The astronomical rhythm of Late-Devonian climate change (Kowala section, Holy Cross Mountains, Poland)

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ARTICLE INFO

Article history:
Received 24 April 2012
Received in revised form
16 January 2013
Accepted 17 January 2013
Editor: G. Henderson

Keywords:
Late Devonian
Milankovitch forcing
limestone-shale rhythmites
Gondwanan glaciation
anoxic black shales
TR-cycles

Abstract

Rhythmical alternations between limestone and shales or marls characterize the famous Kowala section, Holy Cross Mountains, Poland. Two intervals of this section were studied for evidence of orbital cyclostratigraphy. The oldest interval spans the Frasnian–Famennian boundary, deposited under one of the hottest greenhouse climates of the Phanerozoic. The youngest interval encompasses the Devonian–Carboniferous (D–C) boundary, a pivotal moment in Earth’s climatic history that saw a transition from greenhouse to icehouse. For the Frasnian–Famennian sequence, lithological variations are consistent with 405-kyr and 100-kyr eccentricity forcing and a cyclostratigraphic floating time-scale is presented. The interpretation of observed lithological rhythms as eccentricity cycles is confirmed by amplitude modulation patterns in agreement with astronomical theory and by the recognition of precession cycles in high-resolution stable isotope records. The resulting relative time-scale suggests that /C24 800 kyr separate the Lower and Upper Kellwasser Events (LKE and UKE, respectively), two periods of anoxia that culminated in massive biodiversity loss at the end of the Frasnian. Th/U and pyrite framboid analyses indicate that during the UKE, oxygen levels remained low for 400 kyr and /C13Corg measurements demonstrate that more than 600 kyr elapsed before the carbon cycle reached a steady state after a +3‰ UKE excursion. The Famennian–Tournaisian (D–C) interval also reveals eccentricity and precession-related lithological variations. Precession-related alternations clearly demonstrate grouping into 100-kyr bundles. The Famennian part of this interval is characterized by several distinctive anoxic black shales, including the Anulata, Dasberg and Hangenberg shales. Our high-resolution cyclostratigraphic framework indicates that those shales were deposited at 2.2 and 2.4 Myr intervals respectively. These durations strongly suggest a link between the long-period (≈2.4 Myr) eccentricity cycle and the development of the Anulata, Dasberg and Hangenberg anoxic shales. It is assumed that these black shales form under transgressive conditions, when extremely high eccentricity promoted the collapse of small continental ice-sheets at the most austral latitudes of western Gondwana.

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1. Introduction

Throughout the Phanerozoic, the imprint of Milankovitch’s astronomical cycles is recognized in lithological rhythms, as well as in many geochemical and paleoecological proxies (e.g. Bouilla et al., 2011; Fischer and Bottjer, 1991; House and Gale, 1995; Tyszka, 2009). The study of cyclical change in sedimentary archives provides a better insight in the sensitivity of the Earth’s climate system to cyclic variations in the orbital parameters of the Earth (e.g. Lourens et al., 2010; Verschuren et al., 2009) and demonstrates that climatic setting strongly influences the response of climate to orbital forcing (Bouilla et al., 2011; Giorgioni et al., 2012). As a geo-chronometer, astronomical rhythms observed in a sedimentary archive provide insight into absolute and relative timing questions (Ghil et al., 2002; Kuiper et al., 2008; Muller and MacDonald, 2000).

A relevant astronomical imprint into climatic proxies has been successfully demonstrated in diverse cyclostratigraphic studies of Devonian carbonate-shelf archives, exemplified by Chen and Tucker (2003), Crick et al. (2002), De Vleeschouwer et al. (2012a, 2012b), Elrick and Hinno (2007), Elrick et al. (2009), Garcia-Alcalde et al. (2012) and House (1991, 1995). The Devonian system is poorly constrained by radiometric dating (see recent chronologies by Becker et al., 2012; Kaufmann,
and the refined analysis of sedimentary rhythmicity in stratigraphically extended and relatively continuous sequences remains an overall unexploited field and an urgent research aim, as stressed by House (2002) and Racki (2005). This study focuses on the conodont-dated and widely studied Late Devonian shelf-basin successions at Kowala, Holy Cross Mountains (central Poland; see regional geological setting in Chapter 2 and Supplementary material) characterized by distinct limestone-shale rhythmites (Bond and Zatoń, 2003; Fig. 2 in Marynowski and Filipiak, 2007; Fig. 2 in Marynowski et al., 2010; Fig. 3 in Racka et al., 2010; Fig. 3 in Racki et al., 2002; Fig. 1A and B in Racki, 2005; marly facies of Szulczewski, 1971; 1995). We test whether or not this rhythmicity is the result of astronomical forcing, within a climate on the eve of the transition from the Devonian greenhouse to the Carboniferous icehouse (Racki, 2005, p. 15; Streel et al., 2000). In addition, a comprehensive set of other environmental proxies, such as stable isotopes, magnetic susceptibility and gamma-ray spectrometry, which record only minor diagenetic/thermal overprint (Belka, 1990; Joachimski et al., 2001; Marynowski et al., 2011), serve as indispensable tools for the correct interpretation of the observed lithological variations in terms of paleoenvironmental change.

2. Regional and stratigraphic setting

Extensive outcrops of Middle to Upper Devonian reefal and basinal systems are exposed in the Holy Cross Mountains (see Supplementary material), that formed a fragment of the once vast equatorial carbonate shelves of south-eastern Laurussia (Racki, 1993; Racki et al., 2002; Szulczewski, 1995). The centrally located Frasnian Dyminy Reef evolved into a Famennian pelagic ridge, and this shoal was surrounded by drowned, oxygen-depleted deeper-shelf areas (i.e. intrashelf basins): Chęciny–Zbrza to the south, and Łysogóry–Kostomłoty to the north (Racki, 1993; Szulczewski, 1971, 1995).

