Geological Society of America Online Publications

This content has been made freely available by the the Geological Society of America for noncommercial use. Additional restrictions and information can be found below.

GSA Bookstore click www.geosociety.org/bookstore/ to visit the GSA bookstore.

Email alerting services click www.gsapubs.org/cgi/alerts to receive free e-mail alerts.

Subscribe click www.gsapubs.org/subscriptions/ for subscription information.

Permission request click http://www.geosociety.org/pubs/copyrt.htm#gsa to contact GSA

Copyright not claimed on content prepared wholly by U.S. government employees within scope of their employment. Individual scientists are hereby granted permission, without fees or further requests to GSA, to use a single figure, a single table, and/or a brief paragraph of text in subsequent works and to make unlimited copies of items in GSA's journals for noncommercial use in classrooms to further education and science. This file may not be posted to any Web site, but authors may post the abstracts only of their articles on their own or their organization's Web site providing the posting includes a reference to the article's full citation. GSA provides this and other forums for the presentation of diverse opinions and positions by scientists worldwide, regardless of their race, citizenship, gender, religion, or political viewpoint. Opinions presented in this publication do not reflect official positions of the Society.

Notes

© 2009 Geological Society of America

THE GEOLOGICAL SOCIETY OF AMERICA

Limestone-marl alternations: A warm-water phenomenon?

Hildegard Westphal Institut für Geologie und Paläontologie, Universität Hannover, Callinstrasse 30, 30167 Hannover, Germany
Axel Munnecke Institut für Paläontologie, Universität Erlangen, Loewenichstrasse 28, 91054 Erlangen, Germany

ABSTRACT

Ancient limestone-marl alternations are concentrated in settings analogous to loci of aragonite accumulation in the modern world. They typically occur on shelves in the tropical-subtropical climate belt, are far more abundant on passive continental margins than on active ones, and are rare in upwelling zones. In recent studies, aragonite was proposed to play an important role in differential diagenesis typical of most limestone-marl alternations. The coincidence of depositional settings of ancient limestone-marl alternations and modern aragonite accumulation is a strong case for this hypothesis. If confirmed, it could provide a valuable tool for broad-scale paleoenvironmental interpretations. An additional, different type of limestone-marl alternations resulted from the Cretaceous explosion in productivity of calcitic plankton: these pelagic ones are fundamentally different in their style of diagenesis.

Keywords: global maps, paleoenvironment, limestone-marl alternations, rhythmites, aragonite, differential diagenesis.

INTRODUCTION

The distribution of carbonate deposits is dependent on paleoenvironmental conditions such as temperature, salinity, and nutrient levels (e.g., Ziegler et al., 1984; Rao, 1996; James and Clarke, 1997). This is most conspicuous for fossiliferous deposits, in particular for communities with modern analogs, such as hermatypic coral reefs. Limestone-marl and limestone-shale alternations and nodular limestones (for simplification, summarized herein as limestone-marl alternations, regardless of their carbonate contents), in contrast, are less easily interpreted in terms of paleoclimate, because they may contain fewer fossil remains: this might explain why no studies about the global distribution of such rhythmites have been published.

Limestone-marl alternations are known from all Phanerozoic periods and occur in numerous settings from lagoonal to pelagic (see de Boer and Smith, 1994; Einsele et al., 1991). Whether limestone-marl alternations reflect sedimentary rhythms or diagenetic unmixing of relatively homogeneous precursor sediment (e.g., Sujkowski, 1958; Hallam, 1986) is controversial: however, this is not the topic of this paper. Regardless of the origin of the rhythm, most alternations (except for deep-sea pelagic ones; see following) have a diagenetic feature in common that is the basis of our approach: limestones and interbeds have undergone completely different diagenetic processes. This phenomenon is termed differential diagenesis (Reinhardt et al., 2000; Westphal et al., 2000) and is typified by conspicuous differential compaction. In limestones, trace fossils, organic-walled microfossils, and delicate calcareous fossil tests are undeformed to slightly deformed, indicating early lithification. In contrast, marly interbeds are strongly compacted, and trace fossils, organic-walled microfossils, and calcareous tests are deformed.

