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Palaeoenvironmental changes at the Frasnian/Famennian boundary in key European sections: Chemostratigraphic constraints

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Abstract

The study aims to put constraints on global environmental changes, which took place during the Frasnian–Famennian (F/F) transition by using a geochemical multiproxy approach. For this several key European F/F boundary sections deposited in different palaeogeographic settings were selected, including, in addition to the stratotype and parastratotype sections of Coumiac (Montagne Noire, France) and Steinbruch Schmidt/Branau (Germany), respectively, also, some other sections thoroughly characterized by other authors (the drilling Büdesheimer Bach/Prümer Mulde, Germany; Kowala Section, Holy Cross Mountains, Poland; La Serre, France). Changes in the detrital flux along the sections were evaluated on the basis of both variations in mineral composition and in some diagnostic element ratios like Ti/Al. The biogenic flux was assessed as a function of the C_{org} content. The input of nutrients or the palaeoproductivity was determined by the P_2O_5 and Ba in excess. The degree of anoxia during deposition was constrained by determining the concentration of redox sensitive metals (e.g., Fe, Mn) in the bulk sediment, of specific element ratios (e.g., V/Cr), as well as the size of pyrite grains together with the degree of pyritization (DOP) in the Büdesheimer Bach core. The hydrothermal and volcanic influence in the sedimentary record was detected using, e.g., the Al/(Al+Fe+Mn) and Zr/Al_2O_3 ratios.

The Kellwasser horizons are characterized by a general decrease in the detrital input together with the increase of Al-normalized concentration of some of the transition metals. These changes are interpreted as reflecting a relative sea-level rise and a higher hydrothermal influence. In contrast to these, the establishment of dysoxic/anoxic conditions in the depositional environment as well as the increase of organic matter burial are not always restricted to the Kellwasser horizons (KWH). Moreover, the hydrothermal influence can lead to misinterpretation with respect to redox conditions and productivity due to the additional input of some specific elements.

Our results indicate the coincidence of sea-level rise with hydrothermalism and volcanism during the deposition of the KWH in the area of South Laurussia and North Gondwana. The resulting enrichment in metals and nutrients is coupled in several F/F boundary sections with a higher microbial activity, as already observed by some authors. These effects coupled with a general lowering of the degree of oxygenation of the water bodies could have played a significant role in the demise of the biota.

Keywords: Frasnian/Famennian boundary; Mass extinction; Inorganic geochemistry; Primary productivity; Sea-level; Volcanism

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1. Introduction

The Frasnian–Famennian boundary (F/F), also defined as the Kellwasser (KW) bio-event, is one of the “big five” mass extinctions in the earth history. The

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F/F stage boundary has been defined by the Global Stratotype Section and Point (GSSP) in a section exposed near the Upper Coumiac quarry in the southeastern Montagne Noire, France (Klapper et al., 1993). The numerical age of the F/F boundary varies among the different authors between 364 my and 376.5 my (Tucker et al., 1998). In most of the European sections, the KW horizons (Lower and Upper) are recognizable by their dark colour due to enrichment in organic matter. The boundary between the Lower and Upper Rhenana conodont zones corresponds to the top of the lower KW horizon (LKWH), while the limit between the *linguiformis* and *triangularis* conodont zones, defined as the F/F boundary, corresponds to the top of the upper KW horizon (UKWH) (Ziegler and Sandberg, 1990).

The ultimate cause or causes of this mass extinction is still a matter of debate. Some authors favour an impact or multiple impact hypothesis (McGhee, 2001), though no evidences were found in some of the sections (e.g., Steinbruch Schmidt, La Serre; McGhee et al., 1986; Girard et al., 1997). Others postulated a general climatic cooling (Joachimski et al., 2002), though locally warm and humid conditions must have prevailed during the deposition of the KWH, as it was proposed for Steinbruch Schmidt (Devleeschouwer et al., 2002). The onset of global anoxia is also often referred as the main trigger for the F/F mass extinction, though no signs for anoxia was observed in many of the sections (Bratton et al., 1999; Copper, 2002; George and Chow, 2002). Most of the authors emphasize the role of a general eutrophication of the oceans for which they give different explanations, like the evolution of vascular land plants (Algeo et al., 1995), installation of reducing conditions (Murphy et al., 2000a,b), increased terrigenous supply (Girard and Lécuyer, 2002), upwelling (Caplan et al., 1996; Giles et al., 2002) or a more intensive volcano-tectonic activity (Becker and House, 1994; Wilson and Lyashkevitch, 1996; Racki, 1998; Racki and Cordey, 2000; Streel et al., 2000; Racki et al., 2002; Yudina et al., 2002; Ma and Bai, 2002). Sea-level fluctuations were also considered to have played a significant role in environmental changes (Johnson et al., 1985; Buggisch, 1991; Becker, 1993; Joachimski and Buggish, 1993; Muchez et al., 1996; Poty, 1999; Streel et al., 2000; Racki et al., 2002; Devleeschouwer et

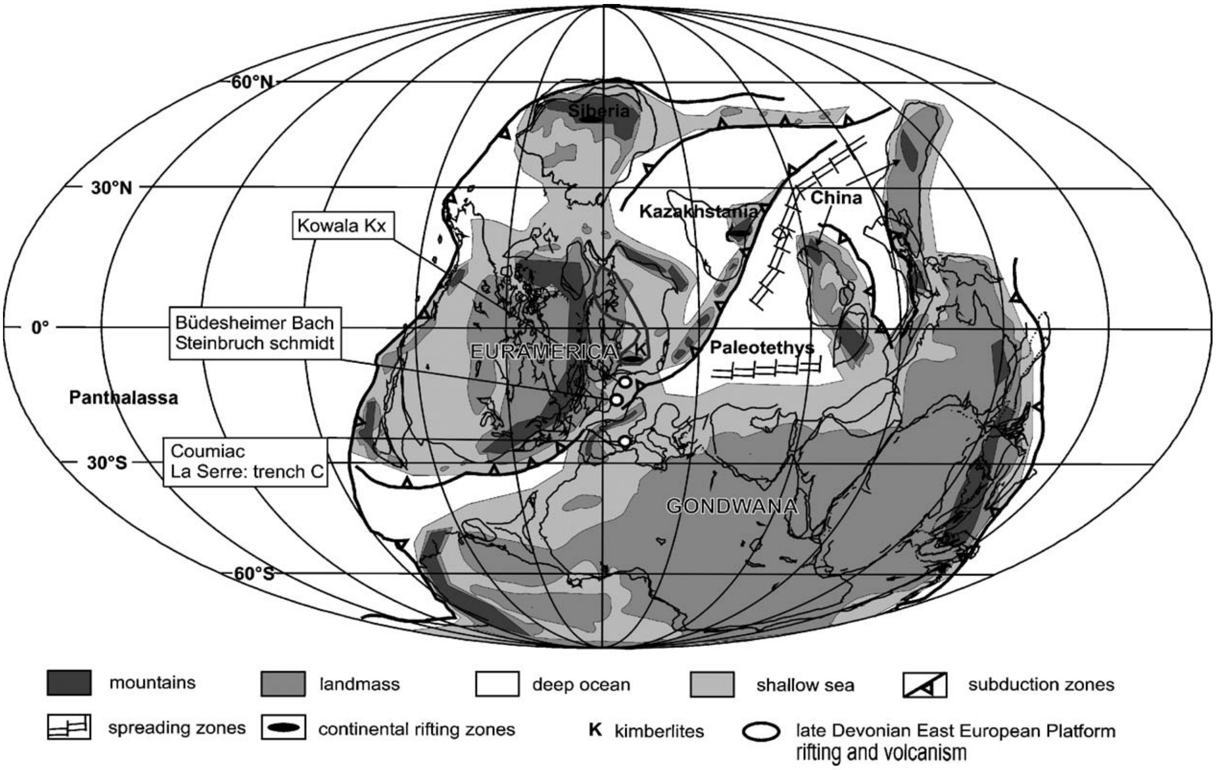

Fig. 1. Palaeogeographic reconstruction of the Upper Devonian (modified after Scotese and McKerrow, 1990; Golonka et al., 1994) with the location of the investigated Frasnian–Famennian boundary sections, the location of spreading zones and continental rifting zones (Racki, 1998) as well as the location of the main areas of late Devonian rifting and associated volcanism of the East European Platform (Wilson and Lyashkevitch, 1996).

al., 2002; Copper, 2002; George and Chow, 2002; Piecha, 2002; Stephens and Sumner, 2003). Finally, some authors preferred a multi-causal scenario to explain the Kellwasser bio-event (Schindler, 1990; Lethiers, 1998; Lethiers and Casier, 1999; House, 2002).

In order to put constraints on possible causes responsible for the demise of the biota during the Frasnian–Famennian (F/F) transition, we aimed at characterizing the environmental changes with respect to detrital input, biogenic input, productivity, redox conditions, as well as hydrothermal and volcanic inputs during the deposition of the Kellwasser horizons by using a geochemical multiproxy approach. For this, five sections were selected (Fig. 1). In addition to the drilling core Büdesheimer Bach (Prümer Mulde, Germany), thoroughly investigated recently by an interdisciplinary research group, the other sections included in the study were selected to have precisely documented macrofaunal stratigraphic record (the parastratotype of Steinbruch Schmidt, Germany, and the stratotype of Coumiac, Montagne Noire, France), to be deposited in different palaeogeographic settings (e.g., La Serre deposited in a deeper facies as compared to Coumiac) as well as to allow a comparison with the results of other geochemical investigations (the well-studied section of Kowala, Poland).

2. Investigated sections

2.1. Kowala (Kx section, Holy Cross Mountains, Poland)

Frasnian–Famennian deposits are well exposed in the Kowala quarry in the southern Kielce region (Fig. 1). The well-known continuous sequence of the Checiny–Zbrza basin (Racki et al., 2002) was frequently sampled for various F/F studies (Joachimski et al., 2001). The Kowala section consists of black carbonaceous shales with intercalated carbonate beds (Fig. 2) deposited in a deep shelf facies. Four lithologic units were described (Vishnevskaya et al., 2002). The F/F boundary was localised by means of conodonts between the *Palmatolepis linguiformis* and *triangularis* zone, as well as based on the presence of a distinctive cherty bed (Racki et al., 2002).

The depletion of seawater in oxygen just after the F/F boundary is indicated in Kowala by Ce anomalies (Girard and Lécuyer, 2002). In their geochemical study on the basinal Kowala section, Joachimski et al. (2001) concluded that anoxic conditions must have prevailed during the late Frasnian and early Famennian. However, this is in contradiction with conclusions based on proxies like the V/Cr ratio (Racki et al., 2002). Additional geochemical investigations indicate a higher Zr/Al_2O_3 ratio near the F/F boundary not only at Kowala, but also in others sections of the south Polish–Morovian shelf basins, suggesting a higher eolian input of fine grained pyroclastic material (Racki et al., 2002). The same study documented also an increase in the biological productivity and in hydrothermal input during the Kellwasser event. Late Devonian volcanic activity was also pointed out in the Kowala 1 borehole (Zakowa and Radlicz, 1990) and in some Moravian sections (Hladil, 2002). Magnetic susceptibility values indicate a transgressive trend at the end of the Frasnian followed by a regressive phase during the earliest Famennian (Racki et al., 2002). An early Famennian eustatic fall as well as an eutrophication and/or disturbance in the marine photic web close to the F/F boundary was postulated in a recent palynofacies study (Filipiak, 2002).

2.2. Büdesheimer Bach (Eifel Mountains, Germany)

The Büdesheimer Bach core (final depth 165 m) was drilled at the north-eastern edge of the Prüm syncline (Eifel Mountains) (Fig. 1). The main stratigraphic units intercepted by the drilling are the Büdesheimer Goniatite Shales and the Ooser Plattenkalk Formation (Middle Adorfian to Nehdenian; Frasnian/Famennian) (Piecha, 1994). The section consists of gray to black coloured calcareous shales including turbiditic limestone beds (Fig. 2). Biostratigraphic dating is difficult because of the scarcity of conodonts in the limestone beds (Piecha, 1994). The twofold occurrence of the base of the late Rhenana zone (LKWH) is considered to be due to tectonic repetition as suggested by lithology and conodont association (Piecha, 1994). The presence of nektic and planktic fauna and the lack of benthos suggest that the pyrite-rich black shale parts were deposited in an euxinic bottom water environment. Bivalve fauna points to a shallow water depth (Piecha, 1994). The positive $\delta^{13}C_{carb}$ excursion during the “Kellwasser horizons” is interpreted in terms of increased burial of organic matter (Joachimski et al., 2002). Based on the conodont color alteration index the sequence shows a thermal overprint at temperature below 100°C (Joachimski et al., 2002).