The large, still active Kowala quarry near Kielce is well established as a major reference site for multifaceted Late Devonian studies. This more than 350 m thick, generally deepening-upward and continuous succession from the Chęciny–Zbrza basin is relatively well-dated using conodonts (Fig. 1), and comprehensively investigated from event-stratigraphical, paleontological and geochemical perspectives (summarized in Racki, 2005). The intensely studied distinctive Frasnian–Famennian and late Famennian bituminozous horizons record several recurrent anoxic pulses that are known to be of global extent (Filipiak and Racki, 2010; Kazmierczak et al., 2012; Marynowski and Filipiak, 2007; Marynowski et al., 2010; 2012; Racka et al., 2010).

Within the largely dark to black rhythmically bedded marly series, late Frasnian to basal Carboniferous lithologic units H–N successions were analyzed for cyclostratigraphy (Fig. 1): (1) The upper Frasnian to lower Famennian interval (sets H–1 to H–4) encompasses the Frasnian–Famennian (F–F) boundary beds and records one of the greatest biodiversity crises of the Phanerozoic, the Late Devonian mass extinction (Bond et al., 2004; Joachimski et al., 2002; Racki et al., 2002). Graded bioclastic limestones (with redeposited reef-builders and brachiopod coquinas) and/or thick (up to 1 m) slump layers occur in the basal (H–1) unit only. An abrupt lithologic change from wavy- and thin-bedded marly deposits, which are highly fossiliferous in places (unit H–2), to cherty limestone strata (H–3), is particularly significant for the F-F passage (Racki et al., 2002). These relatively thick-layered calcareous sets, 6 to 8 m thick, with thin (up to 5 cm) shale breaks, constitute the main lithologic peculiarity within the otherwise uniform marly rhythmic succession of set H. In fact, the succeeding monotonous fossil-impoverished unit H–4, which is more than 100 m thick, includes regularly alternating marly limestones and shales, here analyzed in the lower part only (see also Filipiak, 2009; Marynowski et al., 2011).

(2) The highest exposed interval contains the latest Devonian thicker-layered dark platy limestone-shale couplets, interrupted by the Annulata and Dasberg black shales (set K; details in Marynowski et al., 2010; Racka et al., 2010) and the grey to brownish fossil-rich wavy-bedded to (sub)nodular calcareous set with thin shale partings (Woclumeria limestone, set L, see Supplementary material; Marynowski and Filipiak, 2007; Rakocinski, 2011). The Hangenberg bituminous shale (90 cm thick, total organic carbon (TOC) up to 22.5 wt%), that also records a major biotic crisis, albeit of less significance than the F–F event, occurs above this interval. It is succeeded by a 120 cm thick grey-greenish clayey/tuffite succession with several interbedded limestone layers (the newly proposed set M= sets B and C sensu Malec, 1995; see also Marynowski and Filipiak, 2007, Fig. 2 therein). The Devonian–Carboniferous (D–C) boundary occurs within the upper part of this unit. The Lower Carboniferous comprises a greenish clayey/tuffite interval with four thin black shale intercalations (5 to 15 cm thick) and some nodular carbonate horizons. This recently exposed succession is named herein as set N (=lower part set D sensu Malec, 1995, Fig. 8).

The middle segment of the Famennian succession remains unexplored due to frequent diagenetic nodular lithologies that obscure the depositional rhythmicity (Fig. 1; Marynowski et al., 2007), as well as some fault disturbances and/or covered intervals (Fig. 2 in Bond and Zatoń, 2003).

3. Materials and methods

3.1. Time-series analysis procedure

The frequency composition of lithological variations (shales, marls, micrites, sparites, calcarenites and nodular limestones) were analyzed via spectral analysis. To carry out time-series analysis of lithological variations, each lithology was assigned a different code and a quantified litholog was obtained. Spectral analysis of proxy data, like the isotopic, magnetic susceptibility and gamma-ray spectrometry records, was carried out after detrending and interpolating the records to equally-spaced intervals. Proxy data and quantified logs were analyzed using the multitaper method (MTM: Thomson, 1982) as implemented in the SSA-MTM Toolkit (Ghil et al., 2002).

The MTM-method was performed using 3 discrete prolate spheroidal sequences (DPSS) as data tapers to compromise between spectral resolution and sidelobe reduction. Small variations in accumulation rate behave like phase modulations, and introduce multiple spurious spectral peaks (Muller and MacDonald, 2000). We chose the MTM because it averages these sidelobes into the main peak and thereby gives a superior estimate of the true spectral power. To assess whether or not the strongest spectral peaks are statistically different from the red noise spectrum, the 95% confidence level (CL) is calculated (robust AR(1) estimation, median smoothing window width = (10Δt)−1, Log Fit, f_{frequt}=2/Δt).

The Continuous Wavelet Transform is used to decompose the one-dimensional time-series into their two-dimensional

\[
\begin{align*}
D(t) &= -\log D(t) \\
\log F(t) &= D(t) \\
\log f(t) &= \frac{1}{\Delta t} \\
\end{align*}
\]
time–frequency representation. This method reveals the persistency of (astronomical) periodicities along the studied sections and provides a tool to detect changes in accumulation rate through associated changes in cycle thickness. Wavelet software was provided by Torrence and Compo (1998), using the Morlet wavelet function with wave number 6, zero-padding to the next higher power of 2, spacing between discrete scales ($D_j = 0.25$, smallest scale ($S_0) = 2\Delta t$, and the number of scales = $(\log_2(N\Delta t/S_0)/\Delta j) + 1$.

Frequency-selective filters or Gaussian band-pass filters isolate and extract the components of signals associated with a specific range of frequencies. We employ band-pass filters to assess the behavior of a specific range of frequencies in a studied signal using the Analyseries software (Paillard et al., 1996).

