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Limestone–marl alternations as environmental archives and the role of early diagenesis: a critical review

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“This difference [between shale and limestone] does not find definite expression in the chemical composition but appeals to the eye.”
Gilbert (1895)

Abstract Limestone–marl alternations and other micritic calcareous rhythmites have long appealed to sedimentologists, as they appeared to directly reflect high-frequency environmental change. In particular, when orbital forcing gained popularity amongst sedimentologists and paleoclimatologists in 1980s, such rhythmites seemed to offer an ideal tool for high-resolution chronostratigraphy and environmental reconstruction. However, in spite of the fact that orbital forcing has become a routine interpretation of calcareous rhythmites, and that the processes of formation of calcareous rhythmites are considered well understood, research in the past 10 years again has questioned their primary origin and their direct interpretability. Detailed petrographic, paleontological, and geochemical data from numerous successions through geological time provided the basis for testing whether or not the regular alternation of limestone beds and marl or shale interlayers represents bimodally fluctuating environmental conditions in a direct way. In particular, these data, supplemented by box model simulations, imply that post-depositional alteration (diagenesis) has the potential to not only seriously distort primary environmental signals, but also to mimic primary signals. This questions the use of micritic calcareous rhythmites for high-resolution chronostratigraphy and for environmental interpretations where independent data of diagenetically inert parameters are not available. Diagenetic changes appear to have a yet widely underestimated influence on the appearance of limestone–marl alternations and other calcareous rhythmites. The aim of the present review is to summarize new approaches and give an overview of our

research results in this field of the past decade. This review also aims at pointing to still enigmatic aspects that need to be addressed before the interpretation of micritic calcareous rhythmites can be considered a reliable tool for high-resolution chronostratigraphy and paleoenvironmental interpretation.

Keywords Limestone–marl alternations · Milankovitch cycles · Chronostratigraphy · Calcareous rhythmites · Diagenesis

Introduction: limestone–marl alternations as high-resolution archives of climate change?

The conspicuous appearance of limestone–marl alternations and other micritic calcareous rhythmites has long fascinated geologists. The regular alternation of light-colored cemented limestone beds and darker, softer interlayers is eye-catching, both in outcrop and in cores. Because their macroscopic cyclicity is more subtle, “white-in-white” rhythmites, which lack large amounts of argillaceous material, have only recently also attracted attention (e.g., Scholle et al. 1998; Westphal 1998; Stage 1999, 2001; Westphal et al. 2000) (in the following, the term “micritic calcareous rhythmites” is used to include limestone–marl alternations, limestone–clay alternations, limestone–chalk alternations, and nodular limestones).

The interpretation of sedimentary rhythmites as a record of the Earth’s orbital parameters has a long history and dates back to Blytt (1889) and Gilbert (1895) who tried to link rhythmic sediments to orbital frequencies. Milankovitch (1941) later further developed this idea by linking climate change to the orbital cycles. After Hays et al. (1976), Imbrie et al. (1984) and others established astronomical tuning for the late Pleistocene through analysis of oxygen isotopes, the idea of high-resolution cyclostratigraphy gained fresh attraction, and limestone–marl rhythmites received renewed attention (among many others: Schwarzacher and Fischer 1982; Arthur

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et al. 1984; Cotillon and Rio 1984; Barron et al. 1985; Fischer 1986; Cotillon 1991; Einsele and Ricken 1991).

The concept of orbital forcing since then has been well established, in particular for siliciclastic rhythmic sediment successions from the youngest geologic past, based on the fact that the quasi-periodic rhythmic variations in orbital parameters influence the insolation on Earth (among many others: Kuhn and Diekmann 2002; Liu et al. 2003). Analogously, for calcareous rhythmic successions orbital forcing has developed into a standard interpretation. Varying insolation and resulting variations in climate and oceanography affect carbonate productivity and/or influx of terrigenous siliciclastic sediment into the depositional setting (e.g., various chapters in Berger et al. 1984). Limestone–marl alternations thus appeared to represent a direct record of orbital forcing and as such were thought to provide high-resolution paleoclimatic archives as far back as the Mesozoic and even the Paleozoic (e.g., Elrick et al. 1991; Bellanca et al. 1996; Weedon and Jenkyns 1999). Different superimposed astronomic frequencies were proposed to find their expression in the hierarchical bundling of the couplets (e.g., Schwarzacher 1993; Wendler et al. 2002). On this basis micritic calcareous rhythmites were used as a means of exact high-resolution dating and highly exact age definition of stratigraphic boundaries in the Neogene; for example with a resolution of 1 ka for the Serravallian-Tortonian boundary (Hilgen et al. 2000).

The underlying fundamental assumption for this approach is that the intercalation of lithologies is caused by temporal variations of environmental parameters. While the assumption of a direct link between environmental conditions and the rhythmic appearance is readily demonstrated for young siliciclastic successions, its proof is far from trivial for calcareous successions (cf. Westphal et al. 2004b). Nevertheless, a broad consensus has developed that rhythmic limestone–marl alternations directly reflect environmental fluctuations. This consensus generally was understood as a reliable basis for further interpretations. It was generally accepted that the cause of the intercalation of limestone beds and softer interlayers represents a direct response to changes in environmental conditions, such as (1) productivity cycles of the calcareous plankton (e.g., Seibold 1952; Wendler et al. 2002); (2) dilution cycles, that is, fluctuations in the influx of terrigenous non-carbonate material (e.g., Sarnthein 1978; Holmes et al. 2004); (3) cyclical changes in input of carbonate mud from adjacent shallow-water carbonate factories (e.g., Pittet and Strasser 1998; Munnecke and Westphal 2004); (4) dissolution cycles of the calcium carbonate sediment fraction (e.g., Flügel and Fenninger 1966); or (5) redox cycles at the sea floor (e.g., Berger 1979; Damholt and Surlyk 2004). In many cases, a combination of two or more of these mechanisms was assumed. The basic assumption of all these models, however, is the same: that environmental fluctuations are faithfully translated into the rock record.

Diagenetic alterations of limestone–marl alternations have been discussed in the literature for almost a century

(e.g., Semper 1917; Simon 1939; Illies 1949; Gründel and Rösler 1963; Eder 1982; Arthur et al. 1984; Hallam 1986; Ricken 1986, 1987; Frank et al. 1999). While diagenesis is generally accepted to have modified the lithology of such rhythmites, the extent of these changes is still debated. Most researchers feel that diagenesis merely overprints a pre-existing rhythmic depositional signal (e.g., Ricken 1986, 1987; Einsele and Ricken 1991; Thierstein and Roth 1991; Frank et al. 1999). However, several researchers propose a purely diagenetic formation, as opposed to a primary, environmentally determined origin; or in other words they found no evidence of a primary origin in the rhythmic successions they studied (e.g., Kent 1936; Sujkowski 1958; Gründel and Rösler 1963; Hallam 1964, 1986; Eder 1982; Munnecke and Samtleben 1996).

