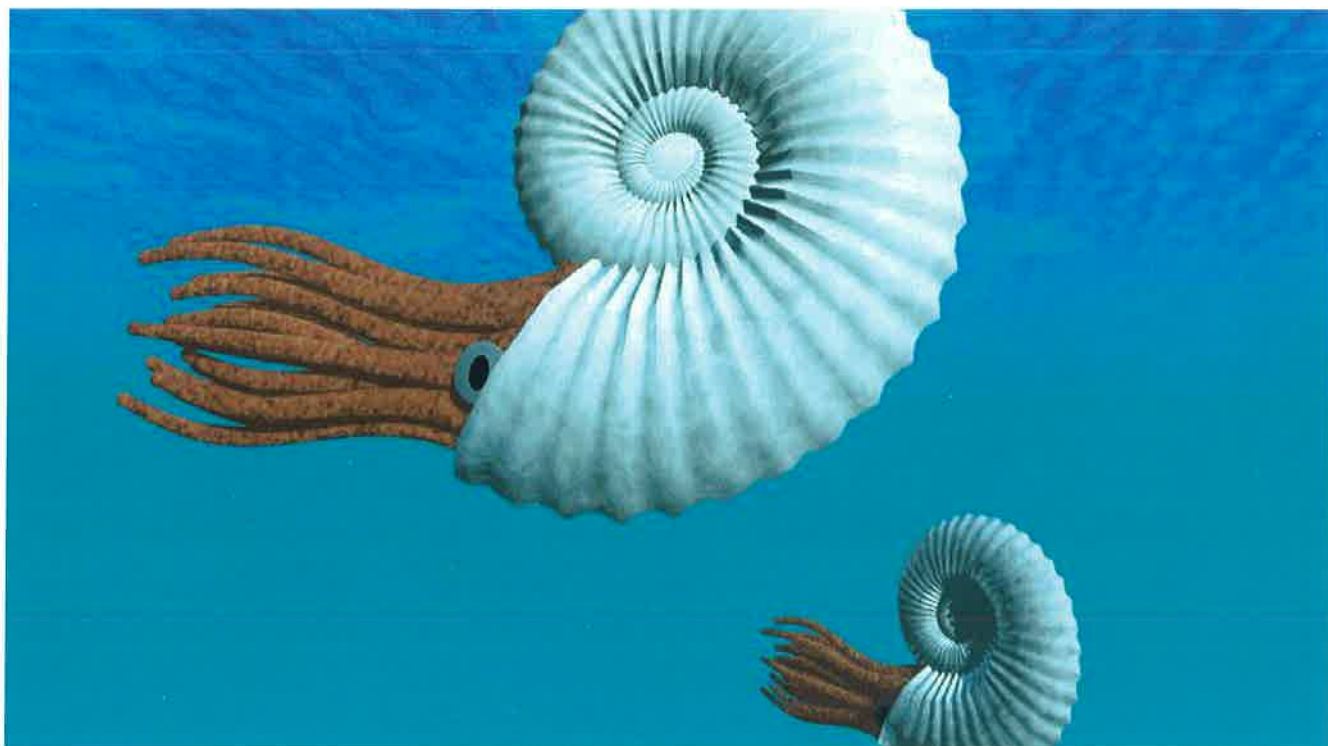


**Influence of paleo-environmental changes during the
Hauterivian (early Cretaceous) on carbonate deposition
along the northern margin of the Tethys:
Evidence from geochemical records
(C, O, and Sr-isotopes, P, Fe, Mn)**



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22 November 2001

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Neuchâtel, le 10 décembre 2001

Le doyen:

A handwritten signature in dark ink, consisting of a stylized 'F' followed by a long horizontal stroke and a large loop at the end.

F. Zwahlen

Abstract

Introduction: An important platform drowning event, recorded in Valanginian shelf carbonates from the northern margin of the Tethys (Helvetic Alps), has been related to a global acceleration of the carbon cycle resulting in a shift from carbonate carbon burial to organic carbon burial. This shift was brought about by the excessive release of CO₂ from flood basalt volcanism in the Parana Basin (Brazil), leading to enhanced greenhouse conditions, intensified weathering, erosion, run-off and the eutrophication of surface waters. During the early late Valanginian, the link between platform drowning and accelerated carbon cycling is expressed in the contemporaneous occurrence of condensed phosphatic horizons in the Helvetic Alps and a global positive $\delta^{13}\text{C}$ shift. During the Hauterivian however, platform destruction, condensation and phosphorite deposition are not mirrored by a positive carbon isotope excursion, but rather by minimum values on a long-term decline.

The principal aim of the here presented work has been to understand this decoupling between platform destruction and eutrophication on one side and the carbon cycle as expressed in $\delta^{13}\text{C}$ on the other side. The element P plays a key role in this research, because it is considered to be a good proxy for weathering and it controls production and thus burial of organic carbon. Carbon isotope records are also important, both as a stratigraphic tool and to get a better grip on carbon cycling during the Hauterivian. A multi-proxy approach (clay minerals, atomic absorption, Sr-, C-, and O-isotopes, organic matter) was used to solve stratigraphic and paleo-environmental problems.

Isotope stratigraphy: High resolution carbon isotope records calibrated with ammonite-biostratigraphic and magnetostratigraphic zonations have been established for the Hauterivian in the Vocontian and Umbria-Marche Basins, respectively. The C-isotope signal for the Hauterivian shows significant variation that can be used to correlate shallow marine sections lacking age-diagnostic faunal elements. C-isotope stratigraphy was successfully applied to correlate the early late Hauterivian *Sayni* zone with magnetozones CM7 and CM6.

Unfortunately, phreatic meteoric diagenesis led to extensive alteration of shallow marine carbonates in the Swiss Jura Mountains rendering C-isotope stratigraphy in these sections extremely difficult. The very negative carbon isotope values can however be used to pin-down an important emersive event during the mid-Hauterivian, which is in accordance with some of the previous proposed models for the sedimentary evolution of the Swiss Jura Platform.

Another promising tool for correlation between basin and platform sections is Sr-isotope stratigraphy. A high-resolution $^{87}\text{Sr}/^{86}\text{Sr}$ record was calibrated in reference sections in the Vocontian Basin with ammonite zonations. The bulk rock signal differs from the belemnite signal and appears to be partly disturbed by diagenesis. *Non-altered* (based on C-, O-isotopes and clay minerals) micrites also show large variations in the Sr-isotope signal, which was attributed to sea level variations and associated changes in weathering fluxes. The sea level variations recognized in the Sr-isotope record correlate well with eustatic sea level charts from different authors. The belemnite and bulk rock records differ because the belemnites recorded a more oceanic, open marine signal, while

the bulk rock samples registered a strong continental signal. The Vocontian Basin may have been a peculiar setting that was not representative for the world oceans of the Cretaceous. A negative repercussion of this work has been that the use of Sr-isotope stratigraphy for bulk carbonate samples for the Hauterivian is limited.

Paleo-environmental change: The negative carbon isotope trend recorded during the early Hauterivian can be explained by the uptake of carbonate deposition under mesotrophic conditions. Increased continental weathering and input of terrestrial organic matter may also be partly responsible for the decreasing carbon isotopic ratios. The increasing carbon isotope ratios during the late Hauterivian are ascribed to a return to increased organic carbon burial under slightly more anoxic conditions. Sea level lowering resulted in the closure of connections with the Boreal realm and cessation of cold water inflow, leading to a decrease in circulation.

That cold water inflow from northern latitudes was important during late Valanginian and early Hauterivian is clearly indicated by oxygen isotope ratios in pristine belemnite guards. These show a temperature decrease of deeper water from the early late Valanginian to early Hauterivian (15 – 11°C). This influx of cold water was related to a second order sea level rise. Hypothermia was an important additional factor for the destruction of oligotrophic carbonate systems along the northern margin of the Tethys.

Other factors that had a negative influence on carbonate producing biota include the increased detrital load of river water entering the Tethys during the late Valanginian and early Hauterivian. Phosphorus burial rates increased dramatically from the late Valanginian to mid-Hauterivian as was shown from the study of 8 sections along a platform to basin transect combined with data for the Valanginian from previous work. P was retained in the sediment under oxic conditions possibly with the help of Fe- and MnOOH on carbonate particles. Carbonate sedimentation rates were relatively fast during the Hauterivian either because of high sea level and/or because of oversaturation of Ca after a prolonged platform drowning phase during the late Valanginian. High Sr/Ca ratios during the early Hauterivian may point to the worldwide diminished deposition of aragonite in reefs and increased deposition of calcium carbonate in the green water mode, (crinoids, bryozoans, echinoderms and sponges).

Phosphogenesis: Drowning phase D2 (Lidernen Horizon; upper part *Nodosoplicatum* – lower part *Ligatus* zones) resulted from an interplay of enhanced weathering and rapid sea level variations. Regression during the end of the *Nodosoplicatum* zone exposed much of the shallow platform, like in the Jura Mountains. Oxidation of pyrite and organic matter during emersion and subsequent flooding during the *Sayni* zone by reducing (dysoxic) watermasses may have released large quantities of nutrients. More important though, was the re-invigoration of coastal upwelling after connections had opened again with the Boreal realm during the *Sayni* zone. Drowning phase D2 is likely to have been of shorter duration as D1 (Gemsättli Beds; *Campylotoxus* zone – lower part *Radiatus* zone), because the early late Hauterivian transgression was not as extensive and connections with the Boreal were rapidly closed again during the late Hauterivian. Phosphorite deposition occurred after reworking of a hemipelagic precursor that was rich in P and Fe. Extensive bioturbation of this bed resulted in glauconitic beds with reworked phosphatic nodules and abundant belemnites.

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It's time to fly away.....

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Maartje, lots of things have happened. Good things, bad things. And although you are not here anymore to be part of these things, you were always in the back of my mind, so maybe you know what I'm talking about.....

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Chapter 1

Introduction

1.1 Introduction

At the Geological Institute of Neuchâtel, Switzerland a long-term research program has been set up to trace continental weathering and establish feedback mechanisms between continental weathering, productivity and (paleo-) climate change. A major objective is to estimate the impact of glaciation on global weathering rates. For comparison, the study of time windows during which weathering was mainly controlled by enhanced greenhouse conditions form an important pillar of this research project.

The element phosphorus plays a key role. In many cases, phosphates are the limiting factor in the capacity of oceanic planktonic communities to transfer atmospheric carbon dioxide into organic substances and phosphates are primarily delivered to the oceans by river run-off. The biogeochemical cycle of P, but also those of Fe, N and Si, are intimately linked with the global carbon cycle, because the available amount of the biolimiting nutrients controls productivity and thus the drawdown of CO₂ from the atmosphere. On the other hand carbon dioxide is an important agent for the weathering of rocks (simplified: $\text{CaSiO}_3 + 2\text{CO}_2 + 3\text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- + \text{Ca}^{2+} + \text{H}_4\text{SiO}_4^{4-}$). An increase in the atmospheric concentration of this greenhouse gas might be regulated through a negative feedback in which increased primary productivity leads to extraction of CO₂ from the atmosphere and its storage as organic carbon in the sedimentary reservoir.

The relevance of this type of study lies in the fact that we are facing an enhanced greenhouse effect possibly of anthropogenic origin. Fossil fuel burning during the past 150 years has considerably increased the partial pressure of CO₂ in the atmosphere from 280 ppmv in pre-industrial times to 360 ppmv present-day values. How this will affect and change global systems is very difficult to assess, because of the complex interplay between the atmosphere, biosphere and geosphere.

Geologists have the means to predict how elevated concentrations of greenhouse gases will impact and alter the face of the earth by studying examples from the past. The Cretaceous period may serve as an example to study past greenhouse climate conditions. We know that the Cretaceous as a whole was a warm period (Hallam, 1984; Barron et al., 1984; Francis and Frakes, 1993), because there is hardly any evidence for glaciation at the poles. Antarctica was not always the ice desert it is today; fossils of trees and crocodiles indicate this was a warm and humid region during much of the Cretaceous. Vegetation reconstructions for the early Cretaceous show that subtropical plants thrived 20° further North as they do today (Vakhrameev, 1978). Warmth may also be inferred from long term sea level rise from the beginning of the Cretaceous to the mid-Cretaceous times (Hardenbol et al., 1998), which probably meant that not much water was locked up in continental ice sheets and glaciers. From different methods and proxies (carbon isotopes, plant stomata, modelling; Barron et al., 1989; Veizer et al., 1999; Retallack, 2001) it was inferred that CO₂ pressure in the atmosphere was much higher (4-6 times) during the Cretaceous than is today (Berner et al., 1983). This increase is thought to have been caused by the excessive release of CO₂ due to volcanic activity. Because of high CO₂ concentrations, weathering, erosion and run-off may have been much more intense.

Phosphorus accumulation rates in marine sediments show several acmes during the Cretaceous, most notably during the Valanginian-Hauterivian, the Aptian, Albian, Cenomanian and Campanian (Föllmi, 1995).

The specific example discussed in this thesis is the relation between carbonate platform crises and continental weathering during the Hauterivian, a period presumably characterized by an enhanced greenhouse effect. The here presented work is centered around limestone sequences exposed in the Helvetic Alps (Switzerland). These present an archive that withholds information on the link between greenhouse climate, trophism in surface ocean water and ecosystem disturbance along the former northern margin of the Tethys ocean. The limestones document how nutrient levels changed and how carbonate producing biota adapted and collapsed in response. From the Valanginian to Barremian carbonate production shifted from a *blue water* mode (oligotrophic, corals and ooids dominated) into a *green water* mode (mesotrophic, filter feeders such as sponges, crinoids and bryozoans dominated) of carbonate production. Intercalated between these limestones are thin glauconitic and phosphoritic horizons. These horizons have been the focus of geologic study for more than a century (Kaufmann, 1867, 1886; Goldschmid, 1927; Fichter, 1934; Schaub, 1936; Schaub, 1948; Schindler, 1959; Funk, 1969; Funk, 1971; Haldimann, 1977; Föllmi, 1986; Föllmi et al., 1994; Wyssling, 1986; Kuhn, 1997; Weissert et al., 1998) and have drawn so much attention because of their often rich macro-fossil assemblages (especially ammonites) which make them excellent marker beds for biostratigraphy and interregional correlation. Because of their highly condensed nature, these horizons mark important events in the depositional history of the Helvetic Alps.

In recent years the paleo-environmental significance of the phosphoritic beds has gained more interest (Föllmi et al., 1994; Kuhn, 1997; Weissert et al., 1998). One firmly established idea is that these horizons mark platform drowning events, during which carbonate production ceased and large parts of the Helvetic Shelf were subject to erosion and condensation. An important paper by Hallock and Schlager (1986) on the role of nutrient excess on the demise of coral reefs led Föllmi et al. (1994) to propose eutrophication as a mechanism to explain the phosphoritic horizons in the Swiss Alps. The causal link between platform drowning and increased nutrient availability is expressed in the contemporaneous occurrence of global positive $\delta^{13}\text{C}$ shifts and phosphate deposition, for example during the Valanginian and Aptian (Föllmi et al., 1994; Weissert et al., 1998). Carbonate platforms along the northern margin of the Tethys were suffocated by high nutrient input through river water flowing in from adjacent landmasses and decreased transparency as a result of high organic (algae) carbon production (leading to high $^{13}\text{C}/^{12}\text{C}$ ratios in biogenic carbonates). Simultaneously occurring global carbon isotope shifts and platform drowning events point to a worldwide mechanism that was behind the deposition of phosphoritic beds in the Alps. In the model of Föllmi et al. (1994) and Weissert et al. (1998) this global mechanism is volcanic CO_2 -degassing. The outflow of large volumes of basalts in the Parana Basin in Brazil during the Valanginian and Hauterivian and the emplacement of the Ontong-Java Plateau during the Aptian are held responsible.

The principal aim of this PhD project has been to understand the mechanisms that led to deposition of phosphoritic beds in the Alps and their relation to continental weathering and erosion during a period of enhanced greenhouse effect. This thesis builds on earlier work by Kuhn (1997) as well as Funk (1971), Wyssling (1986), Föllmi et al. (1994) and Weissert et al. (1998) among others.

1.2 Aims, questions and hypotheses

The red line of this thesis is the so called *Lidernen Horizon*, a Hauterivian (early Cretaceous) phosphoritic horizon that is exposed in the northern Helvetic Alps and subdivides the Kieselkalk Fm in a lower and upper part. This horizon has received little attention so far and its exact stratigraphic position and paleo-environmental significance have remained relatively obscure. It was tried to apply a multi-proxy approach using both stratigraphic tools and proxies for paleo-environmental change. Literature appeared to be a valuable source of additional information.

In **Chapter 2** the model of Föllmi et al. (1994) and Weissert et al. (1998) is outlined using literature. The purpose of this chapter is also to provide the reader with a background on paleo-environmental changes that occurred during the Valanginian and Hauterivian. Specific topics that will be discussed are paleogeography, paleoceanography and paleoclimate, volcanism and tectonism, indications for increased weathering and the relation between the carbon isotope record and phosphorite deposition.

Chapter 3 provides a general background on the chrono- and lithostratigraphy of the studied sections. It summarizes the most important findings of previous work on sections from the Jura Mountains and Helvetic Alps, as well as from the Vocontian Basin in France and Umbria-Marche Basin in Italy.

In **Chapters 4, 5 and 6** reference carbon isotope records for Hauterivian sections from platform, shelf and basin settings are presented that can be used for correlating these sections. Correlation is crucial in understanding the extent of platform drowning events and thus for distinguishing local versus regional and global causes. The phosphoritic horizons are widespread in the Helvetic Alps, but are lacking in the Swiss Jura, which represents the shallow marine platform setting and also disappear towards the basin. The absence of significant biomarkers, such as ammonites, has hampered dating of limestones in the Swiss Jura. A powerful tool that has been widely used in recent years for correlation (such as with the help of the Valanginian global positive carbon isotope shift) of sections is carbon isotope stratigraphy (Ferreri et al., 1997; Grötsch et al., 1998; Jenkyns et al., 1994; Hennig et al., 1999; Lini et al., 1992)).

For the Hauterivian no detailed carbon isotope record is available, so in **Chapter 4** a reference record is defined and discussed. To use this record in the most precise way, it is necessary to calibrate it with some other stratigraphic tool. We have chosen ammonite biostratigraphy, because it is more commonly used than for example magnetostratigraphy. Sections from the Vocontian Basin present the highest resolution

ammonite biostratigraphic zonation and were therefore chosen to serve for calibration of our isotope records. Questions to be answered: *What is the change in C-isotope signature during the Hauterivian and can it be used for correlating sections?*

Besides establishing a calibrated reference carbon isotope curve for the Hauterivian, **Chapter 4** also discusses the paleo-environmental meaning of the carbon and oxygen stable isotope records. *Does the carbon isotope record for the Hauterivian mirror platform drowning events in the Alps, just as for the Valanginian? If not, what were the dominant factors governing carbon cycling during the Hauterivian?*

In accordance with the model, temperature changes should occur parallel with flood basalt activity and CO₂ increase. Because bulk rock oxygen isotope records are often disturbed by diagenesis, belemnites have been used to reconstruct paleo-temperature trends for the Hauterivian. Important questions are: *Is there evidence for a temperature variations during the Valanginian-Hauterivian related to volcanic exhalation of CO₂?*

Chapter 5 investigates the correlation of carbon isotope records calibrated with Vocontian Basin ammonite biostratigraphy and those calibrated with magnetostratigraphy from sections in Italy. Sections in the Umbria-Marche basin represent a more open ocean setting and studying their isotopic signature may independently verify the results from France. Furthermore correlation between these two conventional stratigraphic tools (ammonites and magneto zones) has been hampered because of scarce ammonites in Italian sections. In addition Vocontian Basin sections in southern France have not provided a reliable paleo-magnetic signal. Hennig et al. (1999) have shown that correlation with carbon isotope stratigraphy of Valanginian Italian and French sections improved resolution considerably. So: *Can we apply C-isotope stratigraphy from Italy in Hauterivian sections and improve resolution for the magnetostratigraphic correlation of ammonite zones?*

Chapter 6 aims at using the high resolution carbon isotope records from France and Italy for correlating and dating sections in the Swiss Jura and Subalpine Chains, regions that contain facies without sufficient biomarkers such as ammonites or nannofossils. For this purpose several sections have been investigated and their carbon and oxygen isotope records discussed. The Swiss Jura represents the historical type region for the Hauterivian and Valanginian, however it has been the subject of a long-lived debate between different groups of authors who have very contrasting views on the age of limestone successions in the region around Neuchâtel. Arnaud et al. (1999) consider a large hiatus between the Pierre Jaune de Neuchâtel Fm (early Hauterivian) and Urgonien Jaune and Urgonien Blanc (late Barremian), while Clavel et al. (1995) date these same limestones as early Hauterivian to early Barremian without any interruption. *Can C-isotope stratigraphy help to clarify some of the problems concerning the Pierre Jaune de Neuchâtel and Urgonian Limestones? Does this provide information on the extent of platform drowning along the northern margin of the Tethys?*

In **Chapter 7** the results of a Sr-isotope study are presented and discussed. The Sr-isotope record is another very promising isotope record for deducing correlation and relative dating (McArthur, 1994). The Hauterivian shows a moderate linear rise in ⁸⁷Sr/⁸⁶Sr ratios (Jones et al., 1994) that can be used to correlate sections (Howarth &

McArthur, 1997). However, the record for the Hauterivian is based on few samples (8), so one objective is to produce a high-resolution record based on a large number of samples. Before using the Sr-isotope record on a wider scale sections from the Vocontian Basin will serve again as a reference, just like the carbon and oxygen isotope records. Both bulk rock and belemnite samples have been investigated to get independent records. Although bulk rock samples could produce contaminated Sr-isotope values as a result of leaching of clay minerals and carbonate diagenesis, coarse grained limestones have been used to obtain Sr-isotope records for the early Cretaceous (Jenkyns et al., 1995). To test the use of bulk rock material is imperative, because the shallow platform settings in the Jura do not contain belemnites and other macrofossil debris is rare in the critical interval (Pierre Jaune – Urgonien Blanc). To distinguish between contaminated and uncontaminated Sr-isotope values, the clay mineralogy of the bulk rock samples will be determined with the help of XRD analysis. This is again a double sided cutting sword, because the clay minerals also give insight in weathering, erosion and climatic conditions during the Hauterivian. Important questions are: *How does a high-resolution Sr-isotope curve for the Hauterivian look like and can it be used for correlation? Can we use bulk rock micrites for Sr-isotope analyses?*

To test the importance of continental weathering/erosion and run-off on the observed facies changes in the Alps and elsewhere samples have been analysed for their total phosphate contents. Föllmi (1995) compiled phosphorus accumulation rates from literature. His data show a global increase during the Hauterivian, but resolution is again low. Can we reproduce the same trends by measuring a large amount of samples and what is the relation with the phosphoritic horizons in the Alps. Questions addressed in **Chapter 8** are: *How did weathering change from the Valanginian into the Hauterivian and what were the effects on carbonate sedimentation along the northern margin of the Tethys and worldwide?*

Chapter 9 finally discusses results from an integrated sedimentological, geochemical and paleontological investigation of the Lidernen Horizon. Studying in detail its facies and fossil content should give more insight in prevailing paleo-environmental conditions on the Helvetic Shelf and its chronostratigraphic position. *What was the duration of the condensation phase? How does the sedimentology compare with other better known phosphoritic horizons, like e.g. the Gemsmättli Horizon (Kuhn, 1997)? What processes led to its deposition? And are these mechanisms local, regional or global?*

In **Chapter 10** a synthesis is presented that briefly summarizes the most important findings and tries to integrate the different conclusions.

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Chapter 2

Paleo-environmental change during the early Cretaceous

2.1 Introduction

Drowning was defined by Schlager (1981) as an event during which relative sea level rise outpaces carbonate accumulation so that carbonate platforms become submerged below the euphotic zone. Platform drowning events are paradoxical, because the growth potential of healthy carbonate platforms is much greater than the fastest Holocene sea level rise. Other factors that have been invoked to explain the cessation of carbonate production include: 1) spasmodic pulses in subsidence 2) very rapid pulses of eustatic sea level rise 3) desiccation of an ocean basin 4) hypothermia (platform moves into colder water as a result of plate tectonics 5) (volcanic) upwelling of anoxic waters (Vogt, 1989).

None of the above is fully satisfying in order to explain platform drowning along the northern margin of the Tethys during the late Valanginian and Hauterivian. Subsidence reconstructions by Funk (1985) for the Helvetic shelf show maximum average rates of 20m/Ma, which is far less than the 1000m/Ma taken as a conservative estimate for Holocene platform growth rate by Schlager (1981). Eventhough Mesozoic platforms may have grown slower than Holocene platforms, their growth rates still surpass the most rapid subsidence rates for the Helvetic Shelf. Very rapid pulses of sea level rise are hard to imagine in the absence of Quarternary-type ice caps. Desiccation only applies to isolated ocean basins and not to the Tethyan sea way. Hypothermia by plate tectonics is a long term process, while the phosphatic horizons of the Helvetic Alps are separated by only several millions of years at the most. Upwelling of anoxic waters could be an explanation, but the Valanginian and early Hauterivian do not show pronounced black shales that testify to stratified waters. Volcanic activity was low along the northern Tethyan passive margin so this is not an option either.

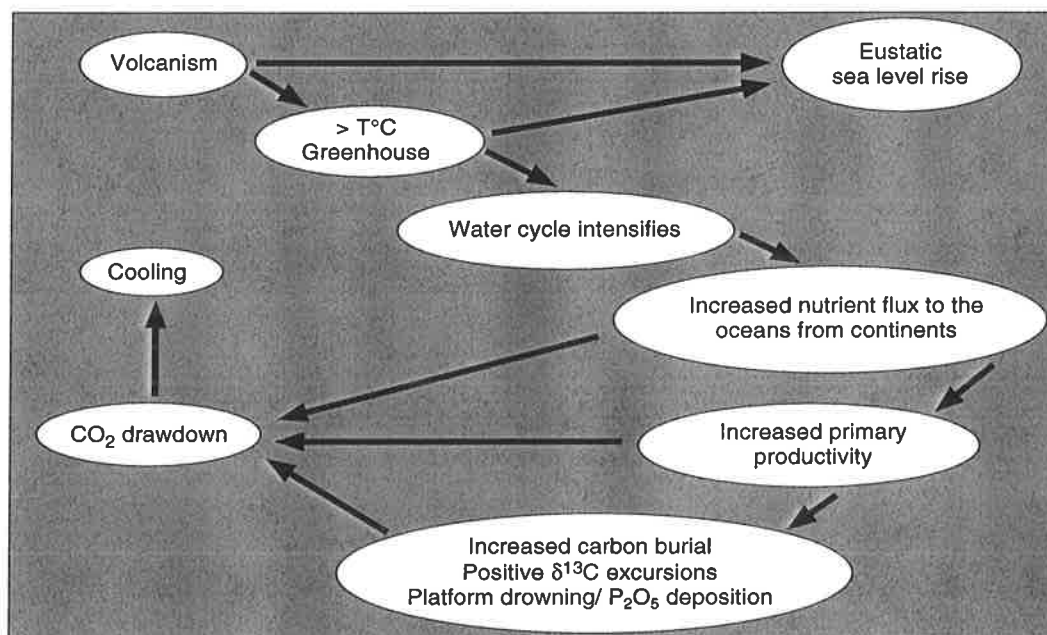


Figure 2. 1 – Feedback mechanisms between emplacement of flood basalts and platform drowning and carbon isotope excursions (modified after Follmi et al., 1994).

Föllmi et al. (1994) and Weissert et al. (1998) suggested that eutrophication was an effective mechanism to drown carbonate platforms during the early Cretaceous. The rationale behind this hypothesis is that important drowning events during the Valanginian and Aptian are contemporaneous with global positive carbon isotope excursions, which these authors interpret as a shift from carbonate carbon to organic carbon production. High organic carbon production resulted from increased nutrient influx from the continents as a response to high CO₂ concentrations in the atmosphere leading to accelerated weathering and erosion. *p*CO₂ increased after the emplacement of large igneous provinces such as the Parana Continental Flood Basalts during the Valanginian and Ontong-Java Plateau during the Aptian.

In the next paragraphs an overview of literature data is presented that further outlines this model (Fig. 2.1). The purpose of this summary is to provide a background on paleo-environmental changes during the Valanginian and Hauterivian.

2.2 Flood Basalt volcanism and tectonism

Flood basalt volcanism in the Parana Basin (Brazil, Fig. 2.2) and on the other side of the South Atlantic in the Etendeka traps (Namibia) is considered to be the driving force behind environmental changes that occurred during the Valanginian-Hauterivian interval (Weissert et al., 1998). Following the Gradstein et al. (1995) timescale and Ar-Ar dating of the basalts by Stewart et al. (1996) and Renne et al. (1992), the main pulse of flood basalt outflow occurred around the Valanginian-Hauterivian boundary (130-132 Ma). The total volume of erupted basalts is estimated at $2.35 \cdot 10^6$ Km³ and covers an area of $1.5 \cdot 10^6$ Km². A review of the relation between flood basalt volcanism and mass-extinction was presented by Wignall (2001). The emplacement of the Parana continental flood basalts (PCFB) did not lead to mass-extinction, but might have caused global warming through emission of CO₂.

An empirically derived formula by Leavitt (1982), can be used to calculate the total amount of CO₂ released from the outflowing basalts. Thus:

$$m\text{CO}_2 = s \cdot f_{dg} \cdot V \cdot d / m.w.\text{CO}_2$$

Where *s* is the weight fraction of CO₂ in the magma (0.002), *f_{dg}* is the fraction of gas released (0.6), *V* is the magma volume, *d* the solid density ($2.9 \cdot 10^{15}$ g/km³) and *m.w.CO₂* is the molecular weight of CO₂ (44 g). Using a volume of $2.35 \cdot 10^6$ km³ for the Parana CFB, the total amount of CO₂ emitted would be $1.85 \cdot 10^{14}$ kg. The numbers used to calculate the amount of CO₂ released are however also dependent on the type of volcanism and composition of the lava. Furthermore, the sedimentary cover through which the lava ascends is a determining factor. One could imagine that the intrusion of igneous rocks into carboniferous coals could potentially release large quantities of CO₂.

Spread out over 0.6 +/- 1 Ma, which is the total duration of the event (Renne et al., 1996), would give an annual release of CO₂ of $3.1 \cdot 10^8$ kg/yr, which is small compared to presentday anthropogenic release of 10^{13} kg/yr CO₂ and very small compared to the total amount of C in the oceans and atmosphere ($5 \cdot 10^{19}$ g C).

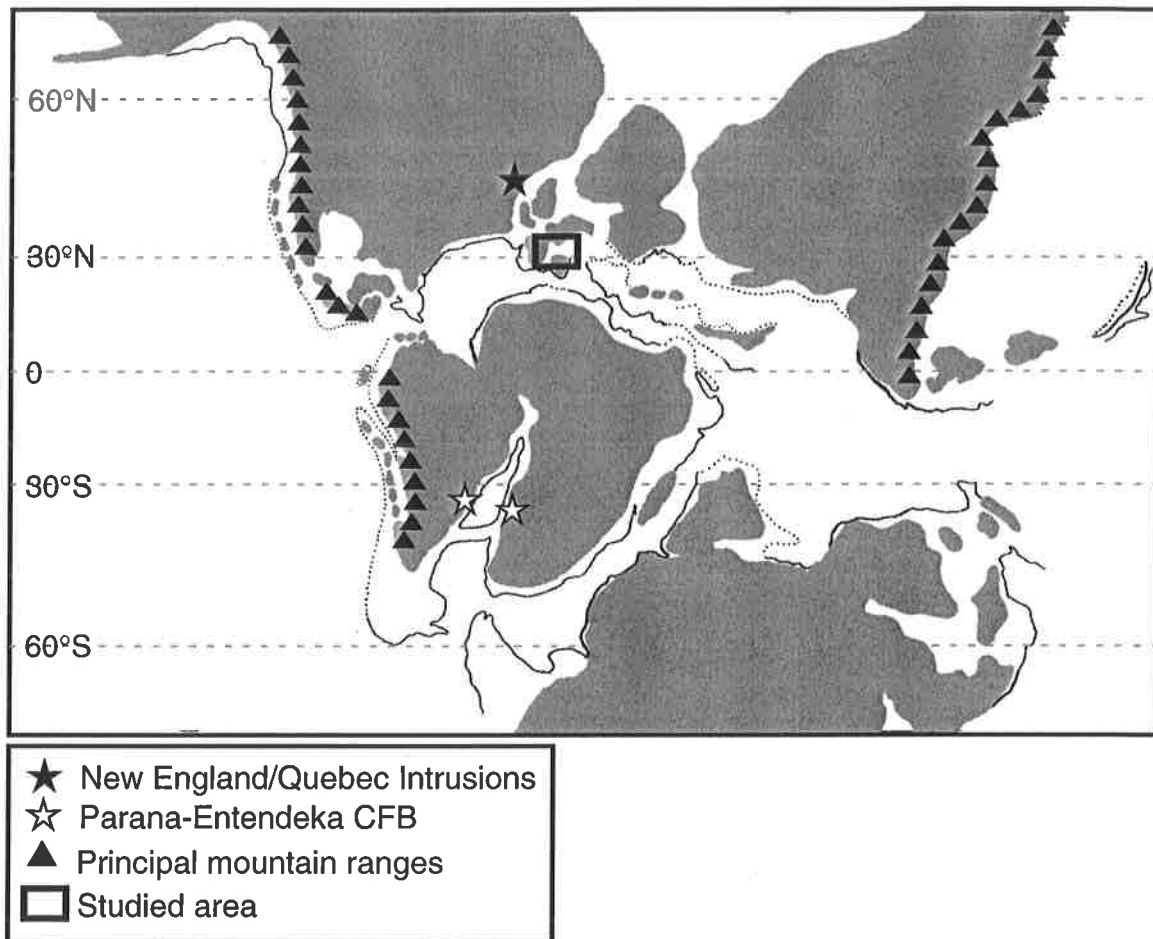


Figure 2. 2 – Paleogeography for the Hauterivian after McSotay (1980).

The calculated CO_2 -flux seems to exclude any direct effects from the PCFB. However, these flood basalts might have been much more widespread as erosion would have diminished their total volume. Tholeiitic dikes in western Angola that are of the same age as the Parana-Etendeka Traps (Marzoli et al., 1999) indicate that igneous activity extended almost 400 km further northeast.

The PCFB possibly mark a phase of increased spreading and maybe of global tectonic activity. Increased spreading rates related to North Atlantic break-up produced four groups of Mesozoic intrusions in New England and Quebec (Canada) of which the fourth was dated as early Cretaceous (starting at 130 Ma, McHone et al., (1984). Other indications for increased rifting stem from the American North Atlantic margin where widespread extrusive and intrusive igneous rocks occur (Hubbard et al., 1988; Jansa et al., 1988). These volcanics range in age from 140-85 Ma, with main pulses in the late Jurassic and earliest Cretaceous (Masson et al., 1986).

Increased spreading and the breaking up of Pangea probably also meant that no major mountain ranges were in the process of formation. Mountain ranges are important for two reasons: 1) Mountain building and steepened relief lead to increased weathering and erosion. 2) Mountain ranges may change atmospheric circulation patterns and can act as traps for moisture. Mountain ranges presumably existed along Cordilleran and East

Asian subduction zones (Ziegler et al., 1988; Figure 2.2). Kuhn (1997) hypothesized that because of a general absence of mountain ranges in continental interiors during the early Cretaceous warm and humid air masses were transported much further land inwards and precipitation might have been more equally distributed across continents, enhancing thereby overall detrital fluxes.

During Valanginian-Hauterivian times rifting was probably more important than uplift (Thiry and Jacquin, 1993). Re-activation of faults and rifting led to the deposition of up to sometimes 6000m thick lacustrine sandstone and shale sequences of Neocomian age along the southwestern margin of the Atlantic (Brazil; Asmus and Campos, 1983). This phase was followed by quiescence and evaporite deposition. In the Iberian Ranges (Southern Spain) re-activation of Hercynian faults led to predominantly terrigenous deposition during the Valanginian-Hauterivian interval (Vilas et al., 1983). Based on clay mineral assemblages from NW Europe Sladen (1983) concluded that uplift during the Berriasian-Valanginian led to extensive leaching and formation of kaolinite. From the Hauterivian to Aptian, due to progressive denudation, illite became more abundant in clay mineral assemblages. After studying thick siliciclastic Wealden type deltaic deposits from the northeastern Atlantic margin off the coast of Morocco, Von Rad et al. (1986) concluded that the Neocomian and especially the Hauterivian corresponded to a major phase of rifting.

A major pulse of tectonic activity occurred around the Hauterivian-Barremian boundary (127 Ma). This phase was accompanied by renewed Parana-Etendeka flood basalt activity on the Rio Grande Rise around 127 Ma (Stewart et al., 1996). Further away, pre-Barremian terranes collided from 125-105 Ma in the Russian northwestern Pacific area (Filatova and Vishnevskaya, 1997). Tectonic uplift occurred in Tunisia along the southern margin of the Tethys, controlling siliciclastic sedimentation during the Hauterivian and Barremian (Burollet et al., 1983). Cheilletz et al., (1999) found radiometric evidence for an Eo-Alpine event around 128 Ma in the internal zones of the Maghrebides (Algeria) related to early thrusting of the Alboran Plate. These authors stress that this event was not unique and that similar ages were found for distensional events in the Pyrenean belt, the North Atlantic, the external Alps and the Sardinian and Calabrian basements.

The effects of spreading during the late Valanginian and early Hauterivian and of uplift during the late Hauterivian and early Barremian are reflected in the sea level record. Spreading caused sea level to rise on a second order scale during the late Valanginian and early Hauterivian (Hardenbol et al., 1998), while uplift during the late Hauterivian may be deduced from general regressive trends that persisted during the early Barremian. This is further discussed in the next paragraph.

2.3 Sea level change and paleoceanography

A late Valanginian transgression is evident over much of Europe (Rawson and Riley 1982). By comparing sea level records for several north European basins, Ruffell (1991) found that certain early Cretaceous sea level events were of eustatic nature because they occur in basins that have very different tectonic histories. In the early

Hauterivian Ruffell delineates two transgressive-regressive cycles. An early Hauterivian transgression is followed by a lowstand and unconformity surface at the early-late Hauterivian boundary (Rawson and Riley, 1982; Ruffell, 1991). In some basins renewed transgression occurs in the early late Hauterivian, but overall the late Hauterivian appears to be mildly regressive (Tyson and Funnell, 1987). The importance of the Polish Furrow as a connection between the Boreal and Tethys decreased during the late Hauterivian, which is evidenced by brackish water deposits in this area. Trends (Fig. 2.3) similar to the western european sea level records are described from the Russian Platform (Sahagian et al., 1996; Pinous et al., 1999) and from Israel (Flexer et al., 1986).

Sea level changes were not incorporated in the model of Föllmi et al. (1994) and Weissert et al. (1998). As discussed above sea level rise is probably an ineffective mechanism to drown carbonate platforms by simply submerging the platform below the euphotic zone, however, it certainly did play a role in the late Valanginian and Hauterivian drownings by bringing about a number of changes: 1) Sea level rise led to the opening of sea straits and changes in circulation. The presence of Boreal ammonites and nannofossils in Tethyan assemblages testify of exchange between high and low latitude watermasses. *Overwelling* of cold waters in the Tethys may have led to hypothermia of sensitive carbonate producers and to upwelling leading to increased organic carbon productivity; 2) Transgression may have leached nutrients from previously deposited lowstand deposits inducing eutrophication in coastal and shelf regions; 3) Flooding of continental margins and establishment of shallow epeiric seas may have facilitated evaporation and therefore also increased precipitation. This further helped to speed up the hydrological cycle (see figure 2.1).

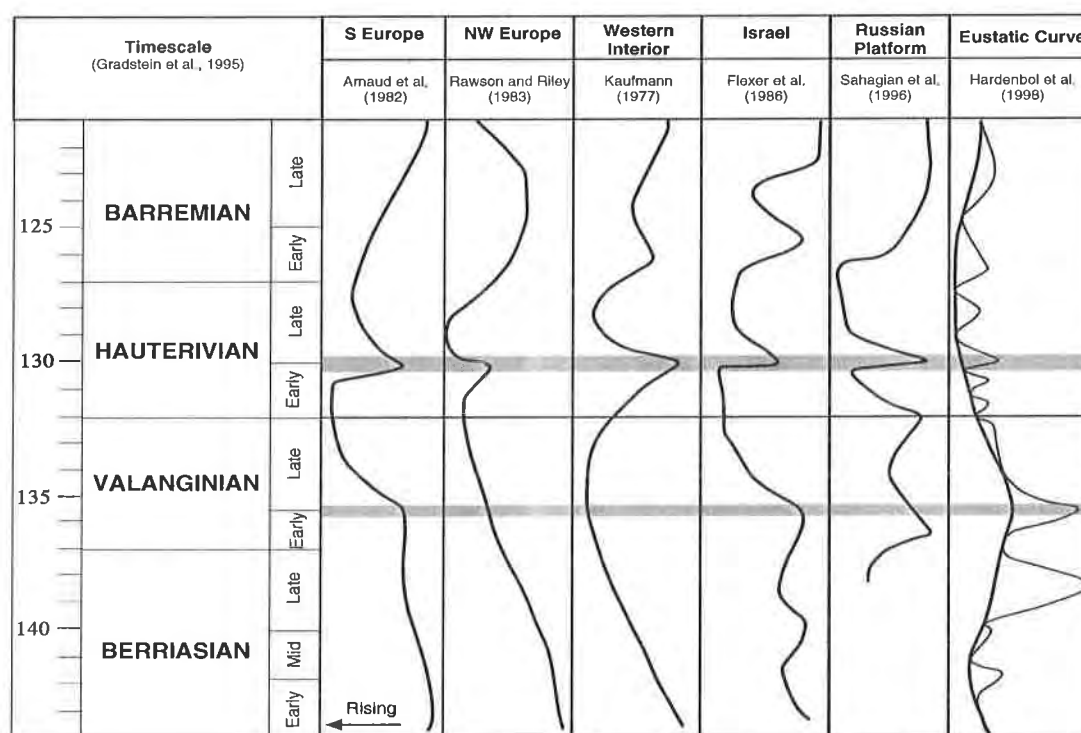


Figure 2. 3 – Sea level records from various basins. The grey lines indicate major sea level lowstands. Note that the mid-Hauterivian regression is the most persistent trend in all the different basins.

Sea level rise led to important changes in ocean circulation during the late Valanginian to early Hauterivian. Reconstructing paleoceanography (Fig. 2.4) for the (early) Cretaceous remains a matter of debate, however using both modelling and geochemical proxies different

authors have obtained similar results. Based on the presence of distinct Arctic belemnites mixed with Tethyan ammonites in California, a cold (deep?) water current is suspected to have flowed southwards along the eastern continental margin of North America (Doyle, 1987; Frakes, 1979). Opening of connections between the Tethys from the Boreal basin over the Polish Furrow and Moscow Platform may have led to increased circulation and influx of cold water in the Tethys. The Pacific was probably characterized by two gigantic gyres (Barron et al. 1984; Barron and Peterson, 1989). East-West trending currents flowing through the Tethys from the Pacific into the North Atlantic were most likely driven by halothermal circulation as opposed to thermohaline circulation existing today. Whether this induced more sluggish circulation and stagnant conditions remains to be seen. In a Tethyan ocean where currents were mainly East-West, North-South currents such as proposed for the Boreal inflow over the Polish Furrow may have had a great impact.

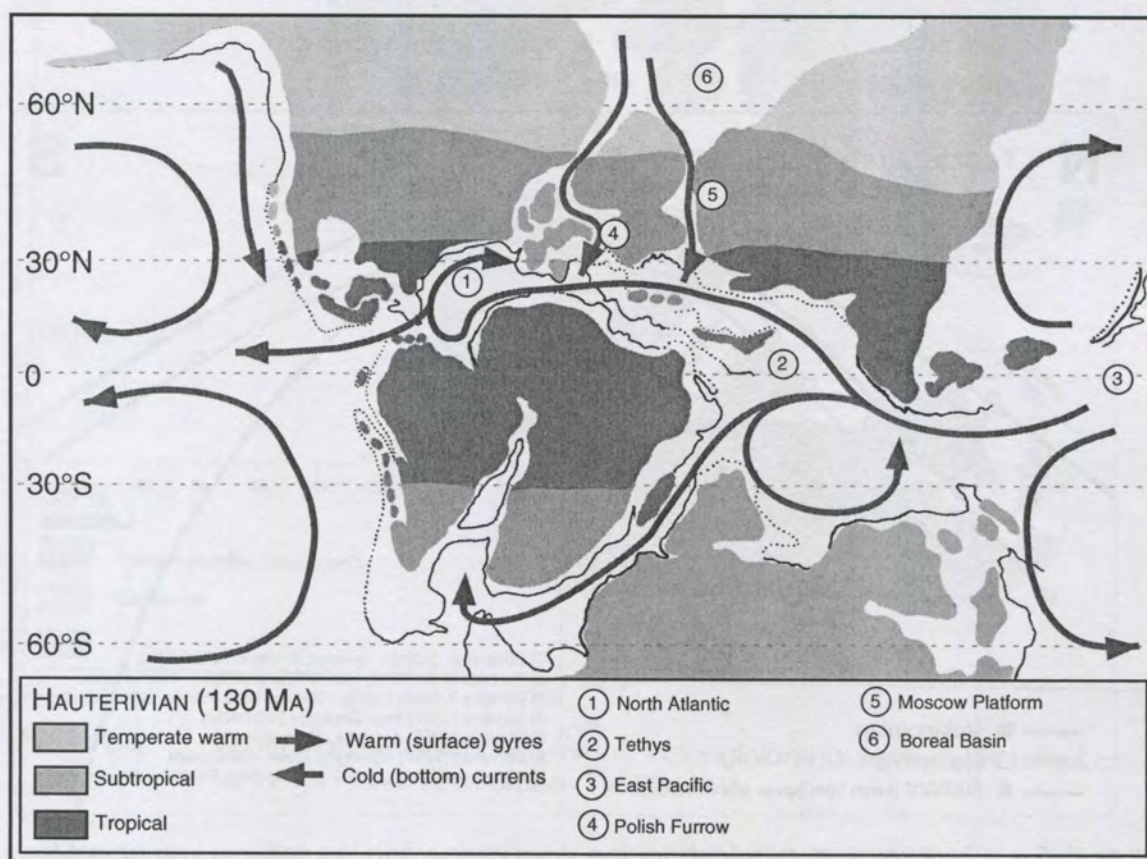


Figure 2. 4 - Climatic zonation after Vakhrameev (1978; 1991). Ocean currents after Frakes (1979) and Doyle (1987).

2.4 Early Cretaceous greenhouse

Lacking evidence for major glaciations or ice caps can be taken as good evidence for generally warmer conditions during the early Cretaceous. Continental configuration is a controlling parameter on the formation of continental ice sheets in high latitudes (Francis and Frakes, 1993). The ocean/continent ratio was 5 during the early Cretaceous for the arctic compared to 1 today (Kuhn, 1997), making the presence of large continental ice sheets unlikely. In recent years doubt has been cast whether the Cretaceous was as warm throughout as formerly thought (Price et al., 2000). Cooler temperatures and maybe even ice formation may have characterized the early Cretaceous of the Arctic and Antarctic, based on the presence of what appears to be ice-rafted debris and glendonites (Kemper, 1983; Francis and Frakes, 1993).

Oxygen isotopes remain the most direct way to estimate paleo-temperatures for Mesozoic and older rocks, although the oxygen isotopic ratio is very liable to diagenesis. Calculated paleo-temperatures from oxygen isotope data from high northern latitudes for the mid-Valanginian show relatively low temperatures around 8°C (Ditchfield, 1997), which is compatible with ice formation.

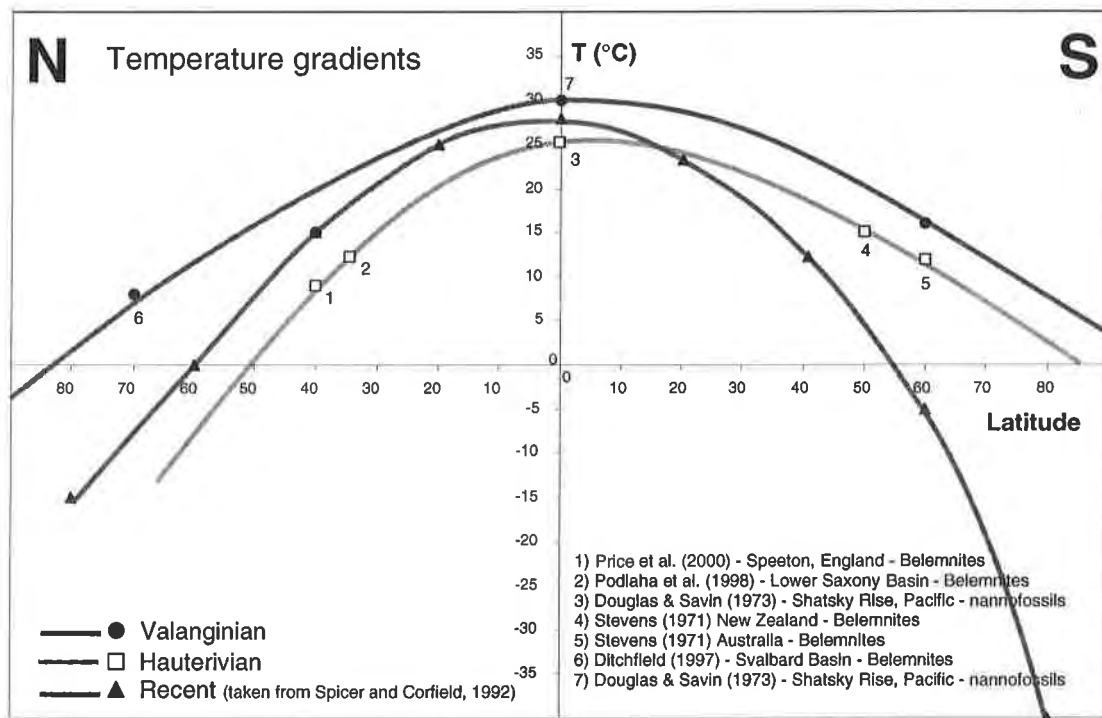


Figure 2. 5 – Temperature gradients for the Valanginian and Hauterivian compared to present-day situation (after Price et al., 2000; Stevens, 1971; Douglas and Savin, 1973; Douglas and Savin, 1975; Podlaha et al. 1998).

At mid-northern latitudes the Hauterivian shows cooler temperatures compared to the Valanginian (Fig.2.5), which extrapolated would mean temperatures below freezing for much of the Arctic. At high southern latitudes temperatures remain relatively elevated for both the Valanginian and Hauterivian compared to today (Fig.2.5). Temperature gradients between pole and equator were however more flattened during the early Cretaceous compared to today. This more equally spread heat may have greatly influenced ocean and atmospheric circulation. The gradient is also more asymmetrical for the early Cretaceous than for today. If the present-day situation represents an interglacial with substantial ice cover, the early Cretaceous probably did neither see an ice-covered Antarctica, nor an ice-covered Arctic in the absence of large continental masses there. The asymmetry in the temperature gradient curve corresponds well to the asymmetry in climatic zonations for the northern and southern hemispheres (Fig.2.4), because in the southern hemisphere subtropical conditions extended towards much higher latitudes.

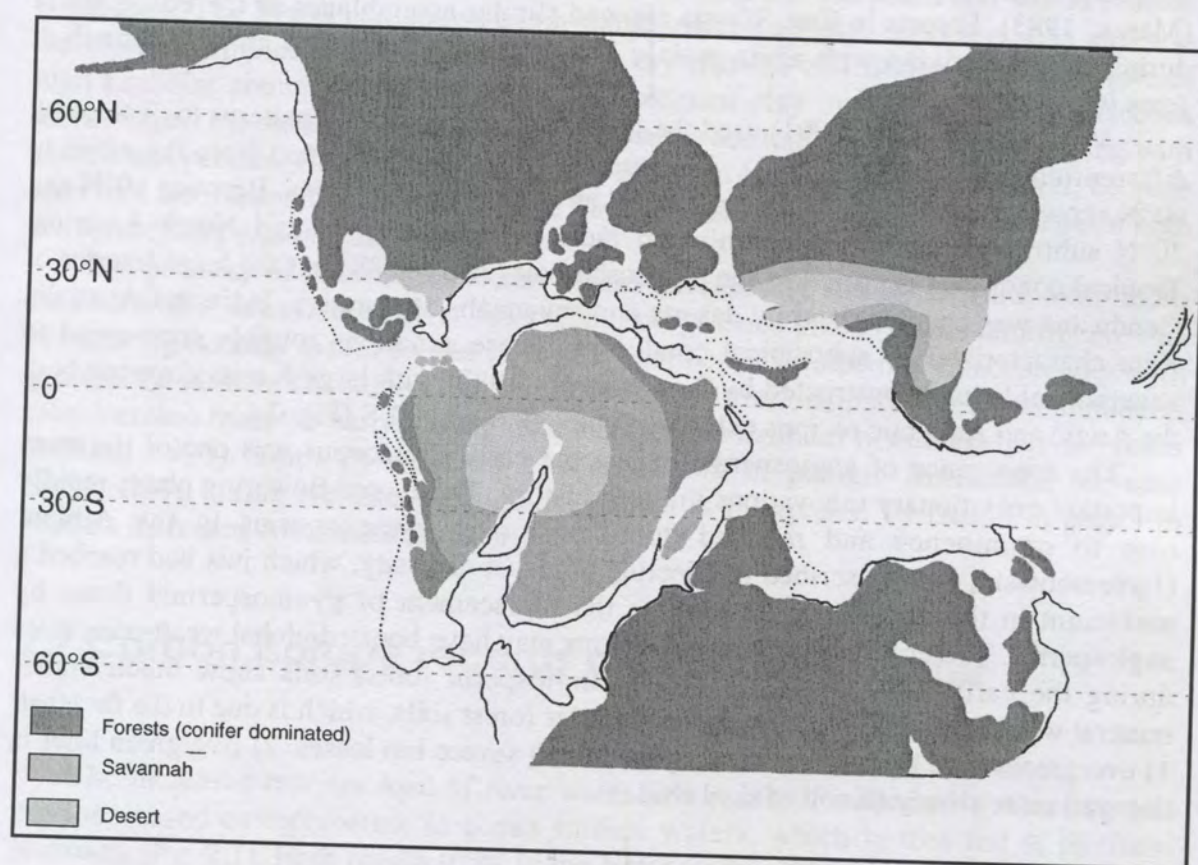


Figure 2. 6 – **Vegetation** reconstruction for the Valanginian-Hauterivian (modified after Kuhn, 1997 and Vakhrameev (1978, 1991).

Further evidence for substantially warmer conditions during the early Cretaceous comes from plant fossils. Plant fossils are paleoclimate indicators par excellence, because they are in direct contact with the atmosphere and are very sensitive to changes in temperature and humid/arid conditions. Plants also have a direct influence on the bio-geochemical cycling of nutrients. The Devonian rise of vascular plants is thought to have increased

continental weathering rates considerably (Algeo et al., 1995). Large-scale reconstructions of early Cretaceous floras was done by (Vakhrameev 1978; 1991). The most important result from his studies is that subtropical plants thrived about 20° further North than today. *Classopollis* pollen are generally believed to be good indicators of aridity and their decreasing abundance from the late Jurassic to early Cretaceous can be taken as evidence for a general increase in humidity (Vakhrameev, 1991).

Allen (1975) mentions fossil tree stems with irregular tree rings from the early Cretaceous Weald (England) that seem to indicate a seasonal wet climate. The common presence of fusain (charcoal) in Wealden sediments points to arid phases during which fires destroyed most of the vegetation (Watson et al., 1996). Further north, vegetation in the Polish Basin was characterized by conifers such as *Taxodiaceae*, *Taxaceae* and *Cupressaceae*. Ferns were represented by *Gleicheniaceae* (Marek 1983). From the Berriasian to late Hauterivian an increase in humidity-indicators occurred, while in the Barremian the assemblage changed significantly towards more aridity-loving plants (Marek, 1983). Forests in East Siberia showed similar assemblages as the Polish Basin during the Hauterivian with again mainly *Taxodiaceae*-forests with an undergrowth of ferns (Golozoubev, 1999).

Vakhrameev (1978, 1991) used the great uniformity in floral patterns to distinguish different climatic zones (Fig.2.4). A temperate-warm zone extended from the arctic to 60°N showing vast forests with conifers and an undergrowth of ferns. Between 60°N and 30°N subtropical conditions dominated most of Europe, Asia and North America. Tropical conditions occurred in the equatorial belt (30°N-30°S) but the large interior of Gondwana was characterized by deserts and savannahs. Antarctica, India and Australia were characterized by subtropical conditions. These zonations roughly correspond to vegetational belts reconstructed by Ziegler et al. (1987) with large forests covering both the Arctic and Antarctic regions extending up to 30°N and 30°S (Fig. 2.6).

The appearance of angiosperms during the early Cretaceous was one of the most important evolutionary innovations in Earth history. These seed flowering plants rapidly rose to prominence and reached dominance over gymnosperms in the Albian. (Jarzembowski, 1995) ascribed the decline in insect diversity, which just had reached a maximum in the earliest Cretaceous, to the replacement of gymnosperm floras by angiosperms. The proliferation of angiosperms may have boosted global weathering rates during the early Cretaceous. Deciduous angiosperm forest soils show much higher mineral weathering rates than evergreen-conifer forest soils, which is due to the fact that: 1) evergreens lose leaves continuously, reducing severe ion losses. 2) Evergreen litter is decayed more slowly (Knoll et al., 1987).

2.6 CO₂ and weathering

Whether hydrological cycling was intensified can only be determined indirectly. Weathering, erosion and run-off should increase if precipitation was increased. Clay mineral abundance, concentrations of phosphorus and other trace elements such as Fe and Mn in marine sediments and paleobotany provide independent evidence for humid conditions during the early Cretaceous. Weathering is controlled by various factors, but probably the most important is CO₂ concentration of the atmosphere. Carbon dioxide is

an agent in the weathering of rocks, generalized as: $\text{CaSiO}_3 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{SiO}_2$. So is there any reason to believe atmospheric concentrations of CO_2 were high during the early Cretaceous?

High CO_2 levels during the early Cretaceous were inferred both from modelling (Berner, 1991; and many other papers) and from several studies on pedogenic carbonates (Lee et al., 1999). From the Berriasian to Albian $p\text{CO}_2$ rose from 2 times to 6 times the presentday concentration. Typical calculated values using $\delta^{13}\text{C}$ from paleosols range from 800 to 3000 ppmv. In a recent paper Retallack (2001) reconstructed CO_2 concentrations from leaf stomata for the past 300 Ma. His data show gradual increasing concentrations from the base of the Cretaceous into the Cenomanian.

Clay mineral assemblages show a clear evolution during the early Cretaceous. The most important trend from the late Jurassic to late Hauterivian is the rapid increase in kaolinite abundance across the Jurassic-Cretaceous boundary (Sladen, 1983; (Hallam, Grose et al. 1991)). Kaolinite is considered as an indicator for warm and humid climate conditions. The Barremian shows again much lower kaolinite concentrations and was therefore interpreted to have been relatively dry (Ruffell and Batten 1990). In spite of high kaolinite abundances, smectite is the dominant clay mineral in early Cretaceous assemblages. Smectites are thought to be indicators for long dry periods alternating with intense wet periods. However, its abundance may also be controlled by sea level, because smectites are transported further offshore than kaolinite and seem to be indicative of high sea level (Thiry and Jacquin, 1993).

The pathway of phosphorus to the oceans is relatively straightforward. With more than 90% of P delivered by river run-off and no gaseous phases in the atmosphere this bio-limiting nutrient makes a good proxy for continental weathering. In accordance with greenhouse climate conditions, high weathering and run-off, phosphorus accumulation rates increase from the early Valanginian to reach a maximum in mid-Hauterivian times (Föllmi, 1995). Both Fe and Mn concentrations in pelagic limestones increase considerably during the late Valanginian, which is interpreted by (Kuhn in prep.) to indicate increased continental weathering.

2.7 Carbon isotope records and organic matter

The increased nutrient load of river water as a result of increased weathering and erosion caused eutrophication in ocean surface waters, which in turn led to platform drowning (fig. 2.1). High productivity in the Valanginian oceans is inferred from $^{13}\text{C}/^{12}\text{C}$ isotope ratios measured from biogenic carbonate. Sections from around the world show a positive $\delta^{13}\text{C}$ excursion (Lini et al., 1992; Föllmi et al., 1994; Weissert et al., 1998) in magneto-zones CM11 and CM12 corresponding to the *Campylotoxus* and *Verrucosum* ammonite zones (Hennig et al., 1999). The Valanginian carbon isotope record is well constrained by studies on pelagic carbonates (Lini et al., 1992 and references therein), hemipelagic carbonates (Hennig et al., 1999), shallow marine carbonates (Kuhn, 1997) and belemnites (Ditchfield, 1997; Podlaha et al., 1998; Price et al., 2000).

The mid-Valanginian positive carbon isotope excursion has been explained as the result of intensified carbon cycling and increased organic carbon (OC) burial (Lini et al.,

1992; Weissert et al., 1998). What is missing are true Valanginian black shales indicating increased OC burial. Organic carbon rich intervals have been described for the Valanginian-Hauterivian from a variety of basins (cf. (Lini et al., 1992), but these seem to be associated with turbidite sedimentation and terrestrial organic matter (Summerhayes, 1981). It seems likely that most organic matter was stored in shallow marine settings or on the continents as the onset of the Valanginian $\delta^{13}\text{C}$ excursion coincides with a major sea level drop (Hardenbol et al., 1998). There are two possibilities, either organic matter was stored on the continents and eroded later or it was stored in shallow marine siliciclastics and re-oxidized when continental margins were flooded during the late Valanginian and early Hauterivian (Weissert et al., 1998). Although poorly constrained thusfar, the late Valanginian to early Hauterivian shows a gradual decreasing $\delta^{13}\text{C}$ trend reflecting probably in part the increased influx of terrestrial organic matter or re-oxidation of organic matter.

Evidence for continental storage of organic carbon comes from early Cretaceous source rocks that are primarily of terrestrial or very shallow marine origin. Valanginian and Hauterivian bitumen-rich lagoonal deposits have been described from the Dinarides (Slovenia; Plenicar et al., 1983). Widespread coal deposits occur in Hauterivian-Albian successions in East Siberia (Golozoubev et al., 1999), while lacustrine oil shales of Hauterivian to Barremian age are described from the Tamtsag Basin, Mongolia (Neves et al., 2000). Berriasian to Hauterivian organic rich lacustrine sediments were discovered in syn-rift basins in Angola and Congo (Karner et al., 1998) and on the eastern Brazilian continental platform (Goncalves et al., 1998).

2.8 Platform drowning and phosphorite deposition

From the early late Valanginian to late Valanginian carbonate platforms showed demise on a global scale. Drowning occurred both along the northern and southern Tethyan continental margins (Masse, 1993; Föllmi et al., 1994; Schlager 1981; 1989). Even platforms that were not attached to any continental landmasses were drowned, like the Apulian platform (Graziano, 1999). In part this demise may have been related to evolutionary trends and ecological changes. Reef ecosystems changed substantially during the early Cretaceous from coral dominated to rudists dominated ecosystems from the Albian onwards (Scott, 1988). From the Hauterivian to Albian, however, these primary carbonate producers co-existed, with corals occurring in slightly deeper water settings than rudists. Scott (1988) explains this ecological turnover as the result of depletion of nutrients in surface waters towards mid-Cretaceous times, when repeated Aptian-Cenomanian anoxic events had resulted in the storage of large quantities of nutrients in the sedimentary reservoir. During the latest Jurassic sponges were common constituents of deeper shelf communities, but their significance decreased during the Hauterivian and they became insignificant afterwards. The Hauterivian could thus represent some transient period towards a new dynamic equilibrium in carbonate production. The ecological changes from blue water facies (dominated by corals) in the Valanginian, to green water facies (dominated by bryozoans, sponges, crinoids) in the

Hauterivian and back to blue water facies (dominated by rudists) in the Barremian stands central in this thesis.

Figure 2.7 presents an overview of main phosphorite occurrences in the Helvetic Alps and phosphate accumulation rates (Föllmi, 1995). It shows together with the $\delta^{13}\text{C}$ record that phosphorite deposition occurred possibly both coupled (Valanginian and Aptian) and uncoupled from carbon cycling (Hauterivian and Albian). The reasons for this decoupling of carbon cycling and phosphorite deposition will be further discussed in Chapter 8.

2.9 Summary and conclusions

It remains difficult to assess whether Parana CFB volcanism had a direct impact, but tectonic activity, spreading and rifting seem to have increased during the Valanginian and Hauterivian. Increased spreading is most evident from a late Valanginian to early Hauterivian eustatic sea level rise, followed by a sharp mid-Hauterivian regression that can be traced over much of the Tethyan and part of the Boreal realms. Although the early late Hauterivian is mainly transgressive, the late Hauterivian is in general considered to show evidence for a mild regressive phase. Spreading might have slowed down during the late Hauterivian and early Barremian giving way to uplift and regression. Sea level possibly helped to drown sensitive carbonate producing communities during the late Valanginian and early Hauterivian as it led to exchange of cold and warm watermasses between the Boreal and Tethyan realms over connections that were previously closed.

Associated with volcanism, an increase in CO_2 is inferred from plant fossils, paleosols and modelling using carbon isotopic ratios. Humid and warm climate conditions during the Valanginian and intensification of the water cycle are indicated by an increase in abundance of kaolinite. During the Hauterivian kaolinite gradually disappeared from clay mineral suites and was replaced by increased amounts of smectite, which seems to point to more seasonally warm and wet climate conditions. Common fusain in Wealden sediments indicate that wet periods were alternating with warm and dry periods. The Barremian is thought to have witnessed more arid conditions.

The Hauterivian continents were covered by dense forest with conifers and ferns. Forest burning during the dry periods may have facilitated weathering and erosion during the wet periods that followed, leading to increased influx of terrestrial organic matter. This is reflected in part in decreasing carbon isotope values for the late Valanginian and early Hauterivian and in abundant terrestrially derived organic matter in shelf sediments from the Tethys and North Atlantic.

High detrital loads of river water entering the Tethys and other basins is evidenced by high concentrations of P, Fe and Mn in marine carbonates of late Valanginian to early Hauterivian age. As a result of high detrital influx, eutrophication is thought to have caused an acceleration of the carbon cycle expressed in a global positive $\delta^{13}\text{C}$ excursion during the mid-Valanginian. During the Hauterivian weathering and erosion remained intense and platforms were drowned several times, most notably during the earliest Hauterivian, mid-Hauterivian and latest Hauterivian.

Carbonate production changed accordingly to changing nutrient levels from oligotrophic in the early Valanginian to mesotrophic in the Hauterivian (siliceous limestones in foramol mode) and back to oligotrophic in the Barremian, when blue water conditions were re-established (with rudists and corals). The late early Valanginian represents a phase of major perturbation (eutrophic) followed by a transient phase during the Hauterivian (mesotrophic). It is during this transient phase that carbonate platforms were drowned frequently as they were under high stress from different factors.

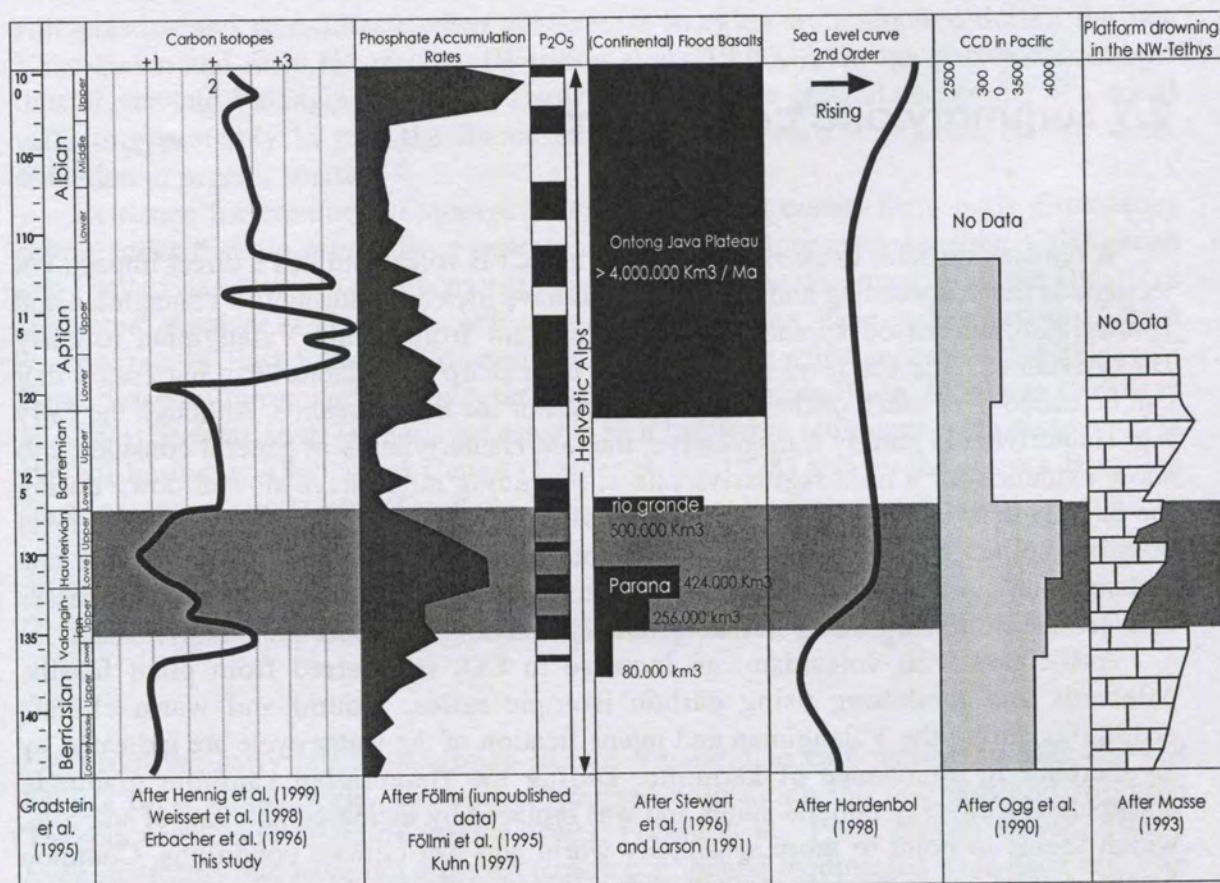


Figure 2.7 – Summarizing diagram showing most important paleo-environmental changes during the early Cretaceous. The red band covers the interval that has been extensively studied for this thesis.

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Chapter 3

Litho-, tectono- and chronostratigraphic framework

3.1 Introduction

In this chapter the regional lithostratigraphic and chronostratigraphic frameworks for 4 studied regions (Jura Mountains, Helvetic Alps, Vocontian Basin, Umbria-Marche Basin) are briefly summarized by highlighting individual key sections. The Hauterivian stage is the principal time period concerned here, but in some cases also the Valanginian and Barremian are treated. The organisation of this chapter follows a platform to basin transect. The sections sampled for this PhD project have often been investigated extensively in the past and the most important findings of previous authors have been incorporated as well. Figure 3.1a and b show the geographic position of all the studied sections.

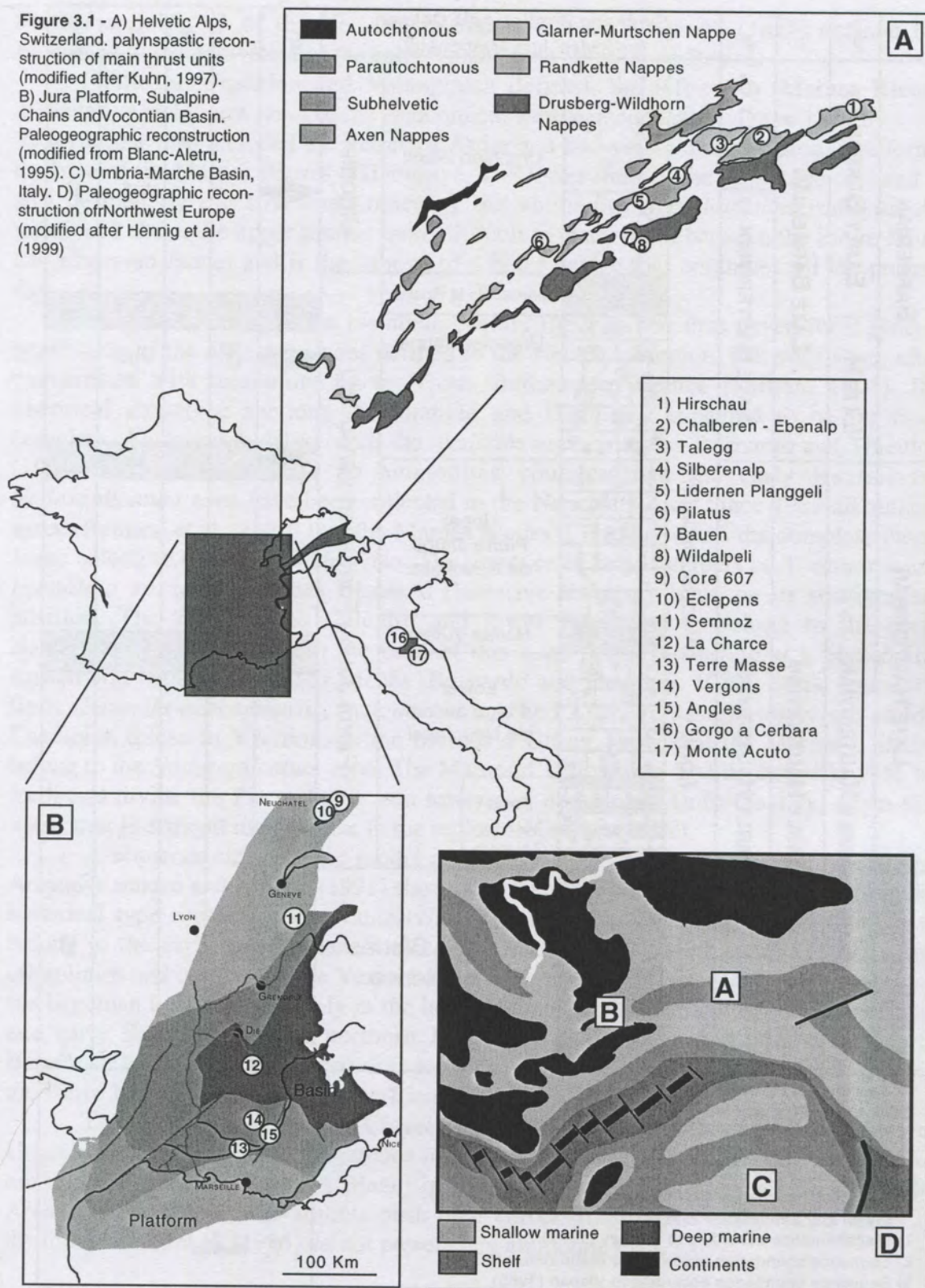
3.2 The Neuchâtel Jura and Subalpine region

3.2.1 Definition of the Hauterivian stage

The Jura Mountains in the area around Neuchâtel have played an important role in geological studies on the early Cretaceous, because it is in this region that the Valanginian and Hauterivian stages were first defined. Figure 3.2 shows the general stratigraphic framework for the surroundings of Neuchâtel. The early history of the definition of the stages is summarized in the following paragraphs.

The *Neocomian* was first introduced by Thurmann (1836) and included the “Terrain crétacé du Jura” of De Montmollin (1835) and “Terrain jura-crétacé” of Thirria (1836). These authors both worked in the Jura mountains and recognized independently from each other early Cretaceous rocks between the Jurassic at the base and the Tertiary (Molasse) at the top. Hence, the Neocomian spanned the whole Cretaceous, but in reality only the Marbre de Batârd, Calcaire Roux, the Marnes Bleues d’Hauterive, the Pierre Jaune de Neuchâtel and the Urgonian were included, because only these lithologic units are present in the region surrounding Neuchâtel. After introduction of the Urgonian by d’Orbigny (1847) the Neocomian was subdivided in a lower oolitic unit and an upper Urgonian facies characterised by rudists. Further precisions were made by Desor (1854) who introduced the Valanginian to distinguish limestones underlying the Marnes Bleues d’Hauterive. Jaccard (1869) separated the Urgonian from the Pierre Jaune by means of the Marnes de la Rusille, a marly horizon not present in the Neuchâtel area. Later on, the Marnes de la Rusille were repositioned between the Urgonian Jaune and Urgonien Blanc (Conrad and Masse, 1989). Jaccard was also the first to recognize a lower Urgonian (Urgonien Jaune) and an upper Urgonian (Urgonien Blanc). The distinction between the Pierre Jaune and Urgonien Jaune remains very difficult due to the absence of any clear biomarker and very similar lithologies (both are yellow and contain abundant ooids).

Figure 3.1 - A) Helvetic Alps, Switzerland. palynospastic reconstruction of main thrust units (modified after Kuhn, 1997). B) Jura Platform, Subalpine Chains and Vocontian Basin. Paleogeographic reconstruction (modified from Blanc-Aletru, 1995). C) Umbria-Marche Basin, Italy. D) Paleogeographic reconstruction of Northwest Europe (modified after Hennig et al. (1999)



1	2	3	4	Synthetic Stratigraphic Column for Swiss Jura (Neuchâtel)				5	6	7	8	9							
BARREMIAN	EARLY BARREMIAN	LATE BARREMIAN	EARLY B.	<i>Nodosoplicatum</i>		Urgonien Blanc	Urgonien				Ju6	F							
																			
	LATE H.		LATE HAUTERIVIAN										Marnes de la Rusille		ϵ		Ju5	E	
																			
LATE HAUTERIVIAN	EARLY HAUTERIVIAN	EARLY HAUTERIVIAN	EARLY HAUTERIVIAN	<i>Loryi</i>		Urgonien Jaune	Pierre Jaune Formation <i>sensu lato</i>		δ'		Ju3								
																			
														Upper Pierre Jaune de Neuchatel		δ		Ju2	D
																			
EARLY HAUTERIVIAN	EARLY HAUTERIVIAN	EARLY HAUTERIVIAN	EARLY HAUTERIVIAN	<i>Radiatus</i>		Marnes d'Uttins	Pierre Jaune Formation <i>sensu lato</i>		γ	D3	Ju1	C							
																			
														Lower Pierre Jaune de Neuchatel					
																			
						Zone Marno- Calcaire	Pierre Jaune Formation <i>sensu lato</i>			D2									
																			
						Marnes Bleues d'Hauterive	Pierre Jaune Formation <i>sensu lato</i>		β			B							
																			
						Marnes Bleues d'Hauterive	Pierre Jaune Formation <i>sensu lato</i>		α	D1		A							
																			
1) Baumberger (1900) & and later works 2) Conrad and Masse (1989) 3) Arnaud-Vanneau and Arnaud (1990) and Blanc-Aletru (1995) 4) Clavel et al. (1995) 5) Hardgrounds and other discontinuities 6) Sequence boundaries after Conrad and Masse (1989) and Clavel and Charollais (1989) 7) Discontinuities according to Rumley (1992) 8) Sequence boundaries according to Blanc-Aletru (1995) 9) Sequence boundaries according to Vieban (1983)								 Cnidarids  Ooids  Glauconite  Detrital Quartz  Rudists											

Figure 3. 2 – Chrono- and lithostratigraphic framework for Swiss Jura

Further splitting up of the Neocomian occurred when Coquand (1871) defined the Berriasian as the equivalent of the early Valanginian (Marbre de Batârd).

With the Urgonian and Valanginian defined, the left-overs (Marnes Bleues d'Hauterive and Pierre Jaune) of the Neocomian, were named Hauterivian in 1874 by Renevier. He also included the Marnes à Astieria, a thin yellow marl horizon, that forms the base of the Marnes Bleues d'Hauterive. The lower limit of the new stage was and is still defined by the first appearance of the ammonite *Acanthodiscus radiatus*. As mentioned above the upper limit is more difficult to place (limit between the Pierre Jaune and Urgonian Jaune) and is the subject of a bitter debate that continues till the present day.

At the beginning of the twentieth century the way was thus paved for a general application of the different stages defined in the Neuchâtel region. But very soon, after comparison with ammonite faunas from southeastern France (Killian, 1895), the historical stratotype sections of Valangin and Hauterive appeared to be far from complete. A general revision of all the available ammonites by Busnardo and Thieuloy (1989) made it clear that no ammonites younger than the early Hauterivian *Nodosoplicatum* zone have been collected in the Neuchâtel Jura. Since 1989 all authors agree (Remane et al., 1989) that the Marnes Bleues d'Hauterive and the complete Pierre Jaune belong to the early Hauterivian. The presence of large numbers of *A. radiatus* and *Leopoldia* sp. in the Marnes Bleues d'Hauterive leave no doubt on its stratigraphic position. The Zone-Marno Calcaire and lower Pierre Jaune belong to the early Hauterivian *Loryi* zone, with the base of this zone possibly starting at a glauconitic hardground within the Marnes Bleues (Busnardo and Thieuloy, 1989). Some ammonite finds (*Saynella neocomiensis*, *Lyticoceras* sp. and *Lyticoceras* aff. *salevense*) at Mt. Chamblon (close to Yverdon) in the Marnes d'Uttins, show that the Marnes d'Uttins belong to the *Nodosoplicatum* zone. The Marnes d'Uttins were first described in 1955 by Jordi and divide the Pierre Jaune in a lower and upper unit. Unfortunately, again this marly unit is difficult to recognize in the region around Neuchâtel.

A sequence stratigraphic model proposed by Arnaud-Vanneau et al. (1990) and Arnaud-Vanneau and Arnaud (1991) shows that there is no late Hauterivian present in the historical type region for the Hauterivian. The upper Pierre Jaune is also thought to belong to the early Hauterivian *Nodosoplicatum* zone. Arnaud et al. (1999) using orbitolinids and correlating the Vercors and northern Jura with sequence stratigraphy put the Urgonian limestones entirely in the late Barremian and state that the late Hauterivian and early Barremian in the northern Jura were probably eroded after a late early Barremian lowstand. Hence, according to these authors a major hiatus is present between the Pierre Jaune and Urgonien Jaune/Blanc.

This view is contested by Clavel et al. (1986, 1987, 1995) who place the lower Urgonian (Urgonien Jaune) limestones in the late Hauterivian and the rudistid facies of the upper Urgonien (Urgonien Blanc) in the early Barremian. However, as shown by Arnaud et al. (1999) these authors push their chronostratigraphic assignments really to the limit. Clavel et al. (1995) do not present any ammonite data.

3.2.2 Sequence boundaries

Because there are so few useful biomarkers within the limestone successions around Neuchâtel (also benthic foraminifera, which have generally long ranges, are rare within the Pierre Jaune), different authors have all tried to distinguish discontinuity surfaces that can be used for regional correlation. Unfortunately every author has a different definition of what a discontinuity surface or sequence boundary is, which has resulted in much confusion on which boundary of one author is correlatable with boundaries recognized by another. From figure 3.2 it becomes quite clear that some boundaries are more important and more easily recognized than others. Boundaries that were recognized in more than two different studies include the top of the lower Pierre Jaune (Marnes d'Uttins), the contact between the upper Pierre Jaune and Urganien Jaune and the base of the Marnes de la Rusille. So these are likely to represent major events. An attempt is made to clarify some of the confusion by discussing several key sections that have been studied during the course of this project.

3.2.3 Core 607

Core 607 (Fig. 3.3 and Fig. 3.4) drilled in the region of Neuchâtel, Swiss Jura Mountains, was first studied by Rumley (1992). Paleogeographically site 607 was situated on a shallow carbonate ramp and it is the most shallow setting studied here. The core was drilled in the southern flank of the Chaumont anticline. The dip varies between 20-30 degrees, which means that the thicknesses in figure 3.3 have to be reduced with 5 to 17% (Rumley, 1992).

