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# The Late Frasnian Kellwasser horizons of the Harz Mountains (Germany): Two oxygen-deficient periods resulting from different mechanisms

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**Abstract**

In the Harz Mountains (Germany), three Late Devonian sections, Aeketal, Hühnertal and Kellwassertal, were analyzed for major- and trace-element concentration. The inorganic geochemical data were used to determine the environmental conditions, associated with the deposition of the two Late Frasnian black Kellwasser horizons in a submarine-rise environment. Low Ti/Al and Zr/Al values and slight enrichment in nutrient- and organic matter-related trace elements (e.g., Ba, Cu, and Ni) suggest that the Kellwasser horizons were deposited during two periods of minimum detrital input but relatively elevated primary production. Enrichments in U, V, and Mo in both black Kellwasser horizons and values of redox indices, including U/Th, V/Cr, and Ni/Co, indicate oxygen-restricted conditions prevailed during the Late Frasnian times. Under oxygen-depleted conditions, reductive diagenesis caused precipitation of iron sulphides, such as pyrite, that are observed with SEM. However, variations in major and trace element concentrations are not similar in the two Kellwasser horizons, particularly regarding redox markers. The Lower Kellwasser horizon seems to be more $O_2$-depleted than the Upper Kellwasser horizon in some German sections.

On the basis of these results, we propose that the two Kellwasser horizons are not caused by identical conditions. The Lower Kellwasser horizon results from increased primary productivity, enhanced by land-derived nutrient-loading and which triggered the anoxic conditions recorded in drowned platform setting. In contrast, the Upper Kellwasser horizon results from the onset of oxygen-impoverished bottom water in the deepest part of the ocean, due to episodic water stratification during maximum Frasnian flooding. Oxygen-depleted water may have impinged shallower environment during the *linguiformis* transgressive pulse. Nutrients would have been released from organic matter decay under reducing conditions and brought up to the photic zone during episodic water mixing.


*Keywords:* Late Frasnian; Kellwasser horizons; Harz mountains; Trace metals; Anoxia; Productivity; Pyrite

## 1. Introduction

The well-known Late Frasnian Kellwasser (KW) horizons are two black, bituminous decimetre-thick

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sequences relatively rich in carbonate (shale-limestone facies) (e.g., Buggisch and Clausen, 1972; Schindler, 1990; Buggisch, 1991; Walliser, 1996). They are well exposed in the Harz Mountains area (Germany), where they were first described in 1850 by Roemer. They are frequently interpreted as resulting from episodes of increased organic-matter (OM) preservation and burial (e.g., Buggisch, 1991; Joachimski et al., 1994, 2002). Coeval with the Frasnian–Famennian (F–F) mass extinction event (Sepkoski, 1986; Copper, 1986; McGhee, 1989, 1996; Hallam and Wignall, 1997; House, 2002), these black horizons have also been observed in numerous shelfal- to basinal settings in North America, Europe, North Africa and South China (e.g., Feist, 1985; Wendt and Belka, 1991; Lazreq, 1992; Ettensohn, 1998; Lazreq, 1999; Yudina et al., 2002; Chen et al., 2005).

To explain the coeval occurrence of black facies and a decrease in biodiversity, several causes have been proposed (Joachimski and Buggisch, 1993; Becker and House, 1994; Algeo et al., 1995; Racki, 1998; Caplan and Bustin, 1999; Murphy et al., 2000a; Joachimski and Buggisch, 2002; Godderis and Joachimski, 2004). The formation of black sedimentary facies is commonly thought to be mainly controlled by oxygen ($O_2$) level in bottom waters and nutrient concentration in surface water. They may result from either (1) improved preservation of organic matter (OM) due to onset of an anoxic water column (preservation model of Demaison and Moore, 1980), or (2) increased marine production, induced by enhanced inputs of nutrients (productivity model of Pedersen and Calvert, 1990); the nutrients may be either delivered with the terrestrial run-off or recycled in situ (e.g., by up-welling or anoxia-induced benthic regeneration of P; see Ingall and Jahnke, 1997; Murphy et al., 2000a). According to the model considered, anoxic conditions are either a consequence or a cause of enrichment in OM. In the last decades, it has been documented that other factors, such as the clastic influx of terrigenous elements, linked to sea-level fluctuations and/or climatic conditions, or oceanic circulation, may also influence the formation of these peculiar facies (Arthur and Sageman, 1994; Murphy et al., 2000a,b; Joachimski et al., 2002; Sageman et al., 2003; Joachimski et al., 2004; Arthur and Sageman, 2004; Tribovillard et al., 2004b; Averbuch et al., 2005; Riquier et al., 2005).

In this paper, we present the results obtained for three sections of the Harz Mountains area, exposing the two KW horizons, based on inorganic geochemistry. Elemental concentrations (major and trace elements) have been measured in order to evaluate the fluctuations in bottom-water $O_2$ level, sea-surface primary productivity and detrital inputs in the marine environments at the F–F boundary along the south Laurussian margin. These data have been complemented by scanning electron microscopy (SEM) observations on polished thin sections that particularly focused on the morphologies and sizes of iron sulphide minerals. The implications of these results for the formation of the KW horizons will be considered at both local and regional scales to assess (1) the possible consequences of early diagenetic perturbations on the depositional record, and (2) possible models concerning the extensive development of black facies during Late Devonian times.

## 2. Geological background

The Harz Mountains are some of the main outcropping Palaeozoic massifs of northern Germany. They form part of the Rheno-Hercynian fold Belt of the German Variscides. This foreland belt evolved from a rifted passive continental margin during the Early Devonian to an orogenic belt in Upper Carboniferous times (e.g., Franke, 2000). During the Late Devonian, the Harz Mountains were located along the southern border of the Laurussian continent, close to the equator (around 15°S according to paleogeographical reconstructions, Golonka et al., 1994; Scotese, 1997; Averbuch et al., 2005). Sedimentation occurred on the gently subsiding northern passive margin of the Lizard-Rhenohercynian Ocean (e.g., Franke, 2000) and is, thus, little influenced by the tectonics of the Eovariscan mountain belt under incipient uplift, some few thousand of kilometres south of the area under study.

The studied three sections, Aeketal, Hühnertal and Kellwassertal, are located in the Upper Harz, i.e., the north-western part of the Harz Mountains (Schindler, 1990) (Fig. 1a). The Upper Harz area is mainly composed of three units (Fig. 1b). The Devonian Anticline consists of Devonian limestones, sandstones and clay schists. The Clausthal Fold Zone is mainly composed of Early Carboniferous graywackes, siliceous schists and clay schists. Lastly, the Acker Bruchberg Zone contains Late Devonian siliceous schists and graywackes and Early Carboniferous quartzites (Gabriel et al., 1997). The Aeketal and Hühnertal sections occur in the Devonian Anticline, whereas the Kellwassertal section occurs in the Claustal Fold Zone. In more detail, the Aeketal and Kellwassertal sections are respectively situated about 10 km and 2 km north of the town of Altenau, whereas the Hühnertal section is situated 1.5 km north-east of the town of Hahnenklee (Fig. 1b). The lithologic and faunal characteristics of the

