Upper Kellwasser Horizon) at Coumiac showing packstones domianted by homoctenids and ostracods and a small, inflated bivalve (upper left of a).

(e.g. at Steinbruch Schmidt) or improving oxygenation elsewhere (e.g. at Kowala). The termination of the Lower Kellwasser anoxic event coincides with the re-establishment of anoxic deposition at La Serre and a change to more shale-prone deposition that probably reflects a long-term deepening event that persisted at least until the *crepida* Zone. The Upper Kellwasser event occurred during this depositional interval, but it is not manifest by any change in the nature of deposition, for example, no 'Cephalopodenkalk' are developed.

7. Wolayer Glacier

The F–F transition at the Wolayer Glacier section (Carnic Alps) occurs within a uniform interval of thick-bedded platform carbonate deposition in which the distinctive double, positive carbon isotope excursion of the latest Frasnian has been recorded (Joachimski & Buggisch, 1993). Petrological examination reveals that thoroughly bioturbated wackestones (biomicrites), lacking any pyrite content, are developed from the end of the Early *rhenana* Zone to the Middle *triangularis* Zone. Thin-shelled bivalves, gastropods, crinoids and entomozoaceans dominate the fossil content. As recognized previously by Joachimski & Buggisch (1993),

there is no record of the Kellwasser anoxic events at this location.

8. Discussion

The degree and duration of oxygen restriction in the Late Devonian seas of Europe was clearly related to palaeobathymetry, with deep water and/or basinal locations, such as Kowala and La Serre, recording prolonged periods of dysoxic/anoxic deposition (Fig. 13). However, pyrite framboid data indicate variation in the intensity of oxygen restriction. The F–F boundary in particular saw the establishment of permanent euxinicity in the Polish basins, with sulphidic waters probably extending up to the photic zone (Joachimski *et al.* 2001). This development of a substantial volume of sulphidic lower water column probably ensured that high energy events, such as storms, were not even able to transiently oxygenate the seafloor in epicontinental basins. This interval also saw the expansion of oxygen-poor waters into shallower water settings, including submarine highs and probably even reef-crest locations. Other shallow-water Polish sections also reveal dysoxic deposition across the F–F transition based upon V/Cr ratio evidence (Racki *et al.* 2002, figs 10, 11).

The Upper Kellwasser anoxic event is thus seen to be intensive and extensive, but the same cannot be said of the Lower Kellwasser event of the early Late *rhenana* Zone. This interval coincides with intensification of anoxia in some German sections but an improvement of oxygenation levels in France and Poland. Feist & Schindler (1994, fig. 7) have previously noted a non-synchroneity between French and German developments of Lower Kellwasser 'dark facies' as have Crick *et al.* (2002), based on magnetic susceptibility correlation data.