It is widely accepted that the calcium carbonate cementing the limestones in the limestone-marl alternations is derived from dissolution in the interbeds (Bathurst, 1971; Ricken, 1986). Seafloor cementation (Shinn, 1969) is unlikely as a general mechanism because not every limestone bed represents a hardground. Cementation by throughflowing pore fluids is improbable because of the low permeability typical for micritic, argillaceous sediments. In the standard model (Ricken, 1986, 1987), the redistribution of calcium carbonate is driven by pressure dissolution of calcite. However, an unsolved problem for this model is the typically uncompacted preservation of limestones (Bathurst, 1970; Shinn et al., 1977), which puts a depth limit to their cementation. The depth difference between the loci required for pressure dissolution in interbeds on one side, and for precompactional cementation of limestone beds on the other side, is not easily explained.

A new model offers a possible solution for this enigma. It assumes aragonite in the interlayers as a source of calcium carbonate cement in the limestones (aragonite in the limestone layers recrystallizes to calcite in place) (Munnecke and Samtleben, 1996; Munnecke, 1997; Westphal, 1998; Munnecke et al., 2001; see also Jenkyns, 1974). Petrographic and paleontological evidence from numerous rhythmic successions has verified this assumption and demonstrated that the model represents a general rule (Westphal et al., 2000; Munnecke et al., 2001).

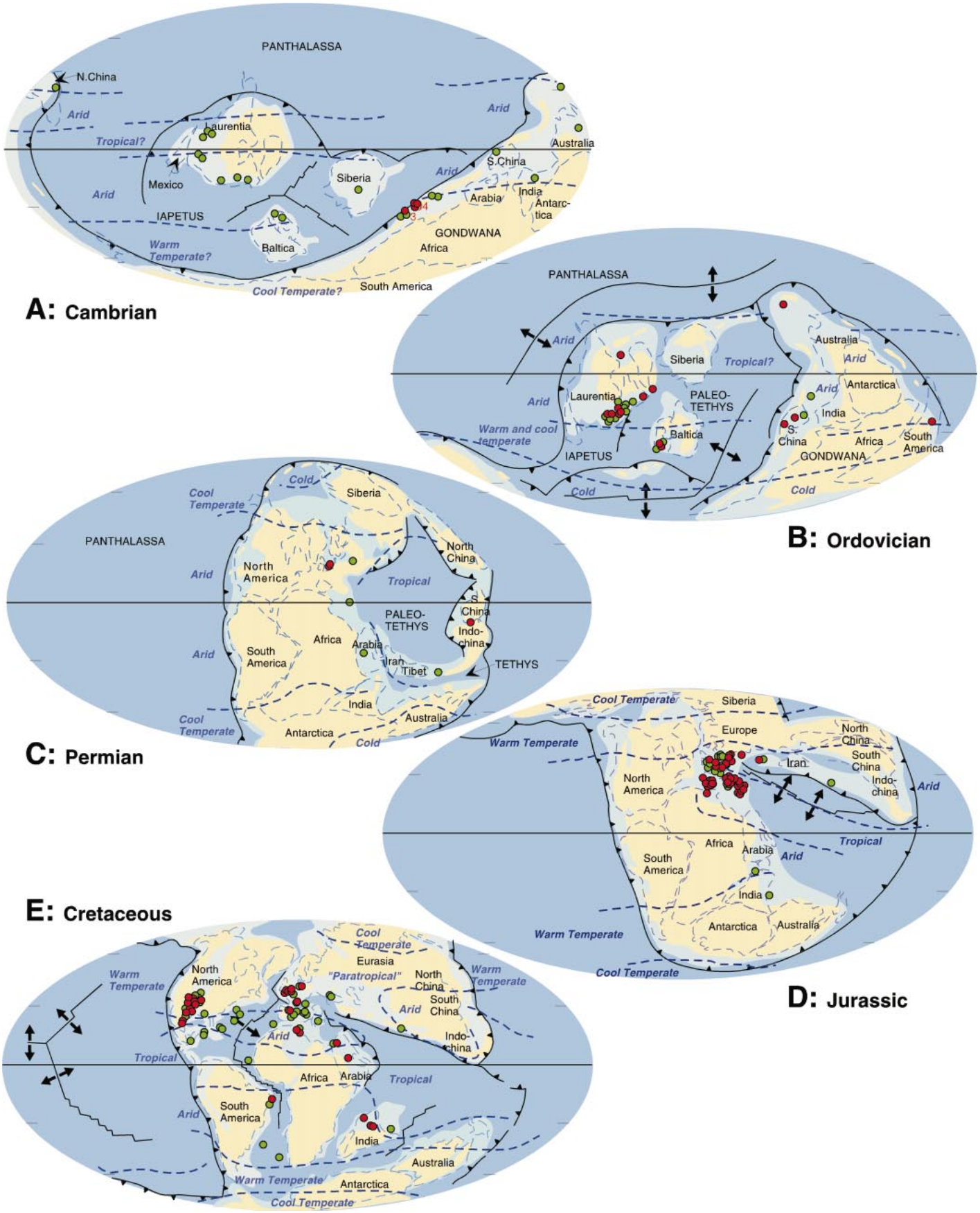
A key principle of the new model is that sedimentary aragonite becomes chemically unstable during early marine burial diagenesis. During progressive burial the sedimentary column passes through a stationary layered early diagenetic environment, and aragonite constituents are selectively dissolved below the lower limit of aragonite stability. The dissolved $CaCO_3$ moves along geochemical gradients through the sediment column and reprecipitates as calcite cement. This process takes place in stable geochemical zones that are likely the result of bacterial oxidation of organic matter (cf. Canfield and Raiswell, 1991). During aragonite dissolution, original calcite components and insolubles are not affected (high-Mg calcite is transformed to low-Mg calcite and dolomite), and the interlayers become passively enriched in those constituents. With increasing sedimentary overburden, they become increasingly compacted. In contrast, the limestones where the dissolved $CaCO_3$ reprecipitates as calcite cement become progressively more calcareous, and mechanical compaction is hindered by cementation. The redistribution of calcium carbonate during differential diagenesis results in the pronounced differences in carbonate content between limestones and marly interlayers observed in diagenetically mature successions. During deeper burial, differential compaction might be further accentuated.

