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ASPECTS OF MIDDLE CRETACEOUS PELAGIC SEDIMENTATION IN SOUTHERN EUROPE;

production and storage of organic matter, stable isotopes, and astronomical influences

P. L. DE BOER

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PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE WISKUNDE EN NATUURWETENSCHAPPEN AAN DE RIJKSUNIVERSITEIT TE UTRECHT, OP GEZAG VAN DE RECTOR MAGNIFICUS PROF. DR. O. J. DE JONG, VOLGENS BESLUIT VAN HET COLLEGE VAN DECANEN IN HET OPENBAAR TE VERDEDIGEN OP WOENSDAG 18 MEI 1983 DES NAMIDDAGS TE 2.45 UUR

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PROMOTOR PROF. DR. P. MARKS
CO-REFERENT PROF. DRS. P. A. SCHENCK

aan mijn ouders

CONTENTS

VOORWOORD

De interesse voor het onderwerp van dit proefschrift werd gewekt door Prof. Dr. S.O. Schlanger in de periode waarin hij als hoogleraar was verbonden aan de Vakgroep Sedimentologie. De samenwerking met hem in de beginfase van het onderzoek heb ik zeer op prijs gesteld.

De aangename en vruchtbare samenwerking met de Groep Organische Geochemie van de Technische Hogeschool te Delft heb ik in hoge mate gewaardeerd. De benadering van de in dit proefschrift behandelde problematiek vanuit de organisch geochemische hoek door Dr. Ir. G. van Graas heeft stimulerend gewerkt.

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SAMENVATTING

Hoofdstuk 1: Een aanzienlijk deel van ons dagelijks energie-gebruik is mogelijk door processen die zich in de aarde hebben afgespeeld tijdens het Onder en Midden Krijt (ca. 100 miljoen jaar geleden). Als gevolg van, nog slecht begrepen, processen die zich afspelen in de Aarde, is in die periode de snelheid, waarmee continenten ten opzichte van elkaar worden verplaatst, toegenomen. In samenhang hiermee vonden een versnelde vorming van nieuwe en een versnelde subductie van oude oceaankorst plaats, met als resultaat een verlaging van de gemiddelde ouderdom van de oceaanbodem. Door de hoge temperatuur en daarmee samenhangend het lage soortelijke gewicht van jonge oceaankorst nam de gemiddelde diepte van de oceaanbodem af. Het dientengevolge gestegen niveau van de zeespiegel (Fig. 1.2) heeft gemaakt dat het deel van de continenten dat door zee werd bedekt aanzienlijk groter was dan tegenwoordig.

Hoofdstuk 2: Hierdoor kwamen grote hoeveelheden elementaire voedingsstoffen (fosfor e.d.), die anders in landafzettingen zouden zijn gefossiliseerd, terecht in de zee. Per oppervlakte eenheid is de organische productie capaciteit van zeeën en oceanen lager dan die van het land. Daardoor ontstond een overschot aan voedingsstoffen in zeeën en oceanen. Tezamen met de trage circulatiesnelheid van het oceaan water en de slechte verversing van zuurstof in het diepere water van de Cretaceische oceanen leidde dit ertoe dat een belangrijk deel van het teveel aan voedingsstoffen in die periode is verwijderd door middel van de opslag van organisch materiaal in diep mariene sedimenten.
Model-berekeningen, gemaakt op basis van de invloed die deze opslag heeft gehad op de $\delta^{13}C$ (een maat voor de verhouding van de stabiele koolstofisotopen C-12 en C-13) van de in zeewater opgeloste koolstofverbindingen en de hieruit gevormde carbonaten, wijzen op een hoeveelheid van ca. 35×10^{20} gram opgeslagen organisch materiaal in de periode van 130 tot 90 miljoen jaar geleden. Dit ligt ca. 20% boven het gemiddelde voor het Phanerozoicum als geheel.
De koolstof die nodig was voor deze grootschalige opslag van organisch materiaal, is waarschijnlijk voor een belangrijk deel beschikbaar gekomen door verhoogde vulkanische activiteit.

Hoofdstuk 3: Voor de bestudering van diep mariene sedimenten zijn in Zuid Frankrijk en in Italie sedimentaire opeenvolgingen bestudeerd. Als gevolg van verticale bewegingen van de aardkorst, zijn deze opgeheven en vormen nu een deel van het land.

Hoofdstuk 4: Het meest kenmerkende van deze afzettingen is een regelmatige afwisseling van kalkige en mergelige banken ten gevolge van een fluctuatie van het gehalte aan (biogeen gevormd) calcium-carbonaat. Vooral in de Italiaanse afzettingen zijn de hoeveelheden van organisch materiaal en calcium-carbonaat in het sediment negatief gecorreleerd.
Uit de analyses komt naar voren dat intervallen met veel organisch materiaal niet, zoals men mogelijk zou verwachten, zijn gevormd in periodes met een grote organische productie, maar dat ze integendeel juist laag productieve periodes representeren. In de situatie waaronder de bestudeerde sedimenten zijn gevormd blijkt een hoog gehalte aan organisch materiaal vooral het gevolg te zijn van een geringe circulatie snelheid van het oceaan water en een daardoor geringe aanvoer van zuurstof naar het diepere water. Het gehalte aan (door planktonische organismen gevormd) calciumcarbonaat is voor de onderzochte opeenvolgingen de beste indicator voor de mate van organische productie.
De regelmatige fluctuaties van het carbonaat-gehalte in vooral de in Italie bestudeerde opeenvolging wordt derhalve toegeschreven aan een wisselende organische productie, welke was gesuperponeerd op een min of meer continue aanvoer van terrestrisch materiaal (kleien e.d.).

Hoofdstuk 5: Fluctuaties in de onderlinge verhouding van de stabiele zuurstof isotopen, O-16 en O-18, in het carbonaat wijzen op relatief lage temperaturen van het zeewater in die periodes, waarin de intervallen met relatief veel carbonaat werden gevormd. Dit bevestigt het eerder geschetste beeld: een goede watercirculatie en een grote organische productie gaan meestal samen met een goede menging van de verschillende watermassa´s; daarbij verlaagt de aanvoer van koel water vanuit diepere niveau´s de temperatuur van het oppervlakte water.
De resultaten van de analyse van de verhouding van de stabiele koolstof isotopen C-12 en C-13 in organisch materiaal wijst op een relatieve toename van de hoeveelheid aangevoerd organisch materiaal vanaf het land in periodes met een lage productiviteit. Dit betekent niet per se een absolute toename van de aanvoer, maar waarschijnlijk een afname van de hoeveelheid in zee geproduceerde hoeveelheid organische stof. Het terrestrische aandeel in het organische materiaal dat door zuurstof-uitputting in de diepzee kon worden gefossiliseerd, nam daardoor toe. Van Graas (1982) die aan het in dit proefschrift beschreven materiaal een organisch geochemisch onderzoek heeft verricht, laat zien dat, voor het van het land afkomstige organisch materiaal, transport door de lucht een belangrijke rol heeft gespeeld.

De verhouding van de stabiele koolstof-isotopen in het carbonaat in niveaux met veel organisch materiaal is in veel gevallen sterk veranderd als gevolg van diagenetische processen. De gevonden $\delta^{13}C$ verhoudingen in opeenvolgingen die onder continue aerobe condities zijn gevormd passen wel in het boven geschetste beeld. Processen die op de $\delta^{13}C$ van het in de fotische zone gevormde carbonaat van invloed zijn, betreffen onder meer temperatuur-afhankelijke fractionering van de stabiele koolstofisotopen tussen de atmosfeer en het zeewater, tussen de terrestrische biomassa en de atmosfeer en de verwijdering van relatief veel organisch materiaal (met een afwijkende, sterk negatieve $^{13}C/^{12}C$-verhouding) uit de fotische zone in periodes met een relatief grote organische productie.

Hoofdstuk 6: Klimaatflucutaties zijn de oorzaak van de regelmatige afwisseling van kalkige en mergelige lagen in het Krijt van de Apennijnen. Zij zijn direct te relateren aan astronomische invloeden, dat wil zeggen aan regelmatige veranderingen van de orientatie van de aardas en van de mate van eccentriciteit van de (niet precies circelvormige) baan van de aarde om de zon (zie Fig. 6.1) met periodiciteiten van onder meer 21.000, 40.000 en 100.000 jaar.
De gelijkenis van de onderlinge verhoudingen tussen de astronomische parameters, zoals berekend door astronomen voor het heden, en zoals gevonden op basis van de veldgegevens uit het Midden Krijt van de Apennijnen, suggereert dat het zon-aarde-maan systeem zich tijdens het Midden Krijt heeft gedragen op een wijze die vergelijkbaar is met het recente verleden.

Hoofdstuk 7: Combinatie van de in de eerdere hoofdstukken verkregen resultaten leiden tot een model, waarin lang periodische cycliciteiten in de eigenschappen van verschillende soorten sedimentaire sequenties kunnen worden verklaard vanuit de invloed die astronomische parameters hebben op de verdeling van klimaatzones over de aarde, op het contrast tussen zomer en winter en op veranderingen hiervan over periodes van vele duizenden jaren.

Appendix: Hierin wordt, vanuit een geheel andere invalshoek (paleomagnetisme) nadere ondersteuning gegeven aan het idee dat astronomische variabelen van invloed zijn op processen in en op de aarde.

CHAPTER 1

INTRODUCTION AND SUMMARY

Large amounts of organic carbon were stored as black shales in pelagic sediments during the Lower and Middle Cretaceous, especially within the Tethyan and North Atlantic oceans and their marginal basins (Schlanger & Jenkyns, 1976; Fischer & Arthur, 1977; Ryan & Cita, 1977; Thiede & van Andel, 1977; Arthur, 1979; Jenkyns, 1980; Scholle & Arthur, 1980; Veizer, Holser & Wilgus, 1980; Weissert, 1981).

Black shales (syn. biopelite, sapropelite) are thinly laminated carbonaceous clayey and marly pelagic sediments without traces of burrowing and benthonic life, mostly rich in organic matter (some up to 20 %) and in certain trace elements. Formation of modern black shales occurs in quiet oxygen-depleted waters, such as stagnant basins (fjords, Black Sea), or below zones of high primary production (e.g. upwelling zones off Peru). In all cases, anoxity results from the fact that renewal of the oxygen stock is insufficient for the oxidation of the sinking dead organic matter.

Although black shale deposits probably have been formed during every period of the Earth's history, they clearly have a greater incidence in distinct intervals. It has been argued that the amount of organic carbon (defined as non-carbonate-carbon) stored in pelagic sediments during the Cretaceous is larger than during any other time interval of that length (Ryan & Cita, 1977). Irving, North & Couillard (1974) state that about 60 % of the total proven oil reserves has been derived from source rocks with an age of 110 - 80 Ma b.p. Tissot (1979) estimates Middle Cretaceous source rocks to have supplied per time unit more than 5 times as much oil to present day reservoirs than the average over the whole Phanerozoic.

Despite the large volume of organic C-rich pelagic sediments of Cretaceous age, their importance has been recognized rather late, in contrast to, e.g., the well known Posidonia Shales or the Kupfer Schiefer. The reason is of course that the latter are well exposed on the continents, whereas Cretaceous black shales have been found especially by deep-sea drilling.

Moreover, Cretaceous black shales, when exposed on land, are not particularly spectacular as regards mineral or fossil content, as are black shales from some other stratigraphic intervals.

Cretaceous deep marine sediments exposed in S. Europe, frequently show a rhythmic pattern of carbonate-rich and marly beds. In the Aptian/Albian part of the series there is a general decrease of carbonate content, the typical rhythmic pattern is less distinct, and the content of organic matter shows an increase (Fig. 1.1).

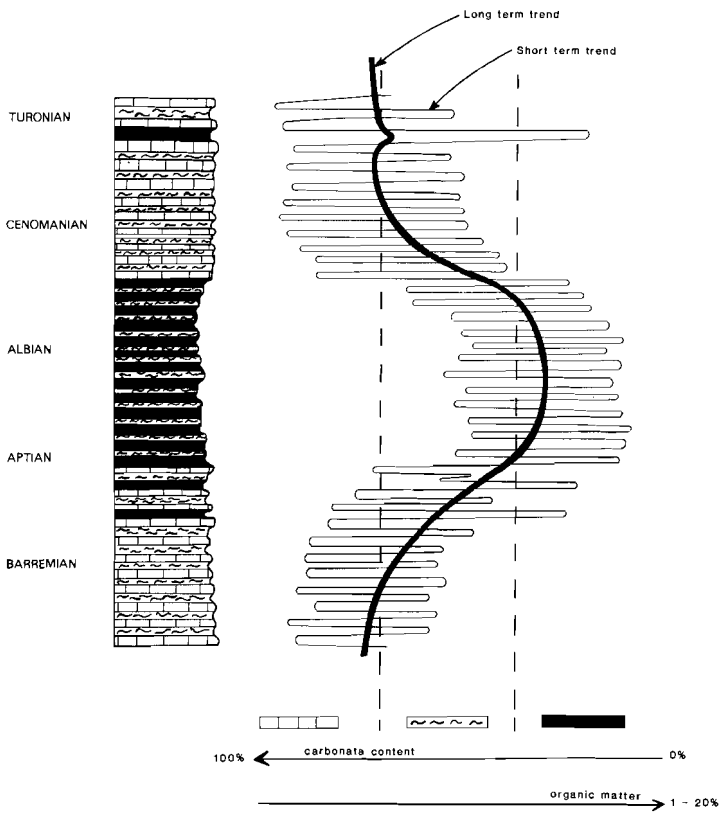


Figure 1.1 Schematic representation of the lithology of Middle Cretaceous pelagic sediments in the Tethyan realm.

In the same time-interval that the large scale storage of organic matter occurred, the oceans showed a great rise of sealevel (estimates are as high as 500 m), which resulted from an increased rate of spreading of oceanic plates (van Straaten, 1973; Hays & Pitman, 1973; Fig. 1.2). This combination of sealevel rise and large scale storage of organic C has also been recognized in other stratigraphic intervals (Bitterli, 1963; Hallam & Bradshaw, 1979; Veizer et al., 1980; Jenkyns, 1980). Most authors agree that these phenomena are related. The problem of the storage of large amounts of organic matter in relation to the large rise of sealevel is treated in chapter 2.

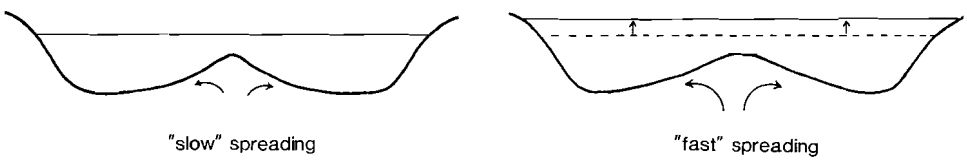


Figure 1.2 Effect of an increased rate of seafloor spreading and of the resulting increase of volume of oceanic ridges upon sealevel. The increase of the total length of oceanic ridges (birth of the South Atlantic Ocean!) also contributed to the rise of sealevel during the Cretaceous.

Another characteristic of the Middle Cretaceous is the low climatic contrast between low and high latitudes (Frakes, 1979; W.H. Berger, 1979). In addition to other possible causes, the absence of polar ice-caps must have been an important factor in this. At present ventilation of deep oceanic waters mainly takes place by the flow of dense and cold well-oxygenated bottom waters, which flow from the polar areas to lower latitudes. This circulation must have been very slow during the Cretaceous, due to the low climatic contrasts, and owing to the fact that continents separated the North Atlantic and Tethyan domains from polar areas. This must have precluded the generation of a strong underflow / bottom current of cold and oxygenated water from high to low latitudes. The importance of this obstruction becomes apparent when the distribution of Middle Cretaceous sediments in the Pacific is compared with that in the Atlantic and Tethys areas (Fig. 1.3).

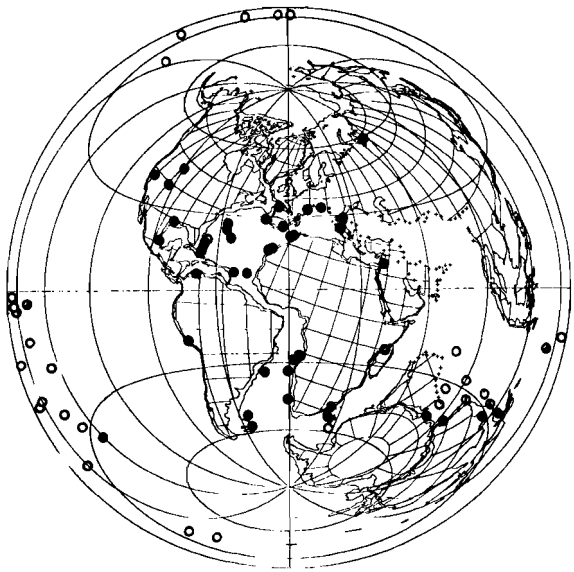


Figure 1.3 Paleoceanographic reconstruction for 100 Ma b.p. with DSDP sites up to leg 60 as far as sediments of that age have been recovered.
Black dots: sites in which considerable amounts of black shales are present in the Middle Cretaceous interval; open circles: sites without extensive amounts of black shales in this stratigraphic interval. Map (with present day coastlines) from Smith & Briden (1977).
Site data from Initial Reports of the Deep Sea Drilling Project

As a transition between a completely oxygenated ocean and a largely anoxic one, the formation of a mid-oceanic anoxic layer is most likely when the underflow of cool waters from high latitudes is insufficient for aeration of the entire water mass (Wilde & Berry, 1982).

In the Pacific direct polar connections remained, and anaerobism occurred only on a restricted scale, mainly on the top parts of seamounts and on the flanks of continental slopes, i.e. at mid-water depths, whereas in the Atlantic and Tethys large parts of the basin suffered anaerobic conditions (Schlanger & Jenkyns, 1976). This situation (Fig. 1.4) indicates that the isolated setting of the North Atlantic was not the only reason for anoxity, but that, on a global scale, conditions were different from the present ones.

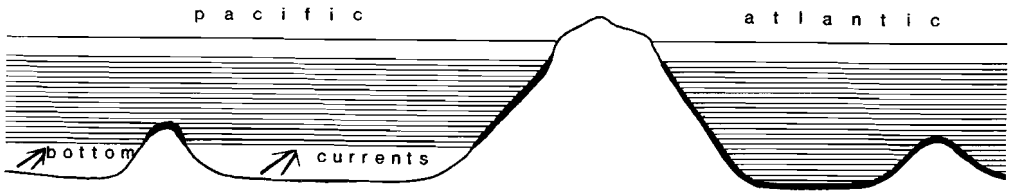


Figure 1.4 Schematic representation of anaerobism in the Tethys and North Atlantic Oceans (right) and the Pacific Ocean (left) during the Middle Cretaceous.

It is attractive to look for an analogue of the Middle Cretaceous black shale deposition among recent anoxic environments where organic C-rich sediments accumulate. However, it appears that, due to the great difference in scale, recent models cannot be simply applied to the Middle Cretaceous situation (chapter 2).

In relation to the decreased velocity of ocean water circulation, changing environmental conditions within the oceans have periodically led to the extinction of a number of foraminiferal species and to the diversification of others (Wonders, 1980). Also a remarkable increase of species diversity of dinoflagellate cysts has been observed during the Middle Cretaceous (Bujak & Williams, 1979; van Erve et al., 1981), and the great radiation of rudists fell within this period. This is in accordance with the idea of Fischer & Arthur (1977) that epochs with a high sealevel, such as the Middle Cretaceous, are polytaxic.

On land, the development of Angiosperms and Mammals showed an acceleration. This seems to confirm the large scale on which storage of organic matter in pelagic sediments occurred. For every atom of carbon which is fixed by photosynthesis and subsequently fossilized, one molecule of oxygen is liberated. The resulting increased oxygen content of the atmosphere must have favoured the respiration system of insects, which is dependent on diffusion through relatively long and thin tracheae. Insects in their turn, play an important role in the reproduction of Angiosperms by pollination. Moreover, most early Mammals were small insectivores (Lillegraven, Kraus & Bown, 1979).
Thus indirectly the storage of large amounts of organic carbon could well have favoured the co-evolution of Insects, Angiosperms, and Mammals.

Pelagic sediments often show very regular lithologic alternations.
In the studied sequences, these alternations are mostly characterized by a fluctuation of the carbonate content. A diagenetic origin has been advocated (cf. Eder, 1982; Walther, 1982) for this kind of rhythm, but the more accepted idea is that they find their genesis in the original process of sedimentation. The carbonate-marl rhythms, their composition, and their origin are discussed in chapter 4.

Analysis of the stable isotope composition of carbonate samples taken from different successions enabled further elaboration of a model explaining the variations of productivity and of supply of the biogenic part of the sediment, which forms the origin of the rhythmicity of the Middle Cretaceous succession (chapter 5).

The regularity of the patterns within the series of alternations of carbonate-rich and marly layers, observed in Italy and France, gave rise to the idea that processes, similar to those which often are stated to be responsible for stadials and interstadials in the ice-ages, i.e. fluctuations of the orientation of the Earth in its varying orbit around the Sun, might have also influenced the sedimentation pattern in these areas during the Cretaceous.
As long as a century ago it was suggested that fluctuations of climate and their record in sedimentary successions might be due to the influences of astronomical parameters (Gilbert, 1894). On the basis of the assumption that sedimentary cycles were astronomically induced, Gilbert gave an estimate for the timespan of an Upper Cretaceous pelagic sequence in Colorado, that fits remarkably well with the results of modern radiometric datings (Fischer, 1980). The ideas about an astronomical cause of the rhythmicity observed in the studied pelagic sections are elaborated in chapter 6.

Adjectives such as high and low, rich and poor, cool and warm, etc. are used frequently in this thesis. In general they are not used to indicate absolute qualifications, but as comparative notions relative to a parameter of adjacent phenomena. Thus, a layer consisting for 70 % of carbonate, may be styled as "carbonate-rich" relative to adjacent layers containing less carbonate, and as "carbonate-poor" or "marly" in the reversed case.

CHAPTER 2

CAUSES OF LARGE-SCALE STORAGE OF ORGANIC MATTER IN MIDDLE CRETACEOUS PELAGIC SEDIMENTS AND RELATED EFFECTS

APPLICATION OF PRESENT-DAY MODELS

(Sub)recent models of open-marine environments with deposition of organic C-rich sediments are represented by:

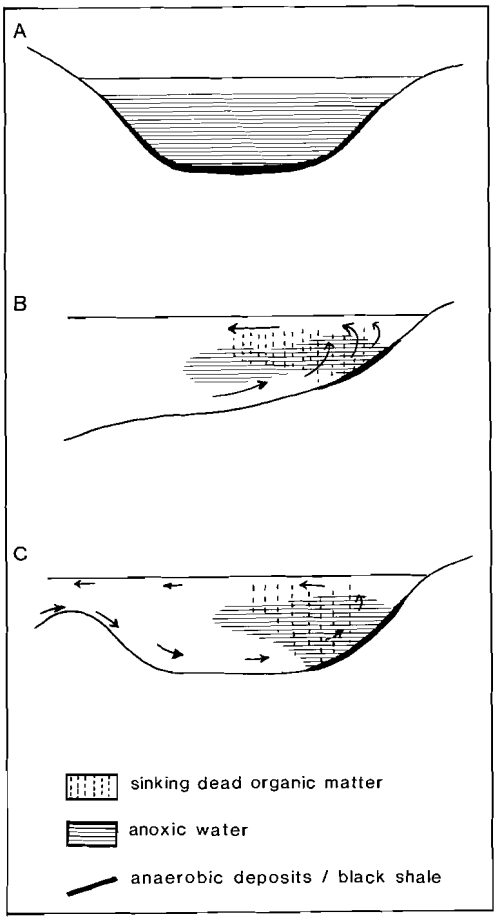


Figure 2.1 Models of black shale deposition:
a. restricted basin;
b. upwelling in the open ocean;
c. estuarine-like circulation system in semi-enclosed basins.

1. - Areas in which the water circulation is slow or stagnant, and where no, or very little, oxygen is supplied to deep water (Fig.2.1. A). Stagnation can result from, and reversely induces, a stratification of the water column, with the denser (colder, and/or more saline) water below. In the Black Sea, e.g., the stratification of the water column is stimulated by the influx of salty dense waters from the Mediterranean and of river waters of low density (Deuser, 1974).
The absence of winters cold enough to cause convective turnovers, prevents extensive mixing and the ventilation of the denser deep water mass.
Downward diffusion and small-scale advection may supply some oxygen to the deep water, but generally this is not enough to eliminate the small amount of sinking dead organic matter, so that parts of the Black Sea are characterized by anoxic deep water, and by the presence of organic C-rich sediments.

2. - Areas with upwelling of nutrient-rich deep waters, a great surface productivity, a large amount of sinking organic matter, and a consequent depletion of oxygen at mid-water depths. (Fig. 2.1 B).
In the open ocean such oxygen-depleted waters occur along the western sides of some of the continents where upwelling of nutrient-rich waters causes a high primary production at the surface, and the consequent sinking of large amounts of organic matter. In this case, oxygen supply in intermediate waters can be insufficient for the digestion of the great quantity of sinking organic matter. In places where such oxygen-depleted intermediate waters join the seafloor, organic matter is incorporated within the sediment under anoxic conditions.