The exception to this history is clearly at the Wolayer Glacier section. The persistent development of oxic conditions at this location may relate to its palaeogeographic location close to a continental margin (Fig. 1). The other studied locations are from the centres of epicontinental seas and basins and were thus far removed from the influence of oceanic circulation regimes. In this regard the Kellwasser events are more comparable to the early Toarcian anoxic event of the Jurassic rather than the oceanic anoxic events (OAEs) of the Cretaceous (Jenkyns, 1985, 1988). The Jurassic event also began in epicontinental basins and expanded into shallower locations but was relatively weakly developed in continental margin locations (Jenkyns, Geczy & Marshall, 1991; Jiménez *et al.* 1996). In contrast, the Cretaceous OAEs are oceanic phenomena and, although encountered in deeper continental shelf locations, they are not well developed in shallow epicontinental seas (Gale *et al.* 2000). These differing characters may help explain
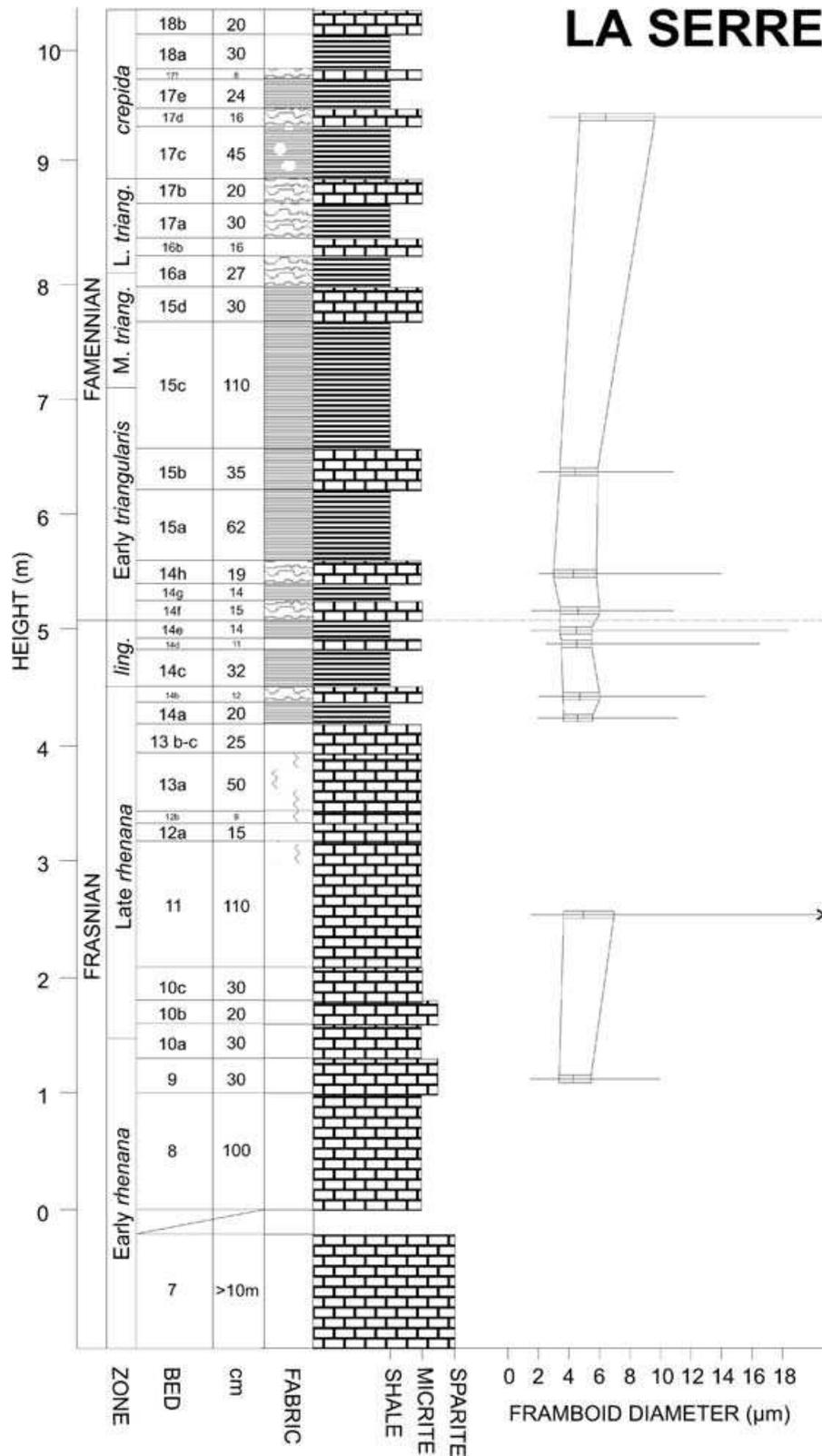
Figure 12. Graphic log of the F–F boundary beds at La Serre, showing framboid diameters. Conodont zonal boundaries are based on Becker & House (1994). For legend see Figure 3.

the different biotic response to these anoxic events. The Cretaceous events are either associated with only slightly elevated extinction rates (e.g. the Bonarelli event: Gale *et al.* 2000) or little perceptible effect on extinction rates at all (e.g. the Selli event: Erba,