HYPOTHESIS AND APPROACH

If aragonite represents a prerequisite for differential diagenesis of limestone-marl alternations, these rhythmites would be expected to be spatially limited to depositional environments with abundant depositional aragonite. To test this hypothesis, we reconstruct the spatial distribution of limestone-marl alternations in five time slices of the Phanerozoic (Cambrian, Ordovician, Permian, Jurassic, Cretaceous) that represent different global climate situations, and cover considerable evolutionary development of marine calcareous plankton. This aims at extracting parameters that influence the distribution of limestone-marl alternations, such as temperature, depositional setting, and paleoceanography. We searched the published literature (common databases and library search; the data compilation is available from the GSA Data Repository[1]) and

[1]GSA Data Repository item 2003027, literature database, is available on request from Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, editing@geosociety.org, or at www.geosociety.org/pubs/ft2003.htm.

© 2003 Geological Society of America. For permission to copy, contact Copyright Permissions, GSA, or editing@geosociety.org.


PANTHALASSA
N.China
Arid
Laurentia
Tropical?
Australia
S.China
Arid
Siberia
Mexico
Arid
Arabia
India
Antarc-
tica
IAPETUS
GONDWANA
Warm
Temperate?
Baltica
Africa
Cool Temperate?
South America
A: Cambrian
PANTHALASSA
Arid
Siberia
Tropical?
Australia
Arid
Arid
Laurentia
PALEO-
TETHYS
Arid
Antarctica
India
Warm and cool
temperate
Baltica
S.
China
Africa
South
America
IAPETUS
GONDWANA
Cold
Cold
B: Ordovician
Cold
Cool
Temperate
Siberia
PANTHALASSA
North
China
Arid
North
America
Tropical
S.
China
PALEO-
TETHYS
Indo-
china
Africa
Arabia
Arid
South
America
Iran
Tibet
TETHYS
India
Cool
Temperate
Australia
Antarctica
Cold
C: Permian
Cool Temperate
Siberia
Warm Temperate
Europe
North
China
Iran
South
China
North
America
Indo-
china
Arid
Africa
Tropical
Arabia
Arid
South
America
India
Antarctica
Australia
Warm Temperate
Cool Temperate
D: Jurassic
E: Cretaceous
Cool
Temperate
Eurasia
Warm
Temperate
North
America
"Paratropical"
North
China
Warm
Temperate
Arid
South
China
Arid
Indo-
china
Tropical
Africa
Arabia
Tropical
Arid
South
America
India
Australia
Warm Temperate
Antarctica
Cool Temperate

