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Decoupling of P- and C_{org}-burial following Early Cretaceous (Valanginian–Hauterivian) platform drowning along the NW Tethyan margin

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Abstract

During the Hauterivian three important phases of platform drowning, phosphogenesis and mesotrophic carbonate deposition along the northern margin of the Tethys are not mirrored by positive $\delta^{13}C_{carb}$ excursions such as during the Valanginian and Aptian, but rather by decreasing to stable trends. The aim of this study is to understand the decoupling of organic carbon and phosphorus burial during the Hauterivian. For this purpose PO_4-concentrations were determined from biogenic limestones from eight sections along a platform to basin transect. Integration with a previously obtained dataset for the Valanginian leads to a biostratigraphically calibrated high resolution phosphorus accumulation rate ($mg/cm^2/kyr$) curve based on 575 data points. From the Late Valanginian to Early Hauterivian phosphorus accumulation rates increased nearly threefold from 0.75 $mg/cm^2/kyr$ to 2.1 $mg/cm^2/kyr$. The phosphorus accumulation rate increase obtained in this study correlates well with a compilation based on ODP and DSDP records, indicating that phosphorus accumulation rates along the northern margin of the Tethys reflect global changes in P in- and output. A global rise in continental P input is thought to have resulted from intensified greenhouse climate conditions leading to increased riverine runoff. Coeval sea-level rise led to re-arrangement of circulation and oxygenation of bottom waters, which meant that P was increasingly well retained by means of Fe- and Mn-oxyhydroxides. Furthermore, the NW margin of the Tethys may have been especially susceptible to phosphogenesis as it was influenced by cold water exchange with the Boreal Realm and prone to coastal upwelling. The Late Hauterivian witnessed sea-level fall, more sluggish circulation along the NW Tethyan margin and also globally lower weathering and erosion rates, leading to generally lower phosphorus accumulation rates. Increased regeneration of phosphorus might have occurred as circulation stagnated and bottom water oxygen levels decreased. Increased phosphorus input into Early Hauterivian oceans did not lead to the production of organic carbon-rich rocks, but rather to increased carbonate carbon burial, also seen in a decoupling between the $\delta^{13}C_{carb}$ record (decreasing) and phosphorus accumulation rates (increasing). Decoupling of these records reflects the ecological recovery of the carbonate system after a prolonged phase of reef destruction during the late Early and Late Valanginian. Carbonate production in the

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green water mode dominated by filter feeding calcitic organisms may have been forced, despite high nutrient levels, in order to bring down increased alkalinity.

Keywords: Valanginian; Hauterivian; phosphorus; carbon isotopes; palaeoceanography; platform drowning

1. Introduction

On geological timescales phosphorus is considered to be the ultimate bio-limiting nutrient and is therefore an important driving force behind the carbon-cycle. The P- and C-cycles are also linked through global continental weathering, which is the primary source for P, a process that consumes CO_2. Understanding the dynamics of the phosphorus-cycle and its interactions with the C-cycle is important because of the role P plays in drawing down CO_2 from the atmosphere by limiting productivity in the oceans (Broecker and Peng, 1982). Phosphorites (i.e. rocks that contain more than 15% of P_2O_5) are not uncommon in the rock record and may serve to understand past changes in palaeoceanography, palaeoclimate and the link between the P- and C-cycles.

During the Phanerozoic, several time periods show an accelerated phosphorus-cycle leading to phosphogenesis and organic carbon burial. One of these periods is the Early Cretaceous, most notably the Valanginian–Hauterivian interval. Lower Cretaceous phosphorite deposits have been described from France (Guillaume, 1966), Morocco (Schlager, 1981), Spain (Gonzales-Donso et al., 1983; Martin-Algarra, 1987; Martin-Algarra and Vera, 1994), England (Jarzembowski, 1988; Taylor, 1990; Taylor, 1991; Poulton et al., 1998), Germany (Mutterlose, 1984), Poland (Kutek et al., 1983), Kazakhstan (Ilyin and Krasilnikova, 1988; Ilyin, 1998), and Chile (Mastandrea et al., 1975; Leanza et al., 1989).

Lower Cretaceous phosphorites in the Helvetic Alps (Switzerland) have received much attention over the past 100 years, because they are important markers in regional geological studies (Heim, 1910–1916; Schaub, 1948; Funk, 1971; Wyssling, 1986; Föllmi, 1986; Kuhn, 1997; Weissert et al., 1998). The phosphoritic beds have been interpreted as platform drowning events (Föllmi et al., 1994; Weissert et al., 1998). In the Helvetic Alps five phases of platform drowning (Lower Valanginian to Lower Cenomanian) in the form of highly condensed phosphoritic beds have been recognised. Early models related the repeated occurrence of condensed and phosphoritic deposits to tectonic movements (Fichter, 1934). Although rapid subsidence and relative sea-level rise can explain condensation, they do not explain the deposition of P_2O_5-rich sediments.

Föllmi et al. (1994) and Weissert et al. (1998) have related drowning events to increased continental weathering/erosion and runoff leading to eutrophication and nutrient poisoning of oligotrophic carbonate producing biota, like corals. These authors have also suggested that platform drowning events were connected to episodes of flood basalt volcanism (Paraña and Ontong–Java Igneous Provinces) inducing greenhouse warming. This suggestion was made after noting that positive excursions in the $\delta^{13}C_{carb}$ record during the Valanginian and Aptian are contemporaneous with phases of platform drowning (D1 and D4 in Föllmi et al., 1994). Increased nutrient influx as a result of increased continental weathering, would have led to increased primary productivity and organic carbon burial, while carbonate carbon burial was slowed down during drowning.

Helvetic drowning phases D2 (Mid-Hauterivian) and D3 (Hauterivian–Barremian boundary) are not mirrored by large scale $\delta^{13}C_{carb}$ positive excursions (Van de Schootbrugge et al., 2000), but rather by decreasing to stable trends. However, global phosphorus accumulation rates calculated from DSDP and ODP data by Föllmi (1995) indicate that the Hauterivian witnessed even higher accumulation rates than the Valanginian, during which a major positive $\delta^{13}C_{carb}$ excursion does occur. Especially the Mid-Hauterivian acme in phosphorus accumulation rates, related to drowning phase D2, presents an interesting problem, because during this time period a minimum in $\delta^{13}C_{carb}$ was recorded (Van de Schootbrugge et al., 2000). The aim of this study is to investigate the discrepancy between phosphorus accumulation rate and $\delta^{13}C_{carb}$ records during the Hauterivian and ultimately to find answers to what mechanism was responsible for platform drowning and phosphogenesis.