For a detailed description of the methodology of proxy record compilation, the reader is referred to the Supplementary material.

Fig. 1. Composite lithological section of the Upper Devonian strata at Kowala (after Szulczewski, 1996, Fig. 8, modified and supplemented in the topmost part by recently exposed sets M and N). The reference succession shows environmental evolution typical of intermittently drowned shelf from reef (units A–C) to foreslope (D–G) to intrashelf basin (H–N).
4. Results and discussion

4.1. Do limestone-marl rhythmites reflect primary environmental change?

Rhythmic alternations between limestones, shales and marls are abundant throughout the entire Phanerozoic. Before any climatic interpretation can be made, or any astronomical cycle can be recognized, the primary origin of the alternations between different lithologies needs to be demonstrated (Westphal et al., 2010). Several arguments strongly suggest that, with some exceptions noted below, diagenesis can be excluded as the driver for the decimeter-scale rhythmic interbedding that dominates the Kowala section. (1) The immature character of the organic matter indicates burial temperatures lower than 75 °C (Belka, 1990). Immaturity to low-maturity is confirmed by an average vitrinite reflectance value of 0.53% (Marynowski et al., 2001), the temperature of maximum release of hydrocarbons (Joachimski et al., 2001; Marynowski and Filipiak, 2007; Marynowski et al., 2007; 2010) and hydrogen, oxygen and conodont alteration indexes (Joachimski et al., 2001). (2) Many primary sedimentary structures are well preserved, including distinctly graded limestone layers, hummocky stratification, trilobite obtrusion deposits, extensive lateral continuity, burrow fills, and web-like structures typical of benthic cyanobacterial mats (Kazmierczak et al., 2012; Marynowski et al., 2011; Racki et al., 2002; Radwanski et al., 2009; Szulczewski, 1971). Moreover, delicate fossils, such as Phyllocarida and other crustaceans, ostracod-shells and aptchi of the goniatite Tornoceras (Deiz, 2006) as well as carbonized thalli of large algae with filamentous internal structure (Fig. 3B in Racki et al., 2002) are superbly preserved. The exceptional preservation of these fossils and sedimentary structures demonstrates minimal diagenetic alternation in this section and thus a limited applicability of the early diagenesis unmixing model (Kazmierczak et al., 2012; Marynowski et al., 2011; Racki et al., 2002; Radwanski et al., 2009; Szulczewski, 1971). Moreover, delicate fossils, such as Phyllocarida and other crustaceans, ostracod-shells and aptchi of the goniatite Tornoceras (Deiz, 2006) as well as carbonized thalli of large algae with filamentous internal structure (Fig. 3B in Racki et al., 2002) are superbly preserved. The exceptional preservation of these fossils and sedimentary structures demonstrates minimal diagenetic alternation in this section and thus a limited applicability of the early diagenesis unmixing model (Kazmierczak et al., 2012; Marynowski et al., 2011; Racki et al., 2002; Radwanski et al., 2009; Szulczewski, 1971). (3) The character of δ13C and δ18O variations in whole-rock samples appear to reflect a predominantly primary signature. Indeed, the isotopic data presented in this study (Figs. 3E and F and 6G and H) fall entirely within the range of δ13C and δ18O for Upper Devonian–Lower Carboniferous brachiopod shell calcite (Giles, 2012; van Geldern et al., 2006; Veizer et al., 1999). Furthermore, the recognized δ13C trends in calcites at Kowala correlate with organic carbon data (Fig. 3E and G; Joachimski et al., 2001) and the δ18O pattern shows the same trends as diagenetically resistant conodont apatites (Fig. 5 in Joachimski et al., 2009). Consequently, in this section, diagenesis appears so moderate that post-depositional incorporation of light isotopes into calcite is negligible. Above all, meteoric diagenesis, paired with strongly distorted isotopic signatures due to the influence of 12C and 16O enriched fluids, is essentially absent in deeper-shelf facies. Indeed, the reported δ13C and δ18O series exhibit frequent enrichments in heavy isotopes of 13C and 18O respectively, which cannot be attributed to diagenetic processes (Joachimski et al., 2001; van Geldern et al., 2006). Pressure solution carbonate re-mobilization is attested by a crudely laminated ribbon-facies in sharp contact with neomorphosed crystal-line carbonate and pressure-welded (stylolominate) argillaceous interbeds (especially in unit H-3; Figs. 12D and 16C in Racki et al., 2002). This conspicuous diagenetic instability of the precursor carbonate muds may be promoted by mass abundance of susceptible opaline skeletons (radiolarians, silicospores) and chert formation near the F–F boundary only (Vishnevskaya et al., 2002). Nevertheless, the isotopic ratios still indicate a primary origin of the alternating lithologies as manifested by the mostly positive δ13C values (Fig. 3E) in the broad F–F transition, concurrent with the global UKE isotopic pattern (Joachimski et al., 2001; Marynowski et al., 2011; Racki et al., 2002). Shallow-burial selective dissolution and cementation of the organic-rich carbonate muds during anaerobic oxidation of organic matter, as well as secondary limestone-shale cyclicity caused by anaerobic methane oxidation, are associated with exceedingly negative δ13C values, as low as −5% to −42% (Coniglio, 1989; Raiswell, 1988). Therefore, early diagenetic processes in the mostly organic-enriched carbonate-clayey deposits (TOC typically > 0.5% in dark shales, but > 20% in the black horizons) are precluded as the driver of the rhythmic bedding.

In the F–F transition, a possible extreme condensation (or even a cryptic hiatus?) embracing the basalmost triangularis Zone should be taken into account, since the (late) Pa. triangularis occurs right at the base of the Famennian (Racki et al., 2002). On the other hand, syndepositional and shallow burrial depth dissolution in starved sedimentation regimes is also commonly documented in the Woculmeria limestone, especially by irregularly wavy inter-layer contacts and the abundance of dissolved aragonite shells (encrustations on cephalopod internal mounds; Rakocinski, 2011).