marked occurrences on paleogeographic maps of Scotese (2001). One dot represents one occurrence regardless of the number of publications dealing with it (number of publications included: Cambrian, 25; Ordovician, 28; Permian, 8; Jurassic, 60; Cretaceous, 87). To minimize bias, we chose a statistical approach and included any limestone-marl alternation we found in the literature, without further filtering. Our distribution maps are influenced by artificial effects. Research history results in a bias of reported limestone-marl alternations toward countries with a tradition of investigating these rhythmites. Publication in local journals (as is tradition in some countries) hinders accessibility. In addition, the uncertainty of paleogeographic reconstructions increases with age while the completeness of the geological record decreases. Nevertheless, the results show consistent patterns, and, in spite of incompleteness, allow for some general conclusions.

DISTRIBUTION OF LIMESTONE-MARL ALTERNATIONS IN TIME AND SPACE

Warm Versus Cool Water

The five time slices have a pronounced concentration of limestone-marl alternations in the warm-water belt. Examples are the Cambrian and Ordovician of North America (Figs. 1A, 1B), the Jurassic of the western Tethys (Fig. 1D), and the Cretaceous of southern Europe and the American midwest (Fig. 1E). Distinctly fewer limestone-marl alternations occur in the warm-temperate realm, and none of the reported successions plot in cool- to cold-water settings.

This preference of limestone-marl alternations for warm-water settings coincides with the distribution of voluminous aragonite production in the present-day world. Most aragonite is produced in the tropics and subtropics (Rao, 1996), where sea-surface waters are oversaturated with respect to aragonite (Kleypas et al., 1999). The potential for aragonite production in the cool- to cold-water realm, in contrast, is considerably lower (Rao, 1996; James and Clarke, 1997).

Continental Margins

More occurrences of limestone-marl alternations are reported for passive margins than for active margins. For example, the western margin of Gondwana with its long-lasting tectonic activity shows a near absence of limestone-marl alternations in the Permian, Jurassic, and Cretaceous (Figs. 1C, 1D, 1E). This reflects the tendency of carbonate platforms to form in areas with restricted terrigenous import and the absence of broad shelf areas at active margins.

In addition, certain areas are conspicuous for an absence of limestone-marl alternations despite being located on warm-water passive margins. In the Ordovician (Fig. 1B), such areas coincide with upwelling zones as deduced from occurrences of phosphorites (Wilde, 1991), such as the western coast of Central America to North America, northern and eastern Norway, and parts of eastern Gondwana. Similarly, in the Jurassic and Cretaceous, upwelling zones including Southeast Asia, Western Australia, parts of Arabia and India, and the west coast of the Americas (Golonka and Krobicki, 2001) are characterized by a virtual absence of limestone-marl alternations. Apparently, cold, organically rich upwelling waters are unfavorable for aragonite deposition (cf. Berner et al., 1978).

Shallow-Marine and Hemipelagic Versus Deep-Sea Pelagic Settings

Limestone-marl alternations are most abundant in shallow shelf areas such as the extensive Tethyan shelf of southwestern Europe in the Jurassic (Fig. 1D), or in the epeiric Midwestern Seaway of the Cretaceous (Fig. 1E). However, they are nearly absent in restricted epeiric seas (Permian, Fig. 1C). In the time slices investigated here, deep-sea pelagic limestone-marl alternations are restricted to the Cretaceous, where they occur in the newly opened Atlantic Ocean basin.