Core 607 contains the early Hauterivian Marnes Bleues d'Hauterive Fm (MBH) at the base which is overlain by the Zone Marno-Calcaire (ZMC). The MBH were not studied in detail by Rumley (1992), because of technical problems. A discontinuity (D1) was placed at the base of the MBH, which marks the base of the Hauterivian. The ZMC in core 607 is made up of fine grained biomicrites with mostly echinoderm debris, reworked micritic clasts and bivalve debris. In more distal settings (e.g. around Geneva) the ZMC shows clearer alternations of limestones with calcareous marls. A hardground is present 7.90 m above the top of the MBH. This discontinuity was termed D2 by Rumley (1992). It consists of a heavily bored submarine glauconitic hardground. Directly on top lies a 9 meters thick fine grained bioclastic wackestone unit, which is particularly enriched in detrital quartz and glauconite. The bioclasts are primarily shell and echinoderm debris. In the top of this unit chert (micro-crystalline quartz and chalcedony) replaces the micrite and bioclasts, which show up as ghost structures in thin section (own observations).

The Pierre Jaune de Neuchâtel Formation (PJN) consists generally of coarse grained crossbedded oolitic and bioclastic pack-grainstones. In core 607 the PJN starts of with oolitic grainstones (6 meters). Most of the ooids have been micritised and are cemented by drusy calcite. Throughout the PJN the ooids have been leached out of the calcitic matrix to a varying extent. The basal 6 meters are followed by a unit that contains again more bryozoan debris and reworked extra- and intraclasts and relatively less ooids. Towards the top of the lower PJN ooid abundance increases again, still showing the extensive leaching.

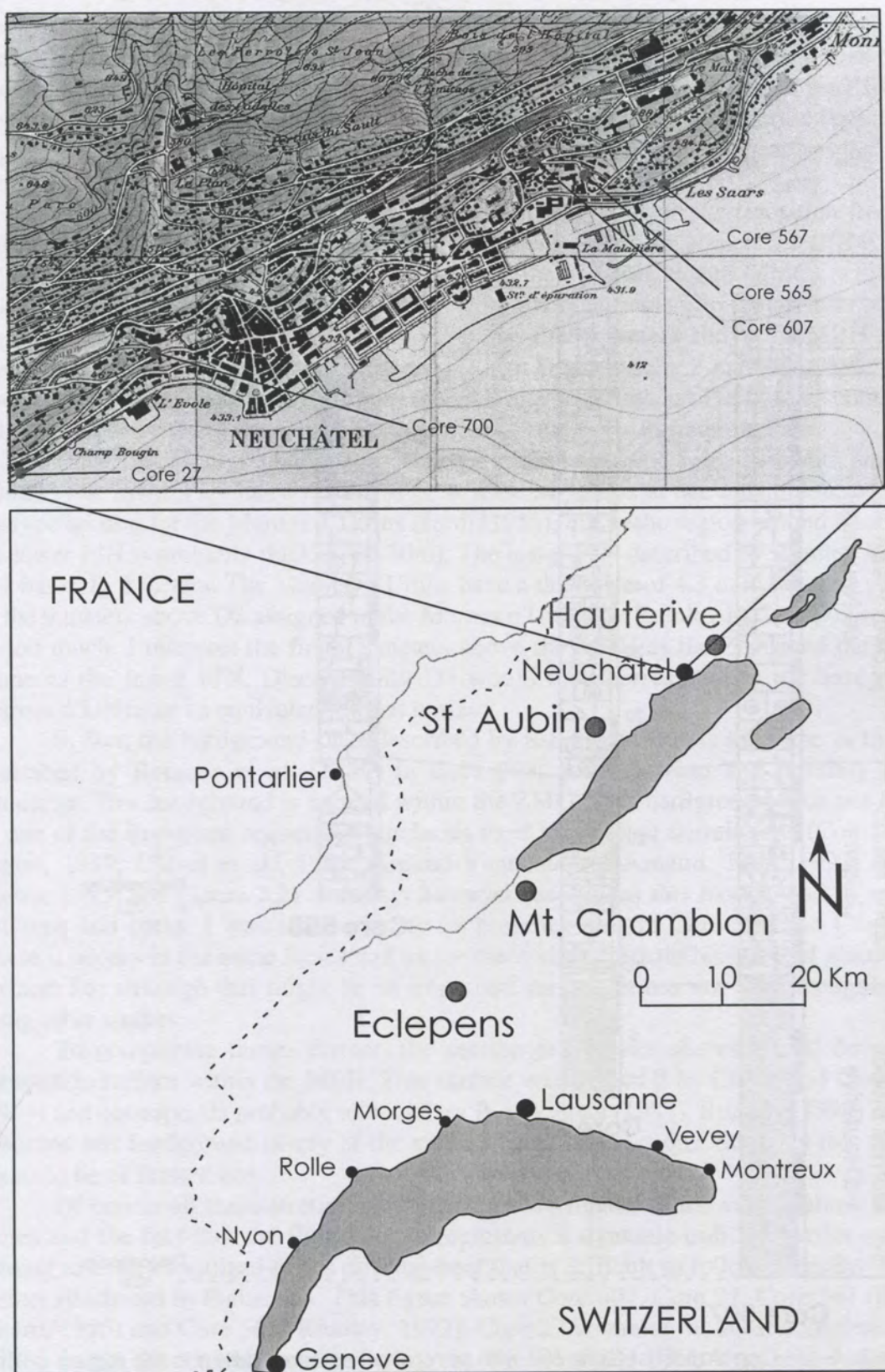


Figure 3.3 – Location maps for cores and outcrops in Swiss Jura Mountains

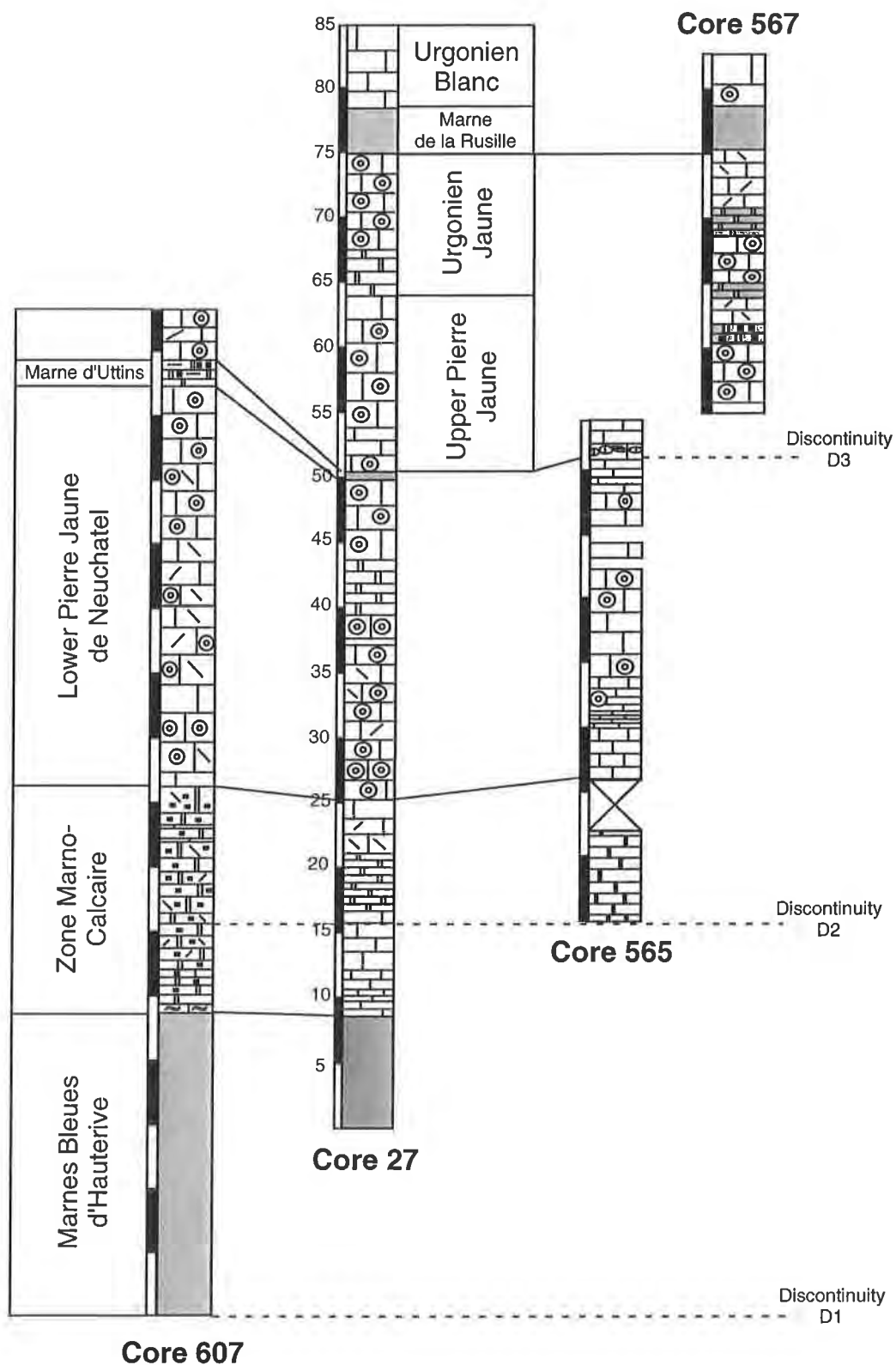


Figure 3.4– Correlation of Core 607 with several other cores drilled in the region around Neuchâtel. Lithology of Core 27 and 567 after Blanc-Aletru (1995) and Core 565 and 607 after Rumley (1992).

Approximately 5 meters below the top of the core Rumley recognized a third discontinuity surface (D3). This surface is marked by the appearance of biomicrites rich in detrital quartz and glauconite. Another striking aspect of this upper part of the PJN is the abundance of small benthic foraminifera just below and above the micritic beds. The uppermost meters of the core are again an oolitic grainstone. Rumley mentions the occurrence of dasycladacean algae in the uppermost meters of Core 607.

The aim of Rumley's thesis was to study in greater detail the transition from the Marnes Bleues d'Hauterive (MBH) into the Pierre Jaune de Neuchâtel (PJN). It is therefore strange that he does not recognize the Zone Marno-Calcaire (ZMC), while this unit clearly marks the gradational transition from the blue marls into the oolitic beds of the PJN (Remane et al., 1989). Rumley takes the first 8 meters above the MBH as the lower Pierre Jaune de Neuchâtel. According to him Discontinuity 2 marks the base of the Marnes d'Uttins, followed by the upper Pierre Jaune de Neuchâtel Fm upto discontinuity D3. The upper 5 meters are placed in the Lower Urgonian (=Urgonien Jaune).

These lithostratigraphic assignments are not in very good agreement with previous studies. The lower PJN has a thickness of at least 14 meters at Mt. Chamblon, which is the type section for the Marnes d'Uttins (Jordi, 1955), but in the region around Neuchâtel the lower PJN is probably thicker (20-30m). The lower PJN described by Rumley in Core 607 has only 8 meters. The Marnes d'Uttins have a thickness of 4.3 m in the type profile, so the 9 meters above D2 assigned to the Marnes d'Uttins by Rumley in Core 607 seem to be too much. I interpret the first 15 meters above the MBH as the ZMC and the Pierre Jaune as the lower PJN. Discontinuity D3 would then correspond to the base of the Marnes d'Uttins or an equivalent of that horizon.

In fact, the hardground (D2) described by Rumley (1992) is the same as the one described by Remane et al. (1989) in Core 208, at Prébarreau and possibly at Le Landeron. This hardground is located within the ZMC. This hardground does not figure as one of the important sequence boundaries used in regional correlations (Conrad and Masse, 1989; Clavel et al., 1989; Arnaud-Vanneau and Arnaud, 1990, 1992; Blanc-Aletru, 1995; see Figure 3.2). Rumley, however recognizes this hardground in several outcrops and cores. I was able to verify its presence also in Core 565 and Core 700, where it occurs in the same facies and as the same characteristic bioturbated glauconitic surface. So, although this might be an important surface, it has not been recognized in many other studies.

To complicate things further, the section at Cressier shows a well developed glauconitic surface within the MBH. This surface was termed β by Clavel and Charollais (1989) and corresponds probably to boundary B of Vieban (1983). Rumley (1992) did not observe this hardground in any of the studied cores and sections. So again this surface seems to be of limited use.

Of course all these stratigraphic problems are related to the very shallow marine facies and the fact that the Pierre Jaune represents a dynamic oolitic barrier system, leading to a very localized facies development that is difficult to follow laterally. This is further illustrated in Figure 3.4. This figure shows Core 607, Core 27, Core 567 (Blanc-Aletru, 1995) and Core 565 (Rumley, 1992). Core 27 is one of the most complete cores drilled in the Neuchâtel area, covering the whole of the PJN, Urgonien Jaune and Urgonien Blanc. Comparison of Core 607 with Core 27 (Blanc-Aletru, 1995) further

proofs that Core 607 probably only spans the lower PJN and shows the great variations in facies and thickness.

3.2.4 Eclepens

The section of Eclepens (Fig. 3.5) was studied by Zweidler (1985), Conrad and Masse (1989) and Blanc-Aletru (1995). The base of the succession is dominated by bioomicrites rich in detrital quartz, followed by mixed bioclastic and oolitic grainstones of the Upper PJN. The oolites are overlain by a more marly horizon rich in coral debris known as the Marnes de la Rusille. This horizon is a marker for regional correlation and represents a distinct break in sedimentation, corresponding to a deepening of the environment. The lower Urgonian (Urgonien Jaune, UJ) is very similar to the PJN both for its facies and appearance and its distinction is sometimes difficult. However, as mentioned above the two are probably separated by a level that is particularly enriched in detrital quartz. The upper Urgonian (Urgonien Blanc, UB) corresponds to the typical Urgonian Facies with rudists and orbitolinids, which are well known from the Vercors Massif and southern France. At numerous horizons dissolved ooids occur and at two levels paleokarsts were observed.

Blanc-Aletru (1995) recognized several sequence boundaries in sections across the Jura Platform which she numbered Ju1-Ju6. She states that Ju1 to Ju3 are clearly of early Hauterivian age (*Radiatus-Nodosoplicatum* zones), while Ju5 and Ju6 are clearly late Barremian. Sequence boundary Ju4 was not dated by Blanc-Aletru (1995), but based on lithologic correlation she considers Ju4 to belong to the late Barremian as well. It is unclear whether this unit is present in Eclepens. According to Blanc-Aletru Ju1 corresponds to the base of the Marnes d'Uttins and thus she correlated it with D2 of Rumley (1992). As discussed above this should be D3 of Rumley (1992). D1 and D2 were not studied by Blanc-Aletru. Boundary Ju2 corresponds to the limit between the Pierre Jaune and Urgonien Jaune, which is the same as d from Conrad and Masse (1989), who see this surface as the boundary between the Pierre Jaune and Urgonien Jaune.

3.2.5 Semnoz section

The Semnoz section (Fig. 3.5 and 3.6), located south of Annecy (France) in the Subalpine tectonic unit known as the Bauges Massif, represents an outer ramp facies. The Lower Hauterivian consists of spiculitic and crinoidal bioclastic pack-wackstones, which are sometimes rich in glauconite. The basal 17 meters of the section probably make up two shallowing up sequences. The upper of these two sequences contains clearly crossbedded limestones. According to Vieban a hardground is present on top of this upper sequence. The crossbedded limestones are overlain by a thick marl sequence with marl-limestone alternations, rich in detrital quartz and sponge spicules that is poorly exposed and was not sampled. This marl sequence is in turn overlain by oolitic crossbedded packstones, marking again a shallowing of the depositional environment.

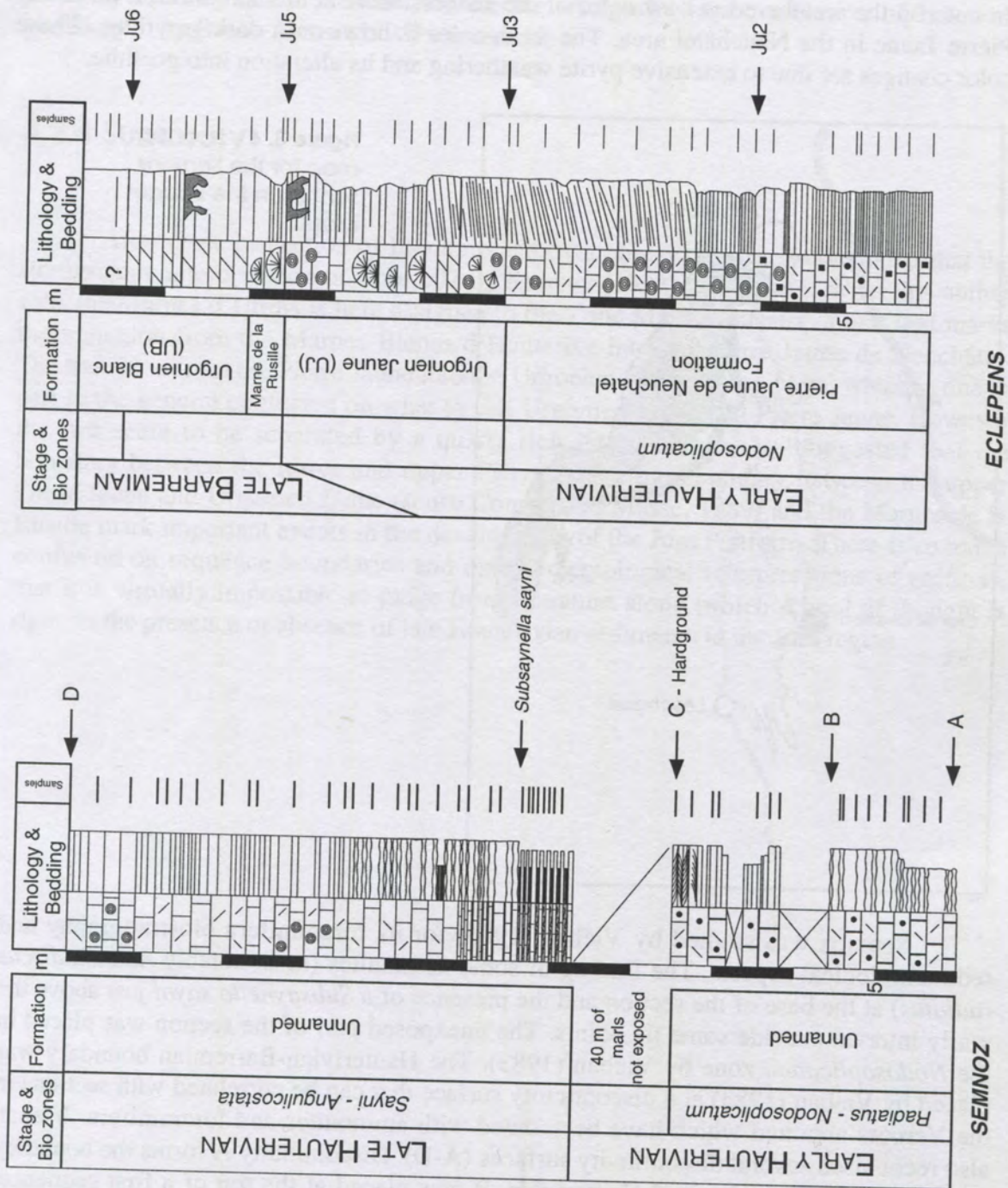


Figure 3.5 – Semnoz (after Vieban (1983) and this study) and Eclepens sections (after Blanc-Aletru, 1995). See text for explanation of sequence

In outcrop the weathered yellow color of the succession at Semnoz reminds a lot of the Pierre Jaune in the Neuchâtel area. The fresh color is however a dark grey blue. These color changes are due to extensive pyrite weathering and its alteration into goethite.

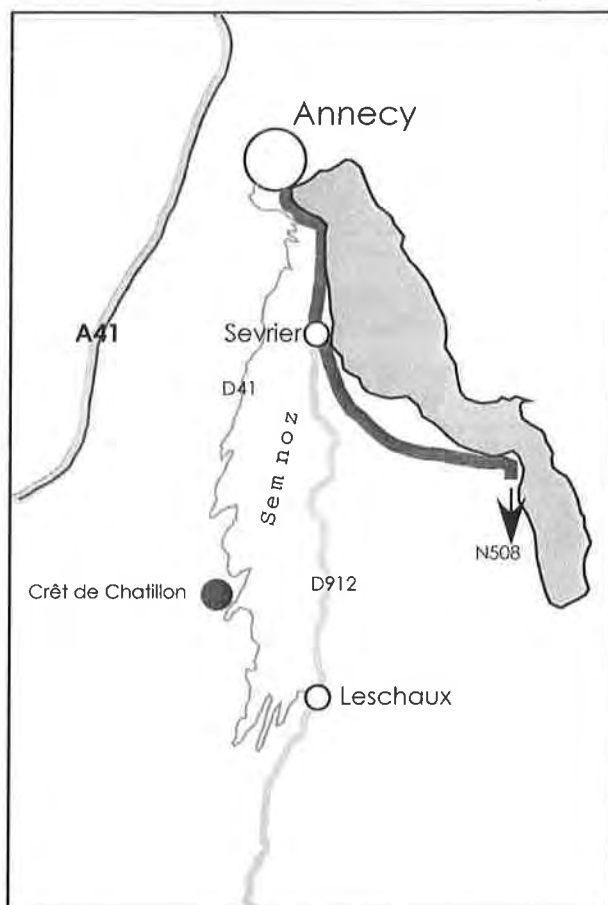


Figure 3. 6 – Location map for the Semnoz section in the Bauges Massif.

Semnoz was studied by Viéban (1983) for its foraminifera biostratigraphy and sedimentological aspects. The finding of some ammonites (most notably *Acanthodiscus radiatus*) at the base of the section and the presence of a *Subsarynella sayni* just above the marly interval provide some tie points. The unexposed part of the section was placed in the *Nodosoplicatum* zone by Viéban (1983). The Hauterivian-Barremian boundary was placed by Viéban (1983) at a discontinuity surface that can be correlated with sections in the Vercors area and which have been dated with ammonites and foraminifera. Viéban also recognised several discontinuity surfaces (A-D). Discontinuity A forms the boundary between the Valanginian and Hauterivian, B was placed at the top of a first sequence, which might be an equivalent of the glauconitic hardground of Cressier and sequence boundary β of Clavel and Charollais (1989). Discontinuity C corresponds to the Marnes d'Uttins and to sequence boundary γ of the same authors. It also corresponds to discontinuity D3 of Rumley (1992) and Ju1 of Blanc-Aletru (1995). So in a basinward direction the Marnes d'Uttins become increasingly thicker, however in the hemipelagic realm of the Vocontian Basin there is no such thick equivalent of the Marnes d'Uttins. Discontinuity D forms the boundary with the Barremian. Because the late Hauterivian is

probably missing in the Neuchatel area, the straightforward correlation of Ju3 with boundary D by Blanc-Aletru (1995) seems odd.

3.2.4 Summary

After close inspection of literature and own observations it is concluded that the stratigraphic interpretation of Core 607 by Rumley (1992) was wrong. What this author calls the Marnes d'Uttins is here assigned to the Zone Marno-Calcaire, a unit that marks the transition from the Marnes Bleues d'Hauterive into the Pierre Jaune de Neuchâtel. The transition from the Pierre Jaune into the Urgonien remains a problem, which is due in part to the general confusion on what to call Urgonien Jaune and Pierre Jaune. However the two seem to be separated by a quartz rich interval. It is also suggested that the boundary between the lower and upper Pierre Jaune, the boundary between the upper Pierre Jaune and Urgonien Jaune (*sensu* Conrad and Masse, 1989) and the Marnes de la Rusille mark important events in the development of the Jura Platform. There is so much confusion on sequence boundaries and on sedimentological interpretations of sections, that it is virtually impossible to judge from literature alone, which school of thought is right on the presence or absence of late Hauterivian sediments in the Jura region.

3.3. The Helvetic Alps

3.3.1 Introduction

Already at the end of the nineteenth century geologists working in the northern Alps had recognized the presence of glauconitic beds that could be used to subdivide the thick limestone successions and for correlations between different Alpine regions. Kaufmann (1867; 1886) was among the first to describe a glauconitic bed at the base of the Kieselkalk (a name also introduced by him) from the Pilatus. An important leap forward was made with the studies of Tobler (1905) and Baumberger and Heim (1907) on ammonite faunas from glauconitic and phosphatic horizons from the Mattstock, Churfirsten and Pilatus areas. The ammonites collected by these authors allowed to place the so-called *Gemsmättli Schichten* (a name introduced by Buxtorf in Baumberger and Heim, 1907) in the Valanginian. Under the name *Rahberg Schichten* a glauco-phosphatic horizon was described by Buxtorf (in Baumberger and Heim, 1907), which clearly contains Hauterivian faunal elements. A coarse sandstone unit is sometimes intercalated or sometimes replaces the Gemsmättli and Rahberg beds. This sandy unit is called the *Pygurus Schichten*, a name derived from the echinoid *Pygurus rostratus* that frequently occurs in these beds. This name appears for the first time in the diary (1840) of Escher von Linth (in Funk, 1971).

In the last two decades of the previous millennium, developing ideas on the chronostratigraphic, sedimentological and paleo-environmental framework of the Helvetic Alps took a flight and was refreshed and updated by numerous publications and theses (Fig. 3.6). A very good summary is provided by Funk et al. (1993). Several broad trends in the development of the Helvetic Shelf during the Valanginian, Hauterivian and Barremian can be recognised (after Kuhn, 1997): In the early Valanginian regression led to the rapid progradation of bioclastic grainstones of the Betliskalk Fm (Strasser, 1979). In the deeper parts of the basin widespread marl deposition occurred (Palfries and Vitznau marls). A first destructive phase of the platform is marked by the deposition of the phosphoritic Bühls Horizon. A next phase of progradation is recorded in the Upper Betliskalk Fm, which consists of spiculitic and bioclastic pack-grainstones. This formation is not everywhere developed along the northern Tethyan margin, which Kuhn (1997) ascribes to erosion and reworking. The distal equivalent of the Betliskalk Fm is the Diphyoideskalk which contains reworked debris from the Betliskalk Fm. The Diphyoideskalk Fm consists of hemipelagic lime-marl alternations with abundant aptychi. In the Vorarlberg region in Austria it continues well into the Hauterivian and contains ammonites from the *Loryi* zone (Wyssling, 1986). In more proximal settings the Upper Betliskalk is overlain by the Gemsmättli complex, which is formed by the Gemsmättli Horizon, Pygurus Schichten and Rahberg Horizon. The Gemsmättli complex represents a major condensation phase that spans the *Verrucosum* to lower *Radiatus* zone and is related to a second order transgression. Phosphorite deposition was much more extended than during the first phase of platform destruction (Bühls Horizon). Ammonites collected from the Gemsmättli Horizon (Kuhn, 1997) indicate that this horizon is

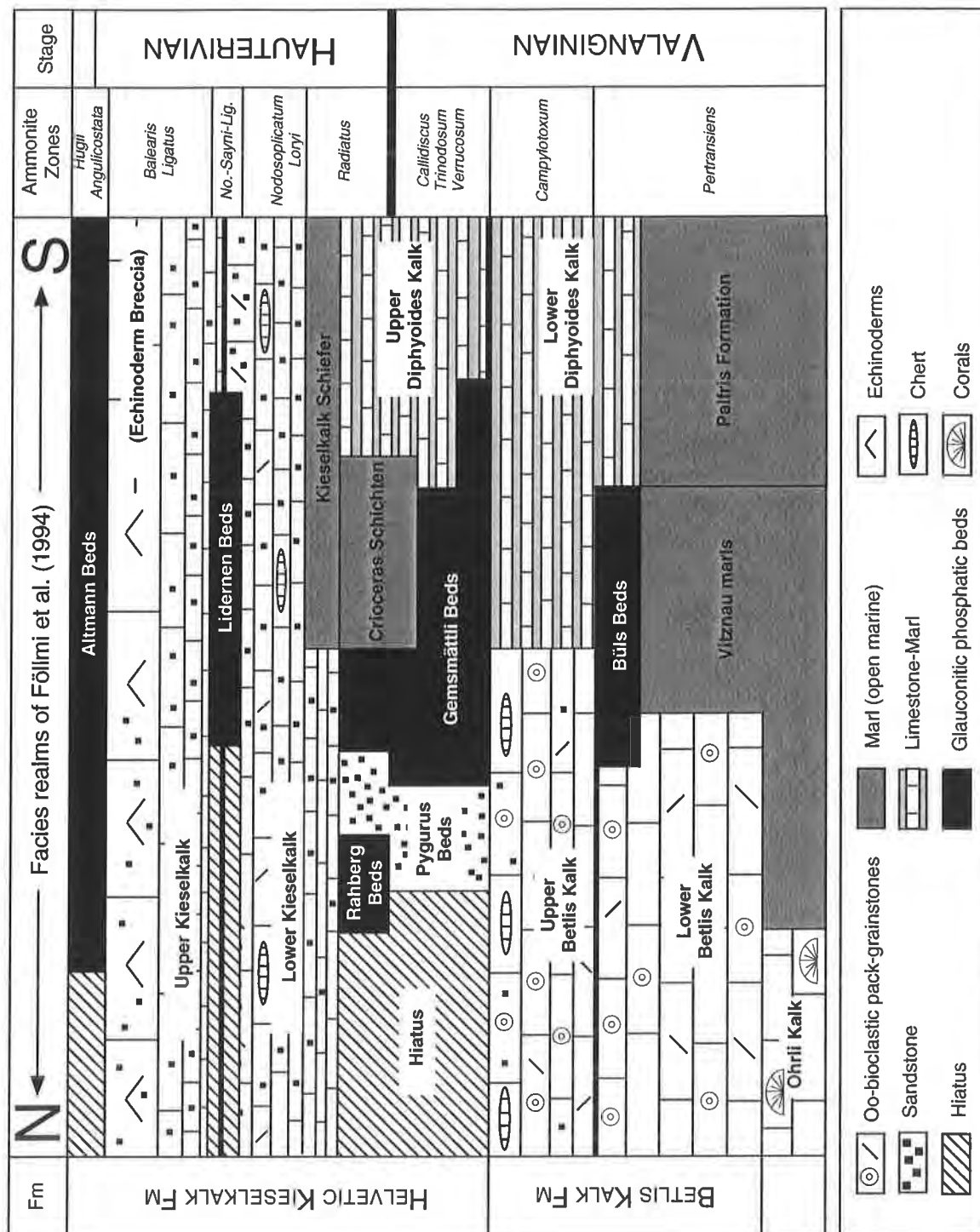


Figure 3.7 – Chronostratigraphic and lithostratigraphic framework for the Helvetic Alps (modified after Kuhn, 1997).

diachronous (and thus transgressive). On top of the Gemsmättli Horizon follows the Kieselkalk Fm, which marks a return to carbonate deposition, rich in crinoid, echinoderm, sponge spicules and bryozoan debris.

In brief, from the early Valanginian to early Hauterivian the northern margin of the Tethys experienced ever deeper marine conditions after a widespread regressive event in the early Valanginian. This deepening is related to a second order eustatic sea level rise (Hardenbol et al., 1998). A major phase of platform destruction occurred during the late Valanginian and is recorded in the Gemsmättli Horizon. Although sea level change can explain the overall development of the Helvetic Shelf, in detail it does not explain the repeated deposition of phosphorite beds. Other factors (water temperature, nutrients) were important too. Föllmi et al. (1994) distinguished three different modes of deposition in this system, which they relate to nutrient status of surface waters along the northern margin: 1) A first mode is called the *Coral-oolite mode*, which represents oligotrophic water conditions, like during deposition of the Lower Betliskalk Fm. 2) A second mode is characterized by mesotrophic carbonate production by abundant filter feeding organisms (*crinoid-bryozoan mode*), tolerant of higher turbidity and nutrient levels. These conditions are recorded in the Upper Betliskalk and Kieselkalk Fm. 3) A *destruction mode*, during which nutrient levels were so much increased that the platform drowned and condensation and phosphorite deposition prevailed (Bühls and Gemsmättli Horizon). So in a way, the Hauterivian represents the aftermath of major changes that occurred during the Valanginian. Let us zoom in now on the Hauterivian and the Helvetic Kieselkalk Fm.

The Helvetic Kieselkalk Fm is a siliceous (both detrital and biogenic) limestone rich in sponge spicules, crinoid and bryozoan debris. The base of the formation is usually formed by shales that grade upwards in marl-limestone alternations. Up to the Lidernen Horizon the beds become thicker and coarser grained and the uppermost metres of the Lower Kieselkalk Mb are often formed by coarse grained sparitic limestones rich in echinoid debris and detrital quartz. The Lidernen Horizon shows great variability in appearance and its thickness varies from 40 cm to 12 meters. Detailed sedimentological and chronostratigraphic data for the Lidernen Horizon are presented in Chapter 9. The Upper Kieselkalk Mb is always thinner than the Lower Kieselkalk and shows thicker bedding. The uppermost part is often formed by a coarse grained bioclastic grainstone rich in echinoderm debris. This horizon is a good marker for mapping and is informally called the *Echinoderm Breccia* (Funk, 1971). The overlying Altmann Schichten are again rich in glauconite, phosphatic nodules, belemnites, oysters and ammonites. Its thickness varies from several meters to tens of meters.

Two sections have been more extensively studied (Talegg and Pilatus) and may serve to further illustrate the stratigraphy and lithology of the late Valanginian and Hauterivian of the Helvetic Alps.

3.3.2 Talegg section

The Talegg section (Fig.3.8 and 3.10), located at the Walensee between Walenstadt and Amden (Switzerland) was first described by Heim (1916) and later

mentioned in the work of Funk (1971). The Talegg section belongs to a relatively deep thrust unit, the so called Mürtschen Nappe. The base of the section consists of about 40 meters of sandy bioclastic and peloidal packstones of the late Valanginian Betliskalk Formation. The contact with the overlying Kieselkalk Fm is sharp and conformable. The Gemsmättli Horizon is not present in this section and a hiatus is assumed between the Betliskalk Fm and the Kieselkalk Fm. The Lower Kieselkalk is made up of fine-bedded sandy wackestones. Bedding becomes progressively coarser and thicker up to the Lidernen Horizon. The top of the Lower Kieselkalk consists of several meters of coarse grained Lidernen Horizon consists of a glauconitic sandy limestone rich in echinoderm debris and belemnites. The Upper Kieselkalk shows generally much thicker bedding and transitions into the Echinoderm Breccia, that is several meters thick in the Talegg section. The Altmann Horizon shows an alternation of marly and glauconitic beds rich in pyrite nodules, belemnites and ammonites. The ammonites are however very poorly preserved and do not allow determination. Compared to the Pilatus section (see below) this section represents a more proximal setting (middle facies realm of Funk et al., 1993), probably inner shelf.



Figure 3.8 –
Location map for
Talegg section at
the border of the
Walensee close to
Amden
(Topographic map
of Switzerland 1:134
– Walensee.
Coordinates:
729010/222150)

3.3.3 Pilatus section

Funk (1969) took the section at the Pilatus mountain (Fig. 3.9 and 3.10), close to Lucerne (Switzerland), as the type section for the Helvetic Kieselkalk Fm. The Pilatus section is situated in the upper Helvetic Drusberg thrust sheet. The easy accessibility and

good exposure make this an ideal outcrop to study phosphoritic horizons of late early Valanginian and Hauterivian age. The base of the succession consists of the Gemsättli Horizon (1m thick) rich in late early and late Valanginian ammonites (Kuhn, 1997) and is conformably overlain by shales which grade upwards in thin bedded sandy limestones, alternating with centrimetric shaly interbeds. Upto the Lidernen Horizon, which divides the Kieselkalk in a lower and upper part, the limestone beds become progressively more massive and the top of the Lower Kieselkalk consists of several meters of coarse grained limestones rich in echinoderm debris. The Lidernen Horizon is a 90 cm glauconitic horizon with phosphatic nodules and has been dated with ammonites in other sections (see Chapter 9) to span the top of the *Nodosoplicatum* zone to the base of the *Ligatus* zone. The Upper Kieselkalk resembles greatly the Lower Kieselkalk, but lacks the 10 meters of shales at the base. It starts off with thin bedded sandy limestones that culminate in approximately 16 meters of massive bedded pure echinoderm breccias. The top of the section is bounded by the glauconitic and phosphatic beds of the Altmann Horizon. The Kieselkalk Fm. itself is extremely poor in any macro- and microfossils that allow direct dating. It has thusfar only been dated indirectly with the help of the phosphatic horizons that are marking its base, its middle and top and by lithologic correlation with other sections. We assume that the shales at the base of the Lower Kieselkalk are corresponding to the Marne Bleues d'Hauterive in the Swiss Jura, which belong to the early Hauterivian *Radiatus* zone. The Lower Kieselkalk would then correspond to the Pierre Jaune de Neuchâtel. Given the age of the Lidernen Horizon, the Lower Kieselkalk Fm would span the *Loryi* and part of the *Nodosoplicatum* zones, while the Upper Kieselkalk Fm would correspond to part of the *Ligatus*, the *Balearis* and lower part of the *Angulicostata* zones. What the equivalents of the Lidernen Horizon and Upper Kieselkalk Mb are in the Jura remains unclear.



Figure 3.9 –
Location map for
Pilatus section close
to Lucerne
(Topographic map
of Switzerland 1170
– Alpnach.
Coordinates:
661795 / 203550

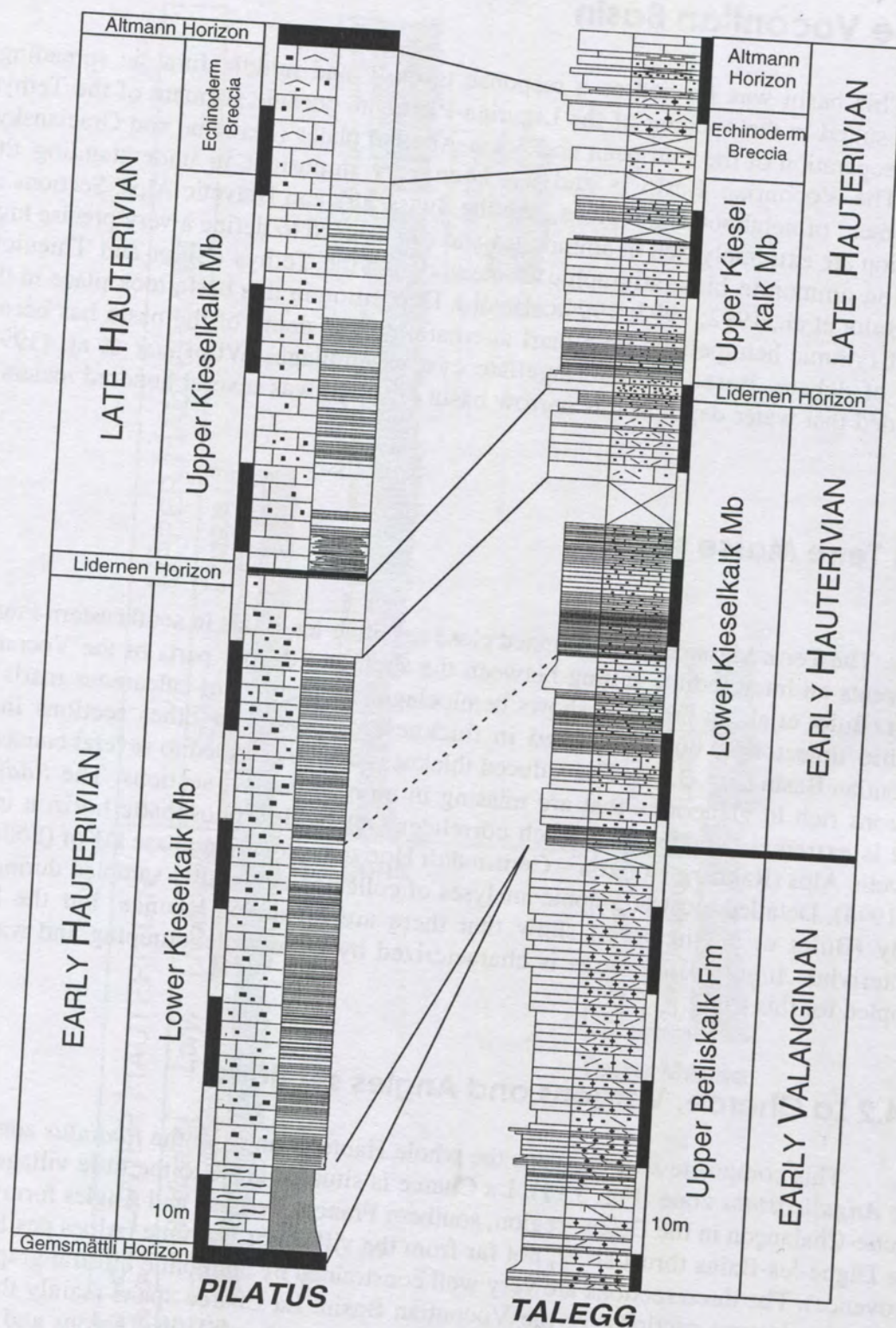


Figure 3. 10 – Litho- and chronostratigraphy for the Talegg and Pilatus sections. There is a large part missing in the Talegg section between the Upper Betliskalk and Kieselkalk.

3.4 The Vocontian Basin

This basin was formed as a response to early and middle Jurassic spreading, which resulted in the opening of the Ligurian-Piemonte oceanic segment of the Tethys and the separation of the European and Adria-Apulian plates (Lemoine and Graciansky, 1988). The Vocontian Basin is and has been very important in understanding the development of neighbouring regions, like the Swiss Jura and Helvetic Alps. Sections in this region are extremely rich in ammonites and can be used to define a very precise high resolution ammonite biostratigraphic framework for the Tethys (Bulot and Thieuloy, 1993; Bulot et al., 1992; 1993; 1994a; 1994b). Deposition in this basin took place in the form of rhythmic hemipelagic lime-marl alternations. The depth of the basin has been a matter of debate. Based on dinoflagellate cyst assemblages Wilpshaar et al. (1997) concluded that water depth in this narrow basin (150km) was several hundred meters at most.

3.4.1 Terre Masse section

The Terre Masse section, situated close to Digne-les-Bains in southeastern France, represents an intermediate setting between the shelf and deeper parts of the Vocontian Basin (Bulot et al., in prep.). It shows hemipelagic alternations of calcareous marls and micritic limestones, but is reduced in thickness compared to other sections in the Vocontian Basin (Fig. 3.11). The reduced thickness can be ascribed to several condensed horizons rich in glauconite that are missing in more expanded sections. The *Radiatus* zone is extremely condensed, which correlates well with a phosphatic horizon in the Helvetic Alps (Rahberg Horizon – Gemsmättli Horizon, drowning phase D1 of (Föllmi et al., 1994). Detailed biostratigraphic analyses of collected ammonites sampled during this study (Bulot et al., in prep.) show that there are no major lacunae, but the latest Hauterivian *Angulicostata* zone is characterized by large-scale slumping and was not sampled for this study.

3.4.2 La Charce, Vergons and Angles sections

This composite section spans the whole Hauterivian from the *Radiatus* zone upto the *Angulicostata* zone (Fig. 3.11). La Charce is situated close to the little village of La Motte-Chalançon in the Drôme region, southern France. Vergons and Angles form part of the Digne-les-Bains thrust sheet, not far from the village of Barrême (Alpes des Hautes-Provence). The three sections are very well constrained by ammonite biostratigraphy and serve as reference sections for the Vocontian Basin. La Charce spans mainly the early Hauterivian (*Radiatus*, *Loryi* and *Nodosoplicatum* zones), while in Vergons and Angles the late Hauterivian (*Sayni*, *Ligatus*, *Balearis* and *Angulicostata* zones) is exposed. The lithology consists of alternating hemipelagic micritic limestones and calcareous marls.

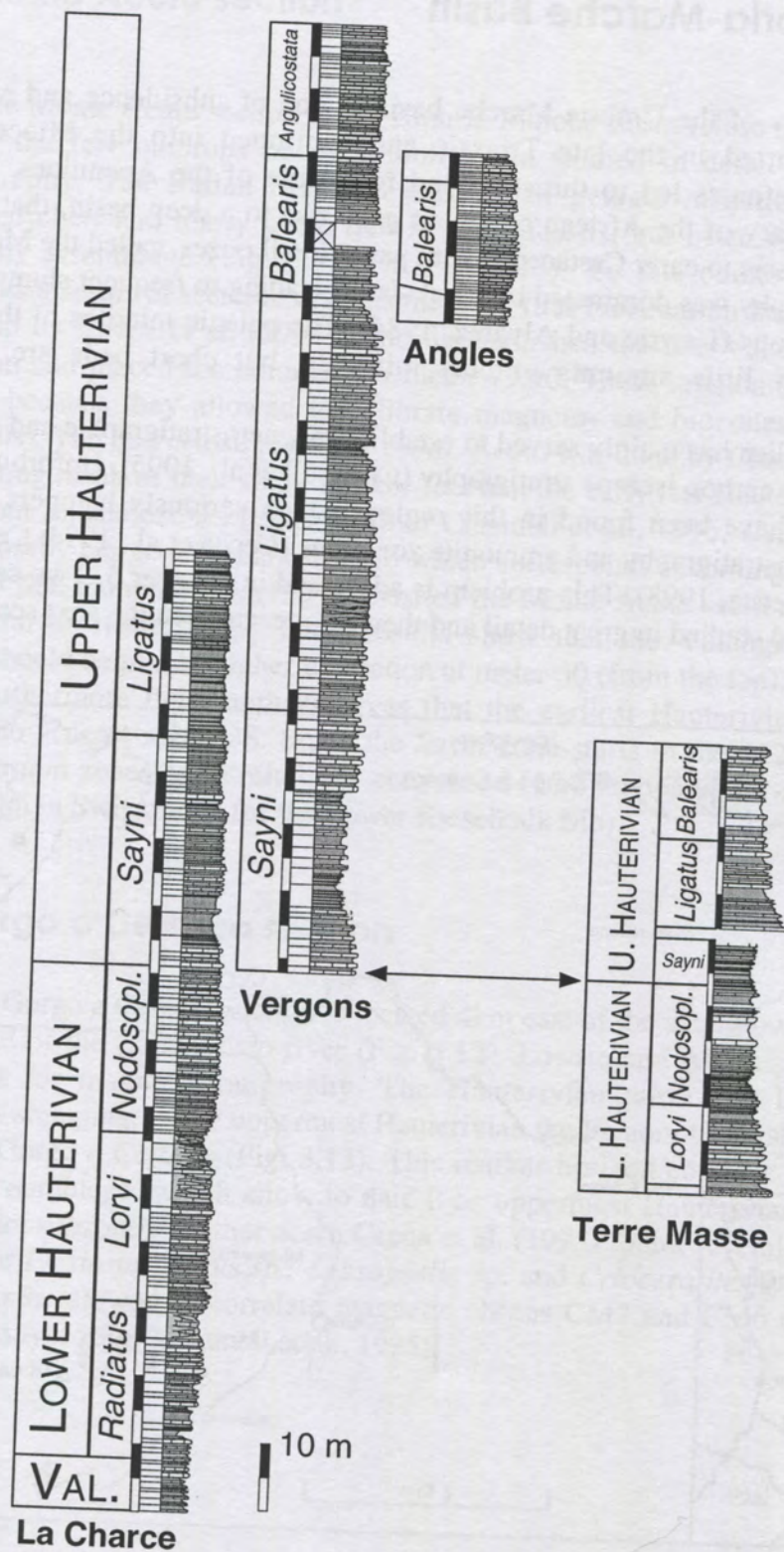


Figure 3. 11- Several key sections for the Hauterivian from the Vocontian Basin

3.5 The Umbria-Marche Basin

The history of the Umbria-Marche basin is one of subsidence and extensional tectonics that started in the late Triassic and continued into the Miocene, when compressional tectonics led to thrusting and formation of the Apennines. Rifting of Adria, a promontory of the African continent gave rise to a deep basin, that was filled from the late Jurassic to early Cretaceous with nannofossil oozes, called the Maiolica Fm. The paleotopography was dominated by block-faults leading to frequent slumping during the early Cretaceous (Lowrie and Alvarez, 1984). The pelagic micrites of the Maiolica Fm contain very little amounts of clay minerals, but chert beds are frequently intercalated.

The Maiolica has mainly served to establish magnetostratigraphic and nannofossil zonations and for carbon isotope stratigraphy (Channell et al., 1995). Unfortunately, very few ammonites have been found in this region, which seriously hampers correlation between magnetostratigraphy and ammonite zonations (Cecca et al., 1994; Cecca, 1995a; Cecca, 1995b; Cecca, 1998). This problem is addressed in Chapter 5. Two sections have been sampled and studied in great detail and they are presented in the next section.

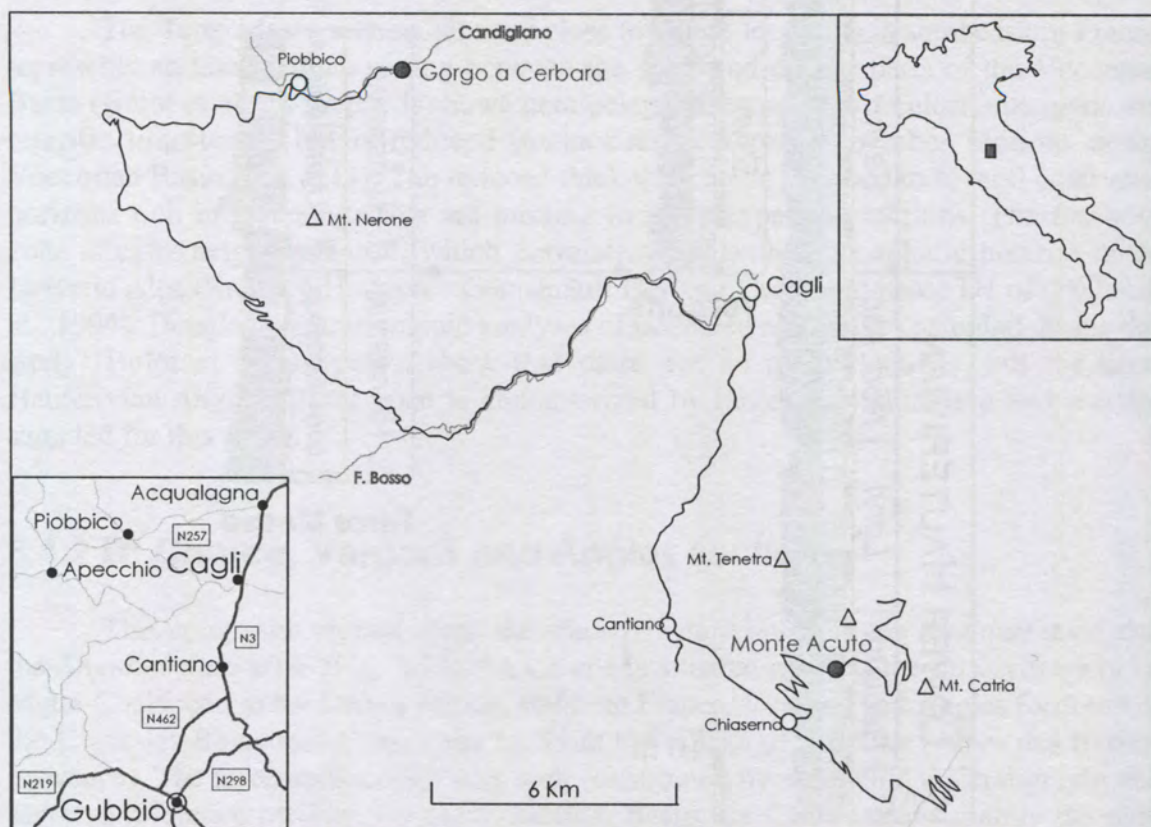


Figure 3.12 – Location maps for Italian Gorgo a Cerbara and Mt. Acuto sections

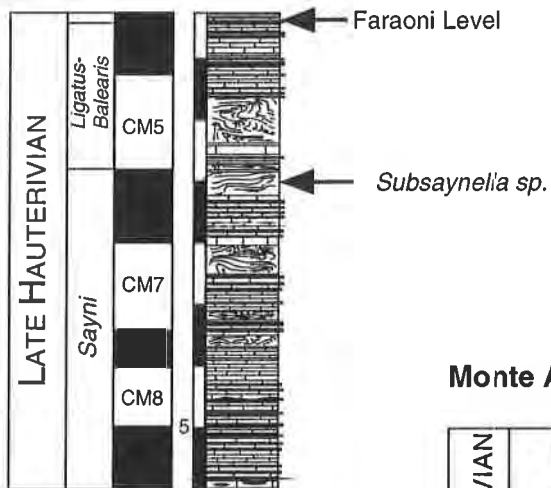
3.5.1 Monte Acuto section

The Monte Acuto section in the Umbria-Marche Basin (close to Chiaserna, Italy) is one of the few outcrops in the Maiolica Fm studied in detail for its ammonite biostratigraphy. The Italian Maiolica consists of pelagic micritic limestones with intercalated chert and marly beds, rich in nannofossils, but often with a depauperate macrofossil assemblage (Fig. 3.12 and Fig. 3.13). To this comes some diagenetic overprint as a result of tectonic displacement. A first biozonation based on ammonites was put up by Cecca et al. (1995), who distinguished the late Valanginian and early Hauterivian and placed the boundary at meter 79.90. These ammonite finds were very important because they allowed to calibrate magneto- and biozones (ammonites and nannofossils). The magnetostratigraphy of Mt. Acuto was done by Channell et al. (1995). An interesting result of their study was the fact that the early late Hauterivian *Sayni* zone spanned four magnetozones (CM9-CM6 in Channell et al., 1995, also after correlation with the closeby Gorgo a Cerbara section) which corresponds according to Channell et al. (1995) to 3 Ma. Faraoni et al. (1997) revisited the Monte Acuto section and added more detail to the biostratigraphy. Their results show that the Valanginian-Hauterivian boundary should be placed higher up section at meter 50 (from the top) of Channell et al. (1995). Furthermore these authors stress that the earliest Hauterivian *Radiatus* zone extends upto at least meter 38. Since the *Sayni* zone starts in meter 22, the *Loryi* and *Nodosoplicatum* zones seem relatively condensed (16m compared to -maximum values of- 400-600m in Switzerland for the Lower Kieselkalk Mb).

3.5.2 Gorgo a Cerbara section

The Gorgo a Cerbara section is located 4km east of the small town of Piobbico in the river bed of the Candigliano river (Fig. 3.12). Lowrie and Alvarez (1984) sampled this section for magnetostratigraphy. The Hauterivian portion is however mostly disturbed by slumping. In the uppermost Hauterivian the Faraoni black shale level is well exposed at Gorgo a Cerbara (Fig. 3.13). This marker horizon contains a relatively rich ammonite assemblage, which allow to date it as uppermost Hauterivian *Angulicostata* zone (*Catulloi* subzone). Further down Cecca et al. (1995) found several more important markers, like *Plesiospitidiscus* sp., *Subsaynella* sp. and *Crioceratites* gr. *duvalii*. These ammonite finds allowed to correlate magnetic chrons CM7 and CM6 to the early late Hauterivian *Sayni* zone (Channell et al., 1995).

Gorgo a Cerbara section



Monte Acuto section

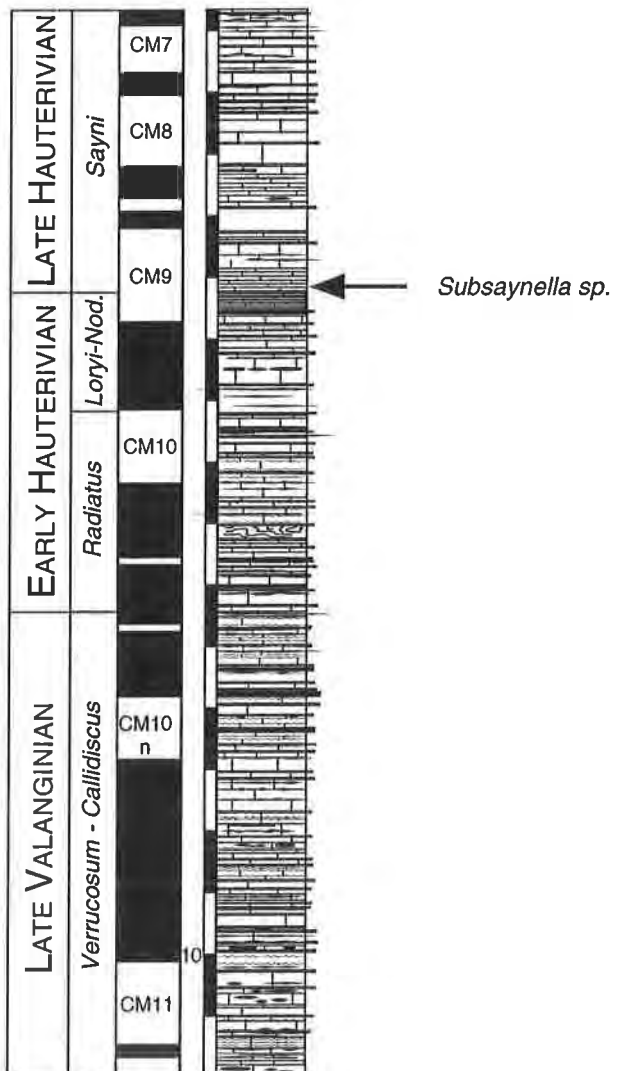


Figure 3. 13 – Monte Acuto and Gorgo a Cerbara sections. Ammonite stratigraphy for Monte Acuto after Cecca et al. (1995) and Faraoni et al. (1997). Ammonite stratigraphy for Gorgo a Cerbara after Cecca et al. (1995). Magnetostratigraphy after Channell et al. (1995).

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Paleoceanographic changes during the early Cretaceous (Valanginian-Hauterivian): evidence from oxygen and carbon stable isotopes

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Abstract

We investigated Valanginian-Hauterivian bulk rock and belemnite samples from Vocontian Basin sections in southeastern France for their stable carbon and oxygen isotope signature. Firstly, because these sections permit calibration with high-resolution biostratigraphy based on ammonites and secondly because detailed isotope studies for the Hauterivian are lacking. The results show that $\delta^{13}\text{C}$ values for bulk rock decrease during the late Valanginian-early Hauterivian with 1‰ and increase again during the late Hauterivian with 1‰. The $\delta^{18}\text{O}$ signal for bulk rock samples is mostly disturbed by diagenesis. The belemnites show carbon and oxygen isotope values that are lower and higher than bulk rock samples respectively. We explain this as the result of the belemnites recording a deeper water signal with lighter $\delta^{13}\text{C}$ values and heavier $\delta^{18}\text{O}$ values, implicating colder water at greater depth.

The overall preservation of the belemnites is very good and permits the construction of a paleo-temperature trend. This trend shows warm deeper water temperatures during the late early Valanginian (15°C) and progressively cooler temperatures during the late Valanginian and early Hauterivian (11°C). During the late Hauterivian temperatures increase again (13°C). We relate this cooling trend for deeper water to a 2nd order sea level rise, which allowed for the exchange of cold Boreal and warm Tethyan watermasses. The influx of cold nutrient rich water had a profound effect on carbonate producing biota along the northern margin of the Tethys during the Hauterivian leading to prolonged phases of condensation and platform destruction. During the early Hauterivian the carbonate system along the northern Tethyan margin shifted into a “green water” mode of carbonate production. High rates of carbonate production under mesotrophic conditions, also observed in other parts of the world, meant that the global carbon cycle became buffered shown by the stable trends in carbon isotopes.

4.1 Introduction

During the late Jurassic and early Cretaceous, a carbonate platform of considerable extent developed along the northern Tethyan margin [1-2]. The evolution of this platform system was punctuated by several phases of platform drowning, most notably during the late early Valanginian to early Hauterivian, and the Aptian. Within the sections preserved in the Helvetic Zone of the northern Alps, the drowning phases are documented by erosional surfaces, hiati, and condensed glauconitic and phosphatic beds, which have been described in numerous publications [1-9].

The large drowning unconformities formed during the late early Valanginian to early Hauterivian (D1 in [2]), the late early to early late Aptian (D4), and latestmost Aptian to earliest Albian (D5) correspond in time to major positive excursions in the stable carbon isotope record [10-11]. This correlation was used to propose a model for the development of the drowning unconformities, which includes major changes in the global carbon budget. In this model, the formation of the large flood basalt provinces at Parí, Kerguelen, and especially Ontong Java is inferred to have led to major increases in atmospheric CO₂ during the Valanginian and Aptian, thereby triggering a row of negative feedback mechanisms, which led to a decrease in atmospheric CO₂ contents. These mechanisms include increases in rates of continental biogeochemical weathering, mobilisation of nutrients and especially phosphorus, productivity and sedimentary burial of organic matter, whereas the rates of carbonate production were decreased leading to phases of widespread platform drowning and phosphogenesis [2, 11].

Since the publication of this model, new age models have been developed for several key areas and further detailed studies have been accomplished in the area of platform deposition [8, 12]. During these studies, the following subjects were shown to be critical and in need of further elaboration:

1) Correlation between the helvetic realm and other regions

Whereas the drowning unconformities are well expressed in the Helvetic realm, they are less well traceable in more proximal areas, such as the Jura Mountains in western Switzerland and eastern France, and more distal areas, such as the Vocontian Trough. This is due to the prevalence of erosional processes during the drowning phases in the proximal areas and to the deposition of more complete, hemipelagic sections in the distal areas, beyond the platform margin (e.g., [1, 8]). Correlation of these sections with those of the Helvetic realm is, for these reasons, ambiguous in most cases. To this comes that the proximal sections are partly poorly dated, due to the scarcity of biostratigraphic markers.

2) Isotope record for the Hauterivian

The carbon isotope data for the Hauterivian, as shown in Föllmi et al. [2] were preliminary and based on sparse and unpublished biostratigraphical records of the Apennine region. Age control was poor and in need of corroboration. The Hauterivian is crucial, however, because of the presence of two drowning unconformities in the late early Hauterivian (D2) and at the Hauterivian-Barremian boundary (D3) in the Helvetic realm, in addition to D1.

3) Correlations of the carbon isotope records and drowning unconformities in the Hauterivian and Albian

Whereas the three main drowning phases in the late early Valanginian – early Hauterivian, early to early late Aptian, and latestmost Aptian to earliest Albian (D1, D4, and D5) correlate with pronounced positive excursions in the stable carbon isotope

record, this relation is less clear for the drowning phases in the late early Hauterivian and at the Hauterivian-Barremian boundary (D2 and D3), because of the above mentioned changes in age assignments in the sections of the Apennines. Also condensed phosphatic beds of Albian and early Cenomanian age, which developed in the Helvetic realm after the final demise of the carbonate platform (at D5) do not show clear correlations to changes in the carbon isotope record.

It is for these reasons that we decided to establish a detailed stable carbon and oxygen isotope record for the Hauterivian, that is independently calibrated by ammonite stratigraphy. This record serves as a reference record, which allows us to better correlate the sections from the above-mentioned regions, as well as to trace the evolution of the drowning unconformities along shelf transects. Furthermore, the detailed isotope record shown here also allows for a comparison with drowning phases D2 and D3. It becomes clear from this comparison that this correlation for D2 and D3 and the stable carbon isotope record is less straightforward as for D1, D4 and D5. We have taken this into consideration and give here a modified model of early Cretaceous platform drowning that accommodates this discrepancy.

4.2 Geological setting

4.2.1 The Hauterivian

The sections from which we sampled material for stable carbon and oxygen isotope analyses are exposed in southeastern France, in the region near Digne-les-Bains (Alpes de Haute Provence) and Nyons (Drôme, Fig. 1c). The sediments sampled for this stable isotope study were deposited along the western margin of the Tethys in a narrow inlet, known as the Vocontian Basin (Figs. 1a and 1b).

The lithology consists of alternations of hemipelagic calcareous marlstones and micritic limestones. In addition to rock samples belemnites were also systematically sampled in order to obtain alternative isotope records from the same sections. Three of the four sections (La Charce, Vergons and Angles) are basinal sections (thickness of 200m), while the fourth one (Terre Masse) is close to the Provençal Platform margin and is therefore less thick (70m). The basinal sections form a composite section spanning the entire Hauterivian.

From a structural point of view La Charce is considered to be autochthonous, Terre Masse parautochthonous and Vergons and Angles are allochthonous. The last two suffered tectonic transport by Alpine orogeny.

The biostratigraphy of all four sections is very well constrained by ammonites and given in Bulot et al. [13] and permits high-resolution calibration of the isotope record. It is for this reason that La Charce, Vergons and Angles have been selected as reference sections for the Hauterivian, Barremian and Valanginian, respectively.

4.2.2 The Valanginian

Hennig et al. [12] made a detailed study of the bulk rock stable isotope signal of Valanginian sediments of southern France. In addition we sampled belemnites from several Valanginian sections for oxygen isotope measurements in order to compare the evolution of this record with the carbon isotope record for bulk rock samples. The section of Barret-le-Bas provided belemnites from the lowermost Valanginian

Pertransiens Zone, while the section of Bourdeaux spans the mid-Valanginian. Some belemnites of late Valanginian age were sampled at La Charce.

4.3 Methods

Stable carbon and oxygen isotope analyses were performed on bulk rock samples from the limestone intervals and on belemnites mostly from the marly intervals for all four sections. The whole rock samples were taken from fresh outcrops; powder was drilled out of the micritic matrix, avoiding bioturbation fabrics. The belemnites were cleaned in 1% HCl and cut along the alveolic line if their size allowed for this. Powder was drilled avoiding the outside laminae and the alveolus, because it has been shown that these parts of the belemnite rostrum are prone to diagenesis [14, 15]. Some belemnites were too small and were crushed entirely.

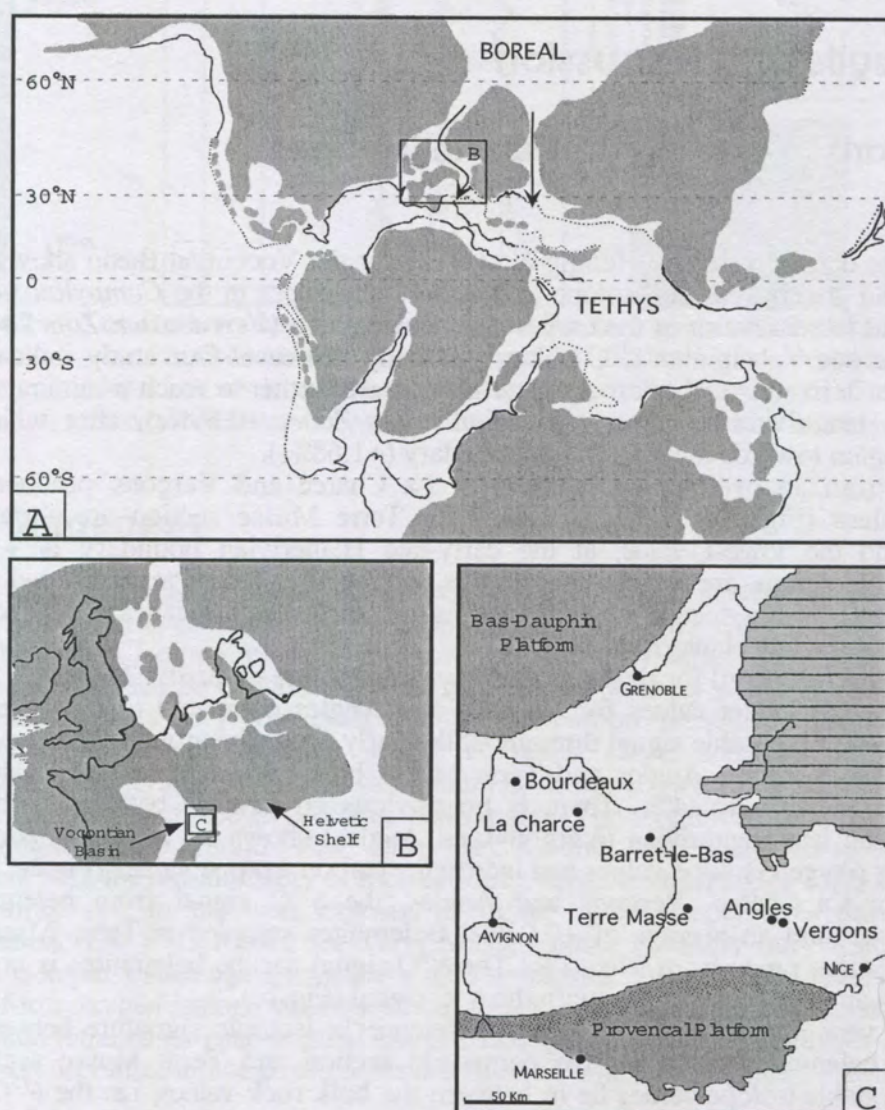


Figure 4.1. a) Paleogeography for the Hauterivian after McSotay [47]; b) Paleogeography for western Europe during the Hauterivian after Michael [37]; c) Paleogeography for the Vocontian Basin during the Hauterivian-Barremian with sample sites.

Approximately 10 mg of powder was reacted with 100% H_3PO_4 at 90°C in an online-automated preparation system. The resulting CO_2 was analyzed at the Stable Isotope Laboratory of the University of Bern with a VG Prism II ratio mass spectrometer. Duplicate measurements proved better than 0.1‰ for the oxygen isotope analyses and better than 0.05‰ for the carbon isotope analyses. The results are expressed relative to the PDB standard.

All belemnites were selected for trace element analyses to assess their diagenetic state, but in some cases little material was left over to perform this analysis. Approximately 1 g of a crushed part of a belemnite was attacked with 1N HCl for 20 minutes at 80°C. The solution was filtered to separate the insoluble residue from the soluble fraction. The soluble fraction was measured for its Mn, Mg, Fe and Sr contents using a Perkin Elmer 5100 PC Atomic Absorption Spectrophotometer (AAS). Precision of replicate analyses was better than 10% for all elements.

Furthermore the texture of some bulk rock and belemnite samples was investigated using a scanning electron microscope (SEM).

4.4 Results and Discussion

4.4.1 Carbon and oxygen stable isotopes

The data obtained by Hennig et al. [12] for the Vocontian Basin show that the Valanginian positive carbon isotope excursion commences in the *Campylotoxus* Zone and reaches its maximum in the earliest late Valanginian (*Verrucosum* Zone, +2.5‰). During the late Valanginian $\delta^{13}\text{C}$ values gradually decrease. Our study indicates that $\delta^{13}\text{C}$ values derived from bulk rock material decrease further to reach a minimum at the early-late Hauterivian boundary (*Nodosoplicatum* Zone, +0.59‰), after which they increase again towards the Barremian boundary (+1.68‰).

Samples from an overlapping interval for La Charce and Vergons produced very similar values (Fig.2a). The $\delta^{13}\text{C}$ values for Terre Masse section are about 0.5‰ heavier and the lowest value, at the early-late Hauterivian boundary is +1.01‰. Although variations are very small in this section, the same general trend can be distinguished, with a decreasing trend during the early Hauterivian and an increasing trend during the late Hauterivian (Fig.2b).

The $\delta^{18}\text{O}$ record for bulk rock displays much more diversity. There is a striking change towards lighter values for Vergons and Angles compared to La Charce. The latter shows a very stable signal throughout the early Hauterivian with values averaging around -1‰. Vergons, Angles and Terre Masse bulk rock samples have values that range from -2‰ to -4‰. There is no obvious co-variance between carbon and oxygen. The late Hauterivian (Vergons and Angles) shows an inverse relation, with decreasing oxygen isotope values and increasing carbon isotope values (Fig.2a, b).

For La Charce, Vergons and Angles, the $\delta^{13}\text{C}$ signal from belemnites is scattering around an average of +0.01‰. Belemnites sampled at Terre Masse have $\delta^{13}\text{C}$ values that range from 0 to +1‰. The $\delta^{18}\text{O}$ signal for the belemnites is noisy, but there is no apparent co-variance with the $\delta^{13}\text{C}$ signal (Fig.2c).

A very interesting result is the difference in isotopic signature between bulk rock and belemnites. Both for the composite section and Terre Masse section the belemnite stable isotope values lie in between the bulk rock values, i.e. the $\delta^{13}\text{C}$ values are lighter for the belemnites, while the $\delta^{18}\text{O}$ values are heavier. A systematic diagenetic offset can be excluded as discussed in the subsequent text.

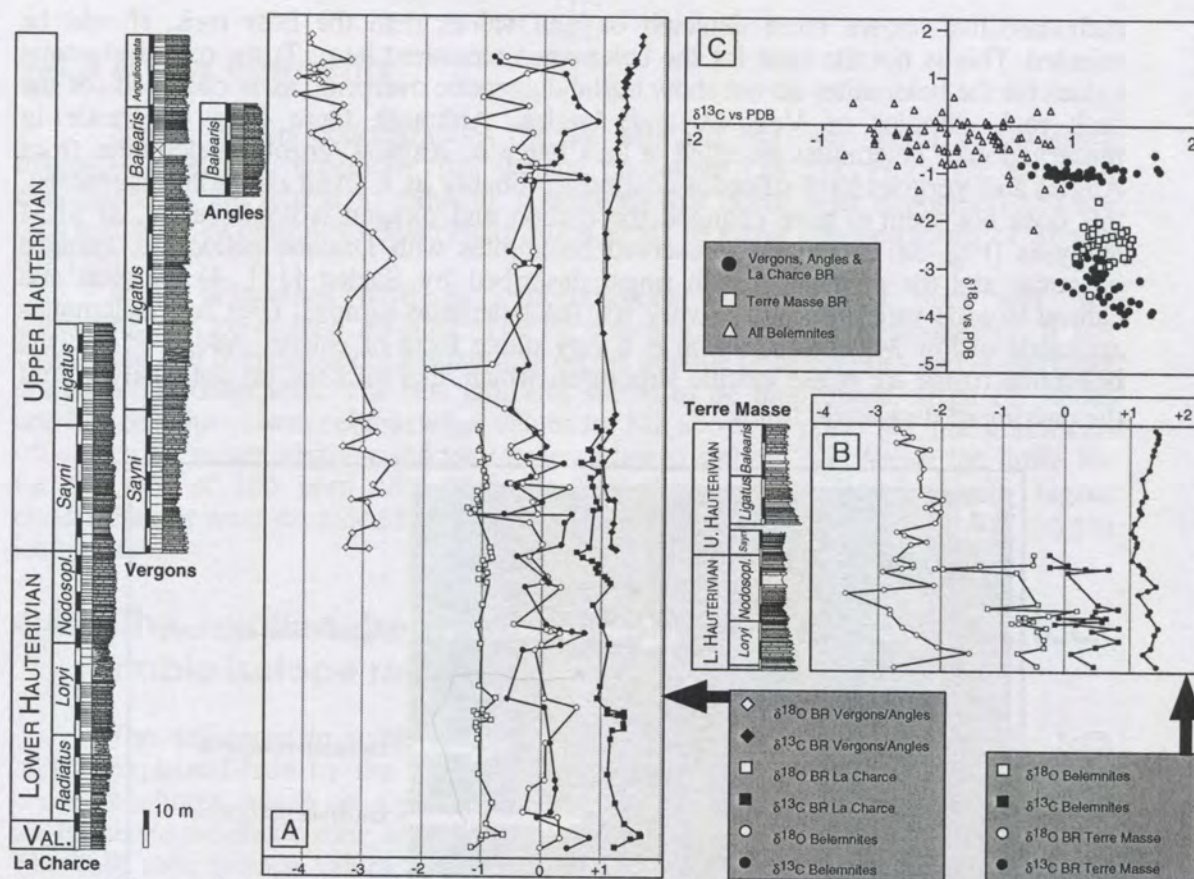


Figure 4.2

a) Carbon and oxygen isotopes for bulk rock and belemnites from La Charce, Angles and Vergons; b) Carbon and oxygen isotopes for bulk rock and belemnites from Terre Masse; c) Crossplot of oxygen versus carbon for different materials and sample locations.

4.4.2 Diagenesis

The advantage of bulk rock material over individual skeletal elements is the average value that is obtained and the smoothing of vital and early diagenetic effects [16]. The carbon isotope record is rather robust and only affected by later stages of diagenesis. This can be explained by the fact that the amount of dissolved carbon in diagenetic fluids is very low compared to the carbon present in the carbonates. Adversely, the oxygen isotopic signal is much more sensitive to diagenetic recrystallization during burial. This last feature is clearly shown from our data from La Charce compared to those of Vergons and Angles. The oxygen isotope data from La Charce show values around -1‰, while Vergons and Angles around -3‰. This is consistent with the burial history of the sections. Vergons and Angles form part of the Digne thrust system and were exposed to higher burial temperatures during alpine deformation. The $\delta^{18}\text{O}$ record for Terre Masse shows probably only mildly altered oxygen isotopic values again consistent with its tectonic history. The relatively heavy and uniform oxygen isotope values for bulk rock samples from La Charce suggest that this section retained its near-original oxygen isotopic signal. SEM analyses show well preserved coccoliths, although the pores are filled in with blocky micro-sparite (Fig 3b and c).

The well preserved nature of the belemnites used in this study is inferred from four observations (see also Table 1): 1) the oxygen and carbon isotope values for the belemnites differ from the bulk rock values in that the carbon isotopes are lighter and the oxygen isotopes heavier than the bulk rock values. This is consistent for the Terre Masse as well as the composite section. According to Haggerty et al. [17] skeletal

carbonate that shows more depleted oxygen values than the host rock, should be rejected. This is not the case for the belemnites measured here. 2) the oxygen isotope values for the belemnites do not show burial diagenetic overprint, as is observed for the bulk rock samples of Vergons and Angles. Although there is a difference in preservation of belemnites sampled at La Charce or Angles/Vergons (belemnites from Angles and Vergons have siliceous coatings, probably as a result of burial diagenesis), this does not seem to have changed the carbon and oxygen isotopic ratios. 3) SEM analyses (Fig. 3a) show well preserved belemnites with laminae pellucidae, laminae obscurae and the original growth rings, described by Saelen [14]. 4) Oxygen and carbon isotope values do not co-vary for the belemnite samples (Fig. 2c). Belemnites are made of low Mg-calcite, which is a very stable form of calcite. Added to that the belemnite rostra are dense calcitic structures, which, like micrites, do not easily permit the passing of diagenetic fluids.

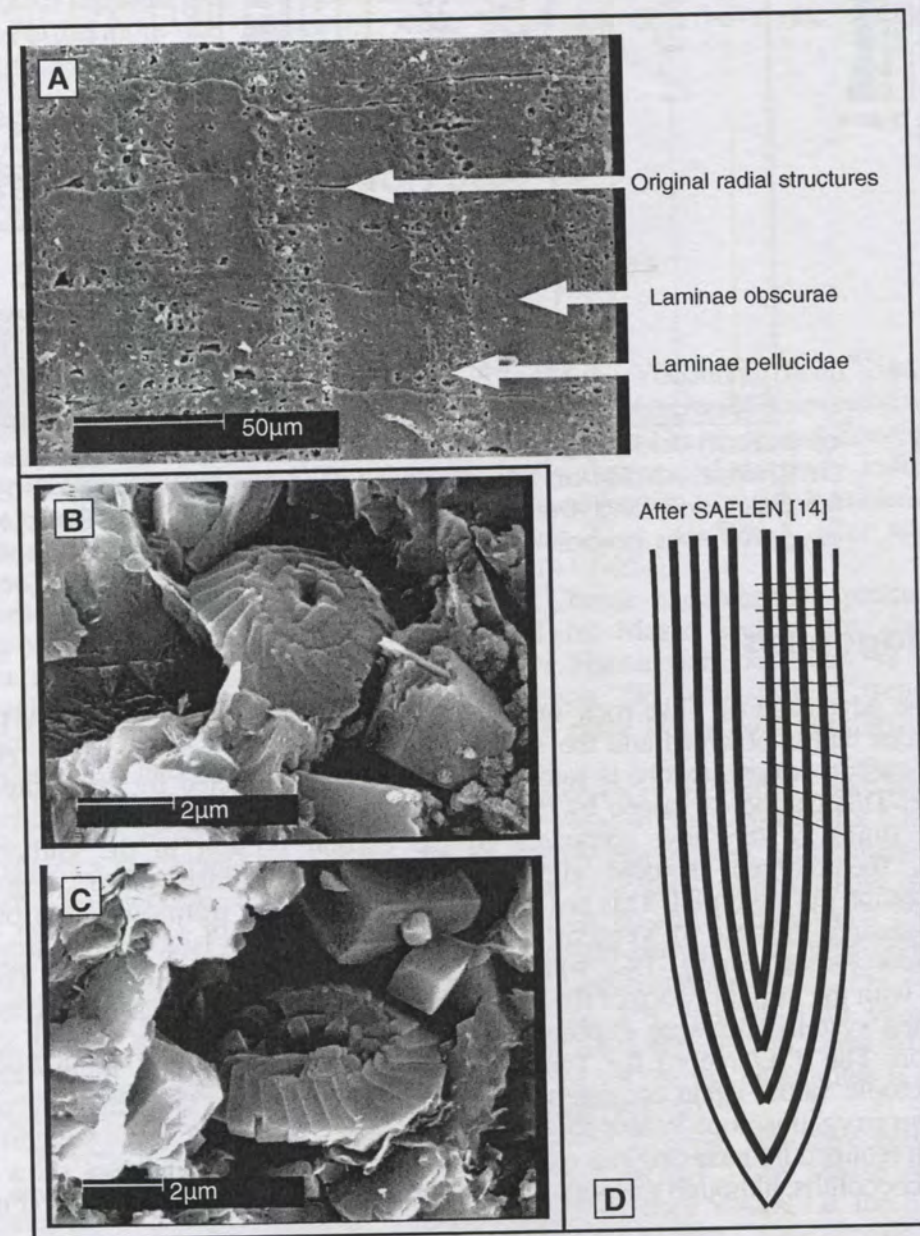


Figure 4.3

a) SEM picture of belemnite rostrum; b) SEM picture of bulk rock sample showing well preserved coccolith with minor overgrowths; c) As in Figure 3b; d) Schematic representation of belemnite rostrum after Saelen [14]

4.4.3 Minor elements

Minor element concentrations (Sr, Fe, Mn and Mg) are useful in assessing diagenetic overprint, especially for skeletal carbonate [18-21]. High Fe and Mn concentrations are related to reducing conditions that occur after deposition and are thus indicative of diagenesis. Recrystallization tends to lower concentrations of Sr and Mg [18].

Most belemnites have Sr concentrations around 1100 ppm and Mn concentrations lower than 30 ppm. The Fe concentration varies considerably. It has been noted that iron can occur as stainings on the outside of belemnites and is therefore not related to diagenesis. The best indicator seems to be manganese. High Fe values and low Sr values always characterize values for Mn above 30 ppm. The maximum cut-off values are rather arbitrary and vary from author to author [22]. We set the limits for Fe and Mn at 300 ppm and 30 ppm respectively and belemnites with higher concentrations were excluded from the temperature trends calculated from the oxygen isotope data.

4.4.4 The relation between the belemnite and bulk rock stable isotope records

The difference in stable isotope values between the belemnites and the bulk rock is explained here by the different ecological habitats of the belemnites and the coccolithophores, which are a primary constituent of the bulk rock. Coccolithophores are limited to the photic zone, and probably do not live deeper than 30-50 meters [23]. The bulk rock isotope values are thus assumed to represent near-sea surface water values.

Belemnites were nektonic animals that preyed on small fish, crustaceans and ammonites [24]. It is likely that belemnites lived primarily on the shelf, in areas of abundant food. The ecology of belemnites might be comparable to the recent squid *Loligo opalescens* inhabits water depths of 120-330 m, but moves into shallower water during the night to feed and mate [24]. Anderson et al. [25] used the oxygen isotope record for belemnites and ammonites to show that belemnites inhabited colder bottom waters than the ammonites. Belemnites were thus primarily nektobenthic. Price and Sellwood [20] concluded that belemnites might have inhabited colder bottom waters, based on different paleo-temperatures for reefs and belemnites.