2.3. Steinbruch Schmidt (Branau, Germany)

The quarry Schmidt is one of the best examined sections, characterised by completeness and by

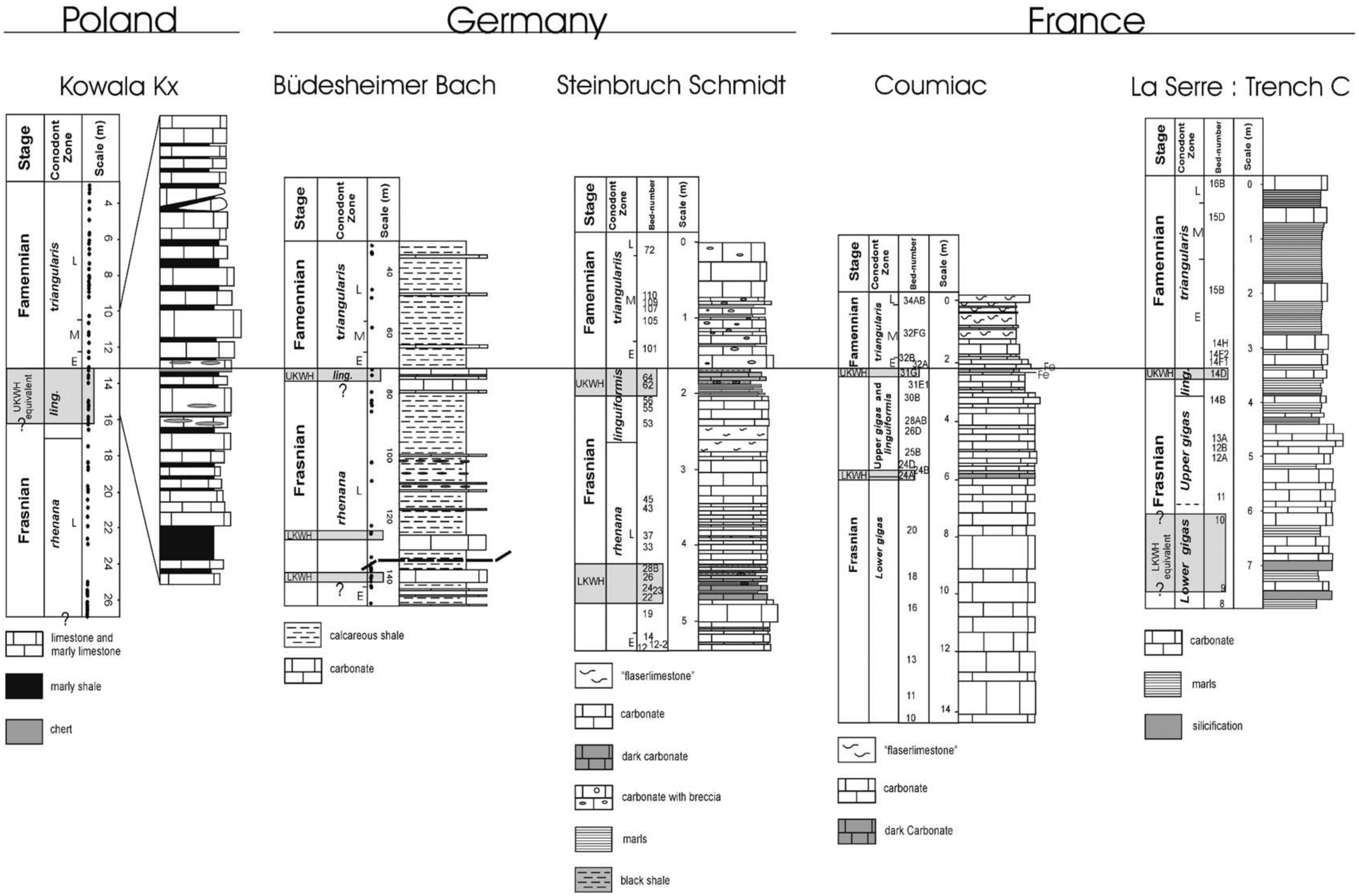

Fig. 2. Lithologs and samples position of the investigated sections. The conodont zones are according to Ziegler (1971) and Ziegler and Sandberg (1990). The Kowala log is modified after Racki et al. (2002), Büdesheimer Bach log modified after Joachimski et al. (2001), Steinbruch Schmidt log modified after Schindler (1990), Coumiac log modified after Becker and House (1994), La Serre log modified after Lethiers et al. (1998) (Bank numbers from Feist, 1990). The sample location is represented in the form of bank numbers or black dots. The question marks correspond to the uncertainties of the KWH equivalent position or the biostratigraphic limits. E: early; M: middle; L: late.

exemplary development of the Kellwasser horizons. The sequence in Steinbruch Schmidt was deposited on a submarine rise, below the wave base level and consists of dark grey to black limestones (KWH, Fig. 2) intercalated within grey cephalopod limestones (Buggisch, 1991). The palaeogeographic environment of the Rhenish Slate Mountains during the upper Devonian corresponds to a siliciclastic carbonate shelf, bordering the old red continent to the south. McGhee et al. (1986) carried out geochemical investigations aiming at the identification of abnormal Ir concentrations, however, without success. Devleeschouwer et al. (2002) defined three main facies in this section, with the Kellwasser horizons representing the basinal environment deposited at an inferred depth of up to 200 m and with the only presence of radiolarians. Magnetic susceptibility values (Devleeschouwer, 1999) clearly suggest variation in the detrital input into the ocean during the early Famennian. The authors interpreted the high kaolinite content at the F/F boundary as an indicator for hot and wet climatic conditions. Schindler (1990) interpreted the deposition of the black shales as a consequence of episodic rises of the anoxic layer. In contrast to a more generally accepted view (Schindler, 1990; Buggisch, 1991) according to which the whole UKWH was deposited under anoxic conditions, Casier and Lethiers (1998) considered only the last 5 cm of the UKWH as anoxic. The two positive carbon isotope excursions reported, also in other F/F boundary sections of central Europe (Joachimski and Buggish, 1993), are interpreted to indicate an enhanced burial of organic carbon.

2.4. Coumiac and La Serre (Montagne Noire, southern France)

The section above the Upper Coumiac quarry was chosen in 1993 by the International Commission on Stratigraphy (ICS) and the International Union of Geological Sciences (IUGS) as the Global Stratotype Section and Point (GSSP) (Fig. 1). The decision was taken because of the exemplary documentation of the transition by means of macrofossil groups (Klapper et al., 1993). The section Coumiac consists of cephalopod and nodular limestones in which are intercalated the KWH, represented by mudstones and wackestones (Fig. 2). Dysaerobic conditions were assigned to the KWH due to faunal and colour changes (Schindler, 1990). Two positive carbon isotope excursions were reported in the vicinity of the KWH (Joachimski and Buggish, 1993). The section is strongly affected by diagenetic alteration (Préat et al., 1999) so that much care was taken after sampling to extract appropriate material for geochemical investigations. The section La Serre is located in the stratotype area of the south-eastern Montagne Noire. The Uppermost Frasnian in the La Serre trench C section consists of alternating dark, carbon-rich marlstones and argilites (Fig. 2). Only the carbonate banks were sampled due to the strong superficial alteration of the argilite. La Serre is considered as a distal basinal time equivalent of the sections deposited on a submarine rise (e.g., Coumiac) (House et al., 1988). Because in the literature for this section, the earlier standard zones (Ziegler, 1971) were used, whereas for the other sections we applied the revised standard (Ziegler and Sandberg, 1990), we adopted the scheme of Klapper and Becker (1999) in order to allow a correlation with the LKWH equivalent. Because in this comparison the top of the Upper *rhenana* zone is corresponding approximately to the top of the Lower *gigas* zone, the LKWH equivalent was placed hypothetically in the bank no. 9, reaching up to the beginning of bank 10 (bank numbers according to Feist, 1990; Schindler, 1990). The magnetosusceptibility event and cyclostratigraphy (MSEC) study by Crick et al. (2002) on the F/F boundary in different localities allowed reasonable correlations in using the La Serre trench C as reference sequence. No evidence for extraterrestrial impact remainders was found in the La Serre trench C section such as high Ir values, Ni-rich spinels or microtektites (Girard et al., 1997). Anoxic conditions prevailing at the F/F boundary and during the early Famennian were postulated based on the ostracod assemblage (Lethiers et al., 1998). Rapid palaeoenvironmental changes were identified based on the variation in the concentration of different palynomorph groups (Paris et al., 1996), with the most remarkable being an exceptional abundance of a single chitinozoan species at the base of the Famennian. This anomaly was ascribed to a conjunction of several factors like higher productivity coupled with a presumed lowering of the ocean water temperature, restricted terrestrial input as well as the disappearance of predators or competitors.

3. Analytical methods

X-ray diffraction technique was used for the identification of major mineralogical phases. The analyses were carried out with an X-ray diffractometer model KRISTALLOFLEX D500 (Siemens). The composition of individual grains was analysed with electron microprobe (SX50; Cameca) in the Laboratory for Electron Microscopy of the University Karlsruhe.

The major element composition of the bulk rock samples and some of the minor elements (V, Cr, Co, Ni) were determined by wavelength dispersive X-ray fluorescence (WD-XRF) analysis, using an instrument model SRS 303 AS (Siemens) with Rh-tube excitation. Conventional fused glass disks were prepared by mixing 1 part of powdered and dried sample material with 4 parts of SPECTROMELT. After properly mixing, the mixture was fused in a platinum crucible. Element contents were evaluated by a fundamental parameter calibration procedure, whereas trace elements were determined using a combined Compton and intensity matrix correction.

Further trace element concentrations were measured by energy dispersive X-ray fluorescence analysis (ED-XRF), using an instrument model SPECTRACE 5000 (Becker Huges). Samples were ground in an agate mortar, taking care to avoid any contamination. For these determinations, an aliquot of ~5 g of sample material was placed into Polystyrol containers and covered with a 6 μm Mylar window prior to measurement. Samples were measured three times using Al, Pd, and Cu primary filters to optimise the excitation of elements emitting X-rays with different energies. Calibration was performed against the reference material GXR-2 (Govindaraju, 1994). For details on the analytical procedure and detection limits for the bulk rock samples, the reader is referred to Kramar (1997).

Carbon Sulphur Analyser (CSA) was used to measure the total carbon and total sulphur content (CSA 5003, Leybold). The inorganic carbon content of the samples was determined with a Carbon Water Analyser (CWA), model CWA 5003 (Leybold).

The reactive parts of Fe and of trace elements were extracted following a slightly modified method after Berner (1970, 1984) and Anderson et al. (1987), by boiling 100 mg of finely ground sample material with 5 ml of 12N HCl. After adding 5 ml of bidistilled water the samples were centrifuged. For the analysis 2 ml of eluate was used diluting it to 100 ml in a volumetric flask. Reactive Fe and trace element concentrations were determined with high-resolution ICP-MS (AXIOM, VG Elemental). The degree of pyritization (DOP) was calculated as $DOP = Fe_{pyrite}/(Fe_{pyrite} + Fe_{reactive})$. Pyrite bound Fe ($Fe_{pyrite}$) was approximated by multiplying the S content with 0.871.

4. Results and interpretation

4.1. Detrital input

To assess the detrital input, the Al-normalized Ti and Si contents were used. In hemipelagic sediments Al is generally regarded as the main conservative element being used as a proxy for clay minerals. High Ti/Al ratio reflects enhanced delivery of riverine detritus (Murphy et al., 2000b; Meyers et al., 2001), because Ti is generally associated with the heavy mineral grains. Thus, increased Ti concentrations relative to Al would reflect relative sea-level fall and coast line progradation and vice versa (Sageman et al., 2003), though it can also represent a higher eolian input (Bertrand et al., 1996) or of volcanic ash (Sageman et al., 2003). The Si to Al ratio reflects the amount of Si in excess to Si bound in aluminosilicates. As such the Si/Al ratio may indicate an enhanced quartz delivery due to eolian input (Pye and Krinsley, 1986; Werne et al., 2002) or mirror increased input of biogenic silicon and thus act as a productivity signal (Davis et al., 1999). In the Kowala section, there is a decrease in the detrital input in the *linguiformis* conodont zone as reflected for example by the Al_2O_3 (Fig. 3) content, but also by the absence of clay minerals. The high Si/Al ratio (Fig. 5) at the same level indicate an increase in biogenic quartz as already observed at Kowala and in other sections of the Morovian shelf by other authors (Racki et al., 2002; Vishnevskaya et al., 2002). These high excess Si contents in the *linguiformis* zone are assigned to siliceous sponge associations and radiolarians (Vishnevskaya et al., 2002). Detrital and biogenic quartz can be easily discriminated, e.g., in a Zr vs. SiO_2 diagram. The high Ti/Al ratio (Fig. 4) is considered to indicate an increased volcanic input, as it was already suggested for the Kowala section based on the Zr/Al_2O_3 ratio and on the amount of the insoluble residue (Racki et al., 2002).

By using the same mineralogical and geochemical approach a decrease of the detrital input was observed in the Büdesheimer Bach core at the level of the KWH. The more proximal facies of this section shows more pronounced variations in the content of muscovite or chlorite. However, because of the scarcity of conodonts in the limestone beds (Piecha, 1994), the biostratigraphic dating of the upper Kellwasser horizon is uncertain. The general lowering of the detrital input not observed in the upper Kellwasser horizon (Fig. 3) would suggest also to consider cautiously the biostratigraphic dating at this level. An increase of the biogenic quartz is preferred to explain the increase of Si/Al ratio in the LKWH (Fig. 5) because radiolarians were found at a depth corresponding to these horizons (Piecha, 1994). The decrease of the Ti/Al ratio (Fig. 4) is interpreted to reflect a relative sea-level rise during this time interval.