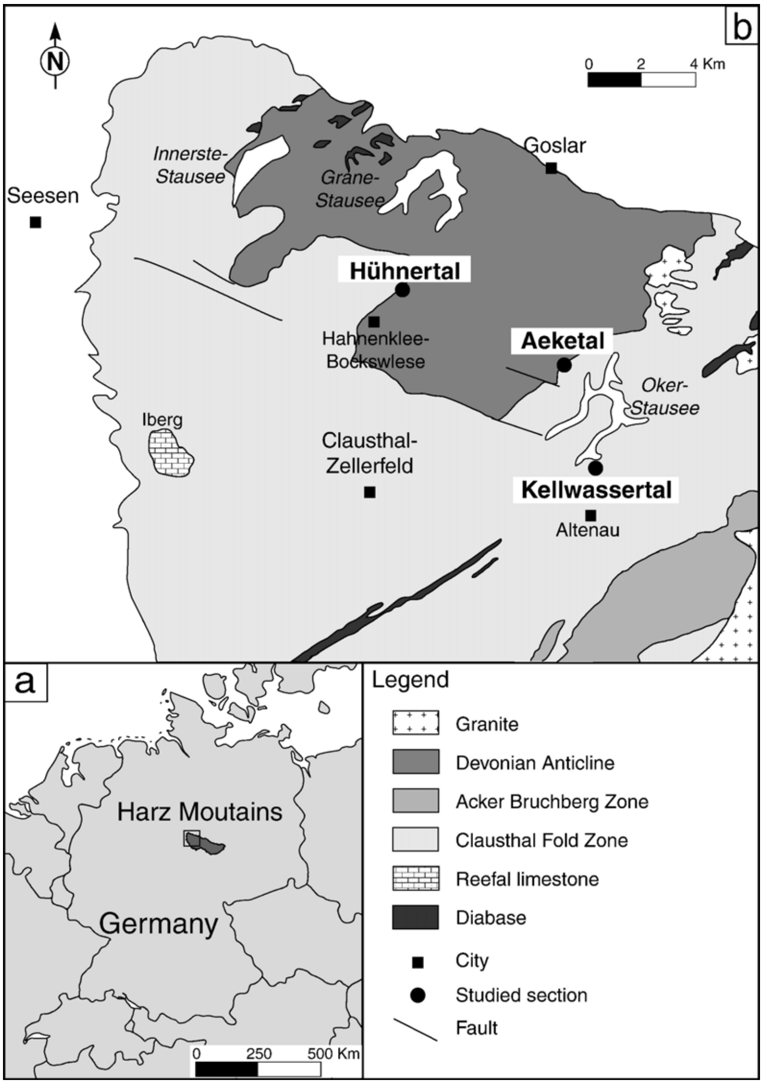


Fig. 1. Location of the studied area (a), and geological sketch of the sampling area in the Harz Mountains (modified from Alberti and Walliser, 1977; Schindler, 1990) (b).

Aeketal, Hühnertal and Kellwassertal sections were described in detail by Schindler (1990, 1993), and Feist and Schindler (1994). The sampled interval records condensed carbonate sedimentation from the Middle Frasnian *jamieae* conodont zone to the Early Famennian Upper *crepida* zone (Fig. 2), but we mainly focus our attention on the time interval from the Lower *rhenana* zone to the Upper *triangularis* zone.

The Late Devonian sequence is about 3.5 to 4.5 m thick and exposes a succession of cephalopod limestone beds, with intercalated calcareous shale levels (Fig. 2). The carbonate content mainly ranges from 60% to 100% for the Hühnertal and Aeketal sections. In the Kellwassertal section, the fluctuations in the carbonate content are more pronounced (5% to 100%) and many marlstone beds are present. The three sections present two black laminated horizons, corresponding to the Lower Kellwasser (LKW) and the Upper Kellwasser (UKW) horizons, which occur at the base of the Upper *rhenana* and in the upper part of the *linguiformis* zones, respectively. The KW horizons may consist of either pure black limestones with the highest % $CaCO_3$ contents, as observed for the LKW horizon in Aeketal and the UKW horizon in Hühnertal, or lenticular lenses of black limestones, alternating with black marls, as observed in the LKW horizon in Kellwassertal and the UKW horizon in Aeketal. Whereas the LKW horizon is about 40-cm thick in each section, the thickness of the

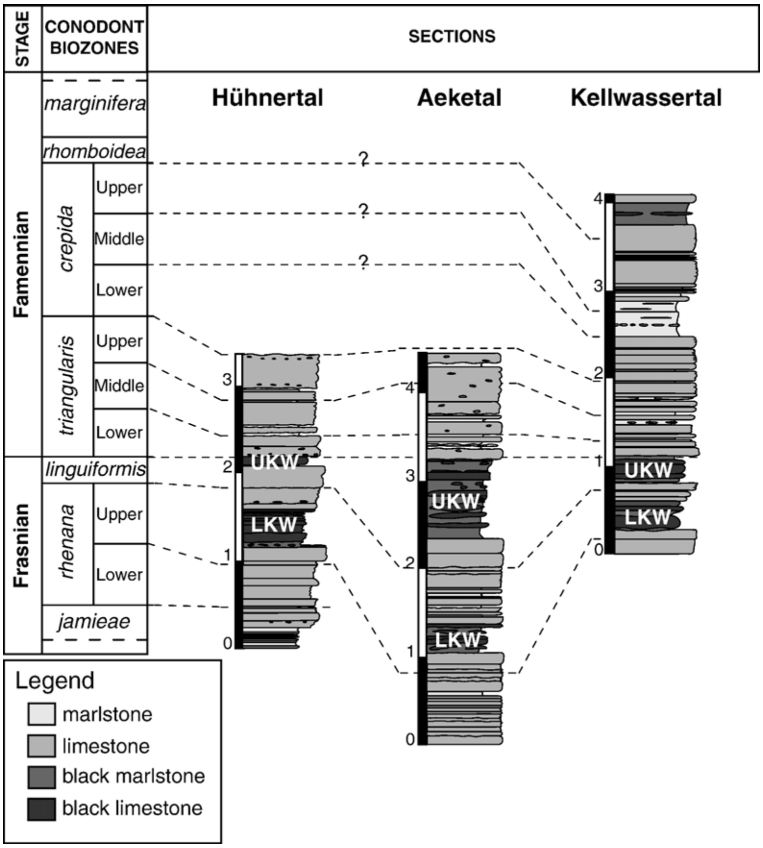


Fig. 2. Lithology, conodont biozonation (from Schindler, 1990) and biostratigraphical correlations between the studied three sections. Scale in meters. LKW and UKW stand for Lower Kellwasser horizon and Upper Kellwasser horizon, respectively.

UKW horizon is more variable, ranging from about 20-cm thick in the Hühnertal section to 90 cm in the Aeketal section. The three sections are thought to correspond to a submarine-rise setting in a pelagic realm, because of the diversified faunas, such as trilobites, ostracods, echinoderms and ammonoids observed in the sedimentary beds. The Hühnertal section is thought to represent the shallowest environment (Schindler, 1990).

## 3. Methods

### 3.1. Inorganic geochemical analyses

Major- and trace-element analyses were performed on selected samples using ICP-AES and ICP-MS, respectively, at the spectrochemical laboratory of the Service d'Analyse des Roches et des Minéraux of the Centre National de la Recherche Scientifique (Vandœuvre-les-Nancy, France). From the three sections, a total of 51 samples were prepared by fusion with $LiBO_2$ and $HNO_3$ dissolution. Precision and accuracy were both found to be better than 1% (mean 0.5%) for major–minor elements, 5% for Cr, Pb, U, V and Zn, and 10% for Ba, Co, Cu, Mo, and Ni as checked by international standards and analysis of replicate samples, respectively.

Sedimentary rocks usually have variable proportions of phases, often biogenic that "dilute" the trace-element abundance relative to crustal averages and mechanisms of enrichment. The most typical biogenic dilutants are calcium carbonate and opal. Thus, to be able to compare trace-element proportions in samples with variable carbonate and opal contents, it is recommended to normalize the trace-element concentration, most commonly to the aluminum content (e.g., Calvert and Pedersen, 1993). For the great majority of sedimentary deposits, aluminum can be considered as an indicator of the aluminosilicate fraction of the sediments, with very little ability to move during diagenesis (Brumsack, 1989; Calvert and Pedersen, 1993; Morford and Emerson, 1999; Piper and Perkins, 2004). However, although Al-normalization is an attractively quick and easy way to normalize chemical data and to present Al-normalized element concentrations in sediment profiles, it must be noted that this methods also present some pitfalls. Van der Weijden (2002) demonstrated that uncorrelated variables (trace metal concentrations) may acquire "spurious" correlations when normalized, and that normalization can also increase, decrease, change sign of, or even blur the correlations between unmodified variables. This is all the more so when the coefficient of variation (standard deviation divided by the mean) of Al concentration is large compared to the variation coefficients of the other variables (Van der Weijden, 2002). In addition, there are also distinct instances when Al should not be used for normalization (Murray and Leinen, 1996). This is the case of marine sediments with a detrital fraction lower than 3–5% and a relative excess of aluminum compared to e.g., titanium (Kryc et al., 2003). The excess Al may be scavenged as hydroxides coated to biogenic particles (Murray and Leinen, 1996; Dymond et al., 1997; Yarincik et al., 2000; Kryc et al., 2003). A part of the excess Al could also result from an authigenic clay mineral formation (Timothy and Calvert, 1998). Nevertheless, such sediments with so reduced detrital fractions are not common.