1994). Much of the marine fossil record comes from epicontinental shelf seas and basins and it is the fate of the inhabitants of these locations that is primarily monitored by extinction rate curves. Thus, the primary development of the Kellwasser (and Toarcian) event in
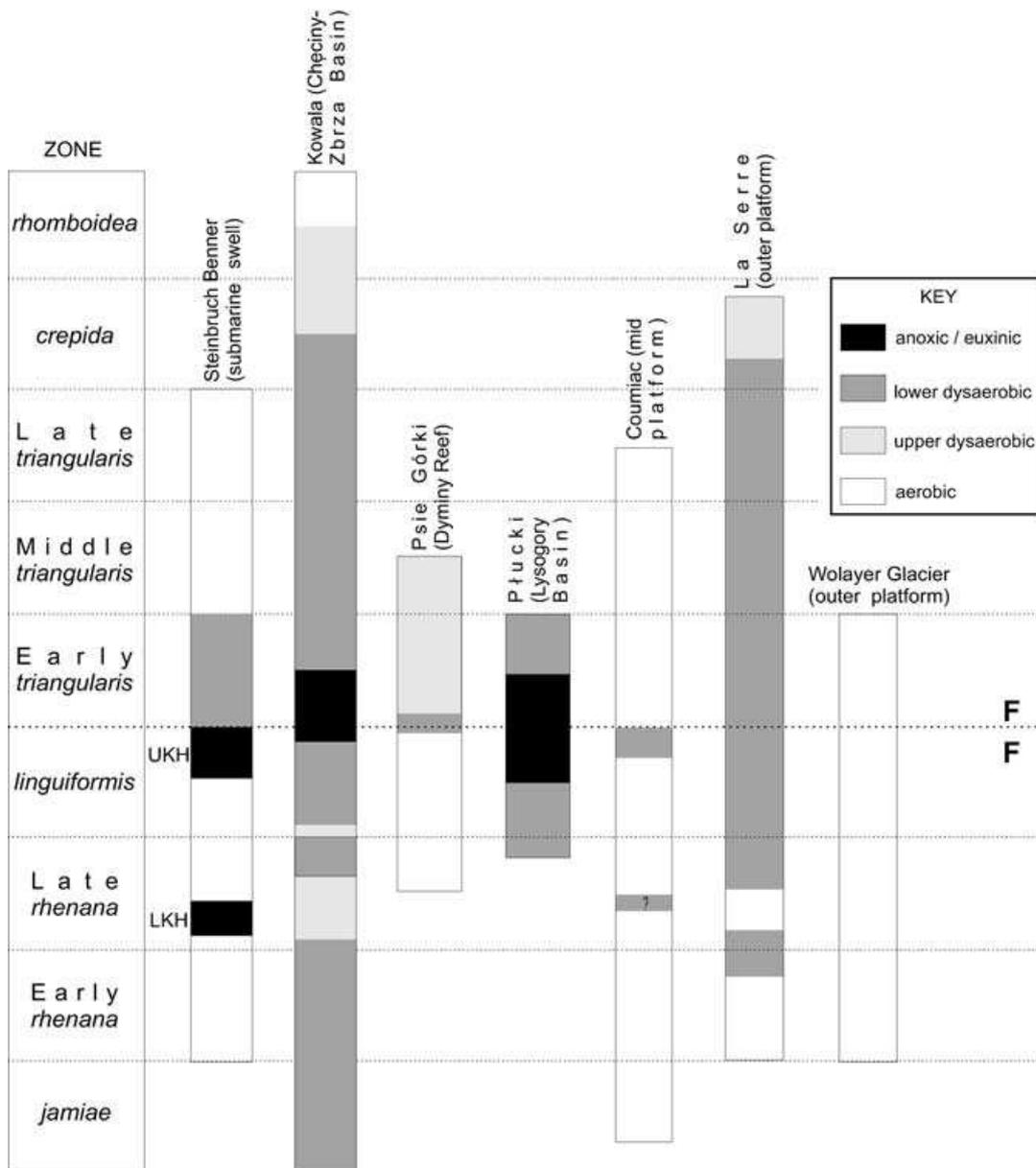
Figure 13. Comparison of oxygenation histories between the study sites. The peak intensity and spread of anoxia coincides with deposition of the Upper Kellwasser Horizon in Germany. In contrast the Lower Kellwasser Horizon in Germany does not mark a European-wide anoxic event (note that oxygenation improves at this level in both La Serre and Kowala).

epicontinental locations effectively removed the habitat of many marine taxa.

The proposed development of anoxia during the F–F interval contrasts with the model of several previous workers. They postulated that anoxic waters were displaced into shelf locations from deep, oceanic settings (Goodfellow *et al.* 1989), either by sinking of dense, cold waters (Wilde & Berry, 1988), or warm, saline waters (Becker & House, 1994). In Joachimski & Buggisch's (1993) variation, enhanced warm, saline bottom water generation on flooded highstand shelves is considered to have intensified the oceanic oxygen minimum zone with the result that anoxic waters spread back across the shelf. Implicit in all these models is the idea that 'deeper anoxic