In the present-day world, shelf areas in low latitudes are the realms of potentially voluminous aragonite accumulation. This includes shallow-water carbonate factories, but also deeper shelf settings in the reach of aragonite exported from these shallow-water factories (e.g., Neumann and Land, 1975; Droxler et al., 1983; Boardman and Neumann, 1984; Wilber et al., 1990), even where the overall depositional facies corresponds to cool-water carbonates due to greater water depth. With the exception of the Cretaceous deep-sea pelagic occurrences, the distribution of limestone-marl alternations coincides with this potential distribution of modern aragonite-bearing sediments. Clearly, saturation of surface waters with respect to aragonite is not sufficient for the accumulation of initially aragonite-bearing sediment; a shelfal shallow-water setting for voluminous aragonite production and a depositional environment above the aragonite compensation depth are required.

A contrasting picture is drawn for the Cretaceous, when, in addition to the shelfal limestone-marl alternations, deep-sea pelagic alternations emerged (Fig. 1E). For the first time in Earth's history, voluminous carbonate sediments accumulated in pelagic settings as a result of the evolution and mass occurrence of calcareous plankton. Large parts of the young Atlantic Ocean seafloor were located above the carbonate compensation depth, and accumulation of calcitic sediments was favored. In contrast to the shelfal alternations, depositional aragonite clearly did not play an important role; this is supported by the accumulation of such successions below the aragonite compensation depth (e.g., Freeman and Enos, 1978). In deep-sea pelagic settings, a fundamentally different type of limestone-marl alternations formed: little or no aragonite was available for differential diagenesis as described here; therefore, early cementation played a lesser role (low diagenetic potential after Schlager and James, 1978; Herbert, 1993), and compaction is ubiquitous in both marl and limestone beds. These new types of pelagic rhythmites, which formed from the Cretaceous onward, occupy a sedimentary setting hitherto not typical for limestone-marl alternations, whereas aragonite-driven rhythmites continued to form in shallow-water–influenced settings.

Of the five time slices examined, three represent calcite seas, whereas the Permian was

Figure 1. Paleogeographic reconstructions of distribution of limestone-marl and limestone-shale alternations (green dots), and nodular limestones (red dots). Each dot represents occurrence reported in published literature (database is available from GSA Data Repository; see text footnote 1). Based on maps from Scotese (2001). Sedimentary units plotted include following: A: Cambrian—Conasauga Group, Sneakover Limestone; Ute, Dismal Gap, Lancara, Cabitza, Kaili, Zhangxia, Rohtas Formations, and others. B: Ordovician—Trenton Group, Upton Group, Cincinnatian Series, Lexington Limestone, Chongson Limestone, Balclatchie Shales; Ponon Trehue, Edinburg, Clays Ferry, Martinsburg, Bull Fork, Drakes, Pamelia, Catoche, Table Point, Whitby, ?Ibbett Bay, Killerod, Yanwashan, Dawan Formations, and others. C: Permian—Rattendorf Group, Lower Magnesia, Khuff Formations, and others. D: Jurassic—Lias, Dogger, Malm, Ammonitico rosso, Bourgogne Marble, Calcaire Grossier, Calcaires a Cancellophycus, Gruenanger, Gintsi, Turmiel, Sarialan, Duodigou, Jomosom, Vaca Muerta Formations, and others. E: Cretaceous—Greenhorn Limestone, Chalk, Maiolica, Scaglia, "Barre du Gattar" Eq., Bagh-Beds, Beckum Beds, Santa Fe Limestone; Muleros, Walnut, Kiamichi, Kelvin, Niobrara, Annona, Demopolis, Cuchillo, Lagrima, Tamaulipas Inferior, Cotinguiba, Zumaya-Algorta, Balgarene, Bahloul, Samhan Formations, and others; Deep Sea Drilling Project Sites in Atlantic Ocean.

a time of a pronounced aragonite sea, and the Cambrian represents a transitional phase (Sandberg, 1983; Wilkinson and Algeo, 1989). In spite of the tendency of abiotic precipitates (Sandberg, 1983) and skeletal mineralogy (Stanley and Hardie, 1999) to follow the general trend of calcite seas and aragonite seas, organisms with calcitic and aragonitic skeletons coexisted throughout the Phanerozoic. Consequently, aragonitic detritus was a potential constituent of carbonate mud, although the portions probably varied according to the ocean chemistry. Therefore it is not surprising that limestone-marl alternations, for which we assume an aragonite-bearing precursor, are also abundant in times of calcite seas.