For this purpose phosphate (PO_4) concentrations were determined from bulk carbonate samples from a wide variety of settings along the northwestern margin of the Tethys. We focused on the element phosphorus because of its obvious connection with the phosphoritic beds, but also because this element is a good proxy for continental weathering, since more than 90% of phosphorus in the oceans is delivered by rivers (Meybeck, 1982; Föllmi, 1996). The phosphate data will be compared with detailed carbon isotope records previously established in sections around the Tethyan basin (Föllmi et al., 1994; Kuhn, 1997; Weissert et al., 1998; Hennig et al., 1999; Van de Schootbrugge et al., 2000). This study is limited to the northern Tethyan margin because sections from this area present in general good bio- or magnetostratigraphic control and because these sections can be directly correlated with the phosphogenic events of the Helvetic Alps. From the PO_4 data phosphorus accumulation rates were calculated which were plotted together with the Hauterivian $\delta^{13}C_{carb}$ records and the global phosphorus accumulation rate curve of Föllmi (1995). Subsequently, a previously obtained PO_4 data set from the Valanginian (Kuhn, 1997) was integrated, which allows us to present a high resolution phosphorus accumulation rate curve based on 575 datapoints for the Valanginian to Early Barremian interval (spanning approximately 11 Myr).

In addition to the larger scale trends in P input and burial, a case study is presented for the type section for the Hauterivian of the Helvetic Alps providing more insight into a number of factors controlling P accumulation, such as redox conditions of bottom waters and surface sediments and biogenic and detrital particle fluxes. An integrated approach, including palynofacies, Total Organic Carbon (TOC) and minor element data (P, Fe), serves to strengthen a proposed model for P accumulation along the NW margin of the Tethys.

2. Methods

The eight studied sections form a basin to platform transect. Five regions have been investigated that are typical of a certain depositional environment along the NW margin of the Tethys (Fig. 1). Sections from the Swiss Jura mountains represent the shallow carbonate platform setting. One section in the Subalpine Bauges Massif (France) represents a southern extension of this platform. This region forms the transition to the Vocontian Basin. Sections from the Helvetic Alps recorded shelf conditions during most of the Early Cretaceous. Sections from the Vocontian Basin (SE France) represent the hemipelagic domain, while sections from the Umbria–Marche Basin (Italy) are representative for the pelagic realm. A total of 403 samples were measured for their total PO_4-concentrations. On incorporation of 172 analyses

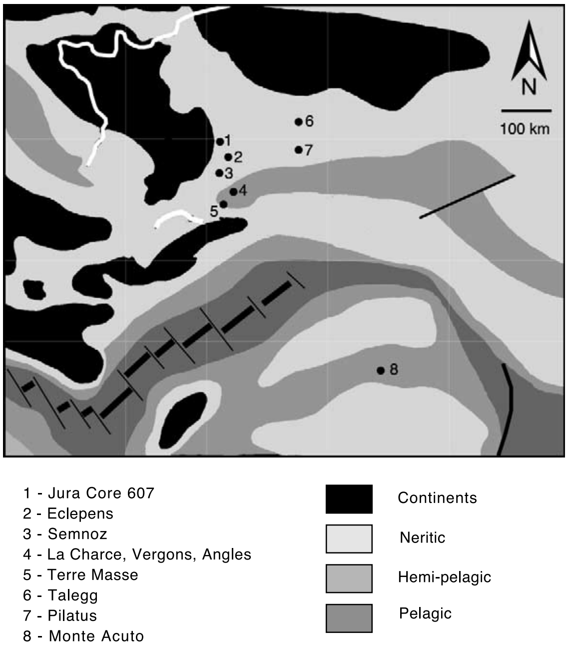

Fig. 1. Palaeogeographic reconstruction of the NW Tethyan margin. The white lines indicate the approximate outline of France (modified from Hennig et al., 1999).

done by Kuhn (1997) a detailed record of 575 datapoints is available now for 12 sections spanning the Lower Valanginian to Upper Hauterivian.

Earlier attempts by Kuhn (1997) to use a sequential extraction technique (Filippelli and Delaney, 1996; Ruttenberg and Berner, 1993) on Lower Cretaceous sediments of the Helvetic Alps, gave no reliable results. Three phases could be distinguished (absorbed, authigenic and detrital), but the measured amount of detrital apatite with that method was found to be too high, sometimes in excess of 80% of the total amount. Microscopic analyses showed no presence of magmatic apatite in detrital residues of Lower Cretaceous limestones. One likely explanation is that diagenesis changed carbonate fluorapatite (authigenic PO_4) to carbonate-poor fluorapatite, meaning that this authigenic phase only dissolves in relatively strong acid and not in weak acids like used in the sequential extraction method to determine the authigenic phase. Therefore, it was decided not to perform the elaborate sequential extraction, but to do the total extraction by reaction with 1N HCl, in order to obtain Total PO_4.

For the phosphate analyses around 100 mg of powdered bulk carbonate was reacted with 1N HCl for 14 h under constant shaking. The solution was centrifuged, diluted ten times and analysed using the Ascorbic Acid Method of Eaton et al. (1995). The solution was mixed with ammonium molybdate and potassium antimonyl tartrate, which in an acid medium react with orthophosphate to form phosphomolybdic acid. This acid is reduced with ascorbic acid to form an intense blue colour. The intensity of the blue colour was determined with a Perkin Elmer UV/Vis Photospectrometer Lambda10 at a wavelength of 880 nm. Individual samples were measured three times and precision proofed better than 5%. Replicate analyses of samples proofed to have a precision better than 10%. To compare results from different sections, that often have varying absolute contents in PO_4, phosphorus accumulation rates are calculated in mg of P per cm^2 per kyr. This is a multiplication of the concentration in P (mg/g), the density (g/cm^3) and the sedimentation rate (cm/kyr). The density was considered constant here for limestones (2.5 g/cm^3). All limestone samples analysed are dense mud to wack/packstones with little or no porosity.

One of the major problems with this calculation is the fact that numerical ages used to calculate sedimentation rates are often poorly constrained. In Hardenbol et al. (1998) the ammonite zones that define the Hauterivian all have the same duration of 710 Kyr. Although it is hard to imagine ammonite evolution proceeded at such a regular pace, this is unfortunately till date the only study that gives realistic durations for Valanginian and Hauterivian ammonite zones. Calibration of magnetostratigraphic and ammonite biostratigraphic zonations from the Umbria–Marche Basin led Channell et al. (1995) to propose that the *Subsaynella sayni* ammonite Zone covered 60% of the Hauterivian stage or 3 Ma (CM9–CM6). New isotope correlation between S France and Italy, however, indicates that magneto zones CM9–CM7 correlate with the *Acanthodiscus radiatus* to *Lyticoceras nodosoplicatum* ammonite zones (Hennig et al., 1999). Another problem is the scarcity of good biostratigraphic markers in shallow marine carbonate settings leading to sedimentation rates being averaged out over large lapses of time. This is best illustrated by the Semnoz section where only one ammonite find (*Subsaynella sayni*, Viéban, 1983) permits to draw the approximate position of the Lower–Upper Hauterivian boundary. In the absence of absolute time durations for the ammonite zones, our accumulation rate curves have to be taken as a first approximation. In spite of these problems, the fact that we reproduce the same patterns in so many sections and from so many different settings suggests that these trends are meaningful and not computational artefacts.