The rhythmical alternations between limestone and shale in the studied intervals of the Kowala section are interpreted to be primary depositional features, even if diagenetically enhanced bedding (Bathurst, 1987) is a feature of some packages and event beds in the succession (e.g. obtrubation trilobite rhythmites; Brett et al., 2012). The associated facies changes reflect repetitive variations in carbonate content, in response to changes in the water column and in the geochemical conditions at the sediment/water interface. These are most probably driven by climate. Indeed, terrigenous clay and silt input is highly dependent on prevailing wind and precipitation patterns, while carbonate productivity is strongly affected by temperature, salinity, storm frequency and wave energy (Erick and Hinov, 2007). The observed lithological variations can thus be used as a continuous high-resolution, 104 yr-scale, record of Late Devonian climate, highly suitable for cyclostratigraphic purposes. For this reason, lithological variations are used as the starting point for time-series analysis and as the foundation for an astronomical cyclostratigraphy. Subsequently, geochemical proxies and their possible cyclical character are placed in the established cyclostratigraphic framework and interpreted in terms of climate change.

4.2. Interval I: the Frasnian–Famennian transition

The time–frequency representation (Fig. 2A) and the MTM-spectrum (Fig. 2B) are combined to give an overview of the dominant periodicities in the lithological variations between shale (coded 0), micrite (coded 2), sparite (coded 3) and calcarenite (coded 4; lithologic log by Bond and Zatonski, 2003, and D. Bond unpublished data). This ranking scheme is chosen to emphasize the alternations between shales and limestones (micrite, sparite and calcarenite). A very strong low-frequency cycle, characterized by 700–1250 cm thick cycles is highlighted (Fig. 2A and B). The wavelet-analysis’ time–frequency representation demonstrates that this cycle is particularly strong in the lowermost Famennian, between 30 and 120 m above the base of the section. Secondly, a strong and distinct spectral peak occurs between a 160 and 256 cm period (Fig. 2B). Wavelet analysis indicates strong spectral power in this frequency range, although the time–frequency representation is characterized by multiple bifurcations (splitting or braiding). The interpretation of these two important cyclical components as the result of an astronomical forcing parameter requires an independent time-control. In this case, time-control comes from conodont zonation based on Szulczewski (1995, 1996), Racki and Balinski (1998) and Racki et al. (2002). The rhenana, linguliformis and triangularis zone span 81.9 m of section. Consensus on the total duration of these
biozones has yet to be reached in the literature. The recalibrated Devonian timescale of Kaufmann (2006) suggested a combined duration of 5.8 Myr for these zones, implying an average accumulation rate of 14.12 m/Myr. De Vleeschouwer et al. (2012b) found that Kaufmann’s (2006) Frasnian chronology overestimated the duration of the entire stage by 17%, and so it is likely that true duration is less than 5.8 Myr. In contrast, Bai (1995) indicated that the rhenana to triangularis zone record only 3.2 Myr of time, which would imply a much higher average accumulation rate at Kowala of 25.6 m/Myr. Most likely, the true combined duration of the rhenana, linguiformis, and triangularis zone lies between these two end-members. Therefore, it is reasonable to assume an average accumulation rate of around 20 m/Myr. In this scenario, the observed 700–1250 cm cycles can be interpreted as the result of 405-kyr eccentricity forcing and the 160–256 cm cycles as the result of 100-kyr eccentricity forcing (Table 1). This interpretation is reinforced by the observed bifurcations in the ~2 m cycles, every 405 kyr, because of the long-eccentricity amplitude modulation of the 100-kyr cycles (indicated by grey circles on Fig. 2A; Meyers and Hinnov, 2010). However, two problems arise with this interpretation: [1] at ~40 m and ~100 m bifurcations in the ~2 m cycles are missing (indicated by ‘?’ in Fig. 2A) and [2] in the lower part of the interval, the low-frequency cycles lack the strong spectral power that would be expected from a phase-coherent and stable 405-kyr eccentricity forcing. Different interpretations can explain these observations in a valid manner. However, the astronomical interpretation is maintained as the listed problems most likely reflect a non-response to orbital forcing (see Supplementary material for a more detailed discussion). Indeed, the 40 m level coincides exactly to the interval

Fig. 2. Periodicities in the lithological variations of the upper Frasnian-Lower Famennian part of the Kowala section. (A) Time–frequency representation resulting from wavelet (Morlet) analysis. Red colors indicate the stratigraphic levels (x-axis) and periodicities (y-axis) that are characterized by high spectral power. The whitish bands and dashed lines indicate the periods associated with 405-kyr (E1) and 100-kyr (E2) eccentricity throughout the section. The bifurcation pattern at the 100-kyr period, indicative for amplitude modulation by the 405-kyr cycles, is shown by rounded rectangles. (B) MTM-power spectra showing distribution of spectral power with 95% confidence level (CL). (C) The E1-filtered lithological signal (purple line). (D) The E2-filtered lithological signal (olive colored line) and its amplitude envelope (purple dashed line). (E) Lithological variations (black solid line). BP=Bandpass.
between the LKE and the UKE recorded by monotonous, clay-rich and fossil-impoverished micrites. Such a long interval (\(\tau/24800\) cm) of unchanged lithology is exceptional at Kowala. Consequently, the loss of low-frequency spectral power in the lower part of this interval is interpreted as the expression of a climate system that was disturbed in such a way that the response to orbital forcing was overpowered. At the 100 m level, an exceptionally long interval of unchanged lithology suggests weak orbital forcing, or a climate system that was insensitive to orbital forcing, or a combination of both. A possible hiatus is considered unlikely because conodont biostratigraphy and microfacies do not reveal any large-scale sedimentary discontinuity (Racki et al., 2002) and the estimated duration between the LKE and UKE (\(\tau/24800\) kyr) is in good agreement with other estimates (Chen and Tucker, 2003; Chen et al., 2005).