CONCLUSIONS

The temporal and spatial distribution of limestone-marl alternations follows a general rule: they are most abundant in settings that favored (in analogy to the modern world) aragonite production and accumulation. This includes shallow-water settings in the warm-water belt as well as deeper water settings to which aragonite was exported (hemipelagic settings). The abundance of limestone-marl alternations in this warm-water realm is areally restricted by a scarcity on active margins, and a near absence in areas of upwelling and in restricted epeiric seas. This distribution pattern supports the hypothesis that aragonite is a prerequisite for the differential diagenesis observed in most such successions. Deep-sea pelagic rhythmites, in contrast, are documented since the Cretaceous, when pelagic calcite productivity vastly increased. With scarce to no initial aragonite, these pelagic limestone-marl alternations are fundamentally different in their diagenesis compared to shelfal limestone-marl alternations that continued to form. These observations make limestone-marl alternations valuable tools for the reconstruction of paleoclimate.

ACKNOWLEDGMENTS

We are grateful to Maria Mutti and Florian Böhm for discussions. We thank Gene Shinn, Luis Pomar, Eric Mountjoy, and an anonymous *Geology* referee for constructive criticism. This work was supported by the German Science Foundation (We-2492 and Fr-1134).

REFERENCES CITED

Bathurst, R.G.C., 1970, Problems of lithification in carbonate muds: Geologists' Association Proceedings, v. 81, p. 429–440.

Bathurst, R.G.C., 1971, Carbonates and their diagenesis: Amsterdam, Elsevier, 620 p.

Berner, R.A., Westrich, J.T., Graber, R., Smith, J., and Martens, C.S., 1978, Inhibition of aragonite precipitation from supersaturated seawater: A laboratory and field study: American Journal of Science, v. 278, p. 816–837.

Boardman, M., and Neumann, A.C., 1984, Sources of periplatform carbonates: Northwest Providence Channel, Bahamas: Journal of Sedimentary Petrology, v. 54, p. 1110–1123.

Canfield, D.E., and Raiswell, R., 1991, Carbonate precipitation and dissolution, *in* Allison, P.A., and Briggs, D.E.G., eds., Taphonomy: New York, Plenum Press, p. 412–453.

de Boer, P.L., and Smith, D.G., eds., 1994, Orbital forcing and cyclic sequences: International Association of Sedimentologists Special Publication 19, 559 p.

Droxler, A.W., Schlager, W., and Whallon, C.C., 1983, Quaternary aragonite cycles and oxygen-isotope record in Bahamian carbonate ooze: Geology, v. 11, p. 235–239.

Einsele, G., Ricken, W., and Seilacher, A., 1991, Cycles and events in stratigraphy: Berlin, Springer, 955 p.

Freeman, T., and Enos, P., 1978, Petrology of Upper Jurassic–Lower Cretaceous limestones, DSDP Site 391, *in* Benson, W.E., et al., Initial reports of the Deep-Sea Drilling Project, Volume 44: Washington, D.C., U.S. Government Printing Office, p. 463–475.

Golonka, J., and Krobicki, M., 2001, Upwelling regime in the Carpathian Tethys: A Jurassic-Cretaceous palaeogeographic and paleoclimatic perspective: Geological Quarterly, v. 45, p. 15–32.

Hallam, A., 1986, Origin of minor limestone-shale cycles: Climatically induced or diagenetic?: Geology, v. 14, p. 609–612.

Herbert, T.D., 1993, Differential compaction in lithified deep-sea sediments is not evidence for ''diagenetic unmixing'': Sedimentary Geology, v. 84, p. 115–122.

James, N.P., and Clarke, J., eds., 1997, Cool-water carbonates: Society for Sedimentary Geology (SEPM) Special Publication 56, 440 p.

Jenkyns, H.C., 1974, Origin of red nodular limestones (Ammonitico Rosso, Knollenkalke) in the Mediterranean Jurassic: A diagenetic model, *in* Hsü, K.J., and Jenkyns, H.C., eds., Pelagic sediments: On land and under the sea: International Association of Sedimentologists Special Publication 1, p. 249–271.