waters *must* [our italics] be brought out of the deeps and spread over previously oxygenated regions of the seafloor' (McGhee, 1996, p. 156). However, it is not a mandatory requirement of anoxic events that they can only begin in oceans as the Upper Kellwasser event demonstrates. Palaeontological support for our viewpoint comes from the successful survival of the deepest water fauna, such as solitary Rugosa (Sorauf & Pedder, 1986) and the Thuringian ostracod community (Lethiers & Casier, 1999), during the Kellwasser crisis, an unlikely occurrence if bathyal and deeper waters were anoxic (Fig. 14). However, deepest water trilobite taxa appear to have fared rather badly compared to their shallowest water cousins (Feist & Schindler, 1994). A further potential counter-argument may be
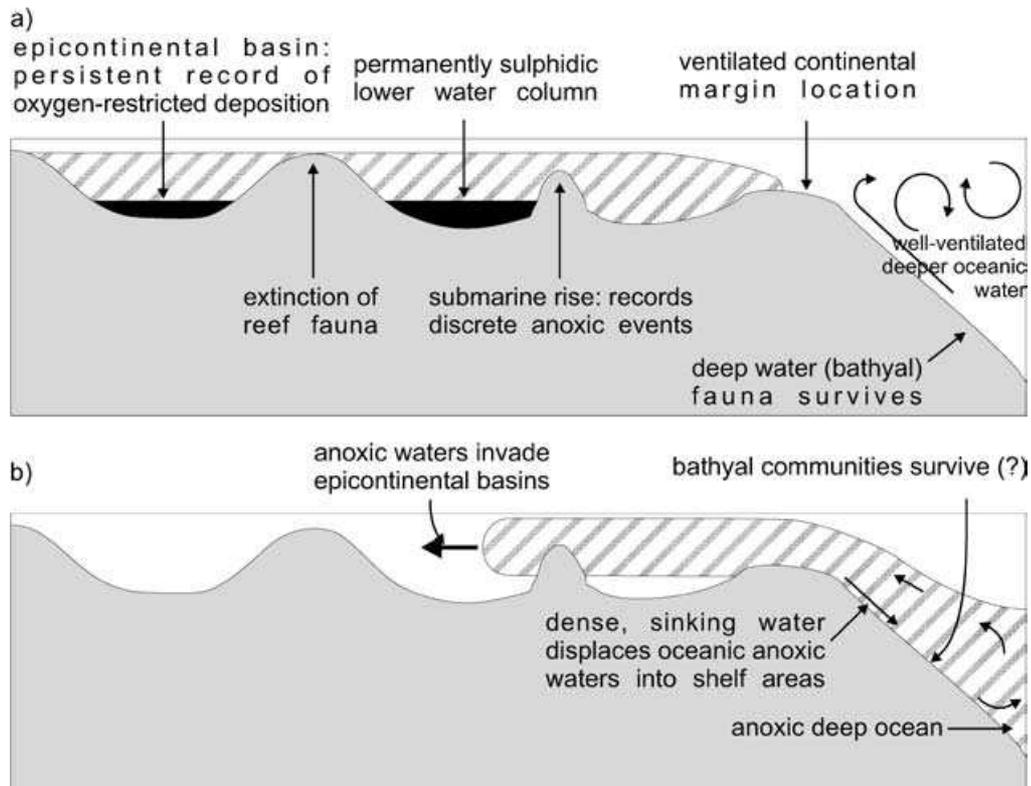
Figure 14. Comparison of model proposed here (a) for the development of anoxia during the Kellwasser anoxic events with previous suggestions (b) that the shelf anoxia was a consequence of oceanic upwelling of deep anoxic waters.

had from contemporaneous changes in pyrite S isotopes that can be interpreted as evidence for stratified, euxinic oceans in the Frasnian (Goodfellow *et al.* 1989, p. 67)

As related above, many authors attribute the F–F extinctions to a rapid, high amplitude sea-level fall that began within the Upper Kellwasser event (e.g. Sandberg *et al.* 1988; Sandberg, Morrow & Ziegler, 2002; House, 2002; Casier *et al.* 2002). However, given that this regression-related kill mechanism attempts to explain the cause of one the great Phanerozoic extinction crises, the evidence is remarkably cryptic. Much reliance has been placed on the changes in conodont biofacies with the sudden increase in *Icriodus* in the Late *linguiformis* Zone providing key data (e.g. Racki *et al.* 2002, fig. 4). In basinal sections this biofacies change is associated with little facies change, persistent euxinic deposition often lasting into the Early *triangularis* Zone. Of the sections studied here, only the very shallow-water Psie Górki section has evidence for emergence (Casier *et al.* 2002) and this occurs in the Dyminy reef complex which is known to record a complex history of active faulting in the Late Devonian (Szulczewski, 1971; Racki, 1990, 1998).