Our results are analogous to the data from Anderson et al. [25] and we interpret the difference in the isotopic record between the bulk rock and the belemnites to reflect different habitats for the belemnites and the coccolithophorids. The lighter carbon isotope values for the belemnites are explained by a net transport of ^{12}C to deeper water lowering the $\delta^{13}\text{C}$ signal measured from the belemnites. Considering the oxygen isotopes for the belemnites, the heavier values represent colder water temperatures at greater depth.

4.4.5 Paleo-environmental implications of the belemnite isotopic record

Having assessed diagenetic overprint we put forward a paleo-ecological model that explains the isotope results obtained from the belemnites. We can use the oxygen isotope record to calculate paleo-temperatures and construct a paleo-temperature trend. We used the equation of Anderson and Arthur [26]:

$$T(^{\circ}\text{C}) = 16.0 - 4.14 (\delta_{\text{c}} - \delta_{\text{w}}) + 0.13 (\delta_{\text{c}} - \delta_{\text{w}})^2$$
and assumed an ice-free world ($\delta_{\text{w}} = -1.2\text{‰ PDB}$, [27]). For these calculations we only used belemnites that met the criteria for Fe and Mn (see Table 1) and calculated the averages per ammonite zone. This was mainly done to compare with other temperature

records, like shown below. The Tethyan paleo-temperature curve of Figure 4 shows relatively warm temperatures for deeper water during the latest early Valanginian (15°C) and a decrease in temperature during the late Valanginian and earliest Hauterivian (11°C). Temperature increases again gradually during the late Hauterivian (13°C). Temperature increases again gradually during the late Hauterivian (13°C).

Taking into account the paleo-geography of the northwestern margin of the Tethys during the Hauterivian (30°-35°N), these temperatures are not unrealistic. Furthermore, our temperatures correspond well with the paleo-temperatures calculated for the Hauterivian by [28-30], which range from 11°C to 15°C for benthic foraminifera and belemnites. It is difficult to compare our results with previous studies, because the time resolution in older work is mostly low. Podlaha [31] provided reliable oxygen isotope data obtained from belemnites sampled in the Germanic Basin. His data set is calibrated with the Boreal ammonite zonation.

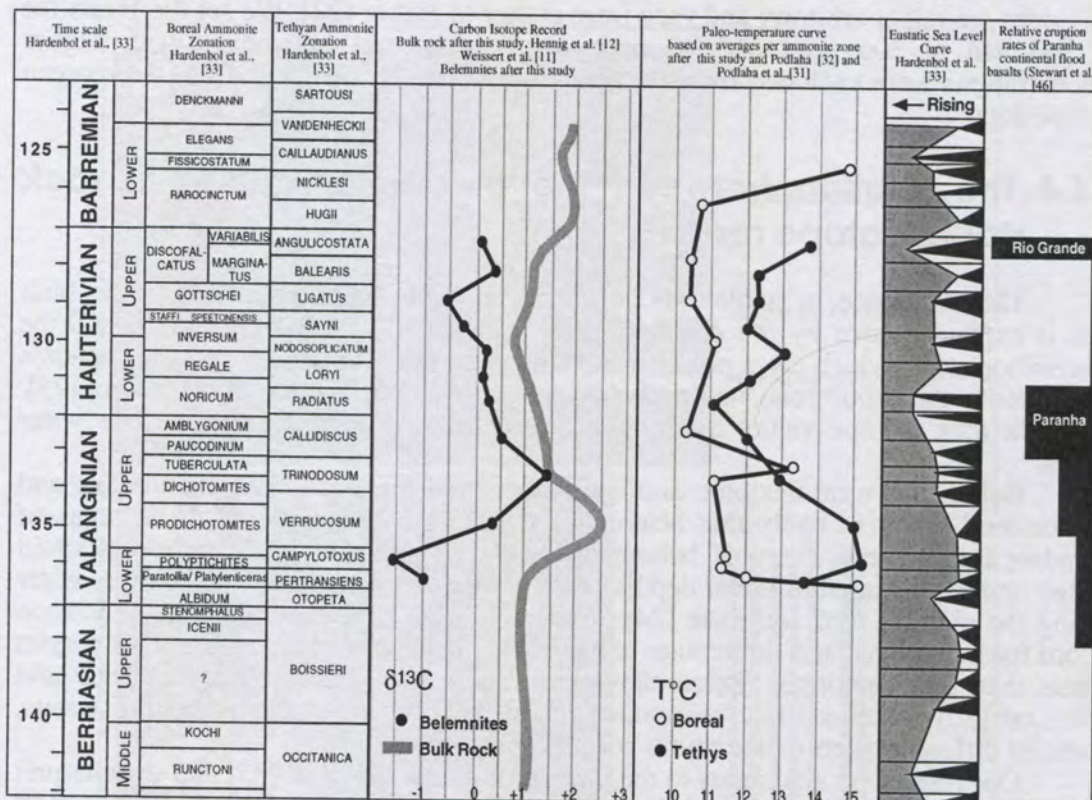


Figure 4.4 Diagram showing temperature trends, carbon isotope records and sea level curve against Boreal and Tethyan biostratigraphic zonations. The sea level curve is from Hardenbol et al. [33].

The temperature curve derived from Podlaha and Podlaha et al. [31,32] does not match the Tethyan curve (Fig.4). The two curves are sometimes diverging, sometimes converging. The Boreal curve shows cooling during the earliest Valanginian, in contrast with the warming trend in the Tethyan curve. Ditchfield [22] also obtained cool temperatures for the early Valanginian from northern high latitudes (Svalbard Basin). During the late Valanginian and early Hauterivian the Boreal curve shows warming again opposed to cooling in the Tethys. Only during the late early Hauterivian and early late Hauterivian the two realms are in the same temperature range, before the curves slightly diverge again in the late Hauterivian. The Barremian appears to be characterized by warming in both realms.

In our opinion the oxygen isotope record is mainly reflecting paleoceanographic changes and the mixing of Boreal and Tethyan water masses. The diverging trend in temperatures during the early Valanginian is coincident with an

eustatic sea level fall, separating the two realms. Whether this sea level low was related to polar ice caps during mid-Valanginian times remains to be seen, but increased temperature gradients from pole to equator during such a glacial period could also be an explanation for the strong difference between the Boreal and the Tethys. The absence of Boreal fauna elements in the Tethys and the extreme provinciality observed in both realms at that time indicate that the connections were closed.

Converging temperature trends during the latest Valanginian, i.e. cooling in the Tethys and warming in the Boreal are contemporaneous with 2nd order eustatic sea level rise [33]. Connections between the Boreal and Tethyan realms were re-established during the late Valanginian and persisted during the early Hauterivian leading to the mixing of cold and warm waters and allowing Boreal fauna, such as ammonites to migrate southwards (Fig.1). During the early Hauterivian the temperatures from both realms are the same, coinciding with general sea level high stand and therefore active exchange of water masses. For the late Hauterivian the temperature curves diverge again, as the connections between the two realms are being closed. The latest Hauterivian to early Barremian temperature increase might correspond to climatic warming [34].

Our data confirm the data and interpretations of Price et al. [35] who observed the same cool water temperatures for the early Hauterivian using oxygen isotope data obtained from belemnites from Speeton (England).

4.4.6 The $\delta^{13}\text{C}$ record and platform drowning

Föllmi et al.[2], Lini et al.[10] and Weissert et al. [11] were the first to recognize that the Valanginian and Aptian positive $\delta^{13}\text{C}$ shifts relate to phases of platform drowning on the Helvetic Shelf and other regions. In their model eutrophication as a result of increased weathering and run-off is the causal mechanism for these platform-drowning events. Increased weathering and run-off are thought to be the product of greenhouse climate conditions that were initiated by flood basalt volcanism and related increases in atmospheric CO_2 [2, 11].

One of the major difficulties with this model is that during the Hauterivian two more phases of platform drowning are not mirrored by positive carbon isotope excursions, but rather by a decreasing to stable trend (Fig.5). The same goes for platform drowning events in the Albian. Apparently another model has to be invoked to explain these drowning events.

How does the carbon isotope record relate to sedimentological changes observed worldwide and in particular to carbonate platforms of the western Tethys during the Hauterivian? The trend to lower $\delta^{13}\text{C}$ values during the late Valanginian to early Hauterivian indicates that carbonate carbon production and burial (a sink for ^{13}C) is prevailing over organic carbon burial. The Hauterivian appears to have been a period of high carbonate carbon production and of high sedimentation rates in general. In some parts of the Swiss Alps (Alvier region) the Lower Hauterivian carbonate succession attains a thickness of 500m [36] and might have been deposited in less than 1 Ma. Ecological change from high diversity oligotrophic to low diversity mesotrophic carbonate producing communities could explain the high carbonate production rates observed in the Swiss Alps. Carbonate platforms developed from a 'blue water facies' with corals and ooids into a 'green water facies' characterized by sponges, crinoids and bryozoans [2]. The Vocontian Basin in the Vercors region (France) contains Hauterivian limestone-marl alternations of 2km thick deposited in 5 Ma [33], giving an average sedimentation rate of 0.4m/Ka for hemipelagic sediments. Michael [37] reports extremely high carbonate deposition rates from the Lower Saxony Basin during the earliest Hauterivian. Ogg et al. [38] noted accelerated carbonate accumulation rates for the Hauterivian based on DSDP sites in the equatorial Pacific.

These high sedimentation rates were only possible if sufficient accommodation space was available. As mentioned above, a second order eustatic sea level rise is

positively correlated with these high carbonate deposition rates [33]. Sea level started to rise during the early late Valanginian. At the same time carbon isotope values start to decrease. Sea level continued to rise during the early Hauterivian. This 'Hauterivian Transgression' is evidenced by the widespread influx of Boreal ammonites in the Tethys and vice versa. Especially connections over the Polish Graben and Moscow Platform come to play an important role [37]. This is consistent with our interpretation of the oxygen isotope data for the late Valanginian and early Hauterivian. The late Hauterivian is characterized by falling sea level and connections with the Boreal realm are closed again [33]. Apparently carbonate deposition slowed down and organic carbon burial increased again, with increasing $\delta^{13}\text{C}$ values. The presence of the Faraoni black shale level in latest most Hauterivian strata can be taken as evidence for this.

The question arises whether sea level also played an important role during the Valanginian positive $\delta^{13}\text{C}$ excursion. Under eutrophic conditions high marine organic carbon production is likely to have led to black shale formation. Lini et al. [10] found evidence for widespread black shale deposition during the Valanginian in the North Atlantic. This was mainly based on DSDP records. Apart from leg 77-site 535 [39], it seems clear that, both from organic geochemical [40,41] and palynological studies [42] the bulk of the organic matter of Valanginian and Hauterivian organic rich levels is in fact terrestrial (site 105, leg 11; site 391, leg 44; site 534, leg 76; site 603, leg 93 [43]). Comparable results were achieved on the southern margin of the Atlantic (Galicia margin, ODP leg 103, site 638) where terrestrial organic matter dominates organic matter rich levels as well. From the Hardenbol et al. chart [33] it can be seen that the mid-Valanginian is marked by an important regression. Weissert et al. [11] acknowledged the problematic absence of black shales during the Valanginian and envisioned reworking of organic matter during the transgressive phase that followed the $\delta^{13}\text{C}$ excursion as a possibility.

In the absence of widespread black shale deposition it is possible that carbon was mainly stored on the continents or in shallow marine settings. Cessation of carbonate carbon production and increased burial of organic carbon in siliciclastic deposits seems a reasonable explanation for the Valanginian positive $\delta^{13}\text{C}$ shift. Either organic carbon was stored during maximum regression in siliciclastic deposits as predicted by Gröcke et al. [44] or during the onset of transgression in coastal areas as predicted by Bohacs and Suter [45].

During the early Cretaceous sea level change on the timescale considered here was probably driven by changes in oceanic ridge volumes. Plotting the pulses in volcanic activity of the Parana-Etendeka Igneous Province [46] next to the eustatic sea level curve (Fig 4.) shows that there is a good correspondence. The Valanginian-Hauterivian is characterized by a considerable increase in ridge volume. This volcanic-tectonic phase possibly led to increased atmospheric CO_2 levels and climate warming. Therefore, we can not exclude that lowered $\delta^{13}\text{C}$ values during the late Valanginian and early Hauterivian might be partly due to the input of juvenile CO_2 with a more negative carbon isotope signature.

4.5 Conclusions

It seems that every phase of platform drowning has to be viewed in the light of its own set of paleo-environmental controls. The model established for the Valanginian and Aptian platform drowning events [2, 11] does not necessarily apply to the Hauterivian and Albian. The early Valanginian carbonate platforms suffered from widespread regression and the shedding of siliciclastics onto the shelf. Organic carbon was stored in coastal and continental settings. The transgression that followed brought cold nutrient rich bottom waters from the Boreal giving rise to a prolonged period of condensation on the Helvetic shelf (D1). Reworking of organic matter and leaching of coastal areas can be an alternative explanation for eutrophic conditions on the Helvetic Shelf.

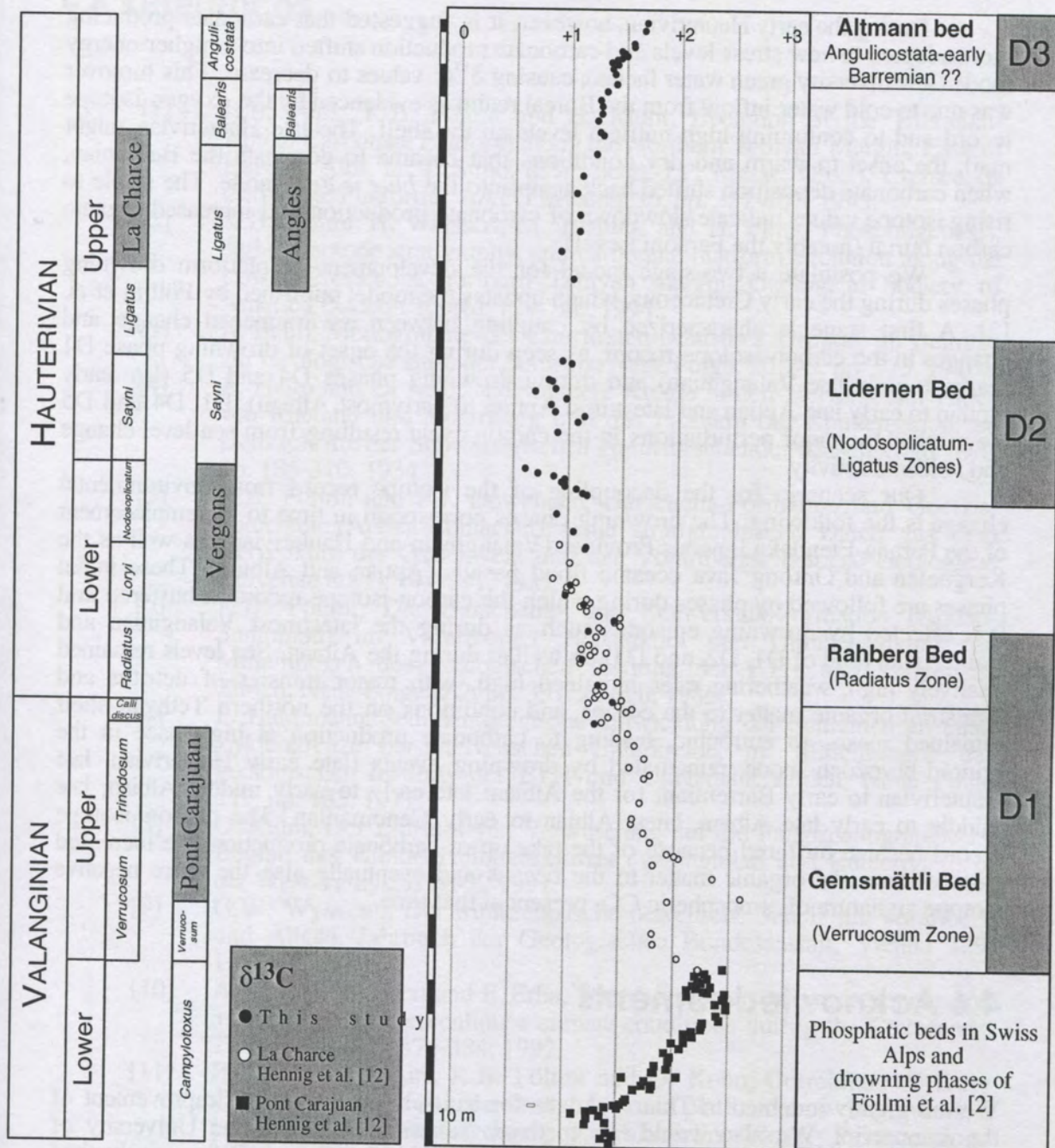


Figure 4.5 - Diagram showing relation between carbon isotope record and drowning events observed in the Swiss Alps. Ammonite zonation from [13].

During the early Hauterivian, however, it is suggested that carbonate producing biota adapted to new stress levels and carbonate production shifted into a higher energy mode (low diversity green water facies), causing $\delta^{13}\text{C}$ values to decrease. This turnover was due to cold water inflow from the Boreal realm as evidenced by the oxygen isotope record and to continuing high nutrient levels on the shelf. The late Hauterivian might mark the onset to warm and dry conditions that became to dominate the Barremian, when carbonate deposition shifted back again into the *blue water* mode. The stable to rising isotope values indicate slowdown of carbonate production and increased organic carbon burial (notably the Faraoni Level).

We postulate a two-stage model for the development of platform drowning phases during the early Cretaceous, which updates the model published by Föllmi et al. [2]. A first stage is characterized by coupling between environmental change and changes in the carbon isotope record, as seen during the onset of drowning phase D1 (early to early late Valanginian) and during drowning phases D4 and D5 (late early Aptian to early late Aptian and latestmost Aptian to earliest Albian). D1, D4 and D5 are marked by major perturbations in the carbon cycle resulting from sea level change and volcanic activity.

Our scenario for the decoupling of the isotope record from environmental change is the following: The drowning phases correspond in time to the emplacement of the Parana-Etendeka Igneous Province (Valanginian and Hauterivian), as well as the Kerguelen and Ontong Java oceanic flood basalts (Aptian and Albian). These initial phases are followed by phases during which the carbon isotope record is buffered and less affected by drowning episodes such as during the latestmost Valanginian and Hauterivian (end of D1, D2, and D3), as well as during the Albian. Sea levels remained relatively high, weathering rates remained high, with major transfer of detritus and terrestrial organic matter to the oceans, and conditions on the northern Tethyan shelf remained meso- to eutrophic, leading to carbonate production at high pace in the crinoid-bryozoan mode, punctuated by drowning events (late early Hauterivian, late Hauterivian to early Barremian; for the Albian: late early to early middle Albian, late middle to early late Albian, latest Albian to early Cenomanian). The carbon isotope record became buffered because of the take up of carbonate production, the increased flux of terrestrial organic matter to the oceans and eventually also the more negative isotope signature of atmospheric CO_2 present at that time.

4.6 Acknowledgements

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Correlation of Valanginian-Hauterivian bio- and magnetostratigraphy by means of $\delta^{13}\text{C}$ isotope records from Italy and France

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Abstract

For the early Cretaceous a detailed magnetostratigraphic framework has been established in the Apennines and southern Alps (Italy), while a high resolution ammonite zonation has been put up in France, based on assemblages from the Vocontian Basin. Correlation of the two stratigraphic tools has been hampered due to scarce ammonites in the early Cretaceous Italian Biancone and Maiolica formations and a too weak paleomagnetic signal in limestone-marl alternations in southern France. Carbon isotope stratigraphy is an important method to improve correlation, provided there is sufficient change in the isotopic signal. Using the mid-Valanginian positive carbon isotope excursion as a reference, Hennig et al. (1999) revised earlier correlations of ammonite- and magneto-zones for the Valanginian.

Here we present carbon isotope records from the Umbria-Marche Basin (Italy), measured from 2 sections (Monte Acuto and Gorgo a Cerbara), which together span the late Valanginian - late Hauterivian interval. We primarily used the Monte Acuto carbon isotope record to correlate with ammonite calibrated isotope records from the Vocontian Basin, because the Gorgo a Cerbara section appears to be unsuitable due to extensive slumping.

The proposed correlation complements and corresponds very well to previous correlations based on carbon isotopes (Hennig et al., 1999). The assignment of CM11 to the *Verrucosum* zone is confirmed. From our correlation follows that in the Monte Acuto section mainly late Valanginian to early Hauterivian sediments are present and that CM9 and CM8 have to be placed in the *Loryi* - *Nodosoplicatum* zones. Consequently, the *Sayni* ammonite zone only spans two magnetozones (CM7 and CM6) and not four (CM9 to CM6) as suggested in previous work. These new assignments have also repercussions for paleo-environmental interpretations of the Italian Biancone and Maiolica formations. In northern Italy chrons CM7 and CM6 are condensed in a conspicuous red nodular limestone interval, that marks a widespread paleoceanographic change during the mid-Hauterivian. This event is contemporaneous with platform drowning and phosphorite deposition along the northern margin of the Tethys observed in the Helvetic Alps, Switzerland.

5.1 Introduction

Refining and tuning of the geological timescale is important for our understanding of geological processes. Two important tools for resolving chronostratigraphic correlation are bio- and magnetostratigraphic zonations on a global scale. Correlation between these zonations is often hampered because of paleo-environmental controls on biomarker distribution, like for ammonites that lack in shallow marine and/or fully oceanic settings, whereas magnetostratigraphy works best in fully pelagic settings. Other problems are related to tectonic overprint, which may disturb any original magnetization, and burial diagenesis that may lead to extensive dissolution of micro- and macrofossils. Further problems exist between the correlation of individual biomarker zonations, such as between nannofossils and ammonites.

These problems become especially apparent in the early Cretaceous, for which detailed magnetostratigraphic zonations exist in Italy, calibrated with nannofossils (Channell et al., 1995), and for which a detailed ammonite biostratigraphy has been established in southern France (Bulot et al., 1994). A relative scarcity of ammonites in the Italian sections and the absence of a reliable paleomagnetic signal in the Vocontian Basin have hampered correlation between the two stratigraphic frameworks.

Carbon isotope stratigraphy has proved its usefulness for correlations within basins and of sections around the world for all time windows (Burns and Matter, 1993; Jenkyns et al., 1994; Ferreri et al. 1997; Grötsch et al., 1998; Immenhauser et al., 1999). Hennig et al. (1999) showed that carbon stable isotopes provide the means to link magnetostratigraphy and biostratigraphy for the Valanginian. The Valanginian $\delta^{13}\text{C}$ record is showing a global positive excursion (see Weissert et al., 1998 for an overview), also recorded in Italy and France (Lini et al., 1992; Channell et al., 1993; Hennig et al., 1999), which was used for correlation. The ammonite-calibrated $\delta^{13}\text{C}$ record of the Vocontian Basin shows decreasing values from +3‰ in the early late Valanginian (*Verrucosum* zone) to +0.5‰ in the late early Hauterivian (*Nodosoplicatum* zone). During the late Hauterivian values increase again to +2‰ in the *Angulicostata* zone (van de Schootbrugge et al., 2000). The results from Hennig et al. (1999) indicate that the correlation between ammonite zones and paleomagnetic zones for the Valanginian-Hauterivian transition, as published by Channell et al. (1995), had to be revised. The most important results from Hennig et al. (1999) are: 1) The correlation of zones CM12 and CM11 with the late early Valanginian *Campylotoxus* zone and early late Valanginian *Verrucosum* zone. 2) Correlation of CM10N with the upper part of the *Verrucosum* zone. In the scheme of Channell et al. (1995) CM10N is correlated with the early Hauterivian *Radiatus-Nodosoplicatum* zones, with the bulk of that zone pertaining to the *Loryi* zone. 3) CM9 was tentatively correlated with the top of the earliest Hauterivian *Radiatus* zone.

This study is complementary to the work of Hennig et al. (1999). Just as for the Valanginian, the carbon isotope record for the Hauterivian may be used to improve resolution of the bio- and magnetostratigraphic framework. Sampling was undertaken of two sections (Monte Acuto and Gorgo a Cerbara) that have delivered some rare ammonites and have a well defined magnetostratigraphy. Based on the available data, these sections span the late Valanginian to late Hauterivian (Cecca, 1995; Cecca et al., 1995). The aim of this paper is to correlate the obtained carbon stable isotope data from

the Umbria-Marche Apennines with records from the Vocontian Basin, in order to improve resolution.

5.2 Methods

Details on the french sections (La Charce, Vergons and Angles) are given in van de Schootbrugge et al. (2000) and in Hennig et al. (1999) for the Pont Carajuan section. The Italian sections sampled for this study (Monte Acuto and Gorgo a Cerbara) have previously been studied by Cecca et al. (1995) and Cecca (1995). The Monte Acuto and Gorgo a Cerbara sections consist of pelagic micrites alternating with more marly centrimetric interbeds and chert layers and nodules. This type of pelagic sedimentation characterizes the Maiolica Formation deposited during the latest Jurassic to early Cretaceous in the Umbria-Marche Basin (Cecca et al., 1995).

For isotope analyses powder was drilled from fresh thick sections and normal procedures were performed to extract the bulk rock carbon and oxygen isotope records. Approximately 10 mg of powder was reacted with 100% H_3PO_4 at 90°C in an online-automated preparation system. The resulting CO_2 was analyzed at the Stable Isotope Laboratory of the University of Bern with a VG Prism II ratio mass spectrometer. Duplicate measurements proved better than 0.1‰ for the oxygen isotope analyses and better than 0.05‰ for the carbon isotope analyses. The results are expressed relative to the PDB standard.

5.3 Bio- and magnetostratigraphic framework

5.3.1 Magnetostratigraphy

Based on nannofossil zonations from Thierstein (1973; 1976), Channell et al. (1992) were able to calibrate magnetic chrons with nannofossil events in several Italian sections. The Valanginian/Hauterivian boundary was placed within CM10N and the Hauterivian/Barremian boundary at the base of CM6. These results added further detail to correlations proposed by Lowrie and Alvarez (1979) who had placed zones CM12 to CM3 in the Hauterivian. Cecca et al. (1994) were the first to integrate ammonites, nannofossils, planktonic foraminifera and magnetic chrons by studying the Gorgo a Cerbara section. Their results indicate a late Hauterivian age for magnetozones CM6 to CM4, with the Hauterivian-Barremian boundary in CM4. Channell et al. (1995) correlated the Gorgo a Cerbara section with other Italian sections with the help of magnetostratigraphy and assigned the Mt. Acuto section to magnetozones CM11 to CM7.

5.3.2 Biostratigraphy

The Monte Acuto and Gorgo a Cerbara sections are key-sections because of their scarce contents of ammonites. Other sections that served for magneto- and carbon isotope

stratigraphy were difficult to correlate with ammonite biostratigraphic zonations, because of their complete lack of ammonites (Lini et al., 1992; Channell et al., 1993).

Cecca et al. (1994) were the first to present ammonite data from the Gorgo a Cerbara section. Important markers for this section include *Plesiospitidiscus* sp. and *Pseudothurmannia angulicostata* and *P. catulloi*, marking the *Ligatus-Balearis* and *Angulicostata* zones, respectively. In a later publication another important marker was mentioned, i.e. *Subsaynella* sp. (Cecca et al., 1995), indicating the early late Hauterivian *Sayni* zone.

The Monte Acuto section was studied by Cecca (1995) and Cecca et al. (1995) for its ammonite contents. Following magnetostratigraphic sampling of Channell et al. (1995) sampling was carried by Cecca (1995) out along the almost unfaulted part of the section. The base of this section contains ammonites indicative of the early late Valanginian *Verrucosum* and *Trinodosum* zones. For the Hauterivian the most important findings in this section are a *Subsaynella* sp. and a *Crioceratites* gr. *duvalii* Leveillé, which were assigned to the *Sayni* zone. Further detail was added by Faraoni et al. (1997), who intensively sampled the severely faulted, but ammonite-rich, part of the Monte Acuto section. Their lithologic log, however, is difficult to compare to the one given in Cecca (1995) and Channell et al. (1995). Faraoni et al. (1997) state that their bed 386 is corresponding to meter 50 of Channell et al. (1995), which gives a tie point. However, the correlation of the strata above metre 50 is impossible because in the log of Faraoni et al. (1997), the slumping reported by Channell et al. (1995) at their meter 43, and photographed by Cecca et al. (1995, fig. 17), is lacking. Based on the presence of a specimen assigned by Faraoni et al. (1997) to *Neocomites flucticulus*, the early Hauterivian *Radiatus* zone starts at meter 50 and extends up to meter 38 (from the top). These authors place the Valanginian-Hauterivian boundary within CM10N at meter 50 and consider CM10 up to meter 38 of Cecca et al. (1995b) to belong to the *Radiatus* zone.

Integration of the ammonite and paleomagnetic data from several Italian sections led to the publication of an ammonite calibrated paleomagnetic zonation for the early Cretaceous by Channell et al. (1995). The Valanginian-Hauterivian boundary was placed within CM11 and the early Hauterivian was represented by magnetozones CM10N and CM10. Taking into account the data presented by Faraoni et al. (1997), the Valanginian-Hauterivian has to be shifted considerably higher up section, within chron CM10N. The early Hauterivian *Radiatus* zone would then span part of the CM10N and CM10 zone. Based on the above the *Sayni* zone, which spans chrons CM6 to CM9, could represent as much as 3 million years (Channell et al., 1995).

The Hauterivian-Barremian boundary is usually placed in the upper part of CM4 (Cecca et al., 1994; Channell et al., 1995), but the late Hauterivian is often disturbed by slumping in many Italian sections.

The discovery of ammonites in Mt. Acuto made it possible to calibrate also microfossils. The results are summarized in Channell et al. (1995). Important markers for the Valanginian-Hauterivian interval are the FO of *T. verenae* in CM12, the LO of *T. verenae* in CM11, the FO of *N. bucheri* at the base of CM10N, the FO of *L. bollii* at the base of CM10, the LO of *C. cuvillieri* at the base of CM8, the FO of *R. terebrodentarius* in CM8-CM7 and the LO of *L. bollii* in CM5-CM4. The significant nannofossil events in the Monte Acuto section are shown in Figure 5.3. Nannofossil events in the Vocontian Basin have been studied by Gardin et al. (in prep.) and the ranges of some of the

important markers for the Hauterivian are quite different from the ones given in Channell et al. (1995). This will be discussed in further detail below.

5.4 Results

The carbon isotope results for the Monte Acuto and Gorgo a Cerbara sections together with all the available bio- and magnetostratigraphic information from previous studies, are presented in Figures 5.1a and b. Oxygen isotopes were also measured, but are not depicted, because they are of no stratigraphical value in this case. In both sections the $\delta^{18}\text{O}$ curve shows stable trends around values of -2‰ , which points to a moderate diagenetic overprint. The carbon isotope trend for the Monte Acuto section is showing high values ($+3\text{‰}$) in the lower part of the section and from 74m onwards values start to decrease. Minimum values are reached in the upper part of the section ($+1.8\text{‰}$). The Gorgo a Cerbara section is showing very little variation, however values slightly decrease from the base of the section ($+2\text{‰}$) to bed 82 ($+1.8\text{‰}$). After a large slumped interval values gradually increase from $+1.7\text{‰}$ to $+2\text{‰}$. Offcourse these variations are very small, however precision of measurements is such that reliable trends maybe discerned.

5.5 Discussion

5.5.1 Correlation with Vocontian sections

The carbon isotope trend observed in Mt. Acuto can be correlated very precisely with a carbon isotope record from the Vocontian Basin, which has been calibrated with ammonites (Figure 5.2). The positive values at the base of the section upto meter 74 are correlated with the *Verrucosum* zone. In the La Charce section in France, spanning the late Valanginian to early Hauterivian, $\delta^{13}\text{C}$ values reach a minimum at the base of the *Sayni* zone ($+0.5\text{‰}$, van de Schootbrugge et al., 2000). Values then gradually increase again towards the Hauterivian-Barremian boundary. The gradual decrease in the Mt. Acuto section from $+3\text{‰}$ to $+1.8\text{‰}$ is correlated with the latest Valanginian to early Hauterivian of the Vocontian Basin. The late Hauterivian increase in $\delta^{13}\text{C}$ values observed in the Vocontian Basin record is not observed in the Mt. Acuto section. From this follows that apparently only early Hauterivian sediments are present in Mt. Acuto. Our correlation shows that the *Radiatus* zone falls within the upper part of CM10N and the base of CM10. Magnetic zones CM9 and CM8 are correlated with the *Loryi* and *Nodosoplicatum* zones of the Vocontian Basin. Zone CM7 in the Mt. Acuto section might be correlated with the *Sayni* zone.

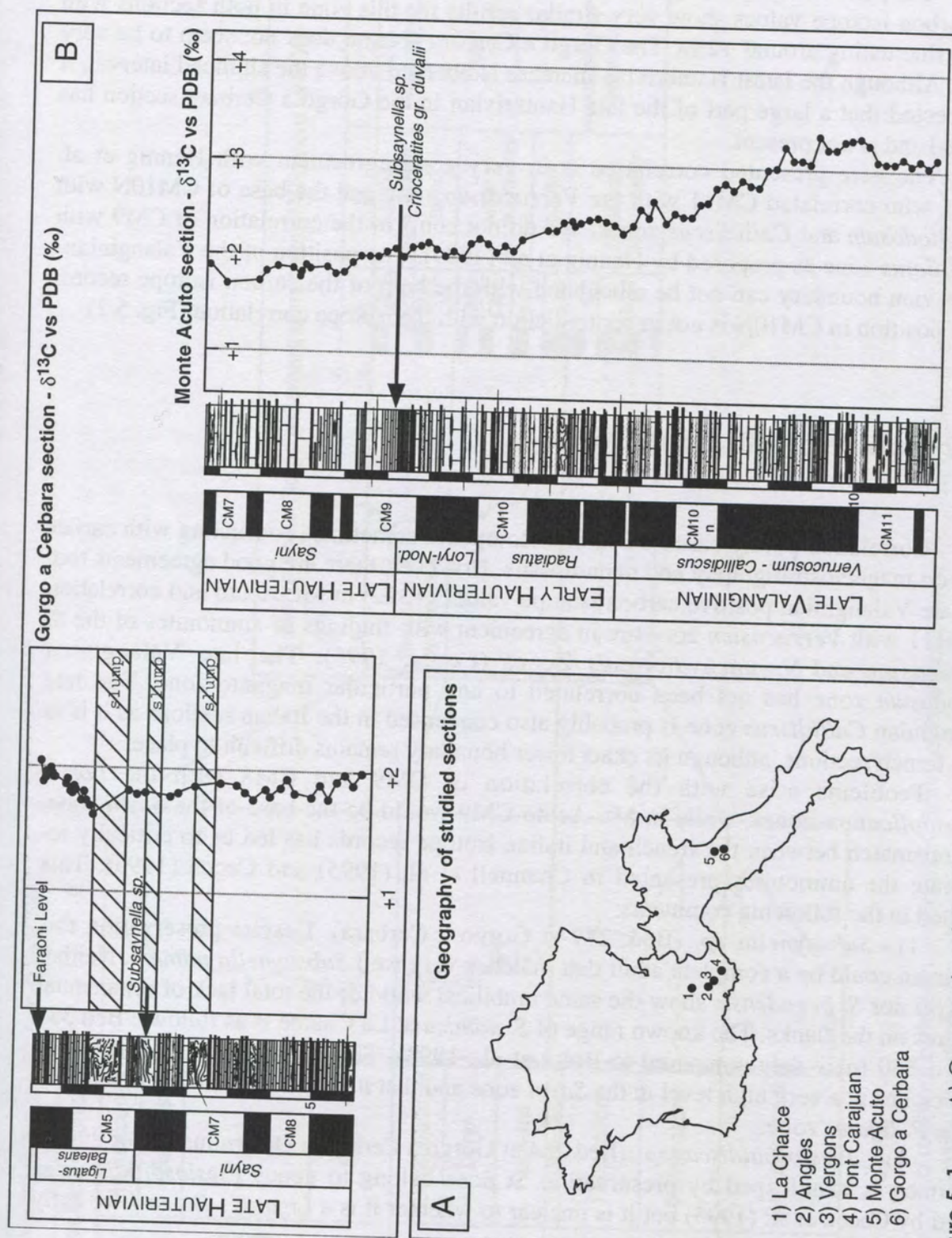


Figure 5. 1 - A) Geography of studied sections. The french sections served for a composite isotope curve for the Vocontian Basin presented in Figure 5.2. B) Carbon isotope records for Monte Acuto and Gorgo a Cerbara

The Mt. Acuto and Gorgo a Cerbara sections are overlapping for zones CM7. The carbon isotope values show very similar results for this zone in both sections with values fluctuating around +2‰. The Gorgo a Cerbara section does not seem to be very useful. Although the latest Hauterivian increase is observed above the slumped interval, it is suspected that a large part of the late Hauterivian in the Gorgo a Cerbara section has slumped and is not present.

The here presented correlation is in very good agreement with Hennig et al. (1999), who correlated CM11 with the *Verrucosum* zone and the base of CM10N with the *Trinodosum* and *Callidiscus* zones. We do not confirm the correlation of CM9 with the *Radiatus* zone as proposed by Hennig et al. (1999). The position of the Valanginian-Hauterivian boundary can not be elucidated with the help of the carbon isotope record, but its position in CM10N is not in contradiction with the isotope correlation (Fig. 5.2).

5.5.2 Problems with correlations

Correlation purely based on carbon isotopes is sometimes conflicting with earlier work on magnetostratigraphy and nannofossils. However, there are good agreements too. The late Valanginian positive carbon isotope values (+3‰) in Mt. Acuto and correlation of CM11 with *Verrucosum* zone are in agreement with findings of ammonites of the *S. verrucosum* and *N. pachydicranus* Zones (Cecca, 1995). The late Valanginian *Trinodosum* zone has not been correlated to any particular magneto-zone. The late Valanginian *Callidiscus* zone is probably also condensed in the Italian sections as it is in most french sections, although its exact lower boundary remains difficult to place.

Problems arise with the correlation of CM9 and CM8 with the *Loryi-Nososoplicatum* zones, while in Mt. Acuto CM9 would be the base of the *Sayni* zone. The mismatch between the french and italian isotope records has led us to critically re-evaluate the ammonites presented in Channell et al. (1995) and Cecca (1995). This resulted in the following comments:

1) - *Subsaynella* sp. (Bed. 277 at Gorgo a Cerbara). Despite preservation this specimen could be a complete adult that matches very well *Subsaynella mimica*. Neither *S. sayni* nor *S. begudensis* show the same umbilical wall nor the total lack of ornamental features on the flanks. The known range of *S. mimica* at La Charce is as follows: Bed 353 to bed 360 (new data compared to Bulot et al., 1993). This means that the LOD of *S. mimica* lies at a very high level in the *Sayni* zone and that its *acme* is restricted to the base of the *P. ligatus* zone.

2) - *Plesiospitidiscus* sp. (Bed 264 at Gorgo a Cerbara): Determination of this specimen is handicapped by preservation. It does belong to genus *Plesiospitidiscus* as stated by Cecca et al. (1995) but it is unclear to whether it is a *Ligatus* - *Balearis* or early *Angulicostata* taxa.

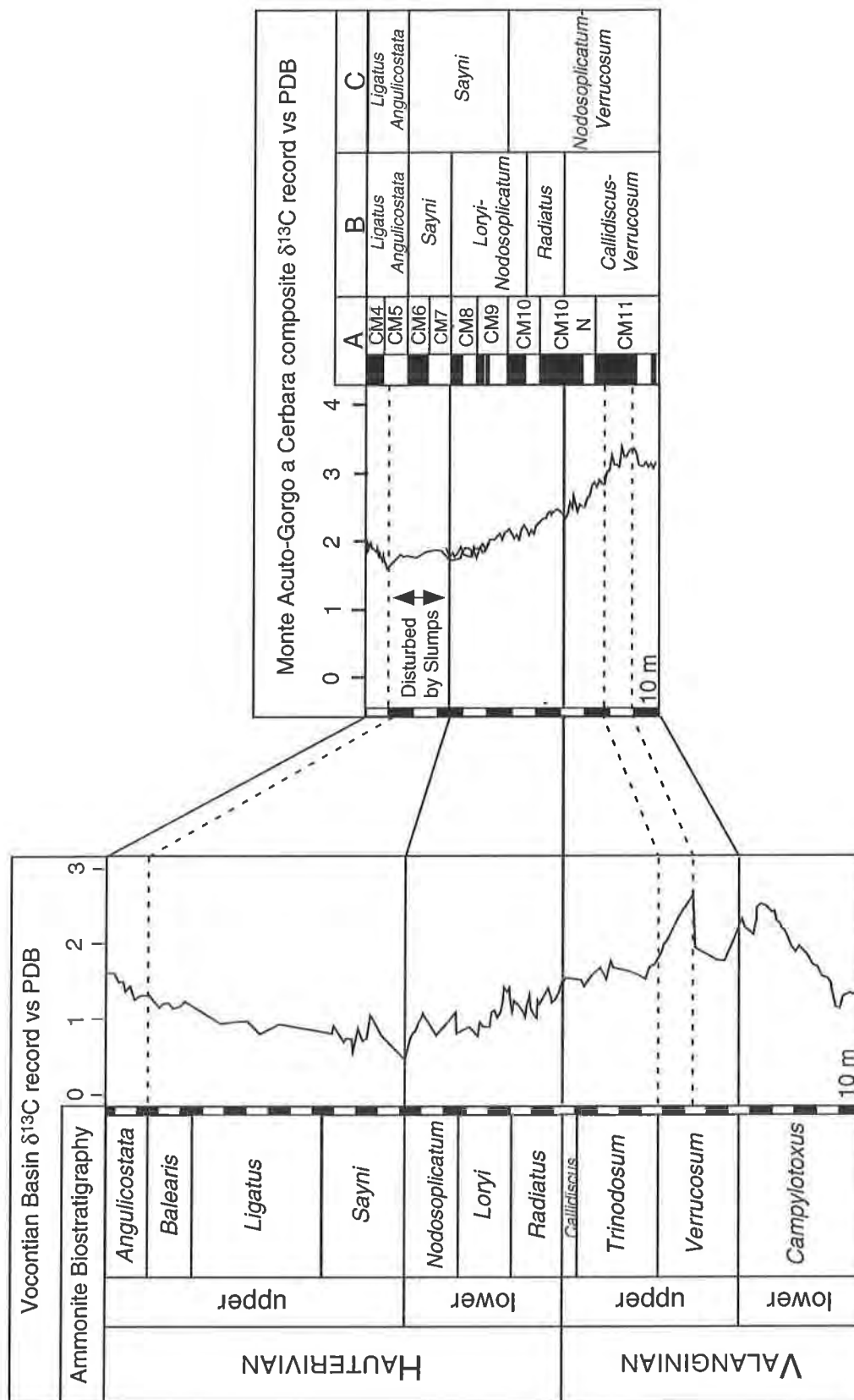


Figure 5.2 – Correlation between Vocontian Basin and Umbria-Marche Basin carbon isotope records. A= Magnetostratigraphy after Lowrie and Alvarez (1979). B= Ammonite zonation based on here proposed correlation and Faraoni et al. (1997). C= Ammonite zonation after Cecca et al. (1995). The Vocontian Basin record is a composite record based on Hennig et al. (1999) and van de Schootbrugge et al. (2000).

3 - *Crioceratites* gr. *duvali*/*villersianus* (Bed 266 at Gorgo at Cerbara) : Weak preservation again but in any case this juvenile specimen clearly belongs to a well "advanced stage" in the *C. duvali* "chronospecies". Such morphologies (at La Charce) appear in the late *Sayni* zone and end well below the *Balearis/Angulicostata* boundary.

4 - *Crioceratites* gr. *duvali* (meter 22 at Monte Acuto). Systematics of the *Crioceratitinae* subfamily is extremely complex. The specimen could possibly belong to the *matsumotoi/quenstedti/curnieri* group instead of to the true *C. duvali* (and allied species such as *C. villersianum*). This is fairly important because at least at La Charce, similar forms of the *matsumotoi/quenstedti/curnieri* group are known to range from the middle part of the *Nodosoplicatum* zone to the lower part of the *Sayni* zone. This might be crucial for correlations with magnetozones.

From this follows that CM6 in Gorgo a Cerbara might be slightly younger (*Ligatus* zone) and chron CM9 in Monte Acuto slightly older (*Nodosoplicatum* zone). In any case these re-assignments correspond better to the results obtained with C-isotope stratigraphy.

However, more problems arise when taking into account the stratigraphic distribution of nannofossils. Figure 5.3 shows the correlation of first and last occurrences of significant species from Monte Acuto and their calibration with ammonite zones based on the work of Channell et al. (1995) and Gardin et al. (2000). The LO of *T. verenae* is placed in both basins at the top of the *Verrucosum* zone, which is confirmed by our isotope correlation and the one from Hennig et al. (1999). The first occurrence of *N. bucheri* was initially placed at the top of the *Radiatus* zone, but with the new ammonite data from Faraoni et al. (1997) this can no longer be defended. The position of the FO of *N. bucheri* in the Vocontian Basin within the *Callidiscus* zone (Fig. 5.3) corresponds better to our isotope correlation. The FO of *L. bollii* occurs in both basins in the *Loryi* zone, but this is not in agreement with the range of the *Acanthodiscus radiatus* zone in Mt. Acuto. *C. cuvillieri* has a last occurrence datum level in Mt. Acuto at the base of chron CM8, which would correspond to the middle of the *Sayni* zone according to Channell et al. (1995) and to the top of the *Sayni* zone after Gardin et al. (2000). Our isotope correlation is not in agreement with both these assignments. Based on the assignment of CM7 to the *Sayni* zone, the first occurrence of *R. terebrodentarius* is placed at the top of this zone by Channell et al. (1995). Gardin et al. (in prep.) find this species in the *Angulicostata* zone in the Vocontian Basin.

All these problems underline the difficulties tying together different stratigraphic tools. Nannofossils might have different ranges in different basins due to differential paleo-environmental controls. Different diagenetic fingerprints, which severely affect nannofossil preservation, may exist in the different basins. In addition, authors may have different concepts of a species. The here presented isotope data might help to clarify these problems.

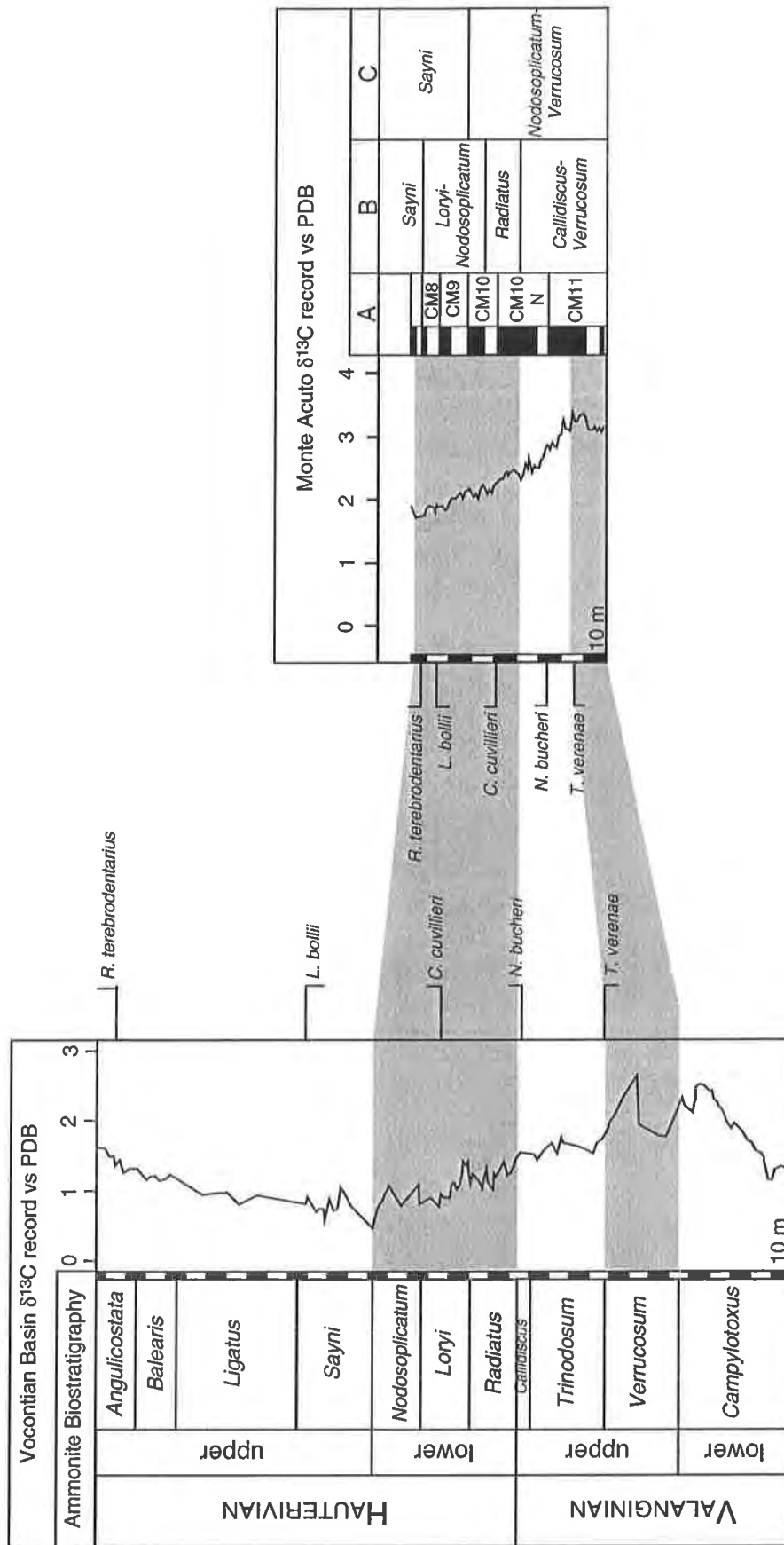


Figure 5.3 – Correlation of isotope curves from Monte Acuto (this study) with C-isotope curve from Vocontian Basin (Hennig et al., 1999; van de Schootbrugge et al., 2000) together with nannofossil zonations from Gardin et al. (2000) and

5.5.3 Other carbon isotope records

A compilation of all the available carbon isotope data for Italian sections from the southern Alps and Apennines was presented in Channell et al. (1995) and calibrated with nannofossils and magnetozones. This carbon isotope record is correlated with the one from the Vocontian Basin in Figure 5.4. The inflection in the Italian curve can very well be correlated with the base of the late Hauterivian in the Vocontian Basin. So again, CM9 and CM8 fall within the early Hauterivian. Overall the decrease from the Valanginian maximum to the mid-Hauterivian is 1.5‰. In the Vocontian Basin this decrease is slightly higher, about 2‰. The increase during the late Hauterivian amounts to 0.5‰ for the Italian sections, while it is 1‰ in the French sections. Differences in both records might be due to different paleo-environmental settings (*hemi-pelagic* for the Vocontian Basin, *pelagic* for the Umbria-Marche Basin) and diagenetic histories.

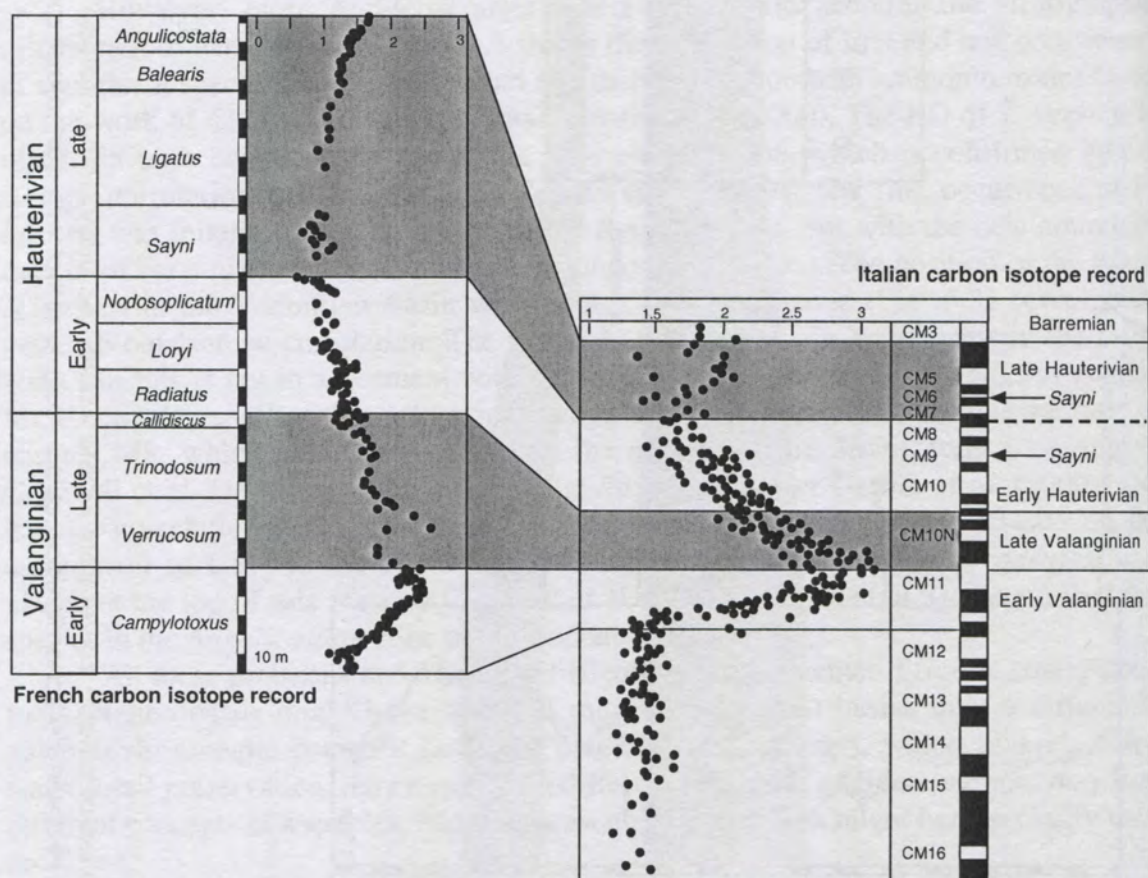


Figure 5.4 - Correlation of french and italian composite carbon isotope curves. The french curve is based on Hennig et al. (1999) and van de Schootbrugge et al. (2000). The italian curve is based on Channell et al. (1995)

Erba et al. (1999) presented a very detailed carbon isotope curve obtained from a core drilled close to Cismon (Apticore Project, Southern Alps, Italy) covering the late Hauterivian to early Aptian. Multidisciplinary research included also micropaleontology and magnetostratigraphy (Fig. 5.5). For the Hauterivian part of the core magnetozones CM9-CM4 were recognized and the Hauterivian-Barremian boundary was placed at the base of CM3 (this is probably a drawing error as in all other authors' publication this boundary is correlated with the upper part of CM4). An important marker bed in this section is the Faraoni black shale level (Cecca et al., 1996), which is dated here and in other sections of Umbria-Marche Apennines (e.g. Gorgo a Cerbara) to the upper part of the *Angulicostata* ammonite zone (Cecca et al., 1998). The carbon isotope curve shows slightly decreasing values for zones CM9 and CM8, descending from +2.2‰ to +1.7‰. Values remain around 1.7‰ upto the Hauterivian-Barremian boundary. No increase is observed towards the Barremian boundary, like for the Vocontian Basin record. Based on the correlations with the records discussed above, it is again suggested that zones CM9 and CM8 are of early Hauterivian age and that the late Hauterivian starts only from CM7 (*Sayni* zone). From our interpretation follows that the late Hauterivian is extremely condensed in the Cismon-Apticore. This is why $\delta^{13}\text{C}$ values seem to stay so stable during the Hauterivian. A similar effect is observed in Gorgo a Cerbara, where the late Hauterivian is slumped.

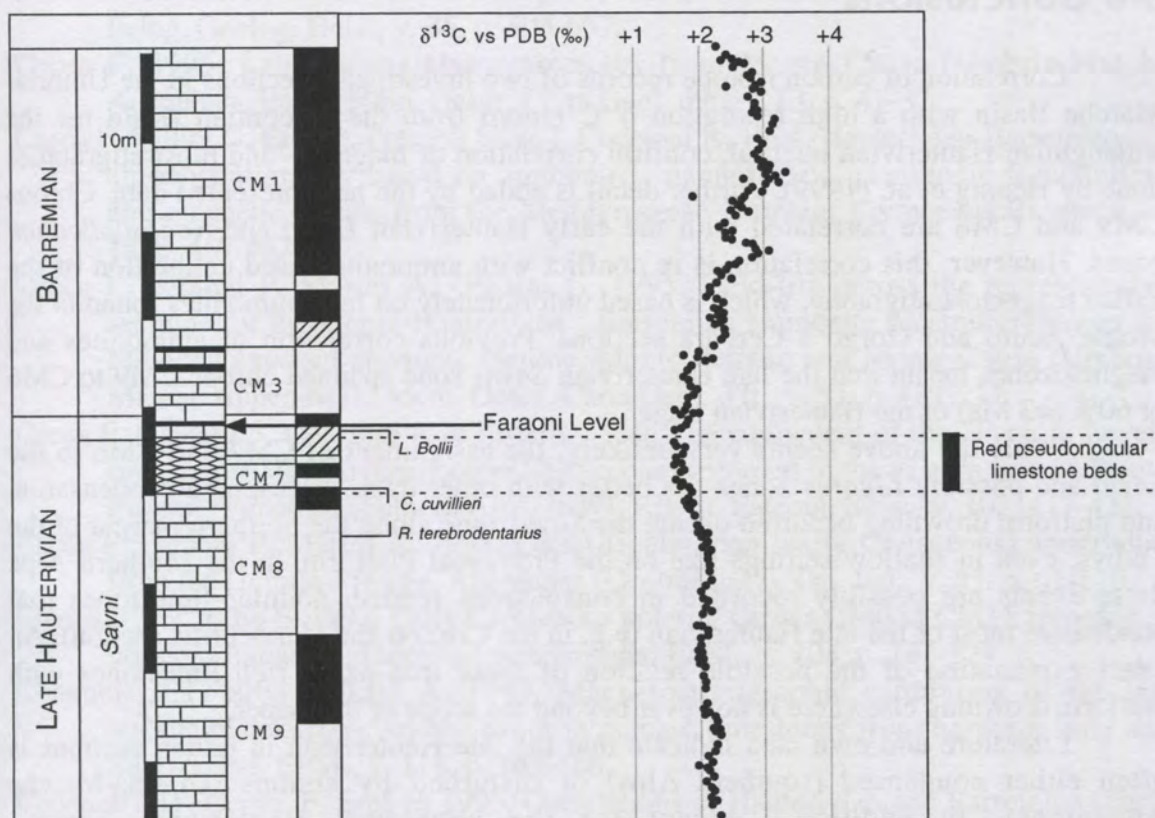


Figure 5.5 – Cismon section (modified after Erba et al., 1999). Note that the carbon isotope values for the Hauterivian show hardly any change, except in the red nodular limestones.

The here proposed correlation might have important consequences for our understanding of the timing of events that characterize the Hauterivian as well as their underlying mechanisms. In the Apticore the late Hauterivian is represented by a conspicuous red nodular level, which stops 60 cm below the Faraoni Level (Cecca et al., 1996). In the north-italian section of Val del Mis the same reddish nodular limestones caused magneto-stratigraphic resolution to be poor for zones CM6 to CM4 (Channell et al., 1993). Condensation during the *Sayni-Ligatus* zones and *Angulicostata* zone (Faraoni Level) is contemporaneous with two major phases of platform drowning on the Helvetic Shelf (D2 and D3 in Föllmi et al. (1994) and van de Schootbrugge et al. (2000)). Overall, carbonate accumulation rates dramatically decreased during the late Hauterivian, something also evidenced by the positive trend in the $\delta^{13}\text{C}$ record, indicating a shift to organic carbon burial. Platform drowning events in the Hauterivian, but also during the Valanginian and Aptian have been ascribed to increased nutrient input (especially P and Fe) from continental weathering and erosion by Föllmi et al. (1994) and Weissert et al. (1998). The reddish nodular limestones in the southern Alps and Apennines might be an equivalent of the mid- and late Hauterivian Helvetic drowning events. However, more research is needed to understand the exact nature of condensation in the late Hauterivian of the Apennines and Southern Alps.

5.6 Conclusions

Correlation of carbon isotope records of two investigated sections in the Umbria-Marche Basin with a high resolution $\delta^{13}\text{C}$ record from the Vocontian Basin for the Valanginian-Hauterivian interval, confirm correlation of magneto- and biostratigraphies done by Hennig et al. (1999). Further detail is added by the here presented data. Chrons CM9 and CM8 are correlated with the early Hauterivian *Loryi* and *Nodosoplicatum* zones. However, this correlation is in conflict with ammonite based calibration of the Italian magnetostratigraphy, which is based unfortunately on few ammonites found in the Monte Acuto and Gorgo a Cerbara sections. Previous correlation of ammonites and magnetostratigraphies meant that the late Hauterivian *Sayni* zone spanned chrons CM9 to CM6 or 60% (≈ 3 Ma) of the Hauterivian stage.

While the above seems very unlikely, the assignment of CM7 and CM6 to the *Sayni* and possibly *Ligatus* zones fits better with other data. Widespread condensation and platform drowning occurred during the *Sayni* zone along the northern margin of the Tethys, even in shallow settings like on the Provencal Platform. In the southern Alps these events are possibly recorded in conspicuous reddish nodular limestones that condensate most of the late Hauterivian (e.g. in the Cismon and Val del Mis section). An exact explanation of the possible relation of these iron-oxide rich limestones with platform drowning elsewhere is however beyond the scope of this paper.

Literature and own data indicate that the late Hauterivian in Italian sections is often either condensed (southern Alps) or disturbed by slumps (Umbria-Marche Apennines). In addition, "except for the uppermost Hauterivian Faraoni Level...ammonites remain very rare in this (Maiolica) facies and furthermore their preservation is very bad" (Cecca, 1995, p. 48). Therefore sections in the Vocontian Basin might prove to be better candidates for defining stratotypes and further efforts should be made to establish a magnetostratigraphic framework for these sections.

5.7 Acknowledgements

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5.8 References

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**Carbon and oxygen isotope records
from Hauterivian shallow marine
carbonate succesions in the
hisotorical type-region (Neuchâtel
Jura, Switzerland) and Subalpine
chain (Bauges Massif, France)**

Abstract

Hauterivian limestone successions of the Neuchâtel Jura (Switzerland), which is the historical type region for the Valanginian and Hauterivian stages, are poorly constrained by biostratigraphic data. This has resulted in a debate on whether the Hauterivian is complete or whether a large hiatus exists between the early Hauterivian Pierre Jaune de Neuchâtel Fm and the Urgonian limestones, which are thought to be of late Barremian age. In the absence of useful biomarkers, C-isotope stratigraphy could be a means to correlate these limestones with successions from the Vocontian Basin, which are better constrained by ammonites and carbon isotopes.

Bulk carbonate carbon isotope records obtained from one core (607) and one outcrop (Eclepens), spanning together the complete early Cretaceous succession of the Jura Mountains, show that oolitic-bioclastic limestones of the Pierre Jaune Fm suffered from a strong diagenetic overprint. Carbon- and oxygen isotopes values for the Pierre Jaune are very negative (-5 and -7‰ vs PDB, respectively). Petrographic observations indicate that extensive leaching occurred, probably as a result of early diagenesis in the fresh water phreatic zone. It is suggested that the diagenetic modification was related to a eustatic lowstand that occurred during the late early Hauterivian *Nodosoplicatum* zone. Exposure of the Jura shallow carbonate ramp also resulted in mixing-zone chert deposition at the base of the exposed succession. Recognition of this important break in sedimentation lends some support to the views of Arnaud et al. (1999) who have recognised large hiatus in the Swiss Jura, in contrast with Clavel et al. (1995) who consider the whole succession complete up to the late early Barremian. In the wake of extensive diagenesis, it is impossible to determine based on the isotope records whether late Hauterivian sediments are present or absent in the Neuchâtel area.

Coeval strata in the Semnoz section (Bauges Massif, France) which are slightly better constrained by ammonites (most notably the finding of a *Subsainella sayni*) and represent a deeper depositional environment, also suffered from diagenesis. This is based on differing isotopic signatures in Semnoz and the Vocontian Basin, which serves as a reference for ammonite calibrated C-isotope records.

6.1 Introduction

Extensive research in the historical type region for the Hauterivian, in the Swiss Jura Mountains close to Neuchâtel, has not provided compelling biostratigraphic evidence to determine whether Hauterivian shallow marine carbonate successions are complete or whether a large hiatus exists between the early Hauterivian and late Barremian (Remane et al., 1989; Clavel et al., 1995; Arnaud et al., 1999). Whereas the Marne Bleue d'Hauterive Fm, the Zone Marno-Calcaire and Pierre Jaune de Neuchâtel Fm (Fig. 6.1) are clearly of early Hauterivian age based on several rare but age-diagnostic ammonites, much uncertainty remains on the stratigraphic position of the lower and upper Urgonian (Urgonien Jaune and Urgonien Blanc). Arnaud et al. (1999) correlate the whole Urgonian of the Neuchâtel region with the late Barremian of the Vercors (France) and argue that the late Hauterivian and early Barremian in the Neuchâtel area were eroded as a result of a eustatic sea level lowstand during the early Barremian. These sediments are now represented by the Bornes bioclastic limestones, which have been interpreted as a lowstand wedge bordering the Vercors platform (Arnaud-Vanneau and Arnaud, 1990). Clavel et al. (1989; 1995) are of the opinion that the succession of the Jura is complete up to the base of the late Barremian after which the Jura platform became subaerially exposed. In a later stage the karstic surface on top of the lower Urgonian was flooded and filled with early Aptian glauconitic sands. Clavel et al. (1995) assign the lower Urgonian (Urgonien Jaune) to the late Hauterivian and the upper Urgonian (Urgonien Blanc) to the early Barremian. Interpretations from both groups of authors rely heavily on sequence stratigraphy and orbitolinids. A sequence stratigraphic interpretation is however difficult, because the Jura Mountains lack the large scale outcrops of the Vercors region. Orbitolinids, a type of benthic foraminifera that lives in shallow marine settings, were probably very much facies dependent and therefore questionable as biomarkers. On top of that some authors have different concepts of important orbitolinid marker species (Schroeder, 1997).

Carbon isotope stratigraphy may help to improve correlations between sections, especially in shallow marine carbonate sequences (Ferreri et al. 1997; Grötsch et al., 1998) that lack biomarkers. This paper discusses bulk carbonate carbon and oxygen isotope records obtained from shallow marine carbonate ramp sections from the Jura Mountains and further South from the Subalpine Bauges Massif (France). The aim is to correlate these records with previously established ammonite-calibrated records in the Vocontian (van de Schootbrugge et al., 2000) and Umbria-Marche Basins (van de Schootbrugge et al., in prep.) and to improve age assignments for these sections. These well calibrated records display a distinct isotope signature for the Hauterivian with a negative trend during the early Hauterivian, that started in the late Valanginian, and a positive trend during the late Hauterivian. In the Vocontian Basin record the inflection in the C-isotope curve lies at the boundary between the early and late Hauterivian.

Ultimately, the reason for getting an improved time frame on Hauterivian successions along the northwestern margin of the Tethys is the fact that important platform drowning events occurred in contemporaneous successions in the Helvetic Alps. These drowning events are recorded in highly condensed phosphoritic horizons of early Hauterivian, middle Hauterivian and late Hauterivian age and are thought to have caused

1	2	3	4	Synthetic Stratigraphic Column for Swiss Jura (Neuchâtel)					5	6	7	8	9			
BARREMIAN	EARLY BARREMIAN	LATE BARREMIAN	EARLY B.	<i>Nodosoplicatum</i>		Urgonien Blanc	Urgonien									
																
																
																
LATE HAUTERIVIAN	LATE H.	LATE HAUTERIVIAN	LATE HAUTERIVIAN			Marnes de la Rusille		Pierre Jaune Formation sensu lato								
																
																
																
EARLY HAUTERIVIAN	EARLY HAUTERIVIAN	EARLY HAUTERIVIAN	EARLY HAUTERIVIAN		Urgonien Jaune	Pierre Jaune Formation sensu lato										
																
																
																
EARLY HAUTERIVIAN	EARLY HAUTERIVIAN	EARLY HAUTERIVIAN	EARLY HAUTERIVIAN		Upper Pierre Jaune de Neuchatel		Pierre Jaune Formation sensu lato									
																
																
																
EARLY HAUTERIVIAN	EARLY HAUTERIVIAN	EARLY HAUTERIVIAN	EARLY HAUTERIVIAN		Marnes d'Uttings	Pierre Jaune Formation sensu lato										
																
																
																
EARLY HAUTERIVIAN	EARLY HAUTERIVIAN	EARLY HAUTERIVIAN	EARLY HAUTERIVIAN		Lower Pierre Jaune de Neuchatel		Pierre Jaune Formation sensu lato									
																
																
																
EARLY HAUTERIVIAN	EARLY HAUTERIVIAN	EARLY HAUTERIVIAN	EARLY HAUTERIVIAN		Zone Marno- Calcaire	Pierre Jaune Formation sensu lato										
																
																
																
EARLY HAUTERIVIAN	EARLY HAUTERIVIAN	EARLY HAUTERIVIAN	EARLY HAUTERIVIAN		Marnes Bleues d'Hauterive		Pierre Jaune Formation sensu lato									
																
																
																
EARLY HAUTERIVIAN	EARLY HAUTERIVIAN	EARLY HAUTERIVIAN	EARLY HAUTERIVIAN		Marnes Bleues d'Hauterive	Pierre Jaune Formation sensu lato										
																
																
																
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EARLY HAUTERIVIAN	EARLY HAUTERIVIAN	EARLY HAUTERIVIAN	EARLY HAUTERIVIAN		Marnes Bleues d'Hauterive		Pierre Jaune Formation sensu lato									
EARLY HAUTERIVIAN	EARLY HAUTERIVIAN	EARLY HAUTERIVIAN	EARLY HAUTERIVIAN		Marnes Bleues d'Hauterive	Pierre Jaune Formation sensu lato										

Figure 6. 1 - Stratigraphic framework for the Swiss Jura Mountains.

by increased influx of nutrients creating eutrophic surface water conditions. The phosphoritic horizons seem to be restricted to shelf environments, because on the shallow carbonate ramp in the Jura no phosphorites were deposited. To understand the exact formation and to be able to delineate local, regional and global mechanisms behind these ecosystem crises, it is necessary to correlate these events with shallow carbonate platform settings.

6.2 Methods

Three sections were studied: Core 607, Eclepens and Semnoz. The first two are situated in the Neuchâtel Jura and the third is located in the Subalpine Chains of the Bauges Massif in France, close to Annecy. Core 607 has previously been studied by Rumley (1992). Eclepens represents a key section for the upper Pierre Jaune and Urgonian and was studied in great detail by Blanc-Aletru (1995). The Semnoz section was selected because it is one of the rare sections that has delivered several age diagnostic ammonites, of which a *Subsalignella sayni* is probably the most important (Viéban, 1983). For details on the sedimentology and description of discontinuity surfaces and sequence boundaries I refer to Chapter 3. The carbon and oxygen isotopes were measured from bulk rock powdered samples at the Geological Institute of Bern. Standard procedures were followed as outlined in van de Schootbrugge et al. (2000). The trace element data were obtained by Atomic Absorption Spectrophotometry. The thin sections were prepared during two previous Ph.D. projects on the Hauterivian of the Swiss Jura (Blanc-Aletru, 1995; Rumley, 1992).

6.3 Results

Core 607

Carbon isotope values remain very constant at around +1‰ throughout the Marnes Bleues d'Hauterive (MBH; Fig. 6.2). The base of the Zone Marno-Calcaire (ZMC) is marked by a small decrease of 0.5‰. Discontinuity 2 (Rumley 1992) does not show any changes. A pronounced negative $\delta^{13}\text{C}$ shift occurs just below the top of the ZMC. Values drop from +0.5‰ to -4‰. Within the Pierre Jaune de Neuchâtel Formation (PJN) the $\delta^{13}\text{C}$ values first slightly increase to -2.5‰ before they descend even further to -5‰, however a positive trend maybe discerned towards the top of the PJN, where values fluctuate between -3 and -4‰.

The oxygen isotope record partly mirrors the carbon isotope record. Values lie around -2 to -3‰ in the MBH. A sharp negative shift with values reaching -7‰ occurs in the basal meters of the ZMC. Again, no major changes are observed for Discontinuity 2. A slight recovery is observed in the middle part of the ZMC. The upper part of the ZMC and lower part of lower PJN show a more gradually decreasing trend from -4 to

-6.6‰. A noisy trend is observed for the remainder of the PJN with values fluctuating between -7 and -5‰.

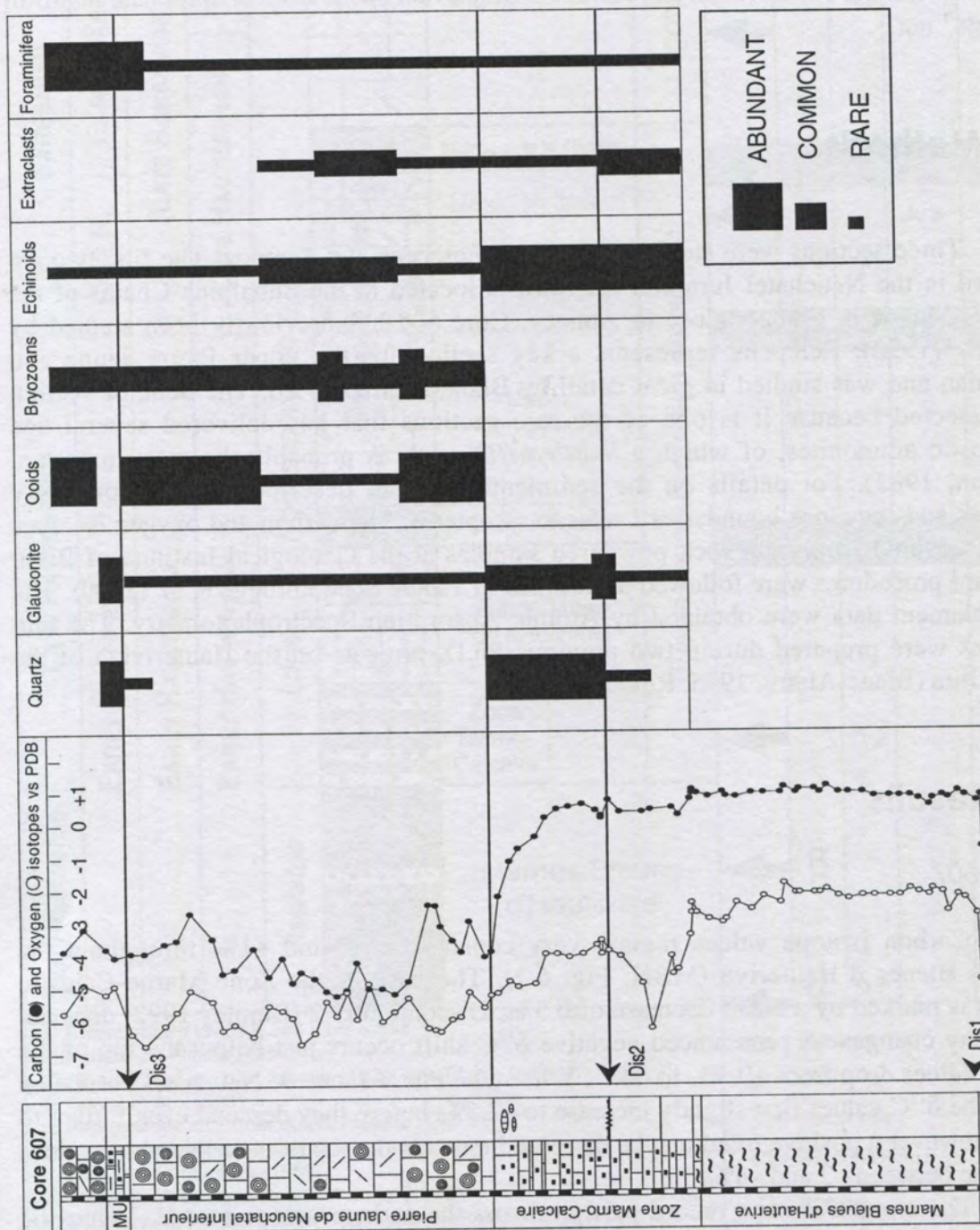


Figure 6.2 - Carbon and oxygen isotope results for Core 607 plotted with main sedimentary aspects. Lithology of core is after Rumley (1992). Dis 1, 2 and 3 are Discontinuity surfaces from Rumley (1992).

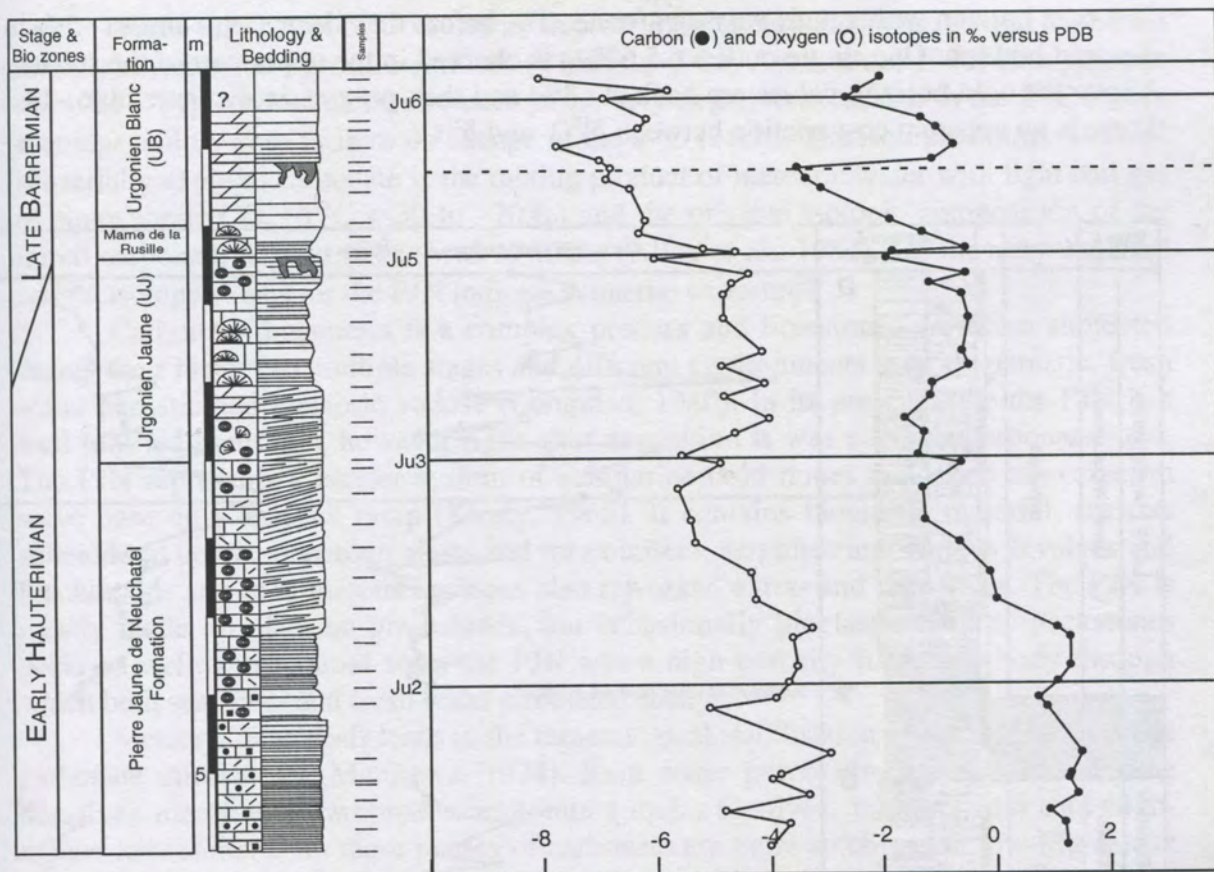


Figure 6.3 - Carbon and Oxygen isotopes for Eclepens. Lithology modified after Blanc-Aletru (1995).

Eclepens

Carbon isotope values are relatively positive varying between +1 and +1.5‰ in the basal 14 meters (Fig.6.3). At the base of a unit consisting of crossbedded oolitic grainstones, $\delta^{13}\text{C}$ values start to decrease and reach minimal values in the top of what Blanc-Aletru (1995) calls the upper PJN. Values slightly increase and remain constant then in the lower Urganian. A short lived negative spike marks the top of the lower Urganian. The Marnes de la Rusille and upper Urganian show two distinct negative shifts. The oxygen isotopes clearly vary in the same manner as the carbon isotopes, albeit slightly more noisy. Values range from -4‰ at the base of the section to -8‰ in the upper Urganian.

Semnoz

The base of the section shows $\delta^{13}\text{C}$ values rapidly increasing from -1‰ to +1‰ (Fig.6.4). Carbon isotope values remain stable upto the top of the first sequence. Oxygen isotopes are fluctuating between -2‰ and -4‰. In the upper part of the section values gradually decrease from 0‰ to around -1‰ and increase again from the base of a first horizon with ooids to reach values of +0.5‰. $\delta^{18}\text{O}$ values are relatively stable upto the

first ooid horizon with values varying around -3‰ before they decrease to almost -5‰ in the ooid horizon. One single outlier (-5.62‰) is observed in the upper part of the section. Above the ooid horizon values are back at -3‰ and then progressively descend to -4‰ . There is no apparent co-variation between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$.

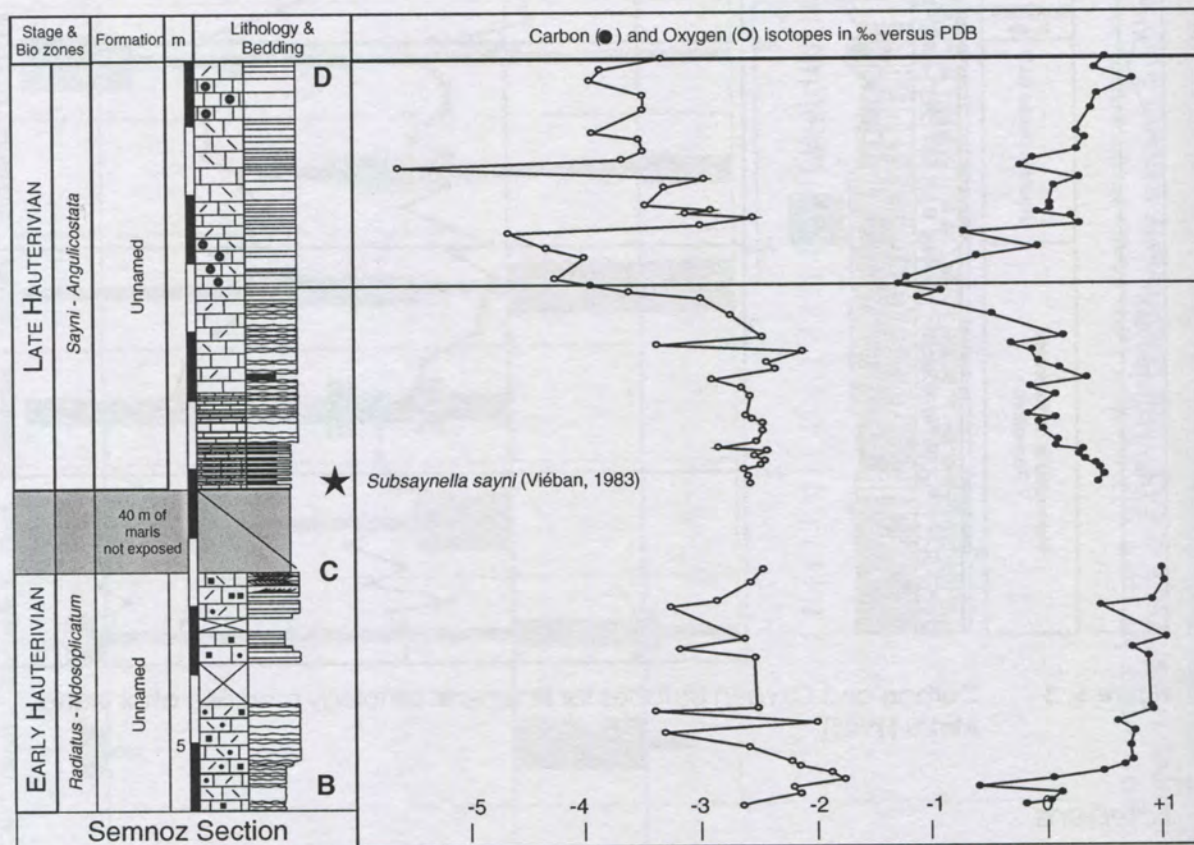


Figure 6.4 - Carbon and oxygen isotope results for Semnoz section. Note large sample gap due to vegetation cover in middle part of section.