Kleypas, J.A., Buddemeier, R.W., Archer, D., Gattuso, J.-P., Langdon, C., and Opdyke, B.N., 1999, Geochemical consequences of increased atmospheric carbon dioxide on coral reefs: Science, v. 284, p. 118–120.

Munnecke, A., 1997, Bildung mikritischer Kalke im Silur auf Gotland: Courier Forschungsinstitut Senckenberg, v. 198, p. 1–71.

Munnecke, A., and Samtleben, C., 1996, The formation of micritic limestones and the development of limestone-marl alternations in the Silurian of Gotland, Sweden: Facies, v. 34, p. 159–176.

Munnecke, A., Westphal, H., Elrick, M., and Reijmer, J.J.G., 2001, The mineralogical composition of precursor sediments of calcareous rhythmites—A new approach: International Journal of Earth Sciences, v. 90, p. 795–812.

Neumann, A.C., and Land, L., 1975, Lime mud deposition and calcareous algae in the Bight of Abaco, Bahamas: A budget: Journal of Sedimentary Petrology, v. 45, p. 763–786.

Rao, C.P., 1996, Modern carbonates—Tropical temperate polar: Hobart, University of Tasmania, 206 p.

Reinhardt, E.G., Cavazza, W., Patterson, R.T., and Blenkinsop, J., 2000, Differential diagenesis of sedimentary components and the implication for strontium isotope analysis of carbonate rocks: Chemical Geology, v. 164, p. 331–343.

Ricken, W., 1986, Diagenetic bedding: A model for limestone-marl alternations: Berlin, Springer, 210 p.

Ricken, W., 1987, The carbonate compaction law: A new tool: Sedimentology, v. 34, p. 1–14.

Sandberg, P.A., 1983, An oscillating trend in Phanerozoic non-skeletal mineralogy: Nature, v. 305, p. 19–22.

Schlager, W., and James, N.P., 1978, Low-magnesium calcite limestones forming at the deep-sea floor, Tongue of the Ocean, Bahamas: Journal of Sedimentology, v. 25, p. 675–702.

Scotese, C.R., 2001, Paleomap Project: http://www.scotese.com/ (July 2001).

Shinn, E.A., 1969, Submarine lithification of Holocene carbonate sediments in the Persian Gulf: Sedimentology, v. 12, p. 109–144.

Shinn, E.A., Halley, R.B., Hudson, J.H., and Lidz, B.H., 1977, Limestone compaction: An enigma: Geology, v. 5, p. 21–24.

Stanley, M.S., and Hardie, L.A., 1999, Hypercalcification: Paleontology links plate tectonics and geochemistry to sedimentology: GSA Today, v. 9, p. 2–7.

Sujkowski, Z.L., 1958, Diagenesis: American Association of Petroleum Geologists Bulletin, v. 42, p. 2692–2717.

Westphal, H., 1998, Carbonate platform slopes—A record of changing conditions: Heidelberg, Springer, 179 p.

Westphal, H., Head, M.J., and Munnecke, A., 2000, Differential diagenesis of rhythmic limestone alternations supported by palynological evidence: Journal of Sedimentary Research, v. 70, p. 715–725.

Wilber, R.J., Milliman, J.D., and Halley, R.B., 1990, Accumulation of bank-top sediment on the western slope of Great Bahama Bank: Rapid progradation of a carbonate megabank: Geology, v. 18, p. 970–974.

Wilde, P., 1991, Oceanography in the Ordovician, *in* Barnes, C.R., and Williams, S.H., eds., Advances in Ordovician geology: Geological Survey of Canada Paper 90-9, p. 283–298.

Wilkinson, B.H., and Algeo, T.J., 1989, Sedimentary carbonate record of calcium-magnesium cycling: American Journal of Science, v. 289, p. 1158–1194.

Ziegler, A.M., Hulver, M.L., Lottes, A.L., and Schmachtenberg, W.F., 1984, Uniformitarianism and paleoclimates: Inferences from the distribution of carbonate rocks, *in* Brenchley, P., ed., Fossils and climate: New York, Wiley, p. 3–27.

Manuscript received 5 August 2002
Revised manuscript received 27 October 2002
Manuscript accepted 1 November 2002

Printed in USA