A selection of 31 argillaceous limestone samples from the Pilatus section was processed for its palynological contents. Samples were alternatively treated with concentrated HCl and HF in order to separate the organic matter from the mineral phases. Sieving was done with a 15-μm sieve and the residues were mounted on slides using glycerine jelly. Counts of at least 200 palynomorphs per slide were made in transmitted light using the palynofacies classification of Steffen and

Gorin (1993). This classification includes recognition of an allochthonous (terrestrial fraction) comprised of pollen, spores, blade and lath shaped inertinite fragments, translucent woody debris and amorphous organic matter and an autochtonous (marine) fraction made up of dinoflagellate cysts, acritarchs, other algae (mostly prasinophytes) and organic walled foram linings. The same sample set was analysed with a Rock-Eval 6 for Total Organic Carbon contents. Iron contents were determined using a Perkin–Elmer 5100 Atomic Absorption Spectrophotometer of the University of Neuchâtel. Approximately 100 mg of bulk rock was reacted with 1N HCl for 20 min at 80°C in a microwave dissolution system. Analyses were calibrated with standard Fe-solutions. Precision proved better than 5% for replicate analyses.

3. Results

Fig. 2 is a compilation of all the gathered data combined with the data reported in Kuhn (1997). Averages were calculated per ammonite zone for each section and averages for all sections per ammonite zone (Fig. 2A,B, respectively). This figure shows that phosphorus accumulation rates are increasing from the Upper Valanginian into the Lower Hauterivian and rapidly decrease in the Upper Hauterivian. Maximum accumulation rates are attained in the *Acanthodiscus radiatus* and *Crioceratites loryi* Zones. Although the P accumulation rates are dominated by sedimentation rates, average PO_4-concentrations also increase during the same interval, indicating that not only sedimentation rates are responsible. The influence of diagenesis is excluded, because the same trends are observed in so many different sections. Furthermore, the two sections that suffered most from tectonic overprint, i.e. Talegg and Pilatus, show similar results even though these two sections belong to different thrust sheets. In the next paragraphs the stratigraphy, lithology and phosphorus contents of each section are briefly presented.

3.1. Inner neritic realm (Core 607, Eclepens, Semnoz)

Core 607 drilled in the historical type region for the Hauterivian, Neuchâtel Jura Mountains (Swit-

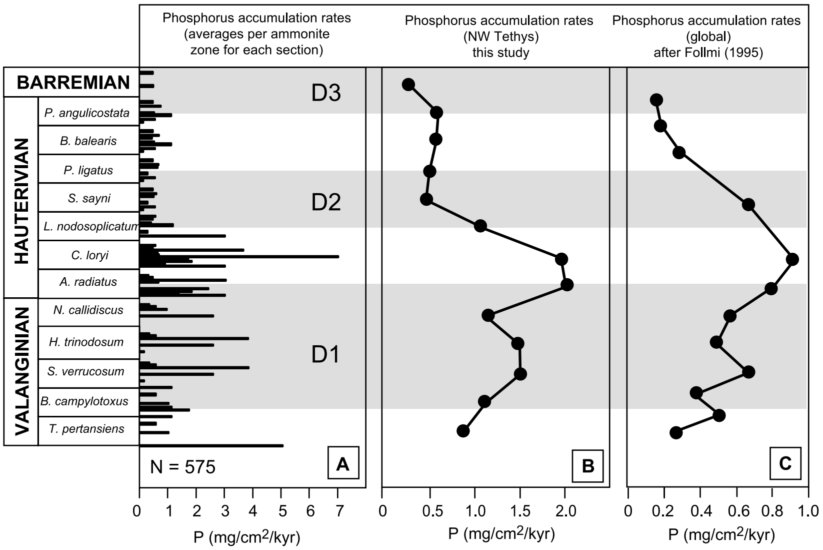

Fig. 2. Compiled P accumulation rates. (A) P accumulation rates within each section (averages per ammonite zone). (B) P accumulation averages for all sections per ammonite zone. (C) Compilation based on ODP and DSDP P accumulation rate data after Föllmi (1995).

zerland), has previously been studied for its sedimentology and biostratigraphy by Rumley (1992). The base of the Hauterivian succession in the Swiss Jura is formed by marly sediments (25 m) of the Marnes Bleues d'Hauterive Formation. These are overlain by shallow marine bioclastic and oolithic limestones of the Pierre Jaune de Neuchâtel (PJN) Formation, which are considered to represent a drowned carbonate platform by Arnaud-Vanneau and Arnaud (1990). The transition between the Marnes Bleues and Pierre Jaune is formed by the Zone Marno–Calcaire Member, which is a biomicritic unit rich in detrital quartz. Whereas the Marnes Bleues are well constrained by abundant *Acanthodiscus radiatus* (lowermost Hauterivian *A. radiatus* Zone), the Pierre Jaune contains almost no diagnostic faunal elements. However, several rare ammonites from the Marnes d'Uttins, intercalated in the Pierre Jaune indicate the *Crioceratites loryi–Lyticoceras nodosoplicatum* Zones (Busnardo and Thieuloy, 1989). Total phosphate values measured for Core 607 show maximum values in the middle of the Marnes Bleues d'Hauterive Formation (3983 ppm). Phosphate concentrations decrease in the Zone Marno–Calcaire Member and PJN Formation to values ranging from 400 to 700 ppm. Phosphorus accumulation rates show corresponding high values for the Marnes Bleues d'Hauterive Formation (>10 mg/cm^2/kyr) and much decreased rates for the Zone Marno–Calcaire Member and PJN Formation (<1 mg/cm^2/kyr).