The details of Late Devonian sea-level changes are worthy of further investigation, with the most recent studies (e.g. Filer, 2002) showing that the eustatic changes may be considerably more complex

than those proposed by Sandberg *et al.* (1988). It is sufficient to note here that the details of extinction timings are closely related to the development of the Upper Kellwasser anoxic event and not to sea-level fall. Thus, many groups go extinct at the onset of Upper Kellwasser deposition, notably many goniatites (Becker & House, 1994), trilobites (Feist & Schindler, 1994) and ostracods (Casier, 1987; Olempska, 2002). This is prior to the postulated end-Frasnian sea-level fall, and suggests that the extraordinarily widespread development of anoxia in the epicontinental seas of Europe, during the Late *linguiformis* Zone, was an important component of the F–F kill mechanism.

References

BALIŃSKI, A. 2002. Frasnian–Famennian brachiopod extinction and recovery in southern Poland. *Acta Palaeontologica Polonica* **47**(2), 289–305.
BECKER, R. T. 1993. Anoxia, eustatic changes, and the Upper Devonian to lowermost Carboniferous global ammonoid

diversity. In *The ammonoidea: environments, ecology and evolutionary change* (ed. M. R. House), pp. 115–63. Systematics Association Special vol. 47.

BECKER, R. T., FEIST, R., FLAJS, G., HOUSE, M. R. & KLAPPER, G. 1989. Frasnian–Famennian extinction events in the Devonian at Coumiac, southern France. *Compte Rendus Academie Science, Paris* serie 2, 259–66.

BECKER, R. T. & HOUSE, M. R. 1994. Kellwasser events and goniatite successions in the Devonian of the Montagne Noire with comments on possible causations. *Courier Forschungsinstitut Senckenberg* **169**, 45–77.

BECKER, R. T., HOUSE, M. R., KIRCHGASSER, W. T. & PLAYFORD, P. E. 1991. Sedimentary and faunal changes across the Frasnian/Famennian boundary in the Canning Basin of Western Australia. *Historical Biology* **5**, 183–96.

BRATTON, J. F., BERRY, W. B. N. & MORROW, J. R. 1999. Anoxia pre-dates Frasnian–Famennian boundary mass extinction horizon in the Great Basin, USA. *Palaeogeography, Palaeoclimatology, Palaeoecology* **154**, 275–92.

BRETT, C. E. & BAIRD, G. C. 1995. Coordinated stasis and evolutionary ecology of Silurian to Middle Devonian faunas in the Appalachian Basin. In *New approaches to speciation in the fossil record* (eds D. H. Erwin and R. L. Anstey), pp. 285–315. Columbia University Press.

BUGGISCH, W. 1972. Zur Geologie und Geochemie der Kellwasserkalke und ihrer Begleitsedimente (Unteres Oberdevon). *Hessisches Landesamt für Bodenforschung, Abhandlungen* **62**, 1–68.

BUGGISCH, W. 1991. The global Frasnian–Famennian "Kellwasser Event". *Geologische Rundschau* **80**, 49–72.

CASIER, J.-G. 1987. Etude biostratigraphique et paléoécologique des ostracodes du récif de marbre rouge du Hautmont à Vodelée (partie supérieure du Frasnien, Bassin de Dinant, Belgique). *Revue de Paléobiologie* **6**, 193–204.

CASIER, J.-G. & LETHIERS, F. 1998. Ostracod Late Devonian mass extinction: the Schmidt quarry parastratotype (Kellerwald, Germany). *Comptes rendus de l'Académie des Sciences de Paris, Earth and Planetary Sciences* **326**, 71–8.

CASIER, J.-G., DEVLEESCHOUWER, X., LETHIERS, F., PRÉAT, A. & RACKI, G. 2002. Ostracods and fore-reef sedimentology of the Frasnian–Famennian boundary beds in Kielce (Holy Cross Mountains, Poland). *Acta Palaeontologica Polonica* **47**, 227–46.

CLAEYS, P., KYTE, F. T. & CASIER, J.-G. 1994. Frasnian–Famennian boundary: mass extinction, anoxic oceans, microtectite layers, but not much iridium? In *New developments regarding the KT and other catastrophes in Earth history*, pp. 22–4. Lunar and Planetary Institute, LPI contribution no. 825.

CHLUPÁC, I., FEIST, R. & MORZADEC, P. 2000. Trilobites and standard Devonian stages. In *Subcommission on Devonian Stratigraphy: Fossil Groups Important for Boundary Definition* (ed. P. Bultynck), pp. 87–98. *Courier Forschungsinstitut Senckenberg* **220**.