Van der Weijden (2002) also showed that the comparison to average shale values might raise some complications. The composition of the commonly used standard shale and, consequently, the reference values of normalized elements are not necessarily representative of the local/regional sediments in the study area. This fact may complicate the comparison of the chemical composition of geological formations that are geographically and/or stratigraphically distinct.

To summarize, Al normalization of element concentrations in usual marine sediments may be considered to be a valuable method to estimate the enrichment in an element relative to a reference sediment, but cannot be used alone to identify and quantify contributions by sediment components other than the detrital fraction (Van der Weijden, 2002). Because the reference shales commonly used to calculate enrichment factors (EF) also present a diagenetic component, the use of EF to estimate limited enrichment/depletion may be delicate. However, when EF show values significantly higher than 1 (from ten- to thousand-fold enrichment), elemental enrichment may be unambiguously deduced. Lastly, the best way to get rid of the normalization bias is–whenever possible–to examine the stratigraphical variations in the EF or the Al-normalized element contents rather than the absolute values, provided the coefficient of variation in Al is not too large, which is generally the case with studies involving high-resolution sampling on stratigraphically limited sequences.

### 3.2. Rock-Eval pyrolysis

Rock-Eval parameters, such as total organic carbon (TOC) content, Hydrogen Index (HI) and $T_{max}$ (Espitalié et al., 1986), were determined using a Delsi Oil Show Analyser at the Earth Science Department of Paris VI-Pierre et Marie Curie University.

### 3.3. SEM analyses

Six samples from the KW Horizons were studied in polished thin sections using an FEI Quanta 200 environmental scanning electron microscope (SEM), operated at low vacuum (about 0.70 Torr and 20.0 kV). The SEM is coupled to an energy-dispersive X-ray spectrometer (EDS) (XFlash 3001), allowing elemental analysis.

## 4. Results

### 4.1. Geochemistry

According to several authors (e.g., Brumsack, 1989; Werne et al., 2002; Sageman et al., 2003; Algeo and Maynard, 2004; Tribovillard et al., 2005, in press, and references therein), the sedimentary geochemical signal records the influence of three types of fractions: (1) a detrital fraction derived from terrigenous (fluvial, eolian, volcanogenic) sources, the main proxies of which are Ti, Zr, Th, and Cr, (2) a biogenic fraction, composed of carbonate, silica or OM, the main proxies of which are Ba, Ni, and Cu, and (3) an authigenic fraction, mainly composed of sulphides and insoluble oxyhydroxides, the main proxies of which are Mo, V, and U.

To determine the origin of the elements studied here (clastic or biogenic supply, authigenic enrichment), the major and trace element abundances were cross-correlated with Al abundance, used here as a proxy for the land-derived aluminosilicate fraction of the sediments. From the $r$ values (Table 1), it clearly appears that (1) Si, Fe, Mg, Na, K, Ti, Ba, Cr, Ni, V, Th and Zr are strongly correlated with Al ($0.90<r<0.99$), (2) Co, Cu Pb, Zn are moderately correlated with Al ($r<0.90$), (3) Mn, Mo and U are poorly to not correlated with Al ($r<0.75$), and (4) both Ca and Sr are negatively correlated versus Al ($r>0.85$). Consequently, most of the major elements (Si, Mg, Na, K and Ti) and some minor/trace elements (Zr, Th and Cr) have a siliciclastic origin and their fluctuations can be related to variations in the detrital influx. Moreover, the anti-correlation existing between Ca and Sr vs. most of major and minor

Table 1
Correlation coefficients ($r$) between Al and selected major and trace elements and level of significance of correlations ($p$, expressed in %)

| | Aeketal ($n$=21) | | Hühnertal ($n$=15) | | Kellwassertal ($n$=16) | |
|---|---|---|---|---|---|---|
| | $r$ | $p$ | $r$ | $p$ | $r$ | $p$ |
| *Major elements (%)* | | | | | | |
| Si | 0.99 | <0.1 | 0.99 | <0.1 | 0.99 | <0.1 |
| Fe | 0.96 | <0.1 | 0.99 | <0.1 | 0.96 | <0.1 |
| Mn | 0.06 | n.s. | 0.47 | n.s. | 0.06 | n.s. |
| Mg | 0.97 | <0.1 | 0.90 | <0.1 | 0.91 | <0.1 |
| Ca | 0.99 | <0.1 | 0.99 | <0.1 | 0.99 | <0.1 |
| Na | 0.96 | <0.1 | 0.87 | <0.1 | 0.98 | <0.1 |
| K | 0.99 | <0.1 | 0.99 | <0.1 | 0.99 | <0.1 |
| Ti | 0.99 | <0.1 | 0.99 | <0.1 | 0.99 | <0.1 |
| *Trace elements (ppm)* | | | | | | |
| Ba | 0.99 | <0.1 | 0.98 | <0.1 | 0.80 | <0.1 |
| Co | 0.95 | <0.1 | 0.74 | <1.0 | 0.61 | <5.0 |
| Cr | 0.99 | <0.1 | 0.99 | <0.1 | 0.99 | <0.1 |
| Cu | 0.64 | <1.0 | 0.85 | <0.1 | 0.54 | <5.0 |
| Mo | 0.52 | <5.0 | 0.11 | n.s. | 0.38 | n.s. |
| Ni | 0.96 | <0.1 | 0.99 | <0.1 | 0.78 | <0.1 |
| Pb | 0.56 | <5.0 | 0.79 | <0.1 | 0.59 | <5.0 |
| Sr | 0.59 | <5.0 | 0.89 | <0.1 | 0.79 | <0.1 |
| Th | 0.99 | <0.1 | 0.99 | <0.1 | 0.99 | <0.1 |
| U | 0.52 | <5.0 | 0.72 | <1.0 | 0.61 | <1.0 |
| V | 0.96 | <0.1 | 0.94 | <0.1 | 0.73 | <1.0 |
| Zn | 0.84 | <0.1 | 0.48 | n.s. | 0.73 | <1.0 |
| Zr | 0.97 | <0.1 | 0.98 | <0.1 | 0.98 | <0.1 |

elements can be interpreted as dilution of geochemical signal by carbonate production. The stratigraphic distribution of some selected elements (Al-normalized) is illustrated in Fig. 3. Broadly speaking, and consistently with the fact that most elements are strongly tied to Al abundance, the distribution of element/Al ratios are rather uniform, but some variations are visible for the KW horizons. In all sections, the stratigraphic profiles of all the redox-sensitive trace elements (Mn, U, Mo and V) and paleoproductivity tracers (Ba, Cu, Ni) exhibit moderate to high enrichments in both KW horizons, relative to the other parts of the sections, where the samples have element/Al ratios at or near average shale values (Fig. 3). Thus, the two KW horizons correspond to the analytical points showing the poorest correlation vs. Al concentration. These enrichments are particularly well expressed within the LKW horizon of the Aeketal section, where the highest values are recorded. Fig. 3 also shows that only the top part of the UKW shows any enrichment in redox and paleoproductivity ratios; the lower portion of the UKW horizon, for the most part, looks like background level. Concerning the lateral variations in elemental concentrations, it is noteworthy that the redox-sensitive metal/Al ratios in the KW horizons of Hühnertal are twice lower than those of the KW horizons of Aeketal. The Kellwassertal section shows intermediate values comparing to the other two sections.

The other major and trace elements have less contrasting fluctuations during the Late Frasnian–Early Famennian times. Ti and Zr are two markers of the detrital fraction of sediments ($r$=0.99 with Al). In the studied three sections, they show rather uniform stratigraphic distributions with the lowest values corresponding to the two KW horizons (Fig. 3). This phenomenon is more accentuated in the Hühnertal and Aeketal sections. Among the detrital proxies, Si is the only major element that shows a well-marked positive peak within the LKW horizon in Aeketal. Iron shows slightly higher Fe/Al values in the KW horizons. Potassium shows similar behaviour.

To summarize, in the three sections, the geochemical composition of the rocks is strongly influenced by the detrital supply, but some elements shows more or less marked enrichment or depletion in the KW horizons (depleted in Ti and Zr, enriched in redox and productivity proxies).