6.4 Discussion

In Core 607 values for oxygen and carbon isotopes in the MBH are comparable to those measured from micrites in the Vocontian Basin for the early Hauterivian *Radiatus* zone and indicate that the MBH has retained a primary signal. The glauconitic hardground of discontinuity 2 is clearly a submarine hardground, characterized by early marine diagenesis that led to precipitation of calcite with a contemporaneous sea water isotopic composition. On the contrary, the very negative $\delta^{13}\text{C}$ values in the PJN can not be correlated with the pristine records of the Vocontian and Umbria Marche Basins, which change by about 1‰ only during the *Loryi* and *Nodosoplicatum* zones. The carbon and oxygen isotope records for the PJN can only be explained as the result of extensive diagenesis.

Negatively offset $\delta^{13}\text{C}$ values in shallow marine carbonates have been explained to indicate subaerial exposure surfaces (Videtic, 1980; Allan et al., 1982; Humphrey et al., 1986). Typical for such carbonates is the very negative excursion in the $\delta^{13}\text{C}$ record accompanied by very little to no change in the $\delta^{18}\text{O}$ record. The isotopic composition of subaerially exposed carbonate is the mixing product of meteoric water with light soil gas or atmospheric CO_2 ($\delta^{13}\text{C} = -30$ to -20‰) and the original isotopic composition of the initial carbonate deposit ($\delta^{13}\text{C} = +1$ to $+3\text{‰}$; (Allan et al., 1982). Do the very negative carbon isotope values for the PJN indicate subaerial exposure?

Carbonate diagenesis is a complex process and limestones are often subjected during their history to multiple stages and different environments (marine phreatic, fresh water phreatic and meteoric vadose (Longman, 1980). In its present state the PJN is a well lithified limestone, however right after deposition it was a friable carbonate sand. The PJN represents a barrier system of submarine ooid dunes deposited above storm wave base on a shallow ramp (Király, 1965). It contains bioclastic material, such as echinoderm debris, bryozoan clasts and foraminifera, serpulids and various bivalves and brachiopods and in numerous horizons also reworked extra- and intraclasts. The PJN is mostly made up of clean grainstones, but occasionally bioclastic-oolithic packstones occur as well. In its initial form the PJN was a high-porosity limestone body through which both sea water and fresh water circulated easily.

Meteoric diagenesis leads to the mineralogical stabilisation of an initially unstable carbonate mineralogy (Matthews, 1974). Rain water percolating through a soil zone dissolves metastable carbonates aragonite (ooids, bivalves, brachiopods) and high-magnesian calcite. Both these phases of carbonate are more soluble than low-Mg calcite and groundwater therefore becomes supersaturated with respect to low Mg-calcite much quicker, while remaining undersaturated with respect to aragonite and high-Mg calcite. As water trickles down, it dissolves the metastable phases and precipitates the stable calcite. Through this process limestones also lose their Mg and Sr. This is illustrated (Fig. 6.5) by the very low Mg and Sr concentrations in the top of the ZMC and the PJN. The manganese concentrations peak at the same level as the most negative carbon isotope values. This manganese is visible in thin sections as diagenetic stainings of Mn-hydroxides (associated with Fe-hydroxides) on bioclasts and ooids. Organic matter (determined with RockEval 6) is also completely oxidized in the PJN, although the low TOC contents may also point to initially low TOC, because oolitic grainstones represent in general unsuitable environments for organic carbon deposition. All these features are typical for a limestone package that has gone through all five diagenetic stages of Land (1970) in the subaerial fresh water environment.

Meteoric diagenesis is a very rapid process and has been shown to convert coral terraces on Barbados from metastable calcite to 100% calcite in 200,000 years (Matthews, 1986). According to Land (1970) the meteoric phreatic zone is the most important of the two meteoric zones for carbonate diagenesis. In this zone cementation produces coarse sparry calcite. Vadose meteoric diagenesis is relatively ineffective in precipitating cements. Once a limestone has been recrystallized in the phreatic zone not much will happen to it in the vadose zone when it is exposed again later on (Marshall, 1992). Re-examination of thin sections previously used by Rumley (1992) to study the sedimentology of Core 607, shows that meteoric diagenesis had a great impact on the

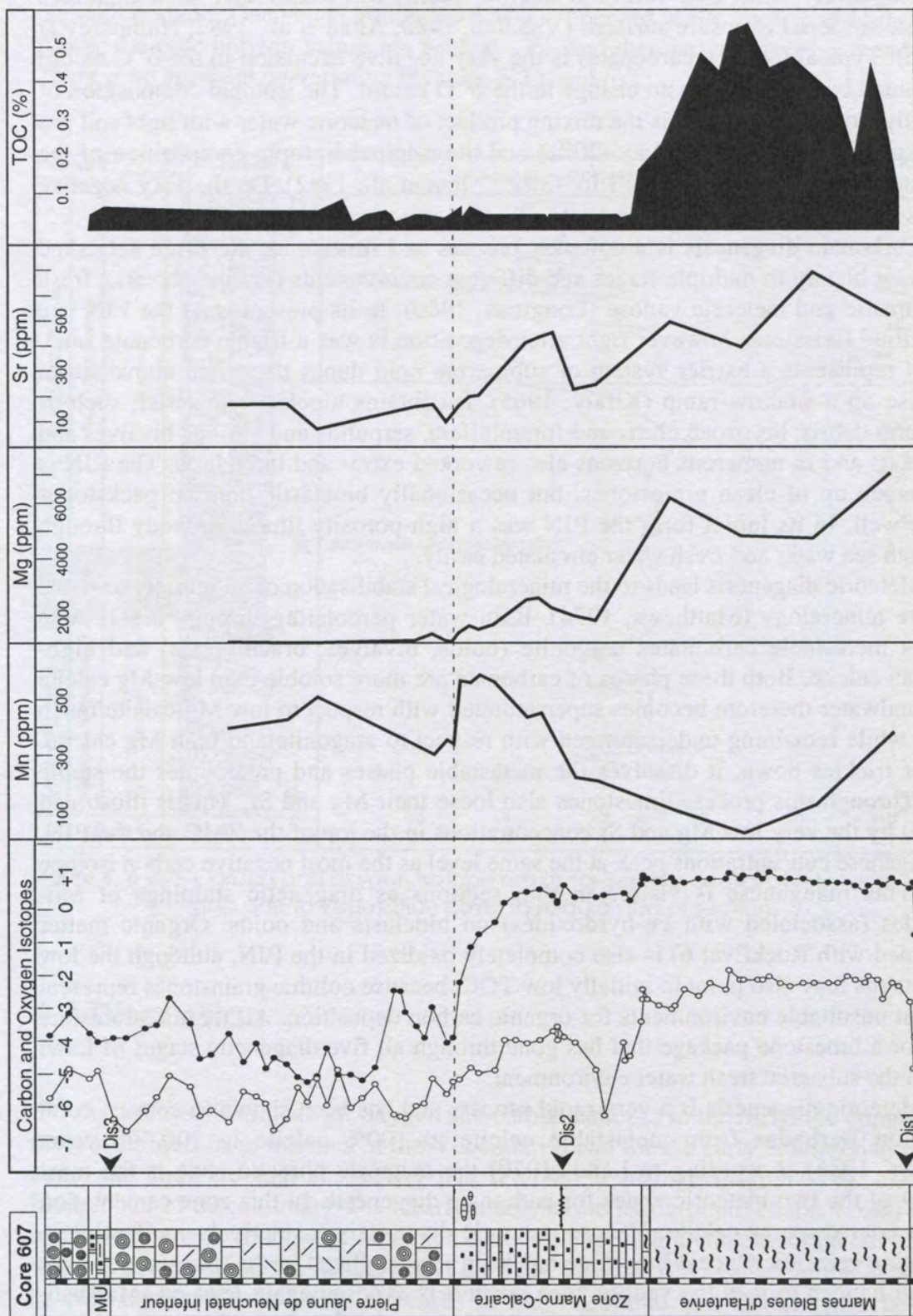


Figure 6.5 - Comparison of isotope data with trace element (Sr, Mg, Mn) and RockEval6 data. The high organic carbon values in the middle part of MBH might be an equivalent of the alauconitic level of Cressier

PJN (see also Plate 6.1 for description of microfacies). Early marine diagenesis probably transformed the ooids in micrite, maybe with the help of blue-green boring algae (Bathurst, 1983). Marine phreatic diagenesis also led to the precipitation of dog-tooth cements, which can be observed as small rims around ooids and bioclasts. These rims are often dissolved, because they consisted of high-magnesian calcite or aragonite. In a later stage meteoric diagenesis led to the infilling of pores by drusy calcite (sparite). In a final stage micritic ooids and micritized bioclasts were selectively (partially or sometimes completely) leached out of the stable calcitic matrix and sometimes also filled with sparry calcite. Selective leaching may explain the second shift in the carbon isotope record that occurs 6 meters above the base of the PJN. In the basal 6 meters of the PJN carbon isotope values increase hand in hand with decreasing oo-moldic porosity (Fig.6.1). The negative shift that follows is probably related to the sudden increase in echinoderm debris, grain size and sparry calcite that fills the larger pores.

Just below the top of the ZMC (and just below the first negative carbon isotope shift) a conspicuous chert level occurs in core 607. Chert occurs as replacement in vugs and molds in the form of chalcedony. Comparison with several other outcrops and cores either from literature or sampled for this study, shows that chert is invariably present between the PJN and the MBH and above Discontinuity 2 of Rumley (1992).

In Figure 6.6 several cores and outcrops from the Neuchâtel Jura are plotted that cover the transition from the Marnes Bleues to the Pierre Jaune. Core 208 was described by (Remane 1989). From this core no chert is described from the ZMC. The authors do report an oyster infested hardground that would correlate with Discontinuity 2 of Rumley (1992). Remane et al. (1989) state that this core closely resembles an outcrop 700 meters from where core 208 was drilled near the Tunnel de Prébarreau. In this outcrop Remane et al. (1989) found chert and a glauconitic hardground (page 34, fig.9 of Remane et al., 1989). Core 565 was studied by Rumley (1992). He places discontinuity 2 at the very base of the core, where he observed a glauconitic nodular hardground. Re-examination of thin sections brought to light the presence of a chert horizon in the top of biomicritic unit rich in quartz and glauconite and echinoderm debris (Fig. 6.5). This unit corresponds to the ZMC of Core 607. The section of Mont Chamblon was described in great detail by Jordi (1955). Also in this outcrop chert is present beneath the PJN, but in this case below Discontinuity 2 (see Fig. 6.5). The outcrop of St. Aubin was sampled during the construction of a tunnel in 1999 and is covered again now. Within the ZMC chert beds occur below largescale crossbedded limestones belonging to the lower PJN. The ZMC and lower PJN are very glauconitic throughout, but two beds are particularly enriched within the ZMC.

Because chert occurs as replacements of bioclasts and ooids it is diagenetic in origin. Knauth (1979) explains the chert formation in shallow marine limestones as the result of mixing meteoric and marine waters. Meteoric waters moving through a limestone body containing biogenic silica (opal-A) will become supersaturated with respect to silica and remain undersaturated with respect to calcite. The PJN, as do most Hauterivian carbonates along the northern margin of the Tethys, contains a considerable amount of sponge spicules, especially in several marly intervals. The sponge spicules are always replaced by calcite.

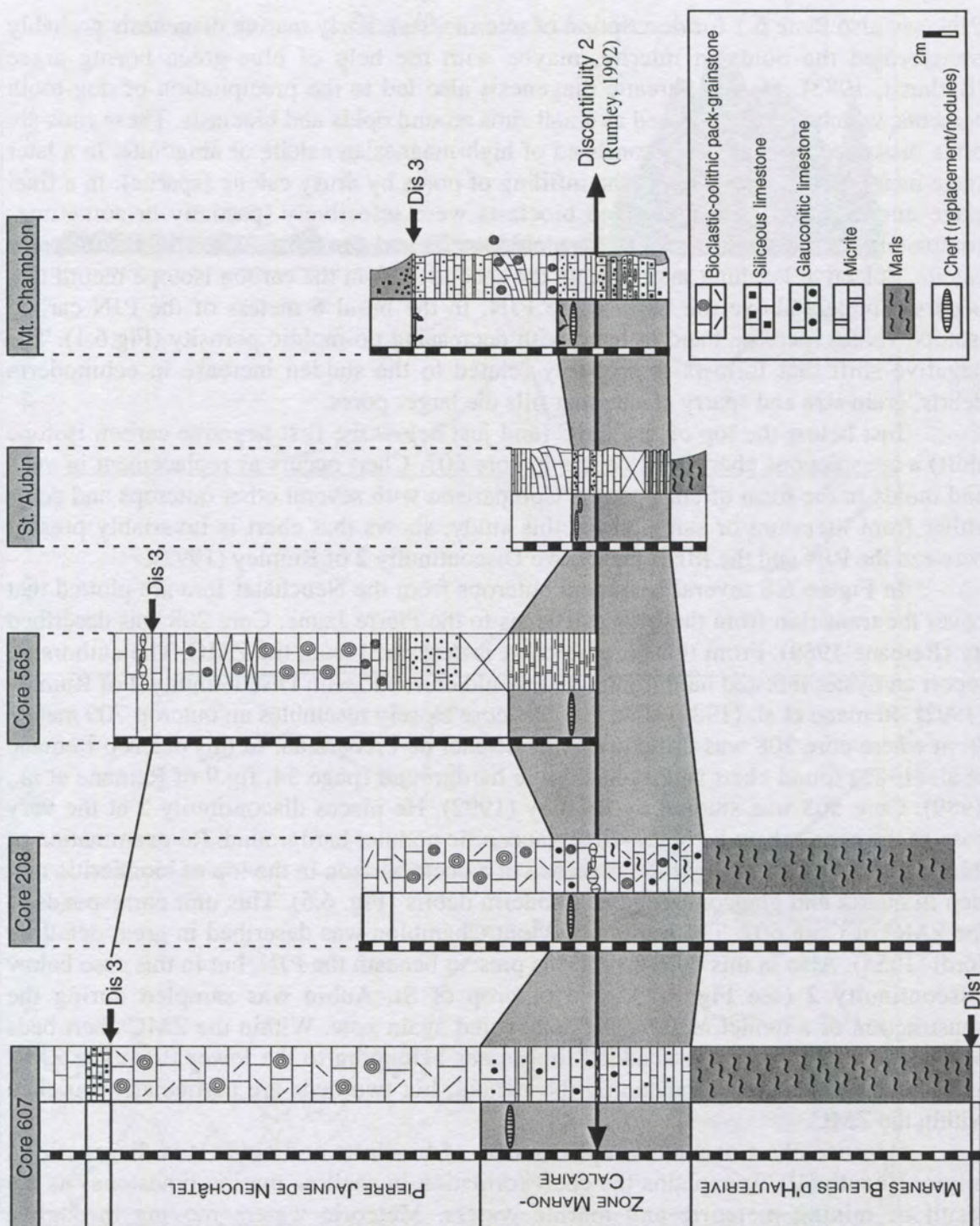


Figure 6.6 – Correlation panel of several cores and outcrops. Core 607 and 565 after Rumley (1992), Core 208 after Remane et al. (1989), St. Aubin (sampled during this thesis project), Mont Chamblon after Jordi (1955).

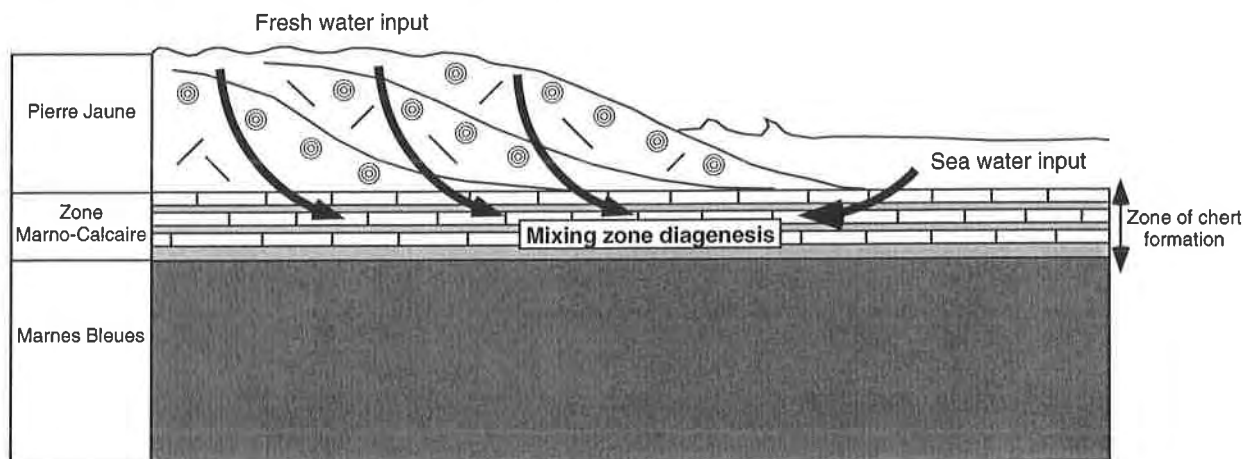


Figure 6.7 Sedimentological model explaining formation of chert horizons below the Pierre Jaune Fm during sea level fall (modified after Knauth, 1979).

The carbon isotopes, the diagenetic history of the oolitic and bioclastic limestones and the chert beds all indicate an important emersive event. Sea level lowstand resulted in subaerial exposure of the ooid shoals of the PJN and a mixing zone of meteoric and sea water was established above the impermeable MBH (Fig. 6.7). But where is the exposure surface located in Core 607? Carbon isotope ratios remain very low throughout the lower PJN upto the top of Core 607, so exposure probably occurred higher up in the sequence.

The isotope records from Eclepens are just as much controlled by lithology as they are in Core 607. The seemingly pristine carbon isotope values in the first 14 meters can be ascribed to the fact that this part of the upper Pierre Jaune is an oo-biomicrite which has been relatively untouched by later stages of diagenesis. Decreasing $\delta^{13}\text{C}$ values correspond to the gradual replacement of micrite by sparite. Correlation of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ records with the sequence boundaries (SB) recognized by Blanc-Aletru (1995) is very good, except maybe for SB Ju2. The $\delta^{13}\text{C}$ record was probably offset several times by subaerial exposure at sequence boundaries Ju3, Ju5 and Ju6. A major negative shift in the upper Urgonian, corresponding to a karstic surface, is not related to a sequence boundary of (Blanc-Aletru, 1995). It is very likely, given the very shallow depositional setting in which the upper Urgonian accumulated, that there are many more subaerial exposure surfaces, which might be identified with the help of C and O isotopes.

The isotope records of Core 607 and Eclepens are clearly different. In the upper part of core 607 carbon isotope values reach -3‰ , while in Eclepens they are $+1\text{‰}$ at the base (Fig. 6.7). If we accept that the isotopic signal from Core 607 is the result of early diagenetic transformation due to subaerial exposure and diagenesis in the meteoric phreatic zone, a major discontinuity surface should be present at the top of the upper Pierre Jaune (or at the base of the Urgonien Jaune sensu Conrad and Masse (1989). It should be recalled that Blanc-Aletru (1995) divides the PJN in three parts: 1) A lowermost part spanning the MBH, ZMC and lower PJN. 2) A middle part spanning the Marnes d'Uttins and the lower part of the Upper PJN bounded by sequence boundary Ju1 at the base. 3) An upper part spanning the upper part of the upper PJN bounded by Ju2 at

the base. The definition of the Pierre Jaune according to Conrad and Masse (1989) seems more logical in the light of the here presented isotope results. Placing sequence boundary Ju2 at the base of the quartz rich interval in Eclepens would also be more in accordance of the here presented results. Sequence boundary Ju2 thus corresponds to a major subaerial exposure surface that led to emersion of the complete PJN. Blanc-Alteru (1995) already recognised this boundary as an erosional and emersion surface. It is however very unfortunate that this part has not been covered by any measurements. Further sampling of the missing strata would help to further elaborate the here presented views.

Evidence for a major discontinuity on top of the PJN lends some support to the views of Arnaud-Vanneau and Arnaud (1990), Arnaud-Vanneau and Arnaud (1991) and Arnaud et al. (1999), who claim that the Pierre Jaune and Urgonian limestones are separated by a major hiatus corresponding to the whole late Hauterivian and early Barremian. However, the results presented above still do not resolve the problem of the presence or absence of late Hauterivian sediments in the Neuchâtel area.

The whole Pierre Jaune has been assigned to the early Hauterivian with the upper Pierre Jaune probably forming the upper part of the *Nodosoplicatum* zone. After comparison with the cycle charts of Hoedemaeker (1995) and Hardenbol et al. (1998), sequence boundary Ju2 might correspond to sequence boundary Ha4 of the latter authors, which represents a major truncation surface that can be followed onto the Russian Platform (Sahagian et al., 1996). Arnaud-Vanneau et al. (1990) state that late Hauterivian sediments were present in the Neuchâtel region, but were later eroded during an early Barremian regressive phase.

The here presented isotope data for Core 607 and Eclepens unfortunately will not elucidate the age of the lower Urgonian (*sensu* Conrad and Masse, 1989), and it is still not excluded that this unit is of late Hauterivian age. Neither confirms this interpretations of (Clavel et al., 1987; Clavel 1995), who do not see evidence for major erosional surfaces and breaks in sedimentation in the Hauterivian of the Swiss Jura.

Problematica

Within the Semnoz section (slightly more open marine facies) the late Hauterivian is present beyond doubt (Viéban, 1983), due to the presence of a *Subsaynella sayni*, marking the base of the late Hauterivian. The carbon isotope record for the Semnoz section shows however a clear trend that resembles very much the Vocontian Basin record. The Vocontian Basin record shows a minimum at the early-late Hauterivian boundary on a long term decreasing trend that starts in the late Valanginian. A minimum on a gradual decreasing trend can be observed in Semnoz, but it occurs too high up in the section, given the presence of a *Subsaynella sayni* approximately 10 meters below the inflection in the $\delta^{13}\text{C}$ curve. The negative carbon isotope trend in the Semnoz section therefore postdates the Vocontian Basin minimum. Interestingly, the isotope results are again in conflict with the finding of *Subsaynella sayni*.

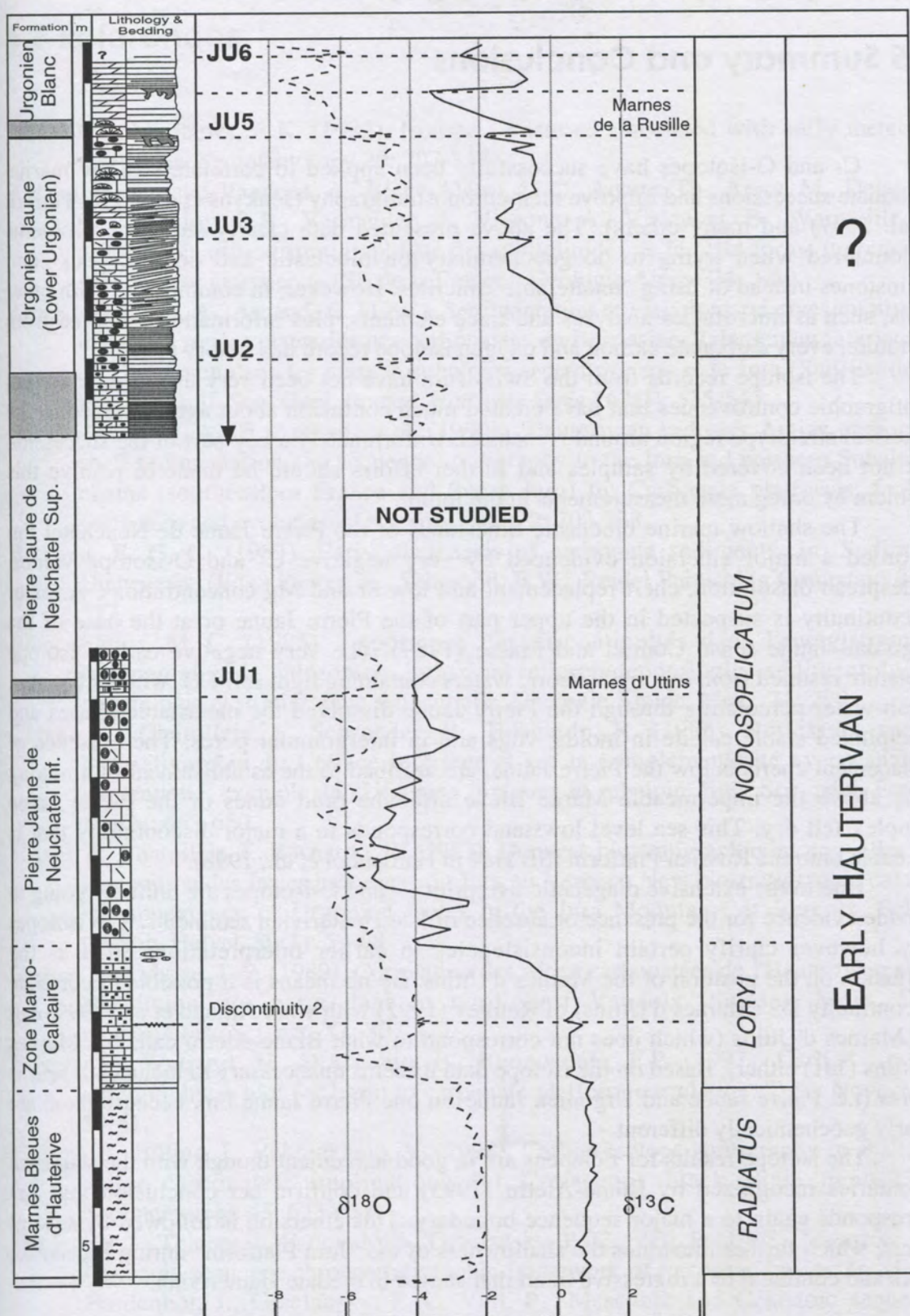


Figure 6.8 - Carbon and oxygen isotope curves for Core 607 and Eclepens. Note that age of the Urgonien Jaune remains elusive.

6.5 Summary and Conclusions

C- and O-isotopes have successfully been applied to correlate shallow marine carbonate successions and improve their chronostratigraphy (Jenkyns et al., 1994; Ferreri, et al. 1997) and many others). The above presented data clearly show the problems encountered when trying to do geochemistry on bioclastic and oolitic pack- and grainstones instead of using "unalterable" micrites. However, in combination with other tools, such as microfacies analyses and trace elements, plus information retrieved from literature, every carbonate carbon and oxygen isotope record has a story to tell.

The isotope records from the Swiss Jura have not been very useful in resolving stratigraphic controversies that have created much confusion about ages assigned to the historical stratotype region around Neuchâtel. Unfortunately a key part of the succession has not been covered by samples and further efforts should be made to resolve this problem by doing more measurements in the future.

The shallow marine bioclastic limestones of the Pierre Jaune de Neuchâtel Fm recorded a major emersion evidenced by very negative C- and O-isotope values, widespread dissolution, chert replacement and low Sr and Mg concentrations. A major discontinuity is suspected in the upper part of the Pierre Jaune or at the base of the Urgonian Jaune sensu Conrad and Masse (1989). The very negative carbon isotope signature resulted from mixing meteoric waters containing light soil CO₂ with carbonates. Fresh water percolating through the Pierre Jaune dissolved the metastable phases and precipitated stable calcite in molds, vugs and in intergranular pores. The presence of replacement cherts below the Pierre Jaune, are ascribed to the establishment of a mixing zone above the impermeable Marne Bleue after the ooid dunes of the Pierre Jaune complex fell dry. This sea level lowstand corresponds to a major discontinuity that is traceable onto the Russian Platform (SB Ha4 in Hardenbol et al., 1998).

Due to the extensive diagenetic overprint C- and O-isotopes are unlikely going to provide evidence for the presence or absence of late Hauterivian sediments. The isotopes may however clarify certain inconsistencies in earlier interpretations such as the confusion on the position of the Marnes d'Uttins. By no means is it possible to correlate discontinuity D2 (Marnes d'Uttins) of Rumley (1992) with what Arnaud et al. (1999) call the Marnes d'Uttins (which does not correspond to what Blanc-Aletru calls the Marnes d'Uttins (Ju1) either). Based on the isotope data it seems unnecessary to include all *yellow stones* (i.e. Pierre Jaune and Urgonien Jaune) in one Pierre Jaune Fm, because these are clearly geochemically different.

The isotope results for Eclepens are in good agreement though with the sequence boundaries recognized by Blanc-Aletru (1995) and confirm her conclusion that Ju3 corresponds again to a major sequence boundary. This emersion is followed by several others, which further illustrates the shallowness of the "Jura Platform" during Barremian times and continual of a regressive trend that started in the late Hauterivian.

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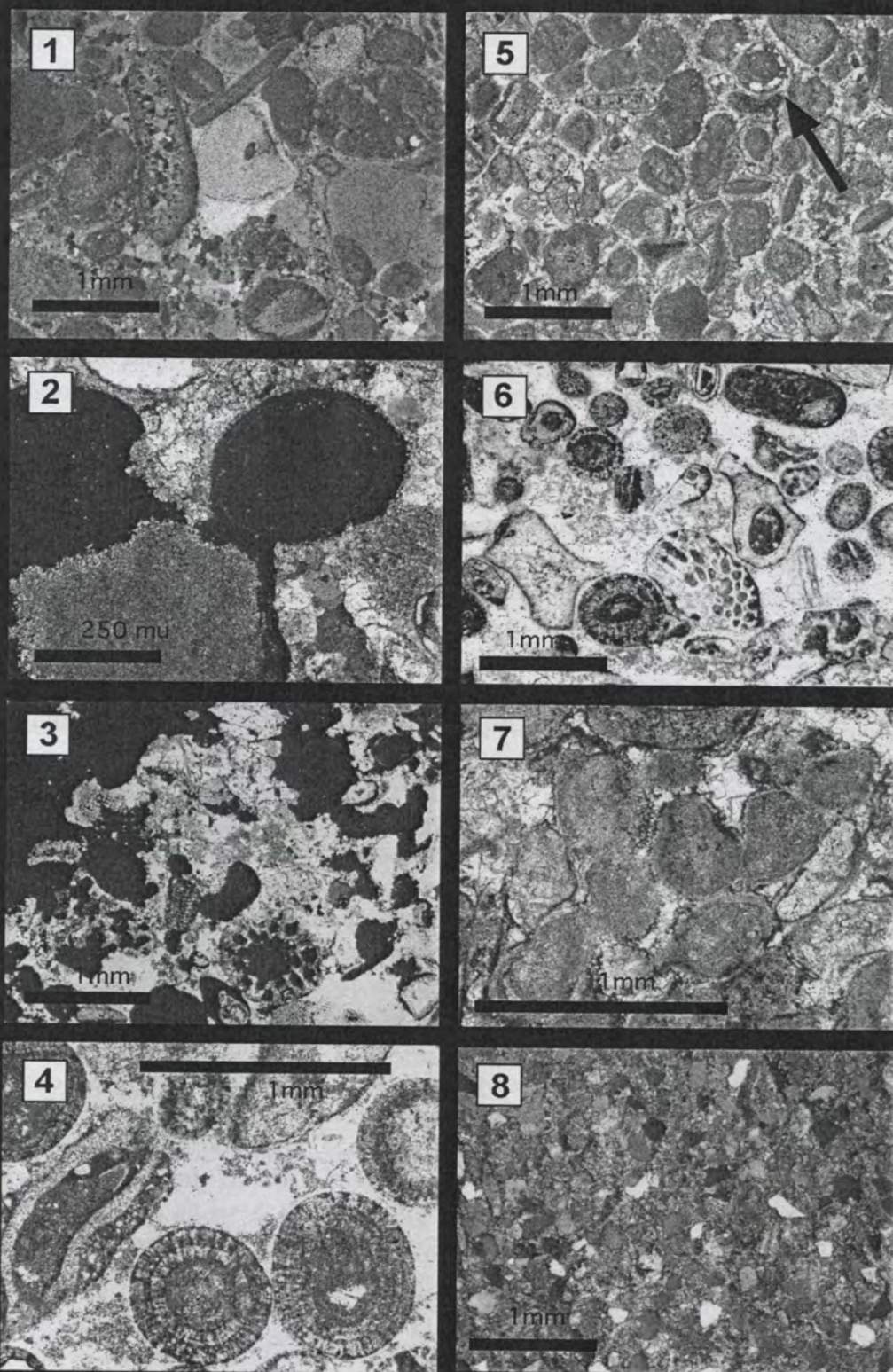
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PLATE 6.1 – Pierre Jaune de Neuchâtel, Core 607, thin sections.

- Figure 1. *Sample 183*. Polarized view, 25x. Bioclastic packstone with abundant echinoderm debris (center of photograph, pink colored). Some small mature ooids may be observed as well. This facies has been completely recrystallised (sparite, syntaxial overgrowths).
- Figure 2. *Sample 196*. Polarized view, 100x. Oolitic grainstone. Large oomoldic porosity after dissolution of micritized ooids (lower part of photograph).
- Figure 3. *Sample 196*. Polarized view, 25x. Larger view as in Figure 2. Note large oomoldic and moldic porosity. In the lower part a bryozoan clast that has also partly been dissolved can be observed. This sample corresponds to the most negative carbon and oxygen isotope values.
- Figure 4. *Sample 200*. Normal view, 50x. Oosparite-Oolitic grainstone. Note well preserved radial mature ooids and partly dissolved micrite within matrix, which has been replaced by sparite.
- Figure 5. *Sample 201*. Normal view, 25x. Oolitic pack-grainstone. Ooids and bioclasts have been mostly replaced by micrite. The micrite has been preferentially leached during phreatic meteoric diagenesis. In the upper right part an ooid with a dissolved cortex (arrow).
- Figure 6. *Sample 208*. Normal view, 25x. Bioclastic-oolitic grainstone. Note difference in preservation between non-micritized ooids and bioclasts that have been replaced by sparry calcite.
- Figure 7. *Sample 210*. Normal view, 50x. Peloidal grainstone. These are probably oolitic pellets (note concentric lines on the outer parts) and not micritized ooids (note irregular form). The dark rims are marine phreatic cements. The pores were later filled in with drusy calcite.
- Figure 8. *Sample 229*. Polarized view, 25x. Sandy mudstone. This type microfacies is characteristic of transgressive phases on to the Jura platform like represented by the Marnes d'Uttins or the Marnes de la Rusille. This sample corresponds to D3 of Rumley (1992) and is here assigned to the Marnes d'Uttins.

PLATE 6.1 - Pierre Jaune de Neuchatel,
Core 607, thin sections



Early Cretaceous (Hauterivian) high resolution $^{87}\text{Sr}/^{86}\text{Sr}$ record for the Vocontian Basin (France)

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Abstract

A high resolution strontium isotope record is presented that is based on early Cretaceous (Hauterivian) bulk carbonate samples and belemnites from three reference sections (La Charce, Vergons and Angles) in southeastern France. These sections permit good calibration of the isotope record with ammonite biostratigraphy. The $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio increases during the Hauterivian confirming earlier research. Belemnites are probably better carriers of the Sr-isotope signal and largely confirm an earlier low resolution study using belemnites. In two sections (Angles and Vergons) the bulk carbonate Sr-isotope record is positively offset when compared to the belemnite data. From $\delta^{18}\text{O}$ data as well as from mineralogical analyses it is concluded that these two sections suffered from burial diagenesis during Alpine deformation. A third section (La Charce), covering mainly the early Hauterivian shows a cyclic pattern of high and low Sr-isotope values measured from bulk carbonate samples, which appear well preserved based on $\delta^{18}\text{O}$ and mineralogy.

We infer that bulk carbonate $^{87}\text{Sr}/^{86}\text{Sr}$ variations in La Charce are reflective of changes in weathering/erosion on the continent related to eustatic sea level changes. This is based on 1) the observation that high $^{87}\text{Sr}/^{86}\text{Sr}$ values are correlated with high detrital input (calcite/quartz+phyllosilicates) and increases in the kaolinite/illite ratio. 2) low $^{87}\text{Sr}/^{86}\text{Sr}$ values correspond to increases in pyrite and organic matter and decreased detrital input. The position of sequence boundaries (Hardenbol et al., 1998) in the La Charce section closely match the high Sr-isotope values. A model that explains why bulk rock recorded extreme variations in Sr-isotopes in contrast to the belemnites is discussed. Cold water inflow at depth (where the belemnites lived) had an oceanic Sr-isotope signature. Surface waters (where coccolithophorids lived) were warm and influenced by fresh water input. Sea level change controlled to what extent surface water was decoupled from deep water. In addition to regressive-transgressive cycles, chemical weathering was much more intense during the Hauterivian leading to greater variation in Sr-isotope ratios.

7.1 Introduction

Over the last two decades Sr-isotope stratigraphy has become an important tool for correlation and dating and has been successfully applied by many authors (e.g. Hodell, 1989; McArthur, 1994; Erba et al., 1999). The $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio of sea water is governed by changes in the input and composition of Sr-isotopes. Various sources, like riverine influx, hydrothermal exchange and marine carbonate recycling, deliver high ratio Sr-isotopes (~ 0.720), low ratio Sr-isotopes (~ 0.704) and intermediate Sr-isotopes (~ 0.708) respectively to the oceans (Faure, 1972). Therefore the Sr-isotope signal is also an important proxy for environmental change. The Sr-isotope ratio of sea water is governed by various processes acting on shorter or longer timescales. Increased spreading rates might lead to lower Sr-isotope ratios due to exhalation of low ratio Sr during basalt formation (Jones et al., 1994a; Jones et al., 1994b). The uplift and subsequent unroofing of the Himalayas and Tibetan Plateau, is thought to have sharply increased the isotopic ratio of sea water over the last 40 Ma (Edmond, 1992; Hodell et al., 1991; Richter et al., 1992; and many others). Third order sea level changes and climate changes in the Milankovitch band width have been invoked to explain shorter term changes that fall within the residence time of Sr (Clemens et al., 1993; Dia et al., 1992; Montanez et al., 1996; Ruppell et al., 1996).

The aim of this study is to improve resolution for the Sr-isotope reference curve for the Hauterivian (early Cretaceous) in order to be able in a later stage to date shallow marine carbonate platform sediments that lack age diagnostic markers, such as foraminifera, ammonites and nannofossils. The Hauterivian part of the global Sr-isotope curve is promising for correlation because of its moderate linear increase. Previous work by (Jones et al., 1994a) does not permit correlation on the subzone and biohorizon level, because it is based on relatively few samples (8 data points for the Hauterivian).

7.2 Methods

Three sections (La Charce, Vergons and Angles) in the Vocontian Basin in southeastern France were sampled (region of les Hautes Alpes de Provence and Drôme), because of good biostratigraphic control which allows for calibration with ammonite zones (Bulot et al., 1992; Bulot et al., 1994). These sections consist of hemipelagic alternating micrites and marls (argillaceous limestones). (Jenkyns et al., 1995) showed that even shallow marine coarse-grained carbonates can retain a primary seawater Sr-isotope signature. In addition to the bulk micrite samples (no marls were measured) we used belemnites. All these samples are part of a larger sample set that was also used for carbon and oxygen stable isotope analyses (van de Schootbrugge et al., 2000).

A total of 82 bulk micrite and belemnite samples was selected and prepared for Sr-isotope analyses. Approximately 5-10 mg of powder was reacted with 1N HCl and the solution was centrifuged immediately to separate the residue. The solution was evaporated and the residue dissolved in 1 ml of 3M HNO_3 . Columns with Sr-spec-pure resin were used to separate Sr from Ca cations. Strontium samples were

stored in 0.01M HNO₃ and before analyses diluted with 0.35M HNO₃. The samples were analysed on a Nu Instruments ® Multiple Collector Inductively Coupled Plasma-Mass Spectrometer (MC-ICP-MS) in static mode at the University of Bern. During the analyses 27 standards were measured with an average of 0.710283 (2 s.d. = 0.000030). The measured values were normalized suite by suite to a NBS 987 value of 0.710256 for comparison with other data. A total of 35 micrite samples was analysed for its bulk rock and clay mineral composition using an Scintag XRD 2000 diffractometer and following standard procedures at the Institut de Géologie of the University of Neuchâtel, Switzerland (Adatte et al., 1996). The belemnites used in this study were examined for diagenetic alteration with the help of trace element analyses (Sr, Mg, Fe and Mn, see van de Schootbrugge et al. (2000) for data and methods).

7.3 Results and discussion

7.3.1 Results

The bulk carbonate Sr-isotope record shows a very noisy trend towards more radiogenic values from the base to the top of the Hauterivian (Fig. 1A). Lowest values are measured for the early Hauterivian *Radiatus* zone (0.707371), while the highest were measured for samples from the latest Hauterivian *Angulicostata* zone (0.707544). Plotted against the trend that was given by (Howarth and McArthur, 1997; Jones et al., 1994a), it can be seen that data extracted from the Vergons and Angles sections, representing the late Hauterivian, are positively offset (Fig. 1A). However, the La Charce data fall within the trend that was given by the above mentioned authors. Belemnites show the same general increase from the base (0.707373) to the top (0.707479) of the Hauterivian (Fig. 1B). All the belemnite data plot within the range given by (Jones et al., 1994a), regardless of their trace element concentrations. The carbonate contents of samples from La Charce is on average 90%. The remaining 10% is formed by various phyllosilicates of which smectite is the most important, making up 80% of the clay mineral assemblage, followed by illite and kaolinite. The clay mineralogy of bulk rock micrites is very different in the La Charce section compared to the Vergons and Angles sections (Fig. 1C-E). Samples from Vergons and Angles have persistently lower amounts of smectites and increased amounts of chlorite (Fig. 1C). Another important trend in the clay-mineral assemblages of Vergons and Angles is the gradual increase in illite for the fraction 2-16 µm (Fig. 1D). Also plagioclase is showing a much higher abundance for Vergons and Angles than La Charce (Fig. 1E). Pyrite is only observed in La Charce (Fig. 2C).

7.3.2 Diagenetic versus primary signal

We confirm that belemnites are good carriers of the oceanic Sr-isotope signal (McArthur, 1994), because our data compare closely to belemnite data from Speeton, England (Jones et al., 1994a). The oxygen and carbon isotopes measured for the belemnites show high $\delta^{18}\text{O}$ (-1‰ to +1‰) and low $\delta^{13}\text{C}$ values (-1‰ to +1‰) compared to bulk rock values, which show lower $\delta^{18}\text{O}$ (-4‰ to -1‰) and higher $\delta^{13}\text{C}$ values (+0.5‰ to +3‰). This was interpreted as reflecting isotopic between deeper water (belemnites) and surface water (bulk rock, see van de Schootbrugge et al., 2000).

The positively offset Sr-isotope values for the Vergons and Angles bulk carbonate samples are clearly linked with more diagenetic alteration. Indications for more diagenesis in Vergons and Angles compared to La Charce include: lower oxygen isotope values (-4‰), recrystallization of smectite and increase in chlorite (also observed by Deconick, 1987), and an increase in plagioclase. The gradual increase in illite (2-16 μm) observed in Vergons and Angles could well account for more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ values, as the presence of more illite would enhance the risk of leaching. The diagenetic modification of Vergons and Angles is the result of higher burial temperatures and recrystallization during Alpine deformation, because these two sections are part of the Digne-thrust system.

La Charce belongs to the autochthonous part of the pre-Alps and was only tilted as a result of Alpine deformation. As a consequence La Charce has been better preserved and has bulk carbonate oxygen isotope values for the Hauterivian varying around -1‰ VPDB (van de Schootbrugge et al., 2000). The bulk carbonate Sr-isotope results for La Charce fit better with previous records for the early Hauterivian, but still show deviating (both high and low) Sr-isotope values when plotted together with the data of Jones et al. (1994a). Mineralogical data further illustrate the relatively little diagenetic overprint on La Charce. Smectites have not been recrystallised and pyrite has been preserved. Erba et al. (1999) correlated high pyrite contents with high Sr-isotope values in the Apticore Project and ascribed this to the formation of H_2SO_4 in sediments rich in pyrite that could possibly have leached Sr from sheet silicates. Our data for La Charce show low Sr-isotope values correlating with high pyrite values. In any case sulfuric acid formed by pyrite would be buffered by the enormous amount of carbonate in La Charce. Another important observation is that the belemnite and bulk rock Sr-isotope records show much more resemblance in La Charce than in Vergons and Angles.

We conclude that the La Charce section is by far better preserved based on the $\delta^{18}\text{O}$ record and mineralogical data and hence the La Charce Sr-isotope results for bulk carbonate samples could reflect a primary signal.

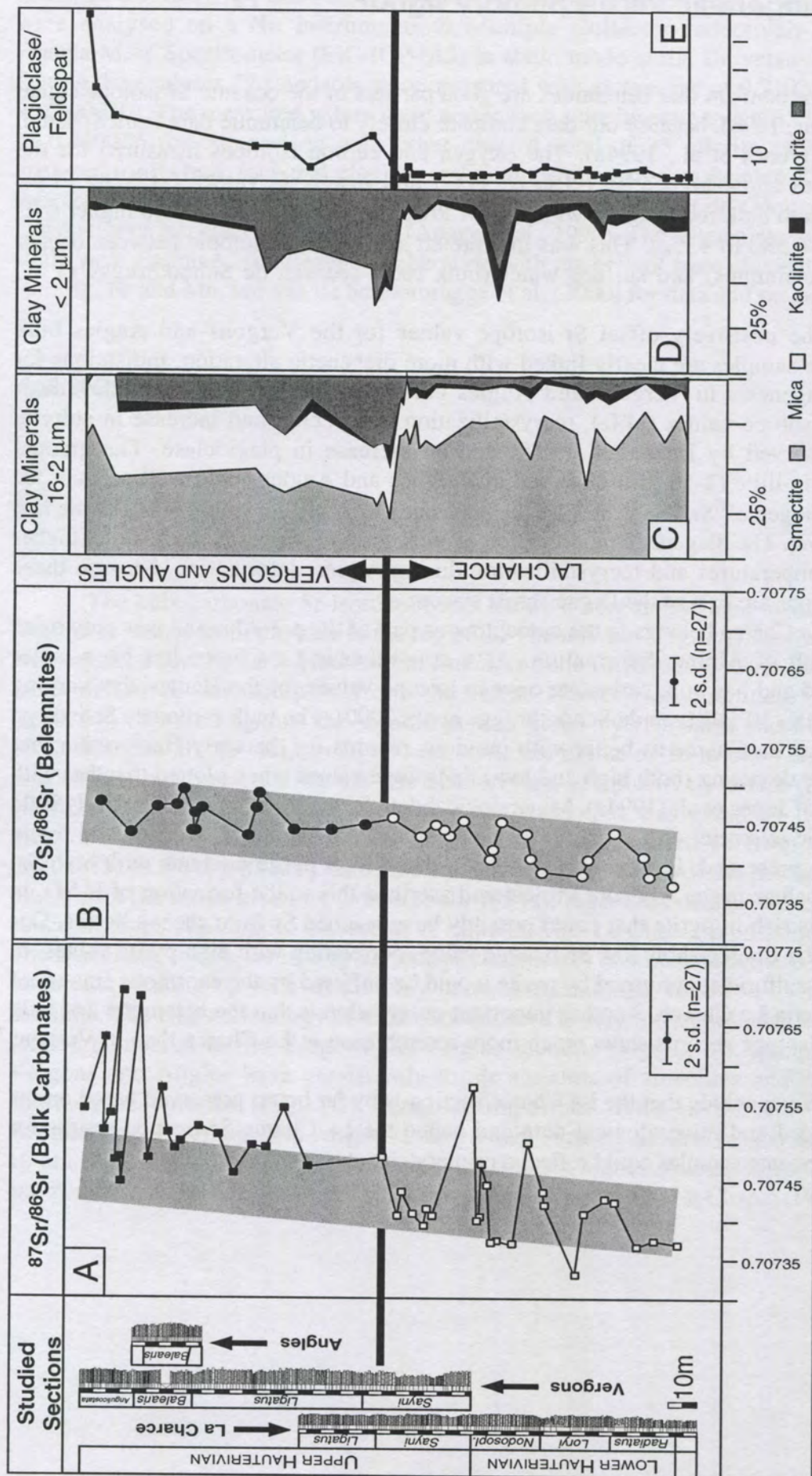


Figure 7.1 – A) Bulk micrite Sr-isotope record. White squares samples from La Charge. Black squares samples from Angles and Vergons. Thick gray band is based on data from Jones et al. (1994a) with error margin included. B) Belemnite Sr-isotope record. White circles La Charge. Black circles Angles and Vergons. Thick gray band as in Fig. 1A. C-E) Clay mineral data for all three

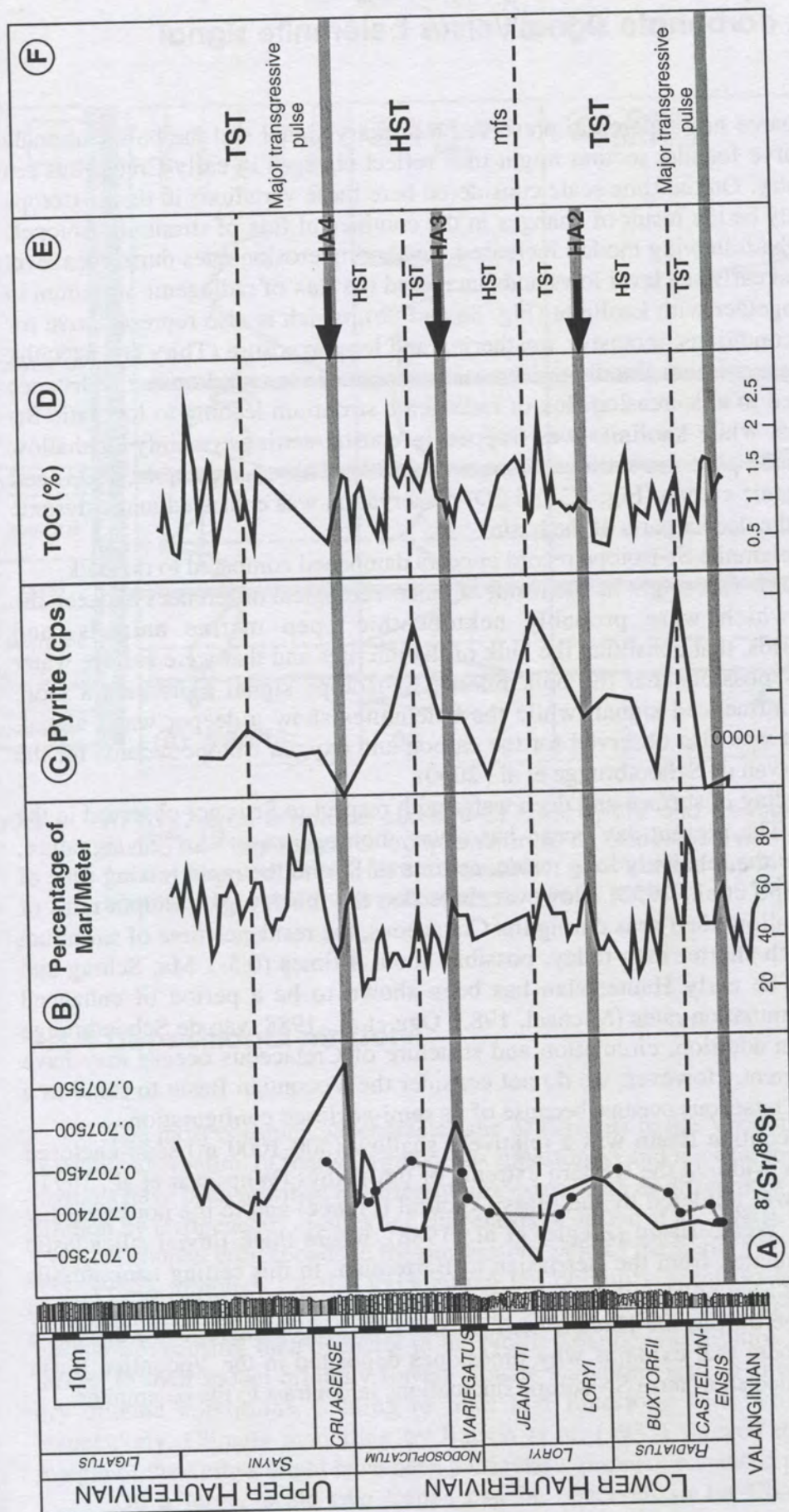


Figure 7.2 –

A) Sr-isotope curve for La Charte based on bulk micrites (line) and belemnites (black dots). B) This curve shows the marl contents per standard unit, in this case per meter. Note the large spikes in the Radiatus and Sayni zones that correspond to transgressive intervals. C) Abundance of pyrite in counts per second. These are brute values from XRD-analysis. D) Total Organic Carbon for La Charte (unpublished data provided by L.G. Bulot). E-F sequence stratigraphic interpretation based on figures A-D. Sequence boundaries were placed at high Sr-isotope values and low pyrite and organic matter

7.3.3 Bulk carbonate signal versus belemnite signal

La Charce has apparently preserved a primary signal and the bulk carbonate Sr-isotope curve for that section might thus reflect changes in early Cretaceous sea water chemistry. On the time scale considered here these variations in the Sr-isotope signal can only be the result of changes in the continental flux of strontium isotopes. We propose the following model: increased weathering/erosion rates during sea level highstands and early sea level lowstands increased the flux of radiogenic strontium to the oceans, together with kaolinite (Fig. 3a and 3b), which is also representative for more humid conditions, intensive weathering and long exposure (Thiry and Jacquin, 1993). During maximum flooding, decreased erosion or increased transport distance would have led to a decreasing flux of radiogenic strontium leading to low ratio Sr-isotope values, while kaolinite was trapped in coastal settings (mainly in shallow marine carbonate platform settings; Deconinck, 1984; Thiry and Jacquin, 1993) and pyrite and organic carbon (Fig. 2C and 2D) preservation was enhanced under dysoxic conditions in the deeper parts of the basin.

The belemnite Sr-isotope record appears dampened compared to the bulk carbonate record. This might be the result of paleo-ecological differences between the belemnites, which were probably nektonic open marine animals, and coccolithophorids, that constitute the bulk of the micrites and that were surface water dwellers. It is possible that the bulk micrite Sr-isotope signal represents a more continentally influenced signal, while the belemnites show a deeper water signal, something that was also observed for the carbon and oxygen isotope records for the same samples (van de Schootbrugge et al., 2000).

Decoupling of surface and deep water with respect to Sr is not observed in the oceans today. The present-day ocean has a very homogeneous $^{87}\text{Sr}/^{86}\text{Sr}$ signature, which is due to the relatively long residence time of Sr and the rapid mixing time of the oceans (Capo et al., 1992). However, based on the much higher output rates of aragonite in shallow shelf seas during the Cretaceous, the residence time of strontium was likely much shorter than today, possibly about 4 times (0.5-1 Ma; Schrag and Stoll, 1996). The early Hauterivian has been shown to be a period of enhanced carbonate accumulation rates (Michael, 1983; Ogg et al., 1988; van de Schootbrugge et al., 2000). In addition, circulation and structure of Cretaceous oceans may have been very different. However, we do not consider the Vocontian Basin to stand as a model for the Cretaceous oceans, because of its semi-enclosed configuration.

The Vocontian Basin was a relatively shallow (500-1000 m) semi-enclosed basin of narrow width at the western extreme of the Tethys (Wilpshaar et al., 1997). To the west it was bordered by the Massif Central (France) and to the northwest lay the continental Weald Basin (Ziegler et al., 1988), where thick fluvial siliciclastic deposits accumulated from the Berriasian to Barremian. In this setting nannofossils proliferated and accumulated thick limestone-marl alternations (in the Vercors region up to 2 km along during the Hauterivian). In the following paragraph we discuss a depositional model that explains why limestones deposited in the Vocontian Basin may have recorded short term Sr-isotope fluctuations in contrast to the belemnites.

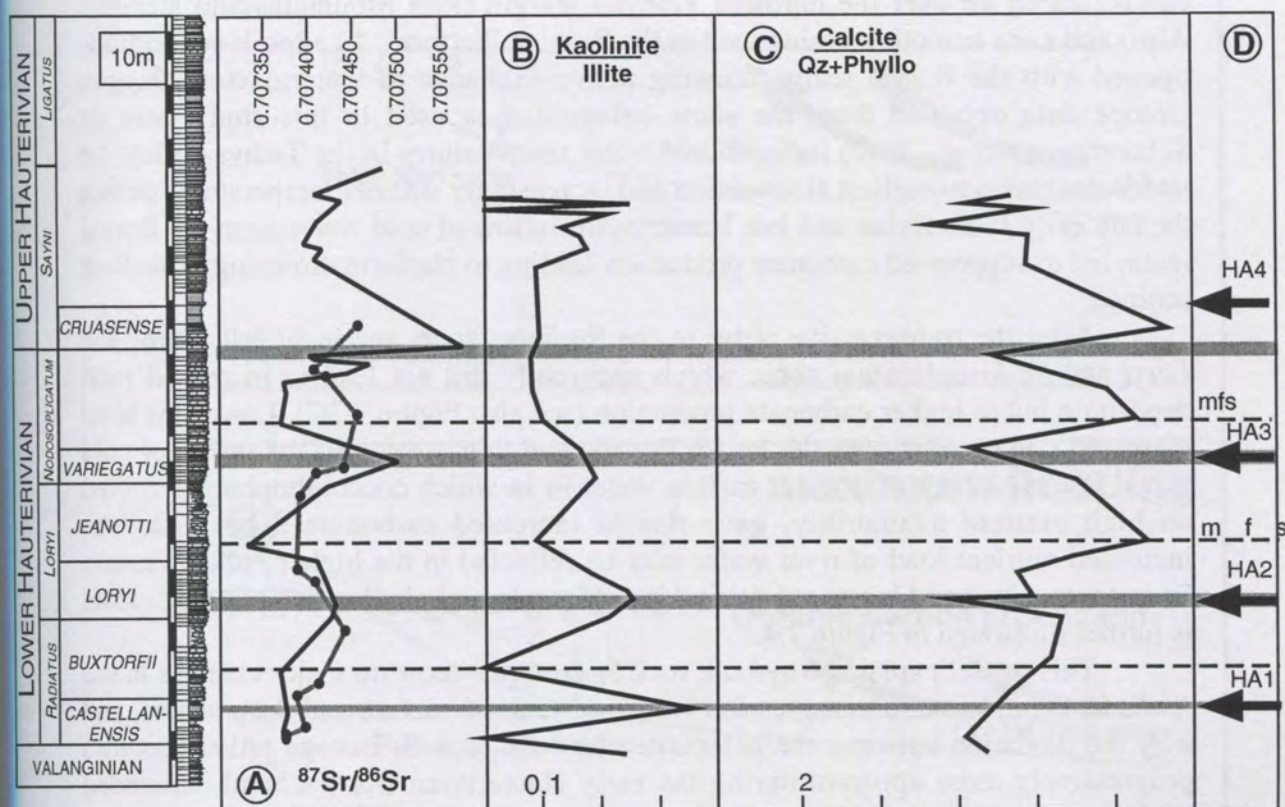


Figure 7.3 – A) La Charce Sr-isotope curve. B-C) Kaolinit/Illite and Detrital input both increases during late highstands or early lowstands. D) Correlation with sequence boundaries from Hardenbol et al. (1998). Correlation of Sr-isotope curve and SB HA4 might be improved by additional measurements in Sayni zone.

7.3.4 Depositional model

The most conspicuous characteristic of deposits in the Vocontian Basin is the rhythmic alternation of marls (argillaceous limestones) and micritic limestones. These rhythms have been ascribed to different processes, such as differences in productivity, dilution by terrigenous clastics and diagenesis (Cotillon et al., 1980). The duration of a typical couplet corresponds to the precession cycle of the Earth's orbit (Cotillon and Rio, 1984), although for the Valanginian the obliquity seems to be the dominant parameter (Giraud et al., 1998). Dean and Arthur (1999) suggested that the main mechanism causing such cyclicity in the North Atlantic was dilution by clay mineral influx. In their model orbitally forced climate variations lead to alternating wet and dry climate conditions, leading to marl and limestone beds with aeolian dust, respectively. Climate modelling by Barron et al. (1985) showed that the northern margin of the Tethys might have been particularly prone to enhanced precipitation.

On a larger scale two trends can be observed in La Charce: an overall decreasing marl content (Fig. 7.2B and 7.3C) from the *Radiatus* zone towards the top

of the *Nodosoplicatum* zone and renewed high marl contents in the *Sayni* zone. These two marl spikes (*Radiatus* and *Sayni* zones) correspond to transgressive pulses that can be traced all over the northern Tethyan margin (Jura Mountains and Helvetic Alps) and even into other basins such as the Russian Platform. As a result connections opened with the Boreal realm allowing active exchange of watermasses. Oxygen isotope data obtained from the same belemnites as used in this study (van de Schootbrugge et al., 2000) indicate cool water temperatures in the Tethys during the late Valanginian to earliest Hauterivian and increasingly warmer temperatures during the late early Hauterivian and late Hauterivian. Inflow of cold water from the Boreal realm led to suppressed carbonate production leading to platform drowning in shallow settings.

After the transgressive pulse in the *Radiatus* zone, sea level fell during the *Loryi* and *Nodosoplicatum* zone, which apparently did not lead to increased marl deposition but to higher carbonate production (see also Figure 7.3C). Lower sea level narrowed connections over the Polish Furrow and thus weakened the influx of cold water. Establishment of a warm surface water lit in which coccolithophorids thrived on high nutrient availability, gave rise to increased carbonate deposition. The increased nutrient load of river water may be reflected in the higher bulk carbonate Sr-isotope values and increased detrital input (quartz and phyllosilicates). Our model is further illustrated in Figure 7.4.

This model explains why bulk rock Sr-isotopes show no major changes in the *Radiatus* zone, because transgression led to well mixed surface and deep waters, and why the deviation between the belemnite and bulk rock Sr-isotope ratios becomes progressively more apparent during the early Hauterivian. As sea level descended surface waters recorded an increasingly larger terrestrial flux of radiogenic strontium. We are aware of the fact that sea level fall leads to the release of low ratio Sr-isotopes from exposed aragonitic carbonates (Stoll and Schrag, 1996). However, the late Valanginian was characterized by widespread platform drowning and condensation (Föllmi et al., 1994; Weissert et al., 1998). Late Valanginian sediments along the northern margin of the Tethys are mainly composed of marls, siliciclastics, siderites and goethitic and iron oolites.

7.3.5 Sequence Boundaries

As stated above our high Sr-isotope values might correspond to late sealevel highstands followed by sealevel fall and they might therefore be used to pin-point sequence boundaries. In this way the Sr-isotope records becomes an important asset to the sequence stratigraphic interpretation of pelagic sediments, which are normally difficult to interpret in terms of sea level changes. Figure 7.3D shows the inferred positions of sequence boundaries and maximum flooding zones. We have tried to compare our sea level fluctuations with the stratigraphic position of sequence boundaries given in (Hardenbol et al., 1998). It shows that there is a good correlation between sequence boundaries HA2 and HA3 with our peak $^{87}\text{Sr}/^{86}\text{Sr}$ values and our inferred sequence boundaries. Sequence boundary HA4 is less well correlated (*Sayni* zone, *Cruasense* biohorizon), but this might be due to a sampling gap (Fig. 7.2F). Another explanation could be that the cyclicity observed in the Sr-isotope record might have been better recorded in a general highstand during aggradation.

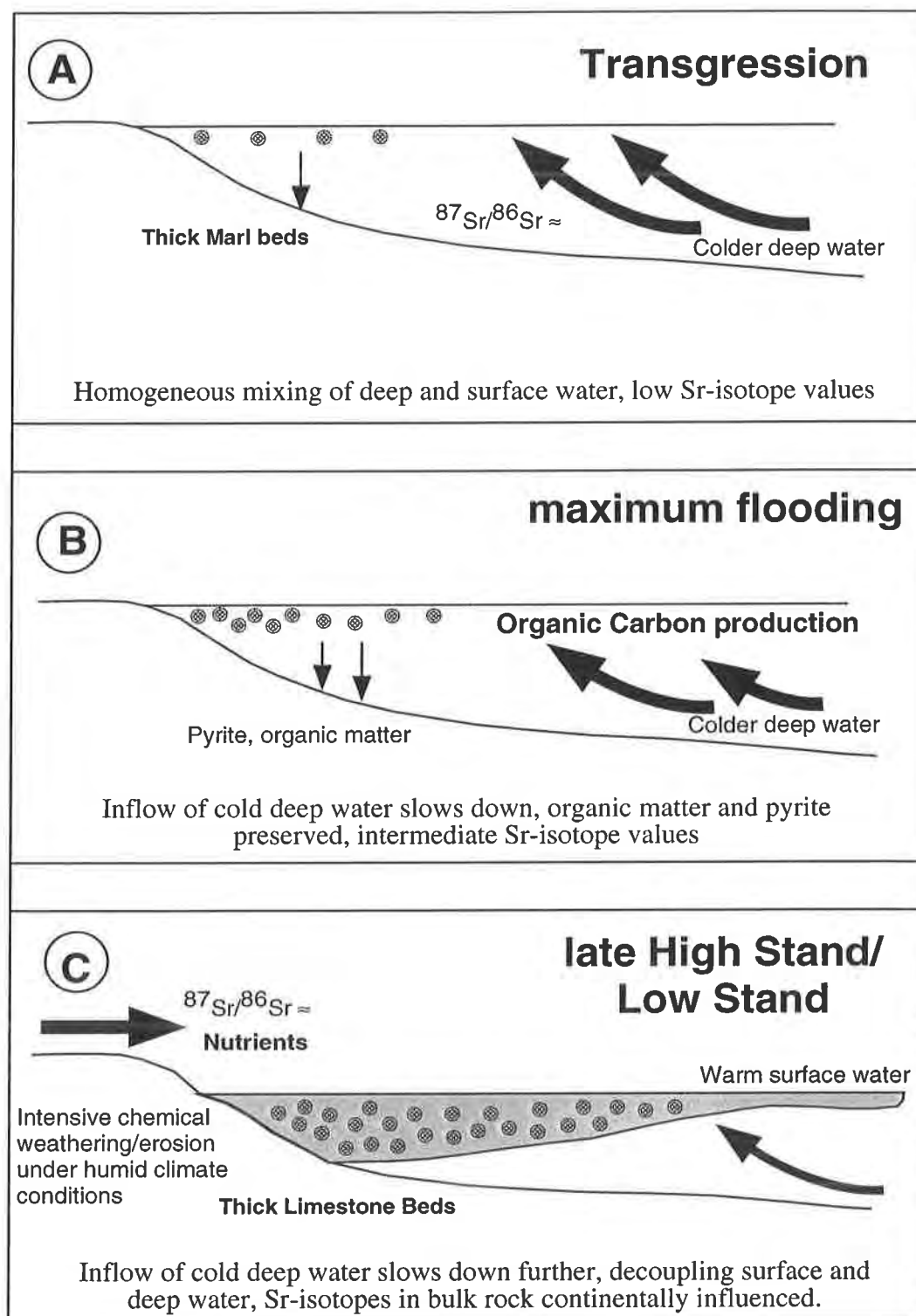


Figure 7.4 – Depositional model for Vocontian Basin. A-C) influence of sea level on marl and limestone deposition. During sea level fall the influence of upwelling is decreased and thick limestone beds accumulate. These record a continentally influenced Sr-isotope signal. During sea level rise influx of cold Boreal water is increased and active mixing results in limestones with a more marine Sr-isotope signature, just as the belemnites registered a marine signal all along.

7.4 Conclusions

We have improved the resolution for the Hauterivian strontium isotope curve based on belemnites and bulk micrites, which will serve future research. Our data are in good agreement with previous work and show the general increase in Sr-isotope values for the Hauterivian also observed in other studies. Our Sr-isotope data measured from micritic samples is however problematic. In the Vergons and Angles sections the bulk rock Sr-isotope record is disturbed by diagenesis, leading to a positive offset in values when compared to our belemnite data and previous work. This diagenetic overprint is also observed in other proxies, like the more negative oxygen isotope values and the clay mineral assemblage. We ascribe this diagenetic overprint to the fact that the Vergons and Angles sections suffered from Alpine deformation.

The La Charce section shows relatively little diagenetic overprint based on oxygen and clay mineral data. Still micrites from this section show Sr-isotope values that are deviating from the general trend for the Hauterivian. Three cycles of low and high Sr-isotope values can be observed. We suggest that this cyclical behaviour of the Sr-isotope curve is related to changes in weathering/erosion induced by 3rd order sea level changes. Correlation with the sequence stratigraphic scheme of Hardenbol et al. (1998) shows that the high strontium isotope values are related to sequence boundaries Ha2-Ha4. Cyclicity would be in the order of 1-1.5 Ma and the Sr-isotope signal is known to respond to such changes (Montañez et al, 1996). The belemnite Sr-isotope record for the same interval appears to be dampened and the variations are within the analytical error. Belemnites might have recorded a more global deeper water signal, while the bulk rock micrites, which consist primarily of coccolithophorids, registered a more proximal surface water signal.

This study also shows the potential problems that can be encountered when using bulk carbonate samples, even if they are seemingly well preserved micrites, for Sr-isotope analyses. Sr-isotope stratigraphy can only be used in accordance with other methods like clay mineralogy, stable isotopes or trace elements analyses. When certain criteria are met and a reasonable paleo-environmental model has been elaborated, only then Sr-isotopes might be used for stratigraphy and other purposes.

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Mesotrophic carbonate production and high P-accumulation rate during the Hauterivian: regulating the Valanginian global carbon cycle perturbation

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Abstract

During the Hauterivian three important phases of platform drowning, phosphogenesis and mesotrophic carbonate production along the northern margin of the Tethys (Helvetic Alps) are not mirrored by positive carbon isotope excursions such as during the Valanginian or Aptian, but rather by decreasing to stable trends. The aim of this study is to understand the de-coupling of organic carbon and phosphorus burial during the Hauterivian. For this purpose PO_4 -concentrations were determined from 8 sections along the northern margin of the Tethys representing a wide variety of depositional environments from inner-neritic to shelf and pelagic settings. Integration with a previously constructed dataset for the Valanginian led to a high resolution P-accumulation rate (PAR) curve based on 575 datapoints.

A gradual increase in PAR is observed from the early Valanginian to mid-Hauterivian and a rapid decrease during the late Hauterivian. The PAR curve obtained in this study correlates well with a compilation based on ODP and DSDP records presented by Föllmi (1995), indicating that phosphorus accumulation rates along the northern margin of the Tethys were controlled by a global mechanism. Mechanisms proposed that could explain a global increase in phosphorus burial are: 1) Increased transfer of P by river run-off under intensified greenhouse conditions, controlling the input. 2) Sea level rise, controlling the output. Sea level rise may have led to a general increase in circulation and oxygenation of bottom waters. The northern margin of the Tethys may have been especially susceptible to phosphogenesis as it was influenced by cold water exchange with the Boreal Realm (van de Schootbrugge et al., 2000) and prone to coastal upwelling.

From the late Valanginian to early Hauterivian phosphorus was probably effectively scavenged by iron and manganese, which also show increased concentrations, assisted by an increased carbonate flux. The late Hauterivian witnessed global lower sea level, decreased circulation and possibly also lower weathering and erosion rates, leading to generally lower P-accumulation rates. Increased re-generation of phosphorus might have occurred as circulation stagnated and bottom water oxygen levels dropped. Overturn of phosphorus enriched bottom water could explain a short lived oceanic anoxic event in the latest Hauterivian (Faraoni Level).

Increased PAR during the early Hauterivian did not lead to increased organic carbon burial, but rather to increased carbonate carbon burial, also seen in a decoupling between the $\delta^{13}\text{C}$ record (decreasing) and phosphorus accumulation rates (increasing). During the early Hauterivian carbonate accumulation rates increased under mesotrophic conditions reflecting ecological recovery after a prolonged phase of reef destruction during the late early and late Valanginian. Mesotrophic carbonate production may have been forced, despite high nutrient levels, in order to buffer the ocean's alkalinity.

8.1 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, because this is the primary source for P which is at the same time consuming CO₂. Understanding the dynamics of the phosphorus-cycle and its interactions with the carbon-cycle is important because of the role the element P plays in drawing down CO₂ from the atmosphere by limiting productivity in the oceans (Broecker and Peng, 1982). Phosphorites (i.e. rocks that contain more than 15% of P₂O₅) are not uncommon in the rock record and may serve to understand past changes in paleoceanography, paleoclimate and the link between the P- and C-cycles.

During the Phanerozoic, several time periods have been shown to be characterised by 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. Early Cretaceous phosphorites in the Helvetic Alps (Switzerland) have received much attention over the last 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 horizons are believed to be related to biocrises and have been interpreted as platform drowning events (Föllmi et al., 1994; Weissert et al., 1998). In the Helvetic Alps five such phases of platform drowning (early Valanginian to early Cenomanian) in the form of highly condensed phosphatic horizons have been recognized. Early models related the repeated occurrence of condensed and phosphoritic deposits to tectonic movements (Fichter, 1934). Although rapid subsidence and relative sea level rise might explain condensation, it did not explain the deposition of P₂O₅-rich sediments.

Föllmi et al. (1994) and Weissert et al. (1998) have related the drowning events to increased continental weathering/erosion and run-off leading to eutrophication and nutrient poisoning of sensitive carbonate producing biota, like corals. These authors have also suggested that the platform drowning events were connected to episodes of flood basalt volcanism (Paraña and Ontong-Java Igneous Provinces) followed by greenhouse warming. This suggestion was made after noting that positive excursions in the $\delta^{13}\text{C}$ record, most notably 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.

From $\delta^{13}\text{C}$ records for the Hauterivian it is seen that the Helvetic drowning phases D2 (mid-Hauterivian) and D3 (Hauterivian-Barremian boundary) are not mirrored by large scale positive excursions (van de Schootbrugge et al., 2000), but rather by decreasing to stable trends, although the latest Hauterivian shows again a trend towards more positive values. This does not correspond to the model of Föllmi et al. (1994) and Weissert et al. (1998). However, global Phosphorus Accumulation Rates (PAR) calculated from DSDP and ODP data by Föllmi (1995) show that the Hauterivian is characterised by even higher accumulation rates than those for the Valanginian, which are correlated with a major positive excursion in $\delta^{13}\text{C}$ values. Especially the mid-Hauterivian acme in PAR, probably related to drowning phase D2, presents an interesting problem, because during this time period a minimum in $\delta^{13}\text{C}$ values was recorded (van de Schootbrugge et al., 2000). The aim of this study is to

investigate the discrepancy between the phosphorus accumulation rate and the $\delta^{13}\text{C}$ records during the Hauterivian and ultimately to find answers to what mechanism was responsible for platform drowning and condensation.

For this purpose phosphate concentrations were determined from bulk carbonate samples from a wide variety of settings along the northern margin of the Tethys. We focused on the element phosphorus because of its obvious connection with the phosphatic horizons, 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). We will compare our phosphate data 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 the possibility of direct correlation with the Helvetic Alps. From the absolute PO_4 data we calculated phosphorus accumulation rates which were compared to both the Hauterivian $\delta^{13}\text{C}$ records and global phosphorus accumulation rate curve of Föllmi (1995). After compilation of the data a previously established database on the Valanginian (Kuhn, 1997) has been integrated, which allows us to present a high resolution phosphate accumulation rate curve based on 575 datapoints. Combination with a high resolution compilation of $\delta^{13}\text{C}$ data might provide insight in processes governing the P- and C-cycles during the early Cretaceous. This paper addresses several topics: 1) How did the accumulation rates of P change from the Valanginian to the Hauterivian and what is the relation with the drowning events and phosphatic horizons? 2) Are the calculated phosphate accumulation rates really indicating increased continental weathering/erosion? 3) What is the relation between the PAR-curve and the carbon isotope record previously established in the Vocontian Basin considering that the carbon and phosphorus cycles are linked.

8.2 Phosphorites in the early Cretaceous

Figure 8.1 represents a schematic transect from the Swiss Jura Platform across the Helvetic Shelf to the Vocontian Basin and Provencal Platform in France. This figure shows the time-space distribution of phosphatic and glauconitic beds in different regions along the northern margin of the Tethys during the Valanginian-Hauterivian. What becomes clear from this figure is the widespread occurrence of phosphorites during the latest Valanginian and especially earliest Hauterivian *Radiatus* zone. This correlates very well with a (global) phosphorus accumulation rate curve constructed by Föllmi (1995), which shows a maximum for this interval (Fig.8.1b).

In the Helvetic Alps the onset of phosphate deposition during the early and early late Valanginian marks an important faunal turnover of carbonate producing biota and as a result also a change in lithology. In proximal sections the phosphate rich deposits are overlying shallow marine carbonate sediments indicative of healthy platforms with corals and bioclastic-oolithic pack-grainstones (Lower Betliskalk Fm). During the late Valanginian and early Hauterivian these platform sediments were replaced by echinodermal-spiculitic wack-packstones (Upper Betliskalk Fm and Kieselkalk Fm).

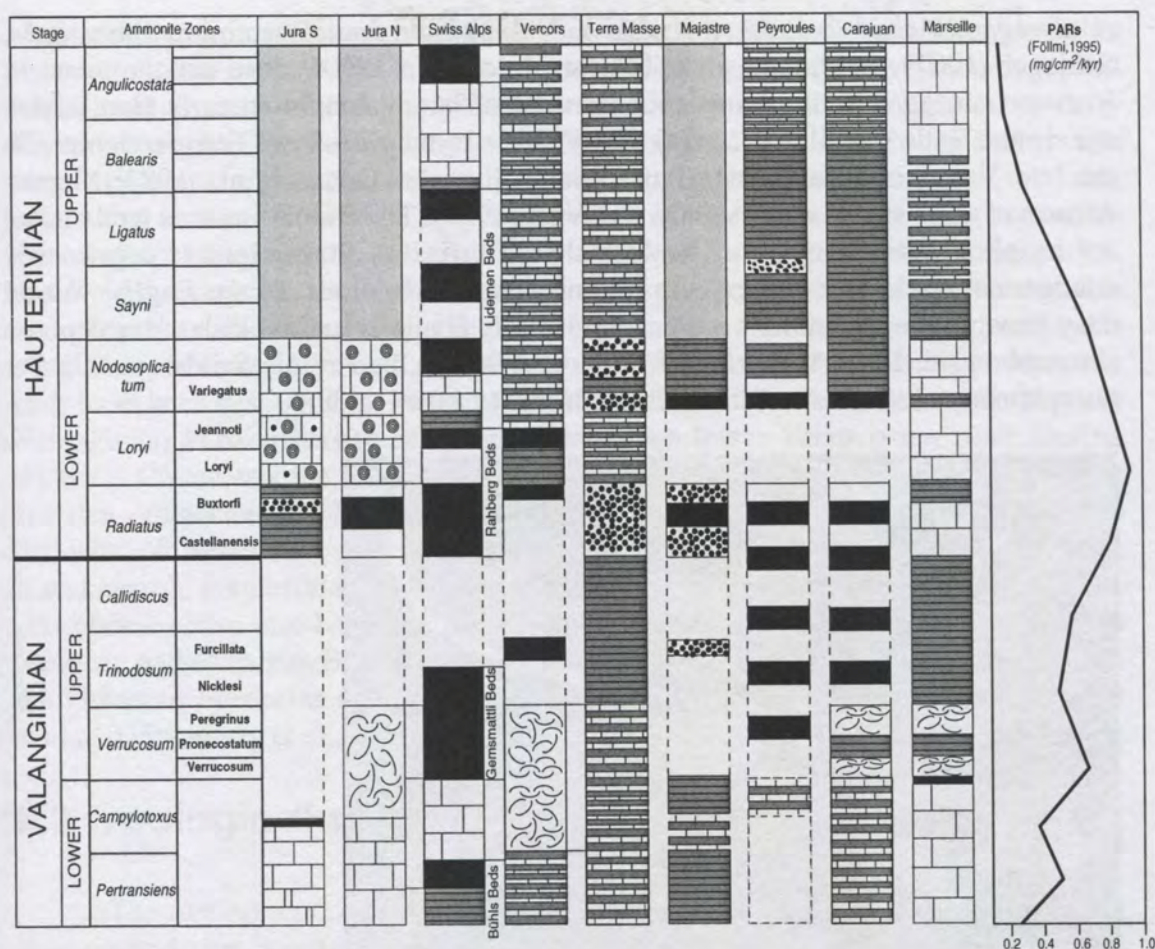


Figure 8.1 – Transect from the Jura Platform through the Vocontian Basin onto the Provencal Platform. This figure shows the widespread deposition of phosphoritic and glauconitic rocks during the latest Valanginian and earliest Hauterivian. Also shown is a phosphate accumulation curve (PAR) from Föllmi (1995) indicating phosphorus burial during this time-interval was a global phenomenon.

These lithologic changes might either be related to sea level rise and/or to changes in nutrient status (mesotrophic conditions). Oxygen isotope records based on belemnites indicate that a late Valanginian to early Hauterivian second order transgression led to the influx of cold Boreal waters in the Tethys, which also negatively affected warm water carbonate producing biota (Price et al., 2000; van de Schootbrugge, 2000). Cold water should normally slow down metabolism and thus carbonate production, however during the Hauterivian carbonate sedimentation rates along the northern margin appear to have been relatively high (sometimes in excess of 50 cm/kyr, e.g. in the Alvier region, Switzerland) compared to other stages (James, 1997). So higher nutrient levels might have been more important in controlling carbonate production during the Hauterivian than cooler water temperatures. (Gammon et al., 2000) suggested that limestones rich in spongal remains are probably more indicative of high nutrient levels than of cooler water temperatures.

The Valanginian-Hauterivian interval was a major phase of worldwide phosphorite deposition, which was not solely restricted to the northern margin of the Tethys. Guillaume (1966) measured several sections in the French Jura for their total phosphate content and found that Hauterivian shallow marine carbonates were

relatively enriched compared to early Valanginian and Barremian limestones. Schlager (1981) mentioned phosphatic nodules in a DSDP core off the coast of Morocco on top of a drowning unconformity of late Valanginian-early Hauterivian age. In the Betic Cordillera (Spain) phosphatic stromatolites have been recognized in the late Valanginian and late Hauterivian (Gonzales-Donso et al., 1983; Martin-Algarra et al., 1987; Martin-Algarra and Vera, 1994). The Boreal Basin is well known for its phosphatic horizons. The “Weald” (Berriasian-Barremian) is a primarily continental siliciclastic facies with marine deltaic incursions. In the English Weald Clay phosphorite concretions are present in early Hauterivian brackish water deposits (Jarzembowski, 1988; Taylor, 1991; Taylor, 1990). In the Ardigly Sandstone Member phosphorite concretions occur in a thin horizon (5-10cm thick).