3. - A third model (Fig. 2.1 C), which combines certain aspects of the above two models, was proposed by Brongersma-Sanders (1971) in order to explain the occurrence of alternating black shale and evaporite deposits.
In this model an estuarine circulation system (i.e. with inflowing deep water and outflowing surface waters) in a semi-enclosed basin (e.g. in the Mediterranean during parts of the Tertiary and the Pleistocene) results in a continuous influx of nutrients carried by inflowing Atlantic deep waters.
Upwelling and organic production occur especially at the inner end of the basin.
Prior to removal from the basin by outflowing surface waters, nutrients (phosphorus, nitrogen, silica, etc.), fixed in organic products sink down into the inflowing bottom current, and thus are kept within the circulation system.
More than in the open ocean, such an estuarine-like system within a semi-enclosed basin can act as a trap for nutrients and organic matter and may lead to anoxity and to the formation of organic C-rich sediments.
The opposite of such situation is seen in the present-day Mediterranean Sea. It can lead to the deposition of evaporites, when the salinity of inflowing surface currents has sufficiently increased by evaporation, before sinking down at the inner end of the basin.
It is obvious that, in semi-enclosed basins, a change of climate, causing changes of the rates of evaporation, and/or of the runoff of fresh water from the land, can cause reversals of these circulation patterns.

Schematizing the above processes, the interaction between the supply of oxygen and organic matter to deep water, and whether or not burial of organic matter as black shale will occur, in response to circulation intensity, surface productivity and oxygen supply, is shown in Fig. 2.2.

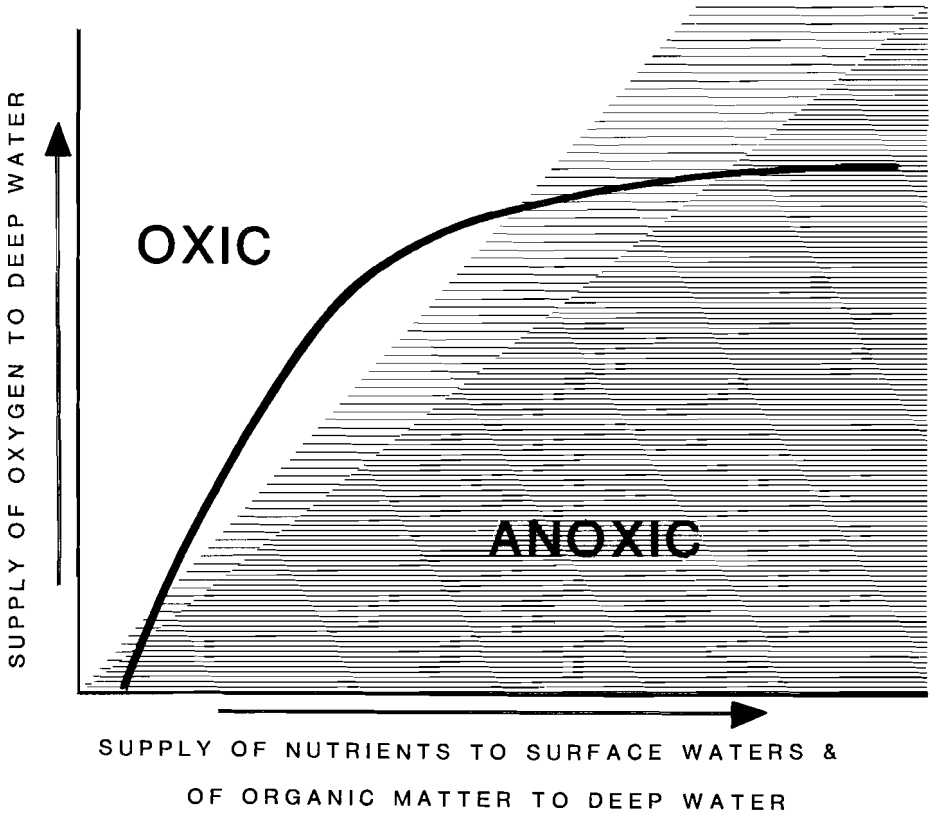


Figure 2.2 Depiction of the interference of surface productivity, rate of sinking of organic matter, and supply of oxygen upon the state of oxygenation in deep water. All these features are related to the circulation intensity. At low or zero circulation velocity, the supply of nutrients to surface waters is low, and as a result the primary production and the removal of organic matter to the deep are low. The renewal of oxygen in deep water is also limited and can easily be insufficient to oxidize the small amount of sinking dead organic matter; anaerobism is the result (cf. Black Sea).
At increasing circulation velocity, the supply of oxygen to deep water increases rapidly relative to the increase of primary production and of supply of organic matter, leading to (well) oxygenated deep water.
In the case of strong circulation and upwelling, abundant nutrient supply induces a large organic production and a transport of large amounts of organic matter to the deep. The supply of oxygen to deep water then is limited by a large consumption in the upper water level, and by the limited solubility of oxygen in seawater: about 8 ml O_2/liter.

In a steady state system, the output of nutrients should equal the input.
If such is accomplished by the formation of organic C-rich sediments, it will depend on the conditions within the relative basin whether it occurs below zones of high production or in stagnant parts (Fig. 2.3).

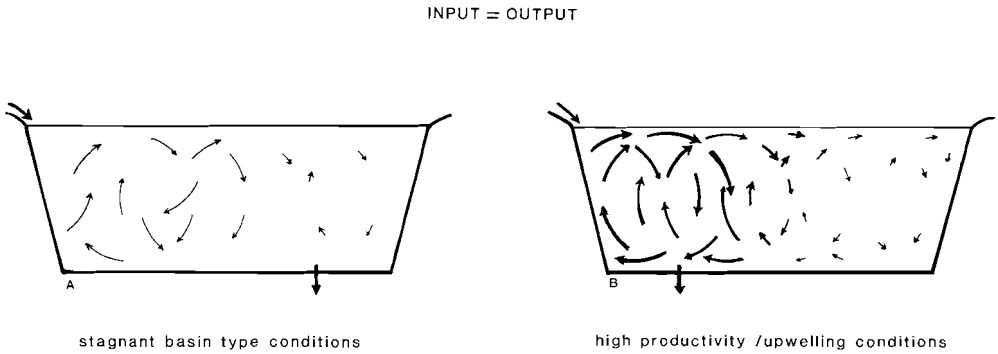


Figure 2.3 In a steady state system, the output of nutrients should equal the input, independent of the total amount of nutrients which the system can cope with. If conditions within the basin vary, and if they lead to the removal of nutrients as a part of organic matter stored under anoxic conditions (i.e. one of the two extremes of Fig. 2.2), then burial of organic matter will occur in areas of lowest circulation velocity when the circulation is slow over the whole basin (A), and below zones of strong circulation and upwelling in basins with a large circulation velocity (B). For most of the Lower an Middle Cretaceous examples, the situation A seems applicable.

The large scale on which black shale formation occurred during the Cretaceous, does not allow the straightforward application of any one of the models depicted in figure 2.1. The modern models all depend on an influx of nutrients from outside the system under consideration. Clearly such a supply of nutrients from elsewhere is a prerequisite for anoxity and black shale deposition (W.H. Berger, 1979).

At the deposition of black shales, a proportion of the nutrients (elements used for photosynthetic processes, such as phosphorus, nitrogen, etc.) is stored into the sediment as a part of the organic matter. Therefore, in order to maintain organic life, a continuous input of nutrients from outside into the system is necessary. For a small anoxic basin, such a supply of nutrients from outside is not difficult to explain. For the Lower and Middle Cretaceous, in which from time to time large parts of, or complete, oceanic basins are inferred to have been anoxic in the deeper parts, it is less feasible.

CIRCULATION VELOCITY

The low ocean water circulation velocity during the Middle Cretaceous (Frakes, 1979; W.H. Berger, 1979), seems to be one of the main causes of the lack of oxygen replenishment and the formation of black shales.
In addition to the low productivity, as indicated by e.g. the small difference between $\delta^{13}C$ of the carbonate of planktonic and benthic foraminifera from that period (W.H. Berger, 1979), oxygen renewal in deep water was so low that the small amount of sinking organic carbon apparently could still consume the available oxygen, and that anoxic sediments could be formed (see chapter 4).

In addition, the very process of a decrease of circulation velocity, leads to a removal of nutrients from the ocean which can be achieved by an increase of anoxic conditions (Fig. 2.4). In a steady state oceanic circulation system, organic matter which sinks to the bottom is largely oxidized and the enclosed nutrients are recycled. When the circulation velocity slows down, not only the supply of oxygen to deep water, but also the recycling of nutrients to the surface is diminished. However, the effective use of the available nutrients by photosynthetic processes, and the settling velocity of the resulting dead organic matter remain constant (or even increase). Thus, an accumulation of organic matter from suspension occurs in deep water, and in the case of insufficient oxygen supply, anaerobism begins or intensifies.
A storage of the excess organic matter and the related nutrients into the sediment then leads to a new equilibrium, with even less nutrients in the system.

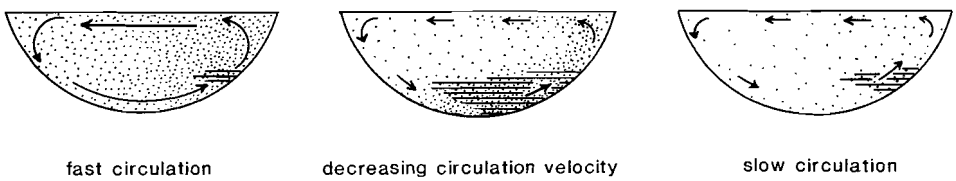


Figure 2.4. The effect of a slowing down of oceanic circulation velocity upon the amount of nutrients in the ocean and upon the degree of anaerobism. A fast circulating system can sustain more nutrients than a slow circulating one, so that at a decrease of circulation velocity nutrients have to be removed. In case of anoxity in deep water, removal as part of sedimentary organic matter is the most obvious way. Horizontal lines indicate anaerobic waters; dots are indicative of the relative amount of nutrients.

Conversely, during an increase of circulation velocity, the system can contain increasingly more nutrients. This explains why after the period with a low oceanic circulation velocity during the Aptian/Albian, the sedimentation rate - which, for the sequence in Umbria, was largely dependent on the contribution of organically produced carbonate (chapter 4) - shows a gradual increase during the late Albian and the Cenomanian (Fig. 2.5).

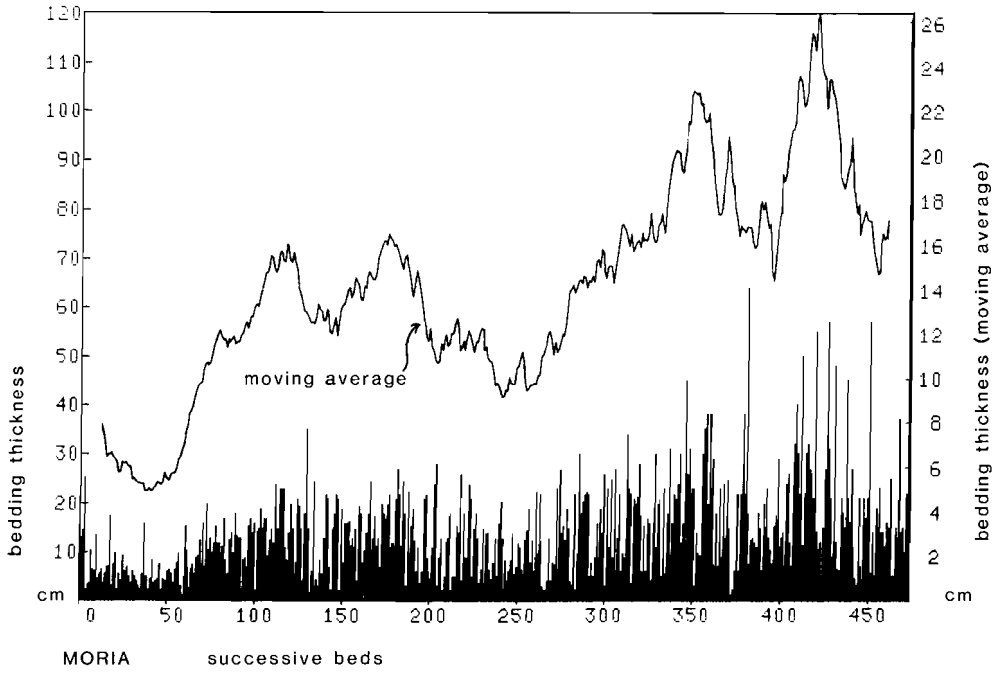


Figure 2.5 Increase of carbonate production in the Tethys during the Late Albian and Cenomanian as shown by the increase of thickness of successive carbonate-rich beds in the Moria sequence, each representing time intervals of about 21,000 years (chapter 6). Vertical bars below with scale in cm at the lefthand vertical axis represent thicknesses of the indivual carbonate-rich beds. Upper curve with scale in cm at the right hand shows the 25 point moving average of these values.

TEMPERATURE AND OXYGEN

Reconstructions by Frakes (1979) suggest that the temperature of the seawater during the Cretaceous was higher than in any other part of the Phanerozoic. Solubility of oxygen in seawater is dependent on temperature; a 5 degree rise in temperature causes a 10% decrease of solubility of oxygen (Riley & Chester, 1971). Thus a rise of temperature as happened during the Cretaceous must have resulted in a diminished transfer of oxygen from the surface to the

deep. Even in the present-day situation, with a strong circulation due to the existence of polar icecaps, the original content of oxygen in polar bottom waters is reduced to about 10% when arriving at low latitudes. "If there were only 2 ml per liter less oxygen in deep waters below 1 km, much of the present Pacific would be anoxic down to 2000 m depth" (W.H. Berger, 1979).

Due to a slight decrease of solubility of oxygen with increasing salinity (cf. Wilde & Berry, 1982), spillage of saline, dense waters from shallow evaporitic settings (Arthur & Natland, 1979) also may have contributed to a depletion of oxygen in deep water.

Radioactive decay of elements within the Earth causes a constant production of heat. Variations in spreading rates and in total volume of oceanic ridges imply an intermittent discharge of energy to the outer sphere of the earth. For the oceanic crust the amount is related to the age, and in the case of young ocean crust the heatflow is about 0.4 cal/cm^2 day (~0.01 J/m^2.sec) (cf. Parson & Sclater, 1977). This means that per year a standing body of 14 meter height can be heated by 1^0. At present, average vertical velocities are some few cm/day, and in areas with strong upwelling, the velocity is of the order of 30 m/year (Tomazak, 1979). Thus, in view of the low circulation velocity during the Cretaceous, an increase in volume of oceanic ridges might well have had a small but significant positive influence upon the increase of ocean water temperature, especially in the deep ocean.

THE CRETACEOUS RISE OF SEALEVEL

As was already stated in chapter 1, the Cretaceous rise of sealevel was suggested to have been caused by an increased rate of spreading of oceanic plates, together with an increase of the total length of mid-oceanic ridges (Fig. 1.2). Pitman (1978) estimates that in this way the Cretaceous sealevel reached a height of about 350 meters above the present one.
New oceanic crust is warm, has a low density, and therefore young ocean floor is situated at rather shallow depths, about 3 km below the (present) sealevel. With increasing age, the temperature of the crust decreases, and because of increasing density the floor sinks down with a decreasing speed of 80 to 15 m. per million years.

Both an increase of the rate of seafloor spreading, and an increase of the length of oceanic ridges, contribute to a decrease of the mean age, thus to a lower mean density, and to a shallowing of the mean depth of the oceanic crust, to be compensated by a rise of sealevel. The increased speed of removal of old oceanic crust by subduction is of course equally important for a decrease of the mean age of the ocean floor.
For example, if in an hypothetical closed basin of 3000 kilometers wide, with two active margins, a spreading center with a spreading rate of 2 x 5 cm/year migrated from one of the edges to the middle of the basin, then the mean age of the ocean crust would decrease from 30 to 15 Ma. This would result in a rise of sealevel of about 500 meter.

EFFECT OF THE LARGE SEALEVEL RISE

It was suggested that "the Cretaceous transgression resulted in the submergence of low-lying coastal plains that were being rapidly populated by dense forests of the newly arrived Angiosperms" (Schlanger & Jenkyns, 1976), and that "much of the mid-Cretaceous world ocean was simply awash with wood" (Jenkyns, 1980).
But, if we look at the actual rates of sealevel rise in response to increased rates of seafloor spreading, these appear to be of the order of 0.01 mm per year (Schlager, 1981). In comparison, the melting of polar icecaps as observed during the Holocene, caused a rise of sealevel that is more than a hundred times faster (cf. Jelgersma, 1961). Yet modern oceans are not flooded with driftwood, and no comparably widespread anoxia and deposition of black shales is observed at present.
Therefore, large scale deposition of black shales during the Cretaceous cannot be attributed simply to the "destructive" effects of a rise of sealevel.
Also, compared to the extra amount of organic matter which was stored within Middle Cretaceous pelagic sediments (4 to 7 x 10^{20} gr C over a period of 40 Ma, see below), the total terrestrial biomass (living 6 to 9 x 10^{17}, dead 10 to 30 x 10^{17} gr C, Bolin et al., 1979) is too small for a significant contribution in the case of a catastrophic transfer to the ocean.

ESTIMATES OF THE AMOUNT OF ORGANIC MATTER STORED IN MIDDLE CRETACEOUS PELAGIC SEDIMENTS

THE EFFECT OF BURIAL OF ORGANIC C UPON LONG-TERM TRENDS OF $\delta^{13}C$ OF OCEAN-DISSOLVED-CARBON

Photosynthetic processes have a preference for ^{12}C over ^{13}C, and thus modern marine organic matter is depleted in ^{13}C by an average of about 25 o/oo relative to its inorganic source, HCO_3^-. Terrestrial organic matter shows a greater variation; on average its $\delta^{13}C$ is lower than that of marine organic matter. When the amount of fossilized organic C exceeds the amount of fossil organic carbon oxidized on the continents, $\delta^{13}C$ of the carbon available in the CO_2 of the atmosphere and dissolved in the ocean, shifts, in the long run to higher values. During the Middle Cretaceous, this is reflected in the $\delta^{13}C$ values of marine carbonates (Scholle & Arthur, 1980; Veizer et al,1980) and of organic matter (Fischer & Arthur, 1977; Erdman & Shorno, 1979). An increase of the order of 3 o/oo of the $\delta^{13}C$ values is found during the Lower to Middle Cretaceous (Fig. 2.8 A).

At first sight one might expect that, in the case of a closed system with an average carbon isotope composition $\delta^{13}C$ = 0 o/oo of the 3.5×10^{19} grams of ocean-dissolved-carbon (mainly as HCO_3^-), as presently dissolved in the ocean, a rise of 1 o/oo of $\delta^{13}C$ of the oceanic inorganic carbon reservoir apparently should be the result of an excess burial of 14×10^{17} gr C. However, the exogenic system is not closed, and the oxidation of organic matter from fossil sediments, brought back to the surface of the Earth, returns light carbon ($\delta^{13}C \sim -25$ o/oo) to the atmosphere and into the ocean, thus counteracting the effect of burial of organic matter. Similarly, the fluxes of weathering and of fossilization of carbonates (with a stable carbon isotope ratio more or less equal to that of ocean-dissolved carbon) contribute to weaken the influence of an excess burial of organic carbon upon the stable isotope ratio in the accessible reservoir.

On the basis of an unspecified model, Scholle & Arthur (1980) state that the 1 o/oo rise of $\delta^{13}C$ of carbonates at the Cenomanian - Turonian boundary would have required a storage of 4.5×10^{20} gr C as organic matter in 2 Ma. This

would be 3 times the present steady state rate of about 0.7 x 10^{17} gr C (in organic matter) per year. It seems an unreasonably large amount. Converted to volume of organic matter it would mean a layer with a thickness of 1.3 meter over all ocean basins. Such an amount is in conflict with the observations as described up to now.

The observed positive excursions of the stable carbon isotope composition in marine carbonates at the Cenomanian-Turonian boundary must be due, at least partly, to diagenetic effects (chapter 5), and our own calculations (below) based on other premises, indicate that the actual storage of organic matter during this short interval was much less.

MODEL SIMULATION

In order to trace the effect that changes in the annual quantity of fossilized organic matter have upon the $\delta^{13}C$ of ocean-dissolved carbon, a simple model simulation was made. For this model only the principal reservoirs and fluxes of the present-day (before the impact of human activities) steady state system were taken into account. They are shown in Table 2.1. The number of decimals given is well in excess of the accuracy of the data. In annual steps the effects of addition and subtraction of the various components on the $\delta^{13}C$ of ocean-dissolved-carbon were calculated.

Considering the differences of opinion between the various authorities about the exact figures, and the number of smaller reservoirs and fluxes omitted, the results of the modelling experiment should be considered as representing an approximation. The input of juvenile carbon added to the (model-) system is assumed to have been removed as organic matter.

	fluxes in 10^{14} gr C/yesr	$\delta^{13}C$
juvenile carbon	0.082	-7 o/oo
weathering of fossil carbonates	1.46	+1 o/oo
weathering of fossil organic matter	0.70	-25 o/oo
fossilisation of carbonates	1.46	+1 o/oo
fossilisation of organic matter	0.782	-25 o/oo

TABLE 2.1 Present-day fluxes and isotope ratios of carbon. Data from Pytkovitch (1973), Hay & Southam (1977), and Scholle & Arthur (1980).

Apart from the flux of buried organic matter and calcium-carbonate, the sum of which was kept constant, the other fluxes were as in Table 2.1. In Fig. 2.6 it is demonstrated how a sudden large change of the amount of organic matter stored annually leads to an initially rapid, but asymptotically decreasing change (per Ma^2) of the stable isotope composition of inorganic carbon in the ocean.

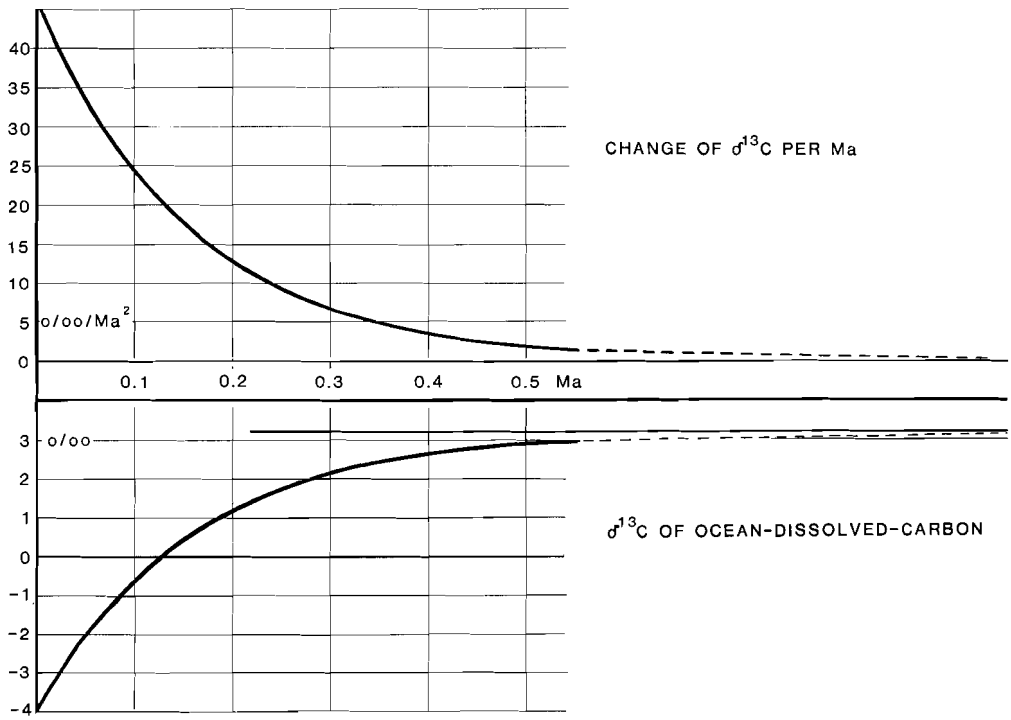


Figure 2.6 Change of $\delta^{13}C$ of marine dissolved carbon (and of carbonates formed simultaneously) resulting from an instantaneous (unrealistic) threefold increase of the net storage of organic matter from 0.37 x 10^{14}gr C per year to 1.0 x 10^{14}gr C/year, and a decrease of the stored carbonate from 1.47 to 0.84 x 10^{14}gr C/year. For the other fluxes used see Table 2.1.

Figure 2.7 gives an impression of the effect which changes in the amount of organic matter buried annually have upon the $\delta^{13}C$ of ocean-dissolved carbon. For example, in the model $\delta^{13}C$ of ocean-dissolved-carbon is, and remains 0 o/oo when the annual storage of organic matter amounts to 0.72 x 10^{17} gr C.

When this quantity is suddenly increased by about 10% to 0.8 x 10^{14}gr C/year, $\delta^{13}C$ will shift to more positive values, starting with a rate of about +6 o/oo /Ma^2, and aiming at a new equilibrium value of +0.9 o/oo.
For equilibrium conditions (with constant $\delta^{13}C$), the relation

$$\delta^{13}C = ((A \times 11.5) - 8.3) \text{ o/oo}$$

can be derived from the data used for the construction of the graph in figure 2.7. In this equation, A is the amount of annually fossilized organic matter in 10^{14} grams.