It is important to note here that in many cases it turns out surprisingly difficult to distinguish between primary and diagenetic features in micritic rhythmites (e.g., Westphal et al. 2004b; Biernacka et al. 2005). However, as Hallam (1986) pointed out, this question is highly relevant: unless a diagenetic formation can unequivocally be distinguished from genuine environmental signals, orbital frequency analysis of such rhythmites will be meaningless. Arthur et al. (1984) point in the same directions when they note that diagenesis renders the cycles of pelagic limestone–marl rhythmites unsuitable for study of primary environmental signals. Nevertheless, the geological community has never considered diagenesis a serious threat of the interpretation of calcareous rhythmites as direct archives of paleoclimate, and environmental interpretation of such rhythmites has long become routine (among many others: chapters in Berger et al. 1984; chapters in de Boer et al. 1994).

Recent research has opened discussion again, shedding doubt on the direct interpretability of many micritic calcareous rhythmites as direct archives of repeated environmental change. The aim of this review is to summarize the past decade's research on this topic and to suggest areas for future research.

Limestone–marl alternations and other micritic calcareous rhythmites

For discussion of potential pitfalls in interpreting micritic calcareous rhythmites, let us first review what generally characterizes such successions. Micritic calcareous rhythmites, including the well-known limestone–marl alternations, consist of two distinct, intercalated, lithologies: limestone beds alternate with softer interlayers that usually consist of shale or marl, but in some cases of soft, or chalky, limestone. The regular and laterally continuous intercalation of the limestone beds, which are more resistant to weathering, and the softer interlayers, renders micritic calcareous rhythmites conspicuous in the field. In cores, a typical expression of calcareous rhythmites is the regular alternation of lighter and darker (e.g., Betzler et al. 1999;

Frank et al. 1999), or of more and less porous layers (e.g., Westphal et al. 2000; Kenter et al. 2001, 2002).

One typical property of many such rhythmites is easily perceived in the field, namely the uncompacted preservation of the limestone beds, usually indicated by undeformed ichnofossils, whereas the interlayers always are more or less strongly compacted. This traditionally is understood as an indication that the limestone beds are mechanically stabilized as a result of early cementation, whereas the interlayers remained largely uncemented (e.g., Kent 1936; Kennedy and Klinger 1972; Ricken and Hemleben 1982; Ricken 1987). Scanning electron microscopy studies support these inferred differences in cementation and have demonstrated that the micritic limestones are tightly cemented, e.g., by microspar cement (Munnecke et al. 1997; Westphal and Munnecke 1997; Westphal et al. 2000).

Numerous rhythmic successions that show the above characteristics deviate from the carbonate content values strictly defined for limestones and marls (see, e.g., Flügel 2004, p866). Here all types of micritic calcareous rhythmites are considered, including classical limestone–marl alternations, lithographic limestones, bedded limestones, and nodular limestones, because they are genetically closely related and represent a genetic continuum (Fig. 1; Munnecke and Samtleben 1996; Munnecke et al. 2001; Munnecke and Westphal 2004). The range of primary mineralogical composition of the precursor sediment in the three-component system aragonite–calcite–clay is reflected in the highly variable morphology of micritic calcareous rhythmites that ranges from nodular to bedded with highly continuous bed thickness (Munnecke and Westphal 2004, 2005).

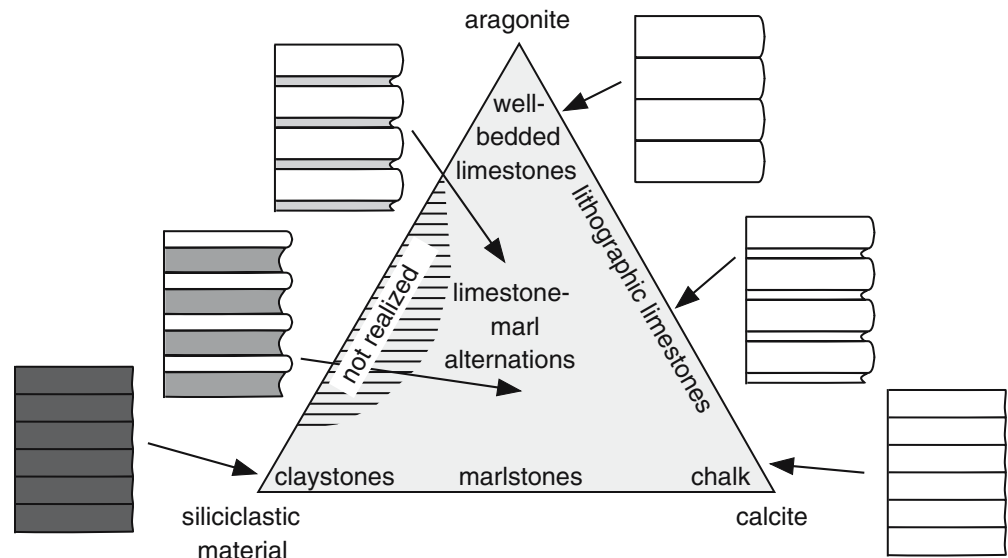
Micritic calcareous rhythmites are known from all geological periods throughout the Phanerozoic, even though in strongly varying abundance (Fig. 2; Westphal and Munnecke 2003; Westphal et al. 2006). They occur in a wide range of depositional settings from lagoonal to hemipelagic, however, in the entire Phanerozoic they are

restricted to the warm-water belt. Within the warm-water belt they exclusively occur in settings with potential aragonite deposition, i.e., in the vicinity of a shallow-water carbonate factory where siliciclastic influx is limited, in the absence of upwelling that could lower water temperature and increase nutrient levels, and outside evaporite basins (Westphal and Munnecke 2003).

Post-depositional alterations

Diagenetic alterations generate systematic differences between limestone beds and interlayers. This observation is independent of the discussion whether or not primary differences had been present in the precursor sediment. While already Sujkowski (1958) and Bathurst (1971) have pointed out that limestone beds and interlayers have undergone different types of diagenesis, the limestones being cemented whereas the marls were subject to dissolution processes, it is generally accepted since Ricken (1986, 1987) that differential diagenesis takes place in limestone–marl alternations (see also Munnecke and Samtleben 1996; Reinhardt et al. 2000; Westphal et al. 2000). Ricken (1986, 1987) interpreted that subtle primary differences were greatly enhanced during diagenesis by pressure dissolution of calcite in the interlayers in the deep burial diagenetic environment, and by resulting calcite cement precipitation in the limestone beds. He termed this phenomenon “diagenetic bedding”. As Ricken pointed out, this implies that original differences in carbonate content between limestone beds and interlayers were much smaller than those present in the diagenetically mature succession (cf. Sujkowski 1958). Similarly, variations in fossil associations and abundance, and in geochemical and petrophysical properties differ more strongly in the diagenetically mature succession than in the precursor sediment (e.g., Westphal et al. 2004b).