The same interpretation holds also for the Steinbruch Schmidt section. The sporadic increase of the Si/Al ratio can be attributed to the presence of radiolarians in the

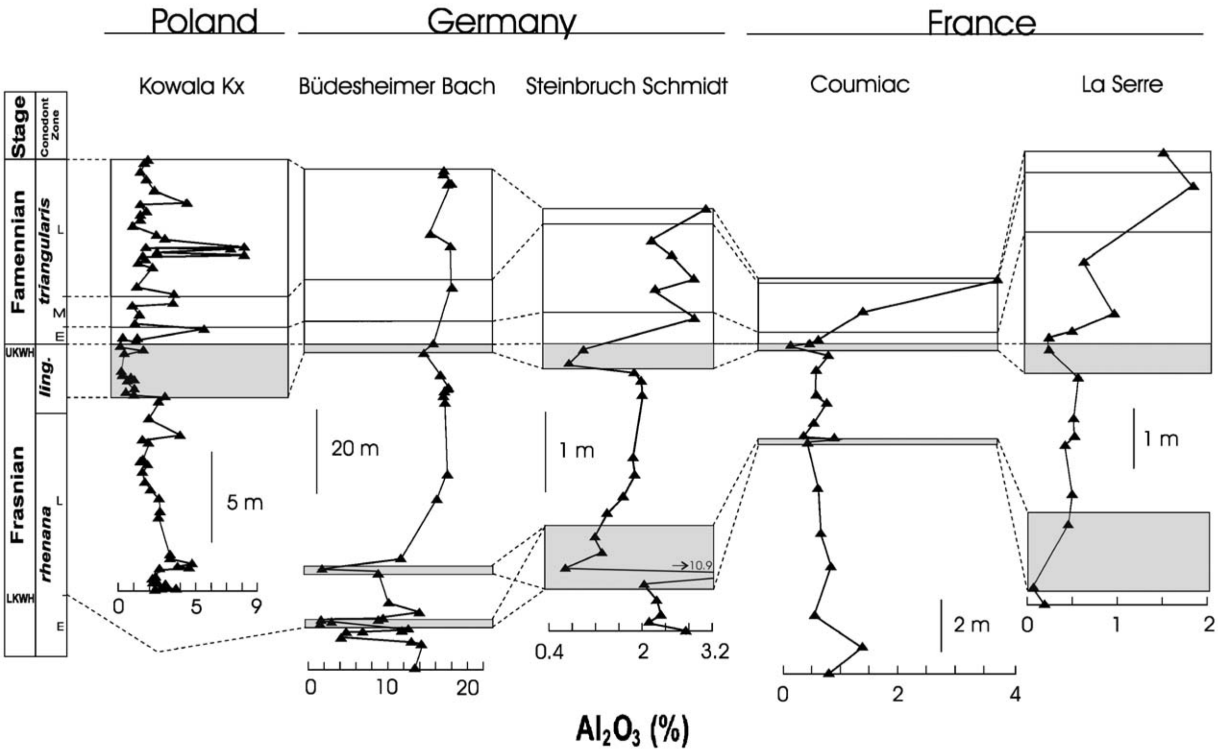

Fig. 3. Distribution of the Al_2O_3 (%) contents along the sections.

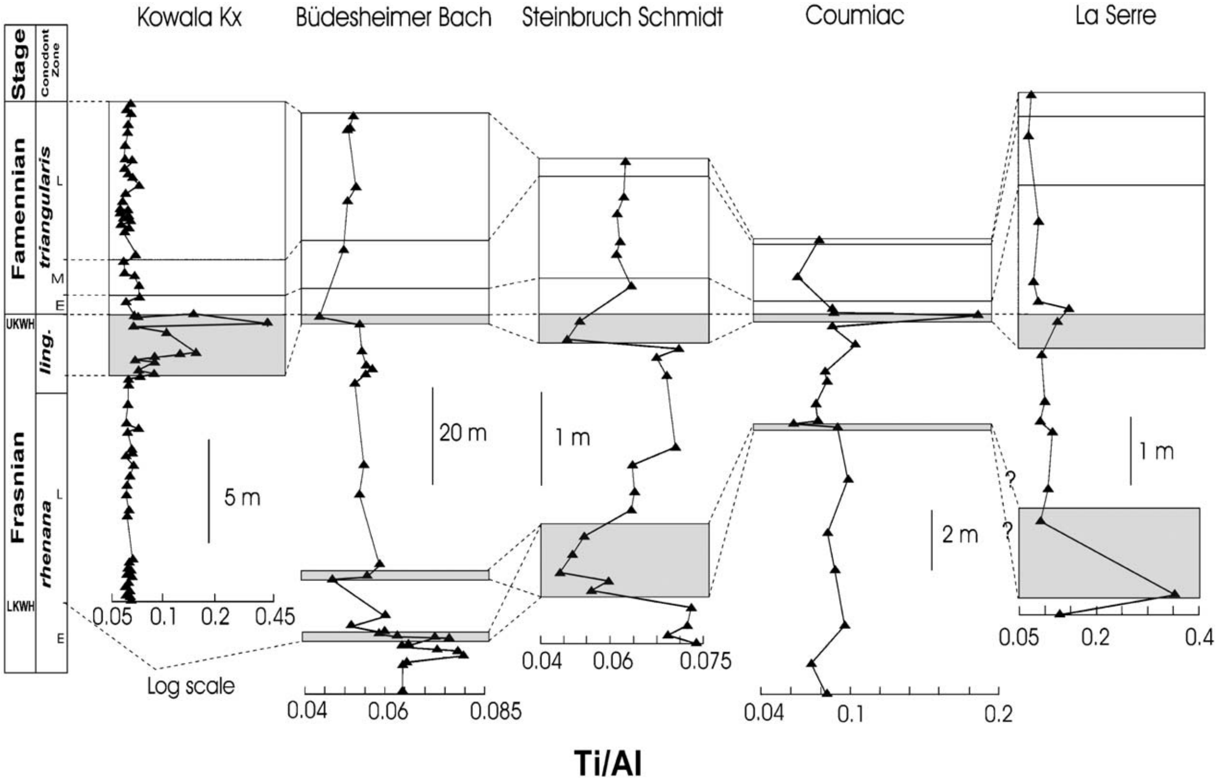

Fig. 4. Distribution of the Ti/Al ratios along the sections.

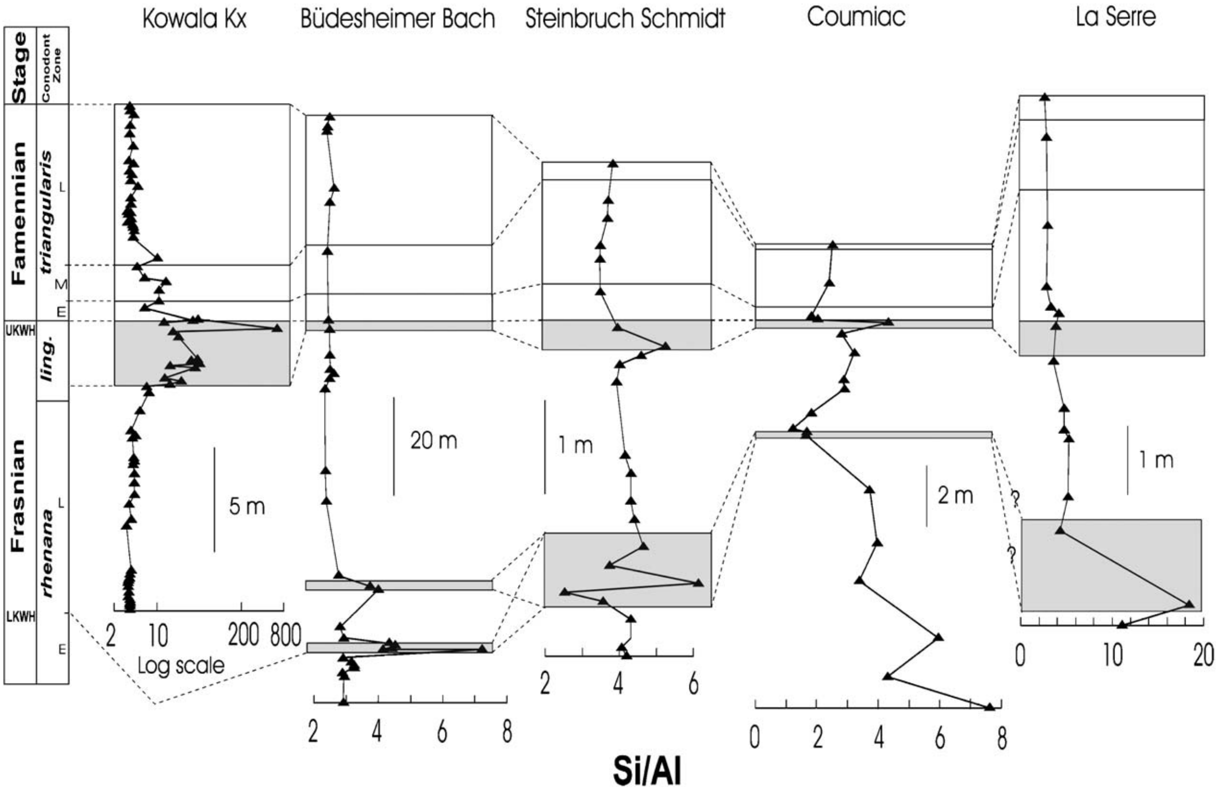

Fig. 5. Distribution of the Si/Al ratios along the sections.

Kellwasser horizons as already observed by Devleeschouwer et al. (2002).

In the two sections of the Montagne Noire, Coumiac and La Serre, the low amount of quartz (not presented) and Al_2O_3 in the KWH also indicate a decrease in the detrital input during this time (Fig. 3). Similar to the Kowala section the increase of the Ti/Al ratio in context of sea-level rise is interpreted to reflect a higher input of volcanic material, especially when it is correlated with the Zr/Al_2O_3 ratio (Fig. 14). The significant increase of Si/Al ratio in the LKW equivalent of the La Serre section occurs in the vicinity of the silicificated banks (terminal parts of banks 8 and 9, Fig. 2). Coupled with higher Ti/Al ratio, the high Si/Al ratios could be ascribed to higher volcanic or eolian input, given that the Zr vs. SiO_2 diagram does not indicate a substantial contribution of biogenic quartz. However, an increase of the Si/Al ratio can also reflect a relative sea-level rise and coastline progradation (Sageman et al., 2003).

The decrease in the detrital input in the Kellwasser horizons is a common feature in all of the investigated sections and is interpreted in terms of a relative sea-level rise during this time. Variations in the Ti/Al and Si/Al ratios could be assigned more probably to local or regional conditions.

4.2. Input of organic carbon

An increase of the organic carbon burial at the time of the KWH deposition is easily recognizable in the European sections, particularly those from Germany and France, by the characteristic presence of dark bituminous limestone (Buggisch, 1991). The Büdesheimer Bach core is a typical example for this (Fig. 6). Nevertheless, as our results show, increased C_{org} contents seems not to be always restricted to the KWH, like, e.g., in Steinbruch Schmidt, where higher concentrations were found also between the two KWH, notably in bank 37. In this section the variation of C_{org} contents is not very pronounced, with values ranging between 1% and a maximum 4%. A relative increase of C_{org} may be due to a decrease in detrital input, i.e., lower sedimentation rates eventually will countersteer the "dilution effect" (Sageman et al., 2003; Sageman and Lyons, 2004). Similarly, in the Coumiac section, the increase of organic carbon content to up to 1 wt.% in the *linguiformis* zone (compared to a mean value of 0.5 wt.

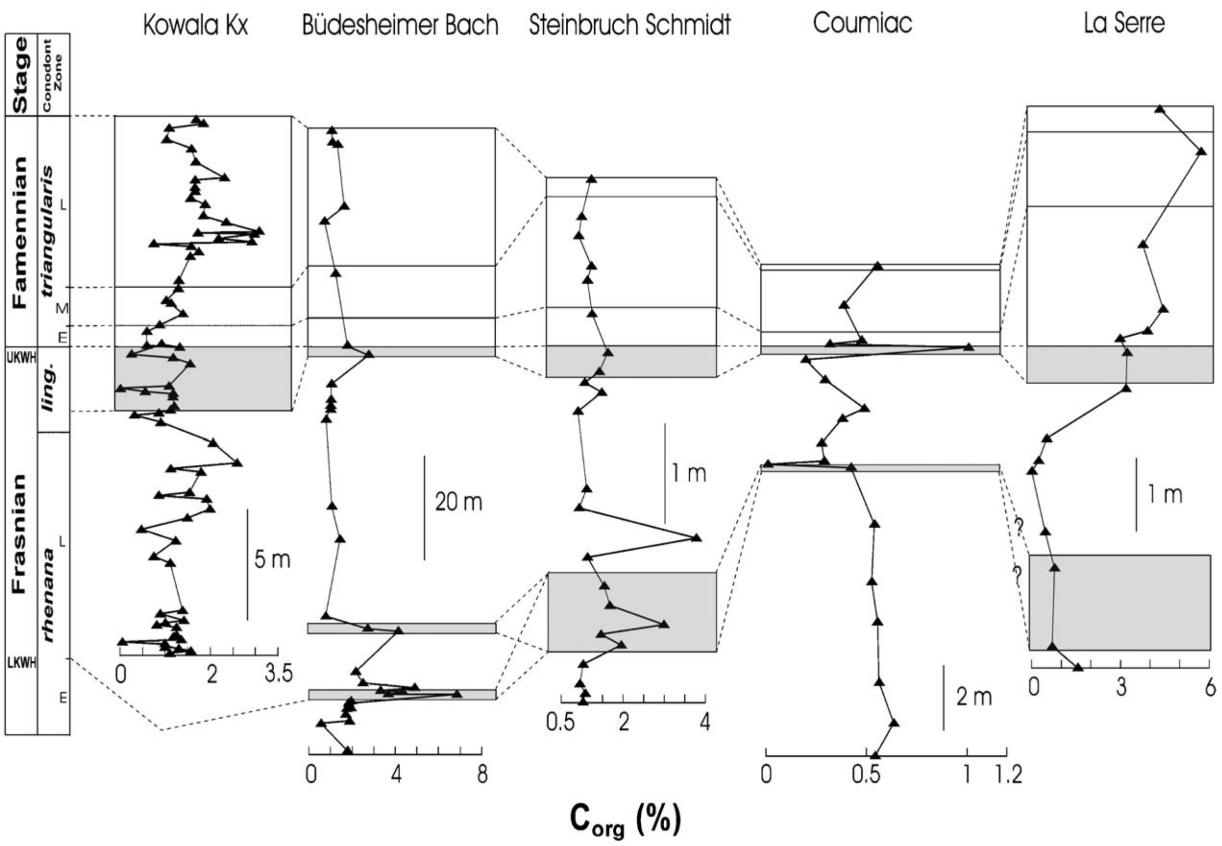

Fig. 6. Distribution of the C_{org} (%) contents along the sections.