COPPER, P. 1998. Evaluating the Frasnian–Famennian mass extinction: comparing brachiopod faunas. *Acta Palaeontologica Polonica* **43**, 137–54.

CRICK, R. E., ELLWOOD, B. B., FEIST, R., EL HASSANI, A., SCHINDLER, E., DREESEN, R., OVER, D. J. & GIRARD, C. 2002. Magnetostratigraphy susceptibility

of the Frasnian/Famennian boundary. *Palaeogeography, Palaeoclimatology, Palaeoecology* **181**, 67–90.

DEVLEESCHOUWER, X., HERBOSCH, A. & PRÉAT, A. 2002. Microfacies, sequence stratigraphy and clay mineralogy of a condensed deep-water section around the Frasnian/Famennian boundary (Steinbruch Schmidt, Germany). *Palaeogeography, Palaeoclimatology, Palaeoecology* **181**, 171–94.

DZIK, J. 2002. Emergence and collapse of the Frasnian conodont and ammonoid communities. *Acta Palaeontologica Polonica* **47**, 565–650.

ENGEL, W., FRANKE, W. & LANGENSTRASSEN, F. 1983. Palaeozoic sedimentation in the northern branch of the mid-European Variscides – essay of an interpretation. In *Intracontinental fold belts* (eds H. Martin and F. W. Eder), pp. 9–41. Berlin: Springer.

ERBA, E. 1994. Nannofossils and superplumes: The early Aptian "nannoconid crisis". *Paleoceanography* **9**, 483–501.

FEIST, R. 1985. Devonian Stratigraphy of the Southeastern Montagne Noire (France). *Courier Forschunginstitut Senckenberg* **75**, 331–52.

FEIST, R. & SCHINDLER, E. 1994. Trilobites during the Frasnian Kellwasser crisis in European Late Devonian cephalopod limestones. *Courier Forschungsinstitut Senckenberg* **169**, 195–223.

FILER, J. K. 2002. Late Frasnian sedimentation cycles in the Appalachian basin – possible evidence for high frequency eustatic sea-level changes. *Sedimentary Geology* **154**, 31–52.

GALE, A. S., SMITH, A. B., MONKS, N. E. A., YOUNG, J. A., HOWARD, A., WRAY, D. S. & HUGGETT, J. M. 2000. Marine biodiversity through the Late Cenomanian–Early Turonian: palaeoceanographic controls and sequence stratigraphic biases. *Journal of the Geological Society* **157**, 745–58.

GIRARD, C. & LÉCUYER, C. 2002. Variations in Ce anomalies of conodonts through the Frasnian/Famennian boundary of Poland (Kowala – Holy Cross Mountains): implications for the redox state of seawater and biodiversity. *Palaeogeography, Palaeoclimatology, Palaeoecology* **181**, 251–98.

GOODFELLOW, W. D., GELDSETZER, H., MCLAREN, D. J., ORCHARD, M. J. & KLAPPER, G. 1989. Geochemical and isotopic anomalies associated with the Frasnian–Famennian extinction. *Historical Biology* **2**, 51–72.

HALLAM, A. 1980. Black shales. *Journal of the Geological Society, London* **137**, 123–4.

HOUSE, M. R. 1985. Correlation of mid-Palaeozoic ammonoid evolutionary events with global sedimentary perturbations. *Nature* **313**, 17–22.

HOUSE, M. R. 2002. Strength, timing, setting and cause of mid-Palaeozoic extinctions. *Palaeogeography, Palaeoclimatology, Palaeoecology* **181**, 5–26.

HOUSE, M. R., MENNER, V. V., BECKER, R. T., KLAPPER, G., OVNATANOVA, N. S. & KUZ'MIN, V. 2000. Reef episodes, anoxia and sea-level changes in the Frasnian of the southern Timan (NE Russian Platform). In *Carbonate platform systems: components and interactions* (eds E. Insalaco, P. W. Skelton and T. J. Palmer), pp. 1–8. Geological Society of London, Special Publication no. 178.

JENKYNS, H. C. 1985. The Early Toarcian and Cenomanian–Turonian anoxic events in Europe – comparisons and contrasts. *Geologische Rundschau* **74**, 505–18.

JENKYNS, H. C. 1988. The Early Toarcian (Jurassic) anoxic event – stratigraphic, sedimentary, and geochemical evidence. *American Journal of Science* **288**, 101–51.