Fig. 1 Genetic continuum of micritic calcareous rhythmites. The proportion of the three initial main components, aragonite, calcite, and siliciclastic material, determines the morphology of the resulting diagenetically mature rhythmite (after Munnecke and Westphal 2004)



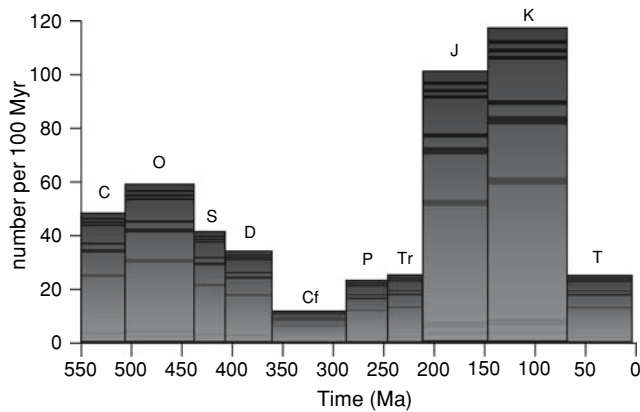


Fig. 2 Distribution of micritic calcareous rhythmites through time as reflected in the published literature (cf. Westphal et al. 2006; Westphal and Munnecke 2003)

One problem with the concept of Ricken (1986, 1987) is, however, that the uncompacted appearance of the limestone beds is incompatible with cementation in the deep burial environment. This leaves the question of the source of the cement in the uncompacted micritic limestones (“cement supply problem” of Bathurst 1970, 1976). The primary porosity in micritic sediments is high (up to 75 or 80%, see Shinn and Robbin 1983; Goldhammer 1997), and large volumes of cement have to be imported for occluding the pore space. At the same time, micritic sediments have an extremely low initial permeability (for modern micritic sediments around 1 md; see Enos and Sawatsky 1981), inhibiting volumetrically important fluid flow through the sediment. Therefore, the calcium carbonate cement has to come from a local source early enough to prevent compaction.

The concept of differential diagenesis in the shallow marine burial diagenetic environment solves this problem (e.g., Munnecke and Samtleben 1996; Westphal et al. 2000; Munnecke et al. 2001). In the marine burial diagenetic realm *sensu* Melim et al. (1995; not to be confused with marine diagenesis = sea-floor diagenesis), aragonite becomes unstable due to microbially mediated alterations such as a subtle decrease of pH of the marine-derived pore water (Melim et al. 2002). In the aragonite-sourced and microbially driven shallow differential diagenetic model, selective dissolution of aragonitic components takes place in the interlayers that, due to loss of volume and due to sediment loading, become compacted, while early cementation of the limestone beds by calcite cement prevents any considerable compaction in these sediments (Fig. 3; Munnecke and Samtleben 1996; Munnecke 1997; Westphal et al. 2000). This is in accordance with the systematic absence of originally aragonitic fossils in the interlayers whereas in the limestone beds, aragonitic fossils are present, usually neomorphosed to calcite (Munnecke 1997; Westphal 1998; Westphal et al. 2000). The apparent enigma of aragonite dissolution in carbonate sediments above the ACD is solved by the fact that such sediments

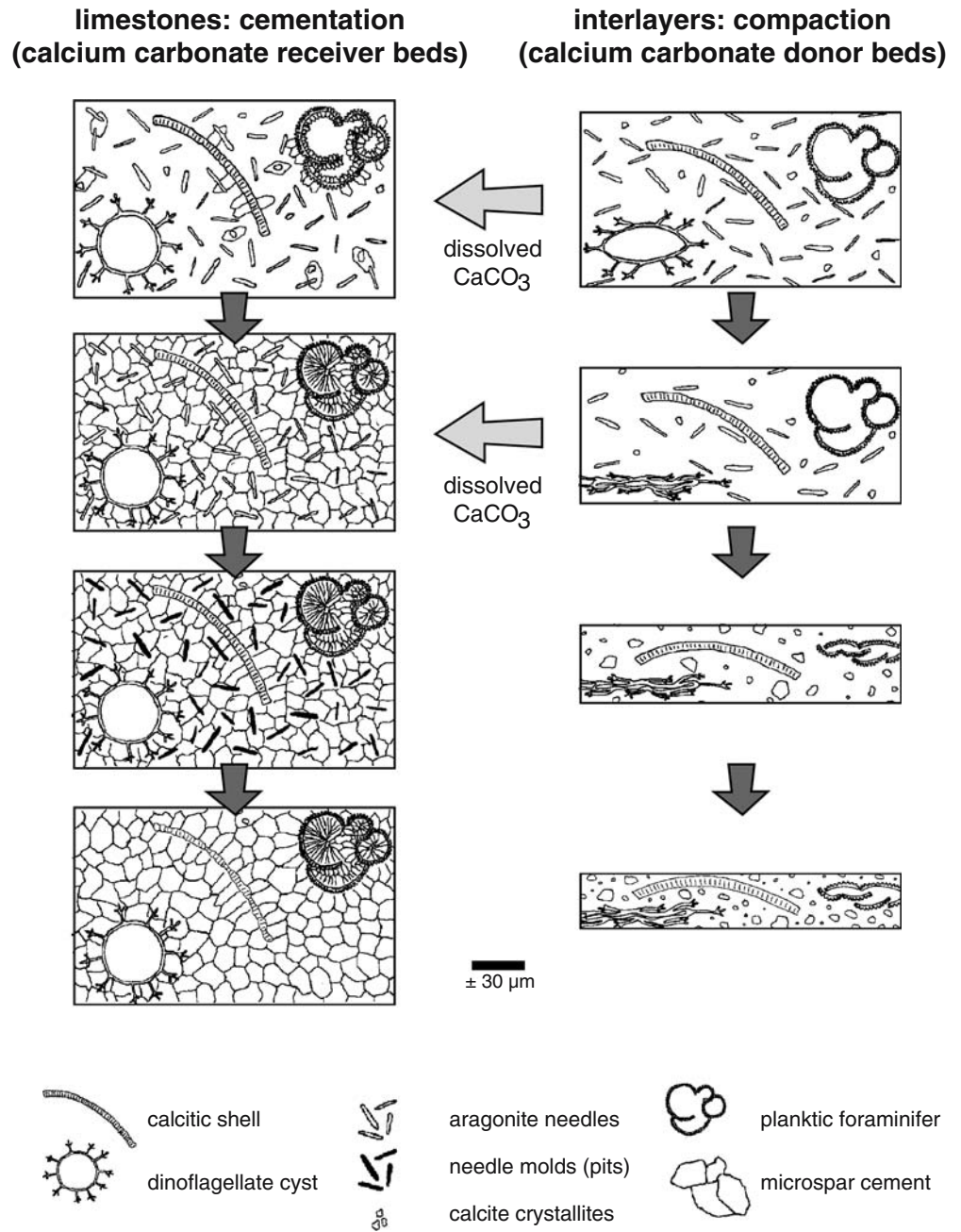
are exposed to undersaturated pore waters due to acids released during decomposition of organic matter in surface sediments despite the fact that the seawater is highly supersaturated with respect to all carbonate minerals (Morse et al. 1985; Walter and Burton 1990; Patterson and Walter 1994). These microbially driven processes could start in sediment depths as shallow as 1 m (Walter and Burton 1990). Minor elements such as strontium and iron (Rude and Aller 1991), and stable carbon isotopes (Walter et al. 1993) in pore water suggest that dissolution of aragonite can occur simultaneously with precipitation of more stable carbonate phases (Patterson and Walter 1994). This coeval low-Mg calcite precipitation is thought to occur as a result of the increased alkalinity since calcite has a lower solubility than aragonite (cf. Munnecke et al. 1997; Melim et al. 2002; Sanders 2003). These processes take place at short distance below the sea-floor, however, how shallow “shallow” means for the differential diagenesis processes has not been determined yet. Independent estimates for the formation of limestone beds or concretions range from between centimeters and decimeters (Möller and Kvingan 1988), 1–5 m below the sediment-water interface (Seibold 1962), less than 5 m (Mullins et al. 1980), to considerably less than 30 m (Noble and Howells 1974).