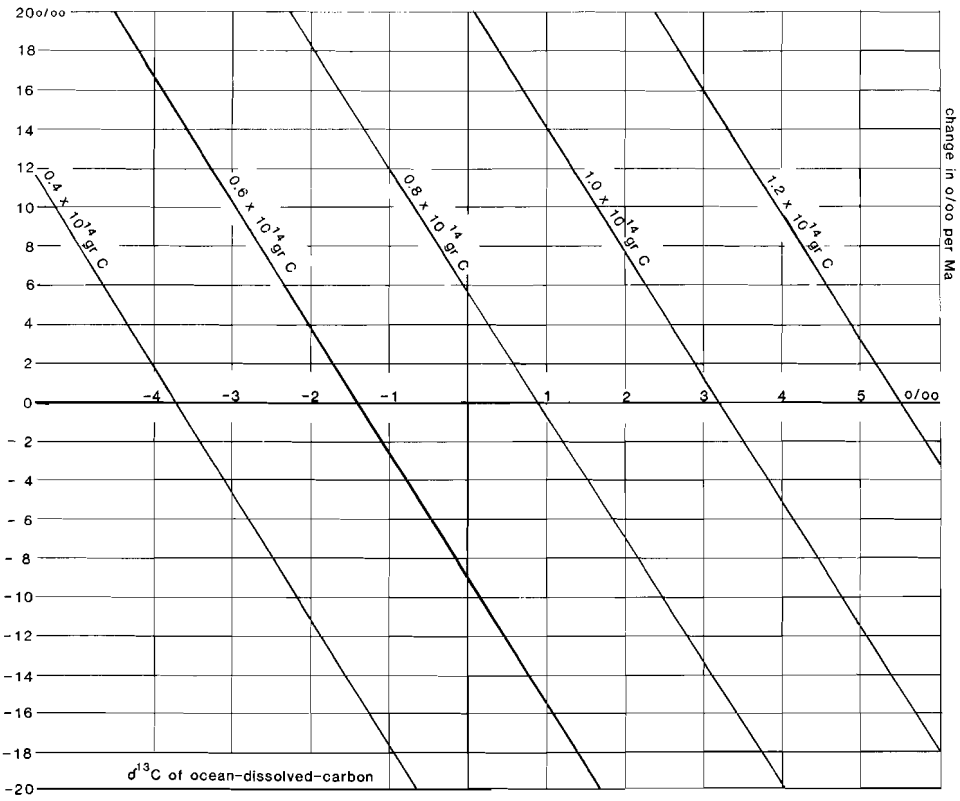


Figure 2.7 Tentative nomogram indicating the effect of changes of the amount of organic matter stored annually upon the stable carbon isotope composition of ocean-dissolved-carbon and marine carbonates. The oblique lines indicate the amount of organic matter fossilized yearly. Sum of the quantities of carbon fossilized as organic matter and carbonate have been considered constant; others as in Table 2.1.
For a 50% increase (0.043 x 10^{14}gr C) of the share of juvenile carbon in the fossilizing organic matter, the values of the horizontal axis are 0.3 o/oo lower.

The initial increase of $\delta^{13}C$ during the Lower and Middle Cretaceous is not as rapid as in the example of Fig. 2.6, but it is rather gradual. The model simulations indicate that a rise of $\delta^{13}C$ as happened during the Cretaceous, would result from a gradual increase of the amount of organic matter stored annually, starting with a very slight extra storage of organic matter to an extra 25 to 40% when $\delta^{13}C$ was highest.
Applied to one of the curves of changing $\delta^{13}C$ values during the Middle Cretaceous of Scholle & Arthur (1980), the model shows the amounts of organic matter stored annually as depicted in Fig. 2.8.

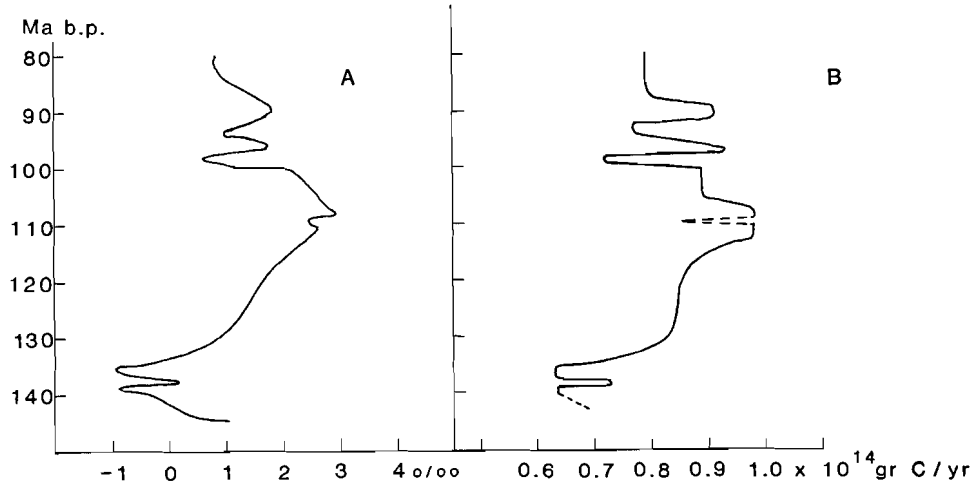


Figure 2.8. Estimates of the amounts of organic matter stored during the Lower to Middle Cretaceous (B) by visual application of the graph of figure 2.7. to $\delta^{13}C$ values of carbonatea from Peregrina Canyon, Mexico (A), Scholle & Arthur (1980: Fig. 4).

Integrating the values of the curve of Fig. 2.8B gives a total amount of about 35 x 10^{20}gr of buried organic matter over the period from 130 to 90 Ma b.p. In view of our present knowledge this is a realistic quantity.

In case of a long-term average of 0 o/oo of $\delta^{13}C$ of ocean-dissolved-carbon during the Phanerozoic, this value of 35 x 10^{20}gr C would be about 21% above average. In the case of 0.6 o/oo as the long-term average (Broecker, 1970, cit. Scholle & Arthur, 1980), the excess would be 13% above the average long-term flux. Averaging over ten million year periods, the largest excess is found in the interval from 120 to 110 Ma b.p. (27 or 19% resp.).

It is stressed that for the results shown in figure 2.8, rough data from only

one section were used. Moreover, only the principal reservoirs and fluxes were taken into account. Therefore, the results only serve to illustrate the effect of increased burial of organic matter in a semi-quantitative way, and the values given should not be considered as being the final answer.

The great discrepancy with the estimates of Scholle & Arthur who suggested a 200% increase at the end of the Cenomanian, is thought to be due to the fact that these authors constructed models from the literature, which refer to long-term (order of 10^8 years) changes, and which include the total sediment reservoir of organic carbon and carbonate carbon.

Our value of 13 to 21% excess storage of organic matter implies an extra storage of 40 to 70 x 10^{19} gr C as organic matter over an interval of 40 Ma.

Assuming deposition of black shales with 4% organic carbon at a rate of 2 cm/Ka over an area of 50 x 10^6 km , and a cumulative time of Cretaceous stagnations of 1 Ma, Ryan & Cita (1977) estimate a subtraction of over 8 x 10^{19} gr C as organic matter. That this value is 5 to 10 times lower than ours, is due to their rather low estimates of the surface area of the euxinic seafloor (5 x 10^7 km) and of the period (1 million years cumulative) over which deposition of black shales did occur.

NUTRIENTS AND THEIR EFFECTS

DERIVATION OF NUTRIENTS FOR THE EXCESS BURIAL OF ORGANIC MATTER

In the modelling of processes which occur in the present day ocean, certain factors can be considered constant.
However, in the long term, such "constants" may change. E.g., during the Cretaceous, the land surface was strongly reduced. On the basis of facies distribution maps, Hallam (1971) estimates that 33 x 10^6 km^2 of the present land surface (148 x 10^6 km^2) was covered by water, i.e. 22%.

The present-day bulk production of organic carbon on land is more or less equal to that of the seas and oceans. Terrestrial photosynthesis amounts to

0.5 to 0.8 x 10^{17}gr C/yr, and marine photosynthesis produces about 0.5 x 10^{17}gr C/yr, Bolin et al. (1979). Nevertheless, the surface area of the land is less than 1/2 of that of the oceans. On the average the organic production per unit area is therefore four times higher on land than in the sea (Thompson, 1978), and therefore also the quantity of nutrients which is incorporated in the cycle. Ajtay, Ketner & Duvigneaud (1979) present data on primary production in terrestrial and marine ecosystems: algal beds, reefs, and estuaries appear to be the only marine environments which approach the high productivity of terrestrial ecosystems. 90% of the ocean surface can be defined as biological desert (Thompson, 1978). In terms of total surface area, highly productive marine ecosystems fade into insignificance when compared to land areas with a high production.

During a transgression, the quantity of terrestrial soils, peat, etc., that is fossilized, decreases, and an equivalent amount of nutrients is, in the long run, transferred to the oceanic realm. If the lower production capacity of marine environments is considered, then it follows that the quantity of nutrients that would have been used by terrestrial vegetation per unit area on the gradually submerging parts of the continents, is more than the amount needed or usable for the marine organic cycle on the same surface. Thus a large and gradual transgression leads to an excess of directly available nutrients in the global exogenic system, part of it in the ocean, which excess will tend to be removed in some way, assuming that the global eco-system tends to regain equilibrium. Considering the slowness of replenishment of oxygen in deep water and the large scale anoxity during the Lower and Middle Cretaceous, one of the means was burial of the excess nutrients fixed in the organic matter in pelagic sediments. In addition, the excess quantity of nutrients must have favoured organic production in the ocean, and therefore also have served as one of the mechanisms driving the system to anoxia.

Phosphorus

Amongst the nutrients needed for the production of organic matter, on the land as well as in the sea, phosphorus is one of the most important, and often the limiting, ingredients.
Solution and erosion of phosphorus from rocks, and addition to the biosphere, occurs almost exclusively on the land, but its burial as a part of sediments

occurs on the land as well as in the sea. Thus the phosphorus cycle shows a surficial flow from the land into the ocean, and a subsurface (sedimentation, burial, tectonics, upheaval, erosion) flow back to the land. The whole cycle covers a period of about 10^9 yr (Pierrou, 1979).

It was estimated that an extra amount of organic matter, equivalent to 4 to 7 x 10^{20}gr C has been stored in the ocean sediments over a 40 Ma period. Assuming an average P:C ratio of 1 : 200 in depositing organic matter, an amount of 5 to 9 x 10^{18}gr P would have been buried in conjunction with this organic matter. This implies an extra flux of 0.1 to 0.2 x 10^{12}gr P per year from the land to the sea, being 10 to 20 % of the present-day natural flux, which is in the range of 1.7 x 10^{12}gr P/year (Garrels et al, 1975) to 0.7 x 10^{12}gr P/year (Delwiche & Likens, 1977). This seems a satisfactory figure considering the decrease of the terrestrial surface by about 20%.
It is noticeable that Stumm (1973) states that small increases of the concentration of phosphorus in the oceans will increase the proportion of the present day ocean floor to be covered by anoxic waters owing to an increase of unoxidized organic production. According to data of Garrels et al. (1975), the amount of mined fossil phosphorus presently added to the land surface as fertilizer, detergent, etc., is about 7 times the natural flux. An increasing portion of this phosphorus will, after transport via ground water and through streams, end up in the sea. As the average age of water withdrawn from the ground is probably of the order of hundreds of years (Garrels et al., 1975), it will take at least several decades for this flux to develop fully, and the influence of nutrient-enrichment of the sea to be felt by an increase of the volume of anoxic ocean waters. In the long run, over hundreds or thousands of years, the resulting increase of oxygen content in the atmosphere because of increased storage of organic matter, may affect the terrestrial biosphere because of a greater incidence of large forest-fires such as experienced recently in Australia.

From the above discussion, one might get the impression that phosphorus will be fossilized only in anaerobic settings as a part of organic matter. However, marine phosphorites deposited under normal, aerobic conditions are well-known from highly fertile areas of shallow depth. Such deposits also formed during the Middle Cretaceous, but no indications were found that this would have been so effective as to contradict the above reasoning.

SOURCE OF THE CARBON OF BLACK SHALES

The above estimates of 4 to 7 x 10^{20}gr carbon having been additionally stored as organic matter in pelagic sediments during the Middle Cretaceous is a multiple of the amount available in the now accessible reservoir (ocean and atmosphere: 3.5 x 10^{19}gr C). Much of it must have been subtracted from the $CaCO_3$ cycle (Garrels & Perry, 1974), as is indicated by the presence of $CaCl_2$-bearing minerals in South Atlantic evaporite deposits (Ryan & Cita, 1977).
Another source of carbon must be juvenile carbon. At present, the flux of juvenile carbon, which is released for an important part from volcanoes, is 8.3 x 10^{12}gr C/yr (Pytkovich, 1973). In relation to the amounts present in the oceans and the atmosphere (3.5 to 4 x 10^{19}gr C) this is a minor quantity, but relative to the steady state fluxes (Table 2.1) it is not to be ignored.
A doubling of the ridge volume during the Cretaceous (Turcotte & Burke, 1978) must have been accompanied by an extra (possibly also double) output of juvenile carbon from young ocean crust. On the basis of Russian literature, Budyko & Ronov (1978) show a graph which also indicates a doubling of the quantity of volcanogenic rocks formed per time-unit during the Cretaceous, in comparison to present-day values. They even suggest that this would have helped to bring about a more than five (!) times higher CO_2 level of the atmosphere. Also Fischer (1981) states that the atmospheric CO_2 might have been enriched by a factor three or four, and he notes that this might have contributed to the increase of global temperature by means of the greenhouse effect, and that this may have been the driving force behind the production and storage of excess organic matter.
Such an increased addition of juvenile carbon to the exogenic cycle would have furnished an important part of the extra quantity of fossilized organic matter during this period.

Oxygen level in relation to the fossilisation of organic matter

By estimating the volume and organic content of mid-Cretaceous pelagic black shales, Ryan & Cita (1977) calculate that an extra burial of 8 x 10^{19}gr of carbon would have caused a 20% rise of the oxygen level of the athmosphere. In analogy to their reasoning, the 4 to 7 x 10^{20}gr C which was additionally stored following the calculations in this paper, should have caused a doubling of the oxygen level. However, Lovelock (1979) shows that, relative to the

present day atmospheric oxygen level, an increase of any importance will have a destructive effect on the terrestrial biosphere because of an exponential increase of the chance of ignition of dead and living organic matter.
Therefore, if the excess burial of organic matter in Cretaceous pelagic sediments did indeed cause an important increase of the oxygen level of the atmosphere, then the starting point whould have been significantly lower than the present-day 21% level.

Increase of oxygen level is known to favour the development of so-called C_4-photosynthesis in Angiosperms. This is a respiration system which evolved through convergent evolution at least some 20 different times within at least ten families of Angiosperms. Its evolution is favoured by high oxygen and low CO_2 levels, and by warm, arid semi-tropical to moist tropical conditions; it can be distinguished from the normal C_3-photosynthesis by the fact that $\delta^{13}C$ of the organic matter formed by C_4-photosynthesis is quite high (-9 to -18 o/oo) relative to that of C_3 organic matter (-23 to -36 o/oo) (Smith, 1976). As yet the oldest examples of species exhibiting C4-characteristics were found in sediments of Pliocene age (Nambudiri et al., 1978), but earlier occurrences can not be excluded.

In order to check if the inferred high O_2 level during the Middle Cretaceous might have led to an early development of C_4-photosynthesis, some analyses of the stable carbon isotope composition of terrestrial organic matter from that time were made. 6 bulk samples of coal from the Utrillas Formation near Escucha (Teruel, Spain) of Middle Albian age show $\delta^{13}C$ values of -22 to -23.5 o/oo, and for isolated Angiosperm tissue from the Dakota Formation (Lower Cenomanian) in Kansas, kindly supplied by Dr.D.L.Dilcher (Indiana University), 5 measurements gave values varying from -25 to -28.5 o/oo. So, although not proving the absence of C_4 photosynthesis, neither these results nor the literature data indicate that C_4 photosynthesis would have been active during the Middle Cretaceous. This indicates that the CO_2/O_2 ratio was not necessarily low during the Cretaceous as compared to the modern ratios.

CAUSES AND RESULTS

In the exogenic cycle, numerous feedback and buffering mechanisms tend to compensate for changes in the chemical system. An increase of the oxygen level in the atmosphere will result in an intensification of oxidation of minerals at the earth's surface (e.g. FeS_2) thus leading to the formation of features such as red beds, gypsum deposits, etc. A rise of the CO_2 level in its turn may induce chemical weathering and thus increase the quantity of available nutrients which reversely serve to the subtraction of CO_2 by photosynthesis, which again is favoured by increased temperatures owing to possible greenhouse effects. Such negative feed-back mechanisms tend to restore equilibrium conditions.

Phenomena that characterize the Lower and Middle Cretaceous include the increased rate of seafloor spreading and volcanism, high sealevels, low ocean water circulation velocity, resulting in widespread anoxia and burial of large amounts of organic matter in the ocean, high global temperatures and low temperature gradients, and the speeding up of evolutionary processes. All seem to be closely interrelated (Fig. 2.9). The position of a number of these features within the series of causes and effects are clear. That of others is questionable.

Undoubtedly, the increased rate of seafloor spreading and the rise of sealevel form the basis for the whole complex of phenomena depicted in figure 2.9. But, for example, it is not clear whether the anoxic deep ocean waters have acted as an active trap, sucking away unoxidized organic matter, or if, reversely, a high CO_2 level and an increased flux of nutrients into the ocean have resulted in a (relative) increase of organic production in the (overall low productive) ocean, a production which was too high for the system to cope with, and thus induced anoxia in deep water.

The complexity of the exogenic system does not allow pure causes and pure effects to be designated, but in all likelihood the intricate connection and interaction of all the processes concerned have forced the system as a whole to arrive at new equilibrium conditions adjusted to the higher sealevel. Apparently the storage of large amounts of organic matter in pelagic sediments was one of the prerequisites.

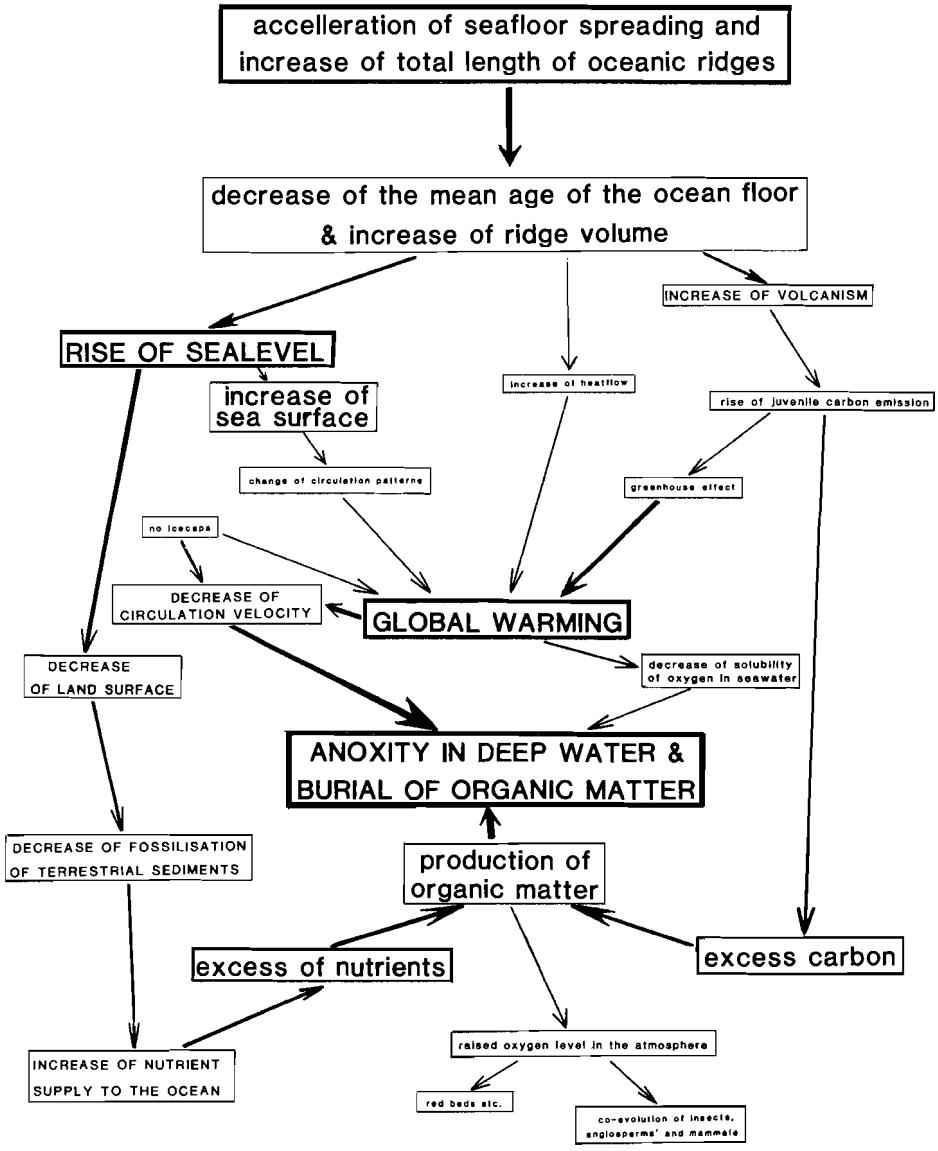


Figure 2.9 Interaction of the processes connected to the great rise of sealevel and the large scale storage of organic matter during the Lower and Middle Cretaceous.

CHAPTER 3

FIELD DATA

Pelagic sediments of Middle Cretaceous age were studied in the field in S.E. France and in Italy (Fig. 3.1).

The sections studied in S.E. France are located near Vergons, Col de Paluel and La Vierre (Fig. 3.1b). The first two have been extensively described by Cotillon, by Moullade, and their co-workers. The sequence near La Vierre (La Vière) was a fresh road exposure.

The field study in the Apennines was concentrated on the Aptian - Cenomanian sequence near Moria. In addition, some other exposures in the area were studied (Fig. 3.1c).

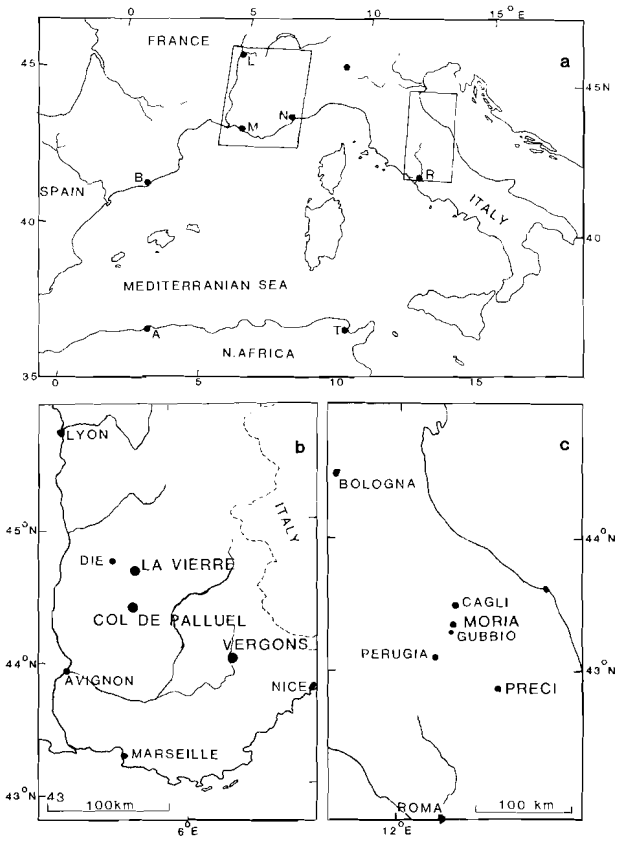


Figure 3.1 Location of the studied fieldexposures

Stratigraphic control was made possible by the presence of foraminifera and dinoflagellates which were studied by P. Marks, A.A.H. Wonders, A.R. Fortuin and A.W. van Erve. These two areas offered two different environments that were the subject of this study; in S.E. France, deposition occurred within the Vocontian Trough, an inland basin adjacent to the Tethys Ocean (Fig. 3.2); the Italian sequence represents a more or less open oceanic environment (cf. Wonders, 1980; Arthur & Premoli Silva, 1982).

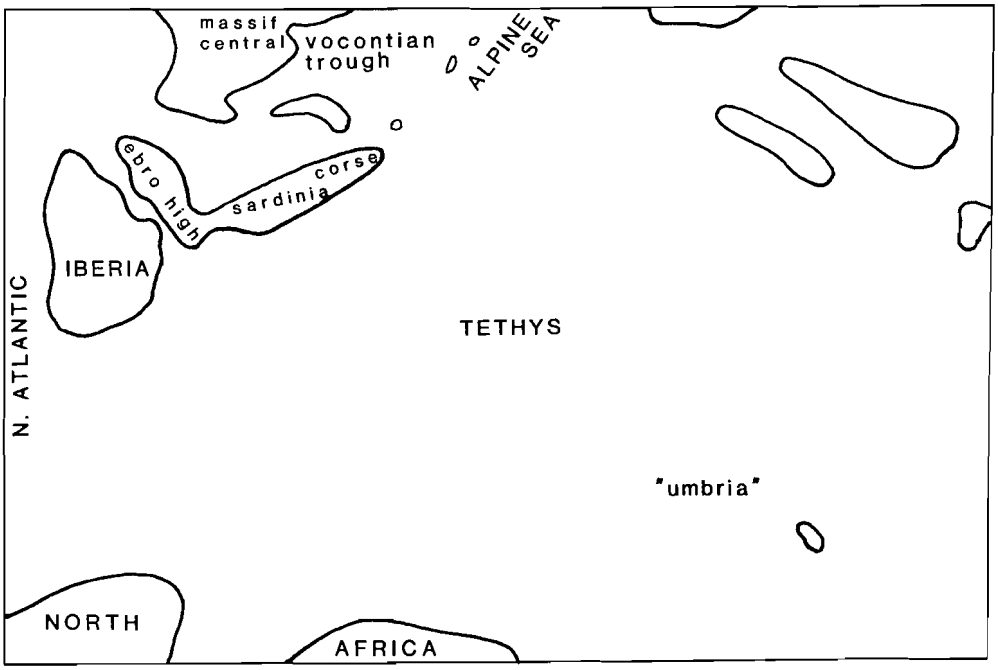


Figure 3.2 Paleogeographic reconstruction of the western Tethys area during the Middle Cretaceous; after various authors.

VOCONTIAN TROUGH, S.E. FRANCE

The Middle Cretaceous pelagic series in SE France resembles the scheme of figure 1.1. The Lower Cretaceous up to the Barremian is characterized by light coloured carbonate beds with marly interbeds. The Aptian/Albian consists of a monotonous succession of dark grey to black marls interbedded with layers with a higher amount of carbonate (Fig. 3.3). Towards the Cenomanian the proportion of carbonate in the sediment increases, and the higher parts of the sequence show a lithologic development similar to the Lower Cretaceous. The Vocontian Basin was enclosed by land masses during deposition of the analysed sequences.