In Fig. 2C and D respectively, the low- and high-frequency cycles were filtered out and the amplitude envelope of the high-frequency cycles is calculated using the Hilbert transform. The amplitude envelope of the 100-kyr eccentricity cycles seems to mimic the pattern of the 405-kyr cycles, as is expected from astronomical theory (Laskar et al., 2004). The similarity between these signals confirms the veracity of the 405-kyr cycles in the lower part of the section, despite the moderate spectral power. At the 40 m and 100 m levels, the non-response to orbital forcing removed the 100-kyr cycles, while the 405-kyr cycle is still observable. Indeed, a \(\tau/240.5\) Myr non-response is not apparent in the 405-kyr bandpass filtered record due to the smoothing inherent in the filtering procedure. The correspondence between the filtered 405-kyr cycles and the 405-kyr pattern in the amplitude envelope of the 100-kyr cycles enables the delineation of 13 complete 405-kyr eccentricity cycles, indicated by purple bands on Fig. 2. Since these thirteen 405-kyr cycles span 105 m, a cyclostratigraphically derived average accumulation rate of 19.9 m/Myr can be calculated. Based on this cyclostratigraphic interpretation, we estimate the time difference between the Lower and the Upper Kellwasser Event (LKE and UKE respectively) to include two 405-kyr eccentricity cycles, i.e. \(\tau/240.8\) Myr. This duration compares well the 10 cycle-sets (100 kyr each) presented by Chen and Tucker (2003) and Chen et al. (2005) between the 4rd-order sea-level transgressions associated with the LKE of the early Late \textit{rhenana} Zone and the UKE of the Late \textit{linguiformis} Zone in Guangxi, southern China. Moreover, it agrees well with the time-difference between the sequence boundary dates of the two latest Frasnian TR-cycles (i.e. respectively 376.0 and
375.2 Ma (Haq and Schutter, 2008), of which the respective transgressions are associated with LKE and UKE anoxic deposition (Bond and Wignall, 2008).

Geochemical proxy data is plotted next to the cyclostratigraphically delineated eccentricity cycles in Fig. 3. The Th/U ratio, a proxy for the intensity of anoxia, shows a gradual increase towards more oxic values throughout the section, with important meter-scale variations superimposed on the long-term trend. The MTM spectral plot of the Th/U ratio in the lowermost 115 m of the section (Fig. 3H) demonstrates a moderate peak of spectral power around 0.00125 cycles/cm, i.e. the frequency at which one would expect the influence of 405-kyr eccentricity forcing. A more important spectral peak (> 95% CL) is observed at frequency 0.0025, indicating ~200-kyr climatic fluctuations. Interestingly, this ~200-kyr rhythm is also observed in the carbon and stromium records of F–F sections from South China (Chen et al., 2005). The source of this signal might be the 174 kyrm amplitude and frequency modulation of obliquity (Hinnov, 2000). However, more high-resolution records are needed to confirm this link. The spectral curve also clearly rises around frequency 0.005 cycles/cm, i.e. the frequency of 100-kyr cycles, but the resolution of the Th/U record is too low to reliably distinguish these cycles. A similar pattern is recorded by the concentration of potassium (K wt%; Fig. 3I), which is mainly a proxy for the detrital clay fraction. The dashed lines in Fig. 3C and D represent the 405-kyr variations of the Th/U ratio and K concentration respectively. In particular, the K concentration follows the 405-kyr cycles that were delineated on lithology. Consequently, it is suggested that stronger lithological variations occur during periods of intense input of detrital clays. The Th/U data in Fig. 3C indicates that during the UKE, oxygen levels remained depleted for ~400 kyrm. This is in agreement with previous estimates based on pyrite framboïds (Bond et al., 2004).

Carbon and oxygen isotopes were measured at decimeter resolution, through a 16 m interval that straddles the F–F boundary. Joachimski et al. (2001) lower-resolution carbon isotope record from another Kowala section is plotted for comparison. The results of MTM and wavelet analyses on the uppermost 115 m of the section (Fig. 3I), which is mainly a proxy for the detrital clay fraction. The dashed lines in Fig. 3C and D represent the 405-kyr variations of the Th/U ratio and K concentration respectively. In particular, the K concentration follows the 405-kyr cycles that were delineated on lithology. Consequently, it is suggested that stronger lithological variations occur during periods of intense input of detrital clays. The Th/U data in Fig. 3C indicates that during the UKE, oxygen levels remained depleted for ~400 kyrm. This is in agreement with previous estimates based on pyrite framboïds (Bond et al., 2004).

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<th>Sed. rate</th>
<th>7.11 m/Myr</th>
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<td>352–628 kyr</td>
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<td>100-kyr eccentricity</td>
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Joachimski et al., 2009). Putting these isotopic records in our cyclostratigraphic framework, it suggests that for the carbon cycle, after the +3% UKE excursion in δ13Corg, more than 600 kyr were needed before a more or less steady state was reached (Fig. 3G).