This model of selective aragonite dissolution and ensuing calcite precipitation explains several otherwise enigmatic features. Among those are (1) the in many cases uncompacted preservation of the limestone beds; (2) the high volumes of cement occluding the primary pore space in a fine-grained low-permeability sediment; (3) the fact that, whereas primary calcitic fossils are present in limestone beds and interbeds, originally aragonitic components are absent from interlayers but are preserved as neomorphoses or molds in the limestone beds. An exception where aragonitic fossils are preserved in interbeds is in early-silicified parts of these interbeds, implying that aragonitic components had also been present in the non-silicified parts prior to diagenesis (Cherns and Wright 2000). Additional support of aragonite as source of the calcium carbonate cement is provided by the global distribution of micritic calcareous rhythmites through Earth’s history that is restricted to settings that are compatible with aragonite deposition (Westphal and Munnecke 2003).

The differential diagenesis model is independent of the presence or absence of rhythmic primary signals in the precursor sediment. It describes the processes of differential diagenesis in micritic, aragonite-bearing sediments in a neutral way. It is currently a matter of debate whether this type of differential diagenesis requires systematic primary variations in the precursor sediment, or whether it can also take place in sediments that lack such rhythmic primary differences (see below).

The importance of post-depositional alterations in the creation of the distinctly rhythmic character of micritic calcareous rhythmites is reflected by the absence of the bipartite precursor sediments in the

Fig. 3 Different diagenetic paths of limestone beds and interlayers. Whereas the limestone beds are cemented early and thus are being mechanically stabilized, the interlayers are compacted and lose calcium carbonate by aragonite dissolution. The interbeds act as cement donors while the limestone beds receive the cement sourced in the interlayers. As a result of differential diagenesis, limestone beds and interlayers continuously diverge with respect to a number of sediment parameters including carbonate contents (modified from Westphal 1998; Westphal et al. 2000)



Quaternary (cf. Westphal et al. 2006), even though the time interval would allow for millennial-scale rhythmites similar to those known from the Paleozoic as described by, e.g., Elrick and Hinnov (1996). This could indicate that diagenesis plays an important role in generating the characteristic features of micritic calcareous rhythmites, thus making the detection of precursor sediment successions difficult (Westphal et al. 2006). Thierstein and Roth (1991) pointed out that repetitive alternations of lithologies in Pleistocene biogenic, calcareous, deep-sea sediments are rare compared to the Cretaceous and explained this by the different climatic and paleoceanographic modes that

acted during the Cretaceous. An alternative explanation could be the pre-diagenetic stage of most such Pleistocene sediments.

Fundamental problems arising from diagenesis in interpreting rhythmites

A consequence of differential diagenesis is that limestone beds and the immediately adjacent (marl, shale, chalk) interlayers follow two diverging diagenetic paths: limestone beds are being cemented, they in many cases are preserved largely uncompacted, their carbonate content

increases relative to the original content, and aragonitic fossils are preserved (usually neomorphosed). At the same time interlayers are being compacted, they remain uncemented, have reduced carbonate content, and no originally aragonitic components are present (Table 1). These different diagenetic paths of limestone beds and interlayers alter many measurable parameters in different ways, including fossil associations, fossil abundances, carbonate contents, absolute contents of insolubles, and stable isotope composition, among others. For all these parameters, the diagenetically mature limestone beds and interlayers are more different than their precursor sediments (Ricken 1986; Westphal et al. 2004b). This poses the question as to how comparable such rock parameters are for the different, adjacent, lithologies (Hallam 1986; Westphal et al. 2004b)?

Differences created by diagenesis could resemble primary differences in the sediment. Additionally, differential diagenesis can potentially mask primary differences. For reliable interpretation it is crucial to unequivocally identify primary signals and distinguish them from diagenetic features (cf. Hallam 1986). However, this task is far from trivial. Diagenetically robust parameters are required for assessing whether or not interpretable primary signals are present, and whether and how diagenetic change influenced the preservation of the environmental record.

Whereas many authors consider diagenesis as an enhancer of primary signals, diagenesis as the origin of the rhythm itself have been rejected by most authors (see, e.g., Einsele and Ricken 1991). For fluid vent systems, Luff et al. (2005) demonstrated that distinct layering of calcium carbonate cemented horizons form even under constant forcing. These authors state that for this system, internal feedback appears to suffice for correlating the cementation laterally, and no external trigger is needed. A reason to question a similar self-organized origin of micritic calcareous rhythmites is the remarkable lateral extension and continuity of individual beds with rather constant thickness that seem to require

some external lateral coordination of the diagenetic mechanisms. It is argued that self-organization over vast lateral distances is unlikely (e.g., Einsele and Ricken 1991; Westphal et al. 2004a).

To some degree diagenesis is obviously able to overrun primary differences, demonstrating the high potential of diagenesis to influence the rock record. In Liassic limestone–marl alternations, sedimentary structures and fossils are documented to crosscut lithologic boundaries, indicating the diagenetic origin of the limestone beds (Kent 1936). In some limestone–marl alternations, coarse bioclastic event layers are seen to pass from discontinuous limestone beds to marl interlayers, in some cases they even are oriented obliquely to the lithological layering (Munnecke and Samtleben 1996). This underlines that a given sediment (the bioclastic layer) can be transformed by diagenesis in both, a limestone bed as well as a marl layer. Conversely, limestone beds as well as marl interlayers can comprise different primary sediments such as mudstone and packstone (Munnecke 1997; Westphal et al. 2006). The pronounced differences in primary sediment composition in these cases are overrun by diagenesis creating new lithologic boundaries.

One other common observation demonstrates the strong influence of diagenesis. Many successions show a repetitive succession of limestone beds and interlayers on a scale of centimeters or decimeters to meters, whereby both, limestone beds and interlayers are intensively bioturbated (e.g., Reboulet and Atrops 1997). However, despite bioturbation, the boundaries between the lithologies are typically well defined and remarkably sharp. This points out that the formation of the boundaries post-dated bioturbation which otherwise would have obscured the boundaries (for other successions it is clearly seen that the bedding pre-dates the bioturbation, where burrows are infilled by the lithology overlying the host sediment, see below).

Unraveling the diagenetically overprinted environmental signal

It follows from the concept of differential diagenesis that potential alterations and distortions caused by diagenetic processes need to be considered for interpreting micritic calcareous rhythmites. A wide range of parameters commonly used for, e.g., frequency analysis and chronostratigraphy is influenced by differential diagenesis. Among these are all properties that are directly or indirectly linked to redistribution of calcium carbonate by dissolution and reprecipitation. Obviously, carbonate contents themselves are altered by differential diagenesis, and therefore, the primary carbonate contents of the precursor sediment of each layer are not easily reconstructed (e.g., Ricken 1987; Munnecke et al. 2001; Munnecke and Westphal, 2004, 2005). The same processes are responsible for the concentration of insolubles such as siliciclastic material and of diagenetically inert trace elements. Also, concentrations of elements that are

Table 1 General petrographic characteristics of limestone beds and interlayers after Munnecke and Samtleben (1996)

	Limestone beds	Interlayers
Primary LMC components	X	X
Primary HMC components	X	X
Primary aragonitic components	X (Neomorphoses)	– (Excl. steinkerns)
Organic microfossils	X	X
Ichnofossils	X	X
Siliciclastic material	X	X
Microspar	X	–
Sparry cement	X	(X)
Compaction phenomena	–	X

Note that clear differences are restricted to primary aragonitic components, and to diagenetic phenomena. Systematic differences in the preservation of aragonitic components supports that aragonite in the interlayers acted as source of the calcium carbonate cement in the limestones

incorporated into calcium carbonate minerals are altered as a result of dissolution and reprecipitation. This applies for example to strontium that enters the pore water during aragonite dissolution and only low amounts are integrated into the calcite cement (and that in some cases is reprecipitated as celestite; e.g., Swart and Guzikowski 1988; Westphal 1998; Melim et al. 2002).