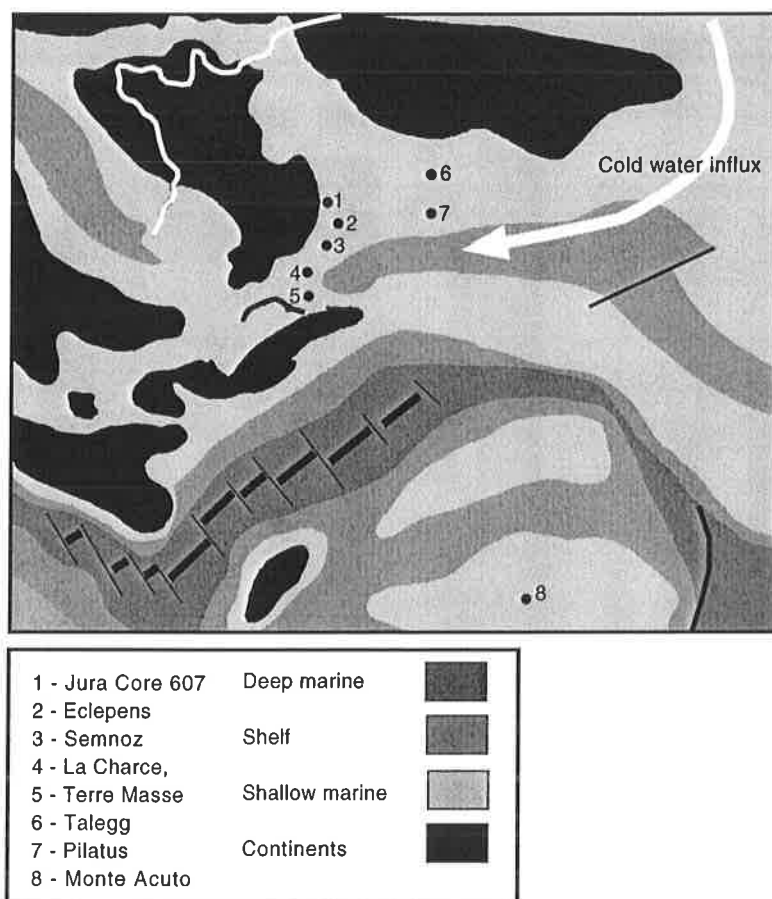


Figure 8.2 – Paleogeography for the northern margin of the Tethys (modified after Hennig et al., 1999). Cold water is presumed to have flowed in from the Boreal realm over the Polish Furrow.

These nodules are in fact a mixture of goethite, siderite and apatite and have probably been reworked during a transgression in the late Valanginian. The English Speeton Clay contains numerous horizons that are enriched in glauconite and phosphorite nodules of Berriasian to Albian age. More particularly, late Valanginian and early Hauterivian are especially enriched in phosphorites and glauconite (Poulton et al., 1998). Again these early Hauterivian beds correspond to a major transgressive sequence deposited on top of a late Valanginian hiatus (*Verrucosum-Callidiscus* zones). The early Hauterivian (*Radiatus* zone) of the Lower Saxony Basin is characterized by the widespread occurrence of phosphorite nodules and glauconitic limestones (Mutterlose, 1984). Those are interpreted as a diachronous transgressive

surface, because in some areas these horizons already occur in the late Valanginian. In the central parts of the basin thick successions of silts and clays have been deposited which contain intercalated phosphoritic-iron nodules of late Valanginian to early Hauterivian age (*Trinodosum-Loryi* zones; Mutterlose, 1984). The Polish Furrow is a very important region for the early Cretaceous, because it represents the only connection between the Boreal and Tethyan Realms that had a direct influence on the northwestern margin of the Tethys. After the seaway got closed during the Berriasian, re-newed opening as a result of a large scale transgression during the late Valanginian and early Hauterivian led to the active exchange of watermasses and fauna. In this small sized sedimentary basin, in the region of Wawal (central Poland) phosphorite beds have been described by Kutek et al. (1983). These 10m thick beds span the early Valanginian *Pertransiens* to early late Valanginian lower *Verrucosum* zone. During the early Cretaceous the Russian Platform was flooded by a shallow N-S stretching sea that connected the Boreal and Tethyan Basins. While economic phosphorite deposits of Berriasian and Valanginian age are widespread (from Moscow to Kazakhstan), Hauterivian phosphorite occurrences are rare (Ilyin, 1988; 1998). phosphorites have also been described from the Pacific Basin. In the west-argentinian Neuquen and Mendoza Basins phosphoritic limestones and phosphate layers occur in the Tithonian-Berriasian and in the late Valanginian to early Hauterivian (Mastandrea et al., 1975; Leanza et al., 1989).

8.3 Geological setting

The studied sections form a basin to platform transect. Five regions have been investigated that are typical for a certain depositional environment along the northwestern margin of the Tethys (Fig. 8.2). Sections from the Swiss Jura mountains represent the shallow carbonate platform setting. One section in the Subalpine Bauges Massif 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 represent the hemipelagic domain, while sections from the Umbria-Marche Basin are representative for the open ocean.

Core 607, drilled in the region of Neuchâtel, Swiss Jura Mountains, has previously been studied for its sedimentology and biostratigraphy by Rumley (1992). The section of Eclepens was studied by Zweidler (1985) and Blanc-Aletru (1995). The base of the Hauterivian succession in the Swiss Jura is formed by marly sediments (25m) of the Marnes Bleues d'Hauterive Fm. These are overlain by shallow marine bioclastic and oolitic limestones of the Pierre Jaune de Neuchâtel Fm, which were considered to represent a drowned carbonate platform by Arnaud-Vanneau et al., (1990). The transition between the Marnes Bleues and Pierre Jaune is formed by the Zone Marno-Calcaire, which is a biomicritic unit rich in detrital quartz. Whereas the Marnes Bleues are well constrained by abundant *Acanthodiscus radiatus* (earliest Hauterivian), the Pierre Jaune contains almost no faunal elements that could be of any use in dating. However, several rare ammonites from the Marnes d'Uttins, intercalated in the Pierre Jaune indicate the *Loryi-Nodosoplicatum* zones (Busnardo and Thieuloy, 1989).

The base of the succession at Eclepens is dominated by mixed bioclastic and oolitic grainstones of the Upper Pierre Jaune de Neuchâtel. 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 late Barremian by (Arnaud et al., 1999) and a large hiatus, that comprises the late Hauterivian and early Barremian, occurs between the Upper Pierre Jaune and Lower Urgonian.

The Semnoz section, located south of Annecy (France) in the Subalpine tectonic unit known as the Bauges Massif, represents an outer ramp facies with spiculitic-crinoidal bioclastic 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 oolitic packstones, marking a shallowing of the depositional environment. This section was studied for its biostratigraphy and sedimentological aspects 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 *Nodosoplicatum* zone by Viéban (1983). The Hauterivian-Barremian boundary was placed by Viéban (1983) at a discontinuity surface that can be correlated with sections in the Vercors area, which have been dated with ammonites and foraminifera.

The Talegg and Pilatus sections are located in the Helvetic Alps, which represent the former 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 southern facies realm characterised by slightly deeper marine conditions. Talegg has been studied by Heim (1910-1916) and Funk (1971). The Talegg section starts off with 50 meters of bioclastic and oolitic packstones of the early Valanginian Betliskalk Formation. The contact with the overlying Kieselkalk Fm is sharp. In the Pilatus section (Funk, 1969) the boundary between the Upper Betliskalk and Kieselkalk is formed by the Gemsmättli Horizon. This phosphoritic horizon contains ammonites from the early late Valanginian to earliest Hauterivian (Wyssling, 1986; Kuhn, 1997). At Talegg the late Valanginian is thus missing. Also missing are 10 metres of shales, present at Pilatus, which are probably an equivalent of the Marnes Bleues d'Hauterive of the Swiss Jura, although this is not confirmed by any ammonite finds. In both sections the Lower Kieselkalk is made up of fine bedded sandy wackestones, that grade in both sections into coarser grained and thicker bedded packstones up to the Lidernen Horizon. This glauconitic-phosphoritic horizon condenses the *Nodosoplicatum*, *Sayni* and lower part of the *Ligatus* zones (van de Schootbrugge et al., in prep.). In the Talegg sections it contains mostly glauconite, while at Pilatus it also contains phosphoritic clasts besides abundant glauconite. The overlying Upper Kieselkalk shows much thicker bedding in general and transitions into the Echinoderm Breccia. On top lies the Altmann Beds which represents a renewed phase of phosphorite deposition and condensation. It is rich in pyrite nodules, belemnites and ammonites, which are however very poorly preserved and do not allow determination. In Austria, Wyssling (1986) was able to date the Altmann Beds as latest Hauterivian (upper part of the *Angulicostata* zone) to earliest Barremian.

The Vocontian Basin is represented by Terre Masse and a composite section consisting of the La Charce, Angles and Vergons sections. In general the sections show hemipelagic alternations of calcareous marls and micritic limestones. Terre Masse is strongly reduced in thickness compared to other sections in the Vocontian Basin, however it contains ammonites that show that the whole Hauterivian is present. The reduced thickness can be ascribed to several condensed horizons rich in

glauconite that are missing in more expanded sections. The *Radiatus* zone is extremely condensed, which correlates well with a phosphatic horizon in the Helvetic Alps (Rahberg Beds – Gemsmättli Beds, drowning phase D1 of Föllmi et al., 1994). The latest Hauterivian *Angulicostata* zone is characterized by largescale slumping and was not sampled for this study. The composite sections is very 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 early Hauterivian (*Radiatus*, *Loryi* and *Nodosoplicatum* zones), while in Vergons and Angles the late Hauterivian (*Sayni*, *Ligatus*, *Balearis* and *Angulicostata* zones) is exposed.

The Monte Acuto section in the Umbria-Marche Basin (close to Chiaserna, Italy) is one of the few outcrops in the Maiolica Fm studied in detail for its ammonite biostratigraphy. The Italian Maiolica consists of pelagic micritic limestones with intercalated chert and marly beds, rich in nannofossils, but often with a depauperate macrofossil assemblage. To this comes some diagenetic overprint as a result of tectonic displacement. A first biozonation based on ammonites was proposed by Cecca, (1995), who distinguished the late Valanginian and early Hauterivian and placed the Valanginian-Hauterivian boundary at meter 79.90. These ammonite finds were very important because they allowed to calibrate magneto- and biozones (ammonites and nannofossils). The magnetostratigraphy of Mt. Acuto was performed by Channell et al. (1995). From their study follows that the early late Hauterivian *Sayni* zone spans four magnetozone (CM9-CM6 in Channell et al., 1995, also after correlation with the closeby Gorgo a Cerbara section) which corresponds to 3 Ma according to Channell et al. (1995). Faraoni et al. (1997) revisited the Monte Acuto section and added more detail to the biostratigraphy. Their results show that the Valanginian-Hauterivian boundary should be placed higher up section at meter 50 (from the top) of Channell et al. (1995). Furthermore these authors stress that the earliest Hauterivian *Radiatus* zone extends upto at least meter 38. Since the *Sayni* zone starts in meter 22 (based on a *Subsaynella* sp.), the *Loryi* and *Nodosoplicatum* zones seem relatively condensed (16m compared to 600m of Kieselkalk in Switzerland, Alvier region). It seems very unlikely that the *Sayni* zone corresponds to 60% of the Hauterivian (5 Ma) and the possibility exists that cross-correlation of the Mt. Acuto and Gorgo a Cerbara sections is hampered by tectonic complications or problems with the assignments of magneto and/or ammonite zones. New carbon isotope data (Hennig et al., 1999; van de Schootbrugge et al., in prep.) seem to indicate that CM9-CM8 belong to the *Loryi* and *Nodosoplicatum* zones.

8.4 Methods

A total of 403 samples from 8 sections were measured for their total PO_4 -concentrations. Together with 172 measurements performed by Kuhn (1997) a detailed record of 575 datapoints is available now for 12 sections spanning the early Valanginian to late Hauterivian along the northern margin of the Tethys.

Phosphorus is primarily stored as phosphate (PO_4), which is present in the sediment in different phases, like authigenic phosphate (Carbonate Fluor Apatite, CFA), absorbed P, detrital apatite, organic P and iron-bound P. By ashing a sample split at 550°C it is possible to obtain the organic phase of phosphate, which is the difference between Total P (TP) and Inorganic P (IP). As was discussed by Ingall et al. (1993), sediments enriched in inorganic phosphorus, as is the case in our study, show small differences between total and inorganic phosphorus, which makes potential errors in organic phosphorus concentrations relatively large. Rockeval 6

analyses showed that organic carbon contents in the samples studied here were in general below detection limit (i.e. < 0.5%). Therefore no samples were pre-heated. Over the last decade sequential extraction methods have been increasingly used to distinguish between different phases of phosphate in marine sediments (Fillipelli and Delaney, 1996; Ruttenberg and Berner, 1993). Earlier attempts by Kuhn (1997) to use the sequential extraction technique on early 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 too high, sometimes in excess of 80% of the total amount. Microscopic analyses showed no presence of magmatic apatite in detrital residues of early Cretaceous limestones. Diagenesis has probably changed carbonate fluor apatite (authigenic PO_4) to carbonate-poor fluor apatite, 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. For this reason we decided not to perform the very 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 hours under constant shaking. The solution was centrifuged, diluted ten times and analysed using the Ascorbic Acid Method of (Eaton, 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 color. The intensity of the blue color can be determined with a photospectrometer (Perkin Elmer UV/Vis Photospectrometer Lambda 10) and through calibration with known standard solutions this will give the concentration of PO_4 in mg/L. 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 , 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 ($2.5 \text{ g}/\text{cm}^3$). 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 make up the Hauterivian all have the same duration of 710 kyr. However, the variations observed in the accumulation rates are larger than this uncertainty, as is illustrated in figure 8.8, where an error margin of 250 kyr is plotted as well.

In addition to the above mentioned problems, the scarcity of good biostratigraphic markers in shallow marine carbonate settings leads to sedimentation rates being averaged out over large lapses of time. This is best illustrated by the Semnoz section (Fig.8.5) where only one ammonite find (*Subsaynella sayni*, Viéban, 1983) permits to draw the approximate position of the early-late 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. 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.

8.5 Results

Core 607 (Fig.8.3)

Total phosphate values measured for core 607 show maximal values in the middle of the MBH (3983 ppm). It is worthwhile to note that in other sections this part of the MBH is often characterised by a condensed glauconitic horizon. Phosphate concentrations decrease in the ZMC and PJN to values ranging from 400-700 ppm. Phosphorus accumulation rates show corresponding high values for the MBH (>10 mg/cm²/kyr) and much decreased rates for the ZMC and PJN (<1 mg/cm²/kyr).

Eclepens (Fig.8.4)

The base of the upper PJN still shows the same order of concentrations observed in the lower PJN in Core 607 (cf. Fig. 8.3) with values reaching up to 500 ppm. Through the upper PJN PO₄-concentrations rapidly decrease to very low values and reach almost zero in the top of the sequence. Accumulation rates show a clear distinction between the PJN and the Urgonian. Although accumulation rates are low in the upper PJN (~ 0.3 mg/cm²/kyr), PAR even decrease further to less than 0.1 mg/cm²/kyr in the Urgonian.

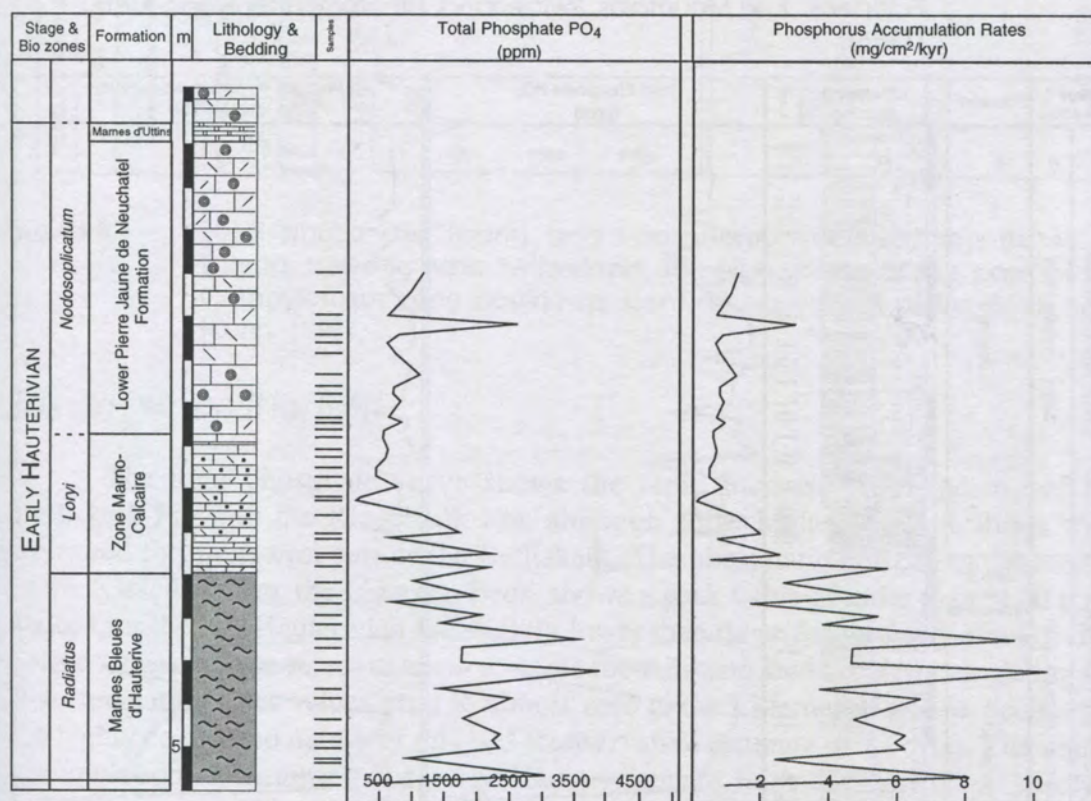


Figure 8.3 – Total phosphate (ppm) and Phosphorus Accumulation Rates for Core 607, Neuchatel, Jura Mountains, Switzerland.

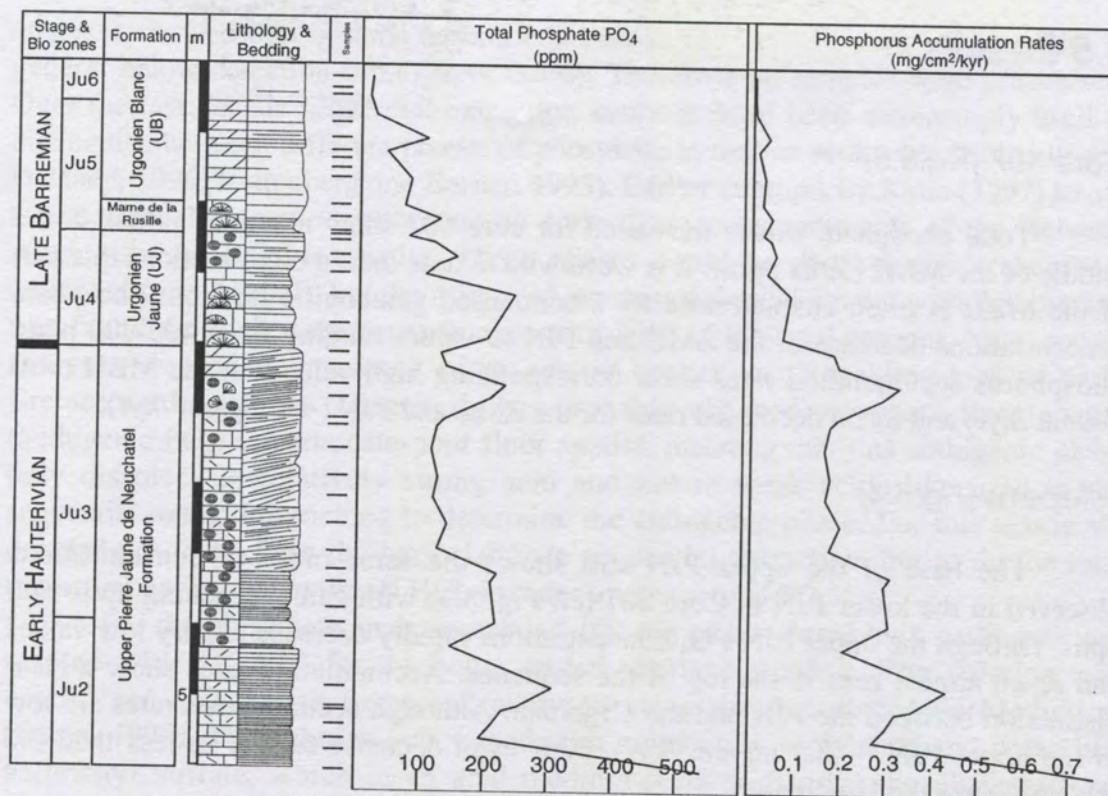


Figure 8.4 – Total phosphate (ppm) and Phosphorus Accumulation Rates for Eclepens, Jura Mountains, Switzerland. Lithology after Blanc-Aletru (1995).

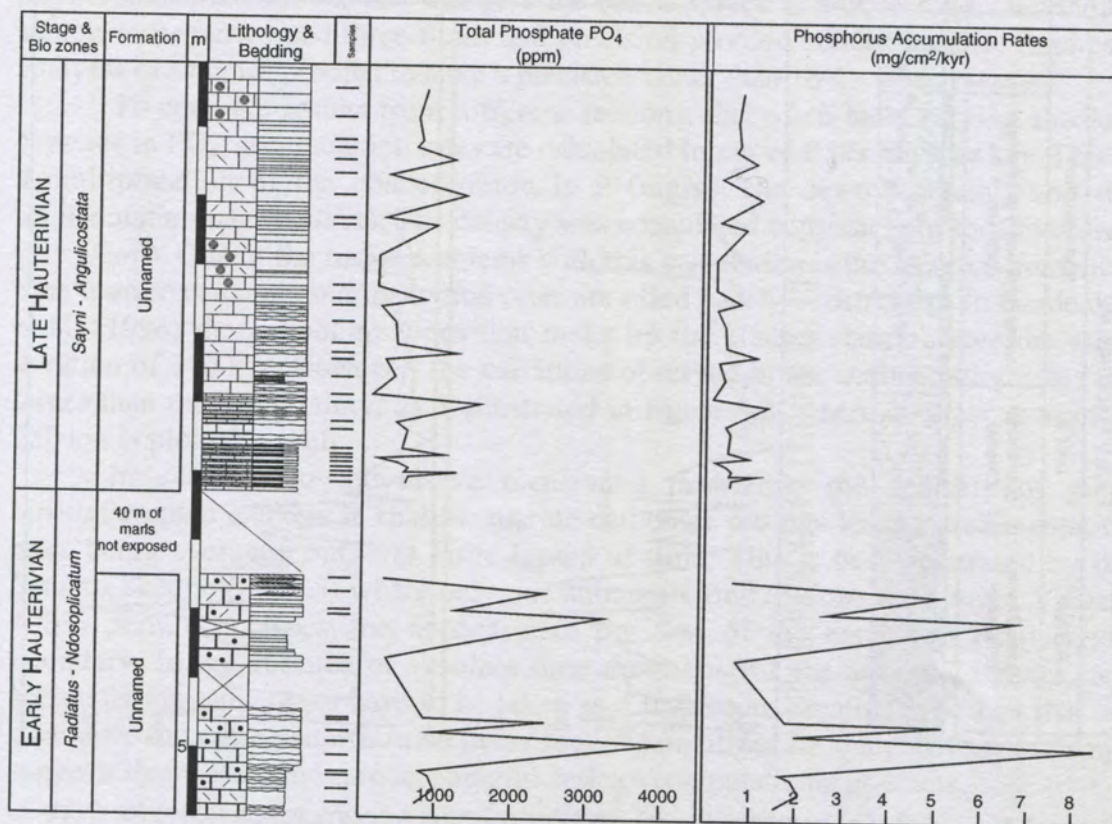


Figure 8.5 – Total phosphate (ppm) and Phosphorus Accumulation Rates for Semnoz section, Bauges Massif, France. Note large difference in PAR for early and late Hauterivian.

Semnoz section (Fig.8.5)

The early Hauterivian shows variable PO_4 -concentrations ranging from less than 500 up to 4000 ppm. The late Hauterivian shows much lower absolute values generally less than 1000 ppm. P-accumulation rates are high (1-8 $\text{mg}/\text{cm}^2/\text{kyr}$) for the early Hauterivian and decreased ($< 1 \text{ mg}/\text{cm}^2/\text{kyr}$) for the late Hauterivian.

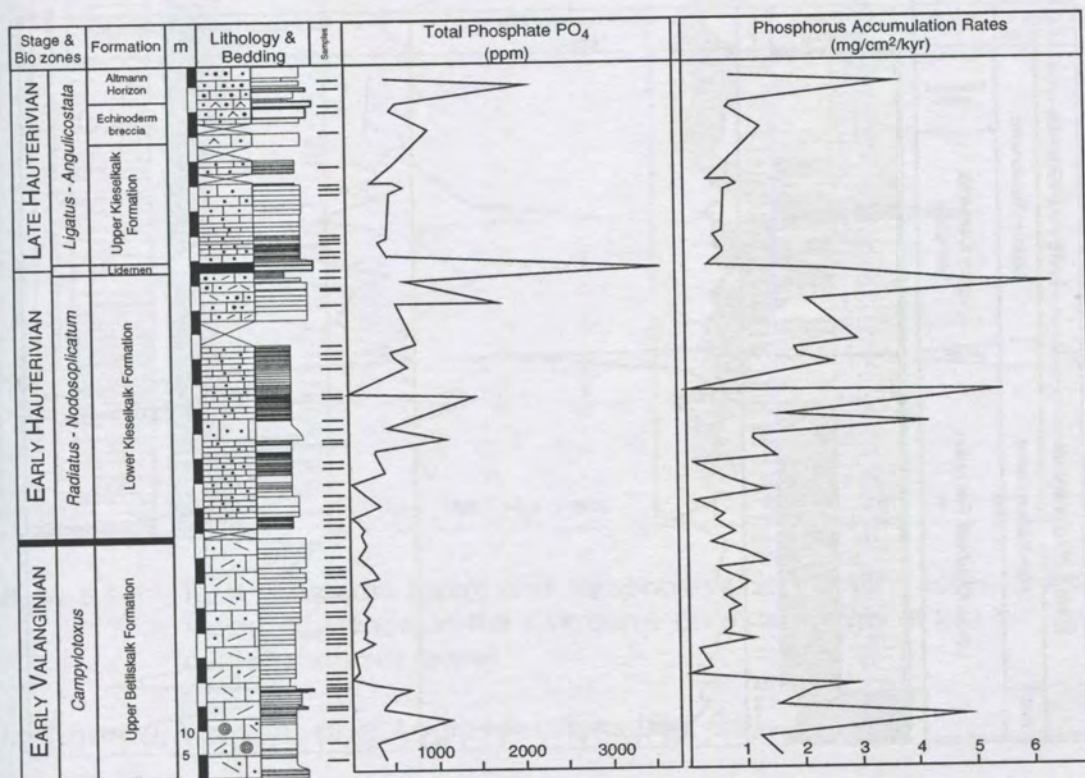


Figure 8.6 – Total phosphate (ppm) and Phosphorus Accumulation Rates for Talegg, Helvetic Alps, Switzerland. The high values at the base of the Campylotoxus zone could represent an equivalent of the Bühls Beds (Kuhn, 1997).

Talegg section (Fig. 8.6)

The total phosphate curve shows the rapid increase from the top of the Betliskalk Fm into the Kieselkalk Fm, although some higher concentrations were measured for the lowest part of the Betliskalk. The phosphatic horizon in the middle of the Kieselkalk Fm, the Lidernen Beds, shows a peak value of more than 3000 ppm. Values for the late Hauterivian are slightly lower than those for the early Hauterivian, before values start to increase again towards the Altmann Beds. When calculating the P-accumulation rates values drop to almost zero in the Lidernen Horizon, because of the highly condensed nature of this bed (conservative estimate of 1.5 Ma). The higher accumulation rates during the early Hauterivian are both due to higher absolute concentrations and higher sedimentation rates, when compared to the late Hauterivian.

Pilatus section (Fig. 8.7)

Average PO_4 -values for the Lower Kieselkalk Fm are around 500 ppm, while they are around 200 ppm for the Upper Kieselkalk Fm. The Lidernen Beds shows

again (see Talegg section) values in excess of 3000 ppm. Accumulation rates illustrate the distinct difference between the early and late Hauterivian. Interestingly, the PAR are very similar to those calculated in the Talegg section. So thrusting during Alpine deformation had no great impact on the concentrations and our age assignments could be quite accurate in spite of absent absolute durations of ammonite zones.

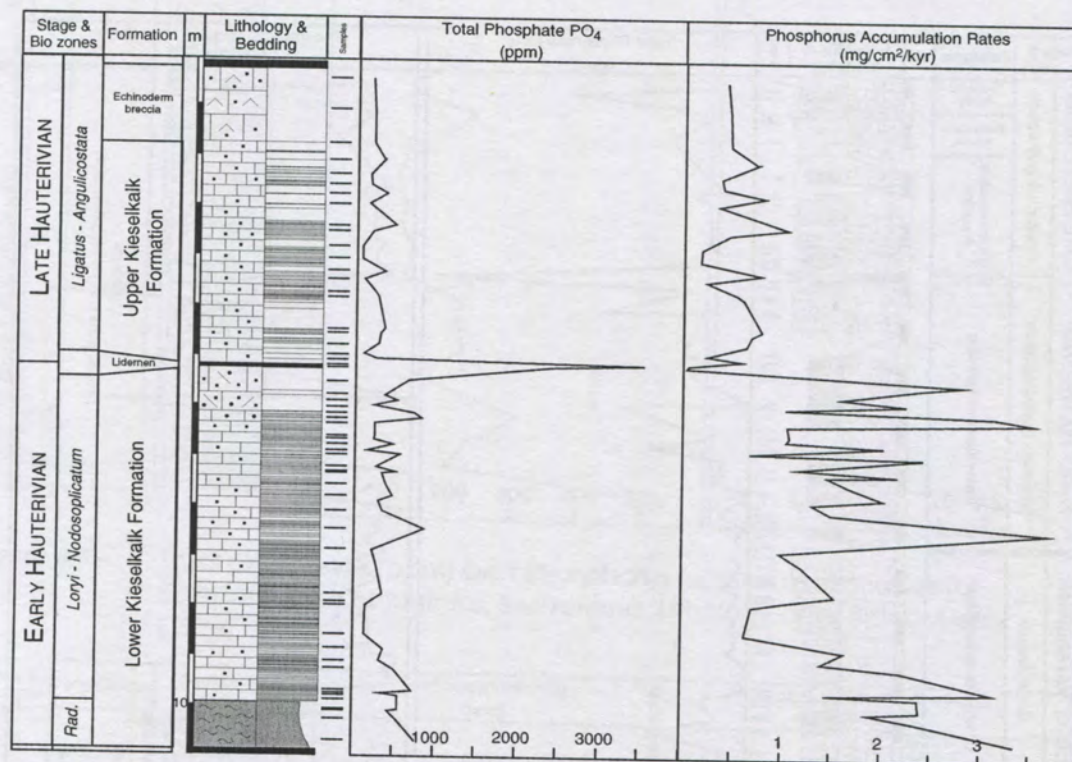


Figure 8.7 – Total phosphate (ppm) and Phosphorus Accumulation Rates for Pilatus section, Helvetic Alps, Switzerland.

Terre Masse section (Fig.8.8)

The fact that Terre Masse represents a more shallow setting than most sections in the Vocontian Basin is also reflected in the PO₄-concentrations which vary between 500 and 1000 ppm with a single outlier (>2000 ppm) in the upper part of the *Nodosoplicatum* zone, which corresponds to a condensed glauconitic bed. Values again are relatively decreased during the late Hauterivian, although the difference with the early Hauterivian is small. Phosphate accumulation rates show slight increase from the *Loryi* zone into the *Nosoplicatum* zone and gradually decreasing PAR upto the top of the *Balearis* zone.

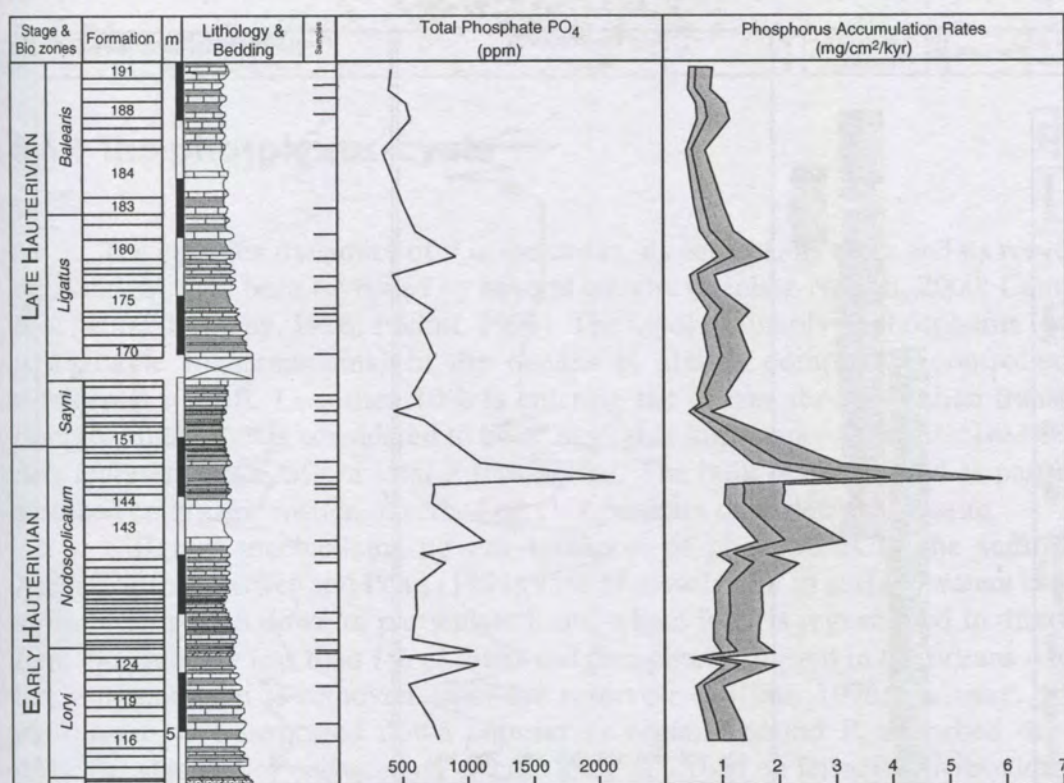


Figure 8.8 – Total phosphate (ppm) and Phosphorus Accumulation Rates for Terre Masse, SE France. In the PAR curve an error margin of 250 kyr (grey contour) is shown as well.

La Charce, Vergons and Angles sections (Fig. 8.9)

PO₄-concentrations show a slightly different development in La Charce with decreasing values during the early Hauterivian descending from around 800 ppm in the *Radiatus* zone to around 400 ppm in the *Nodosoplicatum* zone. For the remainder of the late Hauterivian values range from 600 to 800 ppm. These results are very similar to results obtained by Kuhn (1997) who measured the late Valanginian to early Hauterivian (*Loryi* zone) part of La Charce. His results indicate that concentrations were slightly more elevated during the late Valanginian (between 800 and 1000 ppm). P-accumulation rates show a very different trend than calculated in comparison to those from previously presented sections. PARs are stable around 2 mg/cm²/kyr for the early Hauterivian and increase rapidly from the *Sayni* to *Ligatus* zones to 4 mg/cm²/kyr before accumulation rates decrease again in the *Balearis* and *Angulicostata* zones to about 1 mg/cm²/kyr.

Monte Acuto section (Fig. 8.10)

The new assignments of CM9 and CM8 to the *Loryi-Nodosoplicatum* zones has little consequences for the general picture with increased PAR during the *Radiatus* and *Loryi* zones. Absolute PO₄ values show a slight increase from the latest Valanginian into the early Hauterivian, from 200 ppm to 500 ppm.

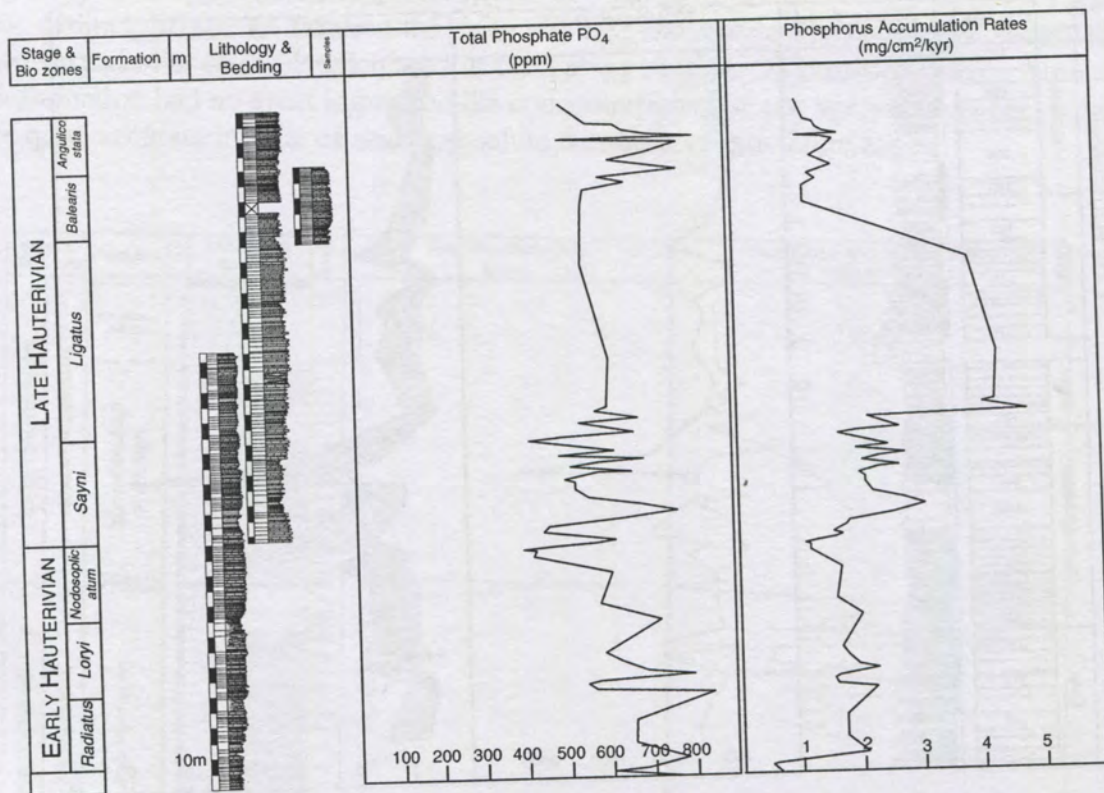


Figure 8.9 – Total phosphate (ppm) and Phosphorus Accumulation Rates for La Charce (left), Vegons (middle) and Angles (right), Vocontian Basin, SE France.

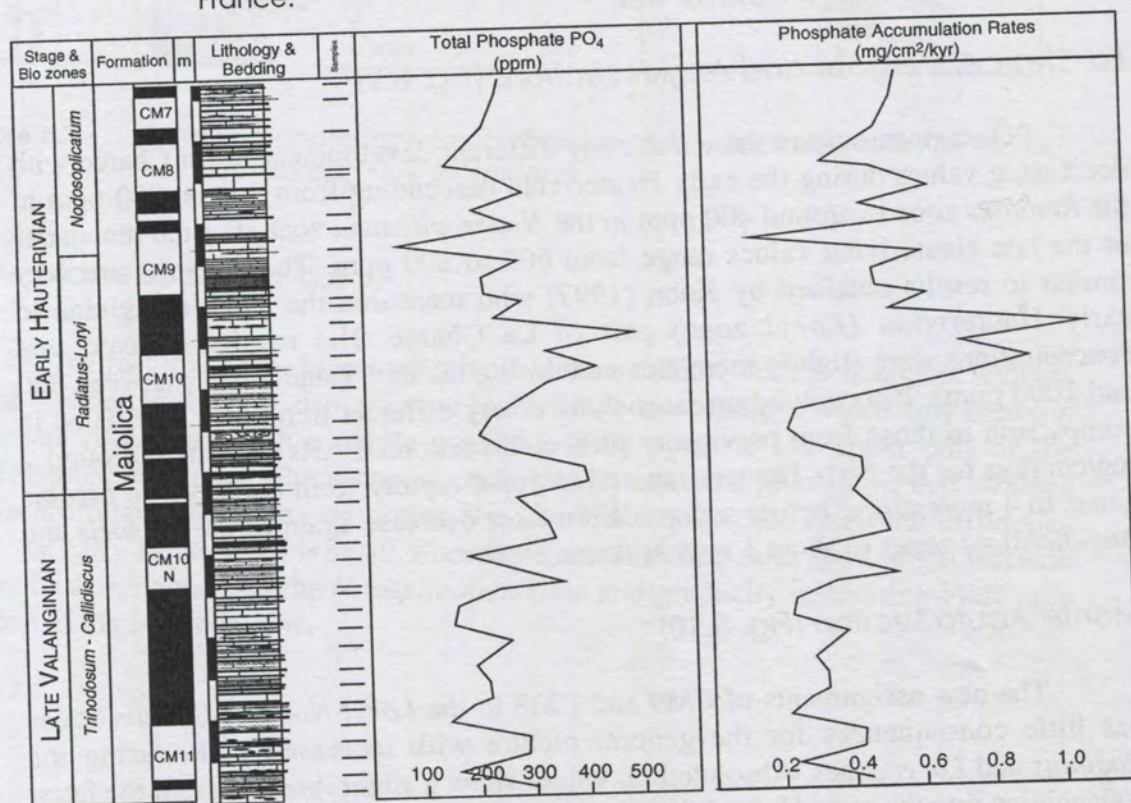


Figure 8.10 – Total phosphate (ppm) and Phosphorus Accumulation Rates for Monte Acuto, Umbria-Marche Basin, Italy. Magnetostratigraphy after Channell et al. (1995).

8.6 Discussion

8.6.1 The phosphorus-cycle

The complex dynamics of P in the ocean, its sources, its sinks and its recycling mechanisms have been reviewed by several authors (Benitez-Nelson, 2000; Compton et al., 2000; Delaney, 1998; Föllmi, 1996). The input of dissolved phosphorus (which is available for organisms) in the oceans is almost completely controlled by continental run-off. Less than 10% is entering the oceans through eolian transport. Hydrothermal input is considered to be of negligible importance. The dissolved P load may represent up to 25% of total P transported. The bulk is transported as part of or adsorbed on organic matter, adsorbed on clay particles or as detrital apatite.

Different mechanisms govern transport of phosphorus to the sediments. According to Broecker and Peng (1982) 95% of dissolved P in surface waters is taken up and transported down in particulate form, where 99% is regenerated in dissolved form. So probably less than 1% of dissolved phosphorus present in the oceans reaches the sediments and is removed from the reservoir (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, which constitutes probably the smallest sink.

The three primary sinks for P are: 1) P in association with organic matter 2) P in association with calcium carbonate and 3) P deposition as authigenic phosphate (carbonate fluor apatite). Of these three, the most important sink is authigenic P, but estimates of its volume are uncertain, because P switches sinks and because non-upwelling sediments can also contain authigenic P. The organic bound P flux can be estimated from the C/P ratio measured from organic matter. Ingall et al. (1990) found that C/P ratios vary with sedimentation rates. Partial oxic respiration leads to an initial preferential loss of P leading to high C/P ratios in sediments accumulating at intermediate (0.002-1 cm/yr) rates. Very low or very high sedimentation rates lead both to low C/P ratios, in the first case because the residual organic fraction (after complete degradation) is enriched in phosphorus and in the second because of enhanced preservation of organic matter. Depending on the redox-state of the sedimentary column preferentially regenerated P can be released to overlying waters or precipitated as authigenic P. The retention of P in the sediment is very dependent on oxygen levels in the sediment and in overlying bottom waters. Aerobic conditions will increase the possibilities for bacteria to effectively store P in the sediment. Dyaerobic conditions decrease microbial P storage and lead to an extensive loss of P from organic matter and a reflux to ocean waters (Ingall et al., 1993).

Bulk storage of P may change as a response to changes in chemical weathering, sea level, MOR spreading rates, glaciation and oceanic circulation. Phosphorite giants appear to be positively correlated with transgressions during warm and humid climate. Upwelling is an important mechanism to introduce nutrients into the photic zone where they become available for organic production (Compton et al., 2000).

8.6.2 General trends

In all the studied sections total PO_4 concentrations always decrease during the late Hauterivian. The reasons for this trend will be discussed below. We exclude a large influence of diagenesis, because we observe the same trends in so many different sections. Furthermore, the two sections that suffered most from tectonic overprint, i.e. Talegg and Pilatus, show very similar results eventhough these two sections belong to different thrust sheets.

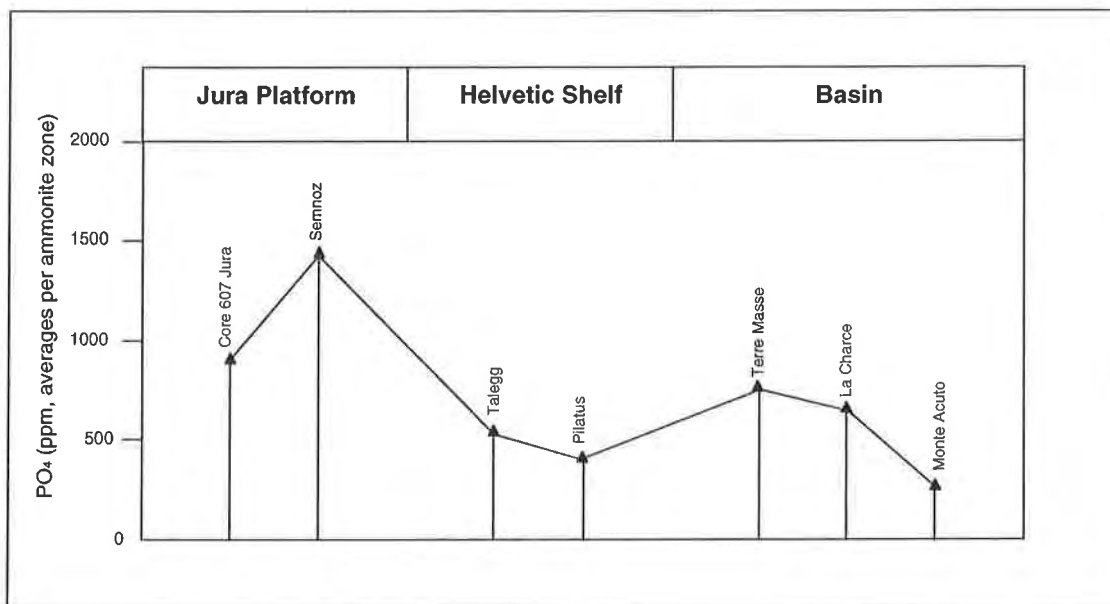


Figure 8.11 – Average PO_4 -concentrations for the early Hauterivian *Loryi* zone along a platform to basin transect.

Figure 8.11 shows a transect across the northern Tethyan margin of PO_4 -concentrations during the early Hauterivian *Loryi* zone. PO_4 -concentrations are maximal in the outer platform region. We would have expected values to be maximal in the Pilatus and Talegg sections, because of a possible relation with upwelling that would be most pronounced in shelf areas. A striking result is that both concentrations and accumulation rates decrease (not depicted, but inferred from Fig. 8.3-8.10) from the platform to the basin during the early Hauterivian. The presence of detrital apatite in shallow marine settings, which would be more influenced by rivers, could lead to slightly elevated PO_4 -concentrations measured for these sections, due to the possibility of leaching during sample preparation. On the other hand, during sea level high stands much of the phosphorus would be buried on the extended shelves, like they existed during the early Hauterivian, and would not be bypassed into pelagic realms (Moody et al., 1981).

P-accumulation rates increase from the platform to the basin during the late Hauterivian, most notably in the composite section of La Charce, Vergons and Angles (Fig.8.9). This is in part due to differences in sedimentation rates, which are a dominant factor in calculating the PAR. Proximal sections show either condensation or much reduced sedimentation rates during the late Hauterivian, especially during the *Sayni* and *Ligatus* zones, while sedimentation rates are high for that interval in pelagic settings. Sea level rise during the early Hauterivian may have shifted sedimentation

more towards the basin margin by the installation of sedimentary conditions leading to condensation on the shelf. An overall regressive phase, maybe punctuated by small transgressions, during the late Hauterivian resulted in expanded basin sections.

8.6.3 Phosphorus Accumulation Rates

Figure 8.12 is a compilation of all the gathered data combined with the data provided by Kuhn (1997), who measured mostly late Valanginian sections in France, Italy and Switzerland. Averages were calculated per ammonite zone for each section and averages for all sections per ammonite zone (Fig. 8.12a and c). This figure shows that PARs are increasing from the early Valanginian into the early Hauterivian and rapidly decrease during the late Hauterivian. Maximal accumulation rates characterise the *Radiatus* and *Loryi* zones. Although the 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 (Fig. 8.12b). Several authors have discussed the correlation between increased bulk sedimentation rates and increased PO_4 -concentrations, due to enhanced preservation of organic matter and reduced regeneration of P (e.g. Ingall et al., 1990).

Along the northern margin of the Tethys the average PAR increased from $0.75 \text{ mg/cm}^2/\text{kyr}$ to $2.1 \text{ mg/cm}^2/\text{kyr}$ from the late Valanginian to early Hauterivian. What are the reasons for a three fold increase in P-burial? As was discussed above (see introduction) increased phosphorite deposition was not restricted to the northern margin of the Tethys, but increased worldwide. A global P-accumulation curve for the last 160 Ma was constructed by Föllmi (1995, Fig.8.12d). From his data a three to four-fold increase can be observed as well, although the calculated values are lower (from $0.2\text{-}0.8 \text{ mg/cm}^2/\text{kyr}$), which is due to the fact that he primarily used data from pelagic sites. This curve should represent a global signal because it is based on DSDP and ODP data coming from a wide variety of basins. Since we find the same trend, the underlying mechanisms for phosphate enrichment in Tethyan northern margin sediments should therefore be global as well. On timescales longer than the residence time of phosphorus (30-80 kyr), the input is thought to equal the output. Or in other words, the buried phosphorus should represent the incoming phosphorus from the continents. We can look at the problem from two sides: 1) what was the source of P and what changes occurred that increased the input? 2) what sinks of P existed and which conditions controlled the output?

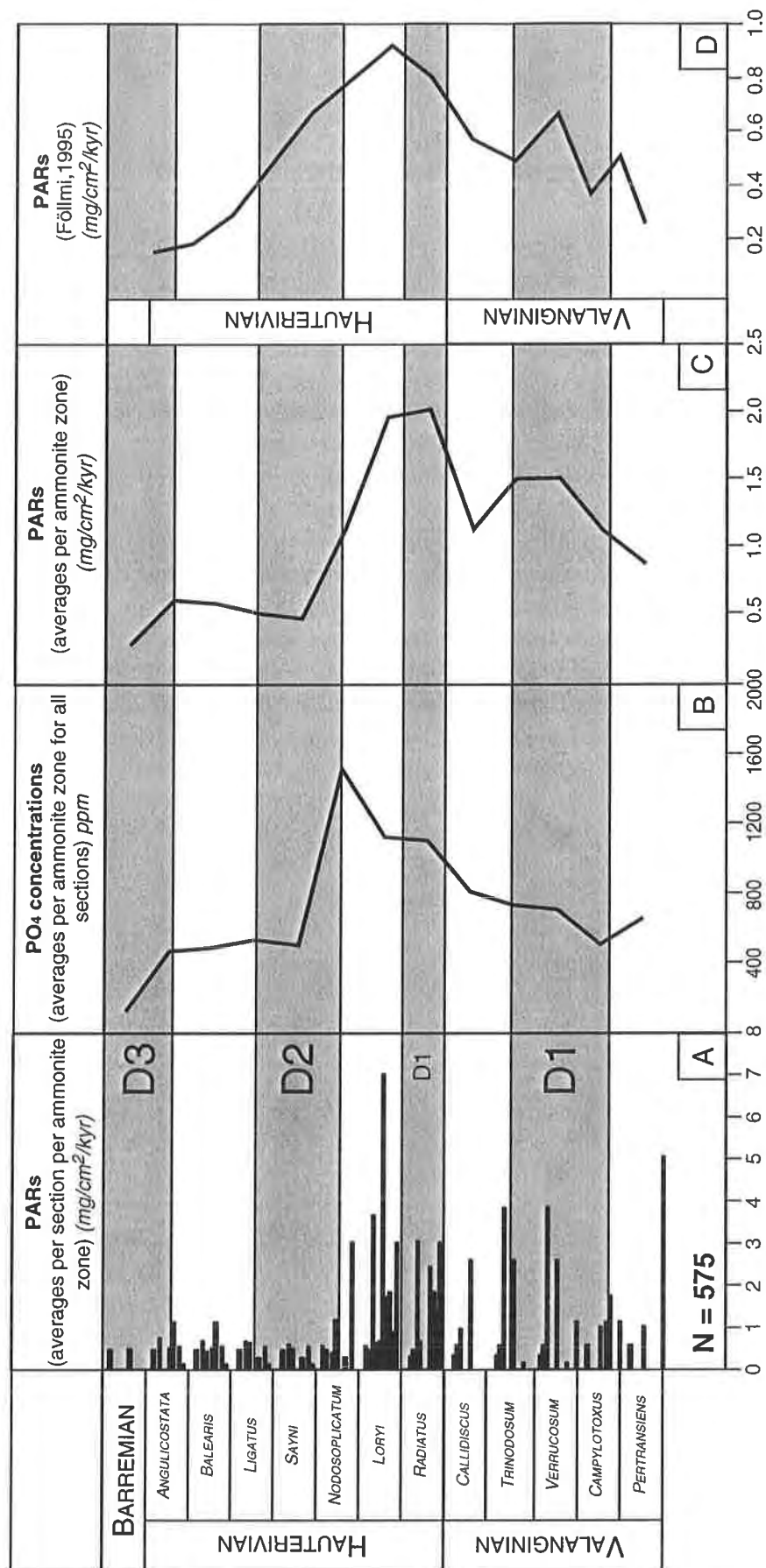


Figure 8.12 – A) Average PAR per ammonite zone for individual sections B) Average PAR per ammonite zone for all sections. C) Average PAR per ammonite zone for all sections. D) PAR curve from Föllmi (1995) based on ODP and DSDP data from the N-Atlantic, Pacific and Indian oceans. Comparison with this curve indicates that the PAR curve obtained from the Tethyan sections represents a global signal. D1, D2 and D3 refer to drowning phases of Föllmi et al. (1994). Drowning occurred also during the late Hauterivian, when nutrient influx diminished.

8.6.4 Phosphorus input

We relate increasing accumulation rates during the Valanginian-Hauterivian to increased continental weathering and erosion. Warm and humid greenhouse climate conditions during the early Cretaceous were probably the main mechanism behind increased continental influx (Weissert et al., 1998). Most authors agree on the fact that the early Valanginian to early Hauterivian interval was in general warm and humid (Marek, 1983; Kemper, 1983; Price et al., 1999) and although the mid-Valanginian might have witnessed a cold spell (Price et al., 1999) the early Cretaceous was essentially ice-free.

Other methods often used to quantify continental weathering include clay mineralogy, palynology and trace element geochemistry. Previous studies on clay mineral assemblages from northwestern Europe (Sladen, 1983; Deconinck, 1984; Ruffell and Batten, 1990; Adatte et al., 1996) showed high abundances of kaolinite during the Valanginian. During the Hauterivian this indicator for warm and humid climate conditions disappears during the early Hauterivian as a dominant clay mineral and is replaced by smectites (Deconinck, 1984). Smectites are more indicative of a seasonally wet climate alternating with more or less dry periods. Major and trace element (Mn, Fe, Mg, Sr, P, REE) data are scarce for the Valanginian-Hauterivian interval. Kuhn et al., (in prep.) show that Fe- and Mn-concentrations are increased during the early Cretaceous in Tethyan sections and around the world and interpret this as evidence for increased detrital input during the Valanginian and early Hauterivian. Kemper (1983) termed the Hauterivian the *geological iron-time* because of widespread iron-rich deposits in the Lower Saxony Basin, Germany. In southern France (Bargème, Var region) iron oolites have been described by Cotillon (1960). Also along the Pacific margin (Chili) iron oolites occur in coastal deposits (Cisternas et al., 1986). Palynofacies studies on ODP and DSDP material from different continental margins indicates that most of the organic matter in Valanginian-Hauterivian sediments is terrestrial (see van de Schootbrugge et al., 2000 for an overview).

An interesting relation exists between terrestrial organic matter, iron, and the formation of iron-oolites. Gehring (1986) explains the formation of Jurassic iron oolites as the result of an increased flux of plant material from continents that were covered by extensive tropical forests. The iron released by lateritic weathering of tropical soils formed organo-metallic complexes in Amazon-type rivers, which upon arrival in lagoons and estuaries were subsequently reduced and the iron as colloids deposited. A similar scenario may apply to iron-rich deposits along Valanginian and Hauterivian continental margins. The Valanginian, being characterized by more humid climate, gave rise to extensive lateritic weathering (Kuhn, 1997). The early Hauterivian (with its seasonal climate) saw frequent fires destroying forests during dry periods, after which both soils and organic matter were easily transported into the oceans during the wet periods. During the late Hauterivian conditions became increasingly drier and run-off was decreased.

The above summary is meant to stress the importance of continental weathering and erosional influx of nutrients (including P, Fe and Mn) during the Valanginian and early Hauterivian. During the late Hauterivian these fluxes decrease as is also shown by our P-accumulation rates. The Barremian, probably drier, maybe also related to a general sea level lowstand, saw a re-installation of oligotrophic carbonate systems along the northern margin of the Tethys.

8.6.5 Phosphorus output

High PARs in the early Hauterivian can not be understood without considering a second order sea level rise that occurred during the late Valanginian and early Hauterivian (Hardenbol et al., 1998). As a result of this transgression connections were established with the Boreal realm and active exchange of Boreal and Tethyan watermasses took place leading to ammonite and nannofossil migrations (Crux et al., 1989). Furthermore, 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. In this respect the northern Tethyan margin may have been in extremely favorable position for phosphorus burial. But how was the P actively stored in the sediment?

Scavenging by Fe- and Mn-oxyhydroxide particles is a very effective method to remove P from the watercolumn, especially around hydrothermal vents (Froehlich, 1982). This hydrothermal scavenging is unlikely to have had some influence on the passive continental margin considered here, but, as was outlined 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 quick, this process is likely to occur in the sedimentary column (Delaney, 1998). Hence, an increase in sedimentary burial of Fe and Mn would increase the potential to retain PO_4 . High bottom water oxygen levels, resulting from increased circulation, would have been a further prerequisite.

We interpret the decreasing PARs during the late Hauterivian to be primarily reflective of decreasing continental influx. However in addition, increasing bottom water anoxicity as a result of different circulation patterns possibly led to an increased re-flux of phosphorus to the water column. As eustatic sea level rise, that dominated the early Hauterivian slowed down, connections with the Boreal realm were probably closed again and the influx of cold oxygen rich waters ceased (van de Schootbrugge et al., 2000).

8.6.6 Relation with drowning events D1, D2 and D3

Although there appears to be a certain cyclicity in platform drowning and phosphorite deposition along the northern margin of the Tethys, every drowning event was likely controlled differently. Drowning phase D1 (late early to early late Valanginian, Böhls and Gemsmättli Beds) marks a first turnover in carbonate sedimentation from the coral-oolite mode to the crinoid-bryozoan mode according to Föllmi et al. (1994). A large sea level drop and a rapid sea level rise during the early late Valanginian probably weakened carbonate platforms, which were then suffocated by high nutrient influxes from the continent. As sea level rose further during the late Valanginian cold water inflow from the Boreal also negatively affected carbonate systems and drowning persisted into the earliest Hauterivian *Radiatus* zone. During the early Hauterivian carbonate systems along the northern Tethyan margin shifted into a new mode of carbonate production with mixed bryozoan, crinoidal and spiculitic carbonate producing assemblages. This community was much more adapted to high nutrient levels and turbidity and produced carbonate at high pace (e.g. on the Helvetic Shelf 600m/Ma in the Alvier region, Switzerland) during the early Hauterivian *Loryi* and *Nodosoplicatum* zones.

The Lidernen Beds (D2 of Föllmi et al., 1994) represent a mid-Hauterivian drowning phase, which is also recognized on the Provencal Platform, albeit not in the form of a phosphatic horizon, but by a pronounced shale interval (Masse et al., 1993). Why did platforms drown if carbonate producing biota were adapted to high nutrient levels? The mid-Hauterivian drowning event was possibly more controlled by sea level changes than by nutrients. The fact is that phosphate concentrations did not rise further after the *Nodosoplicatum* zone and decreased rapidly during the earliest late Hauterivian (Fig. 12c). The end of the *Nodosoplicatum* zone is marked by a major sea level fall (Hoedemaeker, 1995; Hardenbol et al., 1998). The combination of weakening during sea level fall and rapid transgression during the early late Hauterivian *Sayni* zone led to platform drowning phase D2 (Lidernen Beds, late early – early late Hauterivian).

A third phase of platform drowning (D3 in Föllmi et al., 1994) occurred contemporaneous with deposition of the Faraoni black shale level. This relatively short lived anoxic event (< 500 Ka, latest Hauterivian *Catulloi* subzone, (Cecca, 1998; Cecca et al., 1996; Cecca et al., 1994; Cecca et al., 1993) may have resulted from the turn-over of deep anoxic phosphorus rich water during a renewed transgressive phase.

Apparently drowning events are not always directly controlled by continental run-off, since phosphate concentrations steadily increased from the early Valanginian to mid-Hauterivian and carbonate sedimentation re-established itself inspite of mesotrophic conditions. Graziano (1999) came to the same conclusion after studying early Valanginian and Aptian drowning unconformities on the Apulia Platform, a platform that was not influenced by river transported nutrients, but drowned at least three times.

8.6.7 Decoupling of phosphorus accumulation and $\delta^{13}\text{C}$

As discussed above both the input and the output of P increased during the late Valanginian and early Hauterivian and decreased again during the late Hauterivian. Phosphorus is considered to be the ultimate biolimiting nutrient. An increase in the bio-available amount of PO_4 should lead to increased primary productivity and in theory to the deposition of organic carbon rich rocks (Pedersen and Calvert, 1990). The late Valanginian to early Hauterivian shows a long term decrease in $\delta^{13}\text{C}$ values (Hennig et al., 1999; van de Schootbrugge et al., 2000), that does not indicate increased burial of organic carbon but rather of carbonate carbon. Figure 8.13 shows a compiled $\delta^{13}\text{C}$ record together with the average PAR record discussed in Figure 8.12c. This figure clearly shows the divergence during the late Valanginian and early Hauterivian between the two curves and a positive correlation for the early to early late Valanginian and late Hauterivian.

Coupling of the P- and $\delta^{13}\text{C}$ record during the early Valanginian and late Hauterivian appears to be related to sea level lows or regressive phases, while decoupling during the late Valanginian-early Hauterivian corresponds to a second order transgression. Sea level rise created the necessary accommodation space, while at the same time increased nutrient influx from the continents stimulated calcium carbonate production in the *green water* mode. Organic carbon production might have been high, but due to high oxygen levels in deeper waters most of the organic matter was re-oxidized and returned to the surface while phosphorus, initially re-generated, was absorbed by carbonate particles and retained in the sediment under oxic conditions with the help of Fe and Mn. If both the $\delta^{13}\text{C}$ and PAR record represent global trends,

does this mean that carbonate accumulation rates were also increased during the early Hauterivian on a worldwide scale?

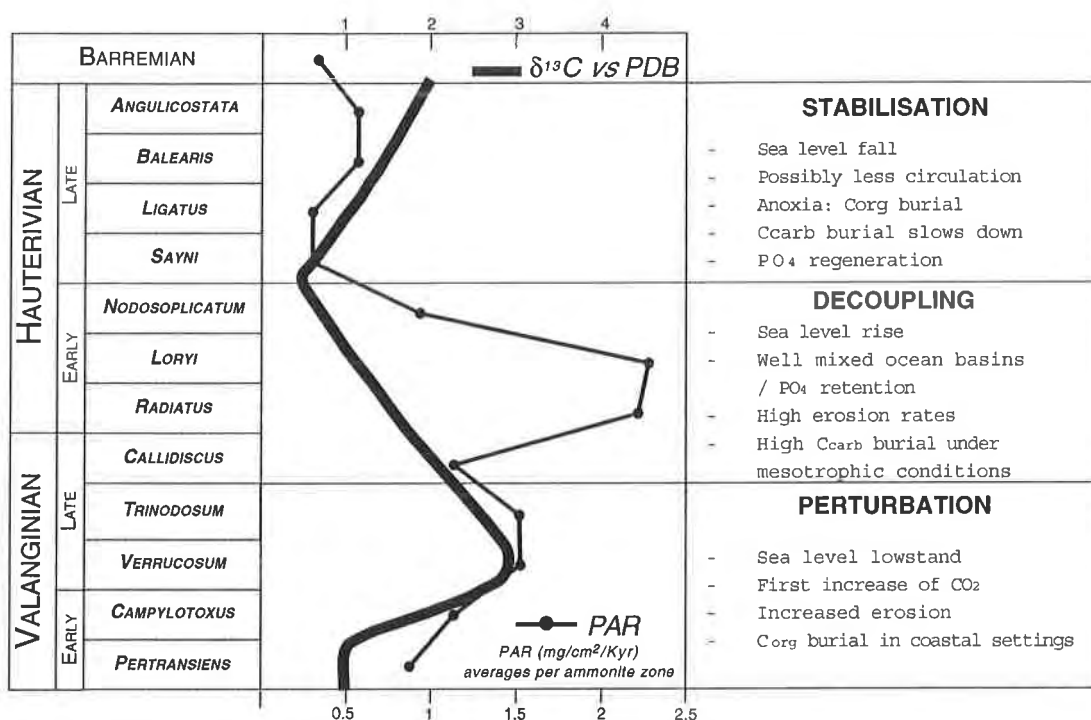


Figure 8.13 – Comparison of a composite carbon isotope curve (thick black line) and average PAR curve from figure 8.12C. Decoupling during the late Valanginian and early Hauterivian is evident from diverging trends. This time-period was characterised by mesotrophic carbonate deposition at high pace. The carbon isotope curve is based on data from Hennig et al. (1999) and van de Schootbrugge et al. (2000) obtained from well preserved bulk rock micrites from the Vocontian Basin.

Renard (1986) compiled a long term data set for Sr/Ca ratios based on DSDP records. From his curve an important increase in Sr/Ca in pelagic limestones can be observed during the Hauterivian (the most important during the early Cretaceous next to the Berriasian). Sr/Ca ratios from Valanginian-Hauterivian limestones cored during ODP leg 103 show increasing ratios upto the mid-Hauterivian (Clauser et al., 1988). High Sr/Ca ratios in pelagic limestones might indicate increased deposition of calcite with respect to aragonite on a global scale. Along the northern margin of the Tethys carbonate deposition was mainly by crinoids, bryozoans and echinoderms all mostly composed of calcite, as opposed to corals, which are primarily made up of aragonite.

The early Hauterivian was a period of forced calcite carbonate deposition in order to decrease alkalinity. Alkalinity was increased both as a result of the prolonged late Valanginian phase of platform destruction and because of ongoing high weathering, erosion and run-off during the early Hauterivian. Ogg et al. (1990), in summarizing the depositional history of the equatorial Pacific suggested that the CCD sharply dropped from the Valanginian to Hauterivian, which might be indicating increased supersaturation with respect to calcium carbonate.

8.7 Conclusions

The late Valanginian and early Hauterivian are characterised by a global increase in phosphorite deposition. Our data, based on 403 measurements from 8 sections spanning the Hauterivian, together with another 172 covering the Valanginian (Kuhn, 1997), confirm an earlier study by Föllmi (1995) in that Phosphorus Accumulation Rates (PAR) gradually increased from the early Valanginian to mid-Hauterivian and decreased during the late Hauterivian. High weathering/erosion rates and increased continental run-off due to an intensified greenhouse climate led to increased inputs of P, Fe and Mn, kaolinite and terrestrial organic matter. Furthermore, cold waters flowing in from the Boreal realm, as is also evidenced by oxygen isotope records from belemnites (Price et al., 2000; van de Schootbrugge et al., 2000), might have stimulated upwelling and thereby increasing productivity and downward transport of P with organic matter. However, high PAR during the early Hauterivian are not related to high carbon burial rates but are positively correlated with increased carbonate sedimentation rates, which seem to have increased on a global scale. As a result of high oxygen levels in bottom water, organic matter may have been re-oxidized and the P set free. Phosphorus was increasingly well retained in the sediment as a result of high carbonate particle fluxes together with increased Fe- and Mn-concentrations.

The observed trends in carbon isotopes and phosphorus burial have led us to distinguish three different stages of platform development and drowning during the Valanginian and Hauterivian:

Perturbation (Fig. 8.13) of the phosphorus and carbon cycles during the early and early late Valanginian was due to the increased influx of nutrients, which led to suffocation of sensitive carbonate producing biota and prolonged phases of reef demise along the northern margin of the Tethys (D1, Böhls and Gemsmättli Beds, Föllmi et al., 1994) and also in other regions. Weakening of carbonate factories was enhanced by sea level fall and shedding of siliciclastics during the mid-Valanginian followed by a second order eustatic sea level rise during the late Valanginian. Initial perturbation was possibly related to a first phase of volcanic activity (Parana Igneous Province). Perturbation is characterised by a simultaneous positive carbon isotope shift and increase in phosphorus burial rates.

Decoupling of the P and organic carbon burial evidenced from increasing PAR and decreasing carbon isotope values during the late Valanginian and early Hauterivian occurred when carbonate factories recovered during the earliest Hauterivian and the system as a whole shifted in a higher energy mode. Carbonate was produced in the green water mode (crinoids, bryozoans, sponges, echinoids) at high pace. We suggest high carbonate sedimentation rates during the early Hauterivian were forced in order to buffer the oceans alkalinity that had increased as a result of a prolonged phase of reef demise during the early and late Valanginian and because of increased weathering/ erosion rates. 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 up connections with the Boreal Realm increased circulation along the northern margin of the Tethys.

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 increased under increasingly dysaerobic conditions resulting from decreased circulation. The deposition of the Faraoni black shales, which was contemporaneous with a third Hauterivian drowning event (D3, Altmann Beds) in the

latest Hauterivian *Angulicostata* zone might be related to the overturn of P-enriched deep waters. A return to less eutrophic conditions when greenhouse climate stabilised correlate with cessation of continental flood basalt formation. A full return to *normal* occurred in the Barremian, when more arid conditions led to carbonate production in the blue water mode (corals and rudists) again.

8.8 References

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**Geochemistry, sedimentology and
biostratigraphy of a mid-Hauterivian
drowning phase: The Lidernen Beds
(Helvetic Alps, Switzerland)**

Abstract

During the Valanginian, the global link between platform drowning in the Helvetic Alps (Switzerland), eutrophic conditions due to increased continental run-off and a shift from carbonate carbon to organic carbon burial is expressed in the contemporaneous occurrence of phosphoritic beds and globally heavier carbon isotope ratios. However, a similar, mid-Hauterivian, phosphogenic event, recorded by the Lidernen Beds, is not mirrored by increased carbon isotope ratios.

A multi-proxy (biostratigraphy, sedimentology, geochemistry and organic matter) study has been performed on different outcrops along the former northern margin of the Tethys with the aim to unravel the complex sedimentary history of the Lidernen Horizon and to evaluate whether local, regional or global factors were involved. Duration of platform drowning was constrained by newly collected ammonites from the Lidernen Beds in the type-section at Lidernen Plänggeli. *Crioceratites cf. duvali*, *Subsaynella sayni* and *Plesiospitidiscus ligatus*, among others, indicate that platform drowning and condensation started in the late *Nodosoplicatum* zone and extended upto the early *Ligatus* zone. Combined geochemical and organic matter analyses (P, Fe/Mn and Sr/Ca) from under and overlying sediments as well as from the Lidernen Beds itself indicate that coastal upwelling of cold water may have played an important role in addition to high continental influx of nutrients, which already stressed carbonate factories.

It is concluded that an important regressive event, witnessed in coeval shallow marine deposits, such as on the Jura Platform, during the latest early Hauterivian (*Nodosoplicatum* zone) preceded drowning. During the earliest late Hauterivian (*Sayni* zone) a rapid transgression of cold nutrient rich waters led to the deposition under dysoxic conditions of an organic matter rich hemipelagic mud with abundant pelagic organisms (ammonites, planktonic foraminifera). This highly condensed unit formed a precursor for phosphate deposition. When a site moved out of the Oxygen Minimum Zone, as sea level rose further, bioturbation intensified (*Thalassinoides*) and the abundant faecal pellets formed the substrate for glauconite formation. Bioturbation also resulted in complete reworking of the initial phosphatic substrate and its transport to deeper water as is evidenced by abundant nodules in deeper settings. As sea level fell during the late Hauterivian, circulation decreased, cold water inflow diminished and upwelling decreased leading again to carbonate deposition.

9.1 Introduction

Cretaceous condensed phosphatic beds occurring in thrust parts (Helvetic nappes in the Swiss Alps) of the former northern margin of the Tethys have been the focus of research for almost a century (Heim, 1910-1916; Goldschmid, 1927; Fichter, 1934; Schaub, 1936; Schaub, 1948; Schindler, 1959; Funk, 1971; Haldimann, 1977; Föllmi, 1986; Wyssling, 1986; Föllmi et al., 1994; Kuhn, 1997; Weissert et al., 1998). These condensed beds are relatively rich in megafossils (ammonites, belemnites, brachiopods, bivalves and echinids among others) compared to under- and overlying sediments, which make them important marker beds in the early and middle Cretaceous stratigraphic framework of the Helvetic Alps (Funk et al., 1993; Föllmi et al., 1994). This paper deals with one of these condensed phosphatic horizons, the so called *Lidernen Beds*, which divides the Hauterivian Helvetic Kieselkalk Formation in a lower and upper member. These beds have not been exactly dated up till now although a mid-Hauterivian age was assumed (Funk, 1971; Wyssling, 1986; Lemaire, 1995; Kuhn, 1997). A first objective of this study has been to constrain duration and extent of condensation with the help of newly collected ammonites.

The Lidernen Beds are not only of great stratigraphic value, but also figure in recent paleo-environmental reconstructions of early Cretaceous platform drowning events. Drowning unconformities in the late Valanginian (D1 in Föllmi et al., 1994) and early Aptian (D4 in Föllmi et al., 1994) were considered by Föllmi et al. (1994) and Weissert et al. (1998) to be linked to global events given their good correlation with contemporaneous global positive carbon isotope excursions. The relation between positive carbon isotope excursions, platform drowning and deposition of condensed phosphatic beds is as follows: During phases of emplacement of large igneous provinces (Parana and Ontong-Java), $p\text{CO}_2$ of the atmosphere was increased inducing enhanced greenhouse conditions. Intensifying of the hydrological cycle under enhanced greenhouse conditions led to increased weathering/erosion and run-off. The increased nutrient load of river water gave rise to eutrophic conditions in shallow marine carbonate platform settings leading to a cessation of carbonate production, condensation and phosphorite deposition. Eutrophic conditions also led to increased organic carbon production and burial and this is reflected in the global positive $\delta^{13}\text{C}$ shifts during mid-Valanginian and Aptian times (Weissert et al., 1998).

Previously established carbon isotope records for the Hauterivian, based on hemipelagic micrites show that the early Hauterivian is characterized by decreasing carbon isotope values (van de Schootbrugge et al., 2000). Interestingly, the Lidernen Horizon (D2 in Föllmi et al., 1994) does not correspond to a major positive carbon isotope excursion, but rather to minimal $\delta^{13}\text{C}$ values, indicating that its paleo-environmental significance might be different than those drowning events occurring in the Valanginian and Aptian. To determine which factors were crucial for platform drowning during the Hauterivian a multi-proxy study of both the Lidernen Horizon and Kieselkalk Fm was performed. In addition to the above mentioned objective, the following topics will be addressed:

- 1) Considering the time involved in the condensed Lidernen Horizon it is very likely that a complex sequence of events is recorded within this phosphatic horizon such as is the case for other phosphatic horizons in the Helvetic Alps (Schaub, 1948; Kuhn,

1997). Several different depositional models have been proposed to explain the formation of these condensed phosphatic horizons, which might be tested by studying in detail sedimentology on a macro- and microscopic scale.

2) Eutrophication is thought to lead to increased primary production of organic matter, because of the increased availability of nutrients. The Valanginian shows globally more positive carbon isotope values, indicating a shift from carbonate carbon burial to organic carbon production and burial. Organic matter (and biological activity) plays an important role in phosphogenesis by transferring phosphate in dissolved form from the water column into the sediment (Froelich et al, 1982; Froelich et al., 1988; Föllmi, 1996). The Lidernen Beds and the Kieselkalk were studied for their palynofacies assemblage in order to determine whether organic matter was important in provoking phosphogenesis.

3) The ratios of Sr/Ca, Fe/Mn and the concentration of total PO_4 from marine limestones present proxies for continental weathering related to climate and sea level (Föllmi, 1995; Stoll and Schrag, 2001; Kuhn et al., in prep.). All of these proxies have shown to increase dramatically from the Valanginian into the Hauterivian, which has been explained as an increase in chemical weathering under intensified greenhouse conditions (Weissert et al., 1998). We present high resolution records from two sections that span the complete Hauterivian and will compare the trends with similar datasets from other localities. This may help to distinguish local factors controlling phosphorite deposition from regional and global mechanisms along the northern margin of the Tethys. It may also provide further clues as to what caused repeated crises in carbonate production on the Helvetic Shelf.

4) Carbon and oxygen isotopes are both useful as stratigraphic tools and as paleo-environmental indicators. We measured the complete Hauterivian of the Pilatus section for its oxygen and carbon isotope signature. Comparison with high resolution records from the Vocontian Basin that have been calibrated with ammonites, may further add precision to the stratigraphy of the Helvetic Kieselkalk. Belemnites from the Lidernen Beds were also measured with the aim of gaining insight in sea water temperature changes during drowning. Upwelling and cold water are both important for phosphogenesis and glauconite formation.

9.2 Geological setting

The studied sections are confined in a narrow tectonic unit, which is called the Northern Helvetic Alps (Switzerland). This northern zone of the Alpine Chain represents the former northern Tethyan Shelf, which was thrust and overthrust in a northward direction during Alpine orogenesis (Fig. 9.1).

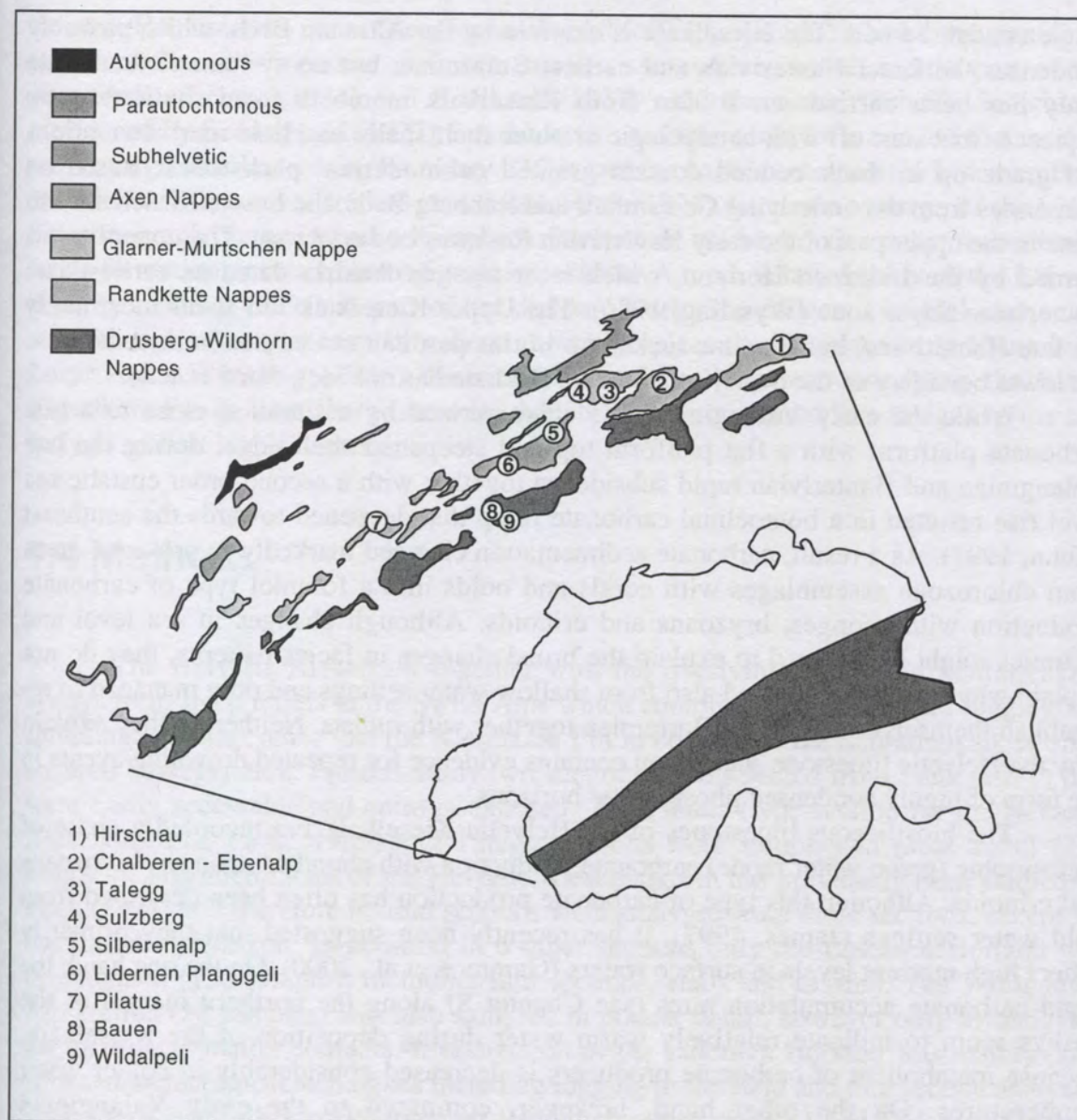


Figure 9.1 – Map of Switzerland showing studied sections in palinspastic reconstruction of the Helvetic Shelf (after Kuhn, 1997 and references therein).

The Hauterivian along the northern margin of the Tethys is represented by the Helvetic Kieselkalk Fm, which consists of a lower and an upper member, separated by a phosphoritic horizon, the so called *Lidernen Beds*. The base of the succession is formed by the early late Valanginian to earliest Hauterivian *Gemsmättli Beds*, which represent a first phase of platform drowning on the Helvetic Shelf (D1 in Föllmi et al., 1994). This horizon is sometimes split or completely replaced by a coarse sand body, called the *Pygurus Beds*. Locally this sand body is overlain by a phosphatic horizon, the *Rahberg Beds*, with an exclusively earliest Hauterivian fauna (Haldimann, 1978; Wyssling, 1986; Kuhn, 1997). In deeper parts of the shelf, the Gemsmättli and Rahberg Beds merge into a

single condensed bed. The Kieselkalk is overlain by the Altmann Beds, which probably condenses the latest Hauterivian and earliest Barremian, but no systematic ammonite study has been carried out so far. Both Kieselkalk members form shallowing up sequences that start off with hemipelagic or outer shelf shales and lime-marl alternations and grade up in thick bedded coarser grained echinodermal packstones. Based on ammonites from the underlying Gemsmättli and Rahberg Beds, the Lower Kieselkalk Mb starts in the upper part of the early Hauterivian *Radiatus* or *Loryi* zone. The upper limit is formed by the Lidernen Horizon, which is at least in Austria dated as earliest late Hauterivian *Sayni* zone (Wyssling, 1986). The Upper Kieselkalk Mb spans most likely the late Hauterivian, but the time locked up in this part can not be determined, because the lower boundary of the overlying Altmann Horizon has not been dated exactly.