A relatively high input of terrestrially derived sediment can be expected, and indeed, to the south, west and north of the area of the studied successions, sandy and conglomeratic intercalations are present.

The land-locked situation may be expected to cause changes of climate to be of influence in a different way as compared to the open ocean. Variations in the precipitation on the land or lateral shifts of deltaic systems will probably affect the inflow of fresh water.
The area was located at a latitude of 30^0 to 35^0N (Smith & Woodcock, 1982).

No indications were found that syn-sedimentary tectonic processes would have significantly influenced the analysed successions.

Figure 3.3 Exposure of the sequence near Vergons, S.E. France.

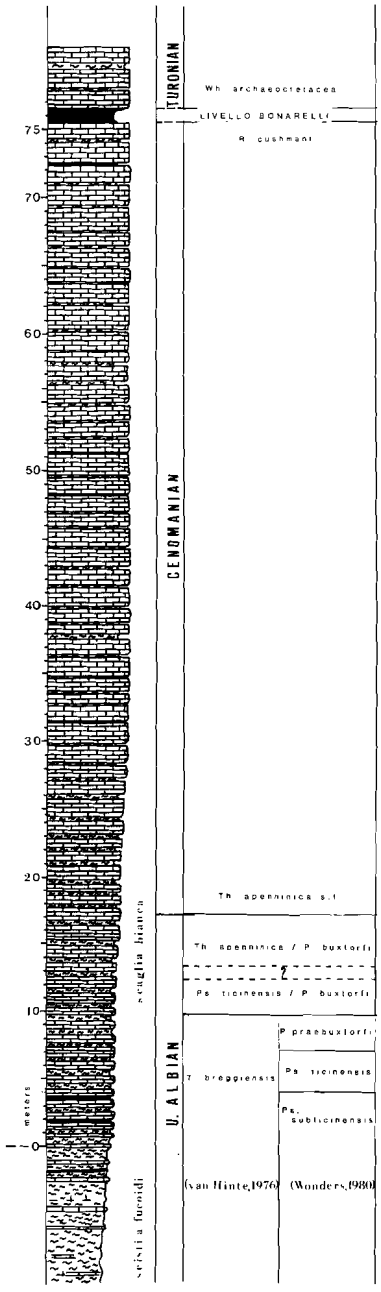
Near Col de Paluel, east of Rosans, two short sections of Middle Albian age, containing laminated intervals, were sampled.
The measured and sampled section near the village of La Vierre was formed during the Lower Cenomanian and covers part of the ticinensis / buxtorfi Zone to the appenninica Zone. Here also special attention was paid to the laminated intervals without benthonic foraminifera.

THE UMBRIAN APENNINES

The Cretaceous pelagic series in Umbria is underlain by Triassic and Lower Jurassic shallow marine carbonates which were largely affected by extensional faulting and subsidence in relation to the opening of parts of the Tethys Ocean (cf. Winterer & Bosellini, 1981; Arthur & Premoli Silva, 1982). Vertical movements caused a deepening of the basin, starting in the lower Jurassic. It is likely that the pronounced submarine relief, that had such an important influence upon the sedimentation during the Jurassic period, continued to play a role during the Cretaceous. This is indicated by the occurrence of small slumps, and by rapid lateral changes of thickness of stratigraphic units. More or less isolated submarine basins may have existed, in which exhaustion of oxygen and accumulation of organic C rich sediments could occur more easily than on the rises. A recent analogue of such a morphology may be the Orca Basin in the Gulf of Texas (cf. Sackett et al, 1979).
The paleolatitude of this area during time of deposition was about 25^0 to 30^0 N (Smith & Woodcock, 1982).

Roughly, the mid-Cretaceous sequence shows the same appearance as the one in SE France (cf. Fig. 1.1), with alternations of carbonate-rich and marly beds up to the top of the Barremian ("Maiolica Limestone") and from the Upper Albian upward ("Scaglia Bianca"). The Aptian and the Lower and Middle Albian are represented by a generally less well exposed, carbonate-poor interval, with dark grey to black and reddish to greenish parts ("Scisti a Fucoidi").

The main studied section near Moria, a small village near Cagli, province of Pesaro and Urbino, is an excellent exposure along the road to the summit of Monte Petrano. This sequence consists of a regular alternation of carbonate-rich and carbonate-poorer beds or marls (Fig. 3.4 and 4.3), and covers the Upper Albian and the complete Cenomanian.
The 75 meters studied (Fig. 3.4), comprise the transition from the Aptian-Albian "Scisti a Fucoidi" to the overlying "Scaglia Bianca". Both contain ichnofossils of the Chondrites-type ("fucoidi"), which are especially frequent in the marls. Often the marls are darker coloured in the middle of the beds than at the rims; they are sometimes completely black.
The contacts between marl and limestone beds are gradational.
The transition from the "Scisti a Fucoidi" to the overlying "Scaglia Bianca" is gradual, and involves an increase of average carbonate content and a



lightening of colour.

The Scaglia Bianca is composed of regularly bedded limestones with bed-thicknesses of one to a few decimeters. The limestone layers are separated by very thin to a few centimetre thick marly interbeds, with gradational contacts. Chert lenses and nodules are present in some of the limestones, especially in the upper part of the sequence.

Stratigraphically the sequence extends from the late Albian (Pseudothalmanninella subticinensis Zone), to the Cenomanian - Turonian boundary (Whiteinella aprica Zone), marked by the Livello Bonarelli, and covers a time-span of ten to eleven million years according to the timescale of van Hinte (1976), and 7.5 to 8.5 Ma according to time scales of other authors (Fig. 3.5) This gives an average sedimentation rate of 0.7 to 0.9 cm per 1000 years.

The Livello Bonarelli is a 1.10 meter composite bed of radiolarite, and black and varicoloured shales. This peculiar unit consists of three parts: a lower alternation of varicoloured argillites and radiolarites, a middle part of black laminated shales, and an upper alternation of varicoloured argillites and radiolarites. The Livello contains 28 ± 5 recognizable couplets of alternating lithologies and/or colours. The radiolaria tests in some of the intervals

Figure 3.4 Schematic section of the Albian/Cenomanian sequence near Moria, Umbrian Apennines. Comparison of timescales of different authors suggests a time period for this interval of 8 to 11 Ma. About 470 carbonate/marl alternations are present in the measured intervals (0 - 75 m).

are sometimes quite large. This could be suggestive of transport by currents or by turbidites, but no structures indicating such processes were found. For a more extensive description of this level see Arthur & Premoli Silva (1982).

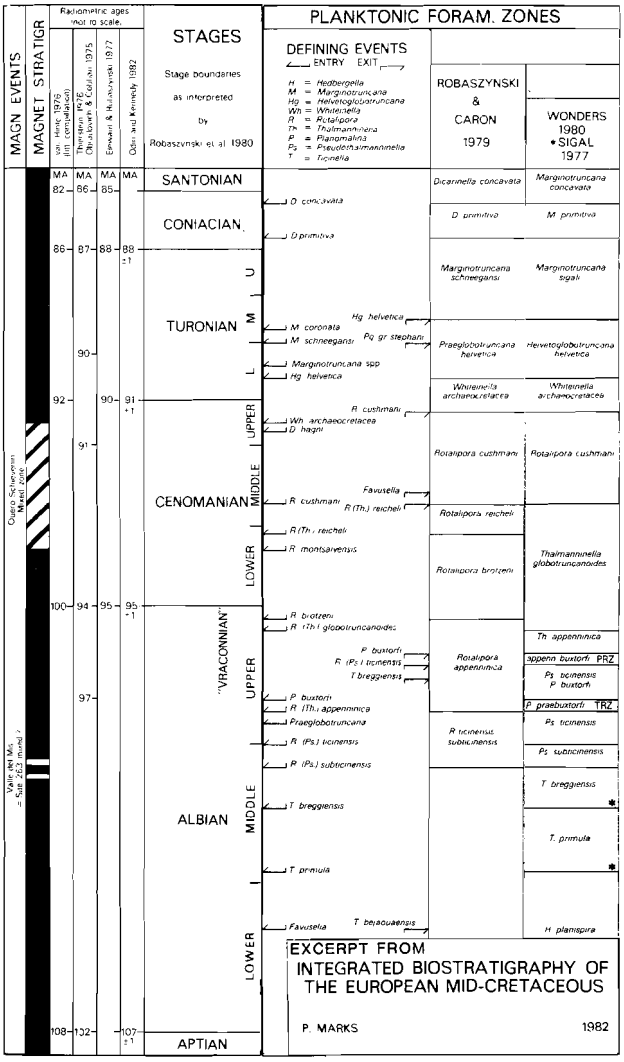


Figure 3.5 Stratigraphic scheme of the Middle Cretaceous (Marks, 1983).

Another section was taken from the "Scisti a Fucoidi" (Aptian - Albian) at the same locality. In the field a rhythmic banding is visible because of an alternation of reddish and greenish colours. The reddish beds are slightly more erosion resistant than the green ones and have a higher carbonate content. Upper Barremian strata west of Acqualagna are distinguished by an alternation of white carbonate-rich intervals and black marls rich in organic matter.
Near the village of Preci, some 80 kilometers southeast of Moria a section was measured for comparison to the main sequence near Moria.

DEPTHS OF DEPOSITION

The Scaglia Bianca was formed at a depth of at least one kilometre (Wonders, 1980). The good preservation of foraminifera shows that deposition occurred well above the carbonate compensation depth, which was at some 3 to 4 kilometers (van Andel, 1975; Winterer & Bosellini, 1981).

The geographic position of the "Fosse Vocontienne", enclosed as it was by land masses, and the absence of mass flow deposits in the analysed successions, puts limits to the depth of deposition of the studied sediments. Assuming a diameter of the basin of 150 km and considering that turbidity currents, of which no traces were found in the studied sections, already may start on a slope of the order of about 0.05 to 0.1 degree (Middleton & Southard, 1978), the depth cannot have been over a few hundred meters.

The difference in depth between the two areas during time of deposition also appears from the Barium content. Due to physico-chemical factors the enrichment of marine sediments by Barium-compounds tends to be greater with increasing depth (Nicholls, 1967). 16 samples from the French sections, analysed by means of neutron activation at the I.R.I. in Delft, show an average Ba-content of 844 ppm, whereas 12 comparable samples from the Albian in the Apennines contain a mean of 1901 ppm.

Figure 3.6 Marnes a Fucoidi (Aptian/Albian) near Moria.

CHAPTER 4

CARBONATE, ORGANIC MATTER, AND PRODUCTIVITY

The pelagic sediments studied in Italy and France, often show a regular bedding which is commonly described as "rhythmic" or "cyclic". This term is applicable to a wide variety of sedimentary phenomena ranging from tidal layerings to long-term cyclothems created by the migration of facies belts.

Regular variations of carbonate content within pelagic sedimentary successions is a characteristic feature in many places, and it has been taken by many as just a quality of pelagic sediments. In the present context, with carbonate-marl rhythms having been formed in a deep marine environment, many of the mechanisms that can create rhythmic bedding do not need being discussed. Turbidite deposits have not been found in the analyzed successions and signs of other forms of mass transport, such as small scale slumping, were only found occasionally.
Two mechanisms are left, that can be held responsible for the origin of carbonate-marl cycles: primary variations in the supply of the sedimentary constituents, and diagenetic processes.

CAUSES OF THE RHYTHMICITY IN PELAGIC SUCCESSIONS

Diagenetic processes

There is a wide-spread opinion that diagenesis is the origin of rhythmic layerings found in pelagic sediments, which opinion is not based on sound data. Einsele (1982) states: "According to our present knowledge on the diagenesis of carbonates, a rhythmic unmixing of a completely homogenous sediment column appears to be very unlikely. In this case the result of diagenesis probably would be a random distribution of limestone nodules within a marly matrix or a nodular limestone with thin and irregular lenses of marl."

During compaction and diagenesis of carbonates, dissolution and reprecipitation of carbonate occurs. Due to physico-chemical conditions, dissolution tends to occur in the marly parts and reprecipitation in the

carbonate-richer parts which contain relatively more nuclei of the stable calcite phase (Einsele, 1982). Notwithstanding the fact that electron microscopy indicates that diagenetic redistribution of carbonate occurred in the analysed sections, the basic cause of the fluctuation of carbonate content is inferred to lie in the original sedimentary environment. Also our data on the stable oxygen isotope composition (see chapter 5) plead against a diagenetic origin of the rhythms.

PRIMARY VARIATIONS OF SUPPLY OF SEDIMENTARY COMPONENTS

In the Italian sequence a negative correlation between the content of carbonate and the one of organic matter is apparent (cf. Fig. 4.1). The organic matter, when present, occurs in the carbonate-poor parts.

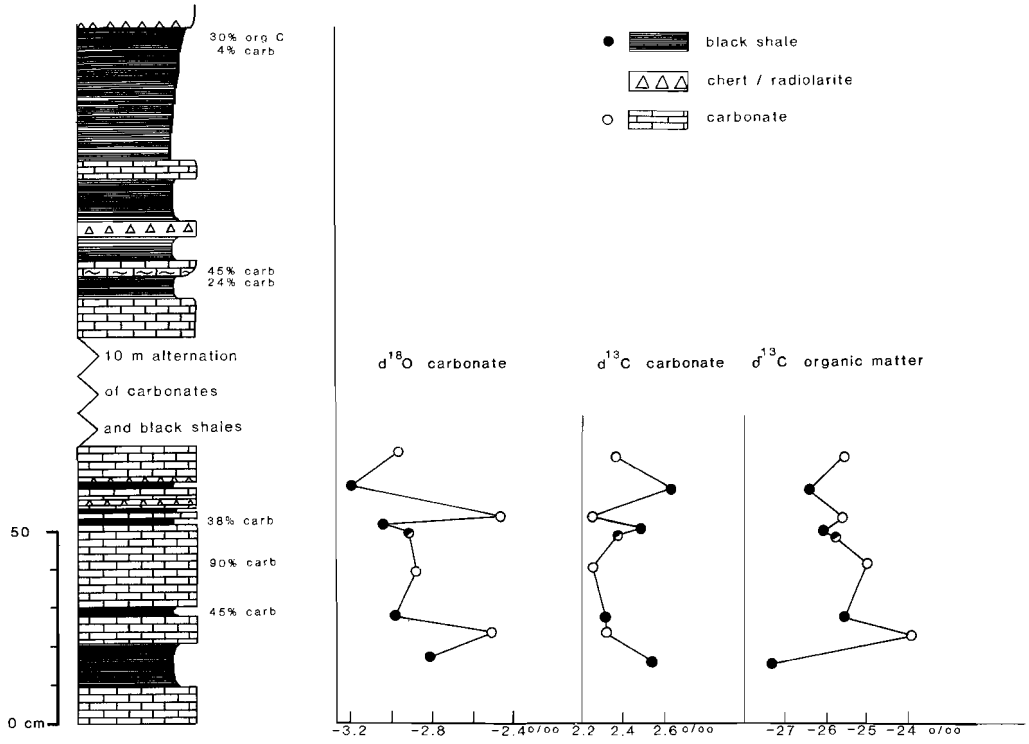


Figure 4.1 Upper Barremian west of Acqualagna

CARBONATE

In the Albian part of the sequence near Moria the carbonate content generally varies between 60 and 80%, the limestone beds containing 5 to 15% more carbonate than adjacent marly beds. The contrast between "carbonate-rich" and "carbonate-poor" intervals in the Scisti a Fucoidi, and in the lower part of the Scaglia Bianca, (Fig. 4.2 , 4.3), is exageratedly accentuated by differential resistance to weathering: differences in $CaCO_3$ content as low as 5 to 10% lead to the formation of massive ledges separated by "shaly" slopes.
In fresh exposures, created by the removal of some decimeters of sediment, the contrast is less visible to the point of disappearance.
The fluctuation of 5 to 15% of the carbonate content seems a rather moderate fluctuation, but it should be realized that an increase of carbonate content from e.g. 50 to 75%, relative to a fixed absolute amount of the non-carbonate portion, implies a threefold increase of the contribution of carbonate.

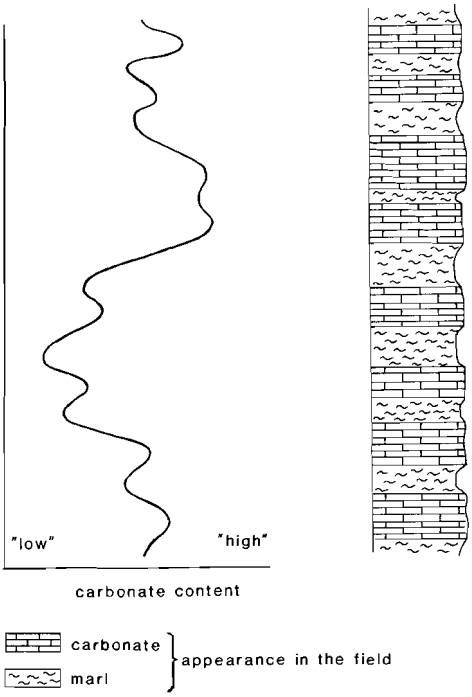


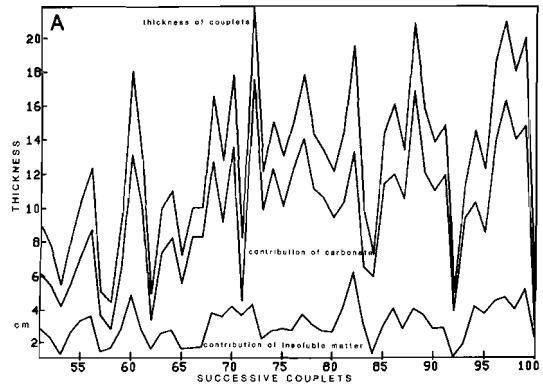
Figure 4.2 The appearance of layers as "marly" or "carbonate" beds is greatly dependent on the character of the adjacent intervals.

Thus, relatively to a fixed amount of insoluble matter a 5% increase of carbonate content implies a 20 to 30% greater contribution of carbonate for the range of values found.
Electron microscopy shows that the larger part of the carbonate consists of calcareous nannofossils.
Microscopic inspection shows that foraminifera have been well preserved (Wonders, 1980). Whereas forams are more prone to dissolution than most calcareous nannofossils, it is concluded that dissolution has not significantly reduced the amount of carbonate, and an average carbonate production of less than 0.002 gr/cm^2 per year can be calculated.
This places the carbonate providing surface waters of this time in the category of present day areas with a very low productivity (cf. Lisitzin, 1972).

Figure 4.3 Part of the Upper Albian near Moria

Calcimetric analyses of the lower 135 couplets reveal that the thickness of the carbonate-marl couplets (calculated as the thickness of each carbonate bed plus half of the thickness of the two adjacent marly beds) is positively correlated with the carbonate content (Fig. 4.4).

The absolute amount of HCl-insoluble matter, including biogenic silica, in each carbonate-marl couplet is, however, more or less constant (Fig. 4.4 A). Expressed as thickness the insoluble residue of the individual carbonate/marl couplets averages to about 3.1 cm.



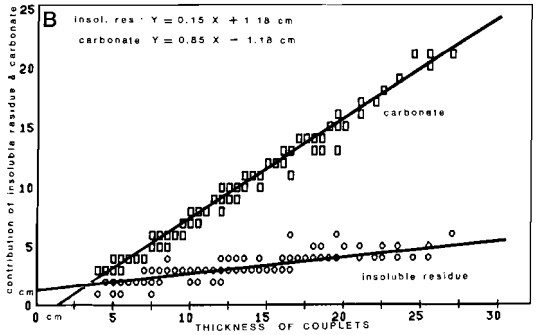


Figure 4.4 A: Thicknesses of the lower 100 carbonate / marl couplets in the Moria sequence, calculated as thickness of carbonate-rich beds plus half of the thickness of the under- and overlying carbonate-poor intervals, contribution to the thickness by carbonate and by HCl-insoluble matter. B: Same data, with the contribution of carbonate and of HCl-insoluble matter (in cm) plotted against thickness.

Thick and carbonate-rich couplets tend to contain slightly higher absolute amounts of insoluble matter. In relation to the total quantity of insoluble matter this difference, however, is small. In view of the fact that the carbonate-marl couplets represent more or less equal timespans, as shall be defended below, three causes can be expected to contribute to the scatter of the amount of insoluble matter in the successive couplets. Firstly, the timespans represented by the carbonate-marl couplets are not exactly equal (chapter 6); thus even a continuous and equable background sedimentation of non-carbonate matter may result in relatively high amounts of insoluble matter in those couplets representing relatively long timespans. Secondly, apart from the regular background sedimentation of non-biogenic sediment, the sinking carbonate was accompanied by additional minor amounts of biogenic silica and/or of non-biogenic matter. In the third place, the thickness of the couplets was defined by calculating the thickness of the carbonate beds plus half of the thickness of the adjacent marly beds. This may have the effect that the values for thickness of couplets, in which the carbonate-rich part represent a long time-span relative to that of the adjacent marly interbeds, used in the calculations, are too high. Indeed, the saw-tooth pattern seen in figure 4.4 B is suggestive of the influence of the last mentioned effect.

Despite these disturbing effects, the data suggest that this sedimentary sequence is the result of a relatively continuous and regular sedimentation of inorganic non-carbonate sediment, with a regularly fluctuating supply of carbonate superimposed.

Assuming deposition from suspension, and no significant redistribution of carbonate by diagenetic processes, the carbonate content must reflect surface productivity.

ORGANIC MATTER

If the organic matter within the black shale intervals is considered, a similar picture develops. A very small primary productivity can produce the quantity of organic matter which is present in Cretaceous black shales, such as found at the top of the Barremian and at the top of the Cenomanian. Because of the good control of the sedimentation rate, the "Livello Bonarelli"

(Cenomanian/Turonian boundary), with a content of organic carbon of up to 20%, is a good illustration. Near Moria it has a thickness of slightly more than one meter. Assuming a constant rate of sedimentation of insoluble matter during the entire Cenomanian, the time for accumulation is of the order of 700,000 years. On the basis of the supposition that the rate of deposition of Al_2O_3 has remained constant, Arthur & Premoli Silva (1982) also arrive at a figure of 700,000 years. A similar calculation on the basis of the Titanium content by the same authors gives a value of 350,000 years.

Fischer (1980) reports about the Bridge Creek Member of the Greenhorn Fm. in Colorado (U.S.A.) which also spans the Cenomanian- Turonian boundary event and probably is the equivalent of the Bonarelli Level in Italy. Fischer estimates the duration of this interval in Colorado to be 800,000 year. This close resemblance, notwithstanding the large distance between the two areas, implies that the event which characterizes the Cenomanian-Turonian boundary was of extensive importance (cf. Schlanger & Jenkyns, 1976).

In the case of a time of deposition of the Bonarelli Level of 350,000 years, settling and burial at a rate of about 0.1 gr org C/cm^2 per 1000 yr would have been sufficient for contributing the organic matter to this interval.
In Recent anoxic environments it was measured that up to 20% of the primarily produced organic carbon eventually reaches the sediment surface (Deuser, 1971). If we apply this figure, a surface productivity of less than a mg C/cm^2 year would have sufficed for the creation of this organic C-rich interval.

This figure may be compared to the primary production in "blue desert" parts of the recent oceans (0.005 to 0.01 gr/m^2 per year, Bolin et al., 1979). It follows again that the surface waters in Umbria during the Middle Cretaceous are comparable to recent oceanic areas with an extremely low productivity. This confirms the idea proposed in chapter 2, that <u>deposition of black shales is not necessarily always the result of a great organic productivity and of an high input of organic matter, but that a lack of oxygen in deep water is at least as important.</u>

On the basis of organic geochemical results, van Graas, et al. (1981) reach the same conclusion.

PRODUCTIVITY AND PRESERVATION

The frequently observed association of high carbonate content and low organic C content, and vice versa, is not a paradox, but it is the logical result of a variation of circulation intensity in slowly circulating and low productive ocean basins. Both, supply of nutrients to the surface waters, with resulting production and sinking of carbonate and of organic matter, and replenishment of oxygen in deep water, are a function of water circulation velocity (Fig. 4.5); in times of strong vertical mixing and upwelling of cool nutrient-rich waters, the nutrient supply to surface waters allows for a relatively high surface production of carbonate as well as of organic matter; at the same time, enough oxygen is provided to deep water to oxidize most of the sinking organic matter. In times of low circulation velocity, the supply of nutrients and the organic production decrease, and this results in a decreased supply of biogenic products to deep water. At the

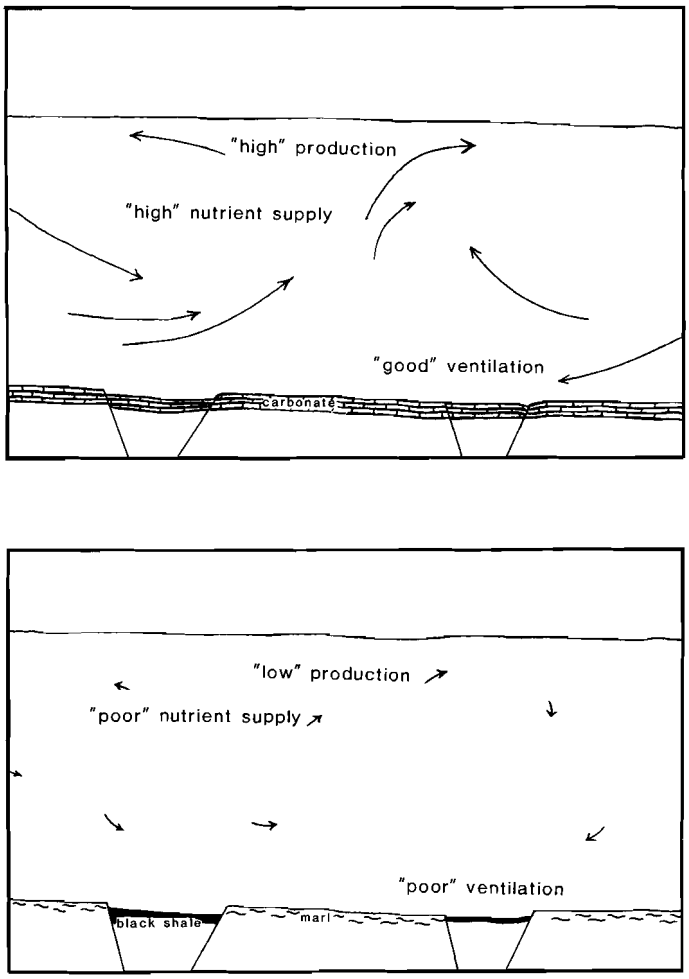


Figure 4.5 Depiction of the reflection of variations of circulation intensity upon the character of pelagic sediments under overall low productive conditions such as found in mid-Cretaceous strata in the Apennines

same time, the replenishment of oxygen in deep water is so much reduced that anoxia starts and that a relatively large part of the organic matter sinking to the bottom cannot be oxidized and is preserved by incorporation within the sediment.