Differential diagenesis also alters stable oxygen and carbon isotope composition differently in limestone beds where cementation takes place and interlayers that are composed mainly of a residue left behind during (partial) calcium carbonate dissolution (e.g., Frank et al. 1999). Thierstein and Roth (1991) point out that isotopic fluctuations are likely to be dominated by bed-specific carbonate dissolution and reprecipitation processes. Diagenesis is known to in many cases overrun the original oxygen isotope signal (e.g., Holmes et al. 2004). Differentiating between primary and diagenetic components of the signal is difficult, rendering stable isotopes problematic for interpretation. Similarly, organic carbon concentration (e.g., Reboulet et al. 2003) is not easily interpreted. The alteration of organic carbon concentration is far from trivial because passive enrichment and dilution by carbonate dissolution and reprecipitation is additionally overlain by consumption of organic matter by microbial activity during marine burial diagenesis, introducing yet another uncertainty.

Physical properties are not easily interpreted in terms of primary signals either, because in carbonates, they are strongly influenced by early diagenesis. This applies for porosity, permeability, sonic velocity, but also for natural gamma ray and color reflectance (e.g., Anselmetti and Eberli 2001; Melim et al. 2001).

Calcareous fossil associations also are altered in different ways in limestones and marls, particularly where aragonitic fossils are concerned (e.g., Cherns and Wright 2000; Wright et al. 2003). Wright and Cherns (2004) point out that fossil assemblages in micritic carbonate sediments generally might only represent residual faunas in terms of both, diversity and abundance, where particularly the mollusks are partly gone. These authors question the usefulness of paleoenvironmental interpretation of such fossil assemblages where it is unknown whether the assemblages represent ecological or taphonomic processes. In many limestone–marl alternations and other micritic rhythmites, fossil assemblages in limestone beds and interlayers differ exclusively in that originally aragonitic fossils are absent from the interlayers, and that calcitic and organic fossils are enriched in the interlayers (Table 1). This, however, does not necessarily reflect a primary signal but could be alternatively explained by the differential diagenesis model, demonstrating the caution required for meaningful interpretation of paleontological data from rhythmites. On this background, differences in the absolute abundance of calcitic nannofossils in limestones and marls for example (cf. Pittet and Mattioli 2002) are not easily interpreted. The difficulties in interpreting originally aragonitic fossil associations are demonstrated by Reboulet

and Atrops (1997) who found strong and systematic faunal contrasts in ammonite associations between limestone beds and marl interlayers in a Valanginian succession. However, the ammonites in limestone beds are preserved as internal molds, whereas in marls the ammonites are pyritized. As the authors state, taphonomic effects cannot be excluded to affect the preserved associations, and in addition the different sampling methods required might introduce additional uncertainties. For example, Seibold and Seibold (1953) state that the minor differences in foraminiferal associations observed in a Jurassic limestone–marl alternation might result from differences in methodology of examination of the two intercalated lithologies.

Calcareous nannofossils are frequently employed for extracting detailed environmental signals recorded in limestone–marl alternations. Here one has to distinguish between studying concentrations of these calcitic fossils, and examining the associations. For many examples, calcareous nannofossil abundance correlates negatively with carbonate content (e.g., Pittet and Mattioli 2002; Reboulet et al. 2003). While this usually is interpreted as indication of carbonate mud import to the locus of deposition from an external shallow-water source during deposition of the limestone beds, this explanation is not the only one possible. Enrichment in primary calcitic components in the interlayers is no less than expected from the fact that the interlayers are uncemented whereas the limestones are cemented (i.e. they have “imported” diagenetic calcite), even if one does not assume that the interlayers have lost any calcium carbonate by dissolution.

Unequivocal evidence for environmental signals recorded in limestone–marl alternations and other micritic calcareous rhythmites is found in characteristics that cannot be produced or distorted by diagenesis. This includes parameters that are independent from carbonate content, are not influenced by the processes of carbonate dissolution and reprecipitation, and are not affected by early diagenetic processes. Among these parameters is the composition (but not absolute concentration!) of certain non-carbonate constituents. This includes for example the ratios of diagenetically inert trace elements, the assemblages of non-carbonate fossils (with the exception of diagenetically susceptible siliceous skeletons), and the clay mineralogical composition. All these characteristics are independent of carbonate contents, are unaltered by diagenetic processes and therefore, are independent of diagenesis (or their diagenetic alterations can be detected), and thus potentially carry a genuine primary signal.

Organic-walled microfossils (palynomorphs) are particularly useful in unraveling paleoenvironmental information from micritic calcareous rhythmites. In many successions, they are excellently preserved, they can be extracted from both lithologies to allow for systematic examination with the same method, and thus provide comparability. Additionally, they yield a wealth of information on paleoenvironmental conditions,

including terrestrial influence such as humidity–aridity cycles (recorded in spores and pollens), and temperatures and nutrient levels of marine waters (recorded in marine palynomorphs) (e.g., Courtinat 1993; Versteegh 1994; Waterhouse 1999). Palynomorphs have been demonstrated to be suitable for detecting paleoenvironmental fluctuations in limestone–marl alternations, e.g., by Courtinat (1993) and Westphal et al. (2000, 2004b). In Jurassic successions, Waterhouse (1999) detected several orbital hierarchies of cyclicity by means of palynology that are not reflected in lithology changes, thus demonstrating the potential of the method. Similarly, the study of calcareous microfossil or nannofossil assemblages (as opposed to mere concentrations) has a high potential for studying environmental signals in micritic calcareous rhythmmites (e.g., Erba et al. 1992; Bellanca et al. 1996; Mattioli and Pittet 2002; Westphal et al. 2004b). They potentially yield information on nutrient levels and nutricline fluctuations where diagenetic bias can be excluded.

Unequivocal information is also recorded in the sediment texture and includes differences in grain size of the non-carbonate fraction such as lithoclasts and quartz grains (however, one has to be certain that the quartz is of detritic origin and not diagenetically formed), sedimentary structures, and bioturbation. Burrows crosscutting limestone–marl boundaries with the adjacent sediment infiltrating the burrows are regarded as one of the clearest signs of primary bedding (e.g., Schwarzacher and Fischer 1982; Elrick et al. 1991; Weedon and Jenkyns 1999). Similarly, bioturbated limestone beds alternating with laminated interlayers (or the other way around) clearly indicate changing conditions at the sea-floor at the time of deposition (e.g., Bottjer et al. 1986; Bellanca et al. 1996). Caution is required, however, because differential compaction can result in the formation of pseudo-lamination in the interlayers.