The MTM spectral curves of our high-resolution isotope data show sharp and strong (> 95% CL) spectral peaks (Fig. 3 and K): δ13C and δ18O display an important spectral peak around frequency 0.011 cycles/cm. Following our astronomical interpretation, these cycles have a duration of ~47 kyr, and cannot be directly attributed to an astronomical forcing factor. In contrast, the elevated spectral power observed for both δ13C and δ18O around frequency 0.027 cycles/cm occurs exactly at the frequency at which one expects the influence of ~18-kyr precession. The recognition of this ~18-kyr period in environmental proxies such as δ13C and δ18O demonstrate the importance of precessional forcing on the Late-Devonian tropical climate. Indeed, in modern tropical environments precession is the most important driver of 104-kyr scale climate change, most often by influencing monsoonal patterns and intensity (Kutzbach, 1981; Kutzbach and Liu, 1997; Tuenter et al., 2003). In comparison with the modern world, Devonian tropical climate potentially exhibited an even more intense monsoonal circulation (Streel et al., 2000), characterized by seasonally wet-and-dry climates (Cecil, 1990); on which precessional variations undoubtedly had a significant influence (De Vleeschouwer et al., 2012a). Despite the fact that 20 Myr separate the present study from the Belgian section analyzed by De Vleeschouwer et al. (2012a), they share a similar paleogeographic setting on the southeastern margin of Laurussia, at a tropical latitude. Thus, a comparable paleoclimatic model can be applied to interpret the precessional cycles observed in both sections. The presence of a precessional rhythm in Frasnian–Famennian climate change at Kowala also explains why eccentricity-related periods show up in the shale-limestone alternations. Eccentricity only marginally influences insolation, but it appears as the envelope of the precession parameter (Muller and MacDonald, 2000).

4.3. Interval II: Devonian–Carboniferous interval

The results of MTM and wavelet analyses on the upper Famennian to lower Tournaisian lithological variations are presented in Fig. 4A. This part of the Kowala section is characterized by shales (coded 0), marls (coded 1), nodular limestones (coded 2) and micrite (coded 2.5; Marynowski and Filipiak, 2007; Marynowski et al., 2010; Racka et al., 2010). This scheme is thought to reflect relative changes in clay-content. In the upper part of the studied interval, an important low-frequency component is suggested at periodicities between 170 and 390 cm. A very strong decimeter-scale cycle is denoted, characterized by a 40–80 cm period. Wavelet analysis suggests that this cycle is persistent throughout the entire Famennian part of the section, though characterized by multiple bifurcations, and that it disappears upon reaching the Tournaisian. Between 1600 and 2900 cm, the importance of a high-frequency cycle with a 8–12 cm periodicity is demonstrated by both MTM and wavelet analysis. The interpretation of the observed cyclicity requires independent data from the sedimentary record.
biostratigraphic time-control: the Annulata Event, recorded in the lower part of this interval occurs within the uppermost trachytera Zone. According to Kaufmann’s (2006) chronology, ~4.7 Myr separate the trachytera conodont zone and the D–C boundary. According to Becker et al. (2012, Table 22.2), the same interval spans 4.1 Myr. Bai (1995) again suggests a shorter duration for the same interval (2.9 Myr), but in this case, the true combined duration of the considered biozones is most probably much closer to the estimates of Kaufmann (2006) and Becker et al. (2012), given the multiplicity of U–Pb ID-TIMS absolute ages available for the latest Famennian (Richards et al., 2002; Streel, 2000; Trapp et al., 2004; Tucker et al., 1998). In the studied section, 25 m span the interval between the Annulata Event and the Famennian/Tournaisian boundary, implying an average accumulation rate of ~5.7 m/Myr. This value is in stark contrast to the 4-times higher accumulation rate found at the Frasnian–Famennian interval of the studied section. For slower accumulation also comes from diverse sclerobionts that utilized the shells of dead cephalopods as a hard substrate for their settlement (uppermost Famennian; Rakocinski, 2011) and from corrosional surfaces related to syndepositional shallow burial-depth dissolution (Berkowski, 2002). Also, as the section becomes much more shale dominated, a slower accumulation could be expected, possibly in response to the shutdown in primary productivity following various extinction events (i.e. a less productive carbonate factory) and to starved sedimentation regimes during the Famennian global climate cooling (Caputo et al., 2008; Isaacson et al., 2008; Joachimski et al., 2009; Streehl, 2000). A ~5.7 m/Myr accumulation rate gives rise to the interpretation of the low-frequency cycles as the result of 405-kyr eccentricity forcing (Table 2). The 48–75 cm cycles match 100-kyr eccentricity cycles and the 8–12 cm cycles can be seen as the result of precessional forcing (Table 2). The extremely low spectral power in the 405-kyr frequency range in the first portion of the record questions this interpretation, as the 405-kyr eccentricity cycle is remarkably phase-coherent and stable. However, the strong bifurcating pattern in the 100-kyr frequency range appears to be a pristine short-eccentricity signal. The lack of spectral power between 0 and 1400 cm is seen as the result of the non-linear recording of climate forcing. Fig. 4C and D shows the bandpass filters at the frequencies of 405-kyr and 100-kyr eccentricity respectively. The amplitude envelope of the 100-kyr cycles, calculated using the Hilbert transform, appears to bundle the 100-kyr cycle in groups of four, as expected from astronomical theory. However, at several stratigraphic positions, a mismatch between the amplitude modulation of the 100-kyr cycles and the 405-kyr cycles is observed. This phase-lagged amplitude modulation does not undermine the astronomical interpretation, as phase and amplitude distortions can be induced by the non-linear translation of sea-level change to offshore sediment flux (Laurin et al., 2005). Mainly based on the amplitude envelope of the 100-kyr cycles, 12 complete 405-kyr eccentricity cycles were delineated and are
indicated by purple bands in Fig. 4. Together, these 12 cycles (4.86 Myr) span 2650 cm, resulting in a refined accumulation rate of 5.45 cm/kyr.

The uppermost Famennian part of the Kowala section (1500–3000 cm) is characterized by cm-scale alternations between limestones and shales. These high-frequency rhythmites were analyzed in more detail to assess the astronomical forcing by precession (Fig. 5). The 40–80 cm cycles are associated with 100-kyr eccentricity while the 8–12 cm cycles are interpreted as the result of precessional forcing. A band-pass filter centered on the frequency of precession shows that the amplitude of the precessional cycles varies significantly (Fig. 5D). The amplitude envelope of the precessional cycles was calculated using the Hilbert transform and compares favorably with the 100-kyr eccentricity cycles. Since the amplitude modulation of precession by eccentricity is expected from astronomical theory, the astronomical interpretation of the different observed cycles is reinforced. Moreover, the dominance of precession may also explain amplitude modulation mismatches between long and short eccentricity cycles, discussed above. Indeed, an important mismatch occurs in that part of the section where precession-related lithological variations can be firmly grouped in 100-kyr bundles, but where grouping in 405-kyr “super-bundles” is much less obvious.