%), absent in the LKWH, is coupled with the lowest amount of detrital component. In contrast, in the La Serre section though there is an evident increase of the organic carbon content in the UKWH, the maximum is reached in the *triangularis* zone. Moreover, the frequently mentioned enrichment in organic carbon in the *linguiformis* zone is sometimes even absent. This is especially evident in the Kowala section, in which the *linguiformis* zone has the lowest content of organic carbon.

Resuming, the enrichment of organic carbon in the KW horizons is not a common feature to all of the sections investigated.

4.3. Nutrient input and productivity

The non-detrital part of P in the sediment was proposed as an indicator for biological productivity (Schmitz et al., 1997). The "P_2O_5 in excess" ($P_2O_5$8*) can be calculated by dividing the P_2O_5 content by the Al_2O_3 content of the sample normalized with the average Al_2O_3 content of the continental crust (e.g., $P_2O_5^* = P_2O_5/(Al_2O_3 \times 15\%)$, Schmitz et al., 1997). With some restrictions, Ba and SiO_2 in excess can be also used as productivity proxies (Schmitz et al., 1997). Nevertheless, the remobilisation of Ba and P under anoxic conditions may alter this signal (Ingall and Jahnke, 1997; McManus et al., 1998), while an increase in the Si/Al ratio (see Section 4.1) may reflect enhanced eolian input instead of higher productivity (Pye and Krinsley, 1986; Werne et al., 2002). Most of the sections are enriched in $P_2O_5^*$ (Fig. 7) in both the *linguiformis* zone (UKWH) and at the base of the late *rhenana* zone (LKWH). Investigations with the electron microprobe allowed a closer characterization of the P and Ba-bearing minerals. In samples from the chert layer representing the Frasnian–Famennian boundary in the Kowala section (Fig. 2), in addition to different P-bearing minerals, like tiny grains (1–2 μm) of xenotime, monazite, and fluoroapatite, more frequently, 10-μm-large crystals of barite were identified. In the Steinbruch Schmidt section, in samples from the UKWH (Bank 62 and 64), fluoroapatite and other P-bearing phases, enriched in REE (La, Ce) were detected. A similar association of P with lanthanids was observed in the UKWH of the Büdesheimer Bach core. Phosphorous

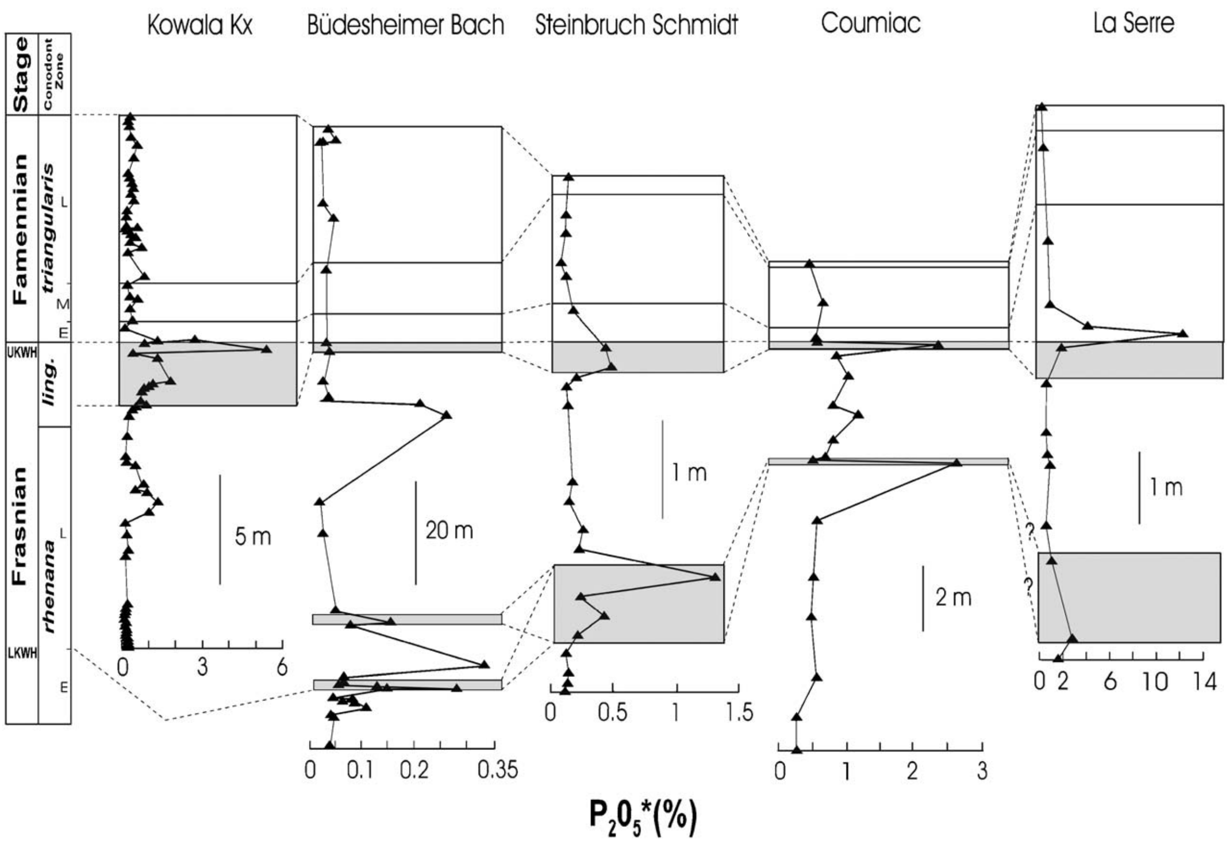

Fig. 7. Distribution of the P_2O_5 content in excess ($P_2O_5^*$) along the sections.

may be associated also with Fe-oxyhydroxides (McManus et al., 1997). The relatively high P content of the conodonts (Girard and Albarede, 1996) may lead to a correlation between P_2O_5* and the abundance of the organisms buried in the sediment. It is noteworthy that in the more typical basinal facies of the Kowala and La Serre sections, the enrichment in P persists until the base of the early *triangularis* zone. The very high $P_2O_5^*$ value in bank 14 (F1 biozone; early Famennian, Fig. 2) correlates not only with a high fluoroapatite content (as evidenced by the microprobe analyses), but also fits well with the high abundance of a chitinozoan species in this bank (Paris et al., 1996). Except for Coumiac, where Ba is below the detection limit in the KWH, the general enrichment of Ba in excess in the KWH (as documented by the presence of barite) could be also due to enhanced productivity (Fig. 8). Nevertheless, under anoxic conditions with intense sulphate reduction (see next section), remobilisation of Ba and P may have occurred, which could have shifted the concentration peaks of these elements relative to the level with the highest productivity. A comparison between nutrient input and organic carbon accumulation (Fig. 6) generally shows a decoupling between productivity and organic matter burial.

Resuming, the enrichment in nutrients or/and the increases of productivity in the KW horizons are common features to all of the sections investigated. These results are in agreement with C-isotope investigations of Joachimski et al. (Joachimski and Buggish, 1993; Joachimski et al., 2001; Joachimski and Buggish, 2002).

4.4. Degree of oxygenation

Different element ratios (e.g., V/Cr, Ni/Co, U/Th, etc.) and the Al-normalized content of redox sensitive or chalcophile elements (e.g., Fe, Mn, U, V, Zn, Pb, Cu, Ni) are used in geochemistry to estimate the degree of bottom water oxygenation during sedimentation (Jones and Manning, 1994; Bratton et al., 1999; Joachimski et al., 2001; Racki et al., 2002; Yudina et al., 2002; Algeo and Maynard, 2004; Cruse and Lyons, 2004). However, because many of these elements (e.g., Pb, Zn, Cu, Co, Ag, Mo) are typically associated with hydrothermal activity (Von Damm, 1995; Eckhardt et al., 1997; Kuhn

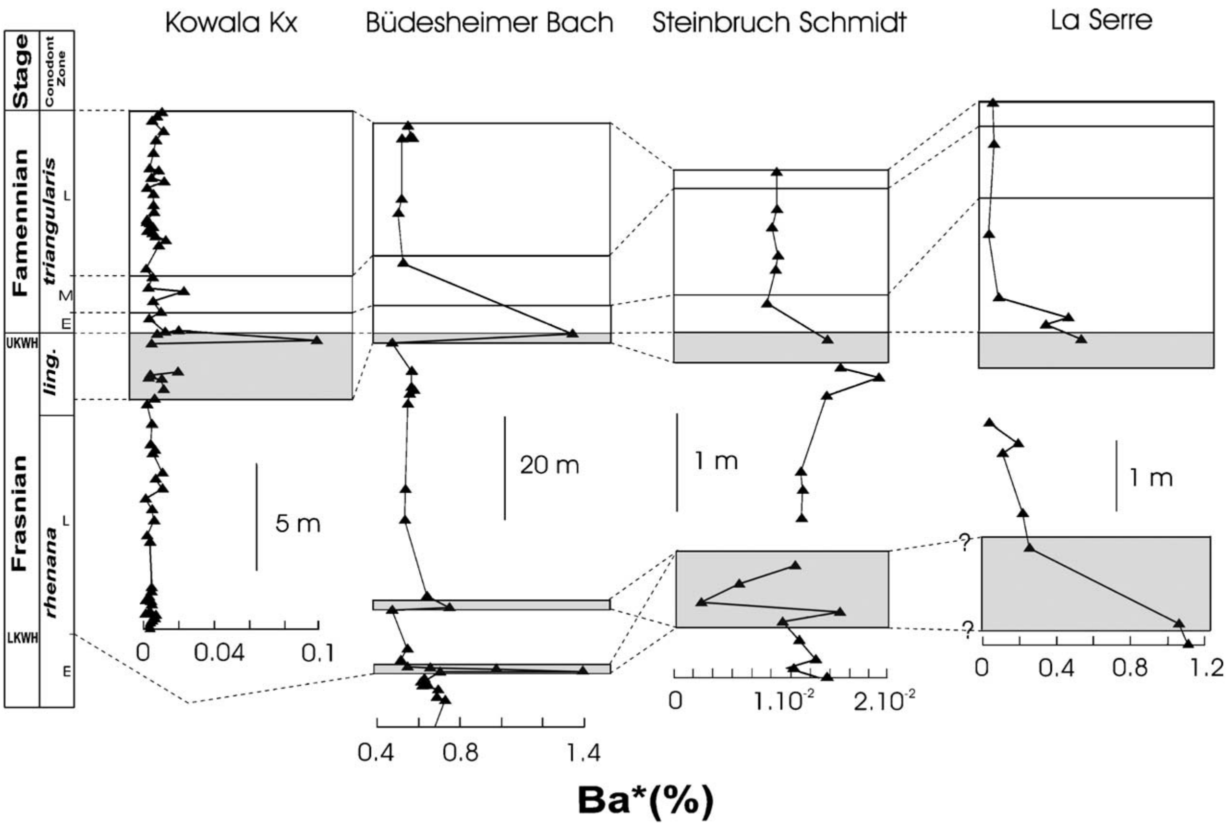

Fig. 8. Distribution of the Ba content in excess (Ba*) along the sections.

et al., 2000; Pierret et al., 2000; Sander and Koschinsky, 2000; Kuhn et al., 2003; Wheat et al., 2003; Hübner et al., 2004) the cause of their enrichment is often ambiguous (Cruse and Lyons, 2004). In this study the use of V/Cr was preferred (Fig. 9), because the concentration of other elements commonly used as a proxy for bottom water oxygenation, like Mo, was often below the detection limit precluding a systematic comparison of the sections. Similarly, the content of typical hydrothermal elements like Pb, Zn, Cu, As or Ag close to or below their detection limits, did not allow a multiparametric analysis of all sections in order to ascertain the relative importance of the redox control versus hydrothermal enrichment. In addition to element contents or ratios, the presence of authigenic minerals formed in a well-constrained redox range is also often used as proxy parameters to assess the degree of bottom water oxygenation. The degree of pyritization of Fe (DOP) is one of the most commonly used geochemical parameters (Berner, 1970, 1984; Leventhal and Taylor, 1990; Middelburg, 1991; Sageman et al., 2003) and could be successfully applied for the Büdesheimar Bach core. Studies in modern anoxic environments, like in the Cariaco basin or in the Black Sea, showed that the presence and size of framboidal pyrite is an even more reliable anoxia proxy (Wilkin et al., 1996, 1997; Wilkin and Barnes, 1997; Wilkin and Arthur, 2000). Framboidal grains less than 5 ìm in size typically indicate anoxic to anoxic–sulfidic conditions. The distribution of pyrite framboids in the KWH was investigated by means of SEM and microprobe, but due to postdiagenetic recrystallization and/or scarcity of pyrite grains, the method found only a restricted applicability in the present study.