The non-carbonate, siliciclastic, fraction can be studied in two different ways: by examining the clay mineralogy, and by measuring the trace elements. In both cases, again not the absolute concentration in the bulk rock, but the relative concentration in the non-carbonate fraction yields the information. For example, variations in the illite to smectite ratio are thought to reflect variations in weathering such as fluctuations of humidity-aridity conditions (e.g., Rachold and Brumsack 2001). Variations in the ratio between elements such as aluminum and titanium that are incorporated into siliciclastic minerals and are inert in the early marine burial environment, can also indicate different source areas, or changes in the type of weathering in the source area, or variations in ocean currents transporting the terrestrial material to the locus of deposition. Relatively few systematic high-resolution studies dealing with the trace element ratios of micritic calcareous rhythmmites exist to date (e.g., Bellanca et al. 1996; Bausch 1997; Westphal et al. 2004b; Biernacka et al. 2005). In clearly primary rhythmmites, this method was demonstrated to

faithfully reflect primary differences in the sediment (cf. I.A. Nijenhuis 1999, unpublished data; Westphal et al. 2006). Interestingly, however, most of these studies show highly correlated abundances of diagenetically inert elements, implying that variations in the composition of siliciclastic material was likely not the steering mechanism for forming those rhythmmites (Fig. 4).

In summary, to obtain reliable data that can be meaningfully interpreted, diagenetically robust and independent parameters have to be examined, preferably in a multi-parameter approach to extract meaningful information. Such studies still are rare, but the few studies published during the past few years produced new and unexpected results (Westphal et al. 2004a; Biernacka et al. 2005). The study of Biernacka et al. (2005) is an example where scrupulous examination of a variety of parameters led to distinction between primary and diagenetic influences.

It is important to note that the absence of a detectable primary signal does not imply that no primary, environmental, signals had been present. Whereas systematic changes in unequivocal indicators (as discussed above) clearly prove primary signals, the absence of such indications is not proof of the absence of environmental changes causing the rhythmic character of the succession. It merely means that one of the three possibilities applies: (1) The evidence of an environmental fluctuation is too subtle to be detected, or (2) it has been destroyed by diagenesis, or (3) diagenesis alone has generated the rhythm. However, the question which of the three is the reason for the lack of any measured environmental signal remains open. Potential external triggers that might not be preserved in the sediment include changes in sedimentation rate that, for example, stabilize the zone of anaerobic methane oxidation, resulting in well-defined concretion horizons (Lash and Blood 2004).

Having pointed out that there is an intrinsic uncertainty regarding the presence or absence of a record of environmental change in micritic calcareous rhythmmites where no unequivocal signals were detected, it is worth mentioning that in an astonishingly high number of rhythmmites environmental changes that are recorded in diagenetically robust, reliable parameters do not correspond to the limestone-interlayer couplets (e.g., Courtinat 1993; Westphal et al. 2004b; Biernacka et al. 2005). The reason is as yet enigmatic, even though various models are proposed by the authors, and new approaches are required for solving the mystery as to what the cause of the rhythmic nature of these successions is.

Theoretically possible effects of differential diagenesis on the record of environmental signals in micritic calcareous rhythmmites

For assessing the possible influence of differential diagenesis on the record of environmental change in

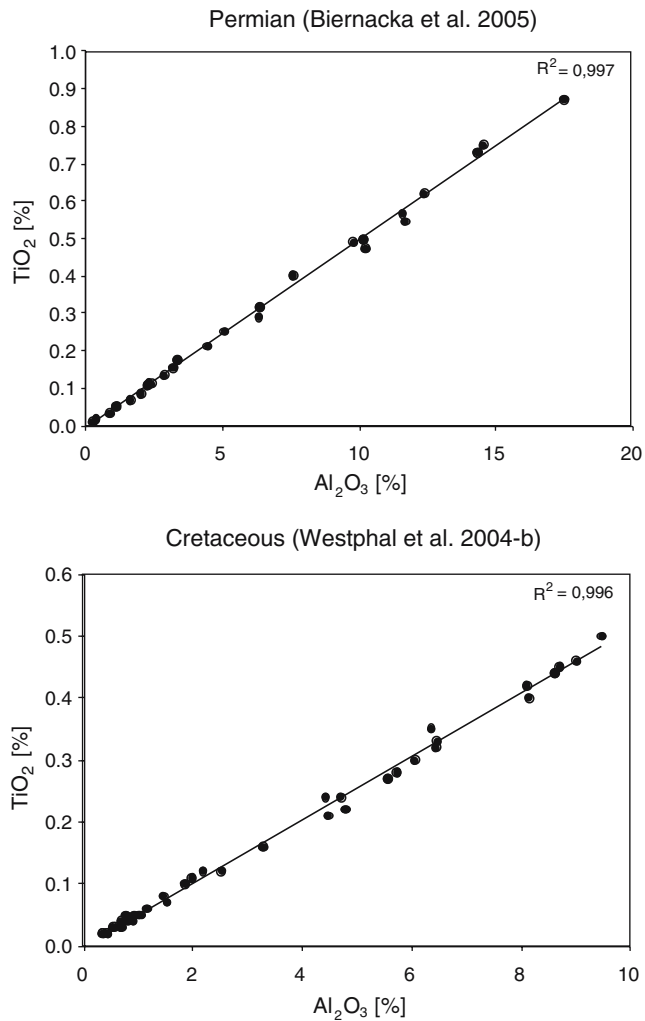


Fig. 4 Diagenetically inert elements titanium and aluminum of two limestone–marl alternations, plotted against each other in order to normalize for calcium carbonate content (bulk rock XRF measurements). High-correlation coefficients demonstrate that, with respect to these elements, the precursor sediment of limestone beds and interlayers was undifferentiated

micritic calcareous rhythmites, computer simulations have been undertaken (Böhm et al. 2003; Westphal et al. 2004a; Westphal et al. 2006). These simulations aimed at exploring potential effects of differential diagenesis, and at assessing the potential role of external, environmental signals on the diagenetic alterations. The model setup was a cellular automaton that implements in a simplified manner the diagenetic model first proposed by Munnecke and Samtleben (1996). This diagenetic model potentially leads to self-organized structures (Fig. 5). Self-organization is a common phenomenon in geological systems, the most well known example being Liesegang rings. Self-organized carbonate cementation layering is known from sediments affected by fluid venting (Luff et al. 2005), where, as in our model, cementation affects permeability and thereby leads to oscillatory cementation patterns.

In the simulation, diagenesis is not capable of producing sustained laterally continuous intercalations of limestone beds and interlayers from homogeneous precursor sediment, but produces evenly or randomly distributed nodules (Böhm et al. 2003). Once an external trigger is introduced into the simulation, implemented as fluctuations in primary aragonite content of the sediment, the diagenetically overprinted bedding exhibits lateral continuity—an external trigger holds up the bedding rhythm in the diagenetic mature succession. However, the limestone-interlayer intercalation does not directly correspond to the primary signal in the precursor sediment, but is distorted. The limestone beds can be shifted in the sedimentary column with respect to the primarily calcium carbonate-rich layer, and frequency analyses reveal that the cement peaks can be displaced or amplified with respect to the aragonite peaks, and new peaks can emerge, whereas others are suppressed (Fig. 6a; Böhm et al. 2003; Westphal et al. 2004a). Even more severe distortions are observed when differential compaction is introduced into the model—non-trivial effects of emerging new frequencies are observed (Fig. 6b; Westphal et al. 2006). This illustrates that for frequency analysis of calcareous rhythmites in the real world, analyzing the present-day thicknesses might lead to distorted results. Bulk decompaction of the entire succession does not solve this problem; each individual compacted interlayer would need to be decompacted to the original thickness in order to transform the succession into the time domain.