Thus, for sediments deposited above the C.C.D. (Carbonate Compensation Depth), the carbonate content seems to provide the best measure of productivity in the surface layer during time of deposition. The organic carbon content primarily reflects whether the rate of replenishment of oxygen in deep water is enough for the oxidation of the sinking and settling organic matter.

It is illustrative that in the present-day Black Sea, sediments with the highest content of organic carbon lie below surface waters with a very low organic production (Shimkus & Trimonis, 1974).

SILICA

The inferred low productivity of the surface waters which supplied the organic matter of the Bonarelli Level seems to be in contradiction with the observed abundance of radiolarians within this interval. Arthur & Premoli Silva (1982) state that in the Apennines the rate of burial of silica was more than doubled during the Cenomanian/Turonian boundary event as compared to the period before. They compare the radiolarian-rich sediments to recent oceanic environments under oxygen minimum zones in highly productive parts of the oceans.

However, compared to sedimentation rates of SiO_2 during the Holocene (Lisitzin, 1972), the mean rate of deposition of about 0.2 gr SiO_2 / cm^2 per 1000 yr, which stands for the Bonarelli Level, is on the low side.
Heath (1974) states that only 4% of silica tests formed in the water column, survives long enough to be buried, and that only 2% avoids post-depositional dissolution and enters the geological record. Data on the global silica budget by Lisitzin (1972) even indicate that less than one percent of the primarily produced silica is buried in bottom sediments.

In general there is a distinct negative correlation between silica and calcite in pelagic sediments, which was ascribed to opposing chemical requirements for preservation (W.H. Berger, 1974).

Taking into account the above arguments, and considering the near-absence of carbonate in the Bonarelli Level, it is probable that the high silica content of the Bonarelli Level reflects a short-term change of chemical conditions rather than representing an extremely high organic production.

VOCONTIAN TROUGH

The average sedimentation rate in the Vocontian Trough is estimated to have been of the order of 2 cm/1000 years. This value is not as accurate as for the Italian example, due to the fact that the measured sections cover only rather short stratigraphic intervals. Productivity and the apport of organic matter seem to have been slightly higher than in the Italian example, but as compared to recent analogues it has been low.

The layers forming the Aptian/Albian sequence near Vergons show a variation of the carbonate content (Fig. 4.6). In the field the differences in composition are accentuated by differential resistance to weathering and erosion, which makes the ligther coloured, more carbonatic layers to protrude, and the darker weathering, more marly intervals to recede (Fig. 3.3).
Analytical data on the content of carbonate and organic matter, as given in figure 4.6, are suggestive of a slightly negative correlation between these two components (corr. coeff. -0.31). However, an increase of the relative amount of one of the sedimentary components automatically implies a relative decrease of the others. When both components are considered independently, i.e. in relation to the quantity of other sedimentary components, no correlation appears to exist between the two variables (corr. coeff. 0.02); the contribution of organic matter and of carbonate to the sediment, therefore, seem to have occurred independently here.

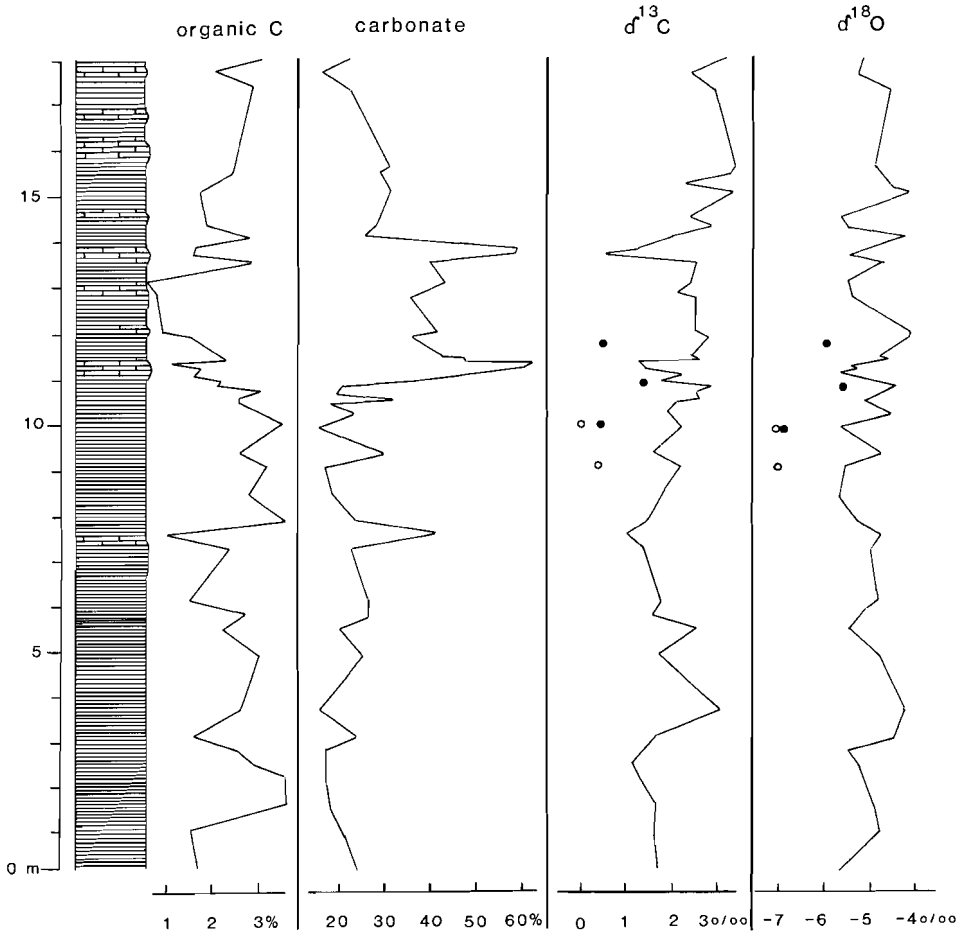


Figure 4.6 Section near Vergons covering the Aptian/Albian boundary. Stable isotope data of bulk samples (curves) by courtesy of Drs. P.A. Scholle and M.A Arthur. Open circles are the isotope data of the carbonate of iso lated planktonic foraminifera and the black dots of that of benthonic foraminifera.

The analytical data for the La Vierre section (Fig 4.7) also show hardly any correlation between the content of carbonate and of organic matter.

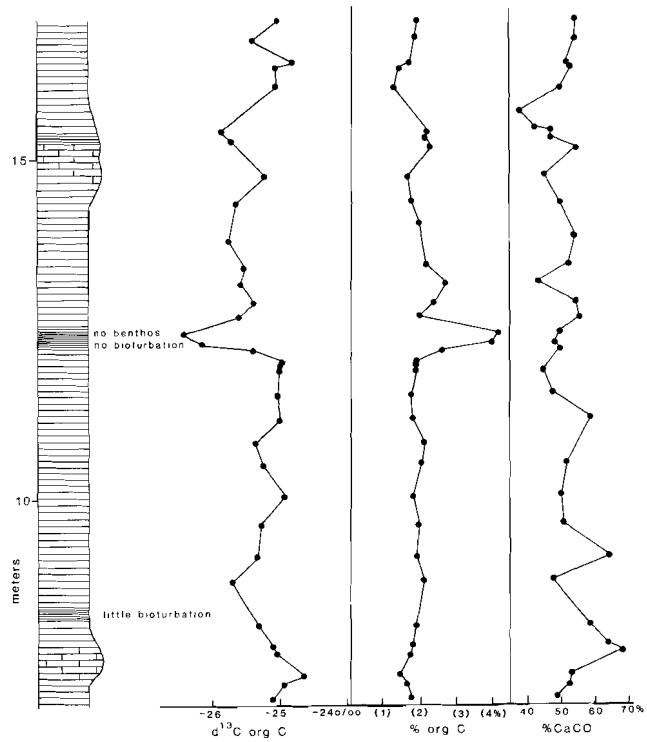


Figure 4.7 Section near La Vierre

Thus, the clear negative correlation between organic matter and carbonate content as was found in the Mid-Cretaceous of the Apennines, is not seen as clearly in the French successions. In figure 3.2, the contrast in paleo-geographic setting of the two areas of study is illustrated. In the open ocean circulation intensity is the main factor in supplying nutrients to surface waters and oxygen to the deep. Other processes may additionally play a role in semi-enclosed inland basins such as the Vocontian Trough, where variations in the influx of fresh river waters with nutrients and organic matter from the land, and where the influx of denser salty water from the other side, or from evaporite settings such as in the modern Black Sea, may have been of major influence. Also processes such as fluctuations in the supply of nutrients by winds, or simply by the diversion of fluvial and / or deltaic discharge patterns, may have played a role.

The near-absence of planktonic foraminifera in a part (Middle to Upper Albian) of the sequence near Vergons where an increase of the quantity of laminated intervals could be observed, and in which the benthic fauna persisted (pers. comm. A.R. Fortuin), suggests a common cause of these two features. This common cause may have been that, in this case, influxes of fresh water disturbed the biological environment in the upper part of the water column and led to a reduction of the oxygen supply to deep water because of stratification of the water column.

The maximum diameter of specimens of Hedbergella sp. from a number of samples from two sections near Col de Paluel was measured (Fig. 4.8).
The size of the specimens in laminated, unbioturbated parts of the succession formed under anoxic conditions, appears to be significantly larger than that of specimens from well-bioturbated parts formed under aerated conditions.
From literature it is known that planktonic foraminifera tend to postpone the breeding of off-spring in the case of a lack of food and thus continue to increase in size. The larger size of Hedbergella sp. found in the anoxic and laminated parts of the succession therefore indicates low viability conditions during the formation of the unbioturbated laminated parts when both oxygen renewal in the deep, and supply of nutrients to the surface waters were low connected with a low circulation velocity (at this place and time). In this example the laminated intervals are not free of pelagic foraminifera as in the previous case. This points to low-nutrient rather than to hostile (low salinity) conditions in surface waters.

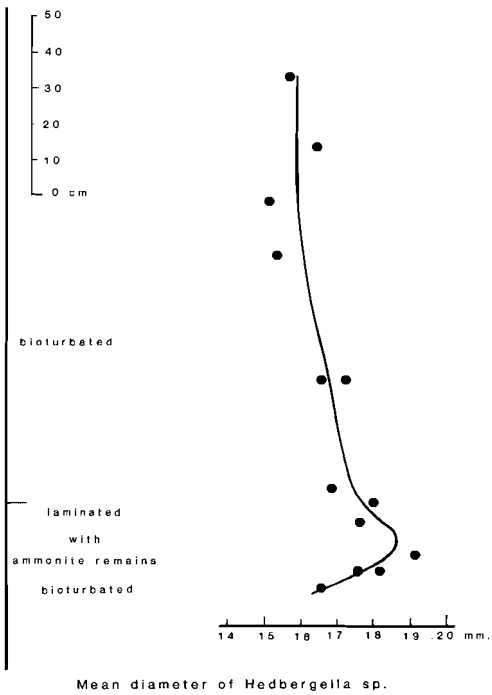


Figure 4.8 Size of Hedbergella sp. specimens in a part of the succession near Col de Palluel (S.E. France).

These examples from different localities in the Vocontian Trough show that in nearshore pelagic settings one should make allowance for the importance of a broader variety of different processes than only the variations in circulation intensity which explain the litologic variations seen in the Italian examples.

To summarize: taking the view that the Cretaceous oceans were characterized by a low circulation velocity and by an overall low organic production (chapter 2), a high carbonate content of pelagic sediments in open oceanic settings reflects a fair water circulation with a relatively high surface production. The related low organic content reflects a relatively good replenishment of oxygen in deep water. The lower carbonate content of the black shale and the marly intervals reflects a (very) low surface production. The relatively still more strongly reduced supply of oxygen to the bottom water allowed anoxity and burial of a part of the (small amount of) organic matter that was produced at the surface (Fig. 4.5).

When variations of circulation intensity are the only factor involved, as seems to have been the case in the low productive and slowly circulating Cretaceous ocean in which the Italian sequence was formed, a clear negative correlation between the content of carbonate and organic matter can result. In land-locked basins other processes, related to the nearness of the land are active and can make that the relations are more complex. A lateral change in the negative correlation between the content of carbonate and organic matter in pelagic sediments can therefore be used to discern trends, indicating the directions towards open oceanic environments, and towards more restricted or marginal settings.

CHAPTER 5

STABLE ISOTOPES

Fluctuations of marine environmental conditions in that part of the water column where the primary production occurs, i.c. the photic zone, are reflected in the stable isotope ratios of the carbonate and of the organic matter. Reversely, the stable isotope composition of sediment samples can provide information about the original environment.
The interpretation of stable carbon isotope ratios has proved to be far more complex than that of stable oxygen isotopes, and the relative importance of the determining factors is less well known.

Prior to the presentation and discussion of the analytical results, factors which influence the stable isotope ratio of biogenic products and their sources are summarized.

STABLE OXYGEN ISOTOPES

$\delta^{18}O$ of ocean water

During the Middle Cretaceous the oxygen isotope ratio of ocean water has been lower by 1.5 to 2 o/oo in comparison with present day conditions, 1 o/oo due to the absence of polar icecaps, and in addition 0.5 to 1 o/oo owing to other causes. Polar ice has $\delta^{18}O$ values as low as -50 o/oo, and Shackleton & Kennett (1975) estimate that the formation of the Antarctic ice sheet caused the $\delta^{18}O$ of the ocean to rise by about 1 o/oo. Long-term variations, probably related to processes such as deposition and erosion of evaporites, almost certainly caused the oxygen isotope composition of the Middle Cretaceous oceans to have been about 0.5 o/oo lower than immmediately before the start of the growth of polar icecaps during the Quaternary (cf. Claypool et al., 1980; Scholle & Arthur, 1980). The difference of about 1.5 o/oo between modern and Cretaceous ocean water should be taken into account when using Middle Cretaceous ratios for the calculation of paleotemperatures.

As icecaps were absent during the Middle Cretaceous, fluctuations of $\delta^{18}O$ cannot be ascribed to glacial effects as during the Pleistocene-Quaternary.

Fractionation during the formation of carbonate and diagenesis

The rate in which ^{16}O and ^{18}O are incorporated within biogenic carbonate, depends on temperature and on salinity. Whereas the discussion below is focussed on open oceanic sediments, the influence of salinity changes is considered to be unimportant. Temperature, however, can have fluctuated. With increasing temperature the $\delta^{18}O$ ratio of newly formed carbonate decreases.

Shackleton & Kennett (1975) suggest the equation

$$T(\text{in } ^{o}C) = 16.9 - 4.38 \times (\delta^{18}O_{carb} - \delta^{18}O_{water}) + 0.10\,(\delta^{18}O_{carb} - \delta^{18}O_{water})^2.$$

Vital effects, i.e. the uptake of stable isotopes by organisms out of chemical equilibrium with seawater, dependent on species and/or environment, may result in variations in oxygen isotope ratio from one species to the other. In the studied series the bulk of the analysed carbonate consists of nannofossils.
For calcareous nannoplankton vital effects were reported to be an unimportant factor (Margolis et al., 1975). Goodney et al. (1980) report a systematic depart from equilibrium, but they also state that the $\delta^{18}O$ ratio of $CaCO_3$ of the nannofossils apparently responds to temperature (see also Kroopnick et al., 1977).
This implies that variations the $\delta^{18}O$ ratio of the bulk pelagic carbonates should be a good measure of variations of the paleotemperature.

Diagenetic processes may lead to changes of $\delta^{18}O$ values of the carbonate, and generally precipitation of carbonate during diagenesis results in a lowering of the $^{18}O/^{16}O$ ratio of bulk carbonate (cf. McKenzie, et al., 1978).

STABLE CARBON ISOTOPES

Factors which define the $\delta^{13}C$ of fossil marine organic matter and carbonate, include the isotopic composition of the inorganic carbon source, fractionation effects during photosynthesis, and possible alterations during settling, burial and diagenesis.

$\delta^{13}C$ OF SURFACE WATERS

Formation of black shales

The $^{13}C/^{12}C$ ratio of marine carbon increases, when a prolonged (in the order of millions of years) net subtraction of organic matter from the active carbon cycle occurs by the formation of black shales; such an increase during the Cretaceous is reflected by, e.g., fossil carbonates (chapter 2).
In the short term, the storage of organic matter in pelagic sediments cannot cause significant changes of $\delta^{13}C$ of ocean-dissolved-carbon.
In the extreme case of black shales with consistently a 5% content of organic carbon, and a sedimentation rate of 5 cm/1000 yr, (which is very high considering literature data and own results), 2 to 3 gram of carbon in organic matter are stored annually per square meter. This is less than a permille of the amount of carbon present within the modern photic zone in a column of one square meter. For the actual (lower) values in the studied sediments (cf. chapter 4), the quantities are less.

The surficial exchange with the atmosphere is the most important factor of refreshment of the carbon in oceanic surface waters. Craig (1957) calculated an exchange rate of 2×10^{-3} mole CO_2/cm^2 per year over the sea/atmosphere interface. The (modern) residence time of carbon in the oceanic surface layer is estimated to be of the order of 5 to 10 years (Kester & Pytkovitch, 1977), and Broecker & Peng (1974) state that the isotopic equilibration time of CO_2 between the mixed layer of the ocean and the atmosphere is about 12 years. Therefore, the residence time of CO_2 in the surface water will not be significantly influenced by a slowing down of ocean circulation. On short term, that is over periods of the order of 10 to 100 Ka, the refreshment of carbon in surface waters is, therefore, sufficiently rapid to compensate for

any change of the $\delta^{13}C$ by local burial of organic matter in pelagic sediments.

It is concluded that, in contrast to the long term effects, the short term intermittant storage of organic matter in pelagic sediments can hardly have influenced the $\delta^{13}C$ of inorganic carbon in the oceanic surface layer.

Vertical mixing and productivity

The larger part of the dead organic matter ($\delta^{13}C \sim -25$ o/oo), sinking down from the photic zone, is oxidized before reaching the sediment surface. Consequently, the $\delta^{13}C$ of inorganic carbon in modern surface waters exceeds that in deep water by a permille or more. The circulation velocity of modern oceanic waters is measured in thousands of years. During the Cretaceous it was slower than at present, and the turnover time must have covered a much longer period. The observed difference between deep water and the surface layer during the Cretaceous (based on the comparison of $\delta^{13}C$ of planktonic and benthonic foraminifera) was less, of the order of 0.5o/oo, (W.H. Berger, 1979). Therefore, fluctuations in the rate of supply of C-depleted deep ocean water to the surface had less influence upon the $\delta^{13}C$ in surface waters during the Cretaceous than at present.
The low circulation velocity of ocean waters implies that $\delta^{13}C$ of the inorganic carbon in the water brought from the deep to the surface represents the influence of the sinking and oxidizing of organic matter averaged over long periods. On the other hand, the transport of organic matter from the photic zone into the deep, i.e. the subtraction of light (low $\delta^{13}C$) carbon has an immediate influence upon the $\delta^{13}C$ in surface waters. Thus, in periods with a "high" production and a relatively high amount of sinking dead organic matter, surface waters in the overall low productive Cretaceous oceans must have shown an increase of $\delta^{13}C$ of the remaining carbon relative to low-productive periods.

In recent oceanic environments it is often seen that the $\delta^{13}C$ of marine biogenic products is low in areas with relatively cool surface waters (Eadie & Jeffrey, 1973; Fontugne, 1978). This feature is probably a derivate from the combination of (1) the fact that high productivity is often caused by the upwelling of cold and deep nutrient rich water, which (2) is generally depleted in ^{13}C, and (3) that exhaustion of the HCO_3^- stock because of high

productivity, can result in the consumption of light dissolved gaseous CO_2 ($\delta^{13}C \sim -10$ o/oo) instead of HCO_3^- ($\delta^{13}C \sim 0$ o/oo) (Goodney et al, 1980).

Primary productivity in the Tethys was shown to have been low, and to be comparable to that in present-day "tropical marine deserts". Therefore, the concentration of HCO_3^- must have been continuously sufficient for photosynthetic processes, so that the dissolved CO_2 stock has been unused.

Fractionation over the air-water interface

In equilibrium conditions, the $\delta^{13}C$ of atmospheric CO_2 is about 7 to 10 o/oo less than that of HCO_3^- dissolved in seawater (Emrich, Ehhalt & Vogel, 1970; Mook, Bommerson & Staverman, 1974). The difference is dependent on temperature; for each degree colder, it increases by about 0.1 o/oo.
A wide scale lowering of the temperature thus leads to a net transfer of ^{12}C from the ocean into the atmosphere and of ^{13}C from the atmosphere into the surface layer of the ocean. As a result, $\delta^{13}C$ in surface waters increases.

Biomass on land

Like marine organisms, the land plant organic matter has a lower $\delta^{13}C$ ratio than the inorganic source due to fractionation during photosynthesis. The degree of depletion is dependent on temperature, $\Delta\ \delta^{13}C \sim +0.4$ o/oo / $(^{o}C)^2$, that is, an increase of temperature leads to higher $\delta^{13}C$ values of the terrestrial biomass (Fraser, Francey & Pearman, 1978). A wide scale climatic warming would therefore result in a net transfer of ^{13}C into the land plant biomass, and, indirectly, in a depletion of ^{13}C in the surface layer of the ocean.

The temperature dependence of carbon isotope fractionation between water, air, and the terrestrial biomass may offer an explanation for the strong negative shift of $\delta^{13}C$ over the Cretaceous-Tertiary boundary, observed in many places. Although the opinions about the exact nature of the boundary event differ, it is agreed that it happened within a short time interval and that it was connected to a global warming. E.g., Romein & Smit (1981) estimate a rise of temperature of more than $8^{o}C$. In combination with other processes, such as a

possible diminishing of the terrestrial biomass (cf. Shackleton, 1977), and the influence of temperature upon the $\delta^{13}C$ of the land plant biomass, such a warming should have caused a transfer of ^{13}C from the surface layer of the ocean into the atmosphere and have contributed to the ^{13}C depletion of surface waters and marine carbonates of that age.

In summary: changes of temperature are of influence upon the $\delta^{13}C$ of carbon dissolved in surface waters by various mechanisms. A decrease of temperature should result in an increase of $\delta^{13}C$ of carbon dissolved in the surface layer, and vice versa.

FRACTIONATION DURING THE FORMATION OF CARBONATE

The isotopic fractionation between inorganic carbonate and dissolved bicarbonate has been reported to be temperature dependent. Emrich, Ehhalt & Vogel (1970) suggest an increase of ^{13}C enrichment of carbonate at increasing temperatures (0.04 o/oo /(^{o}C)^{2}). Kroopnick et al. (1977), on the other hand, state that the $\delta^{13}C$ of calcite decreases relative to the dissolved bicarbonate with increasing temperatures (enrichment 1.7 o/oo at 2 ^{o}C, and 0.9 o/oo at 25 ^{o}C). Whichever of these authors is right, the effect seems to be small.

Species dependent deviations of $\delta^{13}C$ from isotopic equilibrium with seawater in forams occur (Shackleton, Wiseman & Buckley, 1973), but quantitatively the effect is subordinate to other influences (Vincent, Killingley & Berger, 1980). As the carbonate in the analysed sections is made up for the bigger part of calcareous nannofossils, vital effects in foraminifera cannot be important for the values measured on the bulk samples. Margolis et al. (1975) state that "calcareous nannofossils deposit calcium carbonate at or near equilibrium with oceanic surface waters". Therefore, vital effects seem to be negligible in the carbon isotope composition of carbonate in the bulk samples.

	$\delta^{13}C$	estimated response time
1. subtraction of organic matter from the global carbon cycle	higher	10^6 - 10^7 yr
2. increase of upwelling	(lower)	10^2 - 10^4 yr
3. increase of production	higher	10 yr
4. decrease of temperature at the atmosphere/sea interface	higher	10 yr
5. decrease of temperature in the atmosphere (fractionation by the land plant biomass)	higher	10 - 100 yr
6. increase of the volume of the terrestrial biomass	higher	100 - 1000 yr
7. decrease of temperature & fractionation during the formation of carbonate	(higher?)	immediate
8. vital effects	?	

Table 5.1 Summary of the effects of different factors upon $\delta^{13}C$ of biogenic carbonate formed in oceanic surface waters during the Middle Cretaceous.

The different factors influencing the $\delta^{13}C$ of biogenic carbonate in the open ocean are summarized in Table 5.1.