While the early Valanginian was characterized by a situation close to a true carbonate platform with a flat platform top and steepened shelf edge, during the late Valanginian and Hauterivian rapid subsidence together with a second order eustatic sea level rise resulted in a homoclinal carbonate ramp that deepened towards the southeast (Kuhn, 1997). As a result, carbonate sedimentation changed markedly in proximal areas from chlorozoan assemblages with corals and ooids into a foramol type of carbonate production with sponges, bryzoans and crinoids. Although changes in sea level and tectonics might be inferred to explain the broad changes in facies patterns, they do not explain why corals disappeared also from shallow water settings and only managed to re-establish themselves during the Barremian together with rudists. Neither do they explain why the Helvetic limestone succession contains evidence for repeated drowning events in the form of highly condensed phosphoritic horizons.

The biosiliceous limestones of the Helvetic Kieselkalk Fm recorded a phase of mesotrophic (green water mode) carbonate production with abundant sponges, bryozoans and crinoids. Although this type of carbonate production has often been described from cold water settings (James, 1997), it has recently been suggested that they primarily reflect high nutrient levels in surface waters (Gammon et al., 2000). On the one hand, the rapid carbonate accumulation rates (see Chapter 8) along the northern margin of the Tethys seem to indicate relatively warm water during deposition of the Kieselkalk, because metabolism of carbonate producers is decreased considerably in colder water temperatures. On the other hand, however, compared to the early Valanginian oligotrophic mode of carbonate production (Ohrli Kalk and Lower Betlis Kalk), deeper water temperatures were probably considerably lower, something also shown by oxygen isotope data obtained from well preserved belemnites (van de Schootbrugge et al., 2000).

9.3 History of the Lidernen Horizon

The name “Lidernen Schichten” was first introduced by Schindler (1959) following suggestions made by R. Hantke who was studying a well exposed outcrop at Lidernen Plänggeli in the area between Kaiserstock and Rosstock (central Switzerland, (Hantke, 1961). This section is now informally considered as the type section for the Lidernen Beds (Funk, 1971). In previous literature confusion reigned about this glauconitic bed that divides the Kieselkalk Formation in a lower and upper part. Arnold

Heim (1916) used the name “Sentisianus Bank” for a glauconitic rich bed that contained abundant *Toxaster retusus* var. *sentisianus*, somewhere in the middle part of the Kieselkalk. Fichter (1934) and Brückner (1937) used the name “Schiffli Schichten” introduced by Goldschmid (1927), but the latter used this name for a horizon that marked the Valanginian-Hauterivian boundary. Other authors have mentioned the Lidernen Beds in their work, but never studied it in detail. Funk (1971) discusses outcrops of the LH in his monograph on the Helvetic Kieselkalk Formation, but he remains rather inconclusive on its formation or exact biostratigraphic position. A more detailed study of the LH was done by Lemaire (1995) as part of her diploma work. She collected several ammonites and although of very poor quality these allowed to place the LH in the early Hauterivian *Loryi* zone. Wyssling (1986) described a condensed horizon overlying the lower Kieselkalk Fm in Vorarlberg (Austria), which he does not name, but assigns to the late early to earliest late Hauterivian.

9.4 Methods

The Helvetic Kieselkalk together with the overlying Barremian Schrattenkalk always form steep reliefs in the Swiss Alps which complicates their detailed logging and sampling. To this comes that the Kieselkalk Fm in contrast to the Schrattenkalk is often covered by vegetation. For this study two sections were selected from Funk (1971) that were easily accessible and entirely exposed. The Pilatus (type-section for the Helvetic Kieselkalk Fm, Funk, 1969) and Talegg sections were sampled in great detail (250 samples). The microfacies of the Helvetic Kieselkalk Fm has previously been studied by Funk (1971) and therefore no thin sections were analysed from these sections, except for the Lidernen Horizon. In addition in 6 other sections only the Lidernen Horizon was investigated (150 samples, including thin sections, slabs and fossils). The Wildgunten Alp section (30 samples) was also sampled in greater detail, however only investigated for its organic matter contents. Investigation of the Lidernen Horizon was mainly done with sedimentological techniques including logging in the field and thin section analyses. Both the Kieselkalk Fm (Pilatus and Wildgunten Alp section) and Lidernen Horizon (Pilatus, Bauen, Wildalpe, Talegg) were investigated for their organic matter contents. Trace element records (Fe, Mn, Sr, Ca) were determined in two sections (Pilatus and Talegg sections). The Pilatus section was measured for its carbon and oxygen stable isotope record. In addition, several belemnites from the Lidernen Horizon were also measured for their carbon and oxygen isotope signature.

To extract organic matter for palynofacies analyses around 15 g of grounded bulk rock was dissolved in HF and HCl in order to remove all silicate and carbonate minerals. Sieving of the insoluble residue was done with a 15 µm sieve and the organic matter mounted on palynological slides. In every slide at least 200 palynomorphs were counted using light microscopy and classified according to Pittet and Gorin (1997) and Steffen and Gorin (1993) palynofacies classification. Samples were also analysed with the help of a RockEval 6 to determine type and organic matter contents. These data may serve as an independent verification of the optical determinations. For the RockEval 6 about 100

mg of powdered bulk rock was pyrolyzed and oxidized in successive steps. In every run of 26 samples a standard was included.

The trace element data were obtained by dissolving 1 g of powdered bulk rock with 1N HCl for 20 minutes at 80°C. The non-dissolved residue was filtered out and the solution was analysed with a Perkin Elmer 5100 PC Atomic Absorption Spectrophotometer for Fe, Mn and Sr calibrated with standard solutions. The Ca-content was calculated from the dissolved fraction. Precision of analyses proved better than 10% for all elements.

Phosphate was measured using a Perkin Elmer UV/Vis Photospectrometer Lambda 10. Approximately 100 mg of powdered bulk rock was attacked under constant shaking for 14 hours with 1N HCl and the solution centrifuged. Calibration with standard solutions gave precision better than 5%. The absolute PO₄-values were converted in Phosphorus Accumulation Rates (PAR), which are expressed in mg/cm²/kyr, using sedimentation rates and a density of 2.5 g/cm³.

The carbon and oxygen isotope data were measured at the Geological Institute of the University of Bern (see van de Schootbrugge et al., 2000 for details).

9.5 Macroscopic sedimentological aspects

The Lidernen Beds are difficult to recognize in the field, because the whole unit is often less than one meter thick and these beds weather in the same way as the under- and overlying Kieselkalk Fm that can reach thicknesses of several hundred meters. The dark brown weathered appearance of both the Kieselkalk and Lidernen Beds are indicative of presence of pyrite. In the field the Kieselkalk Fm as a whole is easily distinguished from the light grey to beige Valanginian Betliskalk Fm and Diphyoides Limestones and Barremian Schrattenkalk Fm (light grey to blueish).

Another problem is the great variety in LH outcrops even over short distances (< 1 km). This is partly due to the fact that different facies are superposed or occur next to each other as a result of northward overthrusting of the Helvetic nappes, but this can not explain all the differences. In the next paragraphs outcrops are discussed in the context of a palinspastic reconstruction proposed by Funk (1971) and Funk et al. (1993), who distinguished three facies realms for the Helvetic Shelf, a northern, middle and southern.

Northern facies (Fig. 9.2)

Hirschau: This most proximal facies is best studied in the region of Vorarlberg (Austria), where the Kieselkalk Fm consists of crossbedded echinodermal pack-grainstones rich in detrital quartz and sometimes belemnites (Wyssling, 1986). The section at Hirschau is located within the Vorarlberger Säntis Nappe, which is a lateral extension of the Säntis Nappe in Switzerland. At Hirschau Wyssling (1986) described both the Gemsmättli and Altmann Beds plus a third phosphatic horizon dividing the Kieselkalk Fm in two equal parts. In this horizon Wyssling (1986) found a *Subsaynella sayni*, evidence that this bed is an equivalent of the Lidernen Beds of the Helvetic Alps (see below). The actual LH consists of a 10 cm thick micritic horizon with small

phosphatic clasts with a wavy base and no sharply defined upper boundary. Glauconite grains occur dispersed throughout. Small pieces of ammonites and belemnites could be observed in outcrop.

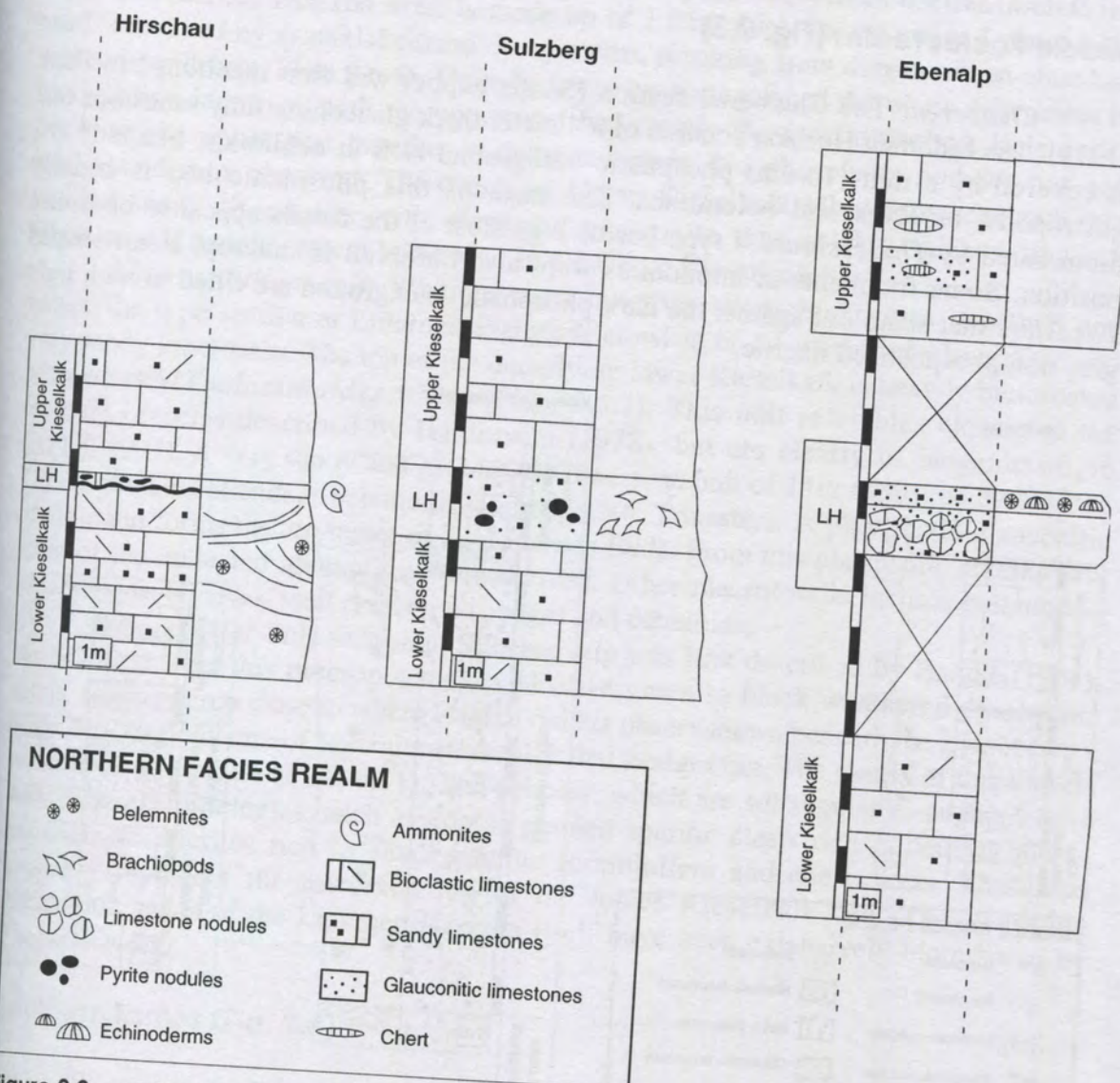


Figure 9.2 – Northern facies realm. Lithology for Sulzberg and Ebenalp after Lemaire (1995). LH = Lidernen Beds

Sulzberg: The Sulzberg section (Axen nappe, Fig.3b) was originally described by (Haldimann, 1977) and studied in more detail by Lemaire (1995). The LH makes up 0.8m of micritic limestone rich in echinoid debris, oysters and brachiopods. The contacts with the under- and overlying Kieselkalk is sharp. Large pyrite nodules of 1-2 cm diameter occur. Glauconite is only present in minor amounts.

Ebenalp: The profile at Ebenalp (Fig. 3c) in the Säntis Nappe (Lemaire, 1995) is poorly exposed and the contacts with the underlying and overlying Kieselkalk Fm could not be observed. The exposed part of the LH consists of two beds: one bed rich in limestone pebbles that float in a glauconitic sandy matrix and one bed purely composed

of glauconitic sandy limestone. This second bed contains abundant *Toxaster sp.* and debris of crinoids, oysters and bivalves. Towards the top small phosphatic clasts occur.

Middle Facies realm (Fig. 9.3)

Chalberen: The Chalberen section (Säntis nappe) was first mentioned in Funk (1971). The Lidernen Horizon consists of a 4 meter thick glauconitic limy sandstone that is covered by a thin (10 cm) phosphatic hardground rich in echinoids, brachiopods, gastropods, bivalves and belemnites. The base of this phosphatic bed is heavily bioturbated by *Thalassinoides* type burrowing. Most of the fossils appear to be in life position. Some fragments of ammonites were also observed in outcrop. Heart-shaped *Toxasters* that stand out against the dark phosphatic background are filled in with light grey non-phosphatized micrite.

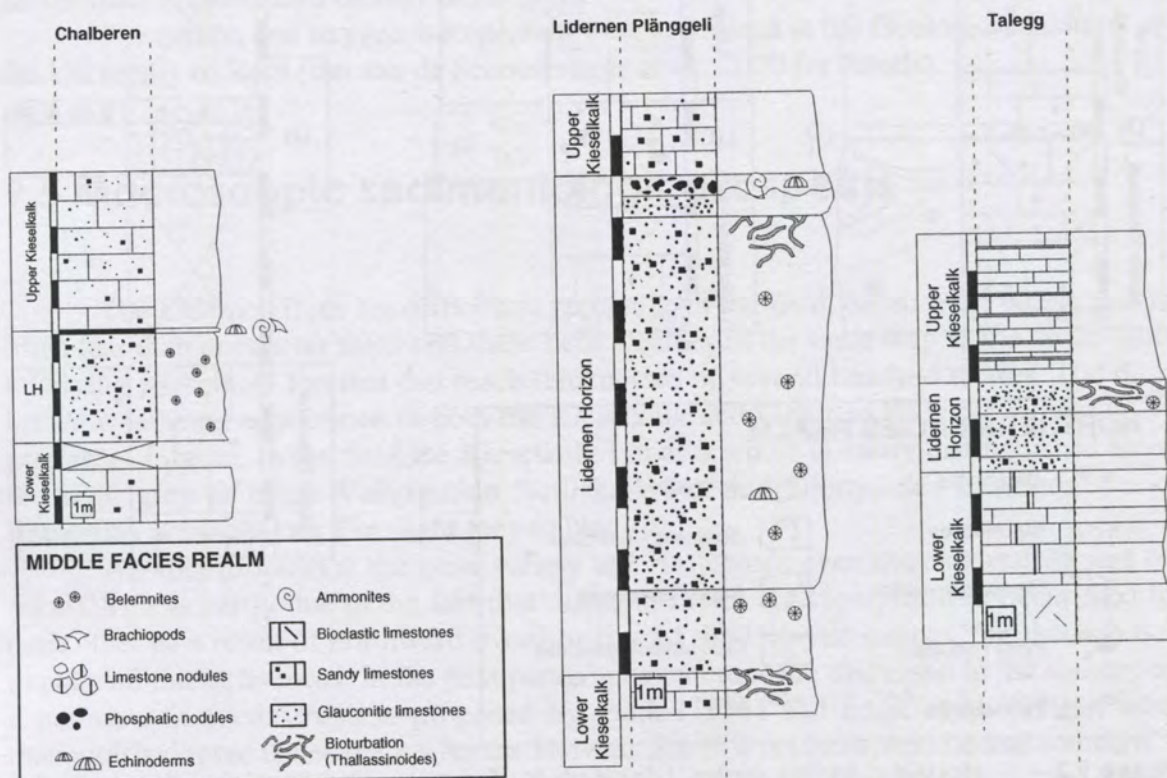


Figure 9.3 – Middle facies realm. Note large variations in lithological development.

Talegg: the Talegg section (Fig.9.3 and Fig.9.9) was sampled more extensively, from the upper part of the Upper Betliskalk Fm upto the Altmann Beds. The first 50 meters consist of sandy bioclastic and pelloidal packstones. At the base of the section oolitic grainstones occur. A small cascade forms the transition from the Betlis Fm into the Kieselkalk Fm. Although this part of the outcrop is inaccessible, the section is visible from the road. Neither the Gemsmättli Beds, nor the marls that normally form the base of the Kieselkalk Fm are present. A large hiatus is thus suspected between the Kieselkalk

and Betlis Kalk. The Kieselkalk starts with regular lime-marl alternations that grade upwards into thicker bedded limestones. Several thin bedded very fine grained limestone beds that overly coarser grained echinodermal pack-grainstones mark the transition to the LH. The Lidernen Horizon itself is made up of 1.85m thick coarse grained glauconitic sands cemented by syntaxial calcite overgrowths, resulting from diagenesis on abundant echinoderm debris (Plate 9.6.4). Three beds can be distinguished that show differences in bioturbation intensity, with the uppermost bed clearly the most disturbed. Belemnites occur in the upper part together with brachiopods. No phosphatic nodules nor any hardground were observed. The overlying Upper Kieselkalk Mb commences with thin bedded sandy limestones with dispersed glauconite that quickly thicken upward. Glauconite is mainly present in burrows in the Upper Kieselkalk.

Lidernen Planggeli: Whereas most outcrops show thicknesses less than one meter, the type section at Lidernen Planggeli consists of 12 meters of glauconitic and very sandy limestones. The top of the underlying lower Kieselkalk is heavily bioturbated with mostly *Thalassinoides* traces (Plate 9.5.7). This unit resembles closely to the tectonic breccias described by Haldimann (1978), but are clearly of biogenic origin (Kuhn, 1997). A very sandy and glauconitic limestone unit of 11m forms the bulk of the LH. It contains abundant belemnites and complete *Toxasters*. A phosphatic glauconitic hardground forms the top meter of the Lidernen Beds. From this phosphatic nodular unit most of the collected ammonites were derived. Other macrofossils include belemnites, brachiopods, bivalves, well preserved sponges and echinoids.

Silberen Alp: This section at Silberen Alp was first described by Hantke (1961). He described from this outcrop 4 meters of olive green to black weathered glauconitic sands. In an outcrop close to where Hantke did his observations, beneath the LH, occurs a polymict conglomerate of several meters thick that wedges out. The matrix of this breccia consists of glauconite (Plate 9.11). The pebbles, which are subangular to angular, have very different lithologies, such as coarse grained sparitic clasts rich in detrital quartz, hemipelagic micrites rich in small benthic foraminifera and chert clasts. The clasts probably represent the reworked top of the lower Kieselkalk Mb. The overlying glauconitic sands of the Lidernen Horizon itself have been extensively bioturbated by *Thalassinoides*.

Southern facies (Fig. 9.4)

Pilatus: In the Pilatus section the whole Hauterivian was sampled. The base of the section consists of marly limestones that grade upwards in thin bedded lime-marl alternations. The marl interbeds become progressively thinner up section until they are only present occasionally. In the lower part of the section, the limestones are wackestones that contain abundant biosiliceous remains (sponge spicules) and detrital quartz, bryozoan, echinodermal and crinoid debris. Most of the sponge spicules have been replaced by calcite and the silica has been concentrated in chert nodules that occur dispersed throughout the Kieselkalk Fm (Funk, 1971). The top of the Lower Kieselkalk Mb is made up of several meters of coarser grained heavily bioturbated (*Planolites*, *Thalassinoides*) pack-grainstones with mainly echinoderm debris and rich in detrital quartz. The top of this lower echinoderm breccia is bioturbated and the burrows are filled in with glauconitic sandy marls from the overlying Lidernen Beds. These marls grade

upwards into bioturbated glauconitic sands that contain pinkish weathered micritic limestone nodules (Plate 9.10). At first sight these appear to be floating within the matrix, but in fact they have been completely dug out of the underlying sediments by bioturbation. This unit is extremely rich in glauconite. Higher up phosphatic nodules and pyritic nodules occur that are clearly polymict. The upper 20 cm is characterized by large amounts of belemnites.

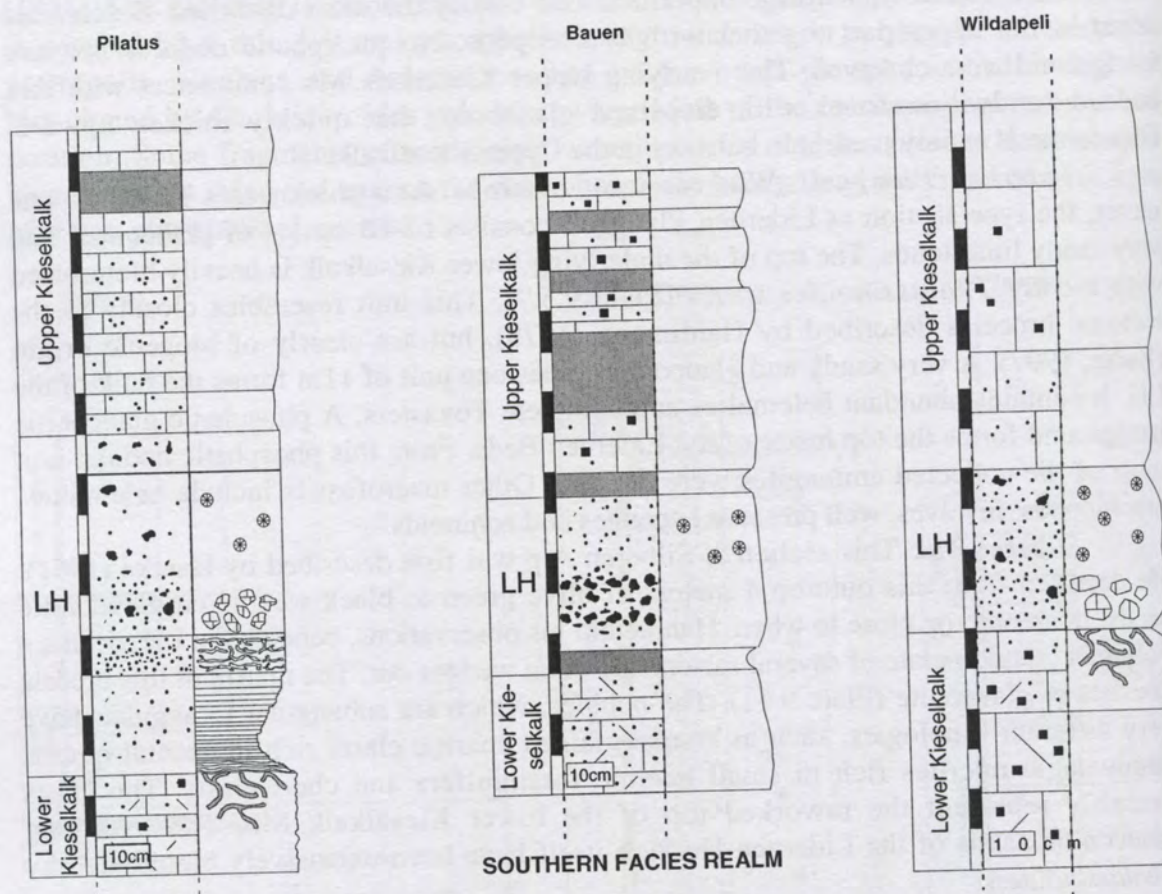


Figure 9.4 – Southern Facies Realm. The Lidernen Horizon is in this realm often less than one meter thick and occurs intercalated between thick limestone succession of the Helvetic Kieselkalk.

Bauen: The section at Bauen (Fichter, 1934) is located in the uppermost Helvetic thrust sheet, the so-called Drusberg Nappe. This very southern facies shows thick hemipelagic limestone deposits of the *Diphyoides* Fm (Plate 9.13.6) dated as late Valanginian to earliest Hauterivian. The *Diphyoides* Fm grades upwards in more marly and sandy equivalents of the lower Kieselkalk Mb consisting of thin bedded micrites alternating with more marly interbeds. According to Fichter (1934) the Kieselkalk Fm reaches a thickness of 600m in this region. The LH forms a 40cm thick glauconitic sandy limestone with numerous well rounded phosphatic nodules in its middle part. Towards the top glauconite and belemnites dominate.

Wildalpel: The section at Wildalpel in the Bauen-Brisen chain belongs to the same thrust unit as the section at Bauen. The appearance of the LH is slightly different.

Pinkish weathered limestone nodules float in a sandy glauconitic matrix. The limestone nodules are mostly micritic and without glauconite. Belemnites are again the most abundant macrofossils. Fichter (1934) found some badly preserved ammonites in this outcrop.

9.6 Microfacies observations and interpretation

Glauconite: glauconite is one of the most common sediment types within the LH. Size and abundance of grains tend to increase towards more proximal settings, except for very proximal settings such as at Hirschau and Sulzberg. The grains are mostly well rounded and the sorting is good. Some grains also show constrictions, which indicates that faecal pellets may have acted as precursors (Funk, 1971). Other indications for this are that within the Kieselkalk Fm itself glauconite is often concentrated in burrows. The color of the grains varies from dark green to whitish green, which is probably the result of diagenesis, since these grains do not show different chemical compositions (Funk, 1971). Glauconite also occurs as infillings of especially echinoid debris and foraminifera.

Odin and Matter (1981) state that glauconitization occurs at depths between 50 to 500m with a maximum abundance on the outer shelf between 200 and 300m water depth. Glauconitization proceeds as an authigenic precipitation of iron-rich, potassium poor, smectite on a parent substrate in a semi-confined environment (cracks, pores). Larger grains are therefore more prone than smaller ones and the interior of grains is often more glauconitized than the outside. In a later stage of glauconitization the smectites are modified by incorporation of potassium. In the Lidernen Beds this parent substrate appears to have been faecal pellets. Low accumulation rates, winnowing and exposure are essential to keep the grains in contact with ambient sea water. Low oxygen levels and relatively cold water (7-15°C) are further prerequisites.

Quartz: Quartz occurs both as biogenic silica and detrital grains. From the lower echinoderm breccia (top of lower Kieselkalk Mb) into the LH quartz increases in size (10-100 µm) and abundance. In Chalberen and Hirschau very large quartz grains (> 1mm) were observed (Plate 9.8.5). Size of quartz grains diminishes towards deeper settings (Bauen, Wildalpel). Quartz in the LH is generally moderately well rounded and well sorted. Chalcedony sometimes replaces parts of bioclasts such as belemnites. The precipitation is diagenetic and probably related to dissolution of sponge spicules, which are always replaced by calcite (Plate 9.4.6).

Phosphate: Phosphatization preceded glauconite formation in the abundant phosphatized lithoclasts and macrofossils that contain no glauconite. However, the matrix of the glauconitic part of the Lidernen Horizon is often also phosphatic, which might have occurred during later (different phase) of phosphatization.

Phosphatic clasts: Phosphatic lithoclasts occur in all sections, but are especially abundant in the northern (Hirschau, Chalberen) and southern facies realms (Pilatus, Bauen, Lidernen Plänggeli). Two types of lithoclasts dominate: 1) spiculitic micrites with very fine detrital quartz (Plate 9.6.2). 2) coarse grained echinodermal packstones, sometimes with glauconite (Plate 9.6.3). The first were deposited and reworked from pelagic sediments overlying the top of the lower Kieselkalk Mb, which formed the parent

material for phosphogenesis as it is often present within the reworked phosphatized ammonites and other macrofossils. The second represent reworked clasts from the uppermost lower Kieselkalk (lower Echinoderm Breccia).

Biogenic components: Reworked phosphatized clasts from the Lower Kieselkalk Fm contain often a rich and diverse benthic foraminifera assemblage (Plate 9.7) as well as abundant very small planktonic foraminifera. In contrast, the glauconitic matrix of the LH is very poor in benthic foraminifera and most were probably reworked (Plate 9.4.5). Several species of benthic and planktonic foraminifera could be determined, but their ranges are often too long to be of any use. Planktonic species include undefined "minute foraminifera" and *Globuligerina* spp. Benthic species like *Gaudryina* sp., *Belorusiella* sp., *Lenticulina* sp. and *Meandrospira favrei* are well known from the Jura Mountains and especially from the early Hauterivian Pierre Jaune de Neuchâtel Fm (Arnaud, 1999; Blanc-Aletru, 1995; Rumley, 1992). The Pierre Jaune de Neuchâtel is a shallow water equivalent of the lower Kieselkalk Mb.

Echinoid debris is the most common type of bioclast within the glauconitic matrix of the LH. Bryzoan debris is relatively rare and seems to be more abundant in shallow settings (Chalberen, Plate 9.8.6). Oysters and bivalve debris also occur mostly in the northern and middle facies realms. Belemnites are always associated with the glauconitic matrix and although they occur in shallow (Hirschau) settings, their abundance increases towards deeper settings.

Bioturbation: Bioturbation played a very important role in the formation of the Lidernen Beds (Plate 9.5). *Thalassinoides* is the most common trace within the glauconitic matrix. Thick bedding in the uppermost Lower Kieselkalk Mb may also be caused by bioturbating activity, blurring any original bedding. The lower Echinoderm Breccia is often extensively bioturbated, creating deposits that resemble intraformational breccias. Similar Valanginian deposits were originally interpreted as the result of synsedimentary tectonic activity along paleofaults (Haldimann, 1977; Strasser, 1979). Kuhn (1997), however, demonstrated for the Gemsmättli Beds that they are of biogenic origin, because these breccias are not particularly related to any paleofaults, but occur over much wider areas. Several phospho-micritic infillings of ammonites from Lidernen Plänggeli contain *Chondrites* type burrows that are either filled in by sparry calcite or more intensively phosphatized micrite (Plate 9.5.5 and 9.5.6). Belemnites suffered more than any other bioclasts from endolithic borings. Some phosphatized extremely fine endolithic borings may suggest that fungal or microbial activity was important during phosphogenesis (Plate 9.5.1).

The presence of *Chondrites* type burrows in the spiculitic phosphatized micrite that fills in ammonites and the *Thalassinoides* type burrows that penetrate into the underlying Kieselkalk are indicative for changing oxygen levels within the sediment and overlying water column. *Chondrites* is thought to be indicative of more dysoxic conditions (Savdra et al., 1986). Phosphatization and glauconitization probably took place under dysoxic conditions at the sediment-water interface and the burrowers that formed the *Thalassinoides*-structures only arrived in a later stage when oxygen levels apparently had risen again.

Reworking: Reworking is evident both on a macroscale as well as on a microscale, such as: 1) In Chalberen reworked ooids (Plate 9.4.3) and reworked lithoclasts with ooids (Plate 9.4.7) were observed. These must have originated from the

Upper Betliskalk, because the Kieselkalk itself contains no ooids. Another option could be that they were reworked from the Pierre Jaune de Neuchâtel Fm. 2) Also in the Chalberen section reworked phosphatized foraminifera occur, that are broken and apparently were reworked from a phosphatic micrite precursor (Plate 9.4.5). 3) Reworking is also indicated by the large amounts of phosphoritic lithoclasts that were reworked from the underlying Kieselkalk. Plate 9.4.1 shows a reworked oyster fragment embedded in a phosphatized micrite.

Pyrite: Pyrite occurs abundantly within the LH. It is present as little framboids dispersed in the matrix or as large pyritized limestone nodules. Some lithoclasts show pyrite enrichment in their outer rims. Organic matter and bioclasts (like benthic foraminifera) are frequently mineralized as pyrite. The size of the framboids has been interpreted as an indicator for water column oxygenation (Wilkin, 1997). Very small framboids ($< 7 \mu\text{m}$) are known to grow within the anoxic water column of the Black Sea, while larger framboids and nodules occur in sediments with overlying oxygenated bottom waters. It is possible that pyritization occurred at a different time as phosphogenesis, maybe related to changed redox-conditions.

9.7 Biostratigraphy

Assigning the Helvetic Kieselkalk Fm to any particular ammonite zone(s) has proved to be extremely difficult due to scarce ammonites and macro- and micro-fossils. Poor preservation of useful microfossils is due to diagenetic overprint during Alpine deformation and diagenesis may also have dissolved ammonite tests. The Lidernen Beds, but also other phosphatic beds, like the Bühls, Gemsmättli, Rahberg and Altmann Beds, are therefore of critical importance as marker beds, because they are generally rich in ammonites and allow for indirect dating of the intercalated Betliskalk and Kieselkalk Fm. Compared to the Valanginian phosphatic horizons (Bühls and Gemsmättli Beds) the Lidernen Horizon is not that rich in ammonites and in general the ammonites are not as well preserved. The Lidernen Beds are often covered by vegetation and the ammonites are difficult to get out of the bed rock. Thusfar the type section of Lidernen Pläggeli has delivered most of the ammonites, which might also have something to do with paleo-topography as will be explained below. Several well preserved ammonites from the Terre Masse section in the Vocontian Basin (France) have been depicted as well in Plates 9.1-9.3 to show how difficult it is to obtain good identifications of the collected specimens and for comparison.

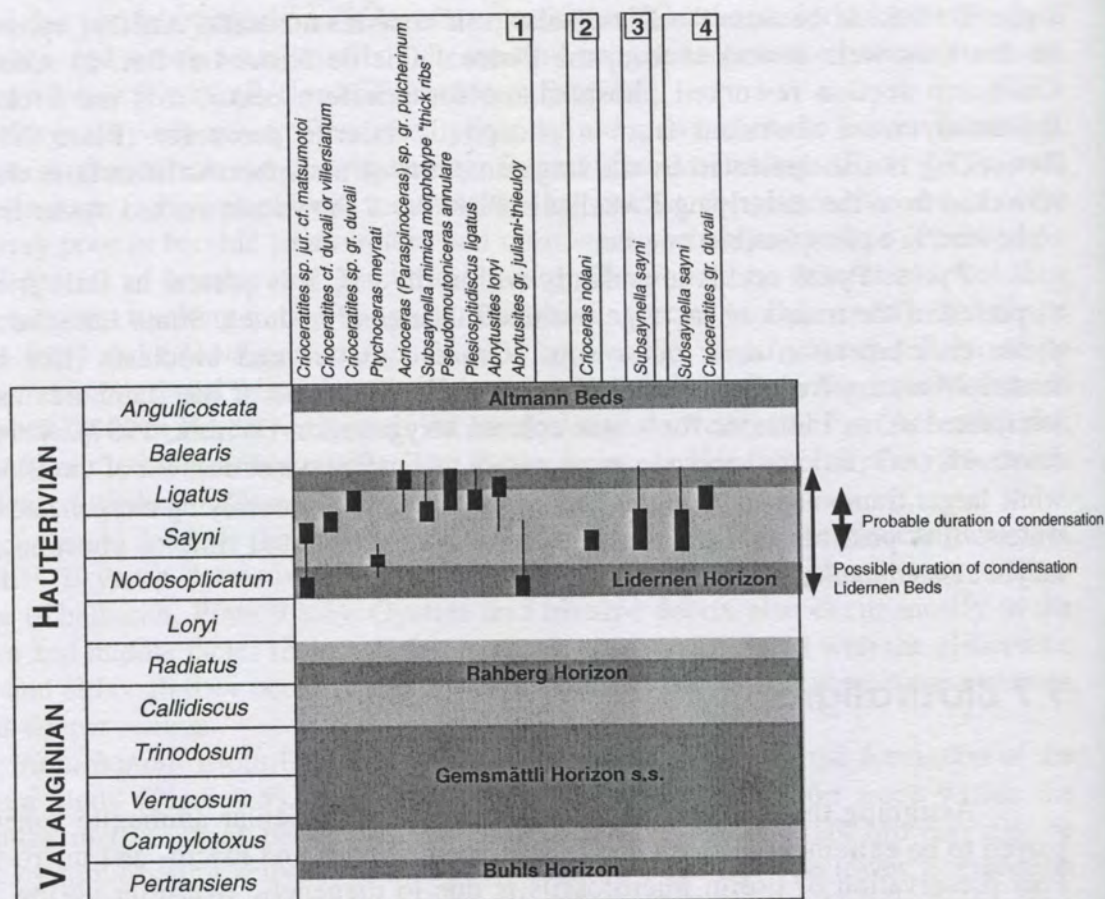


Figure 9.5 - Stratigraphic ranges of ammonites from the Lidernen Horizon. Relation is shown with other phosphoritic horizons of the Helvetic Alps. 1 = this study. 2 = Fichter (1934), 3 = Hantke (1961), 4 = Wyssling (1986).

A list of the ammonites found in the Lidernen Horizon is presented in Table 1, together with other faunal lists of various authors who have collected ammonites from the Lidernen Horizon during previous investigations. The ranges of significant species have been obtained from biostratigraphic studies on Vocontian Basin sections (Bulot et al., 1993; Bulot and Thieuloy, 1993; Bulot et al., 1992). From Figure 9.5 it becomes clear that the bulk of the ammonites from the Lidernen Beds belongs to the late Hauterivian *Sayni* and lowermost *Ligatus* zones, although condensation might have started in the top of the *Nodosoplicatum* zone and possibly continued upto the *Balearis* zone.

A conservative estimate of the time locked up in the Lidernen Horizon would be 1.5 Ma (2 ammonite zones), but this could be much less, as we do not have any absolute time control on ammonite zones for the early Cretaceous. The *Sayni* zone has previously been correlated in the Umbria-Marche Basin in Italy with magnetozone CM9 to CM6 and may have spanned 3 Ma alone (Channell et al., 1995). This creates serious problems for the time involved in the deposition of the Kieselkalk Fm, because if 3.5 Ma (*Sayni* plus *Ligatus*) is condensed in the Lidernen Horizon and an additional 0.5 Ma in the Rahberg-Gemsättli (lower part *Radiatus* zone) and Altmann Horizons (upper part of *Angulicostata* zone), the complete Kieselkalk Fm would have been deposited in 1 Ma.

Location	Name	Number	Remarks
This Study			
Lidernen Planggeli	<i>Crioceratites sp. jur. cf. matsumotoi</i> SARKAR 1955	2	Small incomplete fragments
Lidernen Planggeli	<i>Abrytusites gr. Juliani-thieuloy</i>	3	One complete and two fragments
Lidernen Planggeli	<i>Abrytusites loryi</i>	2	Two fragments
Lidernen Planggeli	<i>Ptychoceras meyrati</i> OOSTER	1	One fragment
Lidernen Planggeli	<i>Bochianites sp. cf. Oosteri</i>	2	Two fragments
Lidernen Planggeli	<i>Acrioceras (Paraspinoceras) sp. gr. pulcherinum</i>	5	Two imprints and three fragments
Lidernen Planggeli	<i>Subsaynella mimica</i> morphotype "thick ribs"	1	Small fragment
Lidernen Planggeli	<i>Plesiospitidiscus ligatus</i> d'ORBIGNY 1841	12	Six complete and six fragments
Lidernen Planggeli	<i>Crioceratites cf. duvali</i> or <i>villersianum</i>	1	Large fragment
Lidernen Planggeli	<i>Nautilus sp.</i>	4	Four fragments
Lidernen Planggeli	<i>Pseudomoutoniceras annulare</i>	1	Small fragment
Lidernen Planggeli	<i>Crioceratites sp. gr. duvali</i> LEVEILLE 1837	2	Two fragments
Lidernen Planggeli	<i>Indeterminable</i>	9	Fragments
G. Wyssling (1986)			
Bersbuch	<i>Crioceratites (Crioceratites) cf. duvali</i> LEVEILLE		Within Kieselkalk Fm.
Hirschau	<i>Subsaynella sayni</i>		Within Lidernen equivalent
R. Hantke (1961)			
Lidernen Pläggeli	<i>Phylloceras perlobatum</i>		
Lidernen Pläggeli	<i>Hemilytoceras sutile</i>		
Lidernen Pläggeli	<i>Hemilytoceras sequens</i>		
Lidernen Pläggeli	<i>Protetragonites</i>		
Lidernen Pläggeli	<i>Subsaynella sayni</i>		
Lidernen Pläggeli	<i>Barremites sp.</i>		
Lidernen Pläggeli	<i>Hamulina sp.</i>		
H.J. Fichter (1934)			
Vorderjochli	<i>Phylloceras sp.</i>		
Vorderjochli	<i>Lytoceras sp.</i>		
Vorderjochli	<i>Crioceras nolani</i>		
Vorderjochli	<i>Crioceras sp. div. Indet.</i>		
Ober Bolgen	<i>Crioceras sp. div. Indet.</i>		
Wildalpe	<i>Crioceras sp. div. Indet.</i>		
Teufelsmunster	<i>Crioceras sp. div. Indet.</i>		
Wildalpe	<i>Hamulina sp.</i>		

Table 1 – Ammonite fauna of the Lidernen Horizon.

This would give sedimentation rates for certain areas (Alvier), where the Kieselkalk is extremely thick, of almost 600m/Ma. Considering a subsidence rate of 20m/Ma (Funk, 1985), the Kieselkalk would have witnessed one of the fastest relative sea level rises ever. However, as already discussed in Chapter 5, the *Sayni* zone probably only spans two magnetozones (CM7 and CM6) and maybe even less, reducing its duration considerably as well. The above reasoning further underlines that the *Sayni* zone (ammonite evolution was probably quite rapid) did not span 3 Ma and that the calibration of ammonites, magnetozones and absolute time scales is in need of further elaboration.

9.8 Carbon and oxygen isotopes

In the Pilatus section, the Lower Kieselkalk shows overall decreasing $\delta^{13}\text{C}$ values, from +1.45 to +0.5‰ from the base of the Kieselkalk to the Lidernen Beds (Fig.9.6). Halfway through the Lower Kieselkalk a small positive shift can be observed, after which values decrease to reach a minimum in the Lidernen Horizon. These two negative $\delta^{13}\text{C}$ trends are accompanied by positive shifts in the $\delta^{18}\text{O}$ record. Oxygen isotopes show a positive trend (–4 to –2.5‰) from the base of the Kieselkalk upto the level where the small positive $\delta^{13}\text{C}$ excursion occurs. The upper part of the Lower Kieselkalk is characterised by slightly more negative oxygen isotope values (–3‰) before a second positive excursion occurs in the Lidernen Beds. The Upper Kieselkalk shows less distinct trends neither for the $\delta^{13}\text{C}$ nor for the $\delta^{18}\text{O}$ records, but the carbon isotope signal descends to +0.2‰ halfway through the Upper Kieselkalk, after which values increase again to reach +0.8‰ in the latest Hauterivian. The oxygen isotope signal appears to co-vary in the same manner, although the variations are larger.

The trend in the carbon isotope signal for the early Hauterivian compares closely with the trends observed in Italy and France. Values gradually decrease during the early Hauterivian as is always the case in all the studied sections (Chapter 4 and 5). However, in France the $\delta^{13}\text{C}$ signal shifts to more positive values during the late Hauterivian (from the base of the *Sayni* zone), while in the Pilatus section the values keep decreasing well after the Lidernen Horizon (which includes the whole *Sayni* zone). It is possible that local factors influenced the carbon cycle on the Helvetic Shelf. The two small scale excursions in the early Hauterivian could correspond to productivity cycles related to third order sea level rises.

Several LH belemnites from three different sites were analysed for their carbon and oxygen isotope signatures (Table 2). The oxygen isotope record of pristine calcite can be used as paleo-thermometer of ambient sea water in which the calcite was precipitated (see Chapter 4). Bottom water temperature on the Helvetic Shelf lay in the range of 15-17°C. The temperatures calculated from the belemnite oxygen isotope data are in accordance with the temperatures envisioned for glauconite formation. The oxygen isotope data is meaningful and not altered by diagenesis, because belemnites from different sections and different thrust sheet show relatively little scatter. Similar bottom water temperatures were obtained using oxygen isotope data from belemnites that lived in the Vocontian Basin (van de Schootbrugge et al., 2000).

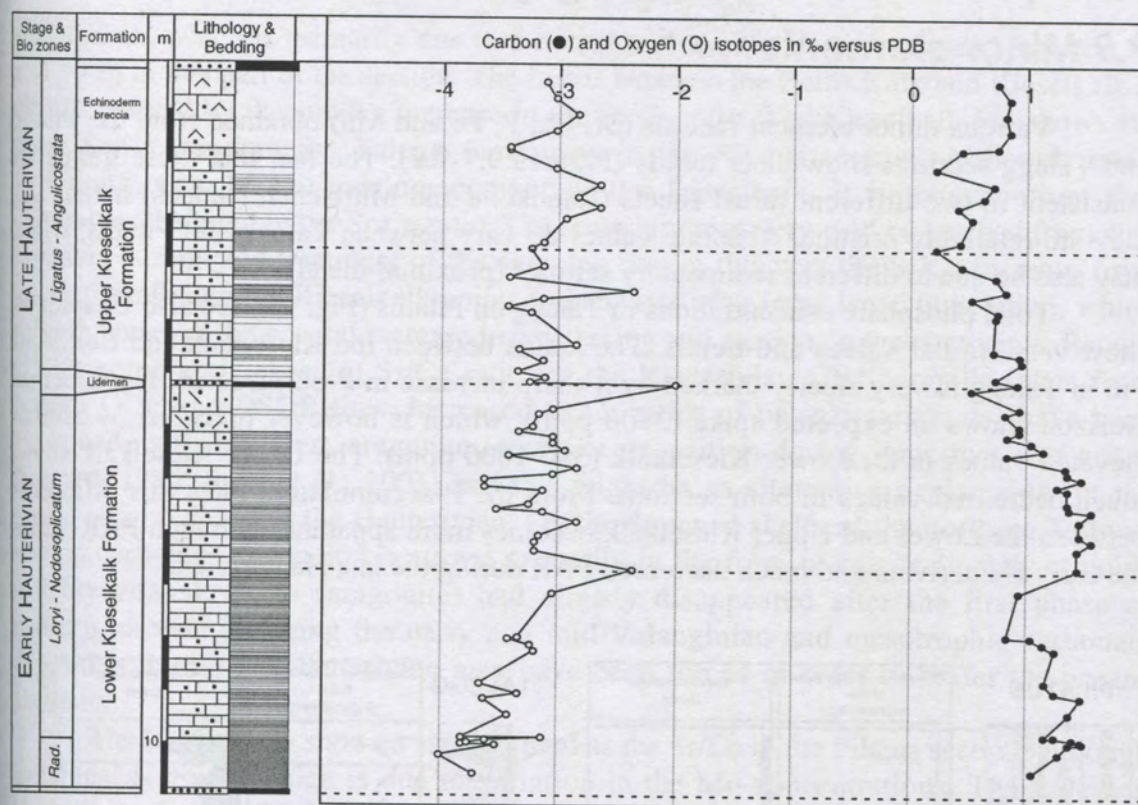


Figure 9.6 – Carbon and oxygen isotope records from Pilatus section, the type section for the Helvetic Kieselkalk.

Sample	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	T°C
<i>Bauen</i>			
BA 3.2	0.60	-1.12	15.7
BA 3.4.0	0.48	-0.86	14.6
BA 3.4.1	0.25	-0.97	15.0
BA 3.4.2	-0.05	-1.37	16.7
BA 3.8	0.25	-1.35	16.6
<i>Pilatus</i>			
PIL 3	-0.18	-0.91	14.8
PIL 4	0.19	-0.42	12.9
PIL 5A	0.24	-0.84	14.5
PIL 5B	-0.23	-0.65	13.8
<i>Wildalpel</i>			
WI 1	0.21	-1.86	18.8
WI 2	0.41	-0.39	12.7
WI 3	0.43	-1.27	16.3
WI 4	0.06	-1.14	15.8

Table 2. Carbon and oxygen isotope data from belemnites

9.9 Minor elements

Various minor element records (Sr, Ca, P, Fe and Mn) obtained from the Pilatus and Talegg sections show clear trends (Figures 9.7-9.9). The fact that these trends are consistent in two different thrust sheets (Randkette and Murtschen Nappes) means that they are relatively pristine. Absolute values do vary between Talegg and Pilatus, which may also be due to different sedimentary settings (proximal-distal).

Total phosphate concentrations in Talegg en Pilatus (Fig. 9.9, see also Chapter 8) show very similar values and trends. The hiatus between the Kieselkalk and Betliskalk Fm in Talegg is very clearly marked by a sharp increase in P-burial rates. The Lidernen Horizon shows an expected spike (3900 ppm), which is however preceded by already elevated values in the Lower Kieselkalk (500-1000 ppm). The Upper Kieselkalk shows much decreased values in both sections. From the P-accumulation rates this difference between the Lower and Upper Kieselkalk becomes more apparent, with high PAR during the early Hauterivian and much decreased PAR during the late Hauterivian.

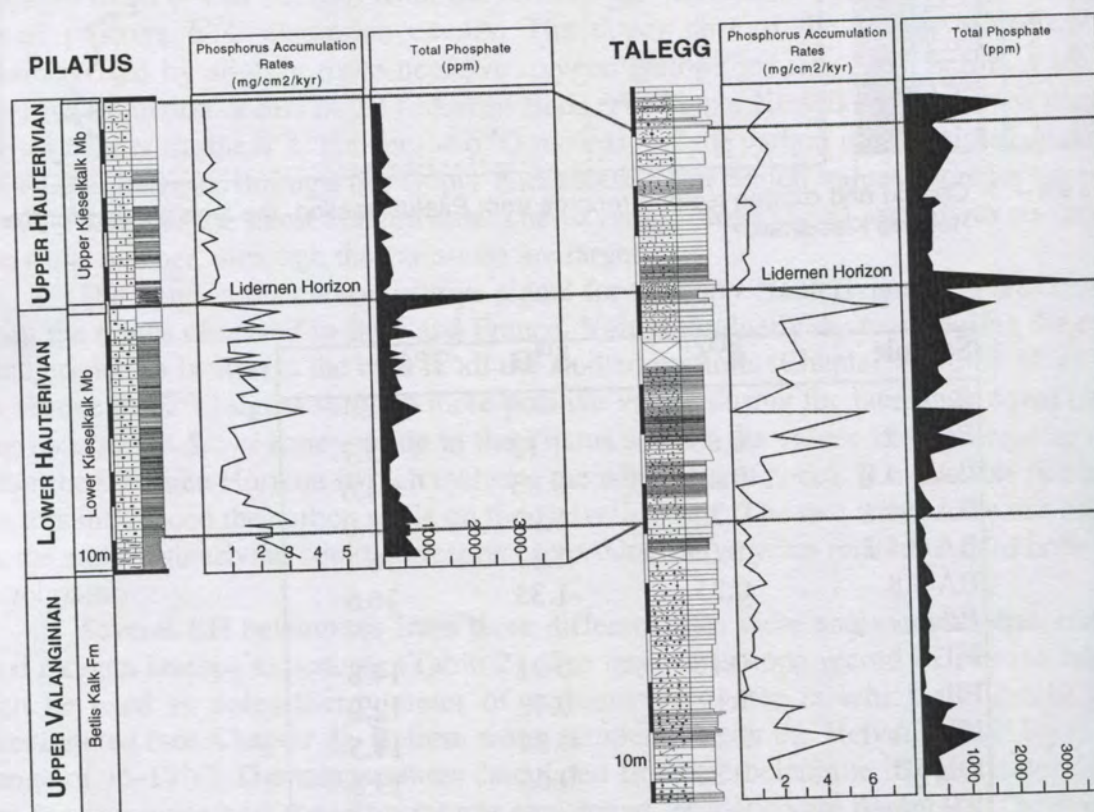


Figure 9.7 – Correlation of Talegg and Pilatus sections by means of total PO_4 concentrations and P-accumulations rates.

The most pronounced trend in both sections is observed in the Sr/Ca ratio which increases up to the base of the lower Echinoderm breccia and decreases rapidly up to the Altmann Horizon in the Pilatus section. The Talegg sections shows low ratios for the

Betlis Kalk, which is primarily due to the very high carbonate percentages (between 80 and 90%) in this part of the section. The hiatus between the Betlis Kalk and Kieselkalk is clearly marked by the sudden increase in the Sr/Ca ratio. The Kieselkalk Fm shows the same Sr/Ca trend in the Talegg section as in the Pilatus section. Although small variations occur in the calcium content of the Kieselkalk, it is the strontium that determines the trend in the Sr/Ca ratio. The strontium may very well be leached from clay minerals during acid treatment of the samples, and in this way the Sr/Ca increase from the Betliskalk into the Kieselkalk points to increased clay input (smectites, illite), which reflects however the general increase in weathering and erosion on the continents. Renard (1986) noted an increase in Sr/Ca ratio for the Hauterivian after compiling data from several ODP and DSDP sites. Increased Sr/Ca ratios of pelagic carbonates have been explained as a shift from aragonite to calcite deposition during important reef crises (Renard, 1986; Stoll et al., 2001) and this might be an alternative explanation for the trends observed during the Hauterivian. On the drowned shelves of the northern Tethyan margin carbonate deposition occurred primarily in the form of calcite (mostly crinoids and bryozoans). Reefs (aragonite) had already disappeared after the first phase of platform drowning during the early and mid-Valanginian and mesotrophic carbonate deposition during the Hauterivian may have been forced in order to buffer the oceans alkalinity.

The Mn/Fe ratio shows a similar trend as the Sr/Ca in the Pilatus section, although the signal is noisy, which is due to variation in the Mn-concentrations. The Lidernen Horizon shows very high Fe-concentrations (18000 ppm), which can be ascribed to the presence of glauconite. The Upper Kieselkalk shows higher Fe-concentrations than the Lower Kieselkalk Mb, which explains why the Mn/Fe ratio decreases for the Upper Kieselkalk Mb.

Fe and Mn are erosional products. The continental flux consists 99% of particulate matter (Bender, 1977; Piper, 1994). The oceanic cycles of Fe and Mn are highly dependent on the redox state of ocean water (and thus oxygen levels). Under anoxic conditions Mn is mainly present in dissolved form as Mn^{2+} or Mn^{4+} , the latter forms $MnOOH$ during oxidation. Iron forms iron sulfide under anoxic conditions and is fixed in the sediment, while under oxic conditions Fe is precipitated as $FeOOH$. Iron is more rapidly oxidized as Mn and therefore more quickly precipitated. In this way Mn and Fe are fractionated in a distal direction, since Mn is likely to be transported further offshore (Force, 1988). The higher Fe-contents of the Upper Kieselkalk probably indicates slightly shallower conditions during the late Hauterivian, while lowered Mn-concentrations may also point to relatively lower oxygen levels.

High P-accumulation rates in the Lower Kieselkalk reflect increased continental influx, probably well oxygenated bottom waters and high carbonate sedimentation rates. This is further corroborated by the high Mn/Fe ratio, which indicates high oxygen levels in bottom water and precipitation of Mn- and $FeOOH$. Oxygen levels may have increased as a result of a second order sea level rise that led to the influx of cold Boreal water. Upwelling of this oxygen (and probably nutrient rich) water may have stimulated productivity and downward transport PO_4 . At the sediment water interface most of the organic matter got re-oxidized and the phosphate was scavenged by iron and manganese hydroxides.

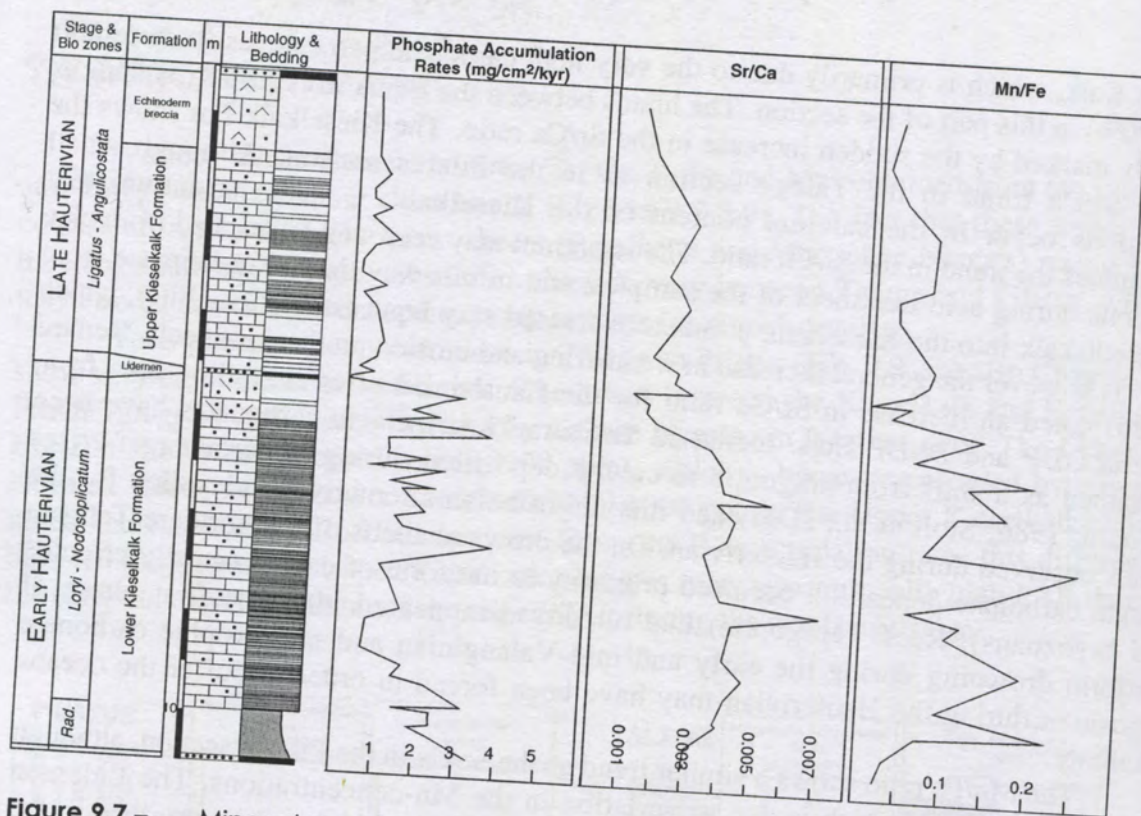


Figure 9.7 – Minor element ratios for Pilatus section.

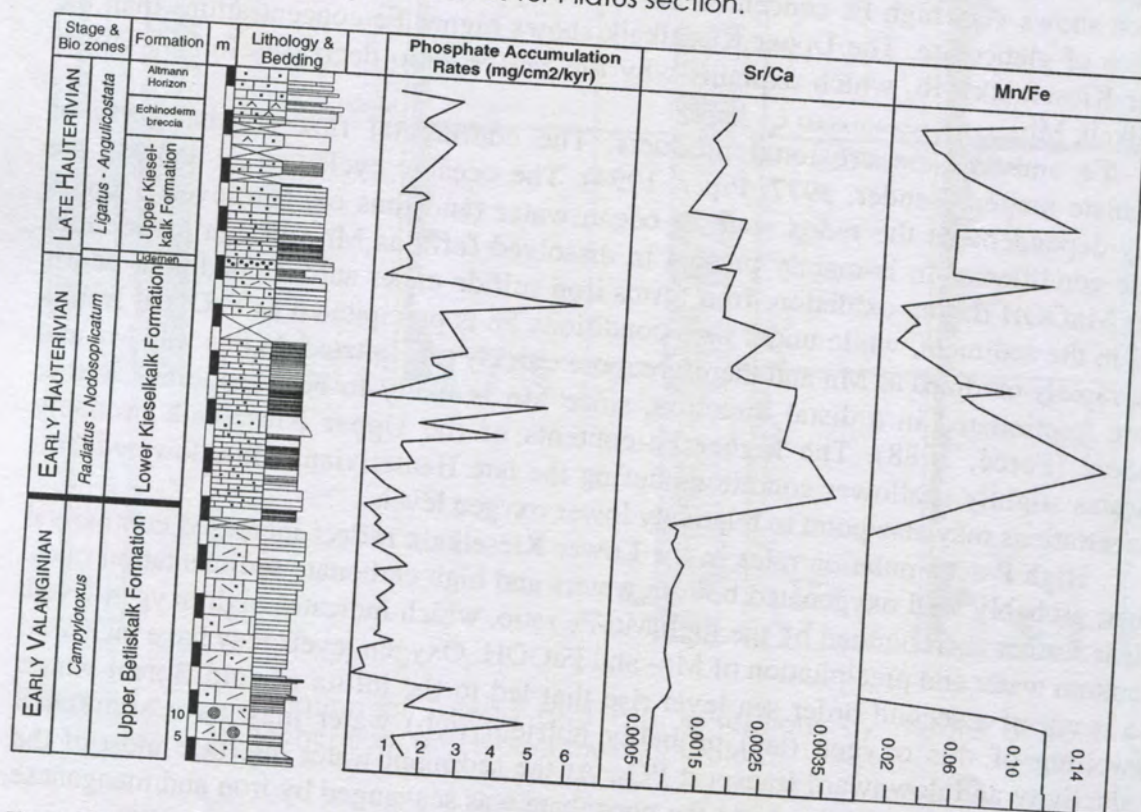


Figure 9.8 – Minor element ratios for Talegg section. Note clear hiatus at the base of the Kieselkalk.

Lower PAR during the late Hauterivian indicate decreased continental influx, decreased oxygen levels and reduced carbonate sedimentation rates. Reduced carbonate sedimentation was a result of sea level fall during most of the late Hauterivian, which also explains decreased oxygen levels as connections with the Boreal realm progressively closed down and the influx of oxygen rich waters declined. Sea level fall and slightly more anoxic conditions are probably also reflected in the decreased Mn/Fe ratio, with higher Fe concentrations in more shallow sediments and lower Mn under more anoxic conditions.

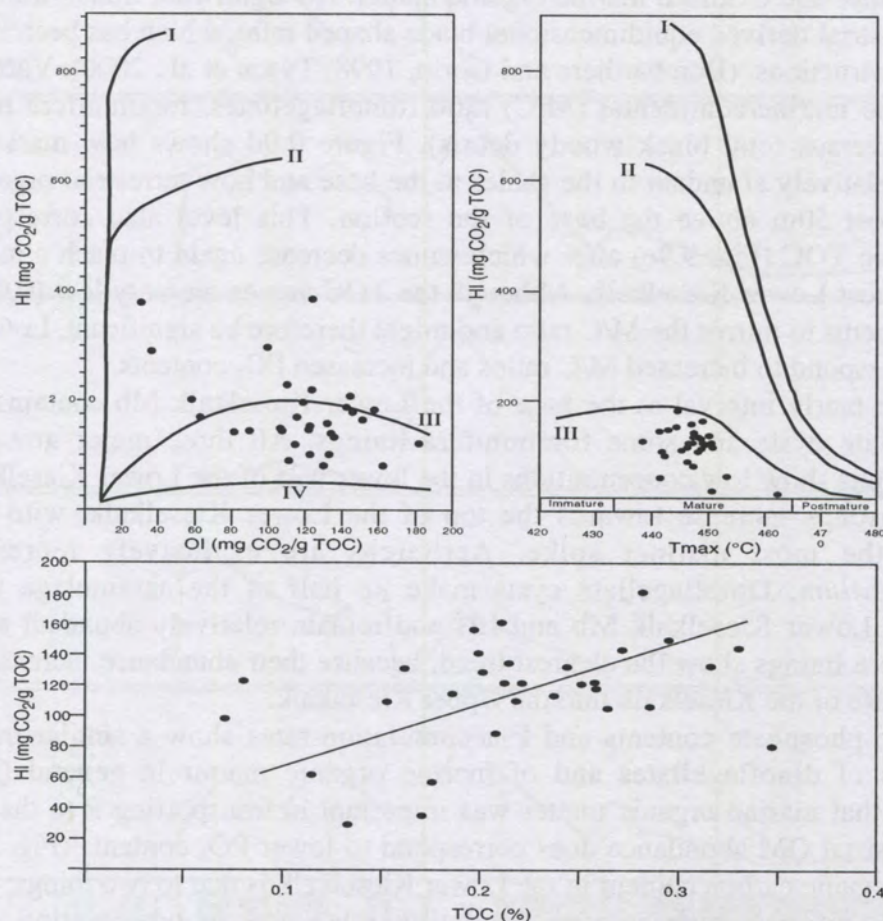


Figure 9.9 – RockEval 6 data for Pilatus section. Decreasing TOC with decreasing HI points to degradation of marine OM.

9.10 Organic matter

Several sections were investigated for their organic matter (OM) contents, but only the Pilatus section (Randkette) produced recognizable OM. Samples from Bauen, Wildgunten Alp, Axen road section (Plate 9.13.5) and Wildalpel produced completely degraded black OM and even oil. The latter points to the extensive burial diagenesis in the more overburdened deeper thrust sheets (e.g. Axen Nappe). Rockeval analyses show that the organic matter in the Pilatus section is mature and suffered from temperatures

between 440° and 450°C (Fig. 9.8b). Preservation of marine phytoplankton remains is in some beds quite poor. The presence of predominantly black OM, which is considered to be the most resistant fraction derived from terrestrial woody debris, can also be related to specific depositional conditions, such as high oxygen levels in ocean water, increased transport distance or decreased marine production.

Palynofacies analyses of the Pilatus section show a mixed terrestrial and marine organic matter source. This is also indicated by the relatively low hydrogen indices characteristic of type-III organic matter (Fig. 9.8a), which includes both terrestrial organic matter and oxidized marine organic matter. No significant trends were observed in the terrestrial derived equidimensional/blade shaped ratio, which has been used in sea level reconstructions (Bombardiere and Gorin, 1998; Tyson et al., 2000). Variation does occur in the marine/continental (M/C) ratio (dinoflagellates, foraminifera linings and acritarchs versus total black woody debris). Figure 9.9d shows how marine organic matter is relatively abundant in the shales at the base and how terrestrial organic matter peaks almost 50m above the base of the section. This level also corresponds to a maximum in TOC (Fig. 9.9e) after which values decrease again to reach a minimum in the uppermost Lower Kieselkalk. Although the TOC values are very low (0.05-0.35%), the trend seems to mirror the M/C ratio and might therefore be significant. Lowered TOC values correspond to increased M/C ratios and increased PO₄ contents.

The marly interval at the base of the Lower Kieselkalk Mb contains abundant dinoflagellate cysts and some foraminifera linings. All three major groups marine palynomorphs show low concentrations in the lower part of the Lower Kieselkalk, while all three groups increase towards the top of the Lower Kieselkalk, with acritarchs showing the most distinct spike. Acritarchs are exclusively represented by *Michrystidium*. Dinoflagellate cysts make up half of the assemblage within the uppermost Lower Kieselkalk Mb and LH and remain relatively abundant afterwards. Foraminifera linings show the clearest trend, because their abundance increases steadily from the base of the Kieselkalk into the Upper Kieselkalk.

The phosphate contents and P-accumulation rates show a similar trend as the abundance of dinoflagellates and of marine organic matter in general (Fig. 9.10) indicating that marine organic matter was important in transporting P to the sediment. High terrestrial OM abundance does correspond to lower PO₄ contents (Fig. 9.10). The low total organic carbon content in the Lower Kieselkalk is due to two things: 1) dilution as a result of high carbonate accumulation rates and 2) preservation. However, preservation does not seem to be related to burial diagenesis, but seems to be primarily syngedimentary. Preservation of dinoflagellates and foraminifera linings is better for the Upper Kieselkalk, which has a similar lithology and burial history as the Lower Kieselkalk. Oxygen levels in bottom waters as well as microbial activity within the sediment are thought to have had a large influence. High oxygen levels in bottom waters during deposition of the Lower Kieselkalk allowed bacteria to actively degrade marine organic matter and store P as CFA in the sediment, which is indicated by the high P-accumulation rates and often highly degraded marine organic matter. During the late Hauterivian oxygen levels dropped and marine organic matter was better preserved, however less CFA deposited.

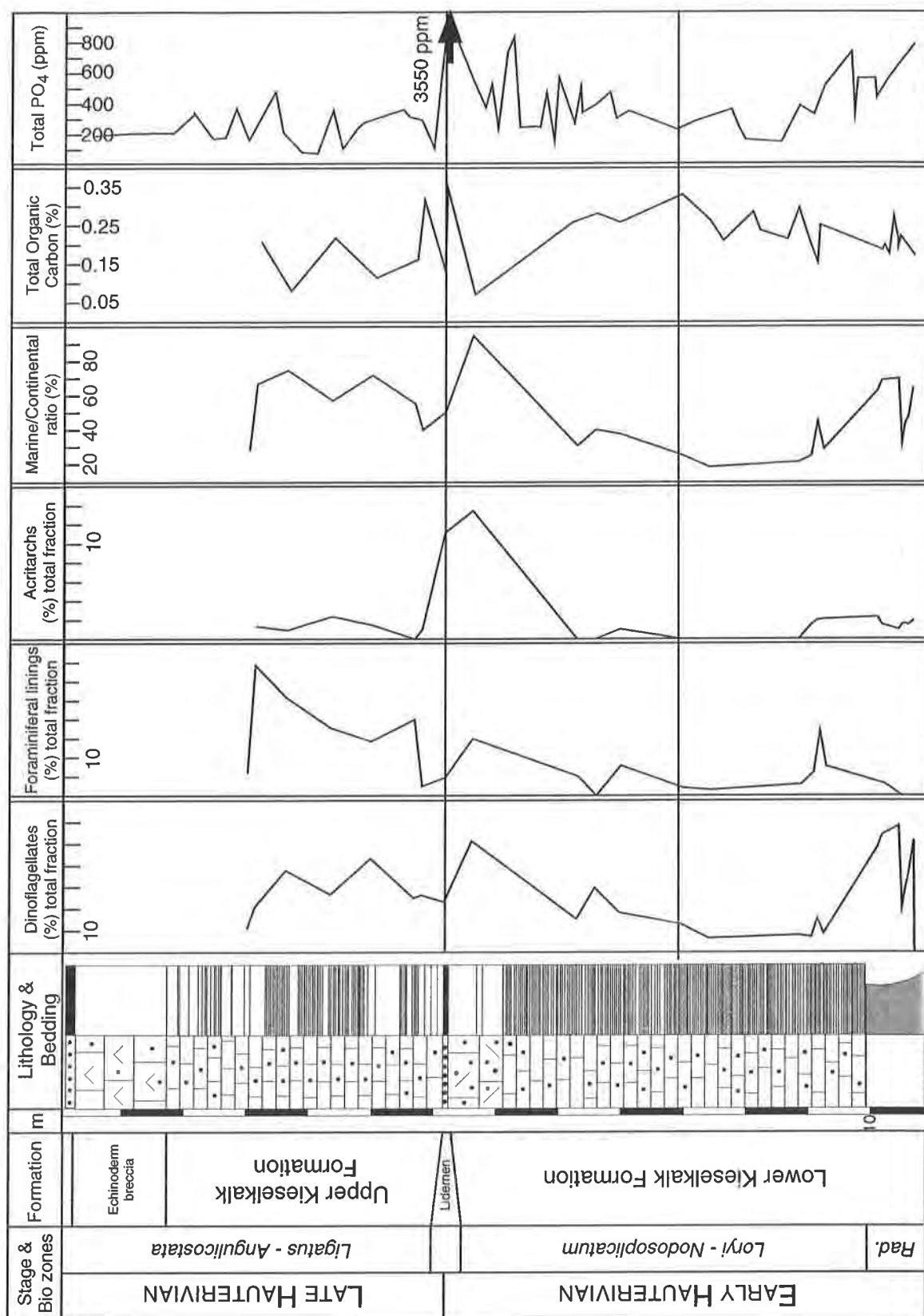


Figure 9.10 – Comparing Palynofacies with PO₄ and TOC

Foraminifera linings remain enigmatic as paleo-environmental indicators. They have been related to anoxic conditions associated with upwelling conditions or simply to shallower marine conditions (Melia, 1984; Powell et al., 1992). The Upper Kieselkalk was probably deposited at shallower depth than the Lower Kieselkalk based on the clearly more regressive nature of the upper part of the Upper Kieselkalk (echinodermal breccia). So the gradual increase in foraminifera linings from the base of the Kieselkalk probably records this regressive trend during the late Hauterivian (*Ligatus-Balearis* zones). It is, however, not excluded that bottom waters were more anoxic during the late Hauterivian.

9.11 Phosphogenesis

The largest sink of phosphorus is that associated with marine organic matter (>40%, (Froelich, 1982). Marine carbonates take up another 40%, mainly within foraminifera and coccoliths, although this sink is also controlled by Fe and Mn-(oxy)hydroxides that retain phosphorus as coatings on carbonate particles. Minor sinks comprise metalliferous sediments close to spreading ridges, fish debris and phosphorites. Recent studies have shown that disseminated CFA may represent a much larger sink than concentrated phosphorites and that large amounts of iron-bound phosphate are locked up in high sedimentation rate siliciclastic deposits, such as deltas (Ruttenberg and Berner, 1993).

The *classical model* for the formation of phosphorites along continental margins is the upwelling model. In this model phosphorus is transferred into the sediment as a component of particulate organic matter deposited in organic carbon rich shales and cherts, commonly associated with upwelling conditions. Early diagenetic in situ precipitation of carbonate fluor apatite (CFA) may occur as pore waters become enriched in inorganic dissolved phosphorus when the organic matter is (microbially) degraded (Glenn et al., 1994). On the Peru-Chile margin strong bottom currents probably help, through winnowing of fines, to keep nodules in the upper 20cm of the sediment column, which is the main locus of CFA deposition. Glenn et al. (1988) showed that a highly porous, organic carbon rich gelatinous mud acts as a precursor for CFA precipitation.

However, not all modern phosphorites along continental margins occur beneath upwelling zones, like on the Peru-Chile margin. Phosphorites along the eastern shelf of Australia are less controlled by seasonal upwelling. In that particular setting low sedimentation rates, bacterial degradation of sparse organic matter and iron-pumping are much more important factors. There are also similarities between the Peru-Chile and East Australian margin (Glenn et al., 1994): 1) CFA precipitation appears to be linked to the sediment-water interface or occurs at shallow burial depths (centimeters) within the sediment. 2) Glauconite is commonly present in both cases. 3) Current activity is in both cases important for reworking and maintaining CFA deposition at or near the water-sediment interface.

So which of these cases applies to the Lidernen Horizon? Kuhn (1997) suggested that organic matter was not controlling deposition of the late Valanginian-early Hauterivian Gemsmättli Horizon, because he found the amount of TOC in general to be

very low. According to Kuhn iron-pumping was the main mechanism controlling phosphogenesis. In Kuhn's model iron and phosphorus influx from the continent were increased during a phase of re-inforced greenhouse conditions. The iron was transported into shallow marine settings, such as the Jura Platform, where Fe^{3+} -minerals were oxidized and formed iron-bound phosphate. These iron-hydroxide particles were then further transported into deeper settings and once in the oxygen minimum zone the iron got reduced and the phosphate was liberated. This may have occurred within the sediment or at the sediment-water interface. In the absence of laminated organic matter rich shales it is thought that CFA deposition took place at the upper and lower boundary of the oxygen minimum zone (Kuhn, 1997).

TOC values are also very low in the Lidernen Beds. However, marine organic matter is positively correlated with increased phosphorus burial within the upper part of the Lower Kieselkalk. Although TOC is relatively low, the Lidernen Beds (and also the Kieselkalk) are relatively rich in pyrite. Pyrite was formed under dysoxic conditions in the sediment in abundance of organic matter. The presence of *Chondrites* burrows in the phosphatized ammonites is further indication for dysoxic conditions. It is therefore possible that TOC contents were initially high, but that later on large amounts of organic matter were either pyritized or degraded by bacteria. This may also point to initially more anoxic conditions.

The spiculitic phosphatized mudstone that fills in sponges, ammonites and echinoderms (Chalberen) may be a remnant of the gelatinous muds similar to the one that act as a precursor sediment on the Peru-Chile margin. These micrites are relatively rich in iron as the pinkish weathered colour of some of the non-phosphatized clasts proves (Pilatus, Wildalpeli; Plate 9.9).

The Kieselkalk Fm was very likely controlled by the activity of upwelling bottom water (see Chapter 8). This mechanism might very well explain the Lidernen Horizon as well. Upwelling may have increased productivity and the export of carbon. The initial phase of drowning was probably associated with expansion of an oxygen minimum zone (OMZ) that covered a wide area of the Helvetic Shelf. Migration of such an oxygen minimum zone over the shelf during a transgression could explain the different redox states the Lidernen Horizon went through and the diachronous nature of many phosphoritic horizons (Kuhn, 1997). Initially low oxygen levels, as a result of high surface water productivity, led to the deposition of organic matter rich mudstone. As the locus of upwelling moved further onshore, CFA precipitation took place under dysoxic to oxic conditions. Pyrite may have formed slightly later. When fully oxic conditions had returned, hardground formation and bioturbation intensified. *Thallasinoides* producing organisms feasted on the phosphatic and organic matter rich muds and excreted abundant faecal pellets. These pellets were glauconitized as the sediment was again within or maybe at the lower boundary of the OMZ and within reach of relatively colder water. Flooding of dysoxic waters onto the shallow carbonate platforms, like the Jura, may have provided the iron necessary for the glauconitization process.

9.12 Sea level changes

As suggested above sea level changes probably played an important role during deposition of the Lidernen Horizon. The late *Nodosoplicatum* zone is characterised by

widespread regression. This regressive event can be followed into Germany (Mutterlose et al., 1998) and onto the Russian Platform (Sahagian et al., 1996). It is followed by a rapid transgressive event during the early *Sayni* zone, leading to condensation and marl deposition along the northern margin of the Tethys (e.g. Vocontian Basin). In the Lidernen Horizon this transgression is seen in the deposition of the spiculitic mudstones that filled the sponges and ammonites.

Sea level change influenced both circulation and erosion during the Hauterivian. As sea level fell during the late early Hauterivian, the influx of cold Boreal water may have ceased and exchange of watermasses and fauna stopped (e.g. ammonites see (Hoedemaeker, 1995); and from nannofossils (Crux et al., 1989). Opening up of connections during the *Sayni* zone gave rise to a new pulse of cold water inflow, which may have been one of the reasons why carbonate producers got drowned. The remainder of the late Hauterivian is generally considered to be more regressive.

9.13 Condensation and reworking

Reworking is one of the dominant processes involved in phosphorite formation. Schaub (1948) summarized two opposing views as to what lead to the mixing of ammonite faunas in many phosphoritic horizons of the Helvetic Alps: 1) A model invoked by Arnold Heim considers much reduced sedimentation rates during a long time span. Ammonites are deposited on top of each other and breaking up of larger specimens results in a muddy matrix with small bioclastic fragments. Fossils are not transported but exposed numerous times. 2) A second model sees reworking as the main cause for condensation and concentration. Fossils are first phosphatized and can withstand constant reworking and winnowing of surrounding matrix by strong current activity. Transportation of bioclasts and nodules is also an important aspect of this type of condensation.

For the Lidernen Horizon it is very likely a combination of the two. Reworking is evidenced by the infilling of ammonites, which is clearly different from the surrounding matrix. Some ammonites from Lidernen Plänggeli have different infillings in different chambers, indicating burial and partial infilling, exposure and renewed infilling during later phases. Schaub (1936) found at least 8 different types of sediment in Albian ammonites from different (bio)zones. That some of the ammonites but also belemnites were occasionally exposed at the seafloor can also be inferred from corrosion and dissolution of belemnites, the extensive burrowing in them and the encrustation by serpulids.

Phosphatization and phosphogenesis occurred before reworking, because also phosphatized lithoclasts of the same sediment type as the infilling of ammonites are present. Reworking is also evident from the number of fragmented and complete ammonites (Fig. 9.12). From macroscopic and microscopic observations it can be seen that most ammonites got broken during deposition and are only present as small pieces. However, the number of non-fragmented ammonites increases upwards. More complete ammonites can be found belonging to the *Ligatus* zone when drowning probably came to an end. This is clearly the result of reworking of older phases of deposition and the fragmentation of ammonites belonging to these older phases of deposition and condensation (*Nodosoplicatum* and *Sayni* zones). Kuhn (1997) did not find such a

relationship for the Gemmättli Horizon. This could indicate that different processes led to the formation of the Lidernen and Gemsmättli Horizons.

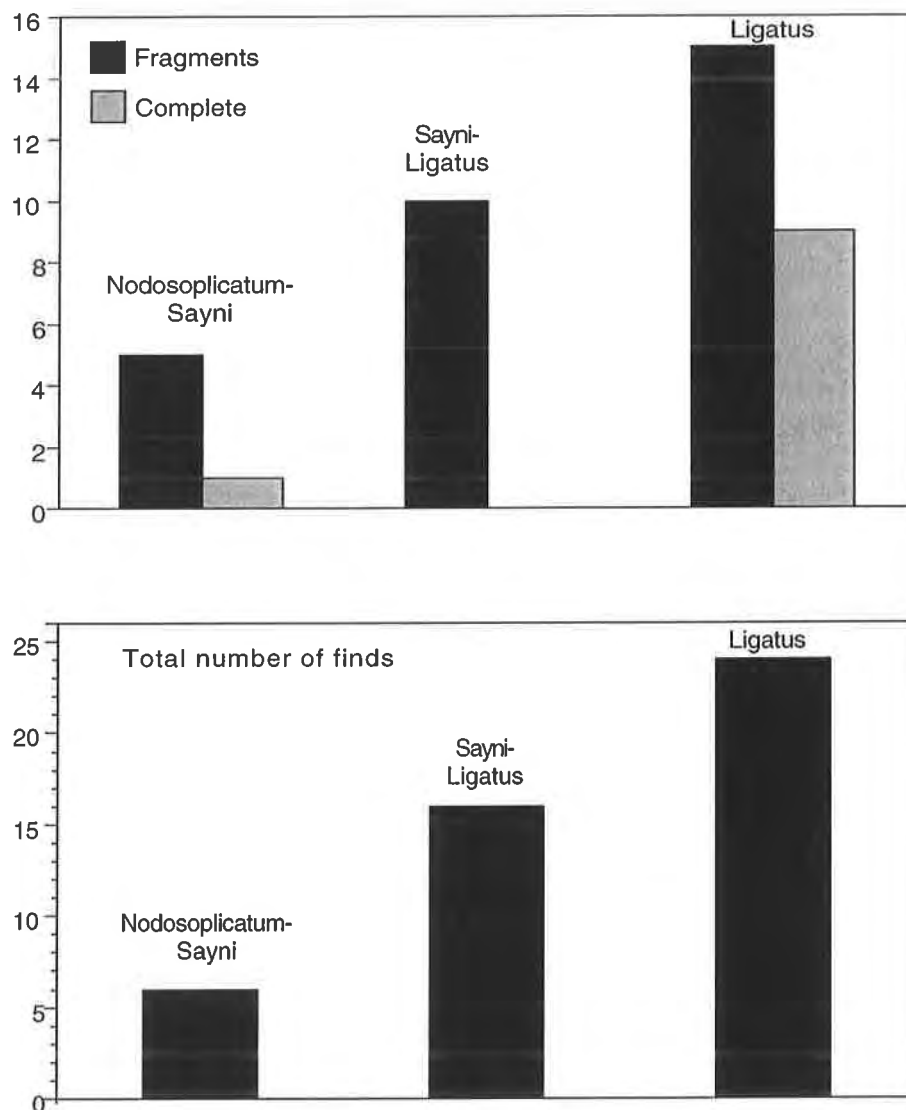


Figure 9.11 – Diagrams showing reworking of ammonites and increasingly fragmentation.

Another important clue for reworking is the presence of different types of phosphatized lithoclasts in the hemipelagic setting (Bauen, Wildalpel, Pilatus and Lidernen Plänggeli). Most of these clasts were derived from the underlying uppermost Lower Kieselkalk Mb and transported into deeper settings possibly by mass-flow processes. LeMaire (1995) found evidence for at least three mass-flow events within the Lidernen Horizon at Bauen, separated by phosphatic crusts.