In addition to element/Al ratios, some redox indices (U/Th, V/Cr, Ni/Co, and V/(V+Ni)) have been calculated and reported as cross-plots in Fig. 4. In the literature (Hatch and Leventhal, 1992; Jones and Manning, 1994), these geochemical indices have been used to derive information on the paleo-oxygen level of the depositional environments (Table 2). For all four indices, the highest values are recorded within the two KW horizons. Nevertheless, the contrast between the samples from the KW horizons and those from the rest of the section varies according to the considered indices. In each section, the samples of the KW horizons have values of the V/Cr and U/Th ratios above 1.25, whereas the non-KW horizons have values that rarely exceed 1 and 0.6, respectively. For the V/(V+Ni) and Ni/Co ratios, the distinction is not as clear. Nevertheless, most of the samples of the KW horizons are characterized by V/(V+Ni)>0.60 and Ni/Co>4. Nevertheless, as discussed by Rimmer (2004), it is not recommended to focus on the absolute values of these elemental ratios, but rather on their relative variations.

## 4.2. Rock-Eval data

The Rock-Eval parameters indicate that the TOC is ranging between 0% and 2%, most values being below 0.5%. Consequently, the other parameters, $T_{max}$ and HI, cannot be used confidently (Espitalié et al., 1986), hence they are of no help to determine the type of OM (II or

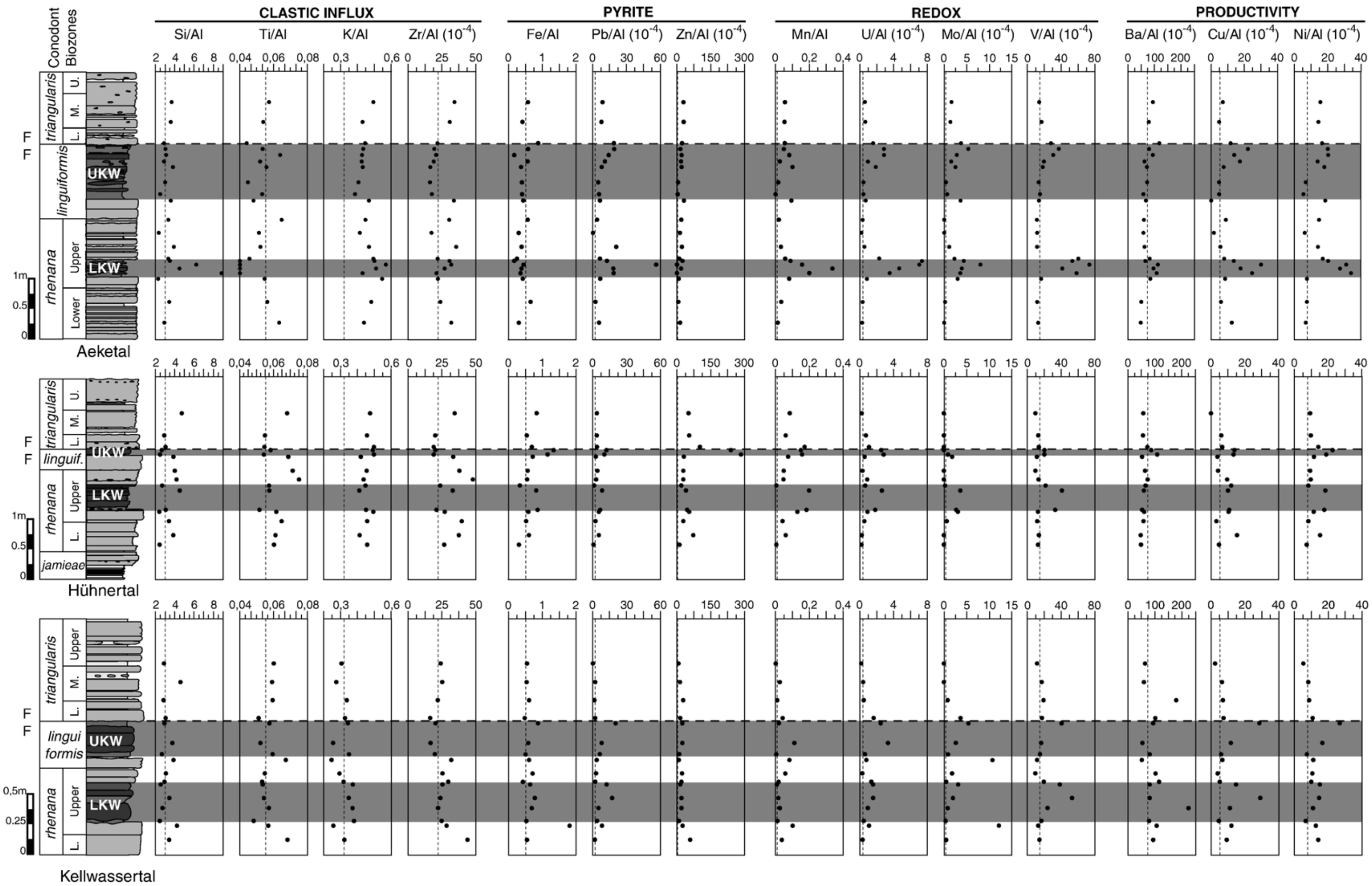


Fig. 3. Normalized metal concentrations in the Aeketal, Hühnertal and Kellwassertal sections. The dashed lines indicate the metal/Al concentration ratios for average shales (Wedepohl, 1971, 1991). Major element/Al ratios are given as weight-ratios and trace element/Al ratios as weight-ratios multiplied by $10^4$. The two shaded bands correspond to the KW horizons.

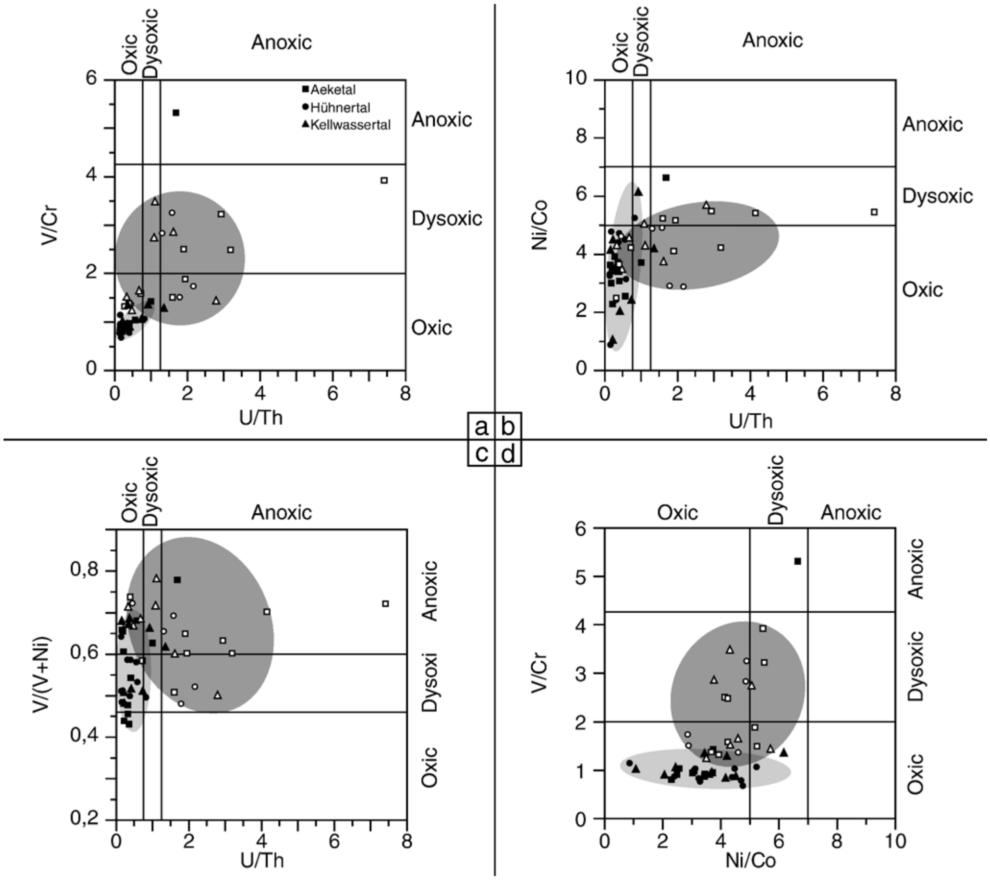


Fig. 4. Crossplot of redox indices. V/Cr vs. U/Th (a), Ni/Co vs. U/Th (b), V/(V+Ni) vs. U/Th (c) and V/Cr vs. Ni/Co (d). Ranges for V/Cr, U/Th and Ni/Co are from Jones and Manning (1994); ranges for V/(V+Ni) are from Hatch and Leventhal (1992). Open symbols: Kellwasser horizon samples. The dark shaded area corresponds to cluster of the KW samples, whereas the light shaded area corresponds to cluster of the no-KW samples.