If it is assumed that a decrease of temperature goes with an the increase of climatic contrasts and of the circulation velocity of ocean waters, then the effects of factors 3, 4, and 5 in Table 5.1 would all influence $\delta^{13}C$ in the same way. Their effect would be counteracted by factor 2 which is sub-ordinate to 3. Factor 1 is only effective over very long periods and can be neglected for the short term. The size of the terrestrial biomass (factor 6) is not only dependent on temperature, but it is also related to other factors, such as precipitation, humidity, and the availability of nutrients on the land.

DIAGENESIS

Irwin, Curtis & Coleman (1977) have put forward a model of burial diagenesis of organic matter in marine sediments. With the increase of burial depth they subsequently distinguish (1) bacterial oxidation, (2) sulphate reduction, (3) bacterial fermentation and (4) abiotic reactions. During (1), (2) and (4), carbon dioxide is liberated with about the same carbon isotope composition as the organic matter from which it is derived (i.e. ± -25 o/oo). Only during bacterial fermentation, which starts after the sulphate is consumed, the CO_2 set free is isotopically heavy, in the order of +15 to +30 o/oo. CH_4 set free at the same time may be as light as -75 o/oo.
Measurements of recent pore waters and young occurrences of natural gas support this idea; $\delta^{13}C$ CH_4 values as low as -80 o/oo are found and $\delta^{13}C$ CO_2 as high as +25 o/oo (Faber, Schmitt & Stahl, 1978; Carothers & Kharaka, 1980; Schoell, 1980).
Also the negative correlation between the sulphate-ion content and the $\delta^{13}C$ of HCO_3^- in oil-field pore waters, shown by data of Carothers & Kharaka (1980), indicates that after the consumption of sulphate, heavy carbon-dioxide is liberated.
The heavy CO_2 released during bacterial fermentation dissolves easily in the pore water. There, it may take part in dissolution-precipitation processes of sedimentary carbonate, and cause an increase of $\delta^{13}C$ in the resulting indurated sediment. Light CH_4-carbon, the other product of bacterial fermentation is <u>not</u> active in the anoxic environment where it is formed. It has to migrate to higher water levels, where it can be oxidized and can influence the $\delta^{13}C$ values of the bulk carbon-dioxide. This oxidation is a slow process. Under modern conditions with well ventilated deep waters, the bulk of the methane which escapes from the seafloor is oxidized at levels above a depth of 500 meters (Brooks, 1979).

The diagenetic influence of heavy carbondioxide, produced during bacterial fermentation, upon the carbon isotope composition of diagenetically altered carbonate was demonstrated by Campos & Hallam (1979). High $\delta^{13}C$ values of $CaCO_3$ from sample station 1474 in the Black Sea (Deuser, 1972) are likely to be the result of the same process.
In a similar way, high stable carbon isotope values in carbonate within organic C-rich intervals reported by Weissert, McKenzie & Hochuli (1979), are suggested to be the result of this diagenetic effect.

ORGANIC MATTER

Marine photosynthetic organisms show a preference for ^{12}C isotopes over ^{13}C in the formation of organic matter; this results in a ^{13}C depletion of 20 to 25 o/oo relative to the composition of the carbon source, which is mainly HCO_3^-. In general, terrestrial organic matter shows lower $\delta^{13}C$ values (-23 to -35 o/oo) than marine organic matter.

Northam et al. (1981) report $\delta^{13}C$ values of Holocene and Pleistocene organic matter from the anoxic Orca Basin (Gulf of Mexico) and from a control core outside of this basin: the variations of $\delta^{13}C$ of the total organic carbon within the sedimentary columns are similar at both sites. The authors conclude that although the lack of oxygen within the anoxic basin served to preserve more organic matter, no unusual processes or chemical changes are operating in anoxic settings at the isotopic level after deposition.
Pyrolysis of organic matter at 500 ^{o}C during 11 days resulted only in small differences in $\delta^{13}C$ between the residue and the original organic matter, the maximum difference being 0.9 o/oo (Chung and Sackett, 1979).

MEASUREMENTS AND RESULTS

ANALYTICAL METHODS

Samples for the analysis of the stable isotope composition of calcites in sediments with much organic matter were heated at 470°C in a helium flow for 30 minutes in order to inactivate the organic matter. After reaction of the powdered samples with concentrated H_3PO_4 at 25°C under initial vacuum conditions for at least four hours, the liberated CO_2 was led through a cold trap (melting aceton, -96°C) in order to remove H_2O, and subsequently trapped by means of liquid nitrogen.
For the analyses of the stable carbon isotope composition of the organic C, carbonate was removed by treatment with diluted HCl; after neutralizing and drying, the samples were heated at 900°C in a 0.2 O_2 atmosphere for 20 minutes. The oxidation products were trapped by means of liquid nitrogen, which next was replaced by melting aceton in order to let evaporate CO_2 and to retain the water. Before measuring, CO_2 was led through a cold trap once again to remove the last traces of water.
The samples were analysed with a Micromass 602 c mass-spectrometer.
The resulting isotope data are relative to the PDB standard.
Duplicates generally do not differ more than 0.05 o/oo.
A systematic difference between duplicates which were analysed some months after each other, is ascribed to a gradual change of the standard gas, and has been corrected for.

S.E. FRANCE

The sequence near Vergons in the "Fosse Vocontienne" in France, from which the stable isotope composition of the carbonate was analysed shows a strong depletion of ^{18}O. This suggests strong diagenetic alterations, which makes the results unsuitable for paleoenvironmental interpretations. Isolated specimens of pelagic foraminifera, mainly Hedbergella spp., which are completely filled with secondary calcite, show aberrantly low $\delta^{18}O$ values (Fig. 4.5).
From the sequence near La Vierre, the stable carbon isotope composition of the organic matter was analysed (Fig. 4.7). Low $\delta^{13}C$ values tend to be found in intervals with high amounts of organic matter.

APENNINES

The carbonate in the carbonate-rich beds shows higher $\delta^{18}O$ values than in adjacent marly beds.

The pattern of the $\delta^{13}C$ of the carbonate is not similar in the various sections. In the Barremian section (Figure 4.1), where true black shales occur, the carbon isotope composition of the bulk organic matter shows the higher values in the carbonate-rich beds, whereas, on the contrary, the $\delta^{13}C$ of the carbonate is higher in the black shale intervals. In series deposited under continuously oxygenated conditions such in the Upper Aptian / Lower Albian part of the Marnes a Fucoidi (Fig. 5.1), the $\delta^{13}C$ values of carbonate in the carbonate-richer parts show a positive deviation from the mean trend.

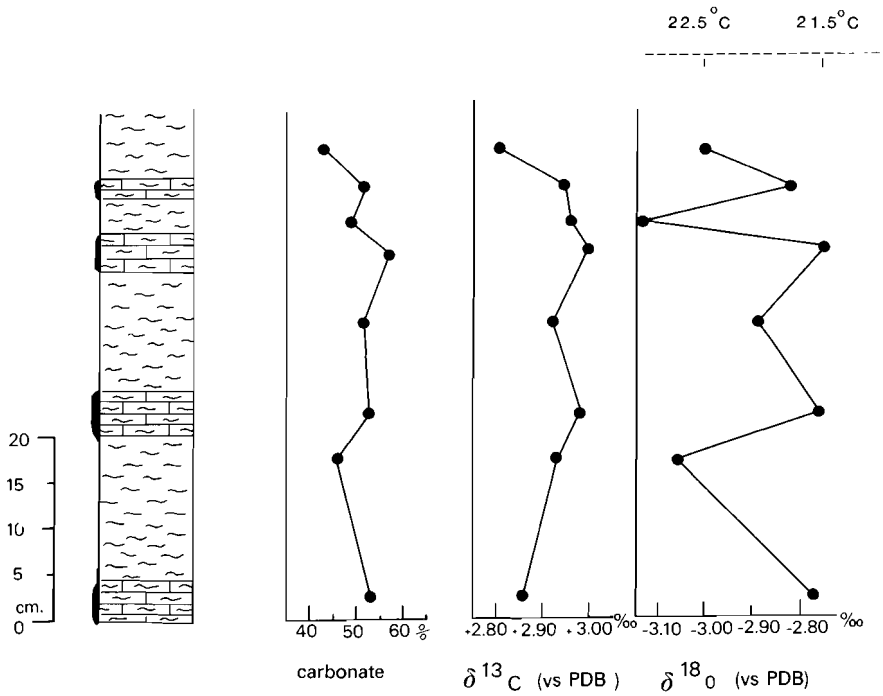


Figure 5.1 Marnes a Fucoidi near Moria (U.Aptian / L. Albian). "Carbonate-rich" beds have a reddish, and the "carbonate-poor" intervals have a greenish colour.

The pattern of $\delta^{13}C$ values from the Upper Albian (Figure 5.2) is hard to interprete. The $\delta^{13}C$ values of "black" intervals, containing only up to 0.66 % organic matter, the dark colours being mainly the result of the presence of pyrite (van Graas, 1982), are relatively high compared to the values of carbonate-rich beds. In the light coloured marly beds lower values tend to be found, but the differences are small.

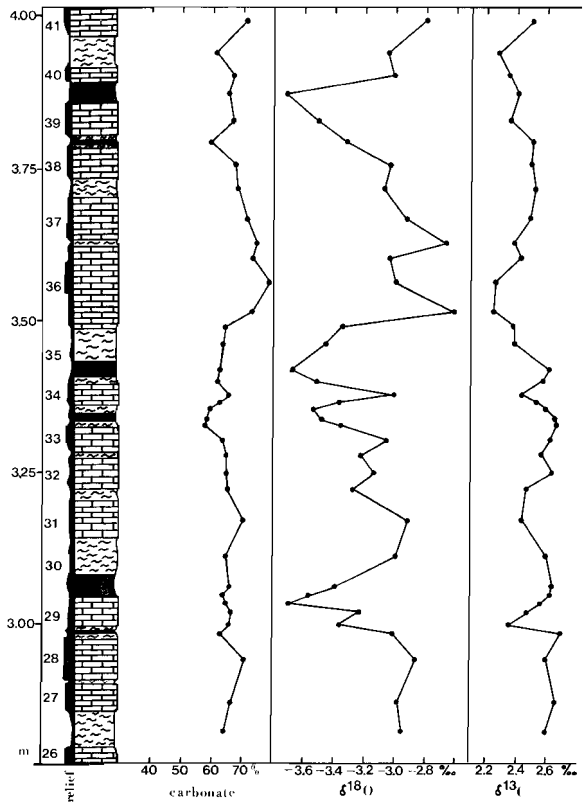


Figure 5.2 Carbonate and stable isotope data from a part of the Upper Albian (Marnes a Fucoidi / Scaglia Bianca) near Moria.

The longer trends seen in the isotope data, covering 4 to 5 carbonate-marl rhythms, will be discussed in chapters 6 and 7.

DISCUSSION

STABLE OXYGEN ISOTOPES

In the Italian succession, the variation in stable oxygen isotope values measured on carbonate in the successive beds parallels the fluctuation of carbonate content: beds with a relatively high carbonate content show the higher $\delta^{18}O$ values and vice versa.

If the rhythmic carbonate-marl successions were uniquely the result of a diagenetic redistribution of carbonate within an originally homogeneous sequence, without initial variations of stable oxygen isotope composition, then diagenesis would have resulted in an oxygen isotope profile that is the mirror-image of the ones which are actually observed. Therefore, a diagenetic origin of the carbonate-marl alternations is improbable.

If diagenesis only emphasized pre-existing differences of carbonate content, then the original amplitude of the observed $\delta^{18}O$ fluctuations whould have been diminished. Accordingly, the original differences of $\delta^{18}O$ values between adjacent intervals must have been equal or larger than those observed.
Considering the measured $\delta^{18}O$ values, and the rather small differences of carbonate content between adjacent carbonate and marly intervals, diagenetic effects cannot have caused important changes.
Therefore, the observed fluctuations should be explained by primary processes.
The discussion of the factors which may influence the $\delta^{18}O$ of fossil carbonates, leaves us with fluctuations of the water temperature in the photic zone as the only reasonable explanation for the observed fluctuations of $\delta^{18}O$.
If a difference of 1.5 o/oo of $\delta^{18}O$ between Recent and Cretaceous oceans is assumed, the oxygen isotope data indicate ocean water temperatures of around 20°C (18°C for $\delta^{18}O$ = - 2 o/oo; 22.5°C for $\delta^{18}O$ = - 3 o/oo). Uncertainty about the exact oceanic oxygen isotope composition during the Middle Cretaceous makes that these estimates are tentative.
Anyhow, irrespective of the absolute values, the oxygen isotope data indicate fluctuations of temperature of a few degrees with the carbonate-richer beds having been formed during periods with cooler surface waters. The differences of temperature do apply to the part of the water column in which the bulk of the carbonate is formed, i.e. mainly the photic zone. It is attractive to attribute these temperature fluctuations to variations of climate.

STABLE CARBON ISOTOPES

$\delta^{13}C$ of carbonate

The original $\delta^{13}C$ values of the carbonate in black shale intervals are suggested to have been strongly modified by extensive activity of bacteria during early diagenesis, in accordance with the above described model proposed by Irwin et al. (1977).
Stable carbon isotope values of carbonate in parts of the studied sequences that were formed under oxygenated conditions in deep water tend to be slightly higher in the carbonate-rich than in the marly beds. In contrast to the values of $\delta^{13}C$ within the black shales, they must reflect the original variations of the environment in which the carbonate was formed. We have seen (Table 5.1), that several mechanisms may have attributed to this effect. Of the different possible mechanisms, changes of organic production and removal of organic matter to the deep, together with the temperature dependence of fractionation of stable carbon isotopes over the air / water interface, are suggested to be the principle factors involved.
Variations of organic production during the Middle Cretaceous have been small (chapter 4), and variations of temperature have not exceeded some few degrees. Therefore, in contrast to the situation in semi-enclosed basins such as in the Mediterranean Sea during the Miocene (cf. van der Zwaan, 1982), variations of $\delta^{13}C$ of biogenic carbonate formed during the Cretaceous in the open ocean must be small, as is indeed actually observed.

organic matter

The measured variation of $\delta^{13}C$ of organic matter exceeds the effects of possible diagenetic alterations.
Relatively low $\delta^{13}C$ values of organic matter in marine sediments are often ascribed to the input of terrestrial organic matter. Although visible plant remains are scarce or absent, van Graas, Viets, de Leeuw & Schenck (1981) show that (eolian) input of terrestrial plant waxes could have contributed significantly to the organic matter in the pelagic sequence near Moria, and thus to the low $\delta^{13}C$ values of the bulk organic carbon in the black shale intervals.
Any supply of terrestrial organic matter via the air is independent of the productivity of surface waters. Thus the proportion of terrestrially derived

input in the total amount of organic matter is likely to be largest in those parts of the sequence that were formed in periods of low marine organic production.

Considering the inferred large influence of terrestrial organic matter upon the $\delta^{13}C$ of the bulk organic matter, it is not probable that the effects of other processes, which can cause slight variations of $\delta^{13}C$ of ocean-dissolved-carbon, and thus of marine organic matter, would be noticeable.

CHAPTER 6

ASTRONOMICAL INFLUENCES ON CLIMATE AND ON SEDIMENTATION

Everything occurring on the Earth is caused by, or subjected to, extra-terrestrial influences. On first sight this term may suggest catastrophic events, much in vogue nowadays, some of which are inferred to have caused conspicious breaks in the sedimentary record, such as the one at the Cretaceous-Tertiary boundary. However, everyday events, such as sunrise and sunset, high tide and low tide, summer and winter, are caused by or dependent on the movements of celestial bodies.

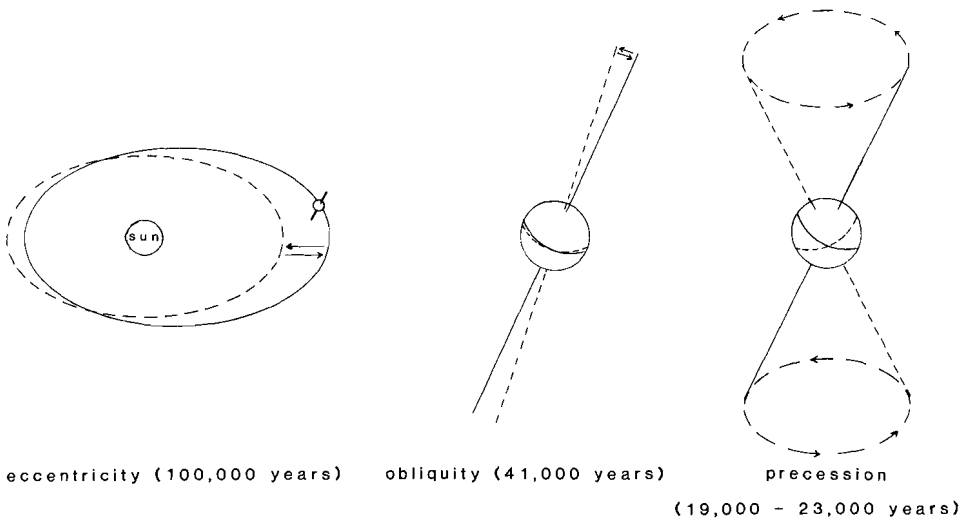


Figure 6.1 Depiction of the long term astronomical variables influencing the climate on Earth.

Over long periods, variations of the position of the Earth's axis in its varying orbit around the sun (Fig 6.1) cause cyclic changes in the amount of solar energy received at the top of the atmosphere, and ipso facto in the climate system of our globe.
The parameters involved are:

1) The varying eccentricity of the orbit of the Earth around the sun, expressed as $\sqrt{(a^2-b^2)}/a$, where a is the semi-major axis, and b the semi-minor axis of the Earth's elliptical orbit around the sun. At present, it has an average periodicity of about 100,000 years. It varies from less than 0.01 to about 0.07,

2) The obliquity or tilt of the Earth's axis with respect to the axis of Earth's orbit around the sun, varying between 22 and 24.5 degrees with a period of, at an average, 41,000 years, and

3) The precession of the Earth's axis which is a variation of the orientation of the Earth's axis with respect to the elliptical path of the Earth around the Sun with a mean period of about 21,000 years.

Exact numerical data describing the amplitudes, periods and phases of these astronomical variables can be found in Berger (1978b).

With the Sun as the main source of energy of the Earth, these astronomical variables are of influence upon the global climate. The eccentricity causes the total amount of energy received by the Earth to vary over the year, since this is proportional to the square of the distance between both bodies. The variation over the year therefore increases with increasing eccentricity.

The obliquity cycle is of influence upon the distribution of insolation on the Earth over the year, and variations are especially felt at high latitudes (van Woerkom, 1953). When obliquity is large, areas at high latitudes undergo large variations in the quantity of solar energy received annually.

The cycle of precession is of major influence on the climate at low latitudes, and it causes both hemispheres to be alternately (with a period of 21,000 years) positioned towards the Sun when the Earth is in its aphelion. In periods in which the northern hemisphere is closest to the Sun during summer and furthest away during winter (i.e. the situation of Fig. 6.1 A), it experiences warm summers and cold winters, while on the southern hemisphere summers are cool and winters moderate. Due to the cycle of precession (Fig. 6.1 C), the reversed situation is seen after about 10,000 years.
Already more than a century ago, changing orbital parameters of the Earth were suggested as a possible cause for climatic change (Croll, 1864). Indeed, the

differences in the intensity and distribution of solar radiation on the suface of the Earth, produced by the combined astronomical influences, results in regular shifts of the "caloric equator" (= the line parallel to the geographic equator where the insolation is maximal) between 10°N and 10°S with a periodicity averaging 21,000 years (Berger, 1978a), and in the length of summer and winter half-years which shows variations up to 34 days (Berger, 1978b).

Changes in the distribution and the intensity of insolation lead to changes of atmospheric circulation patterns. Kutzbach & Otto-Bliesner (1982) calculated that due to the influence of orbital parameters, summer-winter contrasts at about 30°N were much larger 9000 years ago than at present. They state that solar radiation was about 7% higher than at present during summer, and 7 to 8% lower during winter. Also the variation of precipitation and evaporation over the year was more enhanced in comparison with the present, and the amplified seasonal cycle of solar radiation caused by astronomical parameters, should have caused a more intensive monsoon activity 9000 years ago (Kutzbach & Otto-Bliesner, 1982). In this period, the caloric equator was situated at about 3°S against at 3°N at present (Berger, 1978a).

Climate is of major influence upon sedimentary processes and their products, and, considering the long-term effects of astronomical parameters on the climates on Earth, their reflection in the sediment is likely to be present in many places.

EVIDENCE FOR THE INFLUENCE OF LONG TERM ASTRONOMICAL VARIABLES IN THE STRATIGRAPHIC RECORD

ICEAGES

The variation of the volume of polar icecaps during the Pleistocene is a phenomenon which is best-known in the context of long-periodic astronomical influences. The name of Milankovitch is commonly associated with the astronomical explanation of alternating glacial an interglacial periods. For a historical review of his ideas and those of his successors see Imbrie (1982).

Due to fractionation processes during evaporation, and during the transport of water vapour from low to high latitudes, polar ice is strongly depleted in ^{18}O. As a result, the mean $\delta^{18}O$ value of ocean water increases in times of growth of icecaps, and decreases when they diminish in size. The changing $\delta^{18}O$ value of ocean water is recorded in the composition of marine carbonates. Hays et al. (1976) established a correlation between changes in insolation at the top of the Earth's atmosphere, resulting from changes in the astronomical variables, and the global ice volume during the last few 100 Ka as determined by isotopic analysis of deep sea cores. However only 50 to 70% of the variance of the ice volume record can be ascribed to variations of astronomical parameters (Berger et al, 1981). This rather weak correlation is explained by the fact that icesheet/bedrock dynamics have a large response time, leading to a cycle period of about 100,000 years, and thus reducing variations of orbital parameters to a trigger mechanism for the start of growth and melting of the northern-hemispheric icesheets (Oerlemans, 1980; Birchfield et al. 1981; Moore, Pisias & Dunn, 1982). Due to the inertia of icesheet bedrock dynamics, the large amplitude of climatic changes during the subrecent geological history is mainly the result of the very process of growth and melting of icecaps, obscuring the influence of varying orbital parameters.

In geological history, polar icecaps have not been a common phenomenon, and there are no indications that they did occur during the Cretaceous (Frakes, 1979; W.H. Berger, 1979). In the absence of the amplifying effects of polar icecaps, astronomically induced fluctuations of climate are likely to be significantly smaller.

ICECAP FREE PERIODS

In 1894, G.K. Gilbert studied Cretaceous pelagic carbonate-marl rhythms in Colorado (U.S.A.). On the assumption that these rhythms are the result of influences of the 21,000 year cycle of precession, he gave an estimate of the duration of a part of the Upper Cretaceous. Gilbert's estimate was reported to fit well to the results of modern radiometric dating (Fischer, 1980).

Mean periodicities of about 20,000 to 50,000 years have been calculated by different authors for the deposition of individual carbonate-marl couplets in the Cretaceous and the Lower Tertiary of the Apennines. Similar values have been found for other places, for other stratigraphic intervals, and for other sedimentary environments (Table 6.1). It is striking that periodicities reminiscent of the astronomical cycles are often found in sediments which were deposited at latitudes of 20 to 40 degrees.

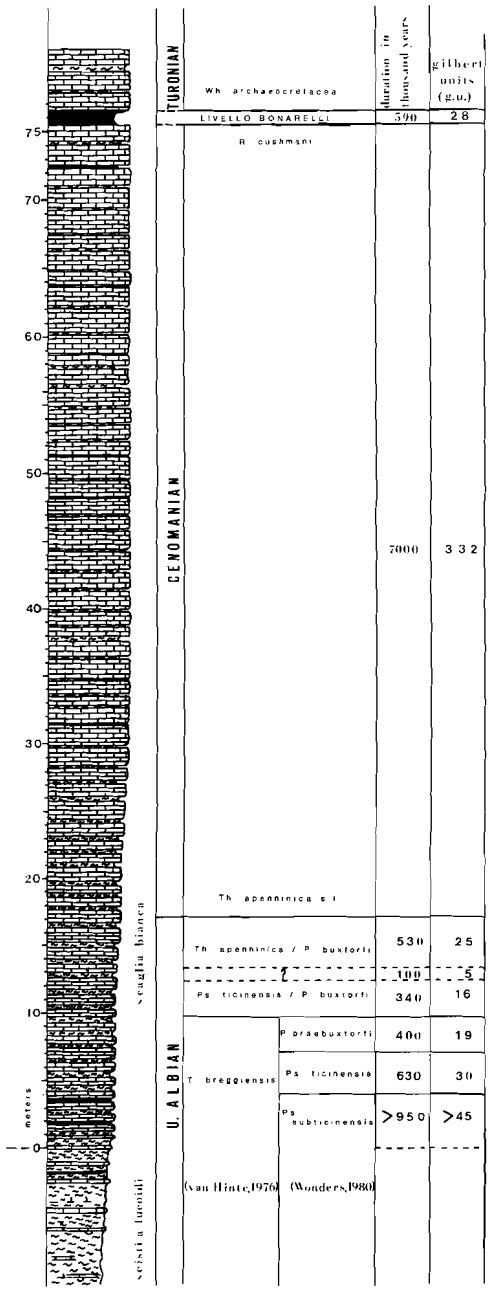
TYPE OF SEDIMENT AND LOCALITY	AGE	PALEOLATITUDE OF DEPOSITION	PERIODICITY IN 1000 yr	SUGGESTED CAUSES of CYCLICITY	AUTHORS
pelagic sediments with variations of carbonate content and oxygenation state; D.S.D.P. site 398	Lower Cretaceous	30 - 35°N	20 - 100 mean 50	periodicity of surface productivity and renewal of oxygen to bottom water	Arthur, 1979
green/black pelagic mudstone; D.S.D.P. leg 43	Albian / Cenomanian	20 - 25°N	17 22 - 43	circulation intensity climate control, precession, obliquity	McCave, 1979
pelagic marl-limestone alternations; Gubbio, Italy	Albian / Cenomanian	25 - 30°N	20 - 100	alternations of carbonate-rich and carbonate-poor periods, emphasized by diagenesis	Arthur & Fischer, 1977
same	Paleocene	30°N	55 - 100	cyclic variations of carbonate productivity; carbonate dissolution cycles	Arthur, 1977
pelagic sediments with variable carbonate and org.C content; D.S.D.P. leg 41	Eocene L.Eocene Eocene	5°S 6°S 1°S	30 - 50 14 - 21 7 - 14	Milankovitch parameters	Dean et al., 1977
shallow marine carbonates; Northern Alps	U.Triassic	30°N	groupings of cycles in numbers of 5	astronomical influences	Schwarzacher, 1954
same	same	same	20 - 100 megacycle groupings of 5 to 8	sealevel oscillations, obliquity cycle	Fischer, 1964
lacustrine deposits N.Jersey, Pennsylvania	U.Triassic	25 - 30°N	19 - 25	precession cycle, climate	van Houten, 1964
lacustrine sediments	U.Triassic		20.5		Olsen et al., 1978
lacustrine deposits Green River Form. Wyoming, Colorado	Eocene	40°N	21.3	fluctuations in lake level, astronomical cycles	Bradley, 1929

Table 6.1 Estimates of the long-term periodicity of sedimentary cycles in various sedimentary environments from various ages.