Sudden Burial (Föllmi, 1996) might have occurred, but was not a dominant process in the preservation of fragile organisms, since the fossils were already phosphatized and reworked as such. Mass-transport was probably an important mechanism though, in concentrating phosphatic clasts in deeper settings, such as in

Bauen and Wildalpel (Plate 9.12). The chaotic appearance of some LH beds with belemnites and other fossils sometimes in vertical position to the substrate in between phosphatic nodules could be further evidence for transport along the shelf. Mass flows were related to extensive bioturbation that produced instable substrates, prone to transport. The breccia of Silberenalp (Plate 9.12) may have formed in such a way.

9.14 Conclusions – Depositional model

After a cold water pulse during the earliest Hauterivian *Radiatus* zone, cold water inflow was possibly less vigorous during the *Loryi* and *Nodosoplicatum* zone, allowing crinoids, bryozoans and sponges to produce at high pace in slightly warmer waters and under mestrophic conditions. Oxygen-levels remained high though in bottom waters. High fertility of surface waters is indicated by high Fe, Mn and P contents in early Hauterivian carbonates.

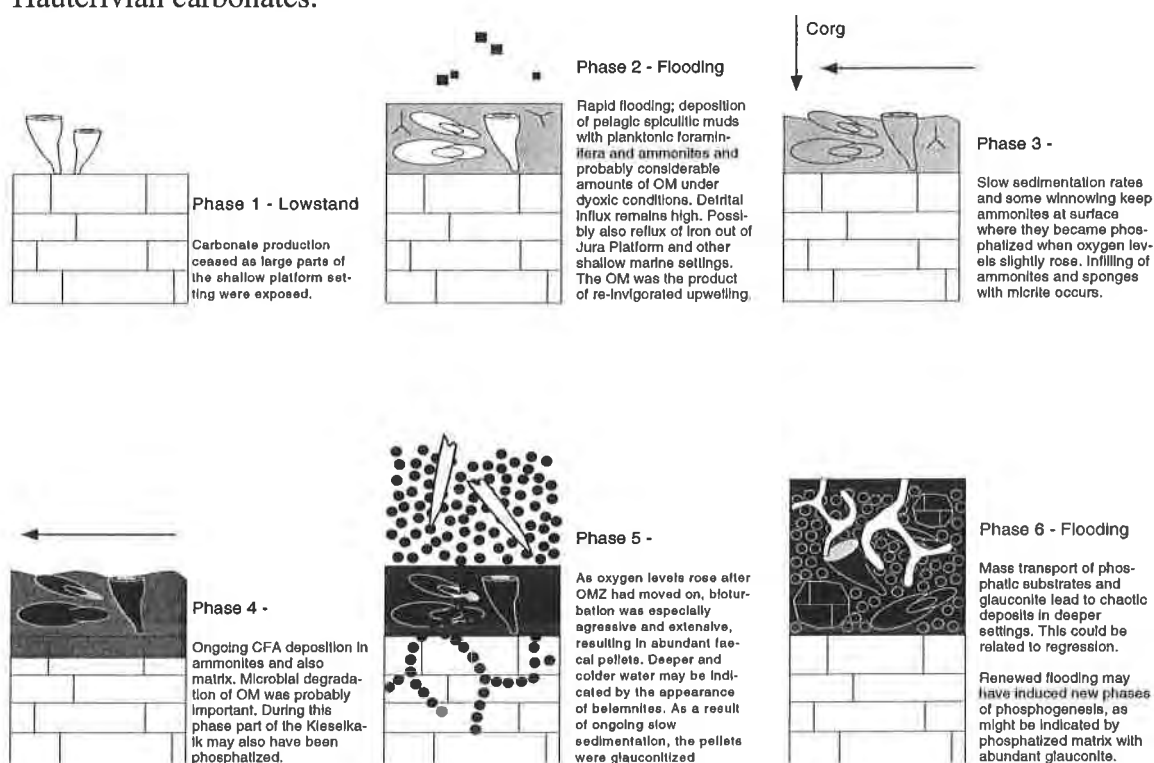


Figure 9.12 – Sequence of events leading up to formation of Lidernen Horizon as it can be observed today in the Helvetic Alps.

It is concluded that eustatic sea level changes in conjunction with elevated detrital input were responsible for deposition of the Lidernen Horizon and drowning on the Helvetic Shelf. A pronounced sea level fall during the late *Nodosoplicatum* zone (Arnaud-Vanneau et al., 1982; Hardenbol et al., 1998), also reflected in the shallowing-up Lower Kieselkalk, led to exposure of shallow carbonate platforms (like the Jura Platform, see Chapter 6) resulting in much decreased carbonate production and export on the Helvetic Shelf.

A rapid sea level rise during the early *Sayni* zone (early late Hauterivian) led to a renewed pulse of cold water inflow from the Boreal and re-invigorated upwelling. Biota,

already weakened by regression, were now suffocated by high nutrient levels and suffered from hypothermia. High nutrient levels may have been brought about by leaching of previously extensively oxidized Fe-rich shallow marine carbonates. High nutrient input and upwelling induced higher organic carbon export and the establishment of an OMZ on the shelf. Dysoxic conditions are evident from *Chondrites* burrows and pyrite nodules in certain sections (Lidernen Plänggeli, Sulzberg). Deeper settings contain only black degraded terrestrial organic matter, indicating oxygen levels here were normal. These sections, like Wildalpel, show therefore also no or less phosphatization.

Pelagic sedimentation during the onset of drowning is indicated by the deposition of spiculitic micrites, that entombed fragile organisms such as sponges and filled in ammonites with planktonic foraminifera. This precursor may still be preserved at Pilatus. Ammonites at the sediment-water interface acted as preferential sites for phosphatization. Sedimentation rates were low in such a setting.

As sea level rose further, upwelling shifted towards shallower settings and the oxygen minimum zone spread further onto the shelf, inducing phosphogenesis in shallower settings. Since all the ammonites come from one site, diachronicity of the Lidernen Horizon can not be proven. As oxygen levels rose again when a site moved out of the OMZ, intensive bioturbation occurred. Abundant faecal pellets were accumulated that were glauconitized at the lower boundary of the OMZ in abundance of terrestrial iron. Glauconite may be indicative for deeper water conditions, which is in accordance with the appearance of abundant belemnites within the glauconitic facies. Reworking occurred as sea level began to descend. Mass-transport of phosphatic lithoclasts and fossil debris occurred as much of the sediment was dug out. Fluctuating sea level, added by high continental iron influx can thus explain formation of the Lidernen Horizon.

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PLATE 1 - Lidernen Horizon Ammonites

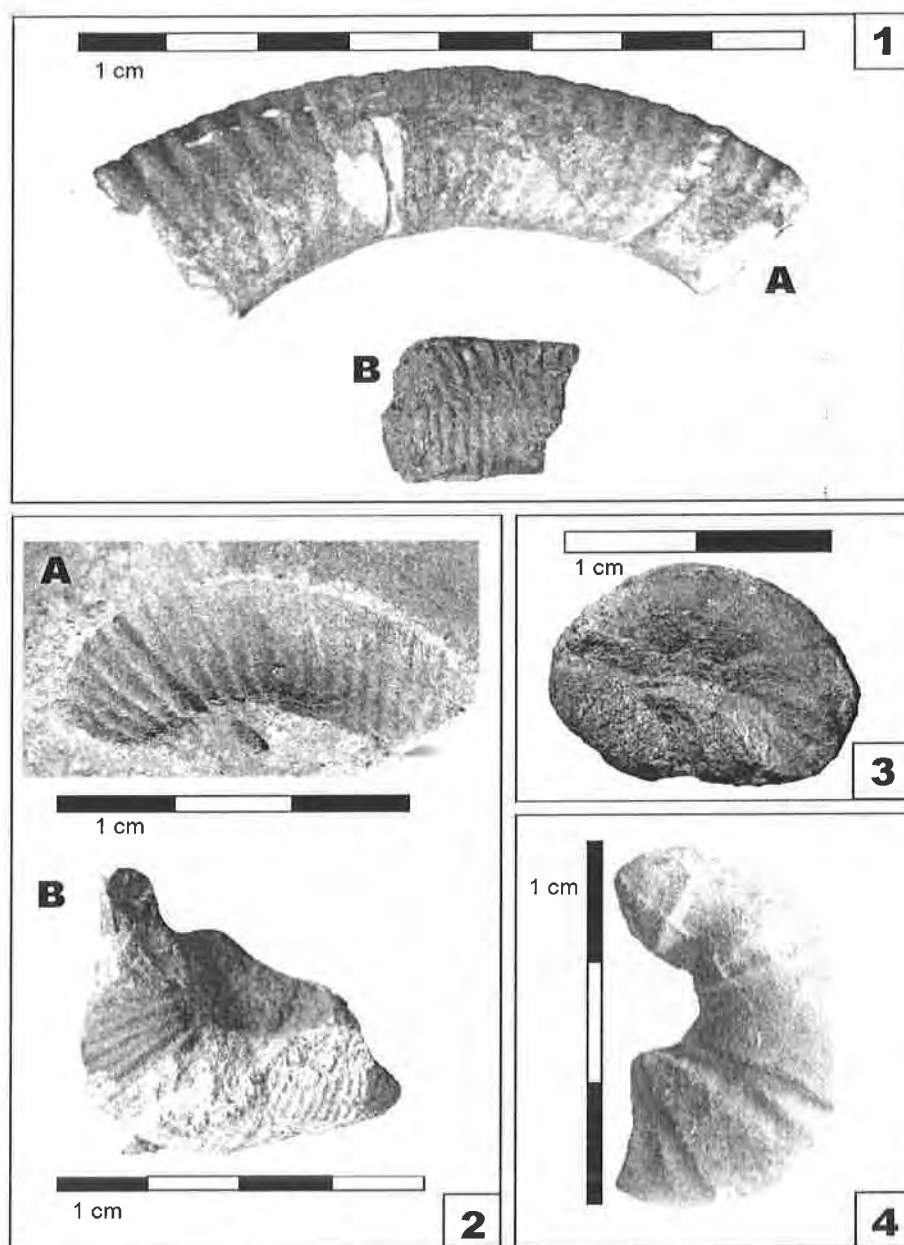


Figure 1a. *Pseudomoutoniceras annulare* (d'ORBIGNY). Terre Masse section, Vocontian Basin, France, specimen for comparison. **Figure 1b.** *Pseudomoutoniceras annulare* (d'ORBIGNY) Lidernen Horizon, Lidernen Plänggeli, central Switzerland. **Figure 2a-2b.** *Acrioceras* (*Paraspinoceras*) sp. gr. *pulcherinum* (d'ORBIGNY) Lidernen Horizon, Lidernen Plänggeli, central Switzerland. **Figure 3.** *Abrytusites* gr. *juliani-thieuloyi* Lidernen Horizon, Lidernen Plänggeli, central Switzerland. **Figure 4.** *Abrytusites loryi* (PAQUIER, 1900) Lidernen Horizon, Lidernen Plänggeli, central Switzerland.

PLATE 9.2 - Lidernen Horizon Ammonites

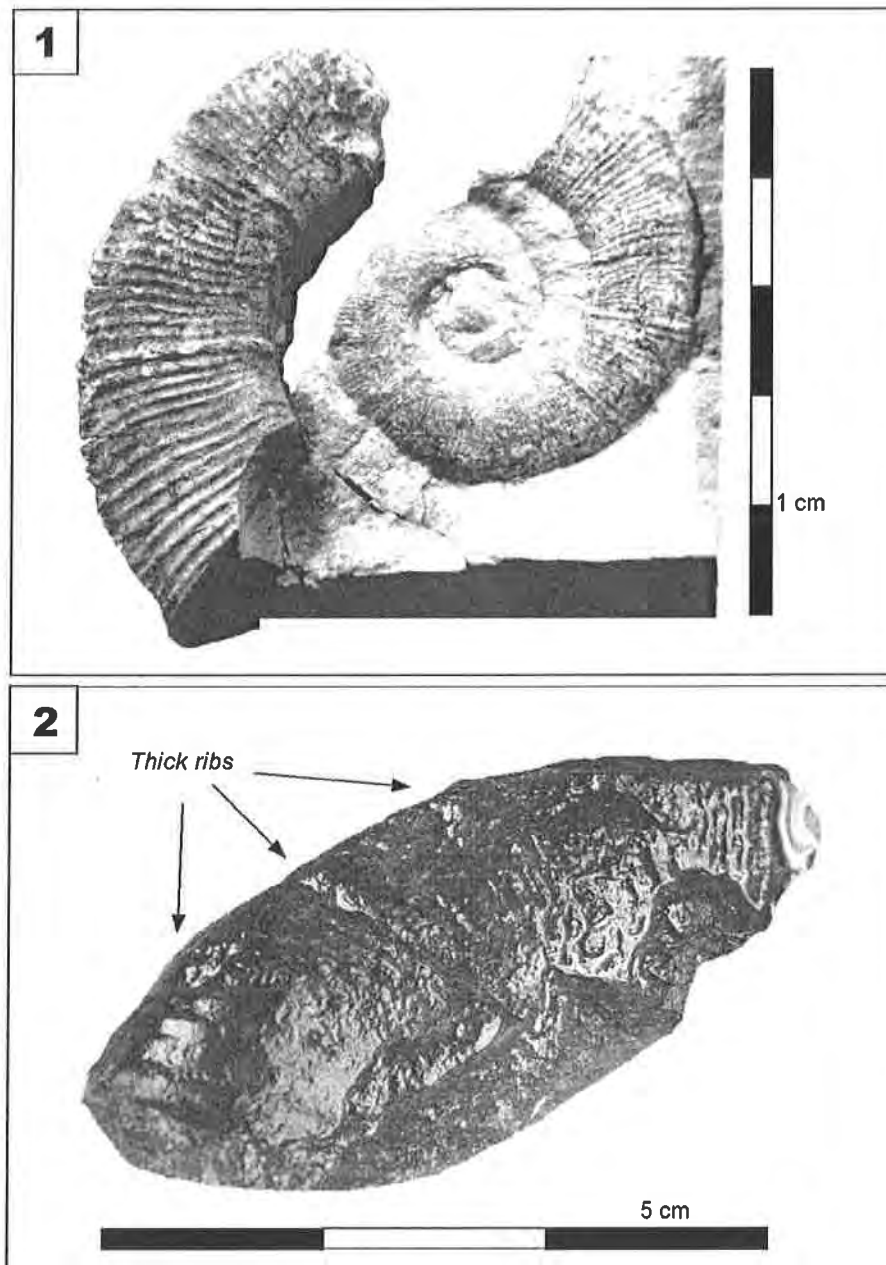


Figure 1. *Crioceratites* sp. juv. cf. *matsumotoi* (SARKAR, 1955). Terre Masse section, Vocontian Basin, France, specimen for comparison. The outer whorl breaks off quite easily after the animal has died and is often found separately, like in Fig. 2. **Figure 2.** *Crioceratites* cf. *duvali* or *villersianum* Lidernen Horizon, Lidernen Plänggeli, central Switzerland. Note constrictions or thick ribs, which are very characteristic for genus *Crioceratites*.

PLATE 9.3 - Lidernen Horizon Ammonites

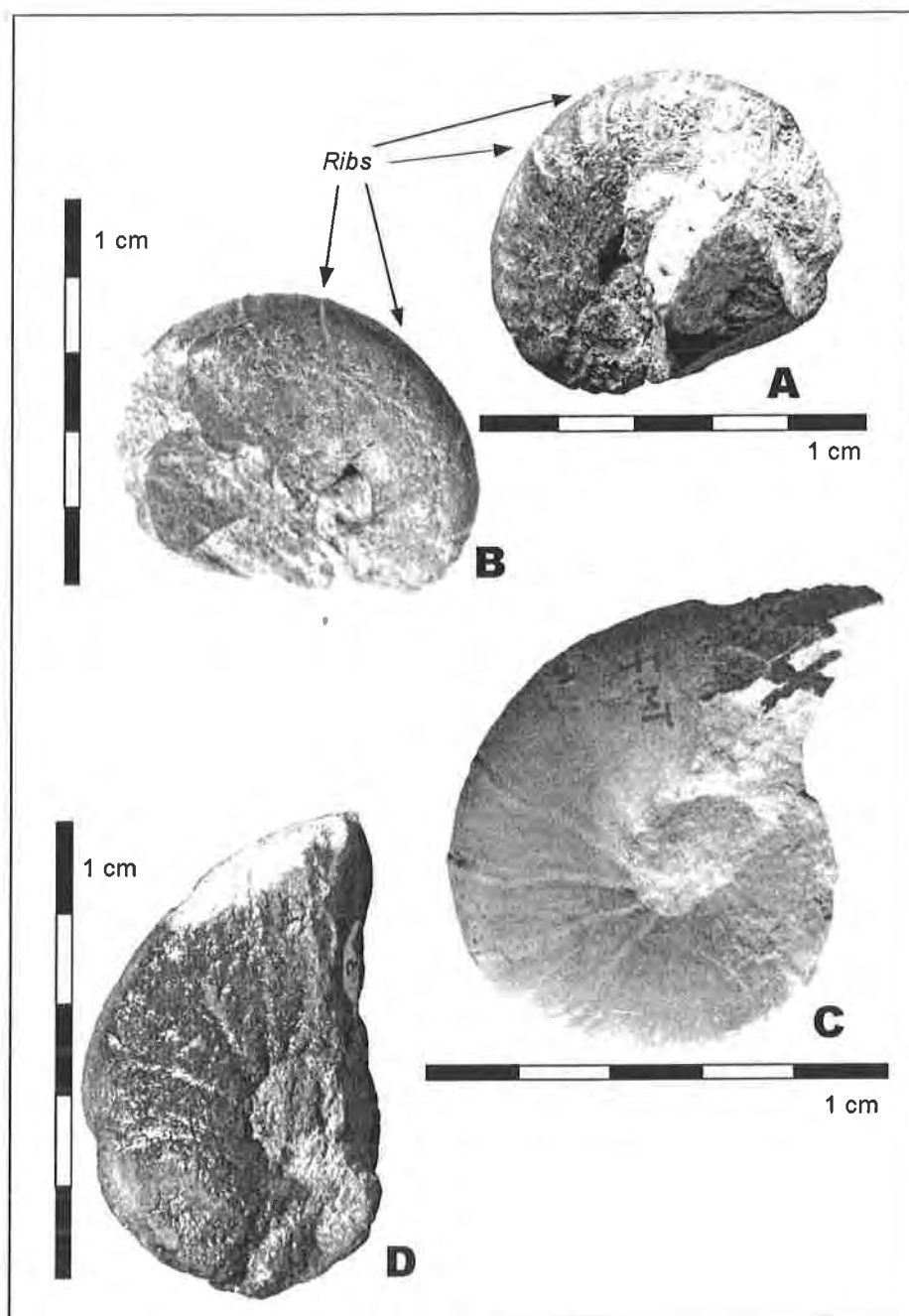


Figure 1a. *Plesiospitidiscus ligatus* (d'ORB, 1841). Lidernen Horizon, Lidernen Plänggeli, central Switzerland. **Figure 1b.** *Plesiospitidiscus ligatus* (d'ORB, 1841). Lidernen Horizon, Lidernen Plänggeli, central Switzerland. Same specimen as Figure 1a, photographed from the other side. Note typical rib forms, just as Figure 1c. **Figure 1c.** *Plesiospitidiscus ligatus* (d'ORB, 1841). Terre Masse section, Vocontian Basin, France. Specimen for comparison. **Figure 1d.** *Plesiospitidiscus ligatus* (d'ORB, 1841). Lidernen Horizon, Lidernen Plänggeli, central Switzerland.

PLATE 9.4 - Lidernen Horizon thin sections

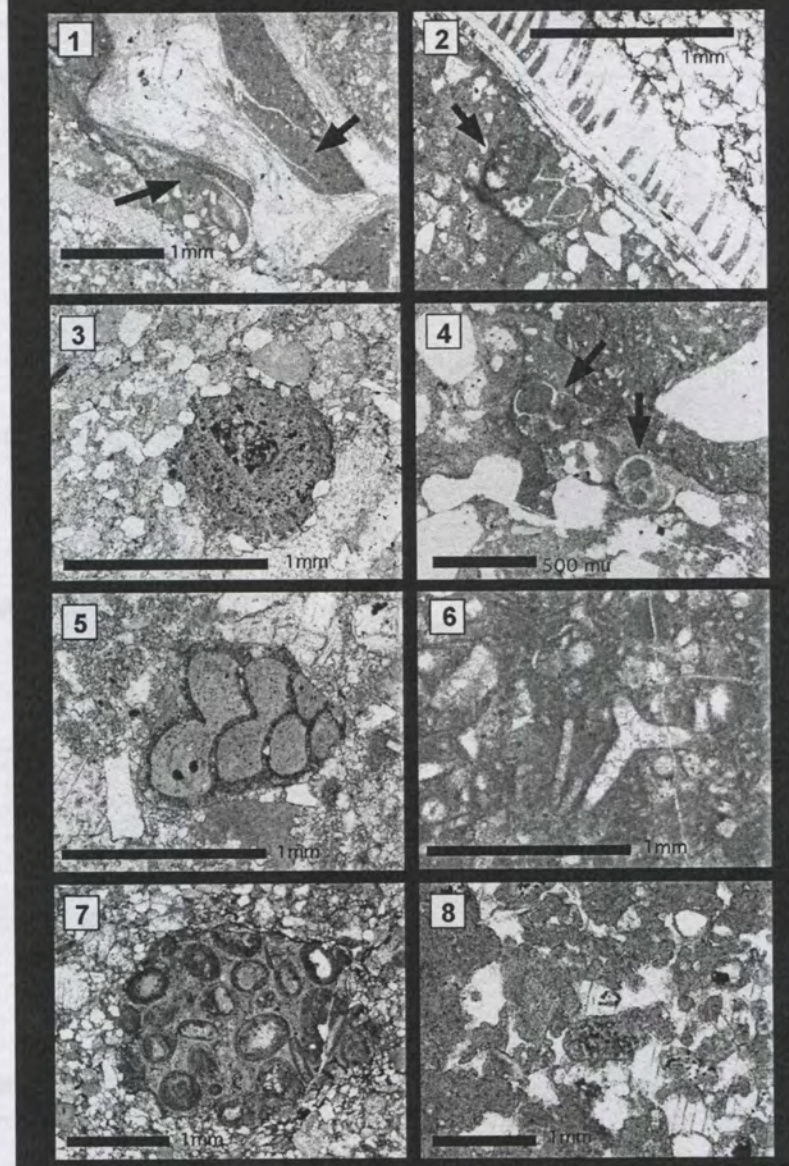


Figure 1. *Chalberen* section. Normal view. Reworked oyster fragment embedded in a phosphatic micrite with fine detrital quartz. **Figure 2.** *Chalberen* section. Normal view. Interior of a brachiopod, filled with a phosphatized micrite with some detrital quartz. Compare outside (upper right corner) which consists of coarse detrital quartz. **Figure 3.** *Chalberen* section. Normal view. Reworked ooid. **Figure 4.** *Lidernen Pläggeli*. Normal view. Inside of an ammonite filled with phosphatized micrite and two minute planktonic foraminifera (arrows). **Figure 5.** *Chalberen* section. Normal view. Reworked benthic foraminifera *Gaudryina* sp. **Figure 6.** *Lidernen Pläggeli*. Normal view. Megasclere. replacement of sponge spicule by drusy calcite. **Figure 7.** *Chalberen* section. Normal view. Reworked lithoclast consisting of oolitic Betliskalk (?). **Figure 8.** *Bauen* section. Normal view. Inside ammonite, infilling by drusy calcite is replaced by phosphorite. Globular structures may point to microbial involvement or burrowing activity.

Plate 9.5 - Lidernen Horizon bioturbation

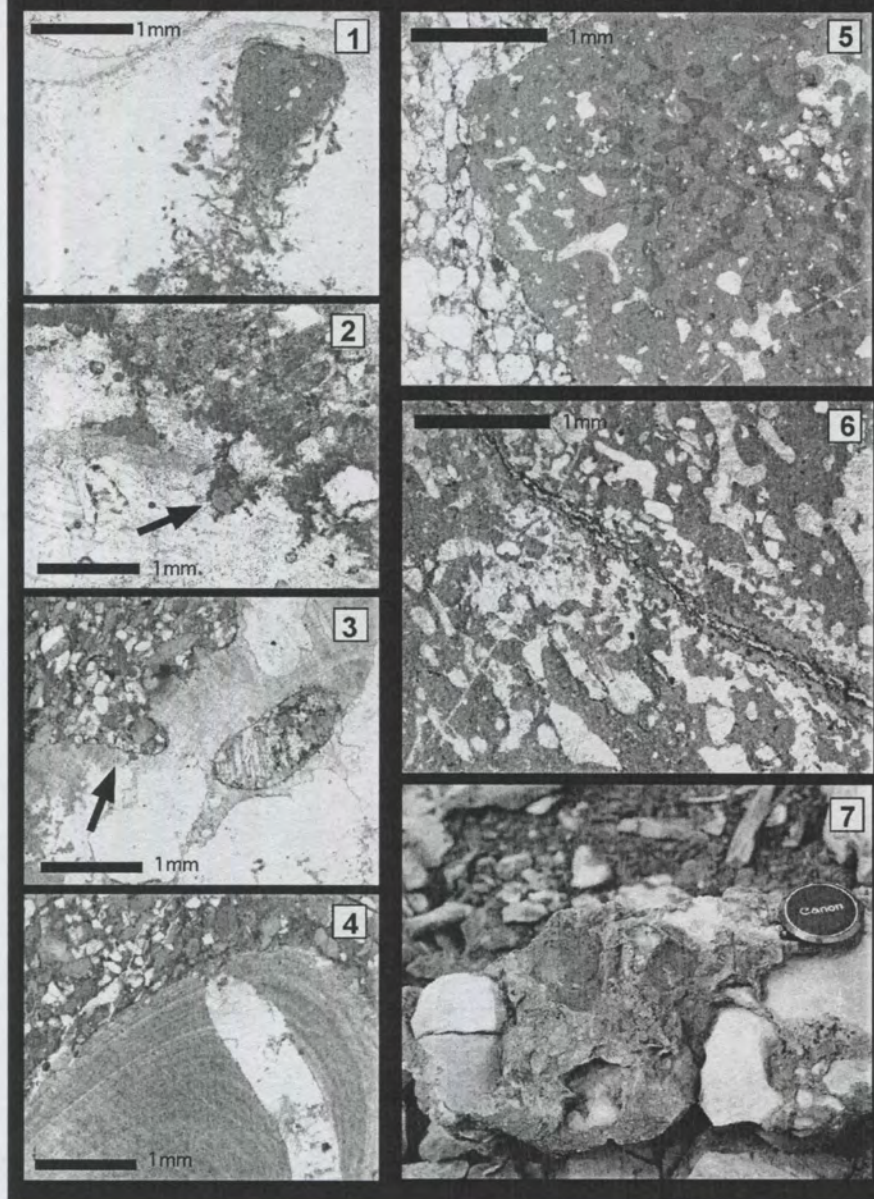


Figure 1. *Chalberen* section. Normal view. Phosphoritic burrow within an oyster fragment. Note small hyphen-like burrowing that extends from central pocket/channel. **Figure 2.** *Bauen*. Normal view. Phosphoritic endolithic borings within belemnite. **Figure 3.** *Pilatus*. Normal view. Burrowed belemnite partly filled with calcite and micritic matrix. Corrosion on outside (upper left side) might be a bite mark (?). **Figure 4.** *Pilatus*. Normal view. Boring in belemnite filled with drusy calcite. **Figure 5.** *Pilatus* section. Normal view. Chondrites borings inside ammonite phospho-micritic infill. **Figure 6.** *Lidernen Pläggeli*. Normal view. Phospho-micritic infill of ammonite boring by Chondrites. The borings are filled by drusy calcite. **Figure 7.** *Lidernen Pläggeli*. Part of Lidernen Horizon. Note how blocks of Lower Kieselkalk Mb float in phosphoritic-glaucinitic matrix.

Plate 9.6 - Lidernen Horizon lithotypes

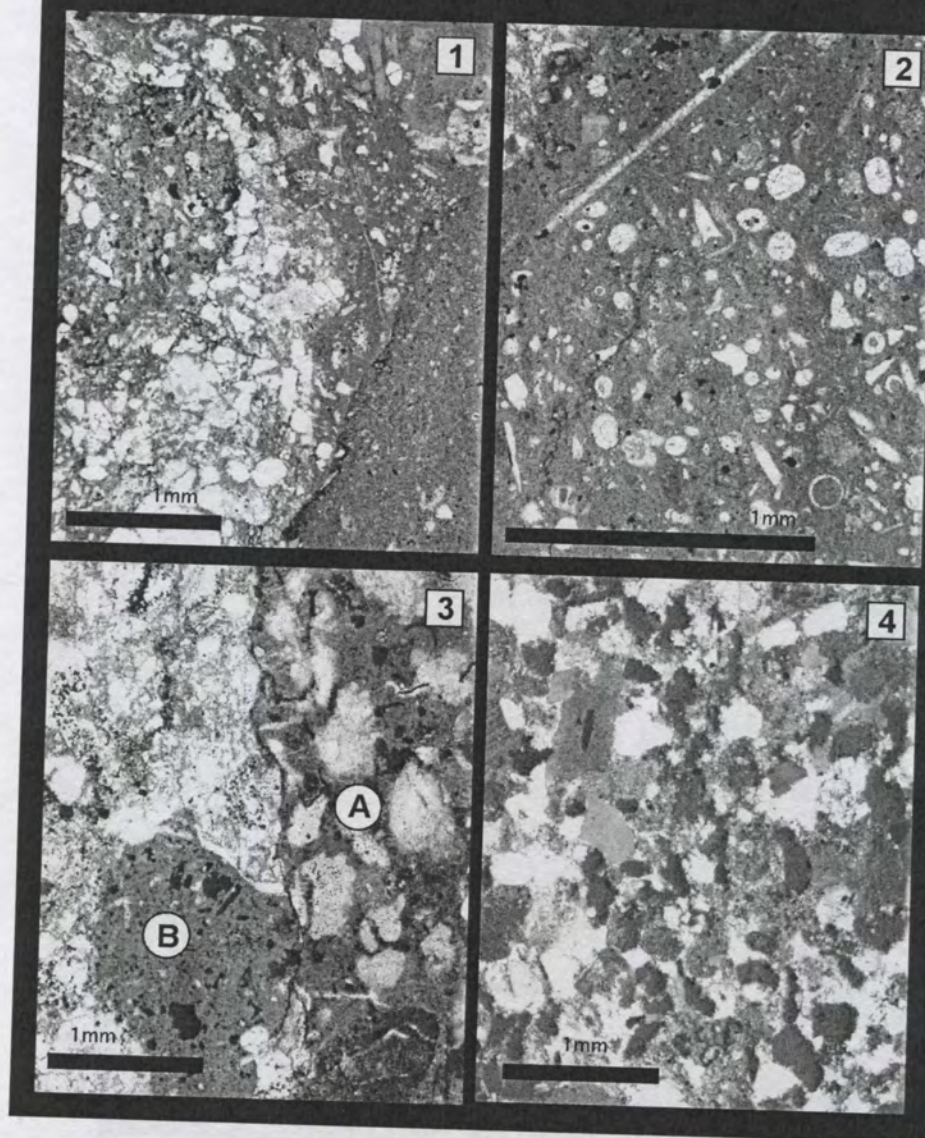


Figure 1. *Chalberen*. Normal View. This thin section shows different lithoclasts. a) Non-phosphoritic slightly pyritic micrite. b) Pyritic quartz rich lithoclast. c) Phosphoritic mudstone with small echinoderm debris and quartz. d) matrix with abundant quartz and glauconite. **Figure 2.** *Chalberen*. Normal view. Phosphatized spiculitic micrite. Some of the central canals still contain the original non-phosphatized micrite (arrow). **Figure 3.** *Hirschau* section. Normal view. Different lithoclasts. a) Spiculitic micrite with pyrite. b) Phosphatized micrite with large glauconite grains. **Figure 4.** *Talegg* section. Polarized view. Detrital quartz and glauconite rich echinodermal packstone. Resembles closely upper part of Lower Kieselkalk, except for glauconite contents.

PLATE 9.7 - Lidernen Horizon Foraminifera

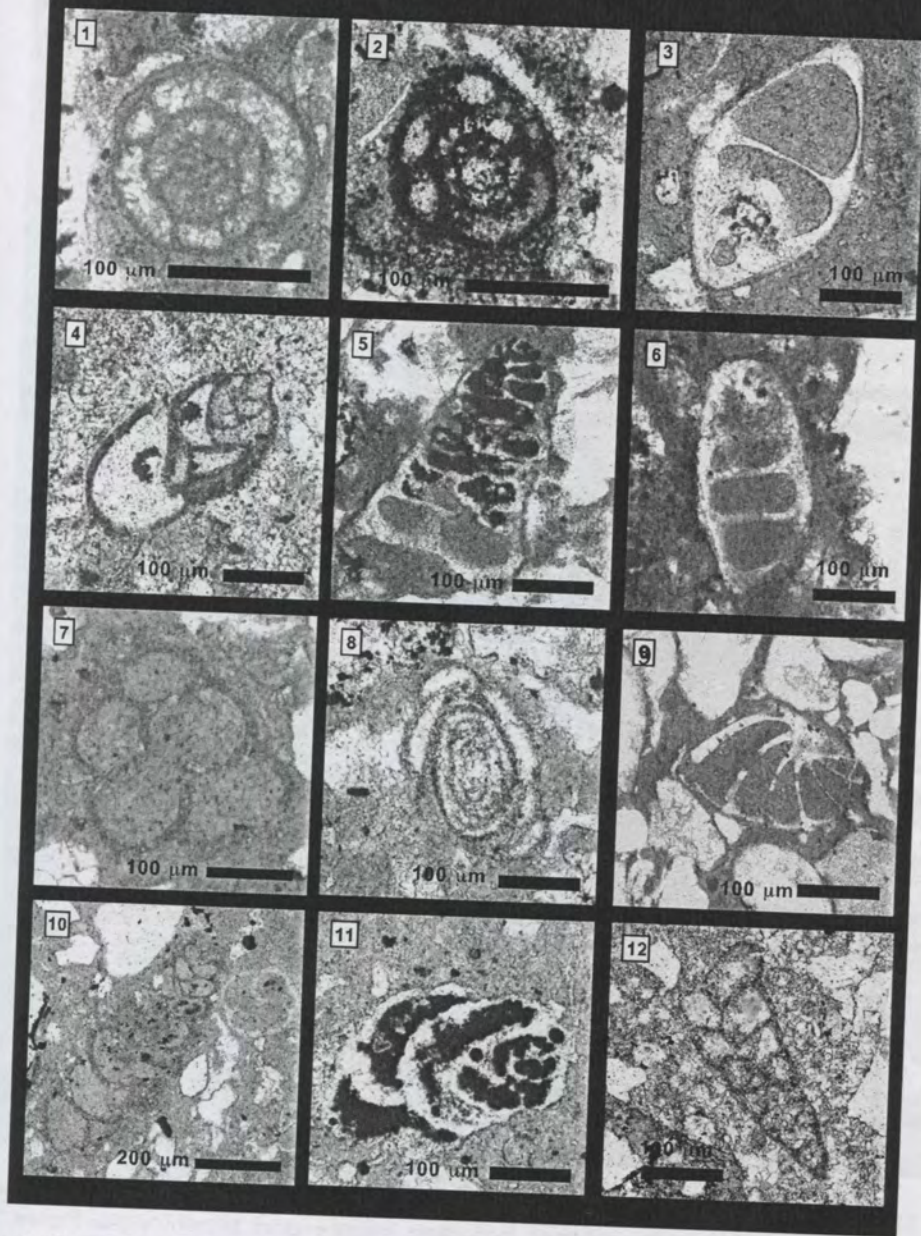


Figure 1. *Meandrospira favrei* - Bauen. Figure 2. *Meandrospira favrei* - Pilatus. Figure 3. *Lenticulina* sp. - Bauen. Figure 4. *?Paragaudryina* sp. - Bauen. Figure 5. *Indet.* - Lidernen Pläggeli. Figure 6. *Lenticulina* sp. - Lidernen Pläggeli. Figure 7. *Verneuilina* sp. - Bauen. Figure 8. *Glomospira glomerosa* - Lidernen Pläggeli. Figure 9. *Lenticulina* sp. - Lidernen Pläggeli. Figure 10. *Indet.* - Bauen. Figure 11. *Indet.* - Lidernen Pläggeli. Figure 12. *Gaudryina tuachensis* - Chalberen

PLATE 9.8 - Lidernen Horizon thin sections

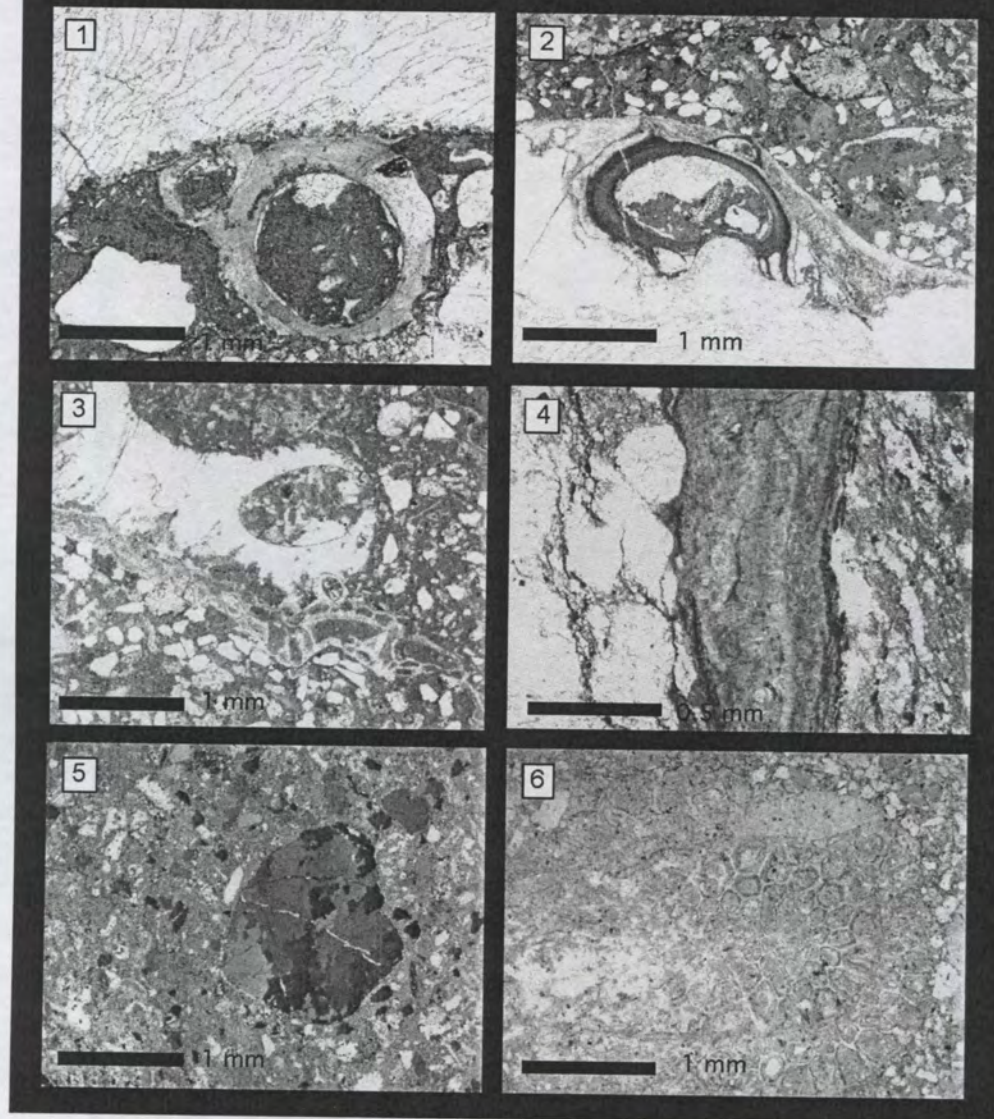


Figure 1. *Chalberen*. Normal view. Serpulids on inside of brachiopod within phosphomicrite. Not small borings on contact between micrite and brachiopod. **Figure 2.** *Chalberen*. Normal view. Serpulid on oyster fragment. **Figure 3.** *Chalberen*. Normal view. Serpulids and algae (?) on a phosphatic lithoclast (lower left part of photograph). **Figure 4.** *Lidernen Pläggeli*. Normal view. Phosphatic stromatolitic crust on outside of ammonite. **Figure 5.** *Hirschau* section. Polarized view. Large detrital quartz grain in detrital quartz rich micrite. **Figure 6.** *Chalberen* section. Normal view. Large bryozoan fragment.

PLATE 9.9 - Lidernen Horizon - Pilatus section

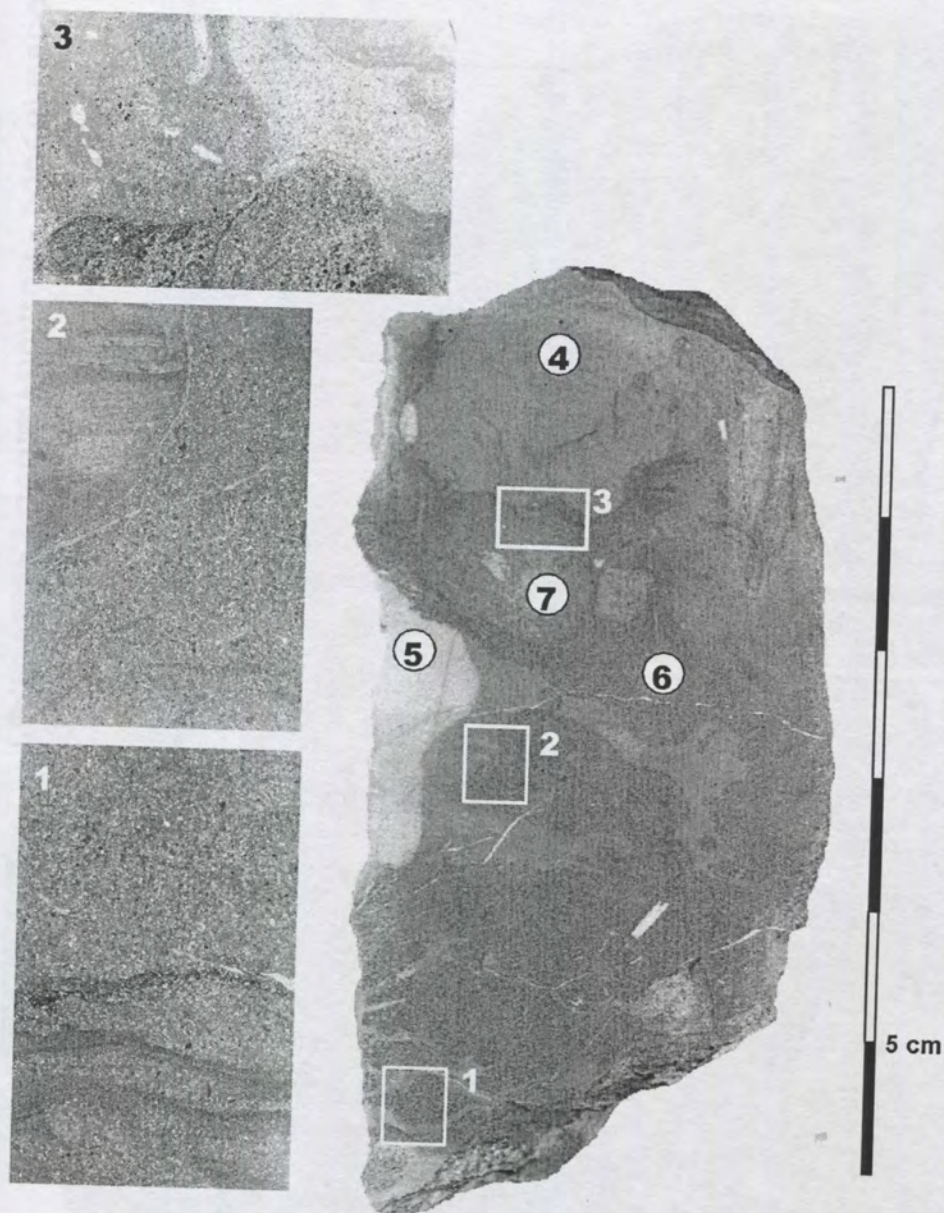


Figure 1. Base of Lidernen Horizon. Brown seams are non-bioturbated remnants of original spiculitic mudstone. **Figure 2.** Contact between glauconitic matrix and spiculitic mudstone. **Figure 3.** This scanned thin section shows different clasts. Lower part pyritized limestone nodule. Upper part reworked clast from spiculitic mudstone. **Figure 4.** Reworked clasts of original substrate for phosphogenesis. **Figure 5.** Idem. Pinkish weathered colour points to relatively high iron contents. **Figure 6.** Glauconitic matrix that resulted from extensive burrowing into 5. **Figure 7.** Pyritized limestone nodule.

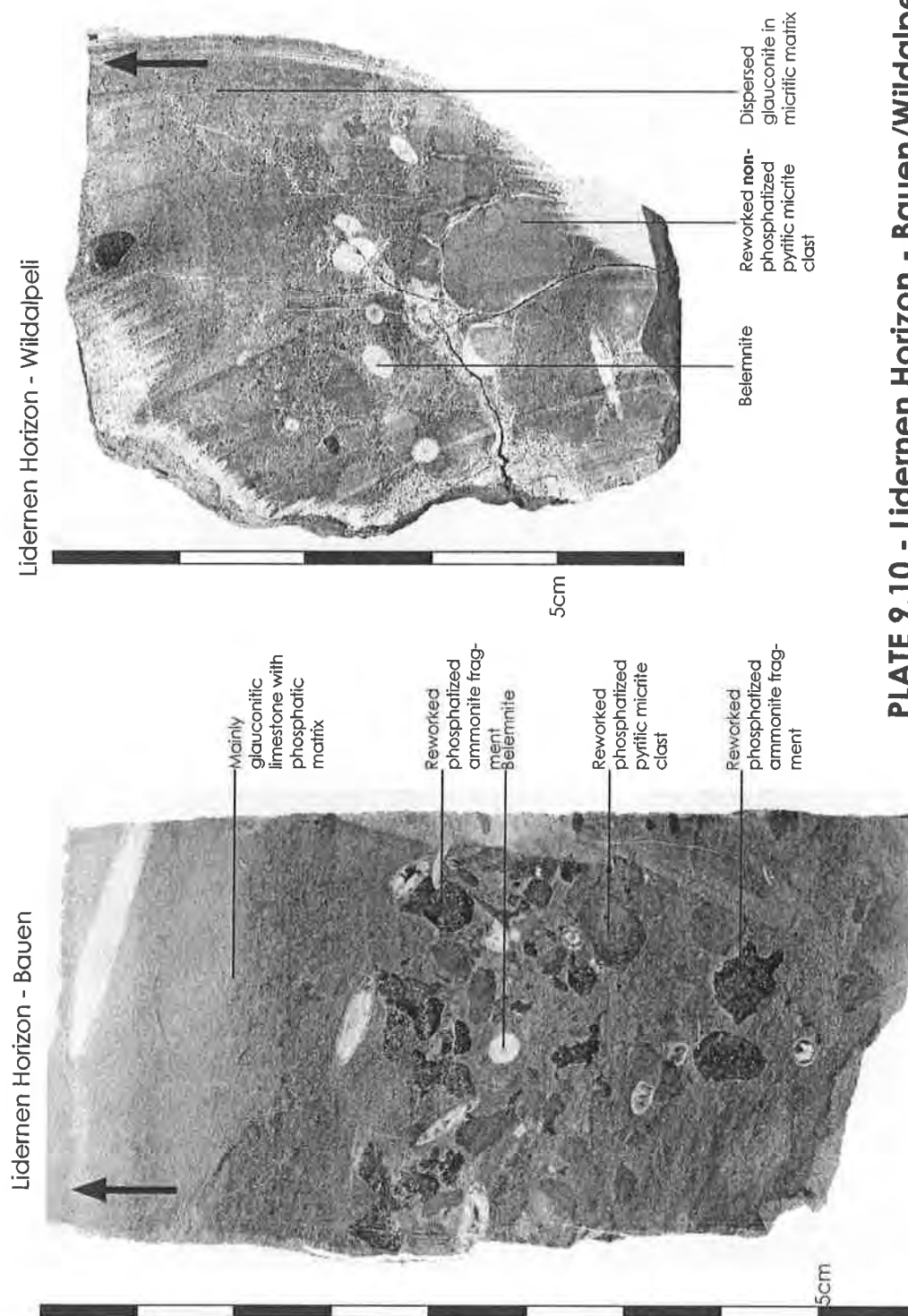


PLATE 9.10 - Lidernen Horizon - Bauen/Wildalpe

Plate 9.11 - Silberrenalp - Lidernen Breccia

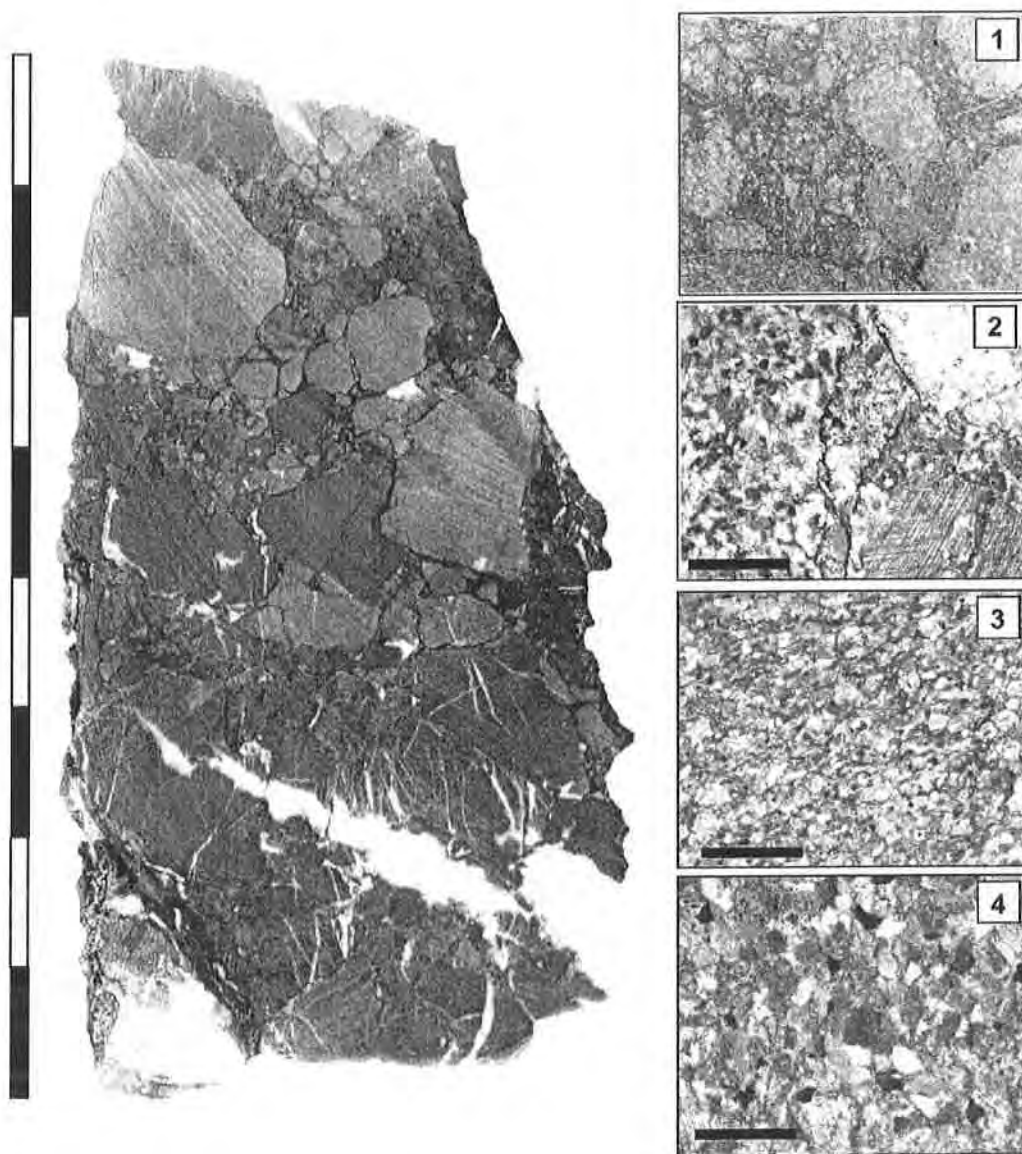


Figure 1. Scanned thin section, showing glauconitic matrix of this polymict breccia. **Figure 2.** Thin section showing polymict nature of breccia. In the upper right, a chert clast from the Kieselkalk. In the lower right hand side, a large echinodermal clast. **Figure 3.** Typical upper part of Lower Kieselkalk reworked as clast. Packstone with abundant detrital quartz and echinodermal debris. **Figure 4.** Idem. Polarized view. Slightly coarser grained as 3.

PLATE 9.12 - Kieselkalk Fm

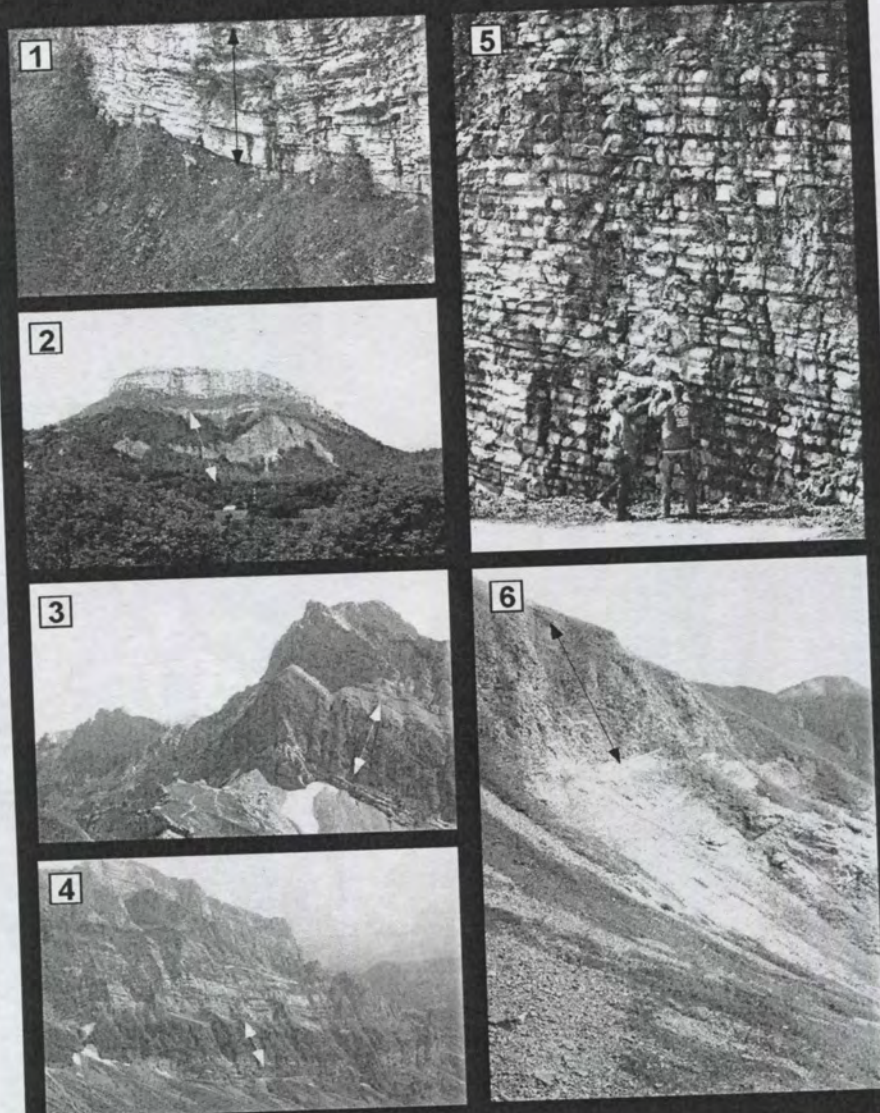


Figure 1. Dosegg section, Austria. Shows contact between Kieselkalk Fm and Palfries marls of early Valanginian age. The contact between the two is formed by the Gemsättli Horizon, which occurs as a thin bed with numerous phosphatic nodules and ammonites. **Figure 2.** Bauges Massif, France. Contact between the Hauterivian (brownish) and Barremian (greyish). This is typical for most shallow settings of the northern margin of the Tethys. **Figure 3.** Altmannsattel, Säntis, Switzerland. Hauterivian succession (green water carbonates) often covered by vegetation. **Figure 4.** Säntis, same as 3. **Figure 5.** Axen, road section. The base of the Kieselkalk in the deeper settings is formed by rhythmic alternations of limestones and marls. Some samples processed for organic matter, only produced oil. **Figure 6.** Bauen-Brisen Chain. Kieselkalk (arrow) overlying the Diphyoides Limestones. Again brownish weathered colour, indicative of high iron (as pyrite) contents.

Chapter 10

Concluding remarks

10.1 Introduction

For more extensive conclusions I refer to the individual chapters. This chapter summarizes the most important findings and outlines some of the remaining questions and problems.

10.2 Carbon isotope stratigraphy

The aim of this thesis has been to understand platform drowning events that occurred during the Hauterivian along the northern margin of the Tethys. Research was focussed on one drowning event in the Helvetic Alps (D2 of Föllmi et al., 1994), the so called Lidernen Horizon. In order to find out whether local, regional or global mechanisms were linked to this phase of platform destruction and phosphorite deposition, correlations with other regions (platform, basin) should first be established. Unfortunately Hauterivian shallow marine carbonate deposits are poor in biomarkers. In order to resolve stratigraphic problems, C-isotopes were used to correlate shallow marine carbonates.

Carbon and oxygen isotope records for the Hauterivian were obtained from a number of sections that represent the former northern margin of the Tethys. A reference curve, calibrated with ammonite biostratigraphy was measured in the Vocontian Basin. The Hauterivian shows a distinct carbon isotope trend in bulk rock micrites, that may be used for correlation. From the early late Valanginian (*Verrucosum* zone) positive isotope shift (+2.5‰; Hennig et al., 1999) to the early-late Hauterivian boundary carbon isotope values decrease with 2‰, of which 1‰ during the early Hauterivian. During the late Hauterivian the carbon isotope values increase again with 1‰. In the Vocontian Basin the minimum in the Hauterivian $\delta^{13}\text{C}$ curve falls exactly at the base of the *Sayni* zone.

Carbon isotope trends in other Hauterivian sections have shown to be more problematic. Bulk rock records from the Umbria-Marche basin show decreasing values during the late Valanginian and early Hauterivian, but the late Hauterivian increase has not been observed. Correlation with the Vocontian Basin record showed that the *Sayni* zone is probably less expanded as previously suggested by Channell et al. (1995). Based on several rare ammonites and nannofossils, these authors proposed that the *Sayni* zone spans magnetozones CM9 to CM6. A new improved correlation shows that the *Sayni* zone probably only spans CM7 and possibly CM6.

Application of C-isotope stratigraphy in the historical type region for the Hauterivian, in the surroundings of Neuchâtel, has proved to be complicated due to extensive diagenetic overprint. Very negative carbon and oxygen isotope values characterize most of the Hauterivian Pierre Jaune de Neuchatel Fm, which has been dated as early Hauterivian. Detailed sedimentological investigations showed that an important sea level fall exposed much of the platform and the carbonates were altered during phreatic meteoric diagenesis. Although the emersion discussed here predates the one of Arnaud et al. (1999) in the early Barremian, such an emersion fits better with the model of these authors, who have suggested that large parts of the Hauterivian and early

Barremian succession are missing. A view that is opposed by Clavel et al. (1995), who see no evidence for emersion during the Hauterivian.

Two other carbon isotope records pose further problems. The minimum values in the Semnoz and Pilatus sections postdate the minimum of the basal *Sayni* zone of the Vocontian Basin. Although diagenetic overprint can not entirely be excluded, the trends occur independent from lithological change. In Semnoz the late Hauterivian positive shift occurs even in coarser grained bioclastic and oolitic pack-grainstones. One way to explain these discrepancies is to envision problems with the determination of ammonites. Both in Semnoz and in the Italian sections (see above) the assignments are based on very few ammonite finds.

10.2 Oxygen isotopes

Oxygen isotope data have served to highlight the influence of sea level changes on carbonate deposition along the northern margin of the Tethys. From the early late Valanginian bottom water temperatures decreased from 15°C to 11°C in the earliest Hauterivian *Radiatus* zone. During the early and late Hauterivian temperatures gradually increase to 13°C. A bottom water temperature decrease during the late Valanginian is connected to a second order sea level rise that led to the active exchange of Boreal and Tethyan water masses.

Although the importance of connections, that got established during the late Valanginian and early Hauterivian, with the Boreal realm had already been shown by numerous studies on the migration of ammonites, nannofossils and dinoflagellates, these indirect inferences are now corroborated by hard data. The waxing and waning of a cold water front probably had a large influence on carbonate deposition along the northern margin of Tethys. The change from carbonate production in a chlorozoan mode to a foramol type of carbonate production was in part due to lowered sea water temperatures.

Important transgressive pulses during the late Valanginian, earliest Hauterivian and early late Hauterivian correspond to pronounced marly intervals in the Vocontian Basin, which may have been caused by re-inforced upwelling and declining carbonate production by calcareous nannoplankton.

The above mentioned time periods also show important platform drowning events which may also have been caused by colder water temperatures. Kuhn (1997), although based on bulk rock oxygen isotope data, showed that the onset of the mid-Valanginian drowning phase D1 was showing probably colder water temperatures. The earliest Hauterivian drowning (Rahberg Horizon) and mid-Hauterivian drowning (Lidernien Horizon) also correspond to lower bottom water temperatures.

10.3 Green water or blue water?

In the model of Föllmi et al. (1994) blue water conditions are characterized by carbonate production in the coral-oolite mode. The Lower Kieselkalk Mb (green water mode, crinoid-bryozoan mode) is time-equivalent with the Pierre Jaune de Neuchâtel Fm, which consist primarily of oolitic grainstones. Contemporaneous deposition of oolites and crinoid-bryozoan limestones may be explained by decoupling of surface waters in

shallow marine settings and deeper water on the shelves and in the basins. This was also proposed to explain the different Sr-isotope signatures for bulk rock (surface water) and belemnites (deep water, Chapter 7).

Under the influence of high continental run-off a warm water lit (less saline?) may have overlain deeper waters which were, at least during the Hauterivian, mainly controlled by upwelling cold water. The Pierre Jaune was initially relatively rich in pyrite, which may be further proof for high detrital input and less well oxygenated surface waters in very shallow coastal settings. Such a setting is typical for upwelling on a carbonate ramp (James, 1997).

10.4 Correlating the Helvetic Shelf and the Jura Platform

Neither carbon isotope records nor strontium isotope records will probably solve the stratigraphic problems of the historical type region for the Hauterivian. A strong diagenetic overprint, together with the problematic Sr-isotope record of the Vocontian Basin, make it hard to obtain reliable records that can be used for correlation, although a higher sample resolution might clarify some of the problems (e.g. missing part in Jura sections). The Lower Kieselkalk Mb is coeval to the Pierre Jaune de Neuchâtel Fm, which consist like the Lower Kieselkalk Mb of two sequences. In the Jura these two sequences consist of 1) Marnes Bleues d'Hauterive, the Zone-Marno Calcaire and the Lower Pierre Jaune and 2) the Marnes d'Uttins and the Upper Pierre Jaune. In the Helvetic Alps these sequences are more difficult to distinguish, but carbon isotope results for the Pilatus sections show two sequences: 1) The first comprises the shales at the base of the Kieselkalk and the lower part of the Lower Kieselkalk Mb. 2) The second the upper part of the Lower Kieselkalk Mb including the lower echinoderm breccia. Although the lower part of the Urgonien Jaune sensu Conrad and Masse (1989) or uppermost part of the Pierre Jaune sensu Blanc-Altru (1995) has been dated as late Barremian by Arnaud et al. (1999), it is not excluded that this part corresponds to the Upper Kieselkalk Mb. As to the question by which unit the Lidernen Horizon is represented in the Jura, there is no way to be exactly sure. The most likely candidate is the glauconitic, sandy oo-micrite, that separates the Upper Pierre Jaune from the Urgonien Jaune sensu Conrad and Masse (1989), like in Eclepens (at the base). There are however few means to proof this, other than lithostratigraphic.

10.5 Globalisation

Increased levels of carbon dioxide in the atmosphere during the Valanginian and Hauterivian could have been caused by a major phase of flood basalt emplacement in the Parana Basin. Although it is unclear how much CO₂ was really released, the outflowing basalts possibly marked a phase of increased spreading and rifting between Africa and South America. Higher CO₂ levels also led to increased weathering rates, following the model of Föllmi et al. (1994) and Weissert et al. (1998). Higher influx of terrestrial weathering products and nutrients seems clear from the conspicuous changes in carbonate sedimentation during the early Hauterivian. Proxies for continental weathering and

erosion, such as concentrations of P, Fe and Mn, in marine carbonates all show increases from the late Valanginian to early Hauterivian.

During the Valanginian eutrophication of surface waters presents a good explanation for global reef demise and increased carbon cycling. During the Hauterivian clay mineral assemblages show decreased abundance of kaolinite and increasingly higher amounts of smectites. Overall, climate appears to have changed from warm and wet during the Valanginian to more seasonally wet, alternating with dry periods, during the Hauterivian. Weathering and erosion were not necessarily less intense though. Widespread iron deposits testify of intense chemical weathering also during the Hauterivian. This iron may have been brought in with detrital loads of river water on clay minerals or on organic matter. It may also in part have been brought in from the Boreal realm or it may have been leached out of lateritic soils that developed during the Valanginian and got flooded during the Hauterivian.

During the early Hauterivian carbonate carbon deposition under mesotrophic conditions may reflect enhanced weathering and erosion rates on the continents and an increase in alkalinity. Flooded shelves, where accommodation space was high, served as sinks for carbonate deposition to buffer the oceans increased calcium contents after a prolonged phase of platform drowning during the late Valanginian. The enhanced deposition of calcite is marked by globally higher Sr/Ca ratios, decreasing carbon isotope ratios and the high sedimentation rates. Although most of the CO₂ released (if any) was consumed by increased weathering and erosion rates, part of it may have been stored as well in rapidly accumulating carbonates.

During the late Hauterivian weathering and run-off decreased, just as sea level descended and carbonate deposition slowed down. This is shown by: 1) decrease in kaolinite abundance. 2) decrease in P-burial rates. 3) decreased Mn/Fe ratios. 4) general decrease in marl deposition. The uptake of organic carbon burial is shown by more positive carbon isotope ratios and may have been related to a decrease in circulation resulting from closed down connections. The late Hauterivian may represent a pre-Barremian dry phase. A change to generally drier conditions during a Barremian arid phase is reflected in the restoration of oligotrophic carbonate platforms. Whether, the late Hauterivian was characterized by lower CO₂ levels and colder climate, remains to be seen.

Platform drowning phases during the Hauterivian (Rahberg and Lidenen Horizon) seem both to be controlled by sea level. Under already elevated nutrient conditions, sea level may have been the ultimate controlling factor. The Lidernen Horizon appears to be related to an important regressive event followed by a rapid transgression. This renewed pulse of cold water inflow in the *Sayni* zone may have re-invigorated upwelling. Phosphate deposition occurred in organic matter rich mudstones containing ammonites and other pelagic fauna. When sea level rise slowed down carbonate deposition was again possible in slightly less cold water, but still characterized by mesotrophic conditions.

Drowning phase D2 of Föllmi et al. (1994) recorded in the phosphoritic Lidernen Horizon was related to global changes such as sea level rise, increased CO₂ pressure and increased nutrient influx. Local or regional factors, such as paleotopography, current systems and sites of upwelling as well distance to river deltas, ultimately controlled where deposition of phosphoritic horizons occurred. Because the Helvetic Shelf was located close to an important sea strait between two different ocean basins, exchange of

watermasses between the Boreal and Tethyan realms left their direct imprint on carbonate sedimentation along the northern margin of the Tethys.

Appendix 1 – Abstracts

Is the $\delta^{13}\text{C}_{\text{CC}}$ record for the Hauterivian of the Vocontian Basin reflecting platform drowning along the northern margin of the Tethys?

B. van de Schootbrugge¹, L.G. Bulot², S.J. Burns³, K.B. Föllmi¹

Three sections consisting of hemipelagic limestone-marl alternations, forming together a composite section spanning the whole Hauterivian stage, were investigated for their carbon and oxygen stable isotopic signature. The Vocontian Basin was chosen, because of the possibility to calibrate the isotope record against a high resolution ammonite biostratigraphy (Bulot et al., 1995). Therefore, the here presented isotope record could serve in the future as a reference to sections with less detailed biostratigraphy, like often encountered in carbonate platform settings.

Analyses were performed on bulk rock samples. Unlike the oxygen isotope signal, the carbon isotope signal is less affected by diagenesis. For the Lower Hauterivian a gradual decrease of 1‰ for the $\delta^{13}\text{C}_{\text{CC}}$ values with a minimum (+0.59) around the Lower/Upper Hauterivian boundary is observed. The Upper Hauterivian shows a gradual increase of 1‰ up to the boundary with the Barremian (+1.65).

Variations in the carbonate carbon isotope record are thought to reflect the efficiency of removal of organic carbon into the sediment with respect to carbonate carbon burial. High $\delta^{13}\text{C}_{\text{CC}}$ values indicate high burial rates for organic carbon and/or low burial rates for carbonate carbon in association, for example, with carbonate platform drowning and oceanic anoxia. The early late Valanginian may have been a period with a high organic carbon to carbonate carbon burial ratio as is evidenced by a positive $\delta^{13}\text{C}_{\text{CC}}$ excursion (e.g., Weissert et al., 1998). This period has been identified as a phase of widespread carbonate platform drowning.

In the late early and late Hauterivian, two further phases of platform drowning have been identified in the northern Helvetic Alps of central Europe, which are less well imaged by the preliminary $\delta^{13}\text{C}_{\text{CC}}$ curve. This may suggest that links between the mode of carbon burial, sea-level and environmental change, and platform drowning may have been different from what is known from the Valanginian and Aptian (e.g., Föllmi et al., 1994). Our goal is, therefore, to explore possible changes in feedback links between the carbon cycle and environmental change through the early Cretaceous.

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Hauterivian carbon isotope record of the Vocontian Basin and its paleo-environmental implications for the Northern Tethys

B. van de Schootbrugge¹, L.G. Bulot², S.J. Burns³, K.B. Föllmi¹

Three sections consisting of hemipelagic limestone-marl alternations, forming together a composite section spanning the whole Hauterivian stage, were investigated for their carbon and oxygen stable isotopic signature. The Vocontian Basin was chosen, because of the possibility to calibrate the isotope record against a high resolution ammonite biostratigraphy. Therefore, the here presented isotope record could serve in the future as a reference to sections with less detailed biostratigraphy, like often encountered in carbonate platform settings.

Analyses were performed on bulk rock samples. Unlike the oxygen isotope signal, the carbon isotope signal is less affected by diagenesis. For the Lower Hauterivian a gradual decrease of 1‰ for the $\delta^{13}\text{C}_{\text{cc}}$ values with a minimum (+0.59) around the Lower/Upper Hauterivian boundary is observed. The Upper Hauterivian shows a gradual increase of 1‰ up to the boundary with the Barremian (+1.65).

Variations in the carbonate carbon isotope record are thought to reflect the efficiency of removal of organic carbon into the sediment with respect to carbonate carbon burial. High $\delta^{13}\text{C}_{\text{cc}}$ values indicate high burial rates for organic carbon and/or low burial rates for carbonate carbon in association, for example, with carbonate platform drowning and oceanic anoxia. For example, the early late Valanginian may have been a period with a high organic carbon to carbonate carbon burial ratio as is evidenced by a positive $\delta^{13}\text{C}_{\text{cc}}$ excursion (e.g., Weissert et al., 1998). This period has been identified as a phase of widespread carbonate platform drowning.

In the late early and late Hauterivian, two further phases of platform drowning have been identified in the northern Helvetic Alps of central Europe, which are less well imaged by the preliminary $\delta^{13}\text{C}_{\text{cc}}$ curve. This may suggest that links between the mode of carbon burial, sea-level and environmental change, and platform drowning may have been different from what is known from the Valanginian and Aptian (e.g., Föllmi et al., 1994). Our goal is, therefore, to explore possible changes in feedback links between the carbon cycle and environmental change through the early Cretaceous.

High resolution Sr-isotope stratigraphy for the Hauterivian of the Vocontian Basin: evidence for 3rd order sea level cyclicity?

van de Schootbrugge¹, B., Adatte¹, T., Föllmi¹, K.B., Bulot², L.G., Kramers, J.D³.

High resolution Sr-isotope stratigraphy has a large potential for dating and correlating sections, especially when used in combination with biostratigraphy and other chemostratigraphic tools (e.g. carbon and oxygen stable isotopes). The $^{87}\text{Sr}/^{86}\text{Sr}$ signal has also been used as a proxy for environmental change, since variations in the isotopic ratio either indicate increased continental erosion (leading to high ratio isotopic values) or increased hydrothermal exchange at MORs (leading to low ratio isotopic values).

The Hauterivian is generally considered to have been a period of warm and humid climate and therefore increased weathering. Weathering probably played an important role in platform drowning events that led to deposition of highly condensed phosphatic beds along the northern Tethyan margin, now exposed in the Helvetic Alps. These biotic crises took place at least three times during the Hauterivian. One of the major problems for establishing a paleo-environmental model to explain these platform drownings is the difficulty in correlating them to other parts of the world. This is primarily due to a lack of age diagnostic fossils in shallow marine settings, like the Swiss Jura platform. The steep increase in the Hauterivian $^{87}\text{Sr}/^{86}\text{Sr}$ isotope signal is an important asset to its use in correlating sections along the northern margin of the Tethys. Our goal is to establish a high resolution $^{87}\text{Sr}/^{86}\text{Sr}$ reference curve to be used in a later stage as a correlation tool and proxy for environmental change.

We analyzed a large number of bulk rock and belemnite samples from the Vocontian Basin in southeastern France. Sections in this region yield a high resolution bio-zonation based on ammonites. The same sample set was used in an earlier study for carbon and oxygen isotope analyses, which showed that the bulk rock samples retained their original $\delta^{13}\text{C}$ signature and that the belemnites suffered from very little diagenetic overprint and can be used for paleo-temperature estimations. Furthermore, we tested the belemnites for diagenetic alteration with the help of trace element analyses (Sr, Mg, Fe and Mn). XRD analyses were performed to check the mineralogy of the bulk rock samples.

The obtained results show the steep increase for the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio from the base (0.707370) to the top of the Hauterivian (0.707544) as observed in earlier work (Jones et al., 1994), although our bulk rock values appear to be positively offset compared to earlier work and show a sharper increase. Belemnites, with Fe-concentrations <150 ppm and Mn-concentrations <30 ppm, give Sr-isotope values that come closest to previous work. However, in previous studies resolution is relatively low (*cf.* (Jones et al., 1994) 8 data points, this study 82 data points), complicating direct comparison. Another particularity of our results is an apparent cyclicity in the bulk rock Sr-isotope values during the early Hauterivian.

We have reason to believe that the Sr-cyclicity corresponds to sea level changes on a million year time scale. Preliminary results of XRD-analyses in order to quantify erosion show that there might be a positive correlation between detrital input

and Sr-isotope variation. Although, at the moment we can not exclude leaching problems during preparation of the samples, we think that this cyclicity is a primary signal, where the high ratio Sr-isotope values correspond to low sea level stands and the low to periods of high sea level. The fact that these cycles are well expressed during the early Hauterivian but not as good during the late Hauterivian is probably due to the fact that the early Hauterivian represents a second order sea level high stand, during which aggradation, rather than progradation, favoured the recording of smaller scale cycles.

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Abstract for oral presentation at EGS 25, 2000, Nice.

Did the Paraña Continental Flood Basalts ignite global change during the early Cretaceous?

B. van de Schootbrugge¹, K.B. Föllmi¹, S.J. Burns² & T. Adatte¹

The emplacement of the Paraña Continental Flood Basalts (PCFB) during the early Cretaceous has been used in paleo-environmental models as the catalyst that sparked off global change. Flood basalt degassing is thought to have led to accelerated carbon cycling, resulting in a mid-Valanginian positive $\delta^{13}\text{C}$ excursion, and to the repeated occurrence of platform drowning events in Valanginian-Hauterivian carbonate series. We investigated belemnite and bulk rock samples of Valanginian-Hauterivian age from the Vocontian Basin, southern France, for their carbon and oxygen isotope record. A paleo-temperature trend constructed, using $\delta^{18}\text{O}$ values extracted from the belemnites, shows warm temperatures (15°C) during the Valanginian positive $\delta^{13}\text{C}$ excursion and rapidly decreasing temperatures during the late Valanginian and early Hauterivian (11°C). During the late Hauterivian temperatures increase again (13°C). We think that these isotopic changes are related to paleoceanographic changes. The observed cooling trend coincides with 2nd order sea level rise and the influx of cold Boreal water in the Tethys. The PCFB might be considered as a marker, rather than a cause, for global change, marking increased tectonic activity and sea floor spreading which led to sea level rise, increased carbon burial and carbonate platform drowning.

Abstract for oral presentation at the EGS 25, 2000, Nice.

Weathering and climate change

Karl B. Föllmi, Rachel Hosein, Kaspar Arn, Federica Tamburini, Tessa van Westrenen, Bas van de Schootbrugge, Philipp Steinmann, and Thierry Adatte

Weathering is important in regulating the long-term carbon cycle. Temporal changes in biogeochemical weathering rates modulate the uptake of atmospheric CO_2 , and changes in biogeochemical weathering rates lead to changes in the release rates of biophile elements (such as P, Si, Ca, Fe), which modulate transformation rates of inorganic carbon into organic carbon through photosynthesis. Variations in weathering may, therefore, exert an important control on a row of globally interlinked processes such as productivity, transformation of inorganic carbon into organic carbon, oxygen contents, as well as climate.

Presently, in the field of research on weathering, several main topics have been identified as partially unresolved: 1) Quantification of weathering rates in the geological past; 2) The degree of dependency of biogeochemical weathering rates on total weathering rates; and 3) The influence of glaciation on total and biogeochemical weathering rates. These topics are relevant to several open questions, such as 1) to what extent did continental weathering contribute to phases of enhanced marine productivity during the Neogene and Quaternary, dependent on climate change; and 2) which types of feedback mechanisms may have developed between weathering and

climate change in the case glaciation events did contribute to enhanced biogeochemical weathering.

Abstract for oral presentation at the EGS 25, 2000, Nice.

Mantle plume activity and environmental change

Karl B. Föllmi¹, Bas van de Schootbrugge¹, Thierry Adatte¹, and Elisabetta Erba²

Massive volcanic events are usually coinciding with rapid environmental change, and causal relationships such as the release of primordial CO₂, and subsequent increases in weathering, marine productivity, and organic carbon burial have been proposed for the majority of them. A close-up examination of major Mesozoic and Tertiary events reveals, however, more complex relationships. The volcanic phases near the Permian-Triassic (P-T), at the Cretaceous-Tertiary (K-T), and at the Paleocene-Eocene boundaries (P-E) are all characterized by extinction events and marked by negative carbon isotope excursions. The volcanic events near the Triassic-Jurassic boundary (T-J) and during the Bajocian (B) are equally correlated with extinction events, but coeval carbon isotope records barely register those events.

The volcanic events in the Valanginian (V), in the Aptian (A), near the Cenomanian-Turonian boundary (C-T) as well as in the middle Miocene (M) correspond to extinction events of medium importance; they are, however, accompanied by important positive carbon isotope shifts. The Toarcian positive carbon isotope shift (T), on the other side, can only doubtfully be correlated to a volcanic event (Karoo). Anoxic events of different extent have been associated with mantle plume activity (P-T, A, C-T, P-E, M, and T?), whereas this has not been observed in relation with the T-J, B, and K-T events. The relation between mantle plume and environmental change may hold up in general; each event seems, however, to be followed by a unique set of feedback mechanisms, for which the boundary conditions remain largely elusive.

High weathering rates during the early Cretaceous and its effect on carbonate sedimentation

Bas van de Schootbrugge & Karl B. Föllmi

Increased weathering and erosion are thought to have led to platform drowning events on the Helvetic Shelf during the early Valanginian to early Cenomanian. A compilation of phosphate accumulation rates (PARs) for the last 160 Ma by Föllmi (1995) shows elevated accumulation rates during the early Cretaceous. Föllmi (1995) ascribed these high PARs to increased erosion under greenhouse climate conditions. High phosphorus input and high primary productivity led to diminished carbonate carbon production and promoted organic carbon burial, as is evidenced from the correlation between positive $\delta^{13}\text{C}$ excursions and platform destruction during the Valanginian and Aptian (Weissert et al., 1998).

During the Hauterivian, which shows three platform crises in the Helvetic Alps, this relation between phosphorus and carbon is less clear. Stable isotope analyses on well preserved micrites from sections in the Vocontian Basin show a decreasing $\delta^{13}\text{C}$ trend during the late Valanginian to early Hauterivian and slightly increasing values for the late Hauterivian. However, detailed investigation of several key-sections along the western and northern margin of the Tethys for their PARs and trace element contents (Fe, Mn, Sr) show that erosion was highest during the late Valanginian to early Hauterivian.

The decreasing $\delta^{13}\text{C}$ values during the late Valanginian to early Hauterivian reflect high carbonate carbon burial rates. High weathering and erosion rates caused a shift in carbonate producing biota, from *blue water* (corals) oligotrophic to *green water* (crinoids, bryzoans and sponges) mesotrophic communities. The fact that platform drowning occurred, even though carbonate producing biota seemed to have adapted to high nutrient levels, means that these crises might not have been related just to nutrient poisoning, but also to oceanographic changes.

Phosphate Accumulation Rates for the Valanginian-Hauterivian: paleoceanographic implications.

Bas van de Schootbrugge & Karl Föllmi

Phosphorus (P) is an essential nutrient and is intimately linked to the carbon cycle, because it controls productivity and therefore export of carbon. Phosphorus is primarily delivered to the ocean through continental weathering and erosion. During the early Cretaceous the link between the carbon and phosphorus cycles has been shown by the contemporaneous occurrence of phosphatic horizons representing drowning events and positive carbon isotope excursions (Valanginian and Aptian).

Detailed investigation of a number (6) of Hauterivian sections along the former northern margin of the Tethys for their Phosphate Accumulation Rates (PAR) combined with other data from the literature allows for the construction of a phosphate accumulation curve that is based on 475 data points. This work largely confirms earlier work by Föllmi (1995). From the Valanginian to Barremian PAR show a maximum during the early Hauterivian (Radiatus-Nodosoplicatum zones), with a gradual increase during the Valanginian and a rapid decrease during the late Hauterivian.

High PAR correlate with high carbonate accumulation rates during the early Hauterivian. Slowdown of PAR during the late Hauterivian correlates with lowered carbonate accumulation rates. This is also reflected by the carbon isotope record for the Hauterivian, with decreasing $\delta^{13}\text{C}$ values during the early Hauterivian and increasing values during the late Hauterivian.

Based on oxygen isotope records for the Tethys the early Hauterivian shows relatively cool water temperatures, which is interpreted as the result of cold water influx from the Boreal realm during a general transgressive phase (van de Schootbrugge et al., 2000). The coincidence of high PAR, mesotrophic carbonate producing biota (crinoids, bryzoans, sponges) and cool water temperatures might point to increased upwelling along the northern margin of the Tethys. The reason that this did not lead to increased C_{org} burial and further drowning might be that carbon cycling was pushed in a higher energy mode from the Valanginian into the Hauterivian. On the whole the Hauterivian represented a stable mode of greenhouse climate, with high atmospheric pCO_2 and high detrital influx (P, alkalinity and terrestrial OM) and during which the ocean became buffered favouring carbonate carbon burial under mesotrophic conditions.