III). The few samples with TOC above detection value show high $T_{max}$ values ($T_{max}$ > 460 °C), indicating that OM is mature. The marked maturation may be ascribed to regional tectonic history (thrusting or heat flow), and may be held responsible for the destruction of a part of the OM content. However, according to Mongenot et al. (1996), the trace-metal content is not markedly affected in sedimentary rocks with strong over maturation (in the case of the elements studied here). Thus, the geochemical message must have been preserved.

### 4.3. SEM–EDS results

SEM observations coupled to EDS microprobe analyses on polished thin sections reveal that framboidal and, very scarce euhedral, pyrite minerals are the most significant iron-bearing phases in the KW horizons. The sizes of framboidal and euhedral pyrites are variable. In each section, the framboidal pyrites are larger than the euhedral pyrites: framboidal pyrites ranging from 2 to 15 μm and most of them being around 8 μm, whereas the euhedral specimens range from 1 to 7 μm, with an average value of 4 μm (Fig. 5a–b). Comparatively, detrital iron oxides (very likely magnetite) are only scarce. An additional point to be noticed is that most framboids are partly or totally weathered to iron oxides but their morphology has been preserved (Fig. 5c).

## 5. Interpretation

### 5.1. Clastic inputs

In the studied three sections, the good correlations of Si, K, Ti, Zr, Fe, Cr vs. Al ($r$ > 0.95) (Table 1), and the rather uniform stratigraphic distribution of K/Al and Fe/Al and, to a lesser degree Si/Al, suggest a rather homogeneous nature for the detrital supply. However, the Ti/Al and Zr/Al ratios show the lowest values for both KW horizons. Ti and Zr are frequently enriched in

Table 2
Correlations between trace-element ratio values and redox zones (bottom-water oxygen levels from Tyson and Pearson, 1991)

| | Oxic zone (8.0–2.0 ml $O_2$/l) | Dysoxic zone (2.0–0.2 ml $O_2$/l) | Anoxic zone (0.0 ml $O_2$/l) |
|---|---|---|---|
| U/Th [a] | <0.75 | 0.75–1.25 | >1.25 |
| V/Cr [a] | <2.00 | 2.00–4.25 | >4.25 |
| Ni/Co [a] | <5.00 | 5.00–7.00 | >7.00 |
| V/V+Ni [b] | <0.46 | 0.46–0.60 | 0.54–0.82 |

[a] Jones and Manning (1994).
[b] Hatch and Leventhal (1992).

the presence of accessory minerals, such as ilmenite, rutile, zircon and augite that are usually associated with the coarser-grained part of fine-grained siliciclastic sediments (Brumsack, 1986, 1989; Calvert et al., 1996; Caplan and Bustin, 1999). The relatively low abundance of Ti and Zr in the KW horizons could thus indicate a decrease in the grain size of the land-derived supply. This grain size decrease could accompany the sea-level rise frequently suggested for the two KW horizons (Girard and Feist, 1997; Hallam and Wignall, 1999; Sandberg et al., 2002; Chen and Tucker, 2003; Godderis and Joachimski, 2004; see discussion in Chen and Tucker, 2004).

Alternatively, Ti and Zr are also two elements frequently referred to as tracers of airborne or eolian detrital supplies (Rachold and Brumsack, 2001). Their relative low abundance could reflect a decrease in eolian supply during the deposition of the KW horizons. This second interpretation is plausible but it demands more hypotheses about the sources of eolian dust, the dominant-wind patterns, and the location of high-pressure cells that one is unable to discuss with the present knowledge about global circulations during the Late Devonian.

The Si/Al ratio shows relatively low values in the KW horizons of the Hühnertal and Kellwassertal sections. This is consistent with both hypotheses: decreased grain size of the detrital supply, including quartz grains, or decrease in the airborne quartz silt abundance (e.g., Tribovillard et al., 2005). However, this Si/Al decrease is not observed in the Aeketal section. In contrast, a strong Si/Al increase is marked for the LKW horizon of the Aeketal section. In that case, the increased presence of $SiO_2$ could be explained by an increase in biogenic $SiO_2$ (silica-secreting organisms) recorded locally (Racki, 1999; see discussion below about the increase in productivity).

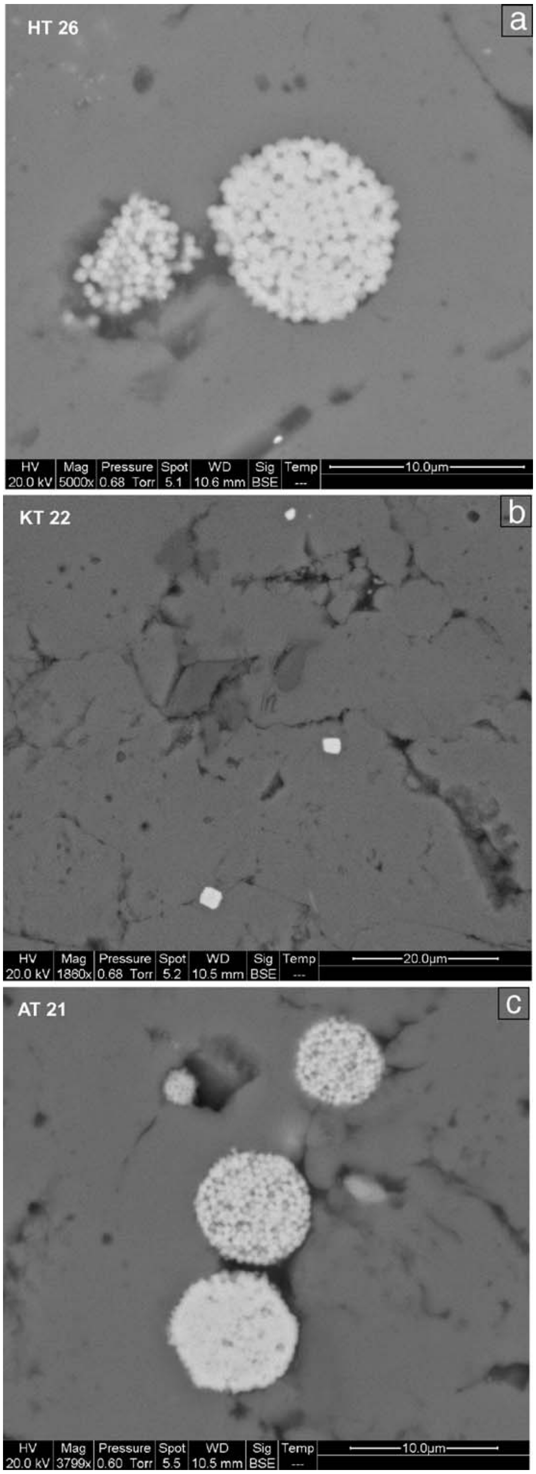


Fig. 5. Backscattered electron microphotographs of framboidal pyrite (sample HT 26, LKW horizon of Hühnertal) (a) and of euhedral pyrite (sample KT 22, UKW horizon of Kellwassertal) (b). (c) Four framboids from sample AT 21 (LKW horizon of Aeketal): two unweathered large ones above and, bottom, a large framboid converted to iron oxides. There is no evidence that the oxidation processes induced a variation in the size of the framboids.