In the simulations, bedding patterns reminiscent of bundling are observed in simulations where a low-frequency aragonite signal is overprinted by a higher-frequency differential diagenetic bedding (Böhm et al. 2003). Bundles are a common phenomenon that usually is interpreted to represent various superimposed orbital frequencies (e.g., Lourens et al. 1996; Pasquier and Strasser 1997). Whereas it is beyond doubt that the bundles represent primary differences, e.g., in the portion of aragonite, the primary or diagenetic origin of the couplets is still discussed for the specific occurrences (e.g., Pittet and Strasser 1998; Munnecke and Westphal 2004).

A common problem in interpreting micritic calcareous rhythmites is posed by additional frequencies, such as the 11 ka frequency, that are not explained by orbital parameters (e.g., Eberli 2000). Such additional frequencies are usually ascribed to non-linear effects in the translation of orbital parameters into the Earth's climate system, or are interpreted as harmonics, however, the exact mechanisms are not understood yet (see Elkibbi and Rial 2001). An alternative explanation of these additional frequencies is post-depositional distortion by differential diagenesis (Westphal et al. 2004a). A related problem was pointed out by Waterhouse (1999) for the Lower Liassic of the UK (with its clearly primary rhythm, see Weedon and Jenkyns 1999; Munnecke et al. 2001) where the same successions were interpreted by various authors as due to the obliquity

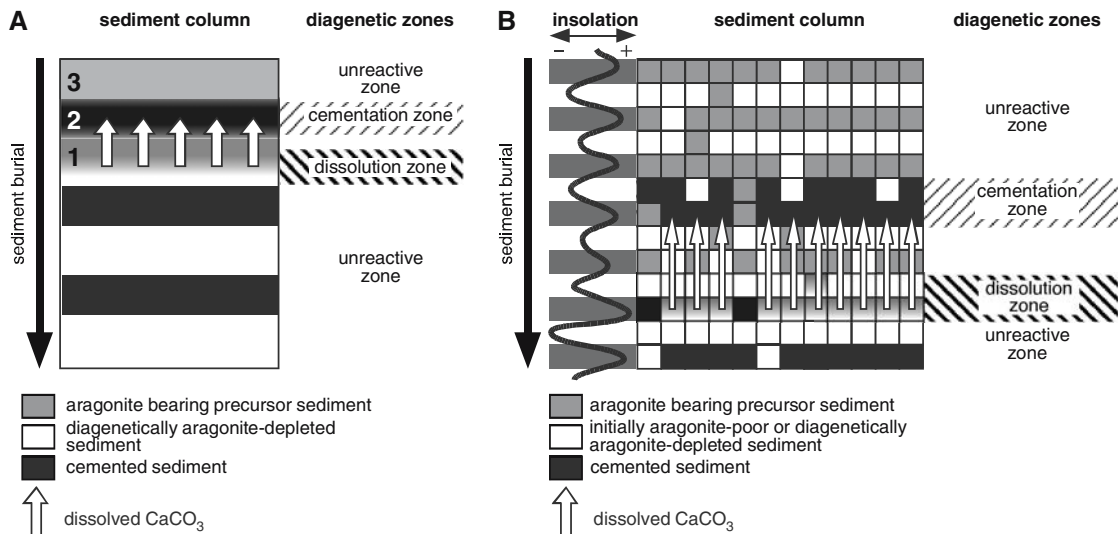


Fig. 5 **A** Sketch of simplified diagenesis model (based on the model by Munnecke and Samtleben 1996), as implemented for the box model simulation. Aragonite-bearing sediment moves through stable diagenetic zones where aragonite dissolution and calcite cementation take place. (I) A layer 2 is cemented by calcite cement derived from dissolution of aragonite in layer 1. (II) Afterwards, the cemented layer 2 enters the aragonite dissolution zone. Little to no dissolution takes place because the aragonite present in layer 2 is “sealed” by cement. As a consequence, no cement is precipitated in layer 3. (III) The uncemented layer 3 enters the aragonite dissolution zone, again aragonite is dissolved and reprecipitated as calcite cement in layer 4. This model explains potentially self-organized diagenetic patterns. **B** Cellular automata model based on

the diagenesis model shown in (A). Sediment being deposited is represented by cells. With each time step, the cells move one layer downward. Three possible states of cells are: 1 “aragonitic”: consisting of aragonite, calcite, and terrigenous material; 2 “cemented”: calcite cement is added; 3 “non-aragonitic”: consisting of calcite and terrigenous material. State 3 cells are either originally aragonite-free, or are diagenetically aragonite-depleted. As a layer passes through the aragonite dissolution zone, aragonite is removed from state 1 cells. For each cell where aragonite is dissolved, two cells in the cementation zone are cemented. External driver (*insolation*) is added that produces primary aragonite cycles. Note diagenetic overprint in the resulting diagenetically mature succession (from Westphal et al. 2004a)

cycle, to eccentricity, to a combination of eccentricity, obliquity and precessional cycles, and to precessional climate forcing (see references in Waterhouse 1999). These inconsistencies could at least partly result from diagenetic distortions. The simulation experiments demonstrated that the potential of diagenesis to distort or mimic primary signals needs to be taken into account. For environmental and chronostratigraphic interpretation, lithology appears not to be reliable enough without other information from diagenetically inert parameters.

Another common difficulty in interpreting the frequencies of micritic calcareous rhythmites is that the proportions in amplitude between the different orbital frequencies are strongly shifted in the rock record; for example the eccentricity signal in many examples is far too strong compared to the other orbital frequencies (e.g., Cleaveland et al. 2002). Kroon et al. (2000) pointed out for a Neogene rhythmic succession that the observed change in proportionality of the original insolation and/or sea-level forcing may have been at least partly a result of diagenesis. The differential diagenesis model discussed here similarly is able to explain changes in proportion by the various diagenetic alterations, namely by differential compaction and cementation dynamics, regardless of a primary or diagenetic origin of the rhythm.

A severe problem in the interpretation of micritic calcareous rhythmites arises where diagenetically inert paleontological or geochemical data show fluctuations that can be interpreted in terms of primary signals such as orbital frequencies; however, these fluctuations do not match lithology changes (e.g., Courtinat 1993; Waterhouse 1999; Rachold and Brumsack 2001). This is also the case for example for an Upper Cretaceous formation studied by Erba et al. (1992), where none of the examined calcareous nannofossil species shows fluctuations in phase with the calcium carbonate content. Erba et al. (1992) suggest that a factor independent from the fertility fluctuations that steer the calcareous nannofossil associations had controlled the carbonate productivity. Similarly, in a Lower Cretaceous rhythmite, palynomorphs and calcareous nannofossils show fluctuating associations that do not correlate with lithology intercalations (Westphal et al. 2004b). In such successions, diagenetic redistribution of calcium carbonate during differential diagenesis has possibly shifted the position of the layers, and the diagenetically mature limestone beds and interlayers do not correspond to the original primary signal.