The section of Eclepens (Swiss Jura) was studied by Zweidler (1985) and Blanc-Aletru (1995). The lower part of the Eclepens section is dominated by mixed bioclastic and oolithic grainstones of the upper PJN Member. The Urgonian of Eclepens can be divided in a lower 'yellow' part still rich in ooids and an upper 'white' part, which corresponds to the typical Urgonian Facies with rudists and orbitolinids. The Urgonian limestones have been dated as Upper Barremian by Arnaud et al. (1999) and a large hiatus, that comprises the Upper Hauterivian and Lower Barremian, occurs between the Upper PJN and Lower Urgonian. At Eclepens, the base of the upper PJN shows the same order of concentrations observed in the lower PJN in Core 607 with values reaching up to 500 ppm. Through the upper PJN PO_4-concentrations rapidly decrease to low values and reach almost zero in the top of the succession. Phosphorus accumulation rates show a clear distinction between the PJN and the Urgonian. Although accumulation rates are low in the upper PJN (~ 0.3 mg/cm^2/kyr), phosphorus accumulation rates decrease even further, i.e. to less than 0.1 mg/cm^2/kyr in the Urgonian.

The Semnoz section, located south of Annecy (France) in the Subalpine Bauges Massif, represents an outer ramp facies with spiculitic-crinoidal bioclastic mud–packstones at the base, sometimes rich in glauconite, overlain by a thick marl sequence with marl–limestone alternations, rich in detrital quartz and sponge spicules, which is poorly exposed. This marl sequence is in turn overlain by oolithic packstones, marking a shallowing of the depositional environment. This section was studied for its biostratigraphy and sedimentology by Viéban (1983). The finding of some ammonites (most notably *Acanthodiscus radiatus*) at the base of the section and the presence of a *Subsaynella sayni* just above the marly interval provide some tie points. The unexposed part of the section was placed in the *Lyticoceras nodosoplicatum* Zone by Viéban (1983). The Hauterivian–Barremian boundary was placed by Viéban (1983) at a discontinuity surface that can be traced back to the Vercors area (France), where it is dated with ammonites and foraminifera. The Lower Hauterivian shows variable PO_4-concentrations ranging from less than 500 up to 4000 ppm. The Upper Hauterivian shows overall much lower absolute values, generally less than 1000 ppm. P-accumulation rates are relatively high (1–8 mg/cm^2/kyr) for the Lower Hauterivian and lower (<1 mg/cm^2/kyr) for the Upper Hauterivian.

3.2. Outer neritic realm (Talegg, Pilatus sections)

The Talegg and Pilatus sections, located in the Swiss Alps, represent the former Helvetic shelf of the northern Tethyan margin. The Talegg and Pilatus sections are part of different thrust sheets that represent different portions of the former shelf (Murtschen and Randkette nappes, respectively). The Talegg section belongs to the middle facies realm of Funk et al. (1993), while the Pilatus section belongs to the further offshore southern facies realm. The Talegg section has previously been studied by Heim (1910–1916) and Funk (1971) and starts off with 50 m of bioclastic and oolithic packstones of the Lower Valanginian Betliskalk Formation. The contact with the overlying Helvetic Kieselkalk Formation is sharp. In the Pilatus section (Funk, 1969) the boundary between the Upper Betliskalk and Kieselkalk is formed by the Gemsmättli beds (D1 in Föllmi et al., 1994). This phosphoritic horizon contains ammonites belonging to the Lower Valanginian to Lower Hauterivian *Busnardoites gr. campylotoxus–Acanthodiscus radiatus* Zones (Wyssling, 1986; Kuhn, 1997). At Talegg the Upper Valanginian is thus missing. Also missing are 10 m of shales, present at Pilatus, belonging to the upper part of the *A. radiatus* Zone. In both sections the Lower Kieselkalk Member is made up of fine bedded sandy wackestones grading into coarser grained and thicker bedded packstones up section. The top of the Lower Kieselkalk Member is formed by the Lidernen Beds. This glauconitic–phosphoritic horizon condenses the *Lyticoceras nodosoplicatum*, *Subsaynella sayni* and lower part of the *Plesiospitidiscus ligatus* Zones (Van de Schootbrugge, 2001.; D2 in Föllmi et al., 1994). In the Talegg section it contains mostly glauconite, while at Pilatus it also contains phosphoritic clasts. The overlying Upper Kieselkalk Member shows thicker bedding in general and transitions into the Echinoderm Breccia, a coarse biosparitic marker bed. On top lie the Altmann beds which represent a renewed phase of phosphorite deposition and condensation (D3 in Föllmi et al., 1994). These beds are rich in pyrite nodules, belemnites and ammonites, which are, however, poorly preserved and do not allow determination. In Austria, Wyssling (1986) was able to date the Altmann beds as uppermost Upper Hauterivian (upper part of the *Pseudothurmannia angulicostata* Zone) to Lower Barremian. In the Talegg section the total PO_4-curve shows a rapid increase from the top of the Betliskalk Formation into the Lower Kieselkalk Member. Higher concentrations were measured for the lowest part of the Betliskalk Formation. The Lidernen beds, show a peak value of 3558 ppm PO_4. Values for the Upper Hauterivian are slightly lower than those for the Lower Hauterivian, before values start to increase again towards the Altmann beds. The phosphorus accumulation rate drop to almost zero in the Lidernen beds. In the Pilatus section (Fig. 3) average PO_4-values for the Lower Kieselkalk Member are around 500 ppm, while they are around 200 ppm for the Upper Kieselkalk Member. The Lidernen beds show again values in excess of 3000 ppm. Phosphorus accumulation rates illustrate the distinct difference between the Lower and Upper Hauterivian, with considerably elevated rates in the Lower Hauterivian.

3.3. Hemipelagic realm (Terre Masse, La Charce/Vergons/Angles)

The Vocontian Basin is represented by a composite section consisting of the La Charce, Angles and Vergons sections and the Terre Masse section. Both sections are composed of hemipelagic alternations of calcareous marls and micritic limestones. Terre Masse is strongly reduced in thickness compared to other sections in the Vocontian Basin, however based on its detailed ammonite biostratigraphy it is possible to infer that there are no major gaps. The reduced thickness can be ascribed to several condensed horizons rich in glauconite that are better developed in expanded basin sections and to its palaeogeographical position on the slope of the Vocontian Basin. The *Acanthodiscus radiatus* Zone in Terre Masse is extremely condensed, which can be correlated with a phosphoritic horizon in the Helvetic Alps (Gemsmättli beds, drowning phase D1 of Föllmi et al., 1994). The uppermost Hauterivian *Pseudothurmannia angulicostata* Zone is disturbed by largescale slumping and was not sampled for this study. In Terre Masse PO_4-concentrations vary between 500 and 1000 ppm with a single outlier (>2000 ppm) in the upper part of the *Lyticoceras nodosoplicatum* Zone, which corresponds to a condensed glaucontic bed. Values decrease again during the Upper Hauterivian, although the difference with the Lower Hauteri-