According to Hoffman et al. (1998) a V to Cr ratio of 5 corresponds to the limit between dysoxic and anoxic conditions (shown as a dashed line in Fig. 9). In the basinal sections of Kowala and La Serre (Fig. 9), the V/Cr values reach the anoxic domain in the lower and middle *triangularis* zone as well as in the middle to upper *Rhenana* zone. In the KWH, the low V/Cr ratios generally indicate oxic/dysoxic conditions. The most significant increase in the V/Cr ratio occurs in the KWH of the stratotype section of Coumiac, though the values still correspond to dysoxic conditions. In Steinbruch Schmidt, there are no noteworthy variations in the ratio of these elements, except for Bank 23 (LKWH) in

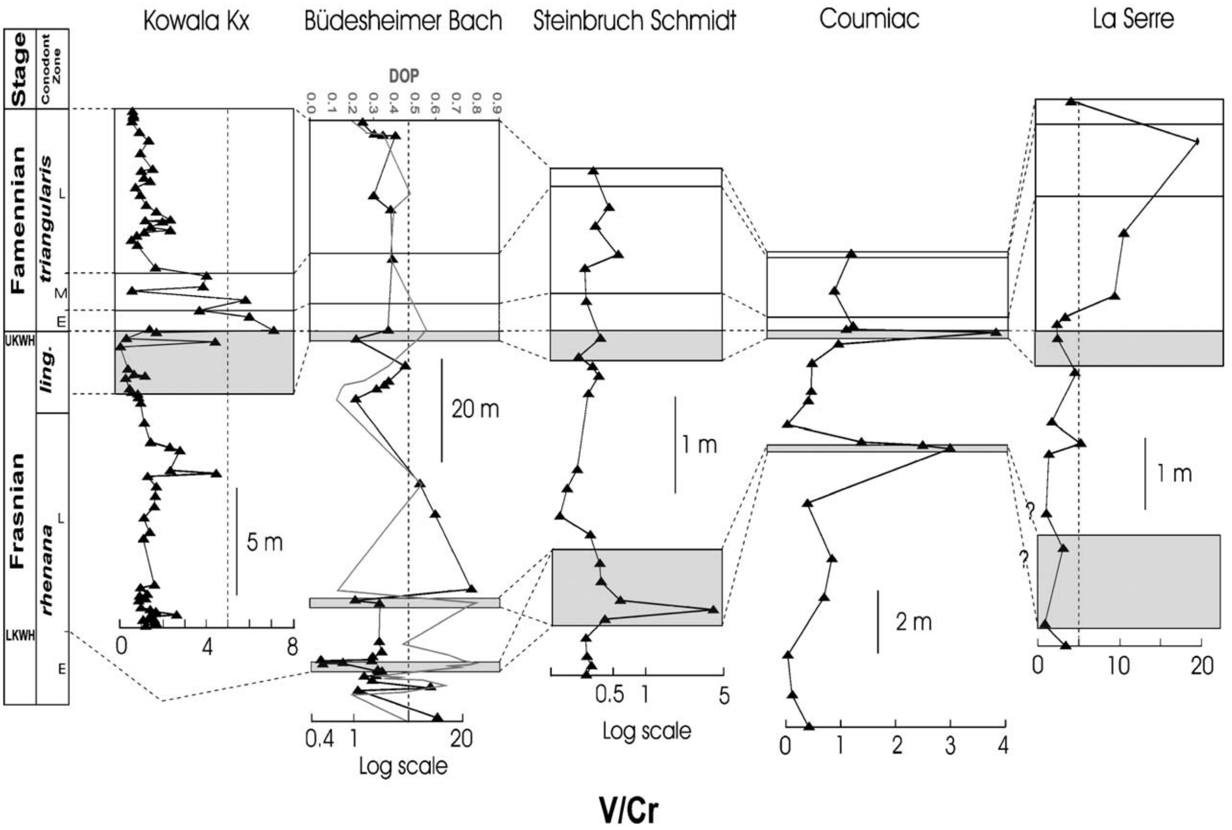

Fig. 9. Distribution of the V/Cr ratios along the sections and of the degree of pyritization (DOP) along the Büdesheimer Bach core. The dashed lines mark the limit between dysoxic and anoxic conditions (Hoffman et al., 1998).

which, however, the increase of V/Cr could be explained by a higher content of clay minerals that adsorbed V. In this section, in addition to the V/Cr ratios, the presence of iron oxides (sometimes in association with pyrite grains) also suggests dysoxic rather than anoxic conditions. The V/Cr ratios in the Büdesheimer Bach core (Fig. 9) apparently contradict the conclusions suggested by the DOP values, because while the V/Cr ratios are low in both KWH, the DOP reach values of up to 0.7 in the LKWH and about 0.6 in the UKWH, suggesting anoxic and dysoxic conditions, respectively. Moreover, most of the pyrite framboids identified with the microprobe are less than 5 μm in size, not only in both of the KWH of the Büdesheimer Bach section, but also in the UKWH of the sections Coumiac (bank 31 g) and La Serre (bank 14 d). A tentative explanation for this apparent inconsistency is given in the next paragraph.

In conclusion, based on the geochemical proxies used, it seems that the deposition of the KW horizons under anoxic conditions is not a common feature to all of the sections investigated.

4.5. Hydrothermal input

The detection of hydrothermal input into a sedimentary record by means of geochemical methods is generally based on the above-average concentration of some diagnostic trace elements such as Cu, Zn, Co, Mo, As, Pb, Ag, Ba, but also on particularities in the distribution of some major elements like Fe, Mn, Si, Ca or Mg (e.g., Von Damm, 1995; Eckhardt et al., 1997; Kuhn et al., 2000, 2003; Hübner et al., 2004). Recent observations in the Juan de Fuca and the North Fidjian Basin (Sander and Koschinsky, 2000; Wheat et al., 2003) showed that the concentration and speciation of Cr in seawater is also widely controlled by hydrothermal activity, and Pierret et al. (2000) demonstrated the utility of the Cr vs. Zr ratio to detect hydrothermal influence. The occurrence of a possible hydrothermal input at the Frasnian–Famennian boundary was already studied by several authors, using the Al/(Al+Fe+Mn) ratio. A value <0.35 is generally considered to be characteristic for metalliferous sediments (Racki et al., 2002; Yudina et al., 2002).

At the level of the KWH, there is a significant decrease in the Al/(Al+Fe+Mn) ratio to values that are in most cases below 0.35 in all of the investigated sections (Fig. 10). X-ray diffraction results indicate that the occasionally low Al/(Al+Fe+Mn) ratios outside the KWH are due to the presence of pyrite. In both of the basinal sections Kowala and La Serre, the low ratios still persist at the base of the early *triangularis* zone. The constant increase in Fe and Mn relative to Al in the stratotype section (Coumiac) up to the base of the upper *rhenana* zone is particularly noteworthy. The less pronounced decrease in the UKWH of the Büdesheimer Bach core is probably due to a stronger continental influence at the transition from Frasnian to the Famennian (Fig. 3). However, the pyrite content does not correlate with the Al/(Al+Fe+Mn) ratio in this section and consequently cannot explain its low values. A statistical evaluation of the data by factor analysis, but even simple cross-plots reveal a significant negative correlation between the Al/(Al+Fe+Mn) ratio and the Al-normalized contents in typically hydrothermal elements like Pb, Zn, Cu, Ag, Ni and As in some of the sections. Investigations with the microprobe allowed a closer insight into the nature of these metal enrichments in some of the KWH samples. In the UKWH of the Steinbruch Schmidt section (Banks 62 to 64) Cu and Pb sulphides (chalcocite, galena) as well as tiny grains (1–2 μm) of As–Sb sulfosalts (possibly getchellite?) could be identified. Additionally, Fe-oxides in association with silica were frequently encountered. In the UKWH of Coumiac (Bank 31 g), the enrichment of Fe relative to Al is due to the presence of pyrite framboids less than 5 μm in size. In the cherty bank of the Kowala section, in addition to sulfides (e.g., sphalerite and Fe-bearing NiAs-sulphide, possibly gersdorffite), V-rich Fe-oxide grains as well as dolomite crystals with low contents of Fe and Mn were found. The mineral speciation of Mn, i.e., the origin of high Mn/Al ratios (Fig. 12) is more difficult to constrain by microprobe analyses. Nevertheless, the strong correlation between the Mn/Al and Fe/Al ratios and the association of slightly elevated Mn concentrations with Fe-oxy/hydroxides (e.g., in Bank 62, Steinbruch Schmidt) indicate that Fe-oxy/hydroxides, Fe-sulphides (mainly pyrite) and possibly dolomite are the main Mn carrier minerals in the KWH.

The Cr/Al ratio in the KWH is high in all of the sections (Fig. 11). In the context of the former annotated inconsistency between the high DOP values and low V/

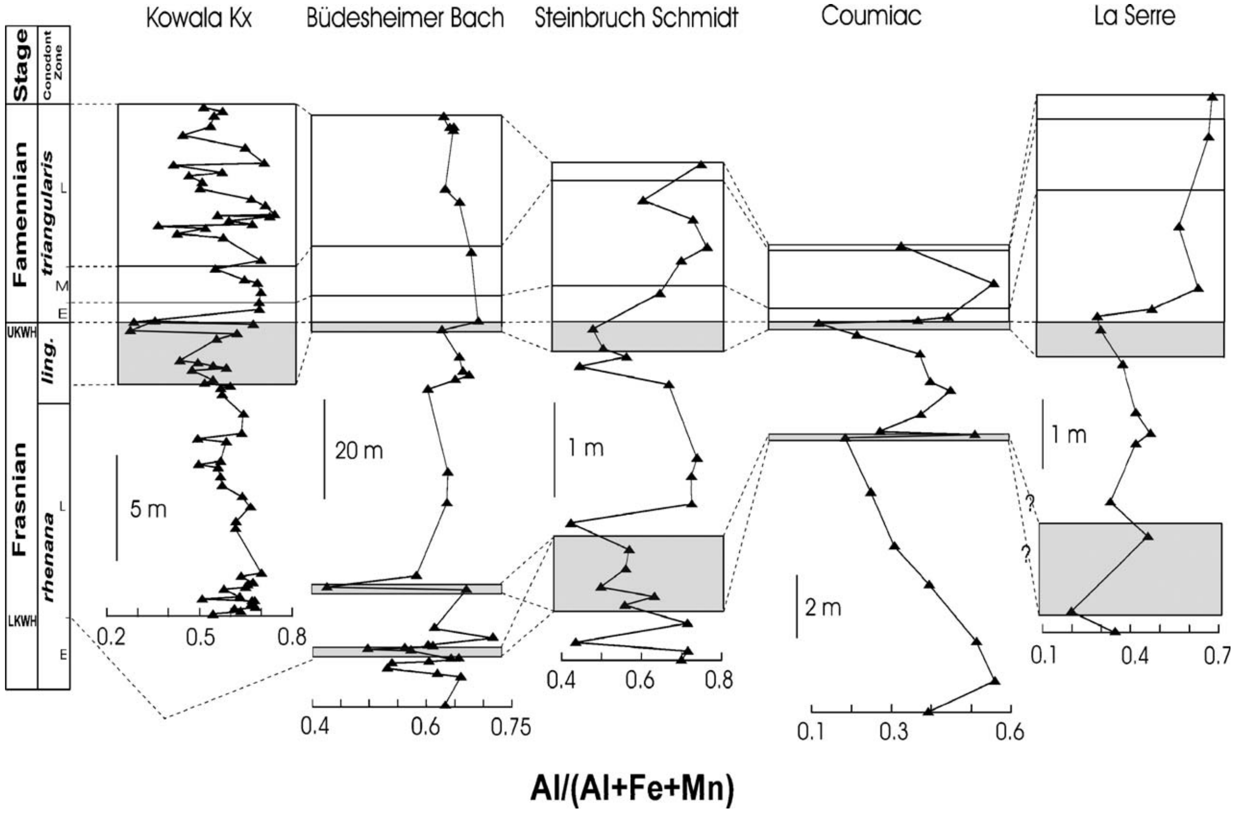

Fig. 10. Distribution of the Al/(Al+Fe+Mn) ratios along the sections.