### 5.2. Redox conditions

For each section, the KW horizons are enriched in Mo, U, V, Cu, Cr, and Ni. These elements that are redox sensitive and/or sulphide forming, and also possible indicators of the OM flux to the sediments (Ni and Cu) can be fixed in high amounts in sediments under reducing conditions (Brumsack, 1986, 1989; Hatch and Leventhal, 1992; Calvert and Pedersen, 1993; Lipinski et al., 2003; Algeo and Maynard, 2004; Meyers et al., 2005; Tribovillard et al., 2005, in press). They may either be precipitated as autonomous sulphides (Co, Zn and Pb), coprecipitated with iron sulphides (V, Ni and Cu), and/or bound to organic matter (V, Mo, Ni, Cu and U). Among the studied trace metals, V, U, and Mo are reputed as redox-sensitive markers (Crusius et al., 1996; Helz et al., 1996; Dean et al., 1997; Zheng et al., 2000; Adelson et al., 2001; Lyons et al., 2003; Algeo et al., 2004, Cruse and Lyons, 2004; Rimmer, 2004; Rimmer et al., 2004; Tribovillard et al., 2004a,b, 2005; Algeo and Lyons, in press). In all three sections, Mo and U are the most enriched elements in the KW horizons compared to the average shale values (entire LKW and upper part of UKW; Figs. 3 and 6). The enrichment in

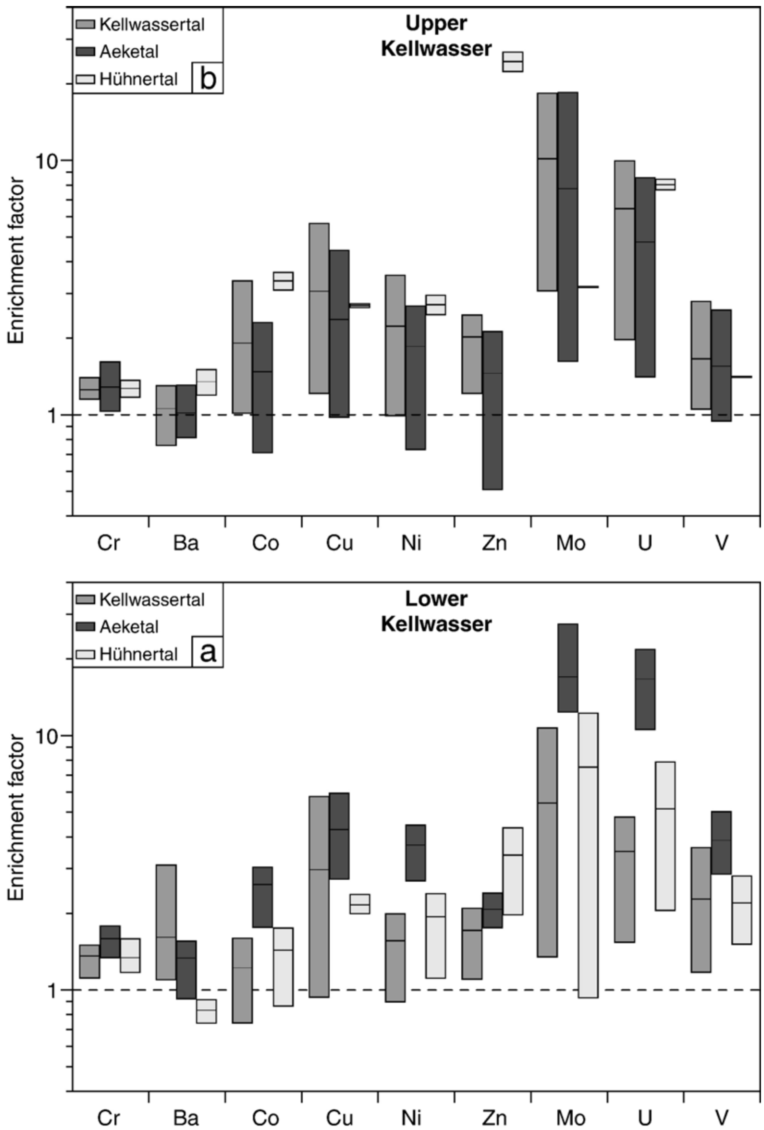


Fig. 6. Comparison of enrichment factor of some trace metals for the two Kellwasser horizons of the studied three sections. The extent of the boxes corresponds to the range of values (min–max) and the inner line to the average value. The enrichment factor for any element (e), $EF_{(e)}$, is equal to $(e/Al)_{sample}/(e/Al)_{shale}$. The dashed line indicates the value for which there is no enrichment/depletion with regards to average shale composition.

Mo and U within the black horizons indicates that the sediments were likely depleted in $O_2$ at the time of deposition of the KW horizons. Between these two redox-sensitive elements, enrichment in Mo within the KW horizons is the highest (Figs. 3 and 6), suggesting the possible presence of dissolved sulphide close to the sediment–water interface (Lyons et al., 2003; Algeo and Maynard, 2004; Tribovillard et al., 2005).

In addition, some redox indices, such as U/Th, V/Cr, Ni/Co and V/(V+Ni), were used. According to Jones and Manning (1994) and Rimmer (2004), these various ratios cannot be used reliably individually, but rather must be considered collectively. In the present case, these proxies behave consistently and show their highest values for samples of the Kellwasser horizons. It means that the most oxygen-poor conditions were met during the KW deposition. However, it is observed that only the upper part of the UKW records oxygen-restricted conditions, whereas the LKW integrally indicates $O_2$-restriction (Figs. 3 and 4). According to the considered ratio, the values point to dysoxic (Ni/Cr, V/Cr) or anoxic (U/Th) conditions. U/Th and V/(V+Ni) are the most and least discriminating proxies, respectively (Fig. 4). Nevertheless, following Rimmer's conclusion (2004), we do not pay too confident attention to the threshold values, and conclude from the ratios with oxygen-restricted conditions for the LKW and the upper part of the UKW horizons.

To summarize, our geochemical data (Al-normalized trace metal abundance and redox ratios) indicate two pulses of bottom water dysoxia to anoxia, coeval with the KW horizons in the drowned platform environments studied here (the entire LKW and the upper part of the UKW horizons).

Lastly, information concerning $O_2$ levels can also be deduced from the Mn/Al ratio. Manganese is frequently depleted in sediments in dysoxic to anoxic environment because manganese oxyhydroxides undergo reductive dissolution and are remobilized as soluble elements ($Mn^{2+}$) (Calvert and Pedersen, 1996; Tribovillard et al., in press). In contradiction to the above interpretation, Mn is relatively enriched in the KW horizons, notably in the Aeketal and Hühnertal sections. The Mn enrichment may be accounted for by the authigenic precipitation of manganese carbonates such as rhodochrosite ($MnCO_3$) or kutnahorite ($Ca(Mn,Mg,Fe)(CO_3)_2$) (Calvert and Pedersen, 1996). These minerals can form where carbonate supersaturation is reached in presence of solubilized $Mn^{2+}$ ions in pore waters. These minerals are thought to form close to the sediment–water interface, in marine anoxic sediments, overlain by oxic bottom waters (Calvert and Pedersen, 1996). In the Aeketal and Hühnertal sections, the KW horizons mainly correspond to pure limestone units, most of samples have $CaCO_3$ content higher than 90%. Good to moderate correlations between Mn/Al and Ca/Al are obtained ($0.69 < r < 0.94$), confirming that Mn could be potentially fixed in carbonate phases.

To summarize, in the drowned platform environments studied here, the two KW horizons correspond to sediments deposited in reducing environments, as indicated by the trace-metal parameters. However, the simultaneous enrichment in redox-sensitive, sulphide-forming elements, and Mn indicate that the sediments must have been reducing and that the redox chemocline (i.e., the boundary between oxidizing and reducing conditions) must have resided within the sediments or, at most, at the sediment–water interface. The chemocline can not have risen durably into the water column, because no such Mn enrichment could have been recorded. Thus, in agreement with Murphy et al. (2000a,b) and Racki et al. (2002), our observations are incompatible with a permanently stratified basin model.

### 5.3. Pyrite framboid size

Our results point out a slight Fe enrichment in the KW horizons unrelated to Al or Ti abundance. Such enrichment may be caused by the presence of syngenetic pyrite (e.g., Werne et al., 2002; Lyons et al., 2003; and references herein). Sedimentary pyrite forms as a consequence of bacterially mediated sulphate-reduction reactions generating sulphide ions ($HS^-/H_2S$) that combine with reactive iron (Berner, 1970, 1984). Several pathways are possible for sedimentary pyrite formation, but, most frequently, pyrite forms via a metastable "FeS" precursor. The transformation of FeS to $FeS_2$ needs the reaction of FeS with intermediate sulphur species such as $S^0$ and $S_x^{2-}$ and has been documented in the laboratory (Rickard, 1975; Schoonen and Barnes, 1991a,b; Wilkin and Barnes, 1996).