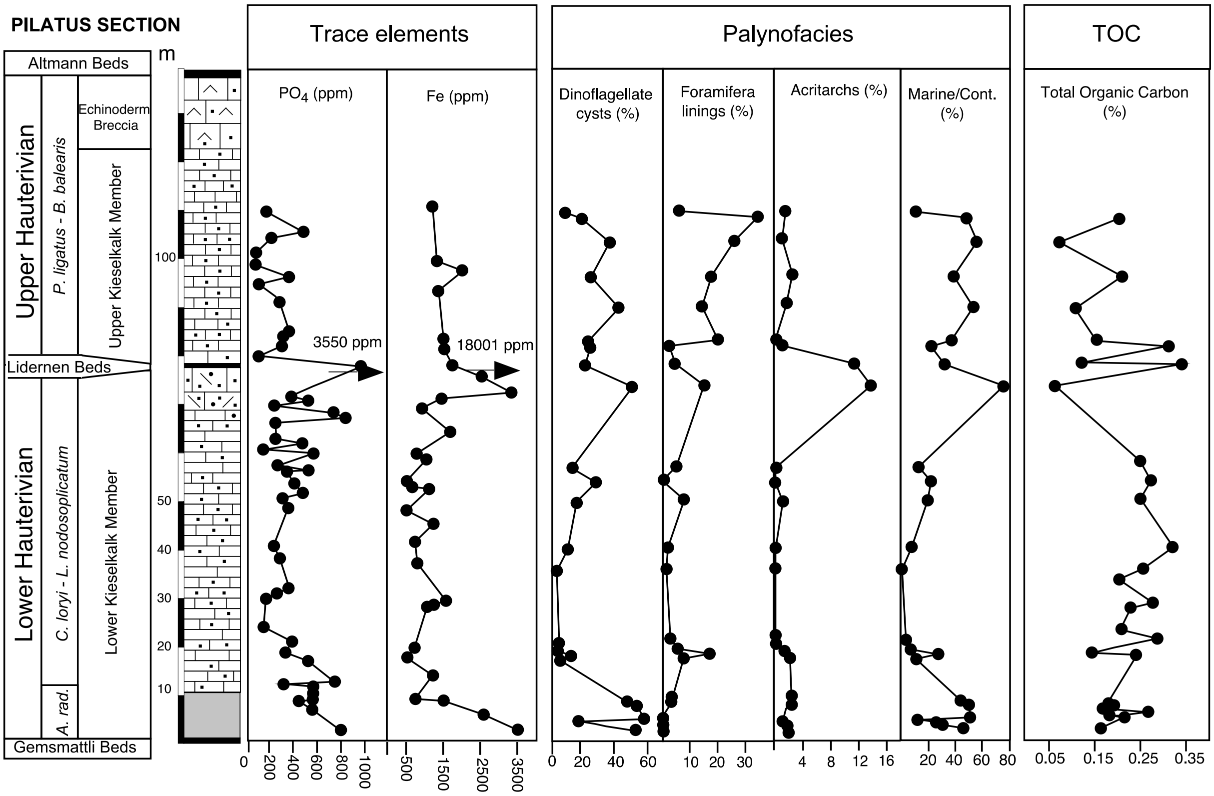

Fig. 3. Integrated study on Pilatus section showing minor element data (P, Fe; left side) vs. organic matter contents. P and Fe peak values in the Lidernen beds are plotted separately, so the trends within the Kieselkalk Formation become clearer. The palynofacies data are all presented as percentages of the total fraction.

vian is small. Phosphorus accumulation rates show a slight increase from the *Crioceratites loryi* Zone into the *L. nodosoplicatum* Zone and gradually decrease up to the top of the *Balearites balearis* Zone.

The composite section is well constrained by ammonite biostratigraphy and the individual sections serve as reference sections for the Vocontian Basin (Bulot and Thieuloy, 1993; Bulot et al., 1992). La Charce spans mainly the Lower Hauterivian (*Acanthodiscus radiatus*, *Crioceratites loryi* and *Lyticoceras nodosoplicatum* Zones), while in Vergons and Angles the Upper Hauterivian (*Subsaynella sayni*, *Plesiospitidiscus ligatus*, *Balearites balearis* and *P. angulicostata* Zones) is exposed. PO_4-concentrations decrease in the Lower Hauterivian, descending from around 800 ppm in the *A. radiatus* Zone to around 400 ppm in the *L. nodosoplicatum* Zone. In the Upper Hauterivian values range from 600 to 800 ppm. P-accumulation rates are stable around 2 mg/cm^2/kyr for the Lower Hauterivian and increase rapidly from the *S. sayni* to *Plesiospitidiscus ligatus* Zones to 4 mg/cm^2/kyr before accumulation rates decrease again in the *B. balearis* and *Pseudothurmannia angulicostata* Zones to about 1 mg/cm^2/kyr.

3.4. Pelagic realm (Monte Acuto)

The Monte Acuto section in the Umbria–Marche Basin (close to Chiaserna, Italy) is one of a few outcrops in the Maiolica Formation studied in detail for its ammonite biostratigraphy. The Italian Maiolica consists of pelagic micritic limestones with intercalated chert (nodules) and argillaceous limestones, rich in calcareous nannofossils, but often with a depauperate macro-fossil assemblage. A biozonation based on ammonites was proposed by Cecca et al. (1995), who distinguished the Upper Valanginian (*Saynoceras verrucosum* to *Neocomites callidiscus* Zones) and Lower Hauterivian (*Acanthodiscus radiatus* to *Lyticoceras nodosoplicatum* Zones). These ammonite finds were important because they allowed to calibrate magneto- and biozones (ammonites and nannofossils). The magnetostratigraphy of Mt. Acuto was established by Channell et al. (1995). Recent carbon isotope correlation with the Vocontian Basin (Hennig et al., 1999; Van de Schootbrugge et al., submitted) indicate that CM8–CM7 belong to the *Crioceratites loryi* and *L. nodosoplicatum* Zones. Absolute PO_4 values show a slight increase from the Upper Valanginian into the Lower Hauterivian, from 200 to 500 ppm. Phosphorus accumulation rates show increasing values from the Upper Valanginian into the *L. nodosoplicatum* Zone.