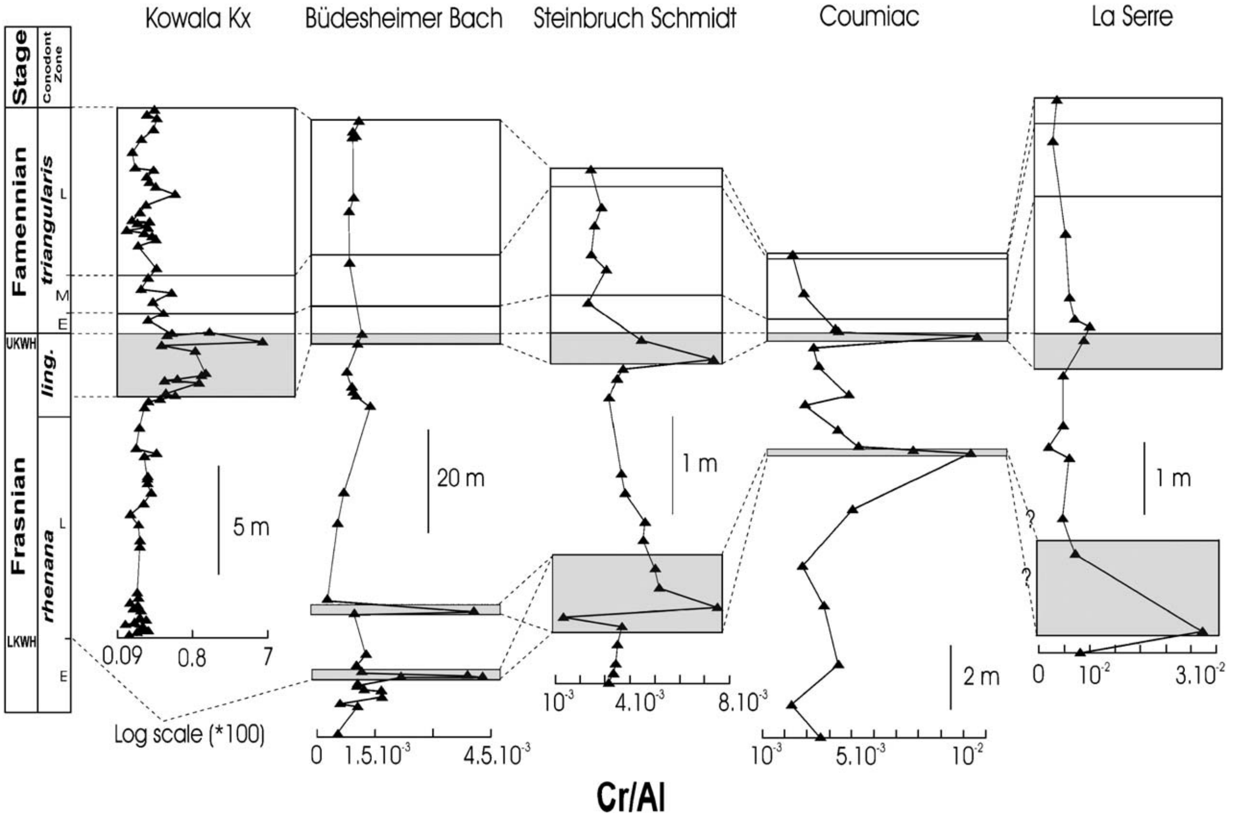

Fig. 11. Distribution of the Cr/Al ratios along the sections.

Cr ratios (suggesting contradictory oxygenation conditions; see Section 4.4) it is especially relevant to notice the parallel increase of the Mn/Al and Cr/Al ratios in the KWH (Figs. 11 and 12). Because of the mobility of Mn under reducing conditions, the Mn/Al ratio is also used as a palaeo-oxygenation proxy (Bratton et al., 1999). However, in cases in which the relative amounts of both Cr and Mn are controlled only by the redox state of the depositional environment, their Al-normalized concentrations should be inversely correlated (Calvert and Petersen, 1993). Consequently, the parallel increase of the Cr/Al and Mn/Al ratios in the KWH could indicate an external (i.e., hydrothermal) input of Cr and Mn to the sediment. The apparently contradictory results indicated by the DOP and V/Cr ratios emphasize the necessity of a careful analysis of the geochemical data in order to avoid possible misinterpretations. In addition to a common hydrothermal source the correlation of the Al-normalized Cr, Fe and Mn contents may be due to the adsorption of Cr on Fe-and/or Mn-oxyhydroxides (Achterberg et al., 1997).

The results presented before (Sections 4.4 and 4.5) indicate that the input into the sediment of Fe of hydrothermal origin may have led–in function of the prevailing redox state–to enhanced formation of either authigenic sulphides (primarily framboidal pyrite) or of Fe-oxides/hydroxides. The temporal proximity of enhanced hydrothermal influence (Coumiac: 31 e1; La Serre: 13 a) and the onset of anoxic conditions (Coumiac: 31 g; La Serre 14 d) in the sections Coumiac and La Serre is interesting and relevant in terms of understanding the mechanisms which eventually lead to the development of anoxia. So, the steady decrease of the Al/(Al+Fe+Mn) ratios up to a minimum in the LKWH at Coumiac, put constraints on the chronology of the events, suggesting a continuously increasing hydrothermal input as the primary cause for the development of anoxia. Moreover, the *triangularis* zone considered to be deposited under anoxic conditions at La Serre (Lethiers et al., 1998; see also Section 4.5) does not present any significant enrichment in Fe or Cr relative to Al (see also the early and middle *triangularis* zone of Kowala, Section 4.5), so that the formation of pyrite was possibly Fe-limited at La Serre during this time. These results indicate that the observed (hydrothermal) signals during the deposition of the KWH cannot be explained by anoxia alone, or in other words, complexation by organic matter (Fig. 6) or the formation

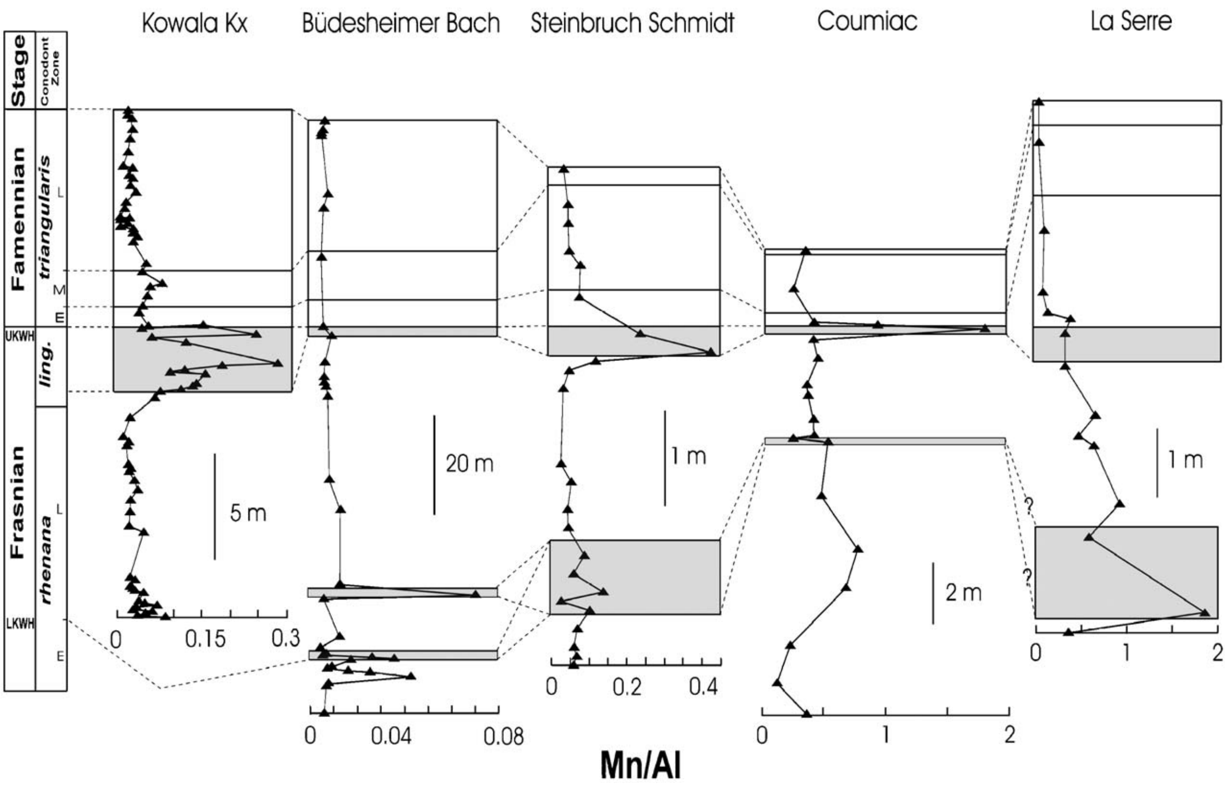

Fig. 12. Distribution of the Mn/Al ratios along the sections.

of authigenic sulphides (Fig. 13) cannot be the primary cause for the observed metal enrichments.

Concluding this section, it could be shown that during the deposition of the Kellwasser horizons there was an increased hydrothermal influence in all of the investigated sections.

4.6. Volcanic input

The Zr/Al_2O_3 ratio is considered to reflect the input of fine grained volcaniclastic particles (Suzuki et al., 1998) and as such was already used as a proxy to assess the amount of volcanic contribution in different Frasnian–Famennian boundary studies (e.g., Racki et al., 2002; Yudina et al., 2002). As mentioned above, the Ti/Al ratio possibly can be interpreted in a similar way. Both proxies show a parallel tendency in all of the sections studied. While in the basinal sections of Kowala and La Serre, the ratios indicate an enhanced volcanic signal, in the UKWH of the Büdesheimer Bach core, this seems to be overlapped by the terrestrial detrital input due to a stronger continental influence (Fig. 14). Studying the volcanic and hydrothermal history of modern ridge segments, Kuhn et al. (2000) observed that the volcanic detritus was strongly concentrated along the central rift valley. Consequently, variations in bottom current may be the reason for the differing distribution pattern observed in the Steinbruch Schmidt section, which has sediments deposited on a submarine rise (Buggisch, 1991). However, other local conditions specific to the German sections could have been involved. Similar to the nutrient (Fig. 7) and the hydrothermal inputs (Fig. 10), the share of volcaniclastic components is also higher at the base of the early *triangularis* zone in the Kowala and La Serre sections.

4.7. Data interpretation by factor analysis

The comparison of the results of different palaeoenvironmental proxies or indicators for each section allows the discrimination between global/regional and local environmental features. Indeed, some of the element ratios used, like the indicators for detrital input (e.g., Ti/Al), reflect more typically local or regional conditions. On the other hand, the general decrease in the Al and/or quartz content in the Kellwasser Horizon could be assigned to a general sea-level rise, as already observed in the South Laurussia and the North Gondwana (e.g., Schindler,

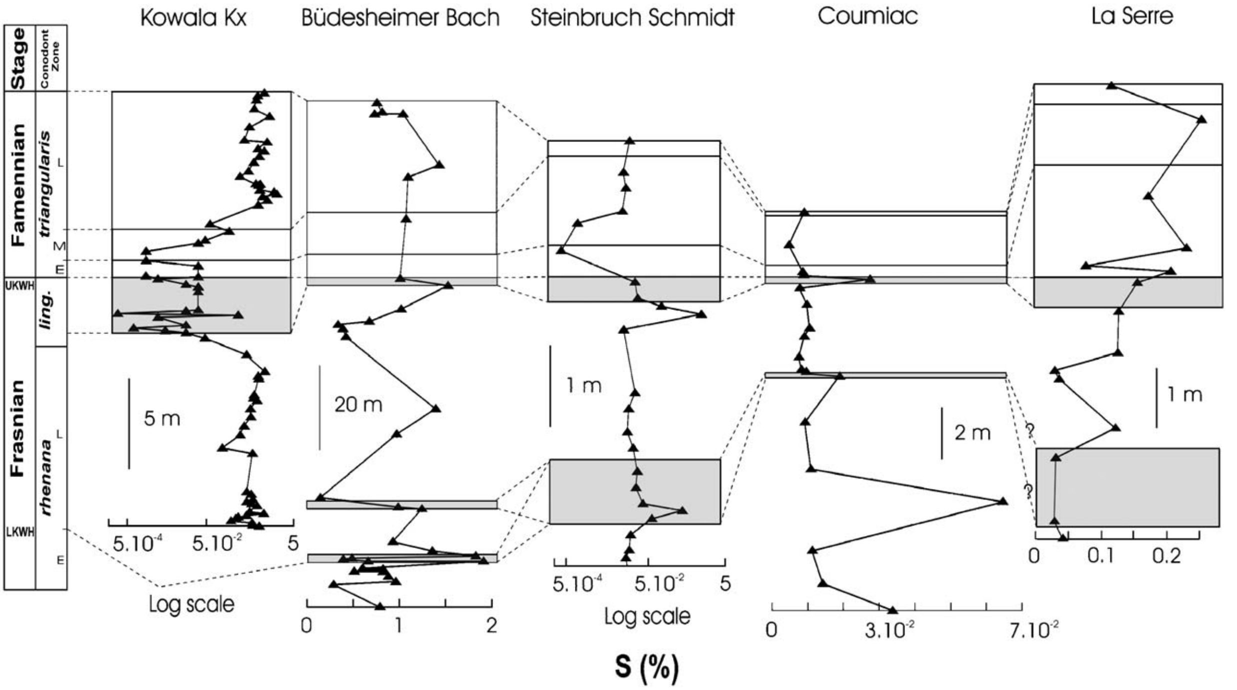

Fig. 13. Distribution of the S contents (wt.%) along the sections.