The oxidized intermediate S species may be produced by $H_2S$ oxidation near the redox boundary by oxidants such as $O_2$, $NO_3^-$, $MnO_2$, FeOOH (Middelburg, 1991; Suits and Arthur, 2000; Schippers and Jørgensen, 2001). In natural environments, the intervention of oxidized intermediate S species appears to be fundamental, and is consistent with the observation that for many environments, the majority of pyrite forms early, near the redox boundary, either in the water column (in euxinic settings) or within the sediments (Goldhaber and Kaplan, 1974; Calvert and Karlin, 1991; Middelburg, 1991; Canfield et al., 1992;

Lyons, 1997; Raiswell and Canfield, 1998; Hurtgen et al., 1999; Wijsman et al., 2001; Lyons et al., 2003; Allen, 2003).

Recent studies of pyrite framboid diameters from a variety of modern and past environments have provided a potential tool to distinguish ancient euxinic conditions from dysoxic–anoxic (non-sulphidic) conditions (Wilkin et al., 1996, 1997; Wignall and Newton, 1998; Taylor and Macquaker, 2000; Lyons et al., 2003; Bond and Wignall, 2005; Wignall et al., 2005). The basic idea is that pyrite growth requires the presence of (partially) oxidized S species ($S^0$) that can be found only close to the redox boundary. Thus, for anoxic sediments found beneath oxic or dysoxic bottom waters, the oxidants required for pyrite growth are supplied by diffusion from bottom waters to the sediment, bioturbation and burrow penetration into the underlying sulphate reduction zone. In a euxinic water column the only favourable place for framboid formation is within the water column, immediately beneath the redox boundary (Wilkin et al., 1996, 1997; Wignall and Newton, 1998; Wignall et al., 2005). In the water column, the pyrite particles sink to the seafloor before they reach appreciable diameters (only small euhedral crystals and small-sized framboid, i.e., a few micrometers large, can form) and no enlargement is observed after deposition (Wilkin et al., 1996, 1997; Wignall and Newton, 1998). Consequently, according to these authors, "euxinic" framboids are smaller and more constant in diameter than framboids formed within sediments underlying oxic or suboxic bottom waters.

Our SEM observations of the KW samples (Fig. 5) reveals the presence of dispersed pyrite framboids, more abundant in the Aeketal and Kellwassertal sections than in the Hühnertal section. The framboid diameters fall within the 2–15-μm range, which are rather considerable sizes. These observations indicate that pyrite growth occurred in presence of relatively abundant $S^0$, allowing the framboid to reach a large size. It is inferred that the paleoenvironmental conditions were not euxinic and that the redox boundary was probably lying close to sediment–water interface. The pyrite data thus confirm the interpretations derived from the geochemical data.

Lastly, the SEM–EDS analyses and observations reveal that pyrite framboids are partly oxidized, with a marked departure of S, indicating that they suffered from severe post depositional alteration. This strong oxidation is most probably attributable to late-diagenesis processes, in an intrusively tectonized area. The results show the partial or total departure of S from the pyrite framboids. It may be inferred that the trace metals, usually associated with pyrite (Ni, Cu, Co, Zn, Mo and Cr) may have also been leached from iron sulphides (at least partly). Consequently, the trace metal concentrations observed here must be looked at as minimum values, probably below the original concentrations at the time of sulphide precipitations.

### *5.4. Productivity conditions*

Both KW horizons record increased Cu/Al and Ni/Al ratios in the three sections. These elements are usually enriched in reduced sediments (Brumsack, 1989; Calvert and Pedersen, 1993). Recent studies (Algeo and Maynard, 2004; Tribovillard et al., 2005) emphasized the fact that Ni and Cu are mainly brought to the sediment in associations with OM and they are retained in the sediment within sulphides (usually solid solution within pyrite) even in the case of complete OM remineralization Thus, Ni and Cu are considered to be reliable tracers of the OM delivery to the sediment (Riboulleau et al., 2003; Algeo and Maynard, 2004; Tribovillard et al., 2005, in press). Thus, the positive peaks of the Ni/Al and Cu/Al ratios recorded here indicate that the KW horizons are interpreted as corresponding to episodes of increased OM influx, possibly recording increased productivity.

Barium is usually considered as a productivity proxy when brought to the sediment as barite (e.g., Dymond et al., 1992; McManus et al., 1998; Tribovillard et al., in press). However, barite ($BaSO_4$) may be sensitive to severe sulphate-reducing conditions (McManus et al., 1998). In the present case, Ba shows subtle enrichments in the KW horizons. These enrichments are coeval to those of Cu and Ni (Fig. 3). These observations suggest some increased productivity at the time of deposition of the KW horizons. However, the relatively low Ba enrichment, compared to Ni and Cu, could indicate Ba remobilization and loss after barite dissolution, as a consequence of the development of strongly reducing conditions below the sediment–water interface. This interpretation is, however, in contradiction with the Mn enrichment, indicating that oxidizing conditions were probably met close to the sediment–water interface. Consequently, the relatively low Ba concentrations are rather interpreted as resulting from moderate productivity increases. The slight increases of productivity resulted in increased delivery of OM and thus Ni and Cu. These elements could be trapped thanks to sulphide precipitation induced by the reducing conditions, the latter being partly induced by the increase OM influx. These interpretations underline the usually intertwined relationships between OM productivity and reducing conditions development. Lastly, a Si/Al peak is marked for the LKW horizon of the Aeketal section (Fig. 3), without coeval peaks of clastic proxies (Ti and Zr). The increased Si abundance must be the echo of a local increased biogenic productivity by silica-secreting organisms, consistent with the coeval enrichment in the abundance of the productivity proxies (Ni, Cu and Ba).

### *5.5. Summary*

Our geochemical data indicate that the two KW horizons correspond to episodes of development of reducing conditions, but the chemocline probably remained at small distance below the sediment–water interface. We have no indications that the redox conditions were constantly reducing, we shall interpret them as dominantly reducing. The LKW event seems to be more intense than the UKW, notably in the Aeketal and Hühnertal sections. The development of reducing conditions is attributed to moderate increases in surface-water productivity during periods of detrital influx decrease that probably reflect the transgressive nature of the KW horizons. These results from inorganic data, presented here, are in agreement with those obtained by Joachimski et al. (1994) concerning the $\delta^{13}C_{carb}$ isotopic signal in the studied three sections.

## 6. Discussion

### *6.1. The contrasting record of the two Late Frasnian anoxic events*

According to previous studies, mainly based on geochemical data (Bond et al., 2004; Riquier et al., 2005; Pujol et al., in correction), the onset of reducing conditions during the deposition of both black KW facies at the F–F boundary seems to be a widespread phenomenon, at least in European and North African areas, on both sides of the Eovariscan Belt. Nevertheless, some authors evidenced the diachroneity of the LKW that is sometimes not developed (e.g., in the Great Basin of the USA; Schindler, 1990, 1993; Crick et al., 2002).

Our results about the Harz sections show that the LKW horizon coincides with the development of dysoxic–anoxic conditions. They are consistent with those of Bond et al. (2004) and Riquier et al. (2005) that demonstrate that the early Upper *rhenana* anoxic event, corresponding to the LKW horizon, is strongly marked in some German sections (e.g., Steinbruch Schmidt) and Moroccan sections (e.g., Anajdam and Bou-Ounebdou), corresponding to submarine rise and platform settings, respectively. However, this anoxic event was not extended to the whole marine domain, as it is not clearly recorded in basinal environments, such as in Kowala (Poland) and La Serre (France) (Bond et al., 2004).Thus, the early Upper *rhenana* anoxic event, corresponding to the LKW horizons, appears to be limited to shallower environments.

In contrast to this first Late Frasnian anoxic event, the *linguiformis* anoxic event, corresponding to the UKW horizon, is recorded in platform and submarine rise settings, as well as in basinal settings (Joachimski et al., 2002; Racki et al., 2002; Yudina et al., 2002; Bond et al., 2004; Tribovillard et al., 2004b; Riquier et al., 2005; Pujol et al., in correction). In many submarine rise and platform sections (e.g., Aeketal, Hühnertal, Bou-Ounebdou), the inorganic geochemical data seem to indicate that the UKW horizon is less enriched in redox proxies (i.e., Mo, U, V), suggesting less reducing paleoenvironments, compared to the LKW horizon. Dysoxic conditions could prevail during the deposition of the second KW horizons in the more proximal settings. In the deepest sections (e.g., La Serre, Kowala Quarry), the oxygen-depleted conditions were strongly marked and could persist up to the Early Famennian (Upper *triangularis*) (Bond et al., 2004; Tribovillard et al., 2004b). According to these statements, it may be supposed that both anoxic events could have had different causes.