3.5. Pilatus section case study

Palynofacies, TOC and Fe-concentration analyses of selected samples from the Pilatus section show several distinct trends (Fig. 3). The most significant are briefly presented here. Dinoflagellate cyst abundance is high at the base of the succession and decreases steadily to low values half way through the Lower Kieselkalk Member. This trends is also reflected in the Marine/Continental ratio (Fig. 3), which is the ratio of all marine palynomorphs vs. all terrestrial palynomorphs. The *Crioceratites loryi* Zone contains predominantly terrestrial organic matter (both lath and blade shaped inertinite). The upper part of the Lower Kieselkalk Member shows again an increase in dinoflagellate cyst abundance. The Marine/Continental ratio reaches peak values within the uppermost Lower Kieselkalk Member, just before the onset of drowning phase D2 (Lidernen beds). The marine fraction is generally dominated by dinoflagellate cysts, but acritarchs and foraminifera linings become more important elements of the palynofacies assemblage towards the top of the section. Acritarchs (predominantly *Micrhystridium* spp.) reach maximum abudance just below and within the Lidernen beds. Organic walled foraminifera linings are extremely abundant in the upper Kieselkalk Member. Total Organic Carbon values are generally low throughout the Kieselkalk Formation varying from 0.05% to 0.35%. These values are considered to be too low to make reliable use of OI and HI values as indicators for source and maturity of the organic matter due to matrix effects. TOC, however, does appear to co-vary with trends in palynofacies and PO_4 contents. Iron concentrations co-vary with PO_4-concentrations and peak in the Lidernen beds (18001 ppm).

4. Discussion

4.1. Phosphorus accumulation rates along the NW Tethyan margin

The input of (bio-available dissolved) phosphorus in the oceans is almost entirely controlled by continental runoff ($>90\%$). Less than 10% is entering the oceans through eolian transport. Hydrothermal input is considered to be of negligible importance. (Benitez-Nelson, 2000; Compton et al., 2000; Delaney, 1998; Föllmi, 1996). Therefore, the most direct way to explain a nearly threefold increase in phosphorus burial along the northern margin of the Tethys from the Upper Valanginian to Lower Hauterivian is an increase in continental weathering/erosion and river runoff. Runoff from landmasses such as the Bohemian Massif towards the north and the Armorican–Central Massifs towards the west is thought to have increased under intensified Early Cretaceous greenhouse climate conditions (Föllmi et al., 1994; Weissert et al., 1998). Conditions along the NW margin of the Tethys have been inferred to have been warm and humid (Kemper, 1983; Price, 1999) based on the presence of abundant kaolinite (Sladen, 1983; Deconinck, 1984; Ruffell and Batten, 1990; Adatte et al., 1996) and Fe/Mn ratios in Tethyan biogenic limestones (Kuhn et al., in prep.).

Drawdown of P into the sedimentary reservoir is governed by various mechanisms. According to Broecker and Peng (1982), 95% of dissolved P in surface waters is taken up by organisms and transported down in particulate form, where

99% is regenerated in dissolved form. So only 1% of dissolved phosphorus present in the oceans reaches the sediments and is removed (Föllmi, 1996; Delaney, 1998). Phosphorus is transported down column as organic bound P, adsorbed on clay particles, adsorbed or occluded on calcitic tests, adsorbed on ferric oxyhydroxides and as apatitic fish debris. Based on the co-variation between the amount of dinoflagellate cysts and phosphorus concentrations in the Pilatus section we suggest phytoplankton may have played an important role in taking up phosphorus and transporting it down column.

Scavenging by Fe- and Mn-oxyhydroxide particles has been shown to be an effective method to remove P from the watercolumn around hydrothermal vents (Froehlich et al., 1982). This hydrothermal scavenging is unlikely to have had any influence on the passive NW continental margin of the Tethys, however, as was mentioned above, the Late Valanginian and Early Hauterivian were also characterised by increased continental Fe and Mn influx. Oxyhydroxides will mainly form as coatings on sedimentary particles and since the dissolved concentrations of Fe and Mn are generally low and descending particles move too quickly, this process is likely to occur in the sedimentary column (Delaney, 1998). Hence, an increase in burial of Fe and Mn would increase the potential to retain PO_4. Well oxygenated bottom waters are further prerequisites for the precipitation of iron, manganese and phosphorus.

The Pilatus case study fits this scenario very well. Co-varying phosphorus and iron concentrations indicate oxygenated bottom water conditions during the *Crioceratites loryi* and *Lyticoceras nodosoplicatum*. Thick bedded limestones underlying drowning phase D2 (Lidernen beds) partly resulted from intense *Thalassinoides* bioturbation, while lower phosphorus accumulation rates in the lower part of the Upper Kieselkalk Member occur in well laminated sediments.

4.2. Phosphorus as a proxy for global change

Phosphorite deposition during the Early Cretaceous was not restricted to the northwestern margin of the Tethys, but increased worldwide. A global P-accumulation rate curve for the last 160 Myr (Fig. 2C) was compiled by Föllmi (1995). From this data set a three- to fourfold increase can be observed as well. Although the calculated values are lower (from 0.2–0.8 mg/cm^2/kyr), which is due to the fact that the data were primarily derived from pelagic sites, this curve represents a global signal because it is based on DSDP and ODP data obtained from a wide variety of basins (cf. Föllmi, 1995). Since the trends in both data sets are similar in shape and magnitude, the underlying mechanisms for phosphorus enrichment along the NW margin of the Tethys should be global as well.

Two global mechanisms exerting control on phosphorus accumulation were at work during the Valanginian to Hauterivian: (1) eustatic sea-level rise, and (2) the outflow of large volumes of flood basalts in the Parana Igneous Province, Brazil (see Fig. 4). Sea-level rise from the Mid-Valanginian to Mid-Hauterivian has been documented from the NW Tethyan margin to the Russian Platform (Sahagian et al., 1996; Hardenbol et al., 1998). The Parana Continental Flood Basalts (PCFB) have been dated from 138 to 131 Myr with a peak in activity around 131 Myr (Early Hauterivian; Stewart et al., 1996). One of the results of the sea-level rise was the establishment of gateways between the Tethys and Boreal. Colder water is thought to have entered the Tethys over the Polish Furrow based on oxygen isotope data from belemnites and migration of fauna and flora (Crux, 1989; Price et al., 2000; Van de Schootbrugge et al., 2000; Fig. 4). The NW Tethyan margin may have been in an extremely favourable position for phosphorus burial. A combination of strong westerlies (Poulsen et al., 1998), offshore currents and replenishment by upwelling Boreal cold nutrient-rich waters may have fueled biological uptake of available phosphorus and its downward transport as organic matter.