Figure 6.2 Field exposure of part of the Upper Albian series near Moria, Apennines

The micro-paleontological data of the sequence near Moria given here were supplied by Dr. A.A.H. Wonders: The good preservation of planktonic foraminifera in most of the sequence allows for a detailed zonation (Wonders, 1978, 1980). All the zones described by Wonders (1975) from Southern Spain were recognized, from the Pseudothalmanninella subticinensis Zone (Wonders, 1980; equivalent to the middle part of the Ticinella breggiensis Zone of van Hinte, 1976) to the top of the Thalmanninella apenninica - Planomalina buxtorfi Zone (= Albian / Cenomanian boundary). As most zonal boundaries are defined by evolutionary appearances of markers, and because gradations from one species to the other could be traced from bed to bed, the record in Moria appears to be complete.

The Cenomanian part of the section was not studied in detail, but from previous studies it is known that the Scaglia Bianca probably is a continuous and complete sequence of Cenomanian pelagic sediments (Premoli Silva & Paggi, 1977; Wonders, 1980).



The entire studied section, excluding the Bonarelli Bed, contains 472 marl-limestone couplets (Fig. 6.3). It covers 11 Ma according to the commonly used scheme of van Hinte (1976). This yields a mean cycle duration of about 21 to 23 thousand years (Ka). According to schemes such as of Obradovich & Cobban (1975) Lanphere & Jones (1978), and Odin & Kennedy (1982) the cycle duration would be less, but at least 16 Ka. See also Figure 3.5 for estimates of the time span of the different stratigraphic zones and stages.

The value of about 20,000 years for the mean period of deposition of the carbonate-marl rhythms is very suggestive of the influence of astronomical variables, especially of the cycle of precession.

Figure 6.3 Columnar section of the interval studied near Moria, showing schematic lithology, planktonic foraminiferal zonation and duration of stratigraphic intervals in Ka based on the assignment of a 21,000 year period for each of the carbonate-marl rhythms.

SPECTRAL ANALYSIS

In order to check whether or not the carbonate-marl alternations found in the field are related to astronomical parameters, thickness values of the lowermost 150 carbonate-rich beds from the Moria section were analysed by means of spectral analysis according to the method of Jenkins & Watts (1968).
As stated by these authors, such analysis does not necessarily imply the assignment of equal time to the intervals between successive observations. Consequently, the spectral analysis of the pattern of thicknesses in the succession of beds does not imply the a priori assignment of equal timespans to the successive carbonate-marl couplets.

The choice of the lowermost 150 cycles was based on the fact that these form the better exposed and least weathered part of the formation, and consequently were measured and sampled with sufficient accuracy. The result of the analysis (Fig. 6.4 shaded) shows a dominant and significant peak at a frequency of 0.234. This indicates a repetition of a distribution pattern in the sequence of bedding thicknesses with a periodicity of about 4.3 (reciprocal of 0.234) CRB (carbonate-rich beds).

The value of 4.3, found in the spectral analysis, is suggestive for the interference between the mean periodicity of the eccentricity cycle (100 Ka) and the most important periodicity of the precession cycle (23 Ka, Berger, 1978a) (100/23 = 4.3).

Measuring only the thicknesses of the carbonate beds implies a strong aliasing, whereas the strongest periodicity in the carbonate signal (i.e the thickness of the carbonate-rich intervals) is taken as the basis of the analysis. Thus, only periodicities amounting to more than twice the period of the sample interval (~ 21 Ka) can be recognized, and the periodicity of 4.3 CRB (100 Ka eccentricity cycle) only indicates a modulation of the major periodicity which is represented by the succession of carbonate-rich beds, and which was shown to be of the order of 21 Ka (precession cycle).

As a check on this result, a model curve, representing the influence of astronomical parameters upon climate, was generated, using the 10 most important amplitudes and periods of the astronomical parameters as given by Berger (1978b Tables). The curve closely resembles the changing position of

the caloric equator in degrees latitude N and S of the geographic equator vs. time. From the model curve, the heights of the successive peaks, representing the successively most northerly positions of the caloric equator in time, separated from each other by timespans in the range of 15,000 to 27,000 years, were subjected to the same spectral analytical method as applied to the Moria data. The dominant peak of the resulting spectral density curve (Fig. 6.4 unshaded), and the one based on the field data show a striking resemblance.

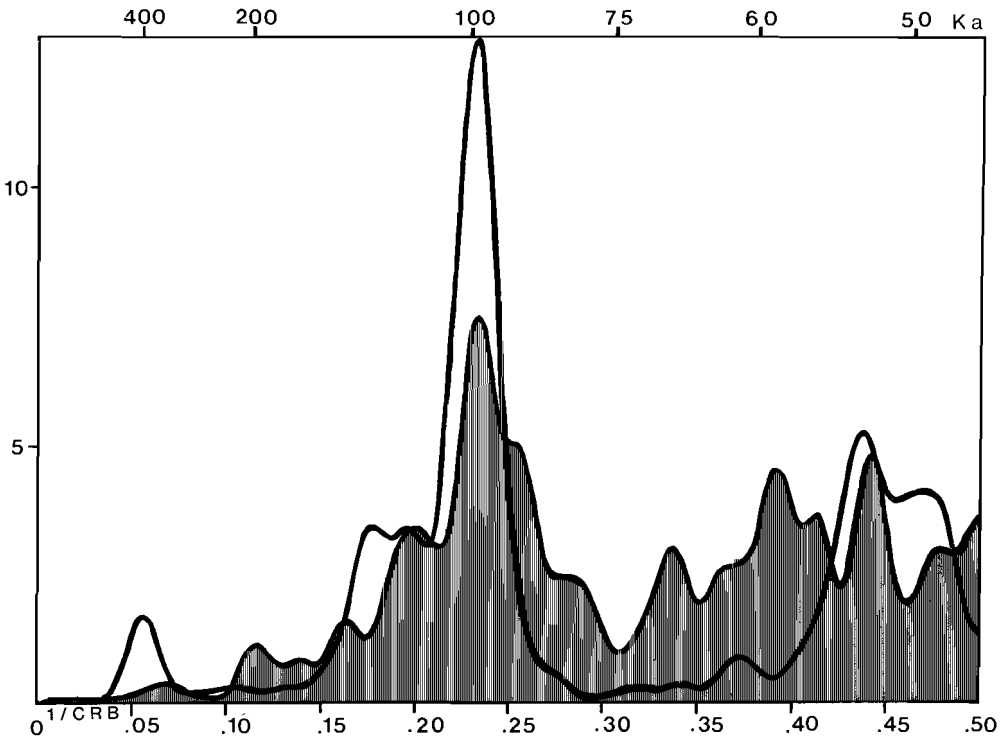


Figure 6.4 Spectral density curves; curve with highest peak value (unshaded) is the frequency spectrum of the successively most northerly positions of the caloric equator. Whereas the successive observations of the extreme positions of the caloric equator are not equaly spaced in time, the time scale above only is an approximation. The shaded curve is based on thicknesses of the carbonate-rich beds nr 1 - 150 (Fig. 6.3). The periodicity at 0.23 CRB / ~100 Ka represents a modulation of the major periodicities in the series of data which are formed by the thickness data of successive carbonate-rich beds, and by the latitudes of successively most northerly positions of the caloric equator.

This strongly suggests that the rhythmic carbonate-marl alternations from the Albian/Cenomanian pelagic sequence in the Apennines do reflect the influence of astronomical parameters upon pelagic sedimentation, that is, that the cycle of precession was the major tuner of the sedimentation process resulting in the formation of the sequence of alternating carbonate-rich and marly beds and that, on the scale of the outcrop, this pattern has been modulated by the influence of the 100,000 year eccentricity cycle.

Cenomanian - Turonian boundary

Carbonate is almost absent in the Livello Bonarelli, the organic C-rich interval at the Cenomanian - Turonian boundary in Umbria.
However, lithological alternations of clayey and silica-rich intervals can be recognized. The state of preservation of the multicoloured claystones in the middle part of the Bonarelli level does not allow the number of lithologic alternations in this part to be counted exactly. The total number of couplets with different lithology and/or colour is estimated to be in the range of 23 - 33 (28±5). The resemblance of this figure to the number of 30 lithologic alternations in the same stratigraphic interval in Colorado (U.S.A.), reported by Fischer (1980; see also chapter 4), suggest a common cause for the rhythmicity in these remote successions.

On the basis of a study of the organic matter from the Bonarelli Level, van Graas et al. (1982) state that the rhythmic alternation of limestones and marls in the Upper Albian and Cenomanian seem to be continued in another form in this particular interval. This would mean that the Bonarelli Level represents a timespan in the range of 480,000 to 700,000 years. It is also in accordance with estimates based on sedimentation rates of non-carbonate sediment and of Al_2O_3 (chapter 4). The sedimentation rate of non-carbonate matter of about 0.15 cm/Ka during the Upper Albian and the Cenomanian thus remained constant at the transition from the Cenomanian to the Turonian (Fig. 4.3 B). The cycle of precession must have been of major influence in the creation of the lithologic alternations in this particular interval.

INFLUENCE OF THE ECCENTRICITY CYCLE

The precession of the Earth's axis causes changes of climate and of sedimentation patterns owing to the fact that the path of the Earth around the Sun is eccentric. In the case of a circular path, the effect of the cycle of precession would be zero. Therefore, variations of the rate of eccentricity should also be of influence. In Fig. 6.5 an impression is given of the wide range of eccentricity rates for the last 5 Ma.

Present-day astronomical observations are not so accurate (Bretagnon, 1982) as to allow exact extrapolations back as far as 5 Million years, but for the purpose of giving an idea of the general pattern, the figure is sufficient.

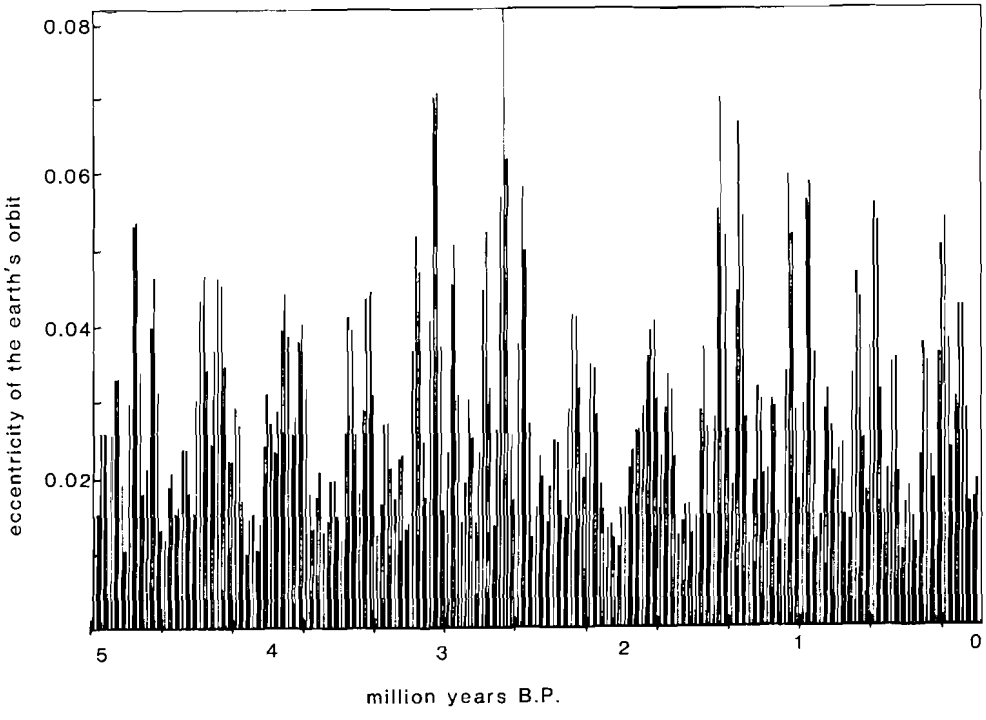


Figure 6.5 Plot of the eccentricity of the Earth's orbit around the Sun calculated with 20,000 year time intervals for the last 5 million years on the basis of data from Berger (1978b).

In the above discussion, the effects of the cycle of precession were shown to be modulated by the alternation of periods of high and of low eccentricity. From Fig. 6.5, however, it appears that, in the long run, the eccentricity varies so much, that a maximum of eccentricity in some time interval can be smaller than a minimum in another. The similarity of character of the long term cyclic trend of bedding thicknesses shown in Fig. 2.5 and the long term variation of eccentricity rates makes it urgent to compare both more closely.

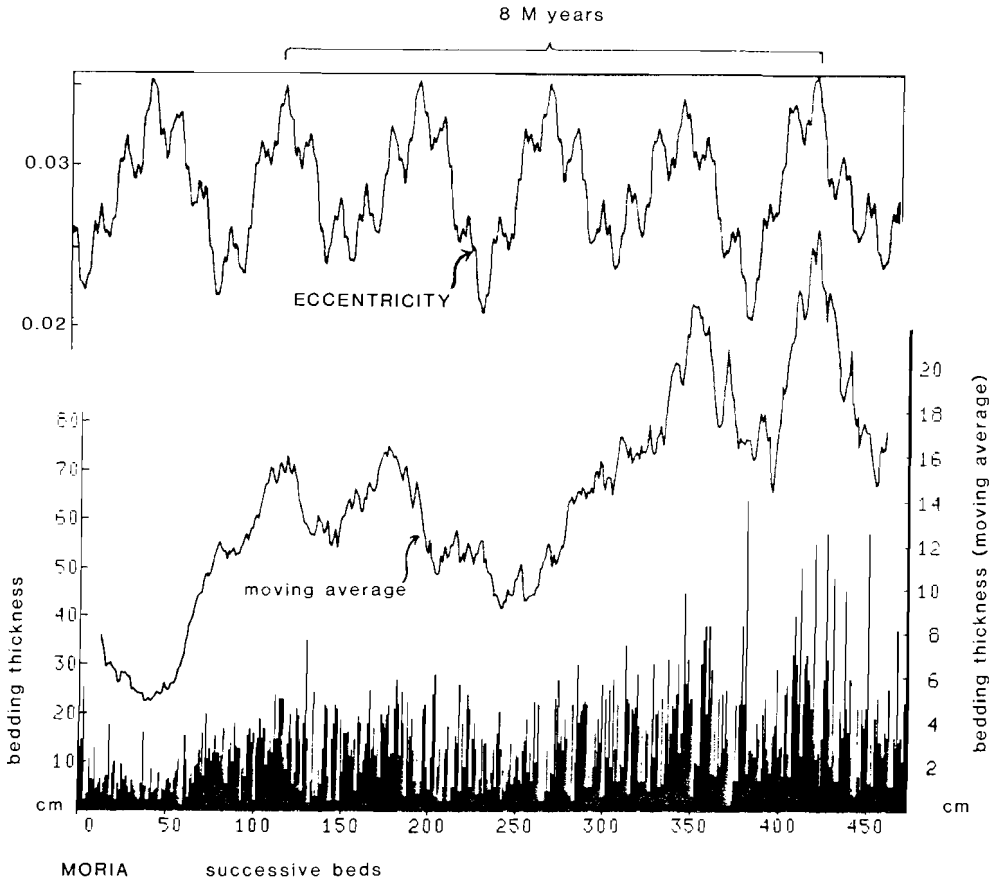


Figure 6.6 Comparison of the distribution of thickness of the carbonate beds near Moria and the rate of eccentricity calculated at 20 Ka intervals. Lower curve: thickness of individual beds; middle curve: smoothed curve (25 point moving average) of the bedding thicknesses; upper curve: smoothed eccenticity values (25 point moving average, i.e. over 0.5 Ma periods with steps of 20 Ka).

In Fig. 6.6 these two features are shown together. The, on first sight, rather irregular pattern with which the eccentricity varies (Fig. 6.5) makes it difficult to recognize it in the sediment. A moving average smoothing was needed to visualize the similarity of the two patterns.
Although the eccentricity curve was calculated by inserting the timespan from 105 to 90 My B.P. into the formula (3) of Berger (1978b) it should not be assumed that the resulting curve would represent the exact ecccentricity values for that period. Rather, it shows the general character of the variations of the eccentricity over millions of years.

Considering the evidence for influences of astronomical parameters upon the pelagic sedimentation system during the Cretaceous, the similarity between the two curves is very suggestive of a relation between the two phenomena. As in the field the attention is often focussed on phenomena with a high frequency, which can be reognized at the outcrop; other features of lower frequency which are superimposed on the first or vice versa, are often not recognized. The effect which diagenesis and weathering have on the appaearance in the field of adjacent layers with precession-related small differences of carbonate content (chapters 3,4), easily lead one to overlook longer term features with a greater amplitude such as the long eccentricity eccentricity effect.

TIMESCALE AND CHANGES OF ORBITAL PARAMETERS THROUGH GEOLOGIC TIME

Having shown that the relation in the frequency domain between astronomical parameters and bedding rhythms in fossil pelagic sediments is an acceptable theory, the next step is to see if it can be used to establish, or as a check on other calculations of, the duration of stratigraphic stages and zones.

If we accept the assumption that the carbonate-marl rhythms do reflect the cycle of precession of the Earth axis, and if we assume that present-day values may be applied to the Cretaceous, i.e. that there are no changes ir astronomical constants from present-day values, the estimate for the timespai of the Th. apenninica / P. buxtorfi and the Ps. ticinensis / P. buxtorfi Zones (Fig. 6.3) together is about half the timespan estimated by van Hinte (1976), and the minimum estimate of 2 Ma for the T. breggiensis Zone practically equals his (Fig. 3.5).

The estimate of a duration of 7 Ma (excl. the Bonarelli Bed) or 7.5 Ma (incl. the Bonarelli Bed) for the interval from the Th. appenninica zone to the top of the Cenomanian falls within the range of estimates of previous authors (9 Ma: van Hinte, 1976; 5 Ma: Obradovich & Cobban, 1975; 5.5 Ma, Odin & Kennedy, 1982).

The durations for the zones given have admittedly been derived from only one section. Errors, either subjective or because of the presence of "noise" in the sedimentary record, should not be excluded. Ideally, estimates from several different sections should be compared.

That such comparison is realistic, is shown in Fig. 6.7, where the thickness distribution pattern of the sequence near Moria is compared to a pelagic sequence in the same stratigraphic interval near the village of Preci, 80 km to the Southeast (Fig. 3.1). Indeed both series can be correlated precisely on the basis of the pattern of thickness distribution of the carbonate rich beds (Fig. 6.7). The position of both subsections relative to the Bonarelli Level confirms the correctness of the correlation.

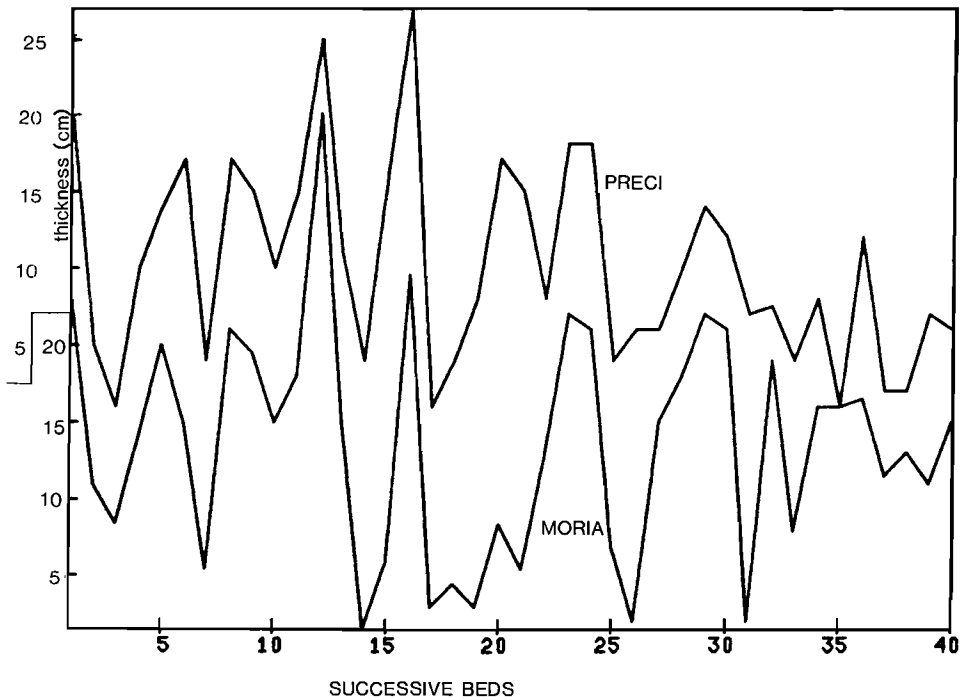


Figure 6.7 Correlation between parts of the Moria and Preci sections.

Occasionally a bed present in one of the two successions is absent in the other or has an aberrant thickness. This is probably due to redeposition processes causing the removal, the arrival, or a change of thickness, of individual layers.

A similar correlation of remote successions with carbonate-marl cycles in the Lower Cretaceous of the Vocontian Basin was found by Cotillon (pers. comm.).

The similarity of the number of lithologic alternations in the Bonarelli Level near Moria, and in the Bridge Creek Member in Colorado (chapter 4), also demonstrates the ubiquity of astronomical parameters upon sedimentation.

An uncertainty about the correctness of the timespans assigned to the Upper Albian and Cenomanian stratigraphic intervals is put forward by the question if the astronomical periodicities as measured at present are valid also for periods as long as 100 Ma ago. The precessional cycle covers at present a mean period of about 21 Ka. Several factors, however, may have caused changes of the mean period of this cycle in the course of geological history. Percentual changes, as recognized in the rotation velocity of the Earth (Pannella, 1971), should not be excluded.
Provisional analyses of cycles from other stratigraphic intervals indeed indicate changes in the ratio between the different astronomical "constants", although for the Middle Cretaceous the difference as compared to the present day may well be small. Therefore it seems useful to introduce a chronology which is independent of present-day time constants.

The duration of stratigraphic intervals based on the counting of precession-induced rhythmic sedimentary cycles is suggested to be expressed in "Gilbert Units", after Gilbert (1894) who was the first to recognize the importance of astronomical influences upon pelagic sedimentary facies.

A "Gilbert Unit" is defined as the (variable) time period between two successive extreme latitudinal positions (north or south) of the caloric equator, induced by the precession cycle (see Fig. 6.3).

The uncertainty about the constancy of astronomical constants through time is illustrated by the results shown in Figure 6.8. If the correlation shown in Fig. 6.6 is correct this would mean that the length of the cycle of precession would have increased relative to the longperiodic variations of the eccentricity fluctuations by 25% since the Cretaceous.

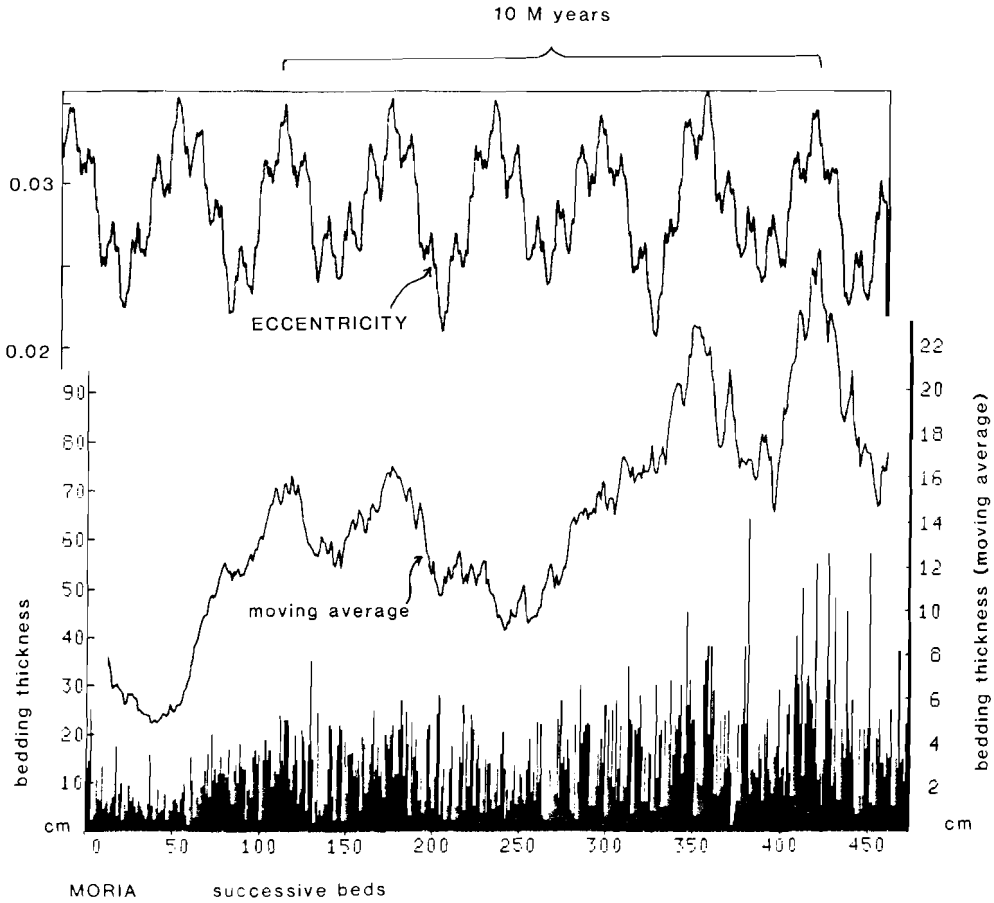


Figure 6.8 Comparison of the distribution of thickness of the carbonate beds near Moria and the rate of eccentricity calculated at 20 Ka intervals. Lower curve: thickness of individual beds; middle curve: smoothed curve (25 point moving average) of the bedding thicknesses; upper curve: smoothed eccenticity values (25 point moving average, i.e. over 0.5 Ma periods with steps of 20 Ka). Upper (eccentricity) time-scale has been compressed relative to the situation in Fig. 6.6

If the correct correlation was as is shown in figure 6.8, the decrease would have been 45%. The other possibility (Fig. 6.9) is that in the middle (badly exposed) part of the sequence near Moria (beds 200 - 300) some other process has played a role. This could be the regular occurrence of unrecognized mass flow transport, or a change in the effect of astronomical influences leading to an increase of cycles per time unit.