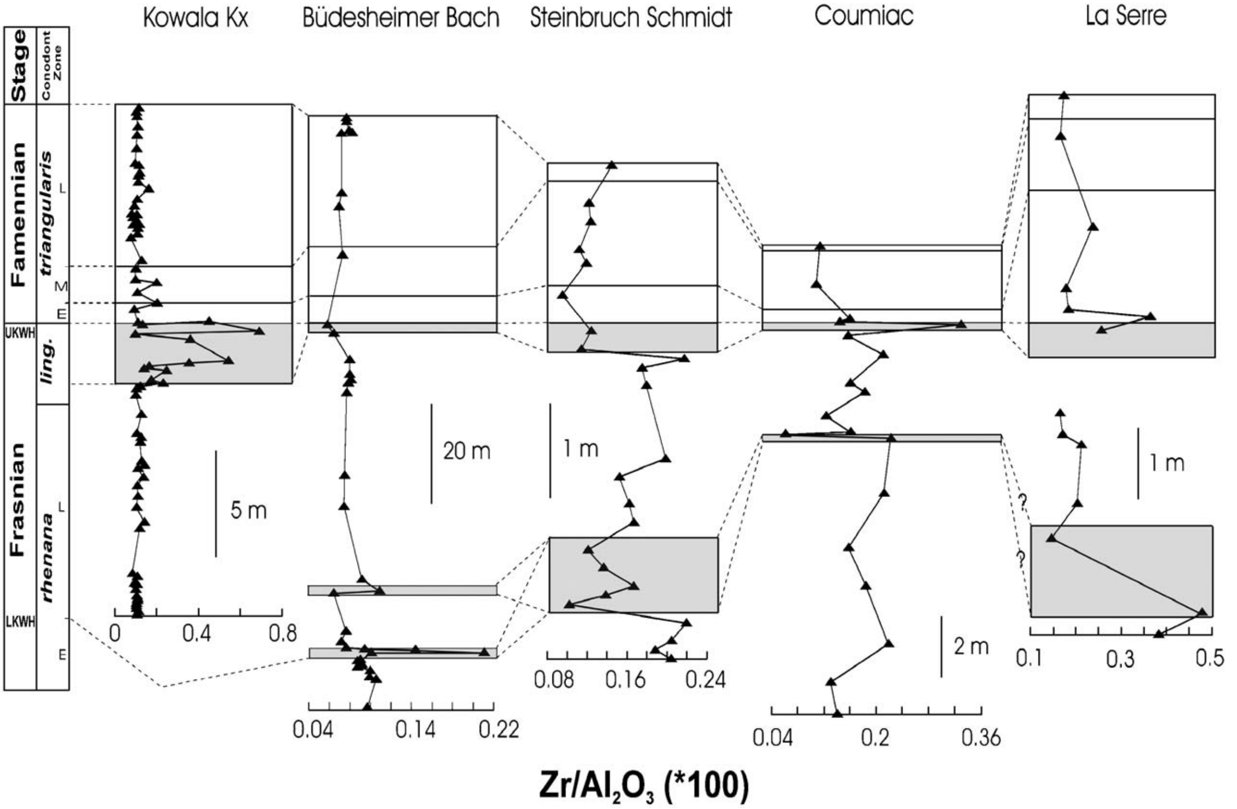

Fig. 14. Distribution of the Zr/Al_2O_3 (*100) ratios along the sections.

1990; Buggisch, 1991). This signal, noticed in all of the sections, could have strongly influenced the other element ratios used, in terms of balance between volcaniclastic background and detrital input. A multivariate statistic study by means of factor analysis, on a cumulative data set from all sections, might yield some additional insights into the complex and intricate relationships between the different proxies. The statistical data analysis was performed using the software package Statistica (StatSoft Inc., USA). To allow a cumulative analysis, before processing, data were normalized for each section separately. The matrix of factor loadings was rotated by the normalized Varimax algorithm. Ba∗ was not included because it could be not evaluated in all sections (i.e., Coumiac). As a hydrothermal indicator, instead of the Cr/Al ratio, the more common Cr/Zr (Pierret et al., 2000) and Fe/Ti ratios (Boström, 1983) were used.

A model with four factors, which explains 73% of the initial variance of the data set, was adopted to assess the relationship between the different parameters (Fig. 15). Factor 1 consists primarily of indicators reflecting potentially volcaniclastic and/or eolian input, as well as sea-level changes (Ti/Al, Zr/Al_2O_3 and Si/Al), but also includes the productivity proxies P_2O_5∗ and Si/Al. The Mn/Al and Cr/Zr ratios, initially used as clues for hydrothermal input and redox conditions, have relatively high loadings on both Factor 1 and 2, suggesting a more complex behaviour. Factor 2 includes parameters commonly used as hydrothermal proxies, with “high” negative loading for the Al/(Al+Fe+Mn) ratio and high positive loading for the Fe/Ti ratio. The opposite algebraic signs are due to the inverse correlation between them. The moderately high negative value for Al_2O_3 indicates that periods of intensive hydrothermal activity generally are coupled with low detrital input. Based on the loadings of C_{org} and S, Factor 3 can be interpreted to reflect redox conditions, with higher deposition of C_{org} and authigen sulfides during anoxic periods, and vice versa during times of normal water oxygenation. The only slightly higher loading of the Mn/Al ratio indicates that in the context of the investigated sections this parameter cannot be used as a reliable proxy for anoxia (see Sections 4.3 and 4.5). Factor 4 includes the V/Cr ratio, which commonly is used as an indicator for anoxic conditions. However, in this case, it is not associated with the anoxia factor, but instead appears to be closely correlated with the detrital input, as expressed by the Al_2O_3 content of the sediment.

The results of the factor analysis are generally in agreement with the conventional interpretation and use of the proxy parameters, but in addition reveal some useful details on the complex interconnections among the different environmental indicators. The results suggest that times of low detrital input and sea-level rise were generally coincident with stronger hydrothermal influence, and sometimes also with a higher eolian and/or volcaniclastic input and productivity. Because the V/Cr ratio is not related to Factor 3 (“anoxia”), but rather to the Al_2O_3 content (detrital input), this indicates that it cannot be used without restrictions as an indicator for redox conditions. Similarly, no variations in Mn/Al ratio can be assigned unambiguously to changes in degree of water oxygenation. As pointed out before (see the section on the detrital input) in the German sections the increase in P_2O_5∗, Mn/Al and Si/Al is not correlated with the Ti/Al and Zr/Al_2O_3 values, which makes necessary the presentation and discussion of the results on individual sections.

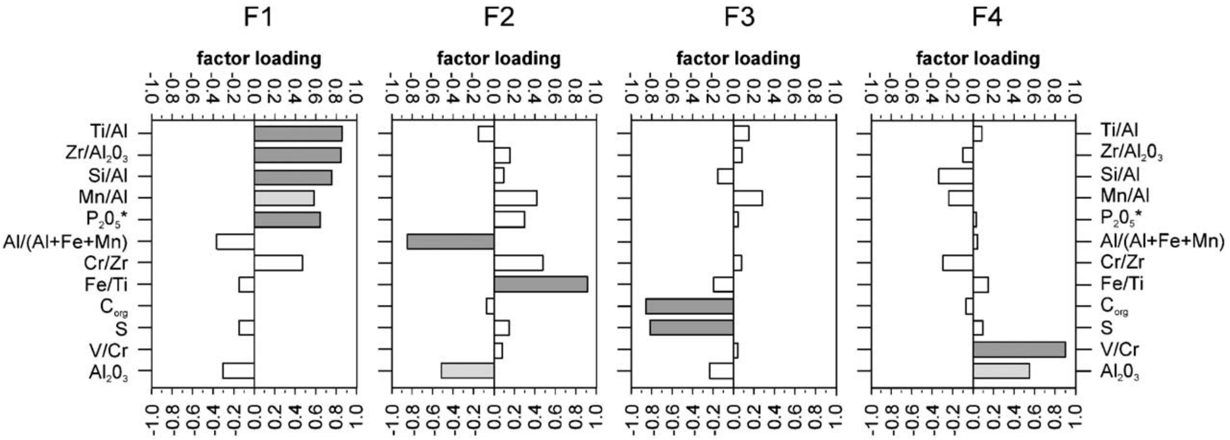

Fig. 15. Factor loadings of the different standardized proxies/indicators used in the palaeoenvironmental study.

Table 1
The results of the proxies/indicators in the Kellwasser horizons for all sections

Factors	Sections	Kowala: Kx section	Büdesheimer Bach		Steinbruch Schmidt		Coumiac: stratotype		La Serre: trench C	
		UKHH equivalent (eq)	UKWH	LKWH	UKWH	LKWH	UKWH	LKWH	UKWH	LKWH eq
Detrital input	Al_2O_3 (%)	–	–	–	–	–	–	–	–*	–
	Ti/Al	+	–	–	–	–	+	no change	+*	+
	Si/Al	+	no change	+	+	Variable (var)	+	–	(+)	+
Organic matter		–	+	+	+ n.r	+	+	no change	(+) n.r	no change
Nutrients input or Paleo-productivity	P_2O_5*	+	no change n.r	+	+	+	+	+	+*	+
	Ba*	+	+	+	+ n.r	(–) (var)	bdl	bdl	+*	+*
Hydrothermal signal	Al/(Al+Fe+Mn)	– 0.35	(–)	–	–	–	– 0.35	– 0.35	– 0.35*	– 0.35
	Cr/Zr	+	(+)	+	+	+	+	+	+*	+
Volcanic input (Zr/Al_2O_3)		+	–	+	–	–	+	no change	+*	+
Oxygen level (DOP; SEM; microprobe)		no change	–	–	no change	no change	–	–	–	?
Remark		Changes in palaeoenvironmental factors common to all of the KWH include: (i) the decrese of the detrital input coupled with sea-level rise; (ii) increase of nutrient input and/or of productivity (iii) a stronger hydrothermal signal.								

bdl: below detection limit; n.r.: not restricted to the Kellwasser horizons; *: including La Serre 14 F1 early triangularis; (): no significant changes.

The results of the interpretation of the environmental indicators are summarized in Table 1. Obviously, trends in C_{org} deposition are correlated with oxygenation level, as indicated by DOP values and observations with SEM. But it is interesting to note that in the section of Steinbruch Schmidt, despite the relative increase in C_{org} content during the Kellwasser event, there is no change in parameters, which are indicative for the degree of oxygenation of the seawater. This could be due to the prevalence of dysoxic rather than anoxic conditions, which are difficult to distinguish unambiguously with the geochemical and mineralogical methods used in this study. The term "no change" used in the table refers to layers, which do not contain the last 5 cm of the UKWH, considered by Casier and Lethiers (1998) as anoxic. However, it is important to mention that according to our results the entire upper Kellwasser horizon was not deposited under anoxic conditions.

5. Discussion

The adopted geochemical multiproxy approach permits to postulate a relative sea-level rise coupled with higher nutrient input during the deposition of the Kellwasser horizons. The intensification of magmatic activity, as indicated by increased hydrothermal and volcanic influence, possibly represents the ultimate cause for the development of a generally more oxygen-deficient depositional environment during this time.

There are growing evidences that the Palaeotethys was a semi-closed basin during the late Devonian (Fig. 1), bordered by the connection between Laurussia and Gondwana to the east (Young et al., 2000), by crustal fragments separating the Palaeotethys from the Panthalassa (or Palaeo-Pacific Ocean) to the west and by the Siberian and Kazakhstanian blocks to the north. In the context of the frequent sea-level oscillations, one must bear in mind this particular palaeogeographic configuration, especially the shallow water depth at the passage between Laurussia and Gondwana to the east (Becker and House, 1994). In analogy to the opening of the Drake passage about 37 my ago, which is considered as the triggering factor for the profound changes in the climate-productivity pattern (Diester-Haass and Zahn, 1996), oscillation in water depth at this shallow passage between the two continental landmasses could have played a key role in the global palaeoclimatic evolution of the late Palaeozoic.

Changes in sea-level as postulated on basis of the detrital input can be hardly explained by changes in volume of the polar ice caps, because there are no evidences for glaciation until the middle of Famennian

(Johnson et al., 1985; Becker and House, 1994). Nevertheless, the absence of evidence of glaciation during a considered geological epoch does not necessarily refute the occurrence of such glaciation, because glacial deposits are notoriously subject to reworking.

Plate tectonic processes, like mid-plate uplift and submarine volcanism, were associated in the Devonian with eustatic sea-level changes (Johnson et al., 1985). In a model of Cathles and Hallam (1991) short-term global sea-level fluctuations were attributed to stress-induced changes in plate density, associated with rapid rift formation. Racki (1998) reviewed the tectonic, volcanic and hydrothermal activity of this time slice and pointed out that tectonism received little attention to explain the puzzling features of the F/F boundary until now. But there is growing evidence for important tectonic and volcanic activity during the F/F transition in the East European Craton (Nikishin et al., 1996, Fig. 1) and in various domains of Eurasia (Veimarn et al., 1997), and on a whole, some authors consider the related cataclysmic events as the primary cause for demise of the biota (Wilson and Lyashkevitch, 1996). A series of arguments can be brought which all support the possible occurrence of such events, like, e.g., initiation of tectonic rifting (Bai et al., 1994; Wilson and Lyashkevitch, 1996), intensification of metallogenic processes (Chen and Gao, 1988; Turner, 1992; Veimarn et al., 1997; Racki, 1998), opening of major back-arc basins (Sengör et al., 1998), intensive silicic exhalative volcanism and island arc volcanism (Algeo, 1996; Racki and Cordey, 2000) as well as massive generation of continental flood basalts (Pripyat–Dniepr–Donets, Wilson and Lyashkevitch, 1996) and plume-influenced cratonic kimberlite and carbonatite emplacement (Kola Peninsula, Kramm et al., 1993). In agreement with these observations, our results also strongly support an enhanced hydrothermal and volcanic activity during the deposition of the KWH. These processes, in connection with a rearrangement of the lithospheric plates (Coffin and Eldholm, 1994; Sheridan, 1997; Kerr, 1998) and a reconfiguration of the subduction zones (Gurnis, 1990) characteristic for the late Devonian (Fig. 1), could be at the origin of the observed relative sea-level rise.

The change from a well-oxygenated environment to dysoxic/anoxic deposition conditions at the F/F boundary, as reported by several authors, cannot be always unambiguously ascertained by means of geochemical criteria. This uncertainty is due not only to the external input of hydrothermal elements, of which some are typically enriched also under anoxic conditions, but also to the positive feedback among hydrothermal processes and anoxia. Based on geochemical modelling, some authors (e.g., Carpenter and Lohmann, 1997) concluded that the flux of S, Fe, Mn, CH_4 and H_2 from submarine hydrothermal systems closely control the burial of organic carbon through the consumption of oxygen by inorganic and/or biologically mediated oxidation processes.