Carbon dioxide emission from flood basalts is widely seen as a cause of global warming and the degassing of the PCFB has been inferred to have lead to an Early Cretaceous greenhouse world (Weissert et al., 1998). Globally humid and warm conditions during the Valanginian–Hauterivian are also shown by global enrichment in Fe

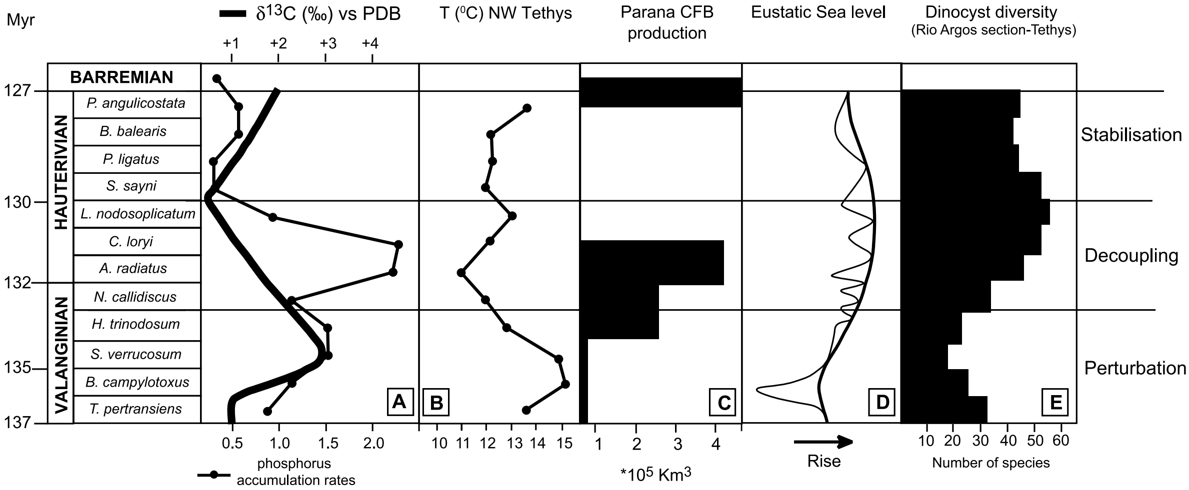

Fig. 4. Three-stage development of platforms during the Early Cretaceous in relation to major palaeo-environmental changes during the Valanginian and Hauterivian. Time scale is after Hardenbol et al. (1998). (A) Coupling and decoupling of P accumulation (curve from Fig. 2) and carbon isotope record (after Van de Schootbrugge et al., 2000 and Hennig et al., 1999) is shown. (B) Temperature record for NW Tethys based on belemnite oxygen isotopes (from Van de Schootbrugge et al., 2000). (C) Parana continental flood basalt production rates taken from Stewart et al. (1996). Lower part of the figure shows flood basalts in Parana Basin proper. Upper part (5*10 Km^3 dated at 127 Ma) is renewed eruption phase on the Rio Grande Rise (Stewart et al., 1996). (D) Eustatic sea-level curve after Hardenbol et al. (1998). (E) Dinoflagellate cyst diversity curve for the Rio Argos (Caravaca) section in SE Spain. Data taken from Leereveld (1995).

and Mn (Cotillon, 1960; Kemper, 1983; Cisternas et al., 1986; Clauser et al., 1988) and the lack of *Classopollis* pollen in palynological assemblages (Marek, 1983; Kemper, 1983). Palynofacies studies on ODP and DSDP material from North Atlantic margins indicate that most of the organic matter in Valanginian–Hauterivian sediments is terrestrial, commonly associated with turbidite sedimentation (see Van de Schootbrugge et al., 2000 and references therein), indicating high detrital input into the young Atlantic.

4.3. P-accumulation and carbonate platform drowning events

Drowning D1 (upper Lower Valanginian to lowermost Lower Hauterivian) marks a significant turnover in carbonate platform sedimentation from the coral–oolite mode to the crinoid–bryozoan mode (Föllmi et al., 1994). This first drowning event is mirrored by a positive $\delta^{13}C_{carb}$ excursion, reflecting slowdown of carbonate carbon burial and increased organic carbon production (Weissert et al., 1998). Lower Hauterivian carbonate ramp ecosystems along the NW Tethyan were dominated by bryozoans, crinoids, echinoderms, and siliceous sponges, a so-called *green water* facies. This community was well adapted to high nutrient levels and turbidity (James, 1997; Gammon et al., 2000), as well as cold water and produced carbonate at high pace during the Lower Hauterivian *Crioceratites loryi* and *Lyticoceras nodosoplicatum* Zones (e.g. 600 m/Myr on the Helvetic Shelf in the Alvier region, Switzerland and 300 m/Myr in basin sections in the Vocontian Basin, France). High carbonate sedimentation rates can also be inferred from an approximately 2 per mil decrease in $\delta^{13}C_{carb}$ during the Late Valanginian to Early Hauterivian (Fig. 4A).

If carbonate factories were up and running during the Early Hauterivian, why did platforms still drown as was the case for the Mid-Hauterivian and uppermost Upper Hauterivian? All platform drowning events probably had their own specific set of controls and it was a combination of factors, not just eutrophication, that gave the final blow. Graziano (1999) came to the same conclusion after studying Lower Valanginian and Aptian drowning unconformities on the Apulia Platform, a platform that was not influenced by river input, but drowned at least three times. In the case of D1 of Föllmi et al. (1994), sea-level fall followed by rapid transgression, cold water influx from the Boreal Basin and increased nutrient transfer from continent to ocean led to a halt in carbonate deposition spanning possibly more than 2 Ma. The Mid-Hauterivian drowning event D2 was possibly even more controlled by sea-level changes. The upper part of the *Lyticoceras nodosoplicatum* Zone is marked by a major sea-level fall (Hoedemaeker, 1995; Sahagian et al., 1996; Hardenbol et al., 1998). The combination of weakening during sea-level fall and rapid transgression during the lowermost Upper Hauterivian *Subsaynella sayni* Zone was almost certainly an additional factor. D3 in Föllmi et al. (1994) occurred contemporaneous with deposition of the Faraoni black shale level. This relatively short lived anoxic event (Cecca et al., 1993; Cecca and Pallini, 1994; Cecca et al., 1996, 1998) may have resulted from the turn-over of deep anoxic phosphorus-rich water during a renewed transgressive pulse. Although *green water* assemblages still prevailed, carbonate production slowed down during the Upper Hauterivian. Carbon isotope records indicate that organic carbon burial increased again during the Late Hauterivian (Van de Schootbrugge et al., 2000).

The observation that phosphoritic beds in the successions studied here accumulated phosphorus at extremely slow rates, while Lower Hauterivian mesotrophic carbonates accumulated P at high rates, presents an interesting paradox. Worsley et al. (1988) put forward the idea that phosphorites are part of a feedback mechanism keeping phosphorus from being buried and available to organisms. These authors stated that contrary to popular believe phosphorites do not indicate increased continental fluxes, but extreme winnowing and scavenging. Transposed to the Hauterivian, this seems to imply that drowning was caused by an absence rather than an overkill of nutrients. Again, sea-level change probably played a large role. Sea-level fall during the Upper Hauterivian may have led to bypassing of phosphorus further offshore (Moody et al., 1981).