The geochemical data available for this interval is not suitable for time-series analysis: for the isotopic proxies (Fig. 6G–I),

| Table 2 | Astronomical interpretation in the upper Famennian–lower Trounaisian part of the Kowala section. |
|-----------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| Sed. rate       | Half biostratigr. acc. rate 2.85 m/Myr           | Biostratigr. derived acc. rate 5.7 m/Myr        | Double biostratigr. acc. rate 11.4 m/Myr        |
| Frequency range | 170–390 cm: 0.6–1.4 Myr                         | 40–80 cm: 140–280 kyr                           | 8–12 cm: 28–42 kyr                              |
|                 | 298–684 kyr                                      | 70–140 kyr                                      | 14–21 kyr                                       |
|                 | 150–342 kyr                                      | 35–70 kyr                                       | 7–10 kyr                                        |
|                 | 405-kyr ecc.                                     | 100-kyr ecc.                                    | 18-kyr prec.                                    |

Fig. 5. Periodicities in the lithological variations of the upper Famennian part of the Kowala section, between 1500 and 3000 cm. This portion is analyzed in detail because it is characterized by high-frequency lithological variations. (A) Time–frequency representation resulting from wavelet (Morlet) analysis. Red colors indicate the stratigraphic levels (x-axis) and periodicities (y-axis) that are characterized by high spectral power. The whitish bands and dashed lines indicate the periods associated with 100-kyr (E2) eccentricity and precession throughout the studied interval. The strong bifurcation pattern at the precessional period, indicative for amplitude modulation by the 100-kyr cycles is shown by rounded rectangles. (B) MTM-power spectra showing distribution of spectral power and 95% confidence level (CL). (C) The E2-filtered lithological signal (olive colored line). (D) The precession-filtered lithological signal (green line) and its amplitude envelope (olive colored dashed line). (E) Lithological variations (black solid line). BP = Bandpass. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
resolution and/or dataset-length are too low; for magnetic susceptibility (Fig. 6C), unequal spacing of data makes MTM and wavelet analysis meaningless. The TOC, TS and CaCO3 concentrations simply reflect lithological variation between shale and limestone, and therefore do not add to the paleoenvironmental information that is already contained in the lithological variations themselves. Excessive burial of organic matter, expressed by the Dasberg, Kowala and Hangenberg black shales, is clearly indicated by increased TOC, TS and decreased CaCO3 concentrations (Fig. 6D–F). All anoxic shales in the studied interval have been interpreted to be the result of repeated transgressive pulses, accompanied by the blooming of primary producers (Joachimski et al., 2001; Kaiser et al., 2008; Marynowski et al., 2010, 2012; Racka et al., 2010). Enhanced bioproduction is reflected by positive δ13Corg excursions of about 4‰, up to values of −25‰ in the limestone enclosing the shales (Fig. 6I). Oxygen isotope excursions associated with anoxic black shale formation.

These values accord with the sequence boundary ages reported by Haq and Schutter (2008), who estimate a duration of 2.4 and 1.8 Myr for the corresponding 3rd-order sea-level changes. Interestingly, a ~2.4 Myr cycle is present in the Earth’s eccentricity. The same correspondence between third-order sea-level changes and long-period ~2.4 Myr eccentricity has been reported for the Mesozoic greenhouse world (Boulila et al., 2011). Hence, one can hypothesize an astronomical influence on the timing of the development of transgressive-regressive (TR) cycles and the associated deposition of anoxic black shales (as has already been suggested for Cretaceous anoxic shales; e.g. Lanci et al., 2010; Mitchell et al., 2008). During greenhouse periods such as the Mesozoic and the Devonian, thermoeustasy or variations in
storage of groundwater and lakes can account for a maximum of 10 m of sea-level change (Jacobs and Sahagian, 1993; Schulz and Schafer-Neth, 1997). Yet, it is clear that the amplitude of sea-level change in the uppermost Devonian was at least 4 to 5 times higher (Haque and Schutter, 2009). Therefore, we suggest that the presence and extent of small continental ice sheets on (western) Gondwana could be strongly influenced by eccentricity. This assumption is supported by Late Devonian glacial marine deposits in Peru, Bolivia and Brazil that record important regional glaciations on the western margin of Gondwana at mid-to-high latitudes (40–50°; Blakely, 2008; Caputo et al., 2008; Issacson et al., 2008). During periods of low eccentricity, austral summer insolation at the high latitudes of the Gondwana continent would not have reached high values, which gives these small continental ice sheets a good chance to survive summer and to continue to grow during the following winter. Thereby, the Earth’s climate is gradually cooled (phase 1 in the oxygen isotope record in Fig. 6H). In contrast, high eccentricity triggers maximal austral summer insolation when \( \alpha = 90^\circ \) (perihelion in December), causing important melting and ice sheet collapse, associated sea-level rise and global warming (phase 2). Global warming combined with late Famennian atmospheric \( {\text{O}_2} \) levels exceeding the 13% threshold for the occurrence of widespread wildfires (Marynowski and Filipiak, 2007; Marynowski et al., 2010; 2012; Rimmer et al., 2004), led to the establishment of optimal conditions for increased primary production and bottom-water anoxia. The enhanced burial of organic carbon reduces the C concentration of the ocean’s surface layer, that is compensated by additional dissolution of \( \text{CO}_2 \) from the atmosphere. The climatic cooling resulting from the drawdown of atmospheric \( \text{CO}_2 \) is reflected by temporarily increasing \( \delta^{18}\text{O} \) values during black-shale deposition (phase 3). This cooling-phase appears to be short-lived (~200 kyr) and is probably counteracted by the astronomical configuration favoring climatic warming (phase 4). Several hundred of kyr’s later, eccentricity and resultant maximal summer insolation in Gondwana weakens, enabling ice to survive summer and accumulate once more (phase 5).