Some authors have also pleaded for a possible connection between periods of intensive hydrothermal circulation and increased microbial activity (e.g., Burns et al., 2000). An excessive bacterially controlled bioproductivity was noticed during the UKW crisis by Joachimski et al. (2001) and Whalen et al. (2002), while other authors proposed a model involving Fe-bacteria to explain the red pigmentation of the KWH observed at Coumiac and Pic du Visoux, France (Préat et al., 1999). Such kinds of bacteria with a high biodiversity (Moyer et al., 1995) are reported from different modern environments. Iron bacteria are found today not only at active deep sea hydrothermal vents (Karl et al., 1988) and in association with ferromanganese concretions (Burnett and Nealson, 1981), but are common also at the water–sediment interface in deep, calm, dysaerobic waters (Ehrlich, 1990). EDAX analysis of bacteriogenic coatings on shells revealed a complex chemical composition with Fe, Mn, Mg, Ca, K, P, Si, and S (Gillan and Cadée, 2000). Such kind of encrustations could have played a major role in the enrichment of some of the elements as described above. Metal toxicity, coupled with drop in water oxygenation had certainly disastrous consequences for living organisms. But also other negative vital effects due to an excessive bacterial activity, such as the decrease of swimming and burrowing ability of benthic organisms (Gillan et al., 2004), the promotion of shell dissolution by bacterial microborers (Knauth-Köhler et al., 1996) or promotion of diffusion of toxic S^{2-} ions into their bodies (Vismann, 1991) may have played an important role in the demise of the biota at the F/F boundary.

By lowering the water transparency or fostering bacterial activity and mucus production, the increase of nutrient availability/palaeo-productivity may have also contributed to a general biotic recession. As well known, water transparency is particularly important for reef building communities (Hallock, 1988). A connection between nutrient excess and microbial carbonate formation was documented in the Late Devonian of the Alberta Basin, Canada (Whalen et al., 2002), though an enhanced nutrient input can also lead to carbonate bioerosion and hiatus as suggested, e.g., by Peterhänsel and Pratt (2001). Indications for an over-fertilization close to the F/F boundary are documented in the Morovian shelf, but also in other regions (Racki, 1998, Racki and Cordey, 2000; Giles et al., 2002; Girard and Lécuyer, 2002; Ma and Bai, 2002; Racki et al., 2002; Yudina et al., 2002). The role of Fe as an important micronutrient with a non-negligible control on productivity (De Baar et al., 1995) should be also taken into account when the cause for a possible over-fertilization of the late Devonian oceans is considered.

The source of an excessive input of nutrients, however, is still a matter of debate. The evolution of vascular land plants (Algeo et al., 1995), upwelling (Caplan et al., 1996; Giles et al., 2002), enhanced terrigenous supply (Girard and Lécuyer, 2002; Tribovillard et al., 2004; Averbuch et al., 2005) or a high volcano-tectonic activity (Becker and House, 1994; Wilson and Lyashkevitch, 1996; Racki, 1998, Racki and Cordey, 2000; Streel et al., 2000; Racki et al., 2002; Yudina et al., 2002; Ma and Bai, 2002) are the most frequently called reasons. According to Sageman et al. (2003) the fluvial nutrient input is mostly restricted to the near-estuarine environment, except for continental scaled watersheds like the actual Amazon river system. Therefore, this hypothesis did not receive much attention as a possible source for an excessive nutrient increase at the F/F boundary. Additionally, the decrease in detrital input as observed in all of the sections, even including the more proximal facies of Büdesheimer Bach, speaks against a nutrient input coupled with increased terrigenous supply, though this argument could be refuted by assuming an enhanced influx of nutrients in dissolved form. In that sense Tribovillard et al. (2004) and Averbuch et al. (2005) ascribed the enhanced influx of nutrients into the ocean to the Eovariscan episode of uplift and the associated intense denudation of continental crust. In this context, a high flux of river-born nutrients (particularly of P) to the ocean should be considered, which could have occurred due to the intensive chemical weathering that followed an excessive volcanic CO_2 exhalation and global warming (Filippeli, 1999; Jones and Jenkyns, 2001). But other causalistic chains, leading to high productivity, can be also envisaged. A remobilisation of nutrients, like N or P from deep basins, under anoxic conditions followed by endo-upwelling seems plausible (Ingall and Jahnke, 1997; McManus et al., 1998), especially if one keeps in mind the increase in the biomass of siliceous biota in some regions during this time (Racki et al., 2002; Vishnevskaya et al., 2002). In their model, Riquier et al. (2005) combined the effect of both tectonic activity (uplift of the Eovariscan belt) and anoxia to explain the increase of nutrient input at the F/F transition. Alternatively, eutrophication due to an excessive release of P, Fe or Si from volcanic ash can be considered (Frogner et al., 2001), as supported by the distinct volcanic/hydrothermal signal at the F/F boundary. To account for periods of high biological productivity and oceanic anoxic events which occurred frequently during Jurassic and Cretaceous times, Jones and Jenkyns (2001) proposed a model according to which these critical episodes resulted as a combined effect of over-fertilization by an excessive input of Fe due to the enhanced production of oceanic crust and the associated hydrothermal activity, coupled with the development of upwelling zones due to increased zonal wind velocities under global warming conditions.

As discussed before, some of the observed environmental changes at the F/F boundary, like, e.g., the high metal contents, can represent the concurring effect of different factors, including specific redox conditions, high bio-productivity and intensive bacterial and/or hydrothermal/volcanic activities (Gillan and De Ridder, 2001). The interaction between these factors makes the environmental interpretation of single geochemical signals often ambiguous. Our results emphasize the necessity for using a multiproxy approach for a variety of different palaeogeographic settings in order to avoid misinterpretations and to recognize palaeoenvironmental trends of global relevance. Additionally, the use of a multiparametric geochemical approach permits to carry out more reliable stratigraphic correlations, like, e.g., in the case of Bank 9 of the La Serre section, which turned out to correspond to the KWH not only in terms of detrital and nutrient input, but also in respect of the intensity of volcanic and hydrothermal influence. Such a correlation was not possible before using only discrete geochemical parameters, like the content in organic C.

Based on the results presented before, we favour a model in which we assign a key role to endogenous/magmatic processes in order to explain the environmental changes which took place at the F/F boundary in the area between the south of Laurussia and north of Gondwana. The endogenous hypothesis was already proposed by several authors to explain the KW crisis (Whyte, 1977; Dvorak et al., 1988; Garzanti, 1993; Becker and House, 1994; Racki, 1998). Others combined the endogenous model with ascribing an additional role to an increased nutrient input and/or a thermal stimulus produced by a massive submarine volcanism and associated phenomena (Vogt, 1989; Coffin and Eldholm, 1994; Vermeij, 1995). There are also some analogies with the model of Kerr (1998), which relate the environmental changes at the Cenomanian–Turonian boundary to the physical and chemical processes connected to the formation of large igneous provinces. Studying the Devonian of the

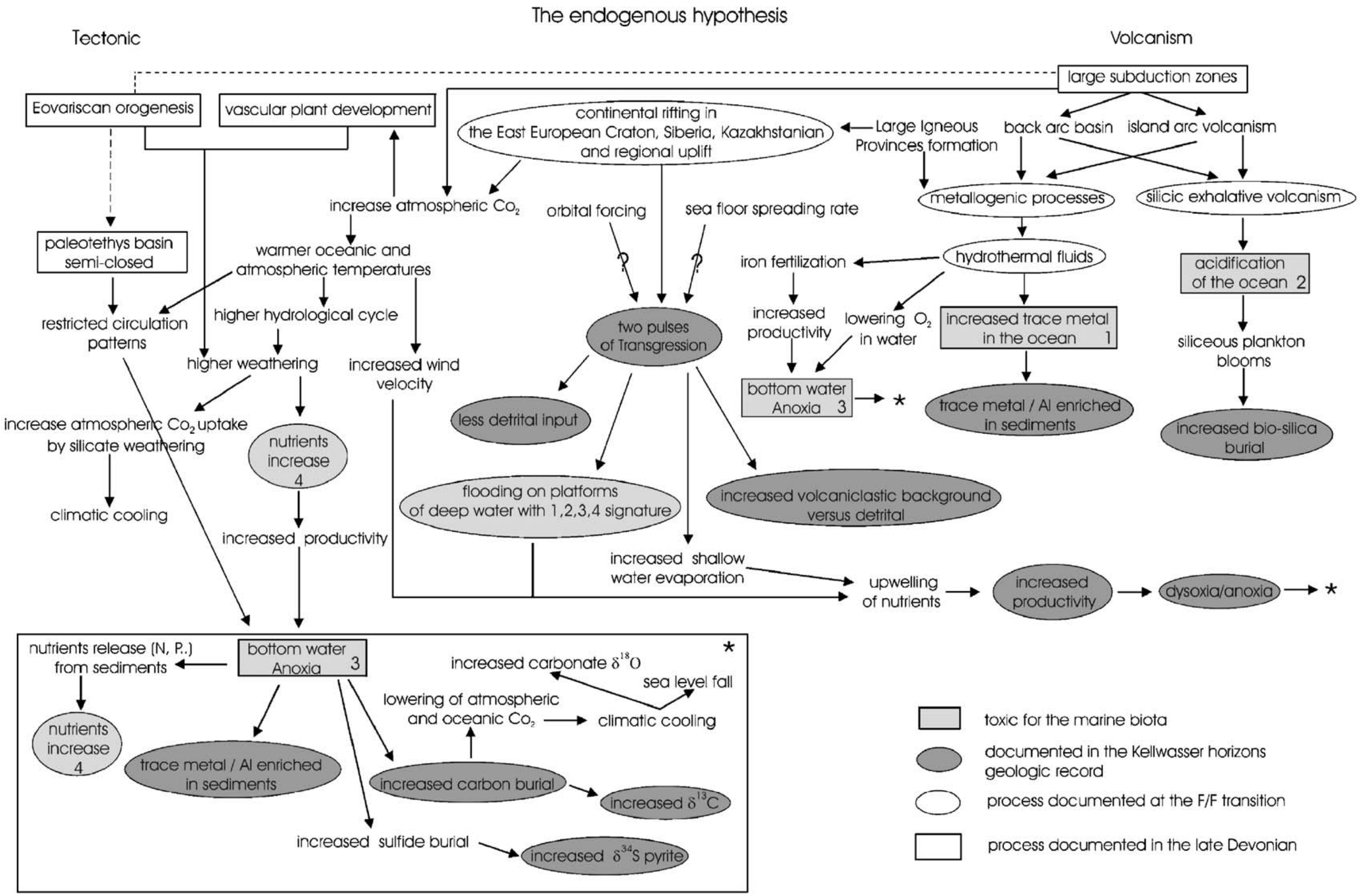

Fig. 16. Flow-chart illustrating the possible links between different processes documented in the Late Devonian or at the F/F transition, the characteristics of the Kellwasser horizons and the induced environmental stress for the marine biota.

Montagne Noire, Becker and House (1994) pointed out the possible role of intraplate volcanism in the development of dysoxia/anoxia and in the occurrence of rapid sea-level fluctuations during the Kellwasser crisis. They traced back the related environmental changes to a variety of mechanisms, like cratonic over-flooding, climatic overheating, upwelling and eutrophication in a quasi-Pangea like configuration of the Palaeotethys. The model presented in Fig. 16 synthesizes the processes already advanced to explain the F/F biotic crisis. In this connection, long-term processes, like the semi-closed configuration of the Palaeotethys in the late Devonian, and short-term processes must be differentiated. Among the characteristics of the Kellwasser Horizons, the rapid sea-level fluctuation seems to be the most important parameter. According to current findings, pulses of continental rifting could explain the rapid eustatic oscillations recorded in the Kellwasser horizons. However, House (2002) favoured a common explanation to all of the late Devonian events, relating the observed transgression-regression cycles to orbital forcing. Other hypotheses, like the development of land plants or tectonic processes are not adequate to explain short-term variations and irrefutable arguments for an impact or multiple impact hypotheses are still lacking. Based on the palaeogeographic reconstruction (Fig. 1), the relative sea-level rise during the KW event as indicated in this study by the decreasing detrital input could have led to the reconnection of bottom water circulation between the Palaeotethys and the western part of Panthalassa, and to a flooding of the southern shores of Laurussia and the northern parts of Gondwana by water enriched in nutrients, metals and impoverished in oxygen (Fig. 16). The driving mechanism for the bottom water circulation could reside in difference in salinity gradient, similar to that between the modern Mediterranean and the Atlantic Ocean. The similarities observed in the development of the Kellwasser horizons in France, Germany and Morocco (Riquier et al., 2005) could be due to the particular palaeogeographic configuration of the area, while distinct features of the individual sections can be attributed to differences in distance to the source of volcanism/hydrothermalism, in bottom water currents (basin morphology, presence of barriers, etc.), in geomorphology or tectonic (proximity of mountains ranges, etc.) and in signal preservation (Zimmerle, 1985).

6. Conclusions

The study brings new geochemical evidences which emphasize the role of tectono-magmatic processes, like volcanism, hydrothermalism and major tectonic movements in the development of the particularities of the Kellwasser horizons deposited close to the southern shores of Laurussia and the northern parts of Gondwana. The results show also that conventionally used markers like the organic matter content or the oxygenation level of bottom waters does not have always-diagnostic values for recognizing the Kellwasser horizons. By the ability of discerning among different processes, a multiparametric geochemical approach as used in the present study allows to draw more reliable palaeoenvironmental conclusions. Finally the observed enrichment in metals, in nutrients and the lowering of the oxygen level in the seawater during the deposition of the Kellwasser Horizons, coupled with an enhanced bacterial activity must have played a decisive role in the major biotic crisis which affected the Frasnian–Famennian transition.

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