One of the rare examples of limestone–marl alternations where primary and diagenetic features can be distinguished is from the Permian of Poland. Biernacka et al. (2005) demonstrate that Permian rhythmites are

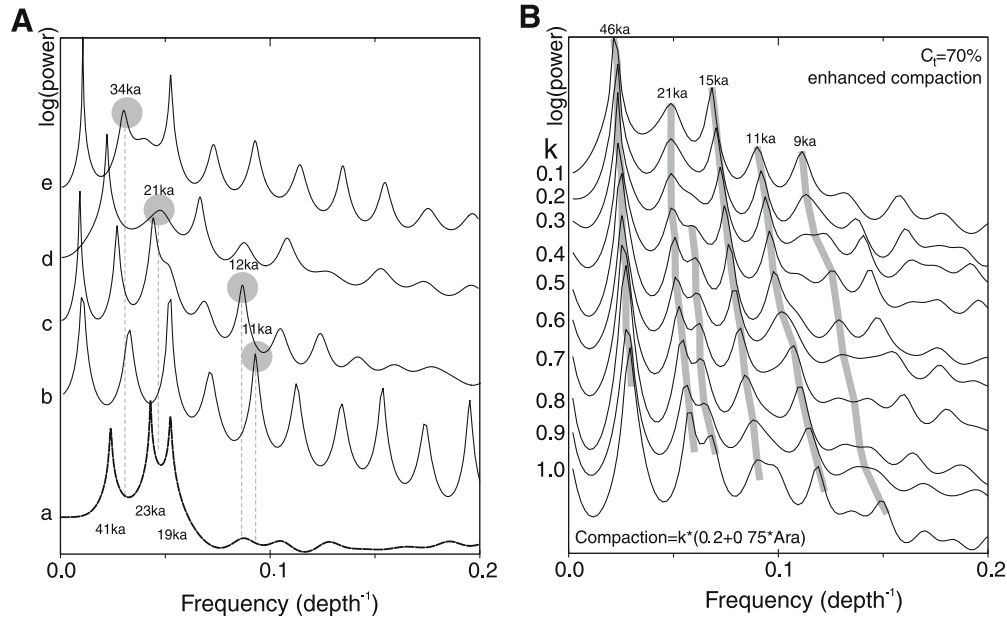


Fig. 6 **A** Power spectra of rhythmic sequences simulated with the cellular automaton. **a** Original signal (insolation spectra) implemented as initial aragonite content. **b–e** Frequency of limestone beds given by the cement portion in the resulting limestone–marl alternation. Simulations are in the time domain, that is, interlayers are not compacted. **b** Spectral peak (11 ka) not present in the input signal emerges. **c** Minor peak in the insolation spectrum (12 ka) is amplified by resonance with the diagenetic cyclicality. **d** Precession frequencies are suppressed. **e** Obliquity cycle period (41 ka) displaced toward shorter wavelength. (modified from Böhm et al.

2003). **B** Effect of compaction on the frequency spectra of modeled limestone–marl alternations. The ten spectra show compaction intensity (k) increasing from top to bottom. Corresponding peaks are connected with *gray bars*. With increasing compaction, spectral peaks are shifted toward higher frequencies and an additional peak emerges at a periodicity of 19–20 ka at high-compaction intensities ($k > 0.4$). High-frequency peaks (periods < 11 ka) show no consistent trends with increasing compaction. Peaks are labeled with the corresponding time domain periodicities (modified from Westphal et al. 2006)

the result of a combination of primary and diagenetic processes. Diagenesis enhanced depositional differences but it shifted the primary layer boundaries. These authors found that in this tempestite-bearing succession cementation and dissolution zones do not reflect original bedding but that incipient new layering formed during early diagenesis that overprinted the depositional bedding.

Interpreting micritic calcareous rhythmites is still far from trivial. However, there are useful tools in detecting primary signals that can be used for the successions where the respective parameters are present and are preserved. Successions that clearly have been devoid of primary aragonite are more easily interpreted where no pressure solution has acted on the calcitic constituents. However, the role of primary aragonite has been underestimated for many micritic calcareous rhythmites (see, e.g., Westphal et al. 2004b).

Conclusions

The aim of this review was to give an overview of new approaches and findings regarding the formation and interpretation of micritic calcareous rhythmites. It also aimed at demonstrating that the topic of limestone–marl alternations is far from being closed. Recent research

once more has opened the discussion by presenting an alternative model of the formation of such rhythmites, by questioning the strict direct interpretability of calcareous rhythmites in terms of environmental fluctuations, and by taking into account the possibility of self-organized effects in diagenesis.

The new model for differential diagenesis by aragonite dissolution in marl layers and calcite cementation in limestone layers in the realm of marine burial diagenesis explains many otherwise enigmatic properties of calcareous rhythmites. This reasoning is independent from the question of whether diagenesis creates the rhythm or only overprints a sedimentary signal. The model is able to explain:

- (1) the usually largely uncompact nature of limestones that could not be explained by earlier diagenesis models;
- (2) the source of the cement occluding the high primary porosity in the low-permeability micrites;
- (3) the typically higher abundance of primarily calcitic components in interlayers compared to limestone layers;
- (4) the absence of originally aragonitic components in interlayers;
- (5) the lack of systematic differences in diagenetically inert parameters such as Ti/Al ratios or palynomorph assemblages.

To overcome the uncertainty introduced by diagenesis, careful study of diagenetically inert parameters is needed in order to ascertain that depositional signals are studied and not diagenetic features. While a purely diagenetic origin of a micritic calcareous rhythmite is inherently not provable, a sedimentary origin can be proven by diagenetically inert parameters. However, it turns out that many successions lack systematic differences between limestones and marls documented in these unequivocal indicators. For such successions, a diagenetic origin of the couplets has to be considered.

Cellular automaton model runs have demonstrated what types of distortions are expected from differential diagenesis. Not only may the bedding be shifted with respect to original, primary signals, resulting in distorted frequencies, but new frequencies can be introduced by differential diagenesis, and others can be suppressed. Severe distortions are additionally introduced by differential compaction; decompaction of the interlayers is required in order to reconstruct the time domain.

On the basis of this knowledge, new open questions arise that, once answered, will deepen our understanding of the nature of micritic calcareous rhythmites and the paleoenvironmental information hidden therein. Clearly, the successions studied in due detail to date are just examples. They do not cover the evolution of atmosphere and ocean chemistry (calcite versus aragonite seas) through time in more than a snap shot way. Detailed and high-resolution sampling, and multi-proxy examination of diagenetically inert parameters of more examples through time and depositional environments will help to provide a solid and reliable basis for understanding and interpreting such rhythmites. Examples from calcite-dominated versus aragonite-dominated tropical carbonate depositional systems are currently being examined to gain better understanding of the influence of nutrient levels determining the biotic systems. Another topic that needs further study is the role of planktic carbonate production through time. A better understanding of the origin of the rhythmites, the processes, and the determinants of their formation will help to turn micritic calcareous rhythmites into robust environmental archives.

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