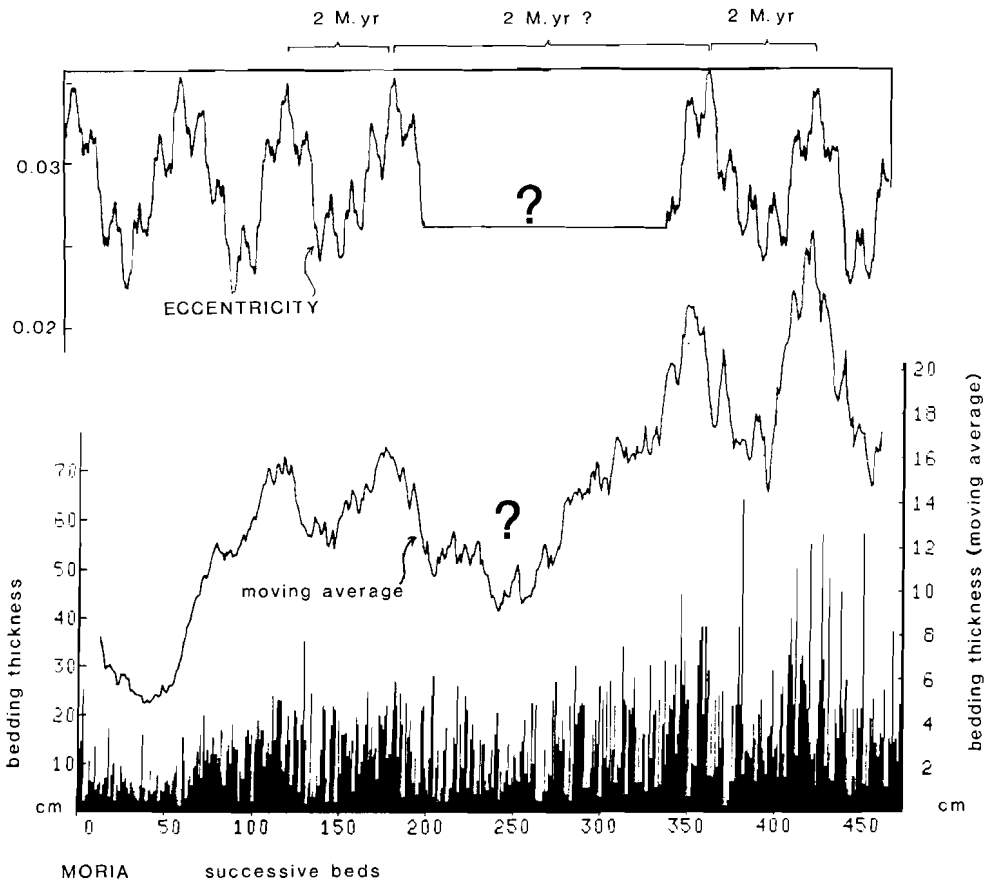


Figure 6.9. Alternative to Figures 6.6 and 6.8.

As yet, on the basis of the present data no answer can be given to this question, but the analysis of more data should provide a solution.

CHAPTER 7

DEPOSITIONAL MODELS

The large scale storage of organic matter in pelagic sediments during the Lower and Middle Cretaceous was not the result of a high organic production, but of a retarded replenishment of oxygen in deep water in combination with an excess supply of nutrients from the continents, and additionally of an excess release of juvenile carbon from volcanoes and from newly formed oceanic crust. Although in this thesis attention was focussed on pelagic sediments, one should realize that in a number of other sedimentary environments (cf. on the Arabian Platform) huge amounts of organic matter have been stored during this period. The wide-scale anoxia in the deep marine environment has been one of the ways in which the global system expressed its striving towards the restoration of equilibrium conditions during the Middle Cretaceous global transgression.

As compared to the situation in modern ocean basins, the circulation velocity and the organic production in the mid-Cretaceous oceans were low. This allowed small variations in the quantity of organic products formed to leave recognizable traces in the sedimentary record of this particular period.

It was shown that the fluctuations of carbonate content in the Cretaceous pelagic sediments in the Umbrian Apennines (Italy) are indeed due to regular fluctuations in the carbonate production in surface waters during the time of deposition (chapter 4). Carbonate-rich intervals represent periods with a relatively good circulation, with a relatively large supply of nutrients to the surface waters, and with, in addition, a fair replenishment of oxygen in deep water. Marly beds and black shale intervals represent periods in which the circulation intensity slowed down, leading to a diminished supply of nutrients to the surface, and to a consequently lower production of carbonate as well as of organic matter. Replenishment of deep water was sometimes reduced to such an extent that the contribution of oxygen was insufficient to fully oxidize the small amount of organic matter that reached the seafloor. Thus anoxity and the formation of organic C-rich sediments could occur. The low productivity conditions at times when the marly and black intervals were formed, also appear from organic geochemical analyses by van Graas (1982).

Carbonate beds generally show higher $\delta^{18}O$ values as compared to adjacent marly intervals (chapter 5). This indicates that the carbonate of the carbonate-rich layers was formed at a water temperature a few degrees lower than that of the adjacent marly intervals. As increases of organic production are often caused by the supply of nutrients by increased vertical mixing in the water column, when cool waters are brought to the surface, this conclusion is fully in accordance with the propositions of chapter 4.

On the basis of systematic differences in fossil content between carbonate and marly layers, Darmedru, Cotillon & Rio (1982) suggest that rhythmic climatic changes are responsible for the origin of similar carbonate-marl rhythms in the Valanginian, Hauterivian and Aptian in the Vocontian Basin.

In the Middle Cretaceous succession in Italy, the rhythms, formed by alternating "high" and "low" amounts of carbonate in the sediment, are clear-cut, because the overall productivity was low enough to allow the small variations of productivity to leave a recognizable record, and also because diagenesis and weathering have led to a type of outcrop in which small variations of the carbonate content can easily be seen.

It was demonstrated in chapter 6 that the process that led to the formation of the carbonate-marl rhythms in the Albian/Cenomanian pelagic succession in the Apennines was forced by astronomical influences. Calculations such as made by Berger (1976, etc.) do indeed show that the intensity and distribution of solar energy over the globe varies, and that at low latitudes the cycle of precession with a periodicity of (at present) an average of about 21,000 years, causes the most pronounced changes of climate.

Fossil examples often seem to be linked to a paleolatitude of about 30°, and the sensitive sedimentary facies which is apparently needed for the formation of bedding rhythms reflecting orbital parameters, seem to exist especially there. It seems not to be accidental that the boundary between tropical and subtropical climates, and the subtropical zone of convergence in the ocean are found close to this latitude.

The ultimate cause of all movements in the ocean is the supply of energy by solar radiation (Defant, 1961). More specifically, climatic contrasts, and temperature and density gradients, between different areas, and over the year, are the main driving force behind water circulation, and behind the supply of nutrient to surface waters.

Orbital parameters cause regular shifts of the position of the caloric equator (Berger, 1978b). Also, the intensity of monsoons (wind and precipitation) changes as a result of astronomical influences over periods of many thousands of years (Kutzbach & Otto-Bliesner, 1982). Comparison of the data from the latter two citations shows that 9,000 years ago a high monsoon intensity in the northern hemisphere coincides with a southerly position of the caloric equator.
In the formulae which describe the summer-winter contrast of caloric insolation and the position of the caloric equator, the astronomical factor $e.\sin\omega$ (e = eccentricity, ω is longitude of perihelion) is of importance (Berger, 1978b). Indeed, from the figures of Berger it is obvious that a southerly position of the caloric equator is accompanied by a large seasonal contrast at low latitudes in the Northern Hemisphere, whereas the summer-winter contrast is low in periods when the caloric equator is located also in the Northern Hemisphere.
The influence which the astronomical parameters have on the climate and on oceanographic processes at low latitudes must have been active also during the Cretaceous.

As polar temperatures were high during the Cretaceous, and as connections with polar areas were of minor importance, circulation in the ocean must have, in contrast to the present day, been driven mainly by processes at low latitudes. That are, an excess of evaporation or of precipitation, leading to differences of density of ocean waters, and differences of atmospheric pressure in time and space.

These considerations and the correlation of the rhythmicity found in the field to astronomical periodicities confirm the earlier suggestions that celestial variables have influenced the sedimentation pattern in the Umbrian area during the Middle Cretaceous.

It may well be that periods with a low seasonal contrast, and/or a low monsoon intensity in the area where the analysed sediments were deposited, were characterized by a relatively pronounced stratification of ocean waters, which had a warm surface layer, poor vertical mixing, a relatively low organic production, and a retarded refreshment of oxygen in deep water.
This extreme situation alternated with periods of more pronounced seasonal contrasts (Fig. 4.4) when an increase of oceanic current intensities reduced the stratification, organic production was relatively high, and surface waters were cool.
This mechanism also explains the fluctuations in $\delta^{13}C$ of the carbonate in the Italian sections by introducing the different fractionation effects which define the isotope composition of biogenic carbonate in the open ocean (Chapter 5: Table 5.1).

As the cycle of precession can exclusively cause fluctuations of climate, owing to the eccentricity of the earth's orbit around the Sun, the maximum amplitude of, precession induced, variations of climate must occur when the rate of eccentricity is highest. In the Middle Cretaceous series in the Apennines the influence of the eccentricity cycle can indeed be recognized from the larger cycles appearing in the fluctuations of the carbonate content and in the isotope data which cover 4 to 5 precession-defined bedding rhythms (Figs. 5.1, 5.2), in the spacing of black, marly levels 4 to 5 carbonate-marl couplets apart, and, on much longer term, in the gradual increase and decrease of average bedding thicknesses (Fig. 6.6). Especially in periods with an extreme eccentricity, with "extreme" changes of temperature and of climate over the year as well as over the 20 Ka precessional period (at low latitudes) one could expect evolutionary steps in living organisms, and also changes of climatic and of oceanographic conditions which can be induced by some trigger mechanism. For the Late Tertiary these relations seem to exist; for earlier periods the search for such features might help to establish a better control of absolute time.

Cyclicity in other sedimentary environments

Two other types of sediment have been reported to exhibit cyclic sedimentary patterns with a periodicity of about 20 Ka: lacustrine sediments (Bradley, 1929; van Houten, 1964, Olsen et al., 1978, Picard & High, 1981) and shallow marine carbonates (Schwarzacher, 1954; Fischer, 1964). It is notable that such deposition also occurred at paleolatitudes of about 30°.

On the land, the northern boundary of desert areas is located at 30 to 40 degrees, as it seems to have been during the Middle Cretaceous (Lloyd, 1982). At latitudes greater than 30° there is an excess of precipitation over evaporation. A precession-induced alternation of dry and wet periods may account for the rhythmicity found within certain lacustrine deposits.

In a similar way variations of climate can influence biological activity.
An equable tectonic subsidence superimposed on a climatically dependent fluctuation of biologic activity could lead to shallow marine carbonate cycles, again with astronomically defined periodicities.
Other climate-dependent features, which might disclose the influence of the cycle of precession on variations of climate, might be found in the typical colour bandings, which characterize paleosols in many places, and in the supply of windblown sediment to marine deposits. In dry periods more eolian material is blown into marine basins than in the case of a wet climate. The prevalence of terrestrially derived wind blown organic matter in some of the marly parts of the sequence in the Apennines (van Graas, 1982), could well be due to such an increase of eolian transport during dry periods.
In an earlier paper (de Boer, 1982), it was suggested that during the Middle Cretaceous the influence of the equatorial upwelling and high productivity zone might have extended to 30 degrees North in times of a northern position of the caloric equator. However, the observed influence of astronomical parameters on atmospheric processes and monsoon intensity at the latitude of 30 degrees produces a more satisfactory model.
It must be conceded that the pelagic system near the geographic equator can be influenced by a changing position of the equatorial upwelling zone caused by shifts of the caloric equator. As the caloric equator passes the geographic equator twice during the 21,000 year cycle of precession, the period of 7 to 14 Ka of Eocene pelagic cycles close to the equator, described by Dean et al. (1977), might fit well a model of astronomically induced sedimentary rhythms.

A recapitulation of the influence of astronomically defined changes of insolation upon the different features as they were when the Albian/Cenomanian succession in Umbria was formed, is given is Figure 7.1.

	position of the caloric equator	
	in the Northern Hemisphere	in the Southern Hemisphere
	----------> 21,000 years <----------	
mean insolation over the year	high	low
mean temperature	high	low
$\delta^{18}O$ of carbonate	low	high
$\delta^{13}C$ of carbonate	low	high (Table 5.1)
summer–winter contrast	low	high
ocean circulation	slow	strong
nutrient supply and organic production	low	high
contribution of biogenic carbonate to pelagic sediments	low	high
replenishment of oxygen in deep water	slow	good
deposition of black shales	possible	unlikely

Figure 7.1 Influence of the cycle of precession on atmospheric and oceanographic processes and their products at about 30°N in the case of an overall slowly circulating open oceanic pelagic system with a moderate supply of oxygen to deep water, as in the Tethys Ocean during the Middle Cretaceous.

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APPENDIX

LONGTERM SECULAR VARIATIONS OF THE MAGNETIC FIELD RECORDED IN LATE ALBIAN PELAGIC SEDIMENTS

J. VandenBerg, P.L. de Boer, and R. Kreulen

INTRODUCTION

Since the pioneering work of Milankovitch, a relation between astronomical, climatic, and geomagnetic variables has been proposed in many studies (1-8). Periodicities suggestive of astronomical influences (100,000 yr eccentricity cycle, 41,000 yr obliquity cycle, and 19,000 - 23,000 yr precession cycle), occur in Quaternary floral and faunal data (7), and in the fluctuations of icecap volume (1,5,8) expressed in the $^{18}O/^{16}O$ ratios of marine carbonates. Warm climates and low magnetic field intensities during the Quaternary were suggested to be related to a high eccentricity of the earth's orbit (2, 3, 4). A correlation between the intensity of the magnetic field and the Earth's obliquity was found in a deep-sea sediment core (9). Berger (5) explained certain variations of global climate as the result of variations of the quantity and distribution of insolation, ruled by astronomical forcing.
Periodicities suggesting astronomical influences have also been found in rhythmic sedimentary successions of pre-Tertiary age (10-19).

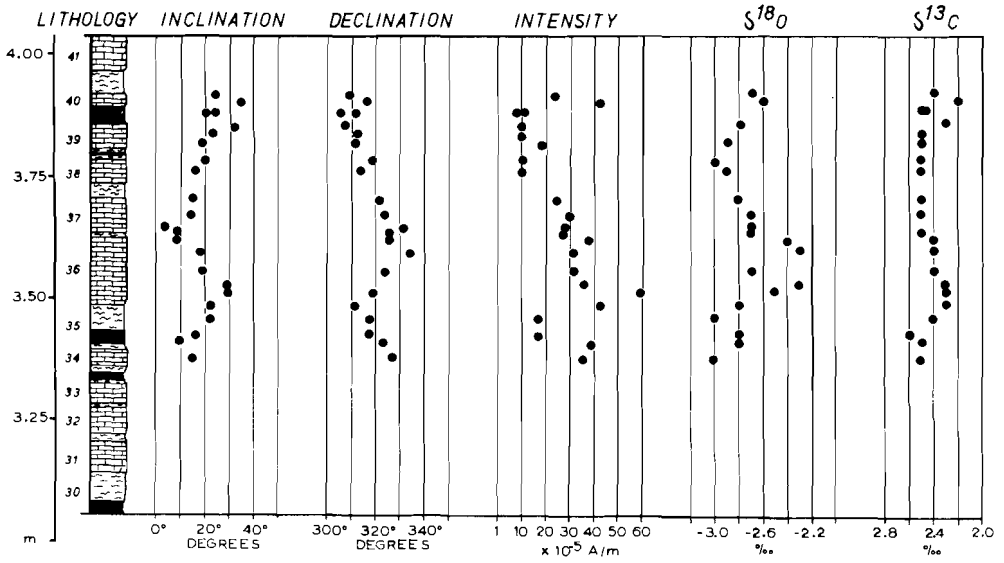
The present study deals with two intervals in rhythmic pelagic carbonates of Upper Albian age which are abundantly exposed in Umbria (Italy).
They belong to a Cretaceous sequence known as the "Moria section" (43° 33'N / 12° 41'E; N.W.Umbria), which was earlier studied for its magnetic properties (20,21). However, no intervals were studied in such detail. The chemical composition and the rhythmic character of the Moria section were studied by de Boer and Wonders (19).
About 90 coresamples were collected in two Late Albian intervals of several meters. The spacing between successive samples is usually less than one centimeter. Due to the low sedimentation rate of these pelagic carbonates (about 0.7 cm/1000 yrs) several thousands of years are covered by each of the one-inch-diameter core samples. Short-term geomagnetic secular variations are therefore averaged out completely within each sample and do not contribute to the Natural Remanent Magnetization (N.R.M.) direction.
Several paleomagnetic researchers (22) have established the primary origin of the N.R.M. recorded in the Cretaceous pelagic sediments of N.W. Umbria (e.g. the Gubbio and Moria sections). The section seems therefore a perfect medium to reveal geomagnetic and chemical variations with periods in the order of several 10,000 years and more.

LABORATORY TREATMENT

Core samples were sliced into cylinders (specimens) of 2.2 x 2.5 cm.
All magnetic measurements were carried out with a ScT cryogenic magnetometer. Following the experience of earlier paleomagnetic studies of the Moria section (20, 21) all specimens were magnetically cleaned applying 6 steps of progressive alternating field demagnetization in the range of 10 mT to 65 mT. The vector path of the total remanent magnetization of each specimen was analysed in orthogonal diagrams, and the primary N.R.M. vector was determined. The primary N.R.M. vectors were corrected for the bedding tilts.
The declination, inclination and intensity were plotted versus height in the sequence and lithology (fig. 1).
Oxygen and carbon ratios have been determined on the same samples used for the paleomagnetic study. Carbondioxide was prepared by reacting the samples with 100% phosphoric acid at $25^{o}C$. Results are given as o/oo deviations from the PDB standard (fig. 1).

RESULTS

The paleomagnetic results show directional variations of more than 20 degrees that are not related to variations in lithology (fig. 1). Especially in the lower interval, where two independent core samples were taken per level, an excellent reproducibility of the magnetic properties is shown. However, variations of the characteristic remanent magnetization (ChRM) intensity were shown to be dependent of lithology and not caused by the geomagnetic field, because initial susceptibility and ARM for the Moria section match the ChRM intensity fluctuations (23). It is therefore assumed that the directional variations of the ChRM reflect geomagnetic variations of Late Albian age with a period of 4 to 5 carbonate-marl couplets, while the ChRM intensity fluctuates mainly with variations in the concentration and the composition of the ferromagnetic mineral fraction. The changes in ChRM intensity are most likely dictated by climatological variations.
The $\delta^{18}O$ profile shows oscillations of 0.8 o/oo, and a periodicity similar to the paleomagnetic data. $\delta^{13}C$ oscillations occur synchronously with $\delta^{18}O$.



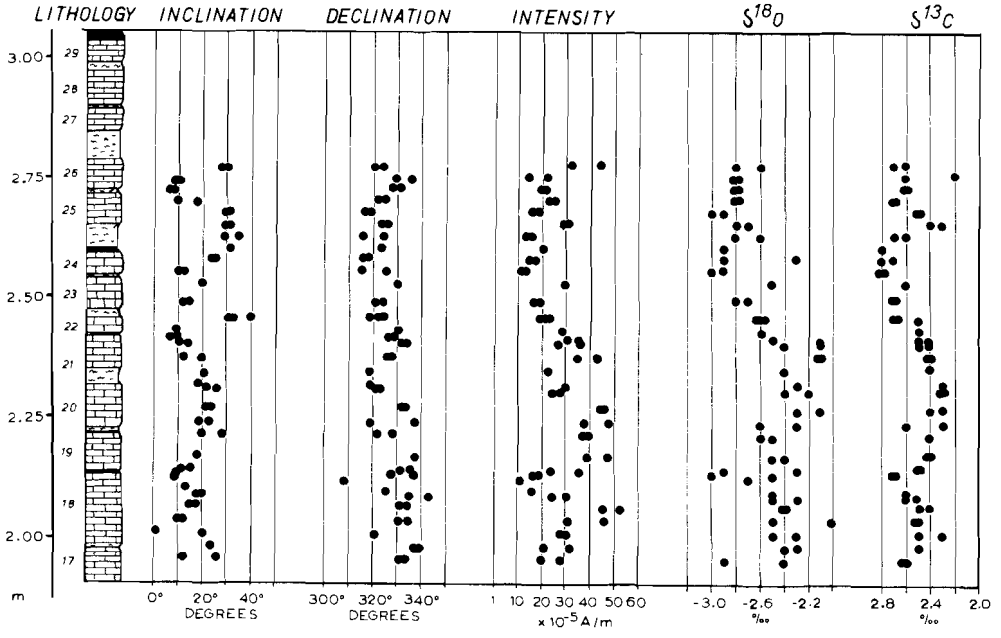


Figure 1. Characteristic remanent magnetization and stable isotope ratios of two pelagic limestone intervals of Late Albian age from N.W. Umbria (Italy).

DISCUSSION OF THE RESULTS

Variations in stable isotope ratios and in paleomagnetic properties can be compared in the figure. For the Albian-Cenomanian pelagic sediments of the Moria section (paleolatitude about 30°N) a relation was suggested between carbonate-marl rhythmicities and astronomical parameters (precession and eccentricity), which cause regular changes of climatic conditions at low latitudes. These changes were suggested to have influenced oceanic circulation patterns, the supply of nutrients and the productivity in surface waters, water temperatures and the supply of oxygen to deep water (24). The bedding rhythms as they appear in the field reflect the cycle of precession. The variation in magnetic and stable isotope data, covering 4 to 5 carbonate-marl couplets, indicate the superposition of the 100,000 year eccentricity cycle. Whereas the black shale intervals, representing periods of warm surface waters, low productivity and poor refreshment of deep water, are found 4 to 5 carbonate/marl couplets apart, they also indicate the superposition of the 100,000 yr eccentricity cycle.
The fluctuation of oxygen isotope data, in phase with the carbonate-marl cycles, which is apparent in other parts of the series, is, in the sections described here, subordinate to the longer trend. Assuming that icecaps were absent (25), and that vital effects, diagenesis, etc. have not been of major influence the oscillation of $\delta^{18}O$ of at maximum 0.8 o/oo would correspond to temperature fluctuations of up to 3°C, with small differences between adjacent carbonate and marly beds, and a more pronounced fluctuation covering 4 to 5 carbonate-marl couplets.

The ChRM vector shows a variation with identical period of 4-5 carbonate-marl couplets , as the oxygen and carbon isotope curves do. This suggests a common cause of the geomagnetic and climatic variations.

The earth´s magnetic field is thought to be generated in the outer liquid core and/or at the boundary of core and mantle. It is very likely that the Earth´s orbital parameters are one of the major factors that control perturbations in the core-mantle dynamics. Consequently any variation in coupling will be reflected directly in the properties of the Earth´s magnetic field. Sofar only Quaternary longterm variations of the paleointensity of the Earth´s magnetic field have been correlated tentatively with the Earth´s orbital parameters.

For the Quaternary, the complex relationship between climate, polar icecaps and astronomical variables, together with the complicated effects of ice-sheet / bedrock dynamics on the distribution of mass within and on the Earth, have hampered to distinguish the very causes and results. The present study adds a record of longterm directional variations of the geomagnetic field from the Middle Cretaceous. The absence of polar icecaps during this period makes it likely that these variations were dictated by astronomical parameters.

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CURRICULUM VITAE

De auteur behaalde in 1968 het diploma Gymnasium β aan het Praedinius Gymnasium te Groningen. In 1972 werd aan de Rijks Universiteit te Groningen het kandidaatsexamen Geologie (G1) afgelegd en in 1976 aan de Rijks Universiteit te Leiden het doctoraal examen Geologie met als bijvakken Sedimentologie en Geofysica.
Sindsdien is hij verbonden aan de Vakgroep, later Taakgroep Sedimentologie, aanvankelijk in Leiden, sinds 1978 in Utrecht.