JENKYNS, H. C., GECZY, B. & MARSHALL, J. D. 1991. Jurassic manganese carbonates of Central-Europe and the Early Toarcian anoxic event. *Journal of Geology* **99**, 137–49.

JIMÉNEZ, A. P., DECISNEROS, C. J., RIVAS, P. & VERA, J. A. 1996. The Early Toarcian anoxic event in the westernmost Tethys (Subbetic): Palaeogeographic and palaeobiogeographic significance. *Journal of Geology* **104**, 399–416.

JOACHIMSKI, M. M. & BUGGISCH, W. 1993. Anoxic events in the late Frasnian – causes of the Frasnian–Famennian faunal crisis? *Geology* **21**, 675–8.

JOACHIMSKI, M. M., BUGGISCH, W. & ANDERS, T. 1994. Mikrofazies, Conodontenstratigraphie und Isotopengeochemie des Frasne/Famenne Grenzprofils Wolayer Gletscher (Karnische Alpen). *Abhandlungen Geologische Bundesanstalt Wien* **50**, 183–95.

JOACHIMSKI, M. M., OSTERTAG-HENNING, C., PANCOST, R. D., STRAUSS, H., FREEMAN, K. H., LITTKE, R., SINNINGHE DAMSTÉ, J. S. & RACKI, G. 2001. Water column anoxia, enhanced productivity and concomitant changes in $\delta^{13}C$ and $\delta^{34}S$ across the Frasnian–Famennian boundary (Kowala – Holy Cross Mountains/Poland). *Chemical Geology* **175**, 109–31.

KLAPPER, G., FEIST, R., BECKER, R. T. & HOUSE, M. R. 1993. Definition of the Frasnian/Famennian Stage boundary. *Episodes* **16**, 433–41.

KREBS, W. 1979. Devonian basinal facies. *Palaeontological Association Special Paper* **23**, 125–39.

LETHIERS, F. & CASIER, J.-G. 1999. Le point sur . . . Autopsie d'une extinction biologique. Un exemple: la crise de la limite Frasnian–Famennian (364 Ma). *Comptes rendus de l'Académie des Sciences de Paris, Sciences de la terre et des planètes* **329**, 303–15.

MCGHEE, G. R. JR. 1996. *The Late Devonian mass extinction.* New York: Columbia University Press, 303 pp.

MYERS, K. J. & WIGNALL, P. B. 1987. Understanding Jurassic organic-rich mudrocks – new concepts using gammaray spectrometry and palaeoecology: Examples from the Kimmeridge Clay of Dorset and the Jet Rock of Yorkshire. In *Marine Clastic Environments* (eds J. K. Legget and G. G. Zuffa), pp. 175–92. London: Graham and Trotman.

OLEMPSKA, E. 2002. The Late Devonian Upper Kellwasser Event and entomozoacean ostracods in the Holy Cross Mountains, Poland. *Acta Palaeontologica Polonica* **47**, 247–66.

PAPROTH, E., FEIST, R. & FLAJS, G. 1991. Decision on the Devonian–Carboniferous boundary stratotype. *Episodes* **14**, 331–6.

PARIS, F., GIRARD, C., FEIST, R. & WINCHESTER-SEETO, T. 1996. Chitinozoan bio-event in the Frasnian–Famennian boundary beds at La Serre (Montagne Noire, Southern France). *Palaeogeography, Palaeoclimatology, Palaeoecology* **121**, 131–45.

RACKI, G. 1990. Frasnian–Famennian event in the Holy Cross Mts, Central Poland: Stratigraphic and ecologic aspects. *Lecture Notes in Earth Sciences* **30**, 169–81.

RACKI, G. 1998. Frasnian–Famennian biotic crisis: Undervalued tectonic control? *Palaeogeography, Palaeoclimatology, Palaeoecology* **141**, 177–98.

RACKI, G. & BALIŃSKI, A. 1998. Late Frasnian Atrypida (Brachiopoda) from Poland and the Frasnian–Famennian biotic crisis. *Acta Palaeontologica Polonica* **43**, 273–304.

RACKI, G., RACKA, M., MATYJA, H. & DEVLEESCHOUWER, X. 2002. The Frasnian/Famennian boundary interval in the South Polish–Moravian shelf basins: integrated event-stratigraphical approach. *Palaeogeography, Palaeoclimatology, Palaeoecology* **181**, 251–98.

RAISWELL, R., NEWTON, R. & WIGNALL, P. B. 2001. An indicator of water-column anoxia: Resolution of biofacies variations in the Kimmeridge Clay (Upper Jurassic, UK). *Journal of Sedimentary Research* **71**, 286–94.