Compared to the Annulata, Dasberg and Hangenberg Shales, the Kowala anoxic shale is a much thinner organic-rich layer. Although it occurs exactly halfway between the Dasberg and Hangenberg Shales, it was probably not triggered by astronomical forcing but rather as the result of regional tectonic activity. Indeed, the Kowala Shale is geographically limited to the Hangenberg Shales, it was probably not triggered by astronomical forcing but rather as the result of regional tectonic activity. Hangenberg Shales, it was probably not triggered by astronomical forcing but rather as the result of regional tectonic activity.

4.4. On the origins of limestone-shale/marl alternations

The limestone-shale/marl alternations in both studied intervals of the Kowala section demonstrate clear orbital signatures of precession and eccentricity and it can be assumed that facies changes reflect a climatic signal. Carbonate-rich layers (limestones) are interpreted to form under warm and dry conditions with less runoff from land, reduced weathering, less frequent storm events (i.e. low dilution by terrigenous influx) and enhanced carbonate productivity. Carbonate-poor layers are thought to result from a lower carbonate productivity under cooler climatic conditions, associated with wetter conditions and enhanced clastic input.

However, the exact same response mechanism is used to explain millennial-scale paleoclimate rhythms, expressed by individual limestone-shale couplets (Chen and Tucker, 2003; Elrick and Hinov, 2007), despite the order of magnitude difference between the sub-Milankovichi and Milankoviči time-scale. To address this discrepancy, accumulation rate, duration of the studied interval and time-scales of the distinguished paleoclimatological rhythms in lithology are compared to the Devonian and lower Carboniferous sections in Elrick and Hinov (2007), the F–F section in Chen and Tucker (2003) and both intervals from this study (Table 3). From this table it is apparent that a high accumulation rate (several cm's/kyr) is needed for lithological variations to record millennial-scale climate change. In sections like Kowala, where accumulation occurs at an order of magnitude more slowly, limestone-marl/shale alternations represent Milankoviči-scale climate change. In summary, terrigenous input to the basin and carbonate productivity vary at both time-scales, but only in rapidly accumulating settings millenial-scale rhythmicity can be registered as lithological variations. On the other hand, only sections characterized by a sufficiently long duration of deposition (e.g. Kowala) are suitable for the detection of Milankovichi-scale cyclicity. Orbital forcing is known to be a powerful driver of climate change, whereas the driver of millennial-scale climate change remains a mystery. The present research reinforces this mystery since the same type of lithological rhythm, driven by similar climate changes, occurs at time scales with an order of magnitude difference.

5. Conclusions

The lithological variations between limestones, shales and marls in the Kowala section (Holy Cross Mountains, Poland) record astronomical forcing. Precession and eccentricity control the cyclical environmental changes that are responsible for the lithological rhythms. The expression of obliquity in the Kowala sedimentary record is weak and intermittent, as is expected during greenhouse worlds (Boulila et al., 2011). The association of lithological alternations with astronomical parameters enables the construction of a cyclostratigraphic framework that suggests a ~800 kyr time-gap between the LKE and the UKE and a ~400 kyr duration for low oxygen levels during the UKE. Isotopic data (\( \delta^{13}\text{C}, \delta^{18}\text{O} \) and \( \delta^{13}\text{C}_{\text{org}} \)) across the UKE exhibit a strong positive shift associated with paleoenvironmental change and destabilization of the carbon cycle. Despite the severe environmental conditions during the Kowala section, lithological rhythms suggest that there were times of warmer and dryer climate conditions, associated with enhanced carbonate productivity and reduced terrigenous input.
perturbations associated with the UKE, the imprint of precession in these isotopic records is clear. The sharp positive isotope shift in δ13C and δ13Corg is interpreted to be the result of enhanced primary production, promoted by increased nutrient-supply coeval with sea-level rise and upwelling of anoxic waters. The consequent burial of large amounts of organic carbon resulted in a drop of atmospheric pCO2, as is suggested by the 1% δ13C positive excursion (4 to 5 C °C cooling). A ~600 kyr recovery for the carbon cycle after the +3% UKE excursion is suggested by the cyclostratigraphic framework. Time-differences between the Annualla, Dasberg, Kowala and Hangenberg anoxic black shales are estimated at 2.2, 1.2 and 1.2 Myr respectively. It is proposed that the formation of the late Famennian Annualla, Dasberg and Hangenberg Shales is related to maxima of the 2.4-Myr eccentricity cycle. These astronomical configurations would have provoked sea-level rise by triggering the collapse of small continental Gondwanan ice-sheets. Thereby, an explicit link between astronomical forcing, eustatic sea-level and marine anoxia for the Late Devonian is proposed.

Acknowledgments

This work is supported by a Ph.D. fellowship awarded by the Research Foundation – Flanders (FWO) assigned to DDV, and a Ph.D. fellowship of the Ministry of Science and Higher Education – Poland (Grant N N307 4272 34) assigned to MR. We would like to thank P. Wignall, M. Zatoń, L. Marynowski and A. Pisarzowska for participation in the field and geochemical analyses which were partly funded by a NERC Ph.D. studentship to DB. M. Joachimski kindly provided unpublished isotope data. PC thanks the FWO project G.078.11). Hercules foundation and VUB research funds for their contribution. The authors thank Dr. Stephen R. Meyers and Dr. Maya Ehrlich for their constructive reviews and Dr. A.-C. Da Silva for positive discussions.

Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.epsl.2013.01.016.

References