### *6.2. The possible causes of the two Late Frasnian anoxic events*

Nowadays, it is frequently considered that the F–F boundary represents an interval of eutrophication and major anoxic events in the oceans, during a “greenhouse” type period (Murphy et al., 2000a,b; Racki et al., 2002; Joachimski et al., 2002; Bond et al., 2004; Tribovillard et al., 2004b; Riquier et al., 2005; but see Ginter, 2002 for the opposite idea and discussion in Sandberg et al., 2002). Environmental changes led to widespread accumulation of organic-rich sediments, the Lower and Upper KW horizons and episode of major biotic turnover (McGhee, 1996). According to several authors (Algeo et al., 1995; Racki, 1998; Murphy et al., 2000a,b; Peterhansel and Pratt, 2001; Joachimski et al., 2002; Racki et al., 2002; Tribovillard et al., 2004b; Averbuch et al., 2005; Riquier et al., 2005), the transition from oxic to anoxic sediments at the F–F boundary occurred in several sedimentary basins all over the world (North America, Europe, China, North Africa) in response to increasing productivity resulting from the Frasnian sea-level rise and corresponding increase in surface water nutrient availability. Additional processes, such as thermohaline stratification and restricted lateral circulation in deep-water settings, are generally invoked to explain the development of oxygen-restricted conditions (e.g., Cruse and Lyons, 2004; Averbuch et al., 2005).

*6.2.1. The influence of productivity*

Based on the geochemical indices used here, it appears that the conditions during accumulation of the both KW horizons were most likely dysoxic, with possible intermittent periods of anoxic conditions, the LKW horizons probably representing the most $O_2$-depleted interval in shallow environments. In addition, the LKW horizon is characterized by periods of relatively increased productivity. For the LKW horizons, where positive peaks of redox indices and productivity markers are recorded, the "productivity" model (Pedersen and Calvert, 1990) could be applied to the drowned platform settings. Increased surface water productivity causes bottom water anoxia by driving benthic $O_2$ demand to exceed $O_2$ supply by water column mixing. According to the model of Algeo et al. (1995) and Joachimski et al. (2002), the primary productivity increase may have been induced by enhanced delivery of terrestrially derived nutrients by rivers. Basing on isotope arguments, Joachimski et al. (2002) rule out any marked influence of upwelling systems for the nutrient supply. Eutrophication would occur in more proximal environments, like platform in Germany and Morocco. The materials (sediments and nutrients) supplied by continental influx are usually deposited or consumed in nearshore environments and consequently the productivity should be limited in remote-offshore settings, far from riverine influx. This may explain why the Upper *rhenana* anoxic event, corresponding to the LKW horizons, is poorly recorded in basinal setting. The low concentration of terrigenous materials in distal setting should have been enhanced by the marine transgression associated with the deposition of the LKW horizon.

For the UKW horizon, where increases of productivity are coeval with milder $O_2$-depletion, compared to the LKW horizons, the application of the "productivity" model may be problematic. Surface productivity did not cause the onset of truly anoxic conditions, in that anoxic conditions only developed below the sediment–water interface, and in the upper part of the UKW horizon. So, it could be envisioned that surface water productivity was not the only triggering factor of reducing conditions in drowned platform setting. The main problem concerning the UKW horizon is that in deeper setting, such as La Serre, peaks of productivity higher than those recorded in platform environments, are recorded within the UKW horizon before the F–F boundary (Tribovillard et al., 2004b; Riquier et al., 2005). Peaks of $O_2$-depleted conditions are also higher than those recorded in platform environments and are observed few cm above the F–F boundary. For distal and deeper parts of basinal settings, the terrestrial influence is minimal and the concentration of terrigenous nutrients should be low. The source of nutrient has to be autochthonous and, thus, likely results from nutrients released from OM decomposition under reducing conditions. Some authors (Murphy et al., 2000a; Riquier et al., 2005) proposed the onset of positive feedback between anoxia–eutrophication–OM decay, based on the model of Ingall and Jahnke (1997) to account for productivity increases within the UKW horizon. So, unlike the Upper *rhenana* anoxic event during which productivity increase, coupled with sea-level rises, was probably the main cause of reducing conditions, the *linguiformis* anoxic-event productivity increase would be one of the consequences of the onset of anoxic conditions in bottom water. Of course, nutrients released from emerged land could have been added to those recycled by OM remineralization (Racki, 1998; Joachimski et al., 2002; Tribovillard et al., 2004b; Averbuch et al., 2005).

*6.2.2. The influence of sea-level fluctuations*

The sea-level change is considered as a major factor for the deposition of black horizons (e.g., Tyson and Pearson, 1991; Arthur and Sageman, 1994; Wignall, 1994; Arthur and Sageman, 2004). During periods of sea-level rise, the depocenters shift landward and the inputs of terrigenous material to deep marine environments are diminished. A decreased dilution of the sedimentary OM by the terrigenous fraction could be a possible factor triggering enhanced OM accumulation. For the last decades, it has been widely accepted that the formation of both KW horizons is linked to short-term transgressive–regressive pulses (Johnson et al., 1985; Sandberg et al., 1988, 2002; Buggisch, 1991). Deposition of both KW horizons occurred during a global Frasnian sea-level rise and corresponded to highstand periods of two punctuated transgressive phases (Johnson et al., 1985; Hallam and Wignall, 1999; Chen and Tucker, 2003, 2004).

In Germany and other areas, representing shallow marine environments (e.g., Morocco), the UKW horizon could result from the progressive impingement of anoxic water from deeper environment onto platform settings. The rise of bottom-water anoxia from deep to shallower setting may have been favoured by the pulse of sea-level rise during the *linguiformis* zone. Anoxia would thus originate from the deep parts of the ocean. The *linguiformis* transgressive phase may have allowed the onset of water stratification in the deepest settings, causing the establishment of anoxic conditions (Tyson and Pearson, 1991). Frequent mixing in platform environments would have cycled nutrients back into sea surface, stimulating higher productivity and introducing dissolved $O_2$ into bottom water. This may explain the observed record toward less reducing conditions during the *linguiformis* anoxic event, compared to the Upper *rhenana* anoxic event.

In platform settings, the UKW facies ended with the beginning of a well-marked Early Famennian sea-level fall (Devleeschouwer et al., 2002; Sandberg et al., 2002); more frequent water mixing and better oxygenation caused the end of deposition of black facies, and this process affected first the more proximal settings. In deeper environments, water stagnation, density contrast, and thus anoxia, were relatively more stable. Thus, reducing conditions could prevail in the basinal environments during F–F transition and could last until early Famennian (Lethiers et al., 1998; Racki, 1998; Joachimski et al., 2001; Bond et al., 2004; Tribovillard et al., 2004b, Riquier et al., 2005).

## 7. Conclusion

Our results allow us to suggest that the formations of the KW horizons occurred during times of oxygen-depletion at or slightly below the water–sediment interface in the relatively shallow environment of present-day Harz Mountains (Germany). Some differences exist between the two black KW horizons. In platform setting, the LKW horizon corresponds to dysoxic to anoxic conditions, whereas the UKW horizon seems to be mainly characterized by dysoxic conditions only. In basinal settings, the contrary is observed. From these statements, two kinds of processes are used to account for the two Late Frasnian black facies. The LKW horizon, corresponding to the Upper *rhenana* anoxic event, and recorded in platform settings, would result from increased productivity in shallow environments, whereas basinal settings kept on with oxygenated conditions. The nutrients causing the increased productivity originated from emerged lands. The UKW horizon corresponds to the *linguiformis* anoxic event and is markedly recorded in basinal environments and, to a lesser degree, in platform environments. In basinal settings, the development of reducing conditions was more drastic with euxinic conditions rising into water column, and lasted longer that in shelfal environments. The basinal settings also recorded more intense episodes of surface-water productivity than the platforms. Thus, the UKW event has mechanisms other than the LKW event. The onset of reducing conditions on the platforms may have two (complementary) causes. The first cause could be the raise of anoxic waters higher up in the water column in response to a marked sea-level rise and their impingement of platforms. The second cause could be the development of eutrophic conditions in basinal environments according to the model by Ingall and Jahnke (1997) of phosphorus regeneration under anoxic conditions (see also Murphy et al., 2000a). The eutrophication could cause the expansion of anoxic conditions in the water column, temporarily reaching and invading shelfal environments. After the contraction of the anoxic water mass, anoxia could still prevail in bottom environments but oxygenated conditions resumed on the platforms.

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