4.4. Decoupling of P- and C_{org}-burial

An increase in overall sedimentation rates should in theory lead to increased organic matter preservation, and therefore to increased P contents (e.g. Ingall and Van Cappellen, 1990). At the same time, increased input of bio-available PO_4 should lead to increased primary productivity and the deposition of organic carbon-rich rocks or even black shales (Pedersen and Calvert, 1990). The Late Valanginian to Early Hauterivian shows a long term decrease in $\delta^{13}C_{carb}$ values (Hennig et al., 1999; Van de Schootbrugge et al., 2000), that do not testify to increased burial of organic carbon but rather to increased burial of carbonate carbon. Fig. 4A shows a compiled $\delta^{13}C_{carb}$ record together with the average phosphorus accumulation rate record discussed in Fig. 2. The most significant trend in Fig. 4A is the divergence between the two curves during the Late Valanginian and Early Hauterivian and positive correlations for the Early to early Late Valanginian and Late Hauterivian.

Coupling of the P- and $\delta^{13}C$-record appears to be related to regressive phases and possibly stagnant conditions, while decoupling during the Late Valanginian to Early Hauterivian corresponds to eustatic sea-level rise (see also Fig. 4). Sea-level rise created the necessary accomodation space and meso- to eutrophoic conditions stimulated calcium carbonate production in the *green water* mode. Organic carbon produced in the process was returned to surface waters, while phosphorus was actively retained in the sediment under oxic conditions. Phytoplankton possibly played a pivotal role in transferring organic matter, and with it phosphorus, from the pelagic to benthic environment. Dinoflagellate cyst diversity along the NW margin of the Tethys (Rio Argos section, southern Spain; Leereveld, 1995) clearly mimics both sea-level rise and phosphorus increase (Fig. 4E). Their diversity increase, which reached a maximum in *Lyticoceras nodosoplicatum* Zone, indicates conditions were optimal to sustain a highly diverse community of phytoplankton. In our view this is further evidence for enhanced circulation and input of P to surface waters.

If both the $\delta^{13}C_{carb}$ and P accumulation rate record represent global trends, does this mean that carbonate accumulation rates increased as well during the Lower Hauterivian on a worldwide scale? Renard (1986) compiled a long term data set for Sr/Ca ratios based on DSDP records. An increase in Sr/Ca ratios in pelagic limestones can be observed during the Hauterivian to Early Barremian. Also Sr/Ca ratios from Valanginian–Hauterivian limestones cored during ODP leg 103 (Galicia Margin) show increasing ratios up to the Barremian (Clauser et al., 1988). High Sr/Ca ratios in pelagic limestones indicate a global increase in deposition of calcite with respect to aragonite in shallow marine settings. This trend in Sr/Ca agrees with a change in carbonate production from the coral–oolite mode to the crinoid–bryozoan mode. Ogg et al. (1990), in summarising the depositional history of the equatorial Pacific, suggested that the CCD sharply dropped from the Valanginian to Hauterivian, which could indicate increased supersaturation with respect to calcium carbonate. The Barremian shows a sharp decrease in Sr/Ca in the above mentioned DSDP and ODP records, which is in line with a re-establishment of oligotrophic mainly aragonitic carbonate producers (corals and rudists) along Tethyan margins.

5. Conclusions

The observed trends in the carbon isotope and phosphorus accumulation rate records have led us to distinguish three different stages of platform development and destruction during the Valanginian and Hauterivian (Fig. 4):

(1) *Perturbation* of the P- and C-cycles during the Early and early Late Valanginian was due to an increase in continental runoff and nutrient influx, which led to suffocation of sensitive carbonate producing biota and to a prolonged phase of reef demise along the northern margin of the Tethys (D1; Föllmi et al., 1994; Weissert et al., 1998). Weakening of carbonate factories was enhanced by sea-level fall and shedding of siliciclastics during the Mid-Valanginian followed by eustatic sea-level rise during the Late Valanginian to Early Hauterivian (Hardenbol et al., 1998). The initial perturbation may have been related to a first phase of volcanic activity starting at 138 Myr (Berriasian–Valanginian boundary) in the Parana Igneous Province (Stewart et al., 1996; Weissert et al., 1998). The perturbation phase is marked by platform drowning, a positive $\delta^{13}C_{carb}$ excursion and an increase in phosphorus accumulation rates.

(2) *Decoupling* of P and C_{org} burial is shown by increasing P accumulation rates and decreasing $\delta^{13}C_{carb}$ values during the Late Valanginian and Early Hauterivian. Decoupling occurred when carbonate factories recovered during the earliest Early Hauterivian and carbonate production shifted in a higher energy mode. Siliceous carbonates were produced in the *green water* mode (crinoids, bryozoans, echinoids, sponges). Sea-level rise played an important role in decoupling the P- and C-cycles by creating the necessary accommodation space for carbonates to accumulate and because opening gateways increased circulation and oxygenation along the northern margin of the Tethys. Remarkably high calcite sedimentation rates during the Early Hauterivian were possibly forced in order to decrease alkalinity that had risen as a result of a prolonged phase of reef demise during the late Early and early Late Valanginian and because of continuing elevated weathering/erosion rates. An extra aggravating factor was a step up in flood basalt production in the Parana Igneous Province (Fig. 4C). Drowning phase D2 (Lidernen Beds) at the end of this decoupling phase was likely directly controlled by sea-level variations imposed on an allready stretched system.

(3) *Stabilisation* during the Late Hauterivian and renewed coupling of the C- and P-cycles is correlated with decreasing carbonate carbon burial rates, lower sea level and probably lower continental weathering and erosion rates. Output of P decreased as output of C_{org} increased under increasingly dysaerobic conditions resulting from decreased ventilation of bottom waters (Ingall et al., 1993). Overturn of P-enriched deep waters in the uppermost Upper Hauterivian *Pseudothurmannia angulicostata* Zone (Faraoni level) may have caused the first of a series of Cretaceous Oceanic Anoxic Events. Thusfar Faraoni black

shales have only been described from hemipelagic sites along the NW margin of the Tethys and are contemporaneous with a third drowning phase on the Helvetic Shelf (D3, Altmann beds). A full return to oligotrophic conditions occurred in the Barremian, when more arid conditions (Ruffell and Batten, 1990) led to carbonate deposition in the *blue water* mode (corals and rudists) again.

The Early Hauterivian represents a peculiar interval during which filter feeding carbonate producers together with siliceous sponges along a huge portion of the NW margin of the Tethys quickly drew down large quantities of biolimiting nutrients (P, Fe, Mn, Ca, and Si) and stored these as mesotrophic carbonates. *Detoxification* of meso-eutrophic surface waters and the transfer of nutrients from planktic to benthic ecosystems may have spurred diversification of especially calcareous nannoplankton, which became very dominant carbonate producers from the Barremian onwards (Renard, 1986).

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