SANDBERG, C. A., MORROW, J. R. & ZIEGLER, W. 2002. Late Devonian sea-level changes, catastrophic events, and mass extinctions. In *Catastrophic Events and Mass Extinctions: Impacts and Beyond* (eds C. Koeberl and K. G. MacLeod), pp. 473–87. Geological Society of America, Special Paper no. 356.

SANDBERG, C. A., ZIEGLER, W., DREESEN, R. & BUTLER, J. L. 1988. Part 3: Late Frasnian extinction: conodont event stratigraphy, global changes, and possible causes. *Courier Forschungsinstitut Senckenberg* **102**, 263–307.

SARTENAER, P., RACKI, G. & SZULCZEWSKI, M. 1998. The late Frasnian rhynchonellid genus *Pammegetherhyncus* (Brachiopoda) in Poland, and its relevance to the Kellwasser Crisis. *Acta Palaeontologica Polonica* **43**, 379–94.

SCHINDLER, E. 1990. Die Kellwasser-Krise (hohe Frasne-Stufe, Ober Devon). *Gottinger Arbeiten zur Geologie und Paläontologie* **46**, 1–115.

SCHINDLER, E. 1993. Event-stratigraphic markers within the Kellwasser Crisis near the Frasnian/Famennian boundary (Upper Devonian) in Germany. *Palaeogeography, Palaeoclimatology, Palaeoecology* **104**, 115–25.

SCHÖNLAUB, H. P. & HISTON, K. 1999. The Palaeozoic of the Southern Alps. *Berichte der Geologischen Bundesanstalt* **47**, 6–30.

SORAUF, J. E. & PEDDER, A. E. H. 1986. Late Devonian rugose corals at the Frasnian–Famennian crisis. *Canadian Journal of Earth Sciences* **23**, 1265–87.

SZULCZEWSKI, M. 1971. Upper Devonian conodonts, stratigraphy and facial development in the Holy Cross Mountains. *Acta Geologica Polonica* **23**, 1–59.

SZULCZEWSKI, M. 1995. Depositional evolution of the Holy Cross Mountains in the Devonian and Carboniferous: a review. *Geology Quarterly* **39**, 471–88.

SZULCZEWSKI, M. 1996. Devonian succession in the Kowala quarry and railroad cut. *Sixth European Conodont Symposium (ECOS VI), Excursion Guide*, Warsaw, pp. 27–30.

WALLISER, O. H. 1996. Global events in the Devonian and Carboniferous. In *Global events and event stratigraphy* (ed. O. H. Walliser), pp. 225–50. Berlin: Springer-Verlag.

WALLISER, O. H., GROOS-UFFENORDE, H., SCHINDLER, E. & ZIEGLER, W. 1989. On the Upper Kellwasser Horizon (boundary Frasnian/Famennian). *Courier Forschungsinstitut Senckenberg* **110**, 247–55.

WENDT, J. & BELKA, Z. 1991. Age and depositional environment of Upper Devonian (early Frasnian to early Famennian) black shales and limestones (Kellwasser Facies) in the eastern Anti-Atlas, Morocco. *Facies* **25**, 51–90.

WIGNALL, P. B. & MYERS, K. J. 1988. Interpreting benthic oxygen levels in mudrocks – a new approach. *Geology* **16**, 452–5.

WIGNALL, P. B. & NEWTON, R. J. 1998. Pyrite framboid diameter as a measure of oxygen deficiency in ancient mudrocks. *American Journal of Science* **298**, 537–52.

WILDE, P. & BERRY, W. B. N. 1988. Comment on: sulfur isotope anomaly associated with the Frasnian–Famennian extinction, Medicine Lake, Alberta, Canada. *Geology* **16**, 86.

WILKIN, R. T. & BARNES, H. L. 1997. Formation processes of framboidal pyrite. *Geochimica et Cosmochimica Acta* **61**, 323–39.

WILKIN, R. T., BARNES, H. L. & BRANTLEY, S. L. 1996. The size distribution of framboidal pyrite in modern sediments: An indicator of redox conditions. *Geochimica et Cosmochimica Acta* **60**, 3897–912.

YUDINA, A. B., RACKI, G., SAVAGE, N. S., RACKA, M. & MAŁKOWSKI, K. 2002. The Frasnian–Famennian events in a deep-shelf succession, Subpolar Urals: biotic, depostional and geochemical records. *Acta Palaeontologica Polonica* **47**, 355–72.