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Appendix 2 - Tables

Table 1 – Carbon and Oxygen isotope data Core 607

Lab#	sample	depth (m)	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$
C-28619	57	0	-3.87	-0.76
C-28620	58	0.2	-4.84	0.83
C-28621	60	0.5	-2.8	0.65
C-28622	62	1.4	-2.32	0.84
C-28623	63	2	-2.22	0.94
C-28624	67	3	-2.71	0.75
C-28625	69	3.4	-2.12	0.83
C-28626	71	4.2	-2.03	0.73
C-28627	73	4.6	-2.22	0.53
C-28628	75	5.4	-2.12	0.73
C-28629	77	6.2	-2.03	0.83
C-28630	79	7	-2.22	0.84
C-28631	81	8	-2.22	0.84
C-28632	83	9.2	-2.22	0.84
C-28633	85	10.3	-2.22	0.94
C-28634	87	11.4	-2.32	0.94
C-28635	90	12.4	-2.22	0.94
C-28636	92	13.4	-2.03	1.14
C-28637	93	14	-2.12	0.94
C-28638	94	14.4	-2.12	1.04
C-28639	97	15.8	-2.12	1.04
C-28640	98	16.1	-2.12	0.94
C-28615	100	17	-1.83	1.13
C-28641	101	17.4	-2.41	0.95
C-28642	104	18.8	-2.22	0.94
C-28643	106	19.8	-2.61	0.95
C-28644	109	21.2	-2.41	0.84
C-28645	111	22	-2.9	0.86
C-28646	112	22.4	-3	0.97
C-28647	114	23.6	-2.9	0.86
C-28648	116	24.6	-2.71	0.96
C-28649	117	25	-2.41	1.05
C-28650	118	25.05	-2.71	0.96
C-28651	119	25.2	-3.39	0.77
C-28652	122	26.2	-4.45	0.29
C-28653	124	26.6	-4.55	0.51
C-28658	127	26.8	-4.03	0.52
C-28659	130	28.6	-6.25	0.47
C-28660	132	29.2	-4.85	0.38
C-28661	136	31.2	-4.02	0.4
C-28662	138	32.2	-3.85	0.76
C-28663	139-2	32.8	-3.53	0.21
C-28664	139-5	32.85	-3.95	0.28
C-28665	140	33.2	-3.69	0.44
C-28666	143	34.4	-3.95	0.63
C-28667	145	35.6	-4.05	0.55
C-28668	147	36.6	-3.96	0.48
C-28669	149	37.6	-3.95	0.23

Lab#	sample	depth	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$
C-28670	151	38.6	-4.86	-0.37
C-28671	153	40	-4.95	-0.74
C-28672	155	40.8	-4.78	-1.11
C-28673	157	41.8	-5.14	-2.19
C-28674	159	42.4	-5.23	-3.87
C-28675	160	43	-5.59	-4.02
C-28676	162	44.2	-5.13	-2.95
C-28677	164	45	-5.88	-3.87
C-28678	166	45.8	-5.96	-3.54
C-28679	168	46.8	-6.32	-3.09
C-28680	170	47.2	-6.27	-2.46
C-28681	171	47.8	-6.23	-2.43
C-28682	176	49.6	-5.3	-4.78
C-28683	178	50.8	-5.71	-5.16
C-28684	180	51.8	-6.01	-5.01
C-28685	183	53	-4.85	-5
C-28686	185	54	-5.93	-4.19
C-28687	187	54.8	-5.12	-5.04
C-28688	189	55.8	-5.83	-5.21
C-28689	190	56.6	-5.4	-5.08
C-28690	192	57.6	-6.33	-4.68
C-28691	194	58.8	-6.68	-4.5
C-28561	196	59.6	-5.88	-4.81
C-28562	198	60.4	-5.65	-4.05
C-28563	200	61.6	-5.51	-4.61
C-28564	203	63	-6.45	-3.75
C-28565	206	64.6	-6.08	-4.4
C-28566	208	65.6	-6.24	-4.52
C-28567	210	66.4	-5.36	-3.44
C-28568	215	68.4	-5.03	-2.66
C-28569	217	69.6	-5.69	-3.48
C-28570	220	70.6	-6.1	-3.58
C-28571	223	72.4	-6.71	-3.89
C-28572	225	73.6	-6.34	-3.88
C-28573	230	75	-4.87	-4
C-28616	233	75.8	-5.12	-3.72
C-28617	236	77.6	-4.83	-3.11
C-28618	240	79.4	-5.71	-3.81

Table 2 – Carbon and oxygen isotope data Eclepens

Lab #	sample EC	depth (m)	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
C-30164	1	0	1.26	-3.93
C-30165	4	1.4	1.24	-3.62
C-30166	6	2.2	0.99	-4.75
C-30167	10	3.2	1.46	-3.27
C-30168	13	4.15	1.32	-3.92
C-30169	15	4.42	1.35	-3.76
C-30170	20	5.77	1.55	-2.88
C-30171	25	8.57	0.92	-5.02
C-30172	28	9.18	0.78	-3.84
C-30173	30	10.2	1.13	-3.62
C-30174	33	11.23	1.37	-3.47
C-30175	38	13	1.34	-3.54
C-30176	42	13.6	1.14	-3.19
C-30177	45	15.38	0.05	-4.16
C-30178	49	17.03	-0.04	-4.25
C-30179	54	18.9	-0.58	-5.25
C-30180	57	20.33	-1.18	-5.3
C-30181	61	22.25	-1.22	-5.53
C-30182	64	23.83	-0.53	-4.76
C-30183	66	24.35	-1.31	-5.45
C-30184	69	25.78	-1.2	-4.53
C-30185	71	26.62	-1.53	-3.92
C-30186	75	28	-1.08	-4.7
C-30187	77	28.85	-1.05	-3.98
C-30189	85	29.88	-0.4	-4.75
C-30190	87	30.83	-0.49	-4.04
C-30192	94	32.9	-0.38	-4.69
C-30194	99	34.38	-0.52	-4.71
C-30195	102	35	-1.07	-4.57
C-30196	104	35.6	-0.43	-4.24
C-30222	106	36.6	-1.81	-5.93
C-30223	108	37	-1.73	-4.46
C-30224	110	37.25	-0.42	-5.04
C-30225	113	38.18	-1.2	-6.18
C-30226	115	39.05	-1.77	-6.07
C-30227	121	40.95	-2.97	-6.33
C-30228	123	41.6	-3.22	-6.74
C-30229	126	42.28	-3.38	-6.66
C-30230	128	42.8	-1.01	-6.85
C-30231	132	43.7	-0.62	-7.6
C-30232	136	44.75	-0.91	-6.19
C-30233	138	45.35	-1.17	-6.01
C-30234	142	46.65	-2.52	-6.78
C-30235	144	47.15	-2.3	-5.66
C-30236	146	47.95	-1.91	-7.92

Table 3 – Carbon and oxygen isotope data Semnoz

Lab#	Sample (SEM)	depth (m)	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
C-27287	2	0.5	-0.22	-2.67
C-27288	3	0.7	0.00	-2.57
C-27289	4	1.25	0.09	-2.18
C-27290	6	1.65	-0.61	-2.24
C-27291	8	2.1	0.03	-1.80
C-27292	10	2.55	0.45	-1.90
C-27293	12	2.95	0.65	-2.18
C-27294	13	3.25	0.72	-2.26
C-27295	15	4.15	0.70	-2.61
C-27296	18	5.05	0.73	-3.35
C-27297	19	5.65	0.59	-2.04
C-27303	22	6.35	0.89	-3.42
C-27304	23	6.55	0.88	-2.55
C-27305	24	9.7	0.86	-2.57
C-27306	25	10.25	0.71	-3.22
C-27307	28	10.85	1.03	-2.65
C-27308	31	12.85	0.44	-3.29
C-27309	32	13.2	0.90	-2.89
C-27310	34	14.35	1.01	-2.59
C-27311	35	15.15	0.98	-2.48
Large Hiatus				
C-27312	36	0.1	0.42	-2.57
C-27313	38	0.65	0.47	-2.59
C-27314	40	1.1	0.43	-2.63
C-27315	42	1.4	0.40	-2.49
C-27316	44	1.7	0.31	-2.45
C-27317	46	2.05	0.25	-2.54
C-27318	48	2.37	0.29	-2.43
C-27319	50	2.62	0.05	-2.86
C-27320	52	3.02	0.07	-2.52
C-27321	53	3.77	-0.06	-2.46
C-27322	54	4.29	-0.09	-2.46
C-27323	55	4.59	0.06	-2.57
C-27324	56	4.81	-0.19	-2.62
C-27325	60	6.15	0.05	-2.57
C-27326	62	6.72	-0.17	-2.65
C-27327	64	7.27	0.33	-2.92
C-27328	65	7.97	0.10	-2.35
C-27329	66	8.42	-0.10	-2.43
C-27330	68	9.17	-0.15	-2.12
C-27331	70	9.62	-0.33	-3.39
C-27332	73	10.19	0.14	-2.47
C-27333	78	11.69	-0.49	-2.74
C-27334	82	12.81	-1.13	-3.00
C-27335	84	13.28	-0.94	-3.62
C-27336	85	13.73	-1.29	-3.95
C-27337	86	14.18	-1.23	-4.26
C-27338	89	15.68	-0.62	-4.00

Lab#	Sample (SEM)	depth (m)	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
C-27339	90	16.28	-0.08	-4.33
C-27340	92	17.35	-0.72	-4.66
C-27345	94	17.87	0.28	-3.01
C-27346	96	18.37	0.19	-2.55
C-27347	97	18.64	-0.08	-3.13
C-27348	98	18.91	0.01	-2.90
C-27349	99	19.21	0.02	-3.47
C-27350	101	20.46	0.06	-3.31
C-27351	102	21.01	0.27	-2.97
C-27352	105	21.86	-0.25	-5.62
C-27353	107	22.36	-0.13	-3.68
C-27354	109	22.91	0.25	-3.50
C-27355	111	23.76	0.33	-3.53
C-27356	112	24.21	0.26	-3.93
C-27357	115	25.76	0.38	-3.50
C-27358	116	26.76	0.44	-3.50
C-27359	117	27.76	0.75	-3.95
C-27360	118	28.51	0.42	-3.87
C-27361	119	29.31	0.51	-3.33

Table 4 – Carbon and oxygen isotope data Pilatus

Lab#	Sample PIL	depth	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
C-29855	7	4.25	1.05	-3.73
C-29854	21	7.55	1.26	-4.02
C-29856	27	9.35	1.35	-3.53
C-29857	28	9.65	1.46	-3.82
C-29858	29	9.95	1.46	-3.76
C-29859	30	10.25	1.38	-3.62
C-29860	31	10.7	1.23	-3.14
C-29861	32	10.9	1.15	-3.82
C-29862	36	15.02	1.35	-3.43
C-29863	42	17.87	1.46	-3.63
C-29864	44	18.79	1.24	-3.34
C-29865	47	20.6	1.15	-3.66
C-29872	57	26.6	1.23	-3.20
C-29873	58	27.8	1.13	-3.25
C-29874	59	28.95	1.04	-3.43
C-29875	60	29.2	0.82	-3.34
C-29876	69	37.2	0.92	-3.05
C-29877	73	41.55	1.41	-2.37
C-29878	76	44.95	1.43	-3.21
C-29879	78	46.75	1.55	-3.21
C-29880	79	47.9	1.44	-3.16
C-29881	82	50.25	1.43	-2.85
C-29882	84	52.2	1.54	-3.14
C-29883	85	52.65	1.35	-3.53
C-29884	87	53.55	1.33	-3.26
C-29885	89	56.05	1.34	-3.13
C-29886	90	56.8	1.25	-3.63
C-29887	91	58.1	1.46	-3.63
C-29888	92	59.1	1.33	-3.05
C-29889	93	60.15	1.32	-2.85
C-29890	95	62.5	0.83	-3.43
C-29891	96	63.45	1.12	-2.95
C-29892	97	64.9	1.02	-3.05
C-29893	98	65.9	0.81	-3.05
C-29894	99	66.9	0.93	-3.34
C-29895	100	67.9	0.92	-3.23
C-29896	102	70.05	0.81	-3.17
C-29897	103	71.05	0.92	-3.05
C-29898	107	74.35	0.57	-1.98
C-29899	109	74.55	0.51	-3.24
C-29900	110	75.65	0.91	-3.05
C-29901	111	76.65	0.72	-3.34
C-29902	114	79.65	0.95	-3.14
C-29903	115	80.65	0.93	-3.34
C-29904	116	81.55	0.70	-2.85
C-29905	118	87.8	0.72	-3.24
C-29906	119	88.8	0.74	-3.42
C-29907	121	91.25	0.51	-3.14
C-29908	123	92.7	0.80	-2.37
C-29913	125	95.2	0.72	-3.43

Lab#	Sample PIL	depth	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
C-29914	127	97.35	0.43	-3.14
C-29915	129	100.45	0.20	-3.24
C-29916	130	101.65	0.42	-3.14
C-29917	134	106	0.51	-2.95
C-29918	135	108	0.40	-2.66
C-29919	136	110	0.61	-2.85
C-29920	137	112.2	0.71	-2.66
C-29921	138	115.1	0.20	-3.04
C-29922	140	118.65	0.42	-3.43
C-29923	141	119	0.73	-3.43
C-29924	142	122	0.83	-3.05
C-29925	143	125	0.81	-2.85
C-29926	144	128	0.84	-3.05
C-29927	145	131	0.74	-3.12

Table 5 – Carbon and oxygen isotope data Terre Masse

Lab#	Sample TM	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
C-25223	112a	1.45	-2.76
C-25224	116a	1.22	-1.57
C-25225	117a	1.35	-2.07
C-25226	120a	1.42	-2.40
C-25227	122a	1.48	-2.64
C-25228	123a	1.49	-2.61
C-25229	125a	1.49	-2.35
C-25231	130a	1.31	-2.84
C-25232	132a	1.34	-2.83
C-25234	141	1.15	-3.54
C-25235	142	1.30	-2.90
C-25236	143	1.44	-2.16
C-25237	144	1.23	-2.94
C-25238	145	1.24	-2.64
C-25239	146	1.21	-2.46
C-25240	147	1.16	-2.47
C-25241	148	1.05	-2.76
C-25242	154	1.13	-2.51
C-25440	155	1.14	-2.28
C-25441	157	1.09	-2.58
C-25442	158	1.03	-2.72
C-25208	1	1.09	-2.11
C-25209	7	1.20	-2.03
C-25210	9	1.17	-2.16
C-25211	11	1.17	-2.26
C-25212	14	1.22	-2.01
C-25213	18	1.27	-2.34
C-25215	25	1.22	-2.36
C-25216	29	1.32	-2.30
C-25217	31	1.38	-2.41
C-25218	33	1.40	-2.22
C-25219	37	1.45	-2.75
C-25220	39	1.47	-2.48
C-25221	41	1.47	-2.63
C-25222	44	1.42	-2.74

Table 6 – Carbon and oxygen isotope data La Charce, Vergons and Angles

Lab #	Sample (LC, VG, AN)	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
C-24373	LC 246	1.24	-1.14
C-25601	249	1.52	-0.97
C-25602	250	1.69	-0.89
C-25603	250	1.71	-0.96
C-25604	251	1.67	-0.61
C-24374	254	1.42	-0.93
C-24375	260	1.27	-0.80
C-24376	265	1.12	-1.03
C-24377	273	1.17	-1.04
C-25605	275	1.22	-1.05
C-24378	276	1.41	-1.08
C-25606	277	1.40	-1.11
C-25607	279	1.35	-0.87
C-25608	280	1.31	-0.90
C-25609	281	1.14	-1.06
C-25610	282	1.41	-1.10
C-24379	283	1.13	-0.96
C-24380	286	0.96	-0.75
C-24381	290	1.01	-1.02
C-24382	294	1.15	-1.00
C-24383	303	1.03	-1.07
C-24384	308	0.88	-0.97
C-24385	314	1.16	-0.90
C-24386	315	1.12	-1.03
C-24387	316	1.06	-0.95
C-24388	317	0.95	-0.90
C-24389	318	0.95	-1.05
C-24390	319	0.92	-0.99
C-24391	320	0.95	-0.93
C-24392	321	0.85	-0.98
C-24393	322	0.70	-0.82
C-24394	323	0.59	-0.84
C-25611	325	0.80	-0.85
C-24395	330	0.88	-1.11
C-25612	331	0.98	-1.23
C-25613	332	0.94	-1.03
C-25614	333	0.93	-1.06
C-24396	334	1.06	-1.08
C-24397	336	1.13	-1.07
C-24398	338	0.86	-0.91
C-24399	341	0.82	-0.94
C-24400	343	0.95	-0.98
C-24401	346	0.67	-1.02
C-24402	347	0.86	-0.90
C-24403	350	0.83	-1.04
C-24404	351	0.80	-1.01
C-24405	357	1.00	-1.06

Lab #	Sample (LC, VG, AN)	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
C-25615	VG -69	1.25	-2.82
C-25616	70	1.19	-3.25
C-25624	74	1.19	-3.11
C-25625	76	1.20	-2.75
C-25626	80	1.21	-2.92
C-25627	80	1.12	-3.14
C-25628	81	1.11	-2.65
C-25629	82	1.07	-2.81
C-25630	84	1.04	-2.51
C-25617	90	1.17	-2.99
C-25618	92	0.96	-3.34
C-25631	96	1.12	-2.75
C-25632	98	1.20	-2.92
C-25619	99	1.16	-3.25
C-25633	100	1.22	-2.79
C-24419	VG 113	1.01	-3.49
C-24420	120	0.90	-3.26
C-24421	125	1.06	-2.90
C-24422	131	1.06	-2.48
C-24423	137	1.03	-2.86
C-24424	142	1.09	-3.38
C-24425	148	1.21	-3.05
C-24426	154	1.27	-3.08
C-24407	AN 10	1.24	-3.17
C-24408	16	1.22	-3.55
C-24409	20	1.25	-3.66
C-24410	26	1.26	-3.92
C-24411	30	1.24	-3.41
C-24416	35	1.30	-3.55
c-24417	40	1.38	-3.35
C-24418	48	1.37	-4.17
C-24427	VG 185	1.35	-3.39
C-24428	187	1.40	-3.73
C-24429	188	1.34	-3.77
C-24430	189	1.39	-3.86
C-24431	190	1.43	-4.12
C-24432	191	1.48	-3.64
C-24433	192	1.46	-3.86
C-24434	193	1.43	-3.93
C-243435	194	1.54	-3.71
C-24436	195	1.55	-3.23
C-24437	201	1.64	-3.93
C-24438	205	1.65	-3.87

Table 7 – Carbon and oxygen isotope data Gorgo a Cerbara

Lab #	Sample GC	Depth (m)	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
C-29487	246	71.18	2.07	-1.87
C-29488	247	71.48	1.92	-1.21
C-29489	248	71.68	1.94	-2.23
C-29490	249	71.88	1.98	-2.35
C-29491	250	72	1.97	-2.32
C-29492	251	72.43	2.02	-2.21
C-29493	252	72.63	1.97	-2.43
C-29494	253	72.78	1.94	-2.07
C-29495	254	72.98	1.94	-2.21
C-29499	258	74.3	1.89	-2.33
C-29500	259	74.5	1.94	-2.29
C-29501	260	74.85	1.83	-2.22
C-29502	261	75.1	1.82	-2.02
C-29503	262	75.3	1.87	-2.39
C-29504	263	75.5	1.84	-2.30
C-29505	265	76.2	1.76	-2.15
C-29506	266	76.5	1.83	-2.11
C-29507	267	76.78	1.76	-2.31
C-29508	268	77.28	1.71	-2.19
C-29509	269	77.68	1.64	-2.46
C-29417	82	82	1.84	-2.18
C-29418	83	83	1.81	-2.39
C-29419	84	84	1.84	-2.26
C-29420	87	87	1.80	-2.43
C-29421	88	88	1.82	-2.32
C-29422	90	90	1.88	-2.14
C-29424	93	93	1.91	-2.13
C-29425	95	95	1.90	-2.30
C-29426	96	96	1.84	-2.34
C-29474	97	97	1.79	-2.20
C-29475	98.5	98.5	1.88	-2.13
C-29476	99	99	1.81	-2.21
C-29477	100.3	100.3	1.89	-1.86
C-29478	101	101	1.96	-2.39
C-29479	102	102	1.85	-2.15
C-29480	104	104	1.81	-2.22
C-29481	105	105	1.92	-1.80
C-29482	106	106	1.80	-2.58
C-29483	107	107	1.94	-2.20
C-29484	108	108	2.01	-1.43
C-29485	109	109	1.92	-2.42
C-29486	110	110	2.02	-2.07

Table 8 – Carbon and oxygen isotope data Monte Acuto

Lab #	Sample MA	depth (m)	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
C-29367	0	0	1.88	-1.98
C-29368	2	2	1.70	-1.74
C-29371	5.9	5.9	1.73	-1.80
C-29372	6.8	6.8	1.83	-1.43
C-29373	8	8	1.88	-1.68
C-29374	10	10	1.87	-1.87
C-29375	10.75	10.75	1.79	-1.83
C-29376	11	11	1.82	-1.83
C-29377	11.5	11.5	1.90	-1.42
C-29431	12	12	1.87	-1.80
C-29378	14	14	1.88	-1.43
C-29379	15	15	1.82	-1.81
C-29380	16	16	1.83	-1.85
C-29381	17	17	1.94	-1.28
C-29382	18	18	2.00	-1.72
C-29432	19	19	1.99	-1.58
C-29383	20	20	2.00	-1.79
C-29433	21	21	2.05	-1.61
C-29434	22	22	2.08	-1.34
C-29435	23	23	2.01	-1.67
C-29436	24	24	2.10	-1.40
C-29437	25	25	2.12	-1.74
C-29438	26	26	2.15	-1.80
C-29439	27	27	2.08	-2.02
C-29440	28	28	2.02	-2.05
C-29441	29	29	2.07	-1.88
C-29442	30	30	2.00	-2.14
C-29443	31	31	2.16	-1.58
C-29444	32	32	2.20	-1.93
C-29445	33	33	2.15	-1.96
C-29446	34	34	2.06	-1.99
C-29447	35	35	2.14	-1.68
C-29448	36	36	2.09	-1.86
C-29449	37	37	2.21	-1.73
C-29450	40	40	2.31	-1.98
C-29451	41	41	2.32	-1.80
C-29452	42	42	2.40	-1.72
C-29453	43	43	2.41	-1.71
C-29454	43.3	43.3	2.36	-1.56
C-29455	44	44	2.40	-1.67
C-29456	45	45	2.43	-2.06
C-29457	46	46	2.44	-2.05
C-29458	47	47	2.42	-1.98
C-29459	48	48	2.39	-1.78
C-29460	49	49	2.29	-2.04
C-29461	50.2	50.2	2.39	-1.87

Lab #	Sample MA	depth (m)	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
C-29462	51	51	2.54	-0.25
C-29463	52	52	2.47	-1.73
C-29388	52.5	52.5	2.63	-1.79
C-29464	54	54	2.42	-0.42
C-29465	55	55	2.52	-1.77
C-29466	56	56	2.47	-2.08
C-29467	57	57	2.47	-2.20
C-29468	58	58	2.61	-1.85
C-29469	59	59	2.63	-2.12
C-29389	60	60	2.78	-1.93
C-29390	61	61	2.84	-1.80
C-29391	62	62	2.78	-1.81
C-29392	63	63	2.87	-1.86
C-29393	64	64	2.83	-1.58
C-29394	65	65	2.81	-1.90
C-29395	66	66	3.00	-1.72
C-29396	67	67	3.02	-1.81
C-29397	68	68	3.23	-1.53
C-29398	69	69	3.10	-1.77
C-29399	70	70	3.09	-1.95
C-29400	71	71	3.06	-2.21
C-29401	72	72	3.35	-1.74
C-29402	73	73	3.22	-1.78
C-29403	74	74	3.22	-2.04
C-29404	75	75	3.29	-2.05
C-29405	76	76	3.32	-1.96
C-29406	77	77	3.33	-2.17
C-29407	78	78	3.26	-2.14
C-29408	79	79	3.10	-2.29
C-29409	80	80	3.08	-2.20
C-29410	81	81	3.08	-1.90
C-29411	82	82	3.12	-2.15
C-29412	83	83	3.06	-2.47
C-29413	84	84	3.11	-2.19
C-29414	85	85	3.05	-2.07
C-29415	86	86	3.12	-1.73

Table 9 – XRD Bulk rock La Charce, Vergons and Angles

Sample	Phyllosilic	Quartz	Calcite	Phyllo	Quartz	Calcite (%)	Indosed	Ca/Ph+Qz
	cps	cps	cps	(%)	(%)		(%)	
LC 251A	1363.8	17556	237738	9.21	3.73	87.07	0	6.73
LC 254A	1095.6	26646	250344	7.59	5.81	82.6	0	6.16
LC 260A	1108.8	18354	264102	7.94	4.14	87.93	0	7.28
LC 265A	921.6	20046	248226	6.37	4.36	89.28	0	8.32
LC 273A	940.2	17574	252108	6.55	3.86	89.59	0	8.61
LC 276A	1461	15294	204054	9.2	3.03	70.11	17.67	5.73
LC 277A	1072.8	14946	222894	7.02	3.08	79.61	10.29	7.88
LC 283A	1224	15954	242172	8.35	3.42	88.22	0	7.50
LC 286A	1050	12882	250086	7.29	2.82	89.9	0	8.89
LC 290A	764.4	14922	244236	5.23	3.22	91.32	0.22	10.81
LC 294A	960	11418	217512	6.22	2.33	76.88	14.57	8.99
LC 303A	1235.4	21648	265038	8.85	4.89	86.26	0	6.28
LC 308A	685.2	13032	211860	4.38	2.63	73.99	19	10.55
LC 314A	828	12864	220980	5.4	2.64	78.65	13.31	9.78
LC 321A	1048.2	23682	262098	7.46	5.31	87.24	0	6.83
LC 325A	623.4	14388	223362	4.08	2.97	79.87	13.08	11.33
LC 334A	720	10968	150888	4.1	1.97	46.86	47.08	7.72
LC 338A	830	16853	194688	5.13	3.28	65.62	25.97	7.80
LC 343A	1463.4	26160	254664	10.23	5.76	84.01	0	5.25
LC 346A	1135.8	17808	229284	7.53	3.72	82.96	5.8	7.37
LC 347A	914.4	21750	259002	6.46	4.84	88.69	0	7.85
LC 348A	751.2	12954	131046	4.12	2.24	39.26	54.38	6.17
LC 350A	995.4	22440	229734	6.6	4.68	83.12	5.6	7.37
VG 93A	1219.8	34098	231204	8.09	7.12	83.71	1.08	5.50
VG 95A	1197	25044	210750	7.62	5.02	73.24	14.12	5.79
VG 99A	567	28446	201498	3.54	5.59	68.67	22.2	7.52
VG 101A	877.8	15468	170724	5.18	2.87	54.95	37	6.83
VG 113A	1156.2	36660	245190	7.9	7.89	84.21	0	5.33
VG 120A	972.6	24594	189276	5.93	4.72	63.01	26.33	5.92
VG 125A	1861.2	37284	237006	12.49	7.88	79.63	0	3.91
VG 131A	1182.6	22854	236904	7.96	4.84	87.03	0.16	6.80
VG 186A	709.2	21204	256038	4.98	4.69	90.33	0	9.34
VG 191A	1184.4	21726	254940	8.3	4.79	86.91	0	6.64
VG 201A	1493.4	20004	228216	9.87	4.16	82.34	3.62	5.87
VG 205A	772.8	19254	264912	5.54	4.35	90.11	0	9.11

Table 10 – XRD Bulk rock La Charce, Vergons and Angles (2-16 μm)

SAMPLE	Smectite	M001	M002	Qtz	K001/C002	K001	K002
LC 251A	8747	24950	13412	40686	6856	2588	3183
LC 254A	11974	18217	11907	55784	0	1973	0
LC 260A	10992	32984	18247	42563	9458	3721	3592
LC 265A	5270	25475	18004	57461	3992	0	0
LC 273A	16221	36150	23277	41562	8490	2908	2685
LC 276A	12279	43809	25683	39510	9453	2338	2091
LC 277A	13368	25832	21025	40990	9382	2345	2269
LC 283A	14029	41239	24471	44592	9399	3703	3120
LC 286A	4442	30988	17030	20810	5507	3071	2821
LC 290A	9625	42709	20691	33603	4755	1604	1993
LC 294A	6829	49678	23192	36271	0	4065	1572
LC 303A	20602	32687	19496	39393	6994	2201	1535
LC 308A	12964	36499	19527	38424	0	2906	1528
LC 314A	11538	4366	24771	40982	6943	1930	1553
LC 321A	9085	20474	16934	43304	5563	2147	2300
LC 325A	8232	42759	23961	46019	6761	2625	1980
LC 334A	3489	49861	22499	35144	4285	1478	1946
LC 341A	6001	33010	15241	35251	6193	737	600
LC 343A	5902	38334	20484	41265	7654	1475	960
LC 346A	5963	43235	16316	35919	5801	1912	1740
LC 347A	10321	36942	22057	41638	7005	1938	1592
LC 348A	6818	36227	7270	19421	7270	1782	1500
LC 350A	7112	40513	22072	43712	7183	2124	2040
VG 93A	5278	12964	9265	61546	16277	0	0
VG 95A	4932	9595	7061	60231	10957	1970	960
VG 99A	1477	4514	4247	59553	8289	0	0
VG 101A	3699	15499	11504	66837	12190	0	0
VG 113A	6294	13236	11512	53461	6636	0	0
VG 120A	6852	20757	17663	69346	12079	0	0
VG 125A	6678	12658	9962	60839	11428	0	0
VG 131A	7253	27311	21885	67019	8516	1039	600
VG 186A	2498	28187	15587	58321	3775	1079	1680
VG 191A	5280	30763	18597	40850	3952	0	0
VG 201A	7343	25004	16217	56084	3744	1479	1920
VG 205A	3388	32212	20194	75216	0	1535	1620

C002	C004	Feldspar	Pyrite	M004	M005	Plagioclase
4268	5248	3149	2111	8607	8607	5758
3244	4140	3582	0	1787	8310	6436
5737	5539	3785	41271	3283	11570	6688
3992	4800	3218	3559	2364	11455	13908
5582	5154	2670	18842	3342	10385	9019
7115	6365	4330	19818	3609	12702	9301
7037	6810	4781	15203	2658	10300	7727
5696	4800	3683	26219	3946	14274	9462
2436	2238	2272	36657	2878	9461	9971
3151	3915	3052	19646	3226	11250	8128
4445	4453	2005	3374	4366	13359	10590
4793	3343	4122	15485	2786	10468	10226
4451	2688	2528	15773	2736	9816	12510
5013	4035	3802	34987	3735	13073	8147
3416	3660	2298	15984	2262	10180	5195
4136	3120	3787	9149	4182	12190	7204
2807	3696	4274	0	3548	13576	7427
5456	4440	2146	9181	2303	8696	4686
6179	4020	1855	8640	4259	13431	4414
3889	3540	1696	10577	2418	9377	8287
5067	4162	3407	14135	3362	13322	4554
5488	4620	5545	8167	3899	10854	5001
5059	4860	3888	8422	3319	14335	3850
16277	8100	2270	0	2722	5622	14789
8987	4380	0	0	2502	5357	13746
8289	4500	0	0	2005	2917	3553
12190	4860	1582	1578	2669	8630	25103
6636	4080	2935	0	13566	6872	13997
12079	5432	2352	0	3195	12058	27928
11428	2994	0	0	2132	6145	9276
7477	4320	2983	0	3867	16990	35552
2696	4200	0	0	2610	9331	78094
3952	3540	1912	0	3328	10454	43015
2265	2940	1872	0	3101	9196	60629
2777	1620	1615	0	3901	11936	93576

Py/Qtz	Qtz 16mu/Qtz <2mu	Illite (%)	Ka (%)	Chl (%)	Fs/Pl	Ka/Mica
0.052	2.86	78.44	8.14	13.42	0.55	0.10
0.000	2.31	77.74	8.42	13.84	0.56	0.11
0.970	2.90	77.72	8.77	13.52	0.57	0.11
0.062	1.95	86.45	0.00	13.55	0.23	0.00
0.453	2.71	80.98	6.51	12.50	0.30	0.08
0.502	3.09	82.25	4.39	13.36	0.47	0.05
0.371	3.90	73.36	6.66	19.98	0.62	0.09
0.588	2.15	81.44	7.31	11.25	0.39	0.09
1.762	2.50	84.91	8.41	6.68	0.23	0.10
0.585	2.44	89.98	3.38	6.64	0.38	0.04
0.093	1.66	85.37	6.99	7.64	0.19	0.08
0.393	4.52	82.37	5.55	12.08	0.40	0.07
0.410	2.10	83.22	6.63	10.15	0.20	0.08
0.854	1.47	38.61	17.06	44.33	0.47	0.44
0.369	2.36	78.63	8.25	13.12	0.44	0.10
0.199	14.39	86.35	5.30	8.35	0.53	0.06
0.000	1.72	92.09	2.73	5.18	0.58	0.03
0.260	1.92	84.20	1.88	13.92	0.46	0.02
0.209	2.07	83.36	3.21	13.44	0.42	0.04
0.294	1.65	88.17	3.90	7.93	0.20	0.04
0.339	2.22	84.06	4.41	11.53	0.75	0.05
0.421	0.98	83.29	4.10	12.62	1.11	0.05
0.193	2.03	84.94	4.45	10.61	1.01	0.05
0.000	2.60	44.34	0.00	55.66	0.15	0.00
0.000	3.14	46.69	9.58	43.73	0.00	0.21
0.000	2.63	35.26	0.00	64.74	0.00	0.00
0.024	3.00	55.98	0.00	44.02	0.06	0.00
0.000	2.13	66.61	0.00	33.39	0.21	0.00
0.000	3.64	63.21	0.00	36.79	0.08	0.00
0.000	2.97	52.55	0.00	47.45	0.00	0.00
0.000	4.14	76.23	2.90	20.87	0.08	0.04
0.000	2.81	88.19	3.37	8.44	0.00	0.04
0.000	1.30	88.62	0.00	11.38	0.04	0.00
0.000	3.29	86.98	5.15	7.88	0.03	0.06
0.000	3.31	88.19	4.20	7.60	0.02	0.05

Table 11 – XRD Bulk rock La Charce, Vergons and Angles (<2 µm)

SAMPLE	Smectite cps	M001 cps	M002 cps	Qtz cps	K001/C002	K002 cps	C004 cps	K001 cps	C002 cps	Smectite %	Illite %	Kaolinite %	Chlorite %	Ka/Illite
LC 251A	67302	22988	7874	14209	13831	3696	5366	5641	8190	64.64	22.08	5.42	7.87	0.25
LC 254A	102969	19061	6698	24179	8460	0	1060	0	8460	78.91	14.61	0.00	6.48	0.00
LC 260A	82858	30853	12321	14698	15312	6180	2400	11029	4283	64.22	23.91	8.55	3.32	0.36
LC 265A	97324	19416	7175	29490	3654	0	2760	0	3654	80.84	16.13	0.00	3.04	0.00
LC 273A	45104	20467	8835	15339	9748	3881	4745	4386	5362	59.88	27.17	5.82	7.12	0.21
LC 276A	39130	14594	4932	12792	9393	2760	4200	3725	5668	62.00	23.12	5.90	8.98	0.26
LC 277A	55208	20444	6145	10499	11741	3427	4562	5036	6705	63.17	23.39	5.76	7.67	0.25
LC 283A	90483	23046	9144	20693	12890	2580	5220	4264	8626	71.57	18.23	3.37	6.82	0.19
LC 286A	14279	16778	6351	8327	5134	1920	2220	2381	2753	39.45	46.36	6.58	7.61	0.14
LC 290A	36053	13115	5109	13776	3534	1320	2640	1178	2356	68.41	24.89	2.24	4.47	0.09
LC 294A	79591	18293	7575	21823	3512	2700	0	3512	0	78.50	18.04	3.46	0.00	0.19
LC 303A	17369	11134	4741	8718	3772	3000	3120	1849	1923	53.82	34.50	5.73	5.96	0.17
LC 308A	52399	18989	6599	18264	4495	1860	2460	1935	2560	69.05	25.02	2.55	3.37	0.10
LC 314A	83496	21471	7884	27866	6087	1380	3240	1818	4269	75.19	19.33	1.64	3.84	0.08
LC 321A	82028	20455	8114	18384	8190	1020	3960	1677	6513	74.12	18.48	1.52	5.88	0.08
LC 325A	80536	20142	8165	3198	6760	1560	3840	1953	4807	74.96	18.75	1.82	4.47	0.10
LC 334A	31082	17232	7237	20377	3173	1680	1740	1559	1614	60.37	33.47	3.03	3.14	0.09
LC 338A	56868	21249	9503	18333	10945	2220	4200	3785	7160	63.85	23.86	4.25	8.04	0.18
LC 341A	33438	16008	5648	19905	6573	1680	2460	2667	3906	59.69	28.58	4.76	6.97	0.17
LC 343A	81700	17467	7664	21720	8992	1560	4380	2362	6630	75.54	16.15	2.18	6.13	0.14
LC 346A	36865	15506	6557	18776	6656	2816	2846	3310	3346	62.45	26.27	5.61	5.67	0.21
LC 347A	49511	21159	13148	19846	9492	0	0	0	0	70.06	29.94	0.00	0.00	0.00
LC 348A	44370	11309	6995	21505	10308	1860	4860	2853	7455	67.24	17.14	4.32	11.30	0.25
LC 350A	60164	19061	7588	23715	11506	0	1500	0	11506	66.31	21.01	0.00	12.68	0.00
VG 93A	8573	12482	6165	19204	20904	3120	10860	4665	16239	20.43	29.75	11.12	38.70	0.37
VG 95A	17731	14029	5800	22667	18862	0	9660	0	18862	35.03	27.71	0.00	37.26	0.00
VG 99A	13317	16813	6797	22298	18612	0	8760	0	18612	27.32	34.49	0.00	38.18	0.00
VG 101A	18433	16562	6259	25133	22860	0	9356	0	22860	31.86	28.63	0.00	39.51	0.00
VG 113A	19644	18667	3470	19057	9402	2160	3780	3419	5983	41.17	39.12	7.17	12.54	0.18
VG 120A	27993	26324	10398	20519	26677	0	9540	0	26677	34.56	32.50	0.00	32.94	0.00
VG 125A	19251	17096	7009	16178	13191	0	5280	0	13191	38.86	34.51	0.00	26.63	0.00
VG 131A	32679	24240	8237	20727	11245	0	3960	0	11245	47.94	35.56	0.00	16.50	0.00
VG 186A	11511	9664	3872	31489	5710	1080	2340	1803	3907	42.82	35.95	6.71	14.53	0.19
VG 191A	9966	13058	5426	17047	2871	0	0	0	0	43.29	56.71	0.00	0.00	0.00
VG 201A	34274	13551	5785	22724	4398	0	0	0	0	71.67	28.33	0.00	0.00	0.00
VG 205A	32676	14736	5892	32325	3226	600	1500	922	2304	64.53	29.10	1.82	4.55	0.06

Table 12 – AAS Pilatus

Samples	CaCO ₃ (%)	Ca (ppm)	Fe (ppm)	Sr (ppm)	Mn (ppm)	Ca/Sr
PIL 7	61	242773	3018	722	73	0.00298
PIL 21	67	268351	2074	820	70	0.00305
PIL 30	58	233393	997	928	70	0.00398
PIL 31	61	244831	242	947	53	0.00387
PIL 36	59	235452	712	984	65	0.00418
PIL 44	58	233563	0	1093	25	0.00468
PIL 50	61	242428	217	986	41	0.00407
PIL 59	64	256406	559	1096	54	0.00428
PIL 62	56	225574	735	1574	84	0.00698
PIL 65	67	269040	1073	1047	57	0.00389
PIL 68	66	262948	302	976	43	0.00371
PIL 74	73	293141	235	975	58	0.00333
PIL 76	64	254806	728	1022	51	0.00401
PIL 80	62	246900	0	1046	19	0.00424
PIL 84	70	280400	629	1028	67	0.00367
PIL 85	55	220653	154	1177	25	0.00534
PIL 88	62	248873	0	962	22	0.00386
PIL 91	69	276568	539	1026	64	0.00371
PIL 92	66	263002	279	1016	53	0.00386
PIL 96	55	218433	1189	742	64	0.00340
PIL 100	70	278003	411	473	54	0.00170
PIL 102	75	299835	938	412	66	0.00137
PIL 104	70	278297	2835	399	71	0.00143
PIL 107	80	320937	2024	298	93	0.00093
PIL 109	51	204681	18101	563	35	0.00275
PIL 111	63	253897	1249	553	60	0.00218
PIL 114	58	233170	1020	532	67	0.00228
PIL 116	67	267998	1010	394	72	0.00147
PIL 121	52	207666	873	525	25	0.00253
PIL 125	62	248139	1522	549	41	0.00221
PIL 127	70	280617	819	519	53	0.00185
PIL 135	64	254861	716	678	49	0.00266
PIL 138	71	283257	2228	571	70	0.00202
PIL 142	90	358180	3242	468	29	0.00131
PIL 145	96	383494	1112	360	25	0.00094

Table 13 – AAS Core 607

Sample	depth	CaCO ₃ (%)	Ca (ppm)	Sr (ppm)	Mg (ppm)	Mn (ppm)	Ca/Sr
607-63	2	67.5	269819	521	12135	380	0.00193
607-83	9.2	60.7	242702	691	7443	122	0.00285
607-97	15.8	76.6	306219	396	7616	21	0.00129
607-112	22.4	73.6	294447	496	10338	105	0.00168
607-132	29.2	91.8	367024	245	1575	207	0.00067
607-136	31.2	90.8	363217	227	1916	220	0.00062
607-140	33.2	80.5	322144	452	2501	361	0.00140
607-143	34.4	81.3	325121	437	3185	449	0.00134
607-145	35.6	81.1	324574	413	3053	434	0.00127
607-151	38.6	89.4	357621	268	1279	562	0.00075
607-153	40	91.2	364806	203	957	586	0.00056
607-155	40.8	82.3	329304	199	1219	560	0.00060
607-157	41.8	80.6	322434	163	698	566	0.00050
607-159	42.4	94.0	376133	131	95	340	0.00035
607-160	43	95.2	380690	99	167	354	0.00026
607-162	44.2	92.7	370668	167	628	302	0.00045
607-166	45.8	95.8	383067	158	162	336	0.00041
607-187	54.8	97.3	389144	72	-	508	0.00018
607-193	57.6	97.4	389779	169	-	426	0.00043
607-203	63	97.1	388489	169	40	395	0.00043

Table 14 – AAS Talegg

Sample	CaCO ₃ (%)	Ca (ppm)	Fe (ppm)	Sr (ppm)	Mn (ppm)	Sr/Ca
TAL 4	95.5	382023	1783	287	211	0.00075
TAL 13	97.8	391038	2430	314	289	0.00080
TAL 17	97.2	388738	2980	376	251	0.00097
TAL 19	98.9	395630	0	411	43	0.00104
TAL 25	96.3	385350	194	352	65	0.00091
TAL 29	98.4	393609	0	371	51	0.00094
TAL 38	98.1	392483	0	379	40	0.00097
TAL 42	99.0	395929	0	450	34	0.00114
TAL 43	98.3	393251	0	396	37	0.00101
TAL 44	98.3	393386	0	366	31	0.00093
TAL 45	96.8	387321	0	378	30	0.00098
TAL 46	96.8	387280	0	390	34	0.00101
TAL 47	98.8	395209	0	341	36	0.00086
TAL 52	58.2	232784	1559	808	98	0.00347
TAL 57	63.0	251811	737	761	108	0.00302
TAL 58	71.5	286082	0	741	95	0.00259
TAL 68	58.5	234083	1591	645	101	0.00275
TAL 71	48.8	195171	2002	539	108	0.00276
TAL 72	62.2	248642	1089	481	92	0.00194
TAL 74	65.8	263154	1822	449	92	0.00171
TAL 75	63.5	253834	1949	436	94	0.00172
TAL 77	57.0	228179	9284	539	103	0.00236
TAL 80	59.9	239413	5412	366	110	0.00153
TAL 81	61.0	243881	4406	376	106	0.00154
TAL 85	66.2	264726	7769	405	97	0.00153
TAL 90	63.9	255569	745	431	78	0.00169
TAL 91	76.7	306685	924	401	61	0.00131
TAL 92	61.5	245978	1324	383	58	0.00156
TAL 101	61.4	245480	1385	443	62	0.00181
TAL 102	97.1	388442	1850	344	224	0.00089
TAL 107	72.6	290418	1560	416	73	0.00143
TAL 108	74.9	299424	2225	381	75	0.00127
TAL 109	75.1	300295	2916	364	79	0.00121
TAL 115	83.5	333879	5821	499	111	0.00150
TAL 116	81.8	327137	2114	502	174	0.00154

Table 15 – Sr-isotope data bulk rock La Charce, Vergons and Angles

Samples #	Ammonite Zone	$^{87}\text{Sr}/^{86}\text{Sr}$	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
LC 254	<i>Radiatus</i>	0.707371	1.42	-0.93
LC 260	<i>Radiatus</i>	0.707375	1.27	-0.80
LC 265	<i>Radiatus</i>	0.707368	1.12	-1.03
LC 273	<i>Radiatus</i>	0.707425	1.17	-1.04
LC 276	<i>Loryi</i>	0.707429	1.41	-1.08
LC 286	<i>Loryi</i>	0.707410	0.96	-0.75
LC 290	<i>Loryi</i>	0.707332	1.01	-1.02
LC 293	<i>Loryi</i>	0.707421		
LC 294	<i>Nodosoplicatum</i>	0.707438	1.15	-1.00
LC 303	<i>Nodosoplicatum</i>	0.707501	1.03	-1.07
LC 308	<i>Nodosoplicatum</i>	0.707372	0.88	-0.97
LC 314	<i>Nodosoplicatum</i>	0.707376	1.16	-0.90
LC 316	<i>Nodosoplicatum</i>	0.707373	1.06	-0.95
LC 318	<i>Nodosoplicatum</i>	0.707446	0.95	-1.05
LC 320	<i>Nodosoplicatum</i>	0.707473	0.95	-0.93
LC 321	<i>Nodosoplicatum</i>	0.707407	0.85	-0.98
LC 322	<i>Nodosoplicatum</i>	0.707401	0.70	-0.82
LC 323	<i>Sayni</i>	0.707572	0.59	-0.84
LC 334	<i>Sayni</i>	0.707407	1.06	-1.08
LC 336	<i>Sayni</i>	0.707416	1.13	-1.07
LC 338	<i>Sayni</i>	0.707395	0.86	-0.91
LC 343	<i>Sayni</i>	0.707410	0.95	-0.98
LC 346	<i>Sayni</i>	0.707540	0.67	-1.02
LC 348	<i>Sayni</i>	0.707438	0.92	-1.02
LC 350	<i>Sayni</i>	0.707407	0.83	-1.04
LC 357	<i>Sayni</i>	0.707483	1.00	-1.06
VG 113	<i>Ligatus</i>	0.707471	1.01	-3.49
VG 120	<i>Ligatus</i>	0.707546	0.90	-3.26
VG 125	<i>Ligatus</i>	0.707494	1.06	-2.90
VG 131	<i>Ligatus</i>	0.707497	1.06	-2.48
VG 137	<i>Ligatus</i>	0.707461	1.03	-2.86
VG 142	<i>Ligatus</i>	0.707511	1.09	-3.38
VG 148	<i>Ligatus</i>	0.707521	1.38	-3.35
AN 16	<i>Balearis</i>	0.707502	1.21	-3.05
AN 20	<i>Balearis</i>	0.707494	1.22	-3.55
AN 26	<i>Balearis</i>	0.707514	1.25	-3.66
AN 30	<i>Balearis</i>	0.707570	1.26	-3.92
AN 40	<i>Balearis</i>	0.707481	1.24	-3.41
AN 48	<i>Angulicostata</i>	0.707687	1.37	-4.17
VG 185	<i>Angulicostata</i>	0.707695	1.35	-3.39
VG 187	<i>Angulicostata</i>	0.707450	1.40	-3.73
VG 188	<i>Angulicostata</i>	0.707481	1.34	-3.77
VG 190	<i>Angulicostata</i>	0.707478	1.43	-4.12
VG 192	<i>Angulicostata</i>	0.707537	1.46	-3.86
VG 194	<i>Angulicostata</i>	0.707635	1.54	-3.71
VG 195	<i>Angulicostata</i>	0.707516	1.55	-3.23
VG 205	<i>Angulicostata</i>	0.707544	1.65	-3.87

Table 16 – Sr-isotope data belemnites La Charce, Vergons and Angles

Sample #	Ammonite Zone	$^{87}\text{Sr}/^{86}\text{Sr}$	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Species	Sr (ppm)	Fe (ppm)	Mg (ppm)	Mn (ppm)
LC 256c	<i>Radiatus</i>	0.707373	-0.05	0.30	<i>Indet.</i>	1638	51	4883	10
LC 258c	<i>Radiatus</i>	0.707395	0.17	-0.28	<i>Pseudobelus brevis</i>	1196	355	2614	19
LC 262c	<i>Radiatus</i>	0.707385	0.25	-0.19	<i>Duvalia spp.</i>	1210	1375	2549	49
LC 264c	<i>Radiatus</i>	0.707410	0.08	0.08	<i>Indet.</i>				
LC 272c	<i>Radiatus</i>	0.707440	0.16	0.09	<i>Indet.</i>	1599	59	3719	12
LC 284c	<i>Loryi</i>	0.707406	0.05	0.59	<i>Pseudobelus brevis</i>	770	102	2810	18
LC 286c	<i>Loryi</i>	0.707386	-0.56	0.05	<i>Indet.</i>	1310	838	3044	58
LC 294c	<i>Nodosoplicatum</i>	0.707390	0.33	0.02	<i>Pseudobelus brevis</i>	709	72	2573	12
LC 301c	<i>Nodosoplicatum</i>	0.707408	0.31	0.10	<i>Indet.</i>	1129	404	2988	21
LC 303c	<i>Nodosoplicatum</i>	0.707439	0.08	-0.46	<i>Hibolithes spp.</i>				
LC 313c	<i>Nodosoplicatum</i>	0.707454	-0.27	0.33	<i>Hibolithes spp.</i>	1407	64	3907	64
LC 315c	<i>Nodosoplicatum</i>	0.707419	0.11	0.02	<i>Hibolithes spp.</i>	1377	46	3277	11
LC 316c	<i>Nodosoplicatum</i>	0.707406	-0.09	0.11	<i>Indet.</i>	1194	725	3162	73
LC 326c	<i>Sayni</i>	0.707455	0.32	0.03	<i>Indet.</i>				
VG 76c	<i>Sayni</i>	0.707437	0.38	-0.20	<i>Hibolithes spp.</i>	1078	150	2630	12
LC 329c	<i>Sayni</i>	0.707444	-0.62	-0.07	<i>Pseudobelus brevis</i>	1212	1434	2525	44
VG 79c	<i>Sayni</i>	0.707451	-0.01	-0.15	<i>Indet.</i>	1724	70	3952	13
VG 82c	<i>Sayni</i>	0.707436	-0.32	-0.53	<i>Indet.</i>	1314	121	2727	10
VG 91C	<i>Sayni</i>	0.707459	0.07	-0.53	<i>Indet.</i>	1446	1031	4284	135
VG 99C	<i>Ligatus</i>	0.707450	-0.53	-0.63	<i>Hibolithes spp.</i>	1353	106	3515	23
VG 109c	<i>Ligatus</i>	0.707444	-0.24	-1.90	<i>Indet.</i>	1359	6496	4239	10
VG 117c	<i>Ligatus</i>	0.707444	-0.59	-0.38	<i>Indet.</i>	1574	41	3718	10
VG 128c	<i>Ligatus</i>	0.707492	-0.07	-0.47	<i>Indet.</i>	1514	294	3729	11
VG 130c	<i>Ligatus</i>	0.707472	-0.33	-0.24	<i>Hibolithes spp.</i>				
VG 133c	<i>Ligatus</i>	0.707436	-0.59	-0.16	<i>Hibolithes spp.</i>	1393	71	3676	15
AN 3c	<i>Ligatus</i>	0.707472							
VG 150c	<i>Ligatus</i>	0.707465	-0.31	-0.24	<i>Hibolithes spp.</i>				
AN 8C	<i>Balearis</i>	0.707443	-0.17	-0.40	<i>Hibolithes spp.</i>	1490	98	3943	10
AN 9C	<i>Balearis</i>	0.707442	0.73	-0.28	<i>Hibolithes spp.</i>	1588	67	4405	10
AN 15C	<i>Balearis</i>	0.707496	-0.42	-0.16	<i>Duvalia spp.</i>	635	799	3949	219
AN 20c	<i>Balearis</i>	0.707475	0.28	-0.32	<i>Indet.</i>	1199	346	2931	12
AN 34C	<i>Balearis</i>	0.707473	0.34	-0.19	<i>Indet.</i>	1297	56	2961	11
VG 181c	<i>Angulicostata</i>	0.707441	0.49	-1.02	<i>Pseudobelus brevis</i>	1464	29	3636	10
VG 197c	<i>Angulicostata</i>	0.707479	-0.83	-0.63	<i>Indet.</i>	1175	76	2951	13

Table 17 – Rockeval6 data for Core 607

Sample	TOC (%)	MINC (%)	Tmax	PC (%)	RC (%)	HI	OICO2	OIRE6	S1	S2
F607-60	0.1	10.2	423	0.01	0.09	0	800	685	0	0
F607-63	0.34	8.6	421	0.03	0.31	53	150	146	0.05	0.18
F607-67	0.45	8.5	422	0.03	0.42	47	196	171	0	0.21
F607-73	0.2	10.3	417	0.01	0.19	25	245	227	0	0.05
F607-77	0.36	8.9	423	0.02	0.34	39	200	168	0	0.14
F607-83	0.44	7.4	423	0.03	0.41	45	184	160	0	0.2
F607-85	0.47	7.1	416	0.02	0.45	36	306	251	0	0.17
F607-90	0.44	7.7	422	0.03	0.41	52	116	113	0	0.23
F607-94	0.56	7.6	424	0.03	0.53	52	127	117	0	0.29
F607-98	0.54	9.1	422	0.03	0.51	39	293	232	0	0.21
F607-100	0.43	7.1	422	0.03	0.4	49	149	142	0.01	0.21
F607-104	0.48	8.5	422	0.02	0.46	38	223	182	0	0.18
F607-112	0.23	8.3	335	0.01	0.22	35	161	139	0	0.08
F607-116	0.16	10.3	419	0	0.16	0	263	223	0	0
F607-119	0.04	9.5	-40	0	0.04	0	1825	1427	0.01	0
F607-122	0.03	10.1	-40	0	0.03	0	833	606	0	0
F607-124	0.04	9.9	-40	0	0.04	0	750	588	0	0
F607-127	0.04	9.9	-40	0	0.04	0	350	326	0	0
F607-130	0.04	9.8	-40	0	0.04	0	275	200	0	0
F607-132	0.04	9.4	-40	0	0.04	0	750	560	0	0
F607-136	0.04	10.2	258	0	0.04	0	1275	927	0	0
F607-1392	0.04	8.9	600	0	0.04	25	1400	1032	0	0
F607-1395	0.03	9.3	576	0	0.03	67	900	655	0.01	0.01
F607-140	0.04	8.9	594	0	0.04	100	625	469	0.01	0.02
F607-143	0.04	9.1	597	0	0.04	75	775	564	0.01	0.02
F607-145	0.04	9.1	597	0	0.04	50	950	691	0.01	0.01
F607-147	0.04	8.9	600	0	0.04	25	900	655	0	0
F607-149	0.04	8.8	591	0	0.04	50	750	545	0	0.01
F607-151	0.04	9	589	0	0.04	50	600	436	0.01	0.01
F607-153	0.06	8.8	594	0.01	0.05	117	17	31	0.01	0.04
F607-155	0.03	8.8	596	0	0.03	67	733	533	0.01	0.01
F607-155	0.06	10.2	601	0	0.06	33	717	521	0.01	0.01
F607-157	0.04	9.1	440	0	0.04	50	700	523	0.01	0.01
F607-159	0.03	8.9	256	0	0.03	0	600	436	0.01	0
F607-162	0.04	10	255	0	0.04	0	375	273	0.01	0
F607-164	0.04	9.9	596	0	0.04	25	225	164	0.01	0.01
F607-166	0.03	8.9	491	0	0.03	0	267	232	0.01	0
F607-168	0.02	8.7	262	0	0.02	50	0	0	0.01	0
F607-170	0.04	10.1	256	0	0.04	0	225	164	0.01	0
F607-171	0.05	8.6	601	0	0.05	20	20	26	0	0
F607-176	0.04	10	587	0	0.04	0	350	255	0.01	0
F607-178	0.02	8.8	603	0	0.02	0	0	29	0	0
F607-180	0.08	10	305	0.01	0.07	50	625	469	0.01	0.03
F607-185	0.05	9.7	260	0	0.05	0	20	26	0	0
F607-190	0.05	9.2	258	0	0.05	0	0	0	0	0
F607-200	0.05	9.5	495	0	0.05	0	0	34	0.01	0
F607-225	0.06	10.8	519	0	0.06	50	0	0	0	0.01
F607-230	0.04	8.1	-41	0	0.04	0	0	14	0	0
standard1	3.01	4.4	420	0.84	2.17	319	44	41	0.22	9.6

Table 18 – RockEval6 Pilatus

Sample	TOC [%]	MINC [%]	Tmax [°C]	HI [mg HC/g TOC]	OI [mg CO2/g TOC]	S2 [mg HC/g]	S1 [mg HC/g]
PIL2	0.17	5.65	450.33	35	289	0.06	0.00
PIL9	0.22	6.99	450.30	122	99	0.27	0.03
PIL11	0.20	7.10	446.70	157	181	0.31	0.05
PIL12	0.21	6.70	446.90	122	152	0.26	0.05
PIL13	0.27	6.11	441.00	144	208	0.39	0.05
PIL16	0.18	6.78	441.10	57	200	0.10	0.02
PIL18	0.20	7.76	447.17	141	185	0.28	0.03
PIL20	0.19	6.95	446.00	115	168	0.21	0.03
PIL35	0.25	4.77	448.67	121	146	0.30	0.05
PIL35	0.24	4.28	448.00	132	101	0.32	0.06
PIL38	0.15	5.30	445.00	109	227	0.17	0.04
PIL40	0.20	5.66	448.40	129	80	0.26	0.05
PIL43	0.30	4.20	444.00	150	163	0.44	0.07
PIL45	0.21	4.53	449.80	135	131	0.29	0.06
PIL53	0.24	4.53	450.50	113	118	0.27	0.04
PIL54	0.29	4.62	441.50	107	144	0.30	0.05
PIL60	0.21	5.36	448.67	161	80	0.34	0.06
PIL63	0.26	3.26	447.83	105	147	0.28	0.03
PIL67	0.33	4.63	442.60	145	176	0.48	0.05
PIL77	0.26	4.11	449.33	118	195	0.31	0.05
PIL81	0.28	3.08	444.20	181	120	0.51	0.05
PIL86	0.26	4.71	446.17	123	219	0.32	0.06
PIL101	0.07	6.68	442.00	99	296	0.07	0.01
PIL106	0.35	8.86	447.00	80	142	0.28	0.02
PIL108	0.13	2.19	462.00	30	378	0.04	0.00
PIL112	0.32	4.66	447.00	133	138	0.42	0.07
PIL113	0.16	6.36	447.83	131	157	0.21	0.02
PIL117	0.11	6.13	453.00	62	167	0.07	0.01
PIL122	0.22	4.91	448.50	110	89	0.24	0.03
PIL128	0.08	7.04	438.00	123	383	0.10	0.01
PIL132	0.21	6.03	446.00	89	142	0.18	0.04

Table 19 – Phosphorus data Core 607

Samples	Depth	Biozones	PO4	Sed. Rates	P	PAR
	m		ppm	cm/kyr	mg/g	mg/cm2/kyr
60	0.5	<i>Radiatus</i>	372	3.2	0.121	0.970
62	1.4	<i>Radiatus</i>	3109	3.2	1.014	8.115
67	3	<i>Radiatus</i>	1334	3.2	0.435	3.481
69	3.4	<i>Radiatus</i>	929	3.2	0.303	2.424
73	4.6	<i>Radiatus</i>	2387	3.2	0.779	6.231
75	5.4	<i>Radiatus</i>	2278	3.2	0.743	5.946
77	6.2	<i>Radiatus</i>	2391	3.2	0.780	6.239
81	8	<i>Radiatus</i>	1810	3.2	0.590	4.724
85	10.3	<i>Radiatus</i>	2568	3.2	0.838	6.703
87	11.4	<i>Radiatus</i>	1427	3.2	0.466	3.725
92	13.4	<i>Radiatus</i>	3983	3.2	1.299	10.395
94	14.4	<i>Radiatus</i>	1788	3.2	0.583	4.668
98	16.1	<i>Radiatus</i>	1802	3.2	0.588	4.702
100	17	<i>Radiatus</i>	3624	3.2	1.182	9.458
104	18.8	<i>Radiatus</i>	1459	3.2	0.476	3.808
106	19.8	<i>Radiatus</i>	2093	3.2	0.683	5.462
109	21.2	<i>Radiatus</i>	655	3.2	0.214	1.711
111	22	<i>Radiatus</i>	2014	3.2	0.657	5.256
114	23.6	<i>Radiatus</i>	1017	3.2	0.332	2.653
119	25.2	<i>Loryi-Nodosoplicatum</i>	2192	3.4	0.715	5.722
122	26.2	<i>Loryi-Nodosoplicatum</i>	462	3.4	0.151	0.528
124	26.6	<i>Loryi-Nodosoplicatum</i>	1704	3.4	0.556	1.946
127	26.8	<i>Loryi-Nodosoplicatum</i>	2263	3.4	0.738	2.584
130	28.6	<i>Loryi-Nodosoplicatum</i>	635	3.4	0.207	0.725
132	29.2	<i>Loryi-Nodosoplicatum</i>	1746	3.4	0.570	1.993
136	31.2	<i>Loryi-Nodosoplicatum</i>	1134	3.4	0.370	1.295
139.5	32.85	<i>Loryi-Nodosoplicatum</i>	112	3.4	0.037	0.128
140	33.2	<i>Loryi-Nodosoplicatum</i>	177	3.4	0.058	0.202
143	34.4	<i>Loryi-Nodosoplicatum</i>	760	3.4	0.248	0.867
145	35.6	<i>Loryi-Nodosoplicatum</i>	425	3.4	0.139	0.485
147	36.6	<i>Loryi-Nodosoplicatum</i>	417	3.4	0.136	0.477
149	37.6	<i>Loryi-Nodosoplicatum</i>	566	3.4	0.185	0.646
151	38.6	<i>Loryi-Nodosoplicatum</i>	605	3.4	0.197	0.691
153	40	<i>Loryi-Nodosoplicatum</i>	525	3.4	0.171	0.600
155	40.8	<i>Loryi-Nodosoplicatum</i>	537	3.4	0.175	0.613
157	41.8	<i>Loryi-Nodosoplicatum</i>	823	3.4	0.268	0.939
159	42.4	<i>Loryi-Nodosoplicatum</i>	623	3.4	0.203	0.712
162	44.2	<i>Loryi-Nodosoplicatum</i>	807	3.4	0.263	0.921
164	45	<i>Loryi-Nodosoplicatum</i>	691	3.4	0.225	0.789
166	45.8	<i>Loryi-Nodosoplicatum</i>	700	3.4	0.228	0.799
170	47.2	<i>Loryi-Nodosoplicatum</i>	1106	3.4	0.361	1.263
176	49.6	<i>Loryi-Nodosoplicatum</i>	727	3.4	0.237	0.830
178	50.8	<i>Loryi-Nodosoplicatum</i>	595	3.4	0.194	0.679
180	51.8	<i>Loryi-Nodosoplicatum</i>	783	3.4	0.255	0.894
183	53	<i>Loryi-Nodosoplicatum</i>	2659	3.4	0.867	3.036
185	54	<i>Loryi-Nodosoplicatum</i>	603	3.4	0.197	0.688

Samples	Depth	Biozones	PO4	Sed. Rates	P	PAR
	m		ppm	cm/kyr	mg/g	mg/cm2/kyr
190	56.6	<i>Loryi-Nodosoplicatum</i>	969	3.4	0.316	1.106
194	58.8	<i>Loryi-Nodosoplicatum</i>	1177	3.4	0.384	1.343

Table 20 – Phosphorus data Eclepens

Samples	Depth m	Biozones	PO4 ppm	Sed. rates cm/kyr	P mg/g	PAR mg/cm2/kyr
EC 1	0	<i>Radiatus-Nodosoplicatum</i>	539.2	1.6889	0.176	0.7427
EC4	1.4	<i>Radiatus-Nodosoplicatum</i>	321.8	1.6889	0.105	0.4433
EC8	2.2	<i>Radiatus-Nodosoplicatum</i>	193.7	1.6889	0.063	0.2669
EC10	3.2	<i>Radiatus-Nodosoplicatum</i>	214.3	1.6889	0.070	0.2953
EC13	4.15	<i>Radiatus-Nodosoplicatum</i>	228.9	1.6889	0.075	0.3153
EC15	4.42	<i>Radiatus-Nodosoplicatum</i>	252.5	1.6889	0.082	0.3478
EC20	5.77	<i>Radiatus-Nodosoplicatum</i>	306.2	1.6889	0.100	0.4217
EC25	8.57	<i>Radiatus-Nodosoplicatum</i>	146.7	1.6889	0.048	0.2020
EC30	10.2	<i>Radiatus-Nodosoplicatum</i>	216.6	1.6889	0.071	0.2984
EC38	13	<i>Radiatus-Nodosoplicatum</i>	209.6	1.6889	0.068	0.2887
EC42	13.6	<i>Radiatus-Nodosoplicatum</i>	218.4	1.6889	0.071	0.3008
EC45	15.38	<i>Radiatus-Nodosoplicatum</i>	124.7	1.6889	0.041	0.1718
EC49	17.03	<i>Radiatus-Nodosoplicatum</i>	139.5	1.6889	0.046	0.1922
EC54	18.9	<i>Radiatus-Nodosoplicatum</i>	118.2	1.6889	0.039	0.1628
EC57	20.33	<i>Radiatus-Nodosoplicatum</i>	124.3	1.6889	0.041	0.1712
EC61	22.25	<i>Radiatus-Nodosoplicatum</i>	115.3	1.6889	0.038	0.1589
EC64	23.83	<i>Radiatus-Nodosoplicatum</i>	123.3	1.6889	0.040	0.1699
EC66	24.35	<i>Radiatus-Nodosoplicatum</i>	134.8	1.6889	0.044	0.1857
EC69	25.78	<i>Radiatus-Nodosoplicatum</i>	205.0	1.6889	0.067	0.2824
EC71	26.62	<i>Radiatus-Nodosoplicatum</i>	229.4	1.6889	0.075	0.3160
EC75	28	<i>Radiatus-Nodosoplicatum</i>	136.6	1.6889	0.045	0.1882
EC77	28.85	<i>Radiatus-Nodosoplicatum</i>	128.9	1.6889	0.042	0.1776
EC85	29.88	<i>Late Barremian</i>	200.4	0.4167	0.065	0.0681
EC94	32.9	<i>Late Barremian</i>	242.8	0.4167	0.079	0.0825
EC99	34.38	<i>Late Barremian</i>	102.1	0.4167	0.033	0.0347
EC102	35	<i>Late Barremian</i>	122.7	0.4167	0.040	0.0417
EC104	35.6	<i>Late Barremian</i>	151.3	0.4167	0.049	0.0514
EC106	36.6	<i>Late Barremian</i>	116.1	0.4167	0.038	0.0394
EC108	37	<i>Late Barremian</i>	75.6	0.4167	0.025	0.0257
EC113	38.18	<i>Late Barremian</i>	124.0	0.4167	0.040	0.0421
EC115	39.05	<i>Late Barremian</i>	69.3	0.4167	0.023	0.0236
EC121	40.95	<i>Late Barremian</i>	79.6	0.4167	0.026	0.0271
EC128	42.8	<i>Late Barremian</i>	41.0	0.4167	0.013	0.0139
EC132	43.7	<i>Late Barremian</i>	104.4	0.4167	0.034	0.0355
EC138	45.35	<i>Late Barremian</i>	22.8	0.4167	0.007	0.0078
EC142	46.65	<i>Late Barremian</i>	13.7	0.4167	0.004	0.0047
EC146	47.95	<i>Late Barremian</i>	16.5	0.4167	0.005	0.0056

Table 21 – Phosphorus data La Charce, Vergons and Angles

Samples	Depth m	Biozones	PO4 ppm	Sed. rates cm/kyr	P mg/g	PAR mg/cm2/kyr
LC 246	1.4	<i>Callidiscus</i>	759.6	0.98	0.248	0.604
LC 249	3.8	<i>Callidiscus</i>	601.8	0.98	0.196	0.479
LC 250	4.6	<i>Callidiscus</i>	680.9	0.98	0.222	0.541
LC 254	8	<i>Radiatus</i>	779.6	3.23	0.254	2.052
LC 260	13.8	<i>Radiatus</i>	654.9	3.23	0.214	1.724
LC 265	21.6	<i>Radiatus</i>	656.2	3.23	0.214	1.727
LC 273	31.4	<i>Radiatus</i>	842.6	3.23	0.275	2.217
LC 275	33	<i>Loryi</i>	562.9	3.47	0.184	1.592
LC 276	35	<i>Loryi</i>	543.4	3.47	0.177	1.537
LC 277	35.8	<i>Loryi</i>	573.5	3.47	0.187	1.621
LC 281	38	<i>Loryi</i>	797.8	3.47	0.260	2.256
LC 283	39.8	<i>Loryi</i>	685.8	3.47	0.224	1.939
LC 286	43	<i>Loryi</i>	625.8	3.47	0.204	1.769
LC 290	46.2	<i>Loryi</i>	587.3	3.47	0.192	1.661
LC 294	58	<i>Nodosoplicatum</i>	721.0	3.41	0.235	2.007
LC 303	63.8	<i>Nodosoplicatum</i>	576.2	3.41	0.188	1.604
LC 308	75	<i>Nodosoplicatum</i>	607.7	3.41	0.198	1.692
LC 314	81.2	<i>Nodosoplicatum</i>	421.3	3.41	0.137	1.173
LC 316	83.5	<i>Nodosoplicatum</i>	426.4	3.41	0.139	1.187
LC 317	84	<i>Nodosoplicatum</i>	395.6	3.41	0.129	1.101
LC 318	85	<i>Nodosoplicatum</i>	471.8	3.41	0.154	1.313
LC 319	85.8	<i>Nodosoplicatum</i>	572.3	3.41	0.187	1.593
LC 320	87	<i>Nodosoplicatum</i>	617.5	3.41	0.201	1.719
LC 321	87.6	<i>Nodosoplicatum</i>	562.6	3.41	0.184	1.566
LC 323	90	<i>Sayni</i>	445.2	4.93	0.145	1.791
LC 325	91.8	<i>Sayni</i>	458.1	4.93	0.149	1.843
VG 73a	94.2	<i>Sayni</i>	634.5	4.93	0.207	2.553
VG 75a	97.2	<i>Sayni</i>	765.3	4.93	0.250	3.079
VG 77a	99.6	<i>Sayni</i>	678.3	4.93	0.221	2.729
LC 330	101.8	<i>Sayni</i>	554.4	4.93	0.181	2.231
LC 334	105.2	<i>Sayni</i>	522.4	4.93	0.170	2.102
LC 336	107.4	<i>Sayni</i>	523.0	4.93	0.171	2.105
LC 338	108.6	<i>Sayni</i>	496.7	4.93	0.162	1.999
LC 341	111	<i>Sayni</i>	580.6	4.93	0.189	2.336
VG 83a	111.4	<i>Sayni</i>	660.1	4.93	0.215	2.656
LC 343	113	<i>Sayni</i>	512.4	4.93	0.167	2.062
LC 346	114.5	<i>Sayni</i>	581.5	4.93	0.190	2.340
LC 347	115.6	<i>Sayni</i>	688.3	4.93	0.225	2.769
LC 350	117.5	<i>Sayni</i>	484.0	4.93	0.158	1.948
LC 351	118.8	<i>Sayni</i>	618.8	4.93	0.202	2.490
VG 93a	122.8	<i>Sayni</i>	413.3	4.93	0.135	1.663
LC 357	124	<i>Sayni</i>	492.0	4.93	0.161	1.980
VG 94a	124	<i>Sayni</i>	480.0	4.93	0.157	1.932
VG 95a	125.2	<i>Sayni</i>	666.6	4.93	0.217	2.682
VG 97a	129	<i>Sayni</i>	534.9	4.93	0.174	2.152

Samples	Depth m	Biozones	PO4 ppm	Sed. rates cm/kyr	P mg/g	PAR mg/cm2/kyr
VG 101a	133.2	<i>Ligatus</i>	573.0	8.69	0.187	4.063
VG 102a	134.4	<i>Ligatus</i>	601.7	8.69	0.196	4.266
VG 113a	152	<i>Ligatus</i>	608.2	8.69	0.198	4.312
VG 142a	186	<i>Ligatus</i>	546.6	8.69	0.178	3.876
AN 10	207	<i>Balearis</i>	552.2	2.64	0.180	1.189
AN 20	212.8	<i>Balearis</i>	559.6	2.64	0.183	1.205
AN 26	215.2	<i>Balearis</i>	660.1	2.64	0.215	1.421
AN 30	217.4	<i>Balearis</i>	596.0	2.64	0.194	1.283
AN 35	220	<i>Balearis</i>	783.7	2.64	0.256	1.687
AN 40	223.6	<i>Balearis</i>	620.7	2.64	0.202	1.336
AN 48	225.8	<i>Angulicostata</i>	706.1	2.69	0.230	1.551
VG 185a	229.4	<i>Angulicostata</i>	785.8	2.69	0.256	1.726
VG 187a	230.2	<i>Angulicostata</i>	690.7	2.69	0.225	1.517
VG 188a	230.8	<i>Angulicostata</i>	499.4	2.69	0.163	1.097
VG 189a	231.4	<i>Angulicostata</i>	824.6	2.69	0.269	1.811
VG 190a	232.4	<i>Angulicostata</i>	714.2	2.69	0.233	1.569
VG 192a	233.8	<i>Angulicostata</i>	656.5	2.69	0.214	1.442
VG 194a	236	<i>Angulicostata</i>	636.3	2.69	0.208	1.398
VG 195a	236.6	<i>Angulicostata</i>	571.1	2.69	0.186	1.255
VG 205a	243.8	<i>Angulicostata</i>	507.5	2.69	0.166	1.115

Table 22 – Phosphorus data Semnoz

Sample	Depth m	Biozones	PO4 ppm	Sed. rate cm/kyr	P mg/g	PAR mg/cm2/kyr
SEM 4B	1.25	<i>Radiatus-Nodosoplicatum</i>	745	2.58	0.243	1.566
SEM 8B	2.1	<i>Radiatus-Nodosoplicatum</i>	1002	2.58	0.327	2.107
SEM 12B	2.95	<i>Radiatus-Nodosoplicatum</i>	916	2.58	0.299	1.926
SEM 13B	3.25	<i>Radiatus-Nodosoplicatum</i>	793	2.58	0.259	1.667
SEM 15B	4.15	<i>Radiatus-Nodosoplicatum</i>	2425	2.58	0.791	5.099
SEM 18B	5.05	<i>Radiatus-Nodosoplicatum</i>	4028	2.58	1.314	8.468
SEM 19B	5.65	<i>Radiatus-Nodosoplicatum</i>	950	2.58	0.310	1.996
SEM 22B	6.35	<i>Radiatus-Nodosoplicatum</i>	2463	2.58	0.804	5.179
SEM 23B	6.55	<i>Radiatus-Nodosoplicatum</i>	851	2.58	0.278	1.789
SEM 24B	9.7	<i>Radiatus-Nodosoplicatum</i>	408	2.58	0.133	0.858
SEM 25B	10.25	<i>Radiatus-Nodosoplicatum</i>	337	2.58	0.110	0.709
SEM 28B	10.85	<i>Radiatus-Nodosoplicatum</i>	985	2.58	0.321	2.071
SEM 31B	12.85	<i>Radiatus-Nodosoplicatum</i>	3224	2.58	1.052	6.778
SEM 32B	13.2	<i>Radiatus-Nodosoplicatum</i>	1258	2.58	0.410	2.644
SEM 34B	14.35	<i>Radiatus-Nodosoplicatum</i>	2438	2.58	0.795	5.125
SEM 35B	15.15	<i>Radiatus-Nodosoplicatum</i>	298	2.58	0.097	0.627
SEM 38B	40.65	<i>Sayni-Angulicostata</i>	593	1.03	0.194	0.500
SEM 40B	41.1	<i>Sayni-Angulicostata</i>	628	1.03	0.205	0.529
SEM 42B	41.4	<i>Sayni-Angulicostata</i>	1277	1.03	0.417	1.076
SEM 42B	41.4	<i>Sayni-Angulicostata</i>	569	1.03	0.186	0.479
SEM 44B	41.7	<i>Sayni-Angulicostata</i>	625	1.03	0.204	0.527
SEM 46B	42.05	<i>Sayni-Angulicostata</i>	485	1.03	0.158	0.409
SEM 48B	42.37	<i>Sayni-Angulicostata</i>	225	1.03	0.073	0.189
SEM 50B	42.62	<i>Sayni-Angulicostata</i>	1093	1.03	0.356	0.921
SEM 52B	43.02	<i>Sayni-Angulicostata</i>	543	1.03	0.177	0.458
SEM 54B	44.29	<i>Sayni-Angulicostata</i>	609	1.03	0.199	0.513
SEM 56B	44.81	<i>Sayni-Angulicostata</i>	465	1.03	0.152	0.392
SEM 60B	46.15	<i>Sayni-Angulicostata</i>	1575	1.03	0.514	1.327
SEM 62B	46.72	<i>Sayni-Angulicostata</i>	143	1.03	0.047	0.121
SEM 65B	47.97	<i>Sayni-Angulicostata</i>	439	1.03	0.143	0.370
SEM 68B	49.17	<i>Sayni-Angulicostata</i>	313	1.03	0.102	0.264
SEM 70B	49.62	<i>Sayni-Angulicostata</i>	1257	1.03	0.410	1.059
SEM 73B	50.19	<i>Sayni-Angulicostata</i>	468	1.03	0.153	0.395
SEM 78B	51.69	<i>Sayni-Angulicostata</i>	445	1.03	0.145	0.375
SEM 82B	52.81	<i>Sayni-Angulicostata</i>	247	1.03	0.081	0.208
SEM 84B	53.28	<i>Sayni-Angulicostata</i>	838	1.03	0.273	0.706
SEM 86B	54.18	<i>Sayni-Angulicostata</i>	209	1.03	0.068	0.176
SEM 90B	56.28	<i>Sayni-Angulicostata</i>	218	1.03	0.071	0.183
SEM 96B	58.37	<i>Sayni-Angulicostata</i>	972	1.03	0.317	0.819
SEM 98B	58.91	<i>Sayni-Angulicostata</i>	293	1.03	0.095	0.247

SEM 101B	60.46	<i>Sayni-Angulicostata</i>	1362	1.03	0.444	1.148
SEM 105B	61.86	<i>Sayni-Angulicostata</i>	338	1.03	0.110	0.285
SEM 109B	62.91	<i>Sayni-Angulicostata</i>	1203	1.03	0.392	1.014
SEM 111B	63.76	<i>Sayni-Angulicostata</i>	695	1.03	0.227	0.585
SEM 112B	64.21	<i>Sayni-Angulicostata</i>	775	1.03	0.253	0.653
SEM 115B	65.76	<i>Sayni-Angulicostata</i>	713	1.03	0.233	0.601
SEM 117B	67.76	<i>Sayni-Angulicostata</i>	834	1.03	0.272	0.703

Table 23 – Phosphorus data Terre Masse

Sample	Depth m	Biozone	PO4 ppm	Sed. rates cm/kyr	P mg/g	PAR mg/cm2/kyr
TM 116A	4.1	<i>Loryi</i>	769	1.47	0.25080	0.920
TM 117A	5.56	<i>Loryi</i>	724	1.47	0.23621	0.866
TM 120A	8.9	<i>Loryi</i>	544	1.47	0.17750	0.651
TM 122A	10.66	<i>Loryi</i>	1078	1.47	0.35167	1.289
TM 123A	11.4	<i>Loryi</i>	479	1.47	0.15639	0.573
TM 125A	11.8	<i>Loryi</i>	1042	1.47	0.34003	1.247
TM 127A	12.88	<i>Nodosoplicatum</i>	576	2.27	0.18781	1.064
TM 130A	14.4	<i>Nodosoplicatum</i>	584	2.27	0.19056	1.080
TM 132A	15.22	<i>Nodosoplicatum</i>	605	2.27	0.19722	1.118
TM 138A	17.54	<i>Nodosoplicatum</i>	597	2.27	0.19467	1.103
TM 141A	19.6	<i>Nodosoplicatum</i>	826	2.27	0.26955	1.527
TM 142A	20.42	<i>Nodosoplicatum</i>	639	2.27	0.20846	1.181
TM 143A	21.5	<i>Nodosoplicatum</i>	1129	2.27	0.36821	2.087
TM 144A	24.9	<i>Nodosoplicatum</i>	729	2.27	0.23785	1.348
TM 145A	26	<i>Nodosoplicatum</i>	744	2.27	0.24260	1.375
TM 146	26.52	<i>Nodosoplicatum</i>	737	2.27	0.24049	1.363
TM 147A	27.04	<i>Nodosoplicatum</i>	2122	2.27	0.69243	3.924
TM 148	28.4	<i>Nodosoplicatum</i>	1097	2.27	0.35803	2.029
TM 154A	32.12	<i>Sayni</i>	669	1.47	0.21837	0.801
TM 155A	32.9	<i>Sayni</i>	434	1.47	0.14167	0.519
TM 157A	33.66	<i>Sayni</i>	627	1.47	0.20470	0.751
TM 158	34.44	<i>Sayni</i>	583	1.47	0.19029	0.698
TM 1	37.74	<i>Ligatus</i>	752	1.60	0.24527	0.981
TM 7	40.56	<i>Ligatus</i>	647	1.60	0.21097	0.844
TM 9	41.22	<i>Ligatus</i>	703	1.60	0.22935	0.917
TM 11	41.72	<i>Ligatus</i>	746	1.60	0.24336	0.973
TM 14	43.64	<i>Ligatus</i>	486	1.60	0.15850	0.634
TM 18	44.94	<i>Ligatus</i>	430	1.60	0.14029	0.561
TM 22	46.52	<i>Ligatus</i>	918	1.60	0.29954	1.198
TM 25	48.78	<i>Ligatus</i>	605	1.60	0.19752	0.790
TM 29	51.08	<i>Balearis</i>	509	1.60	0.16620	0.665
TM 31	55.82	<i>Balearis</i>	356	1.60	0.11624	0.465
TM 37	58.58	<i>Balearis</i>	568	1.60	0.18545	0.742
TM 39	60	<i>Balearis</i>	535	1.60	0.17467	0.699
TM 41	61.18	<i>Balearis</i>	404	1.60	0.13175	0.527
TM 44	63	<i>Balearis</i>	420	1.60	0.13700	0.548

Table 24 – Phosphorus data Talegg

Samples	Biozones	PO4 ppm	Sed. rates cm/kyr	P mg/g	PAR mg/cm2/kyr
TAL 4	<i>Campylotoxus</i>	377	5.20	0.1231	1.600
TAL 6	<i>Campylotoxus</i>	290	5.20	0.0946	1.230
TAL 8	<i>Campylotoxus</i>	1139	5.20	0.3716	4.830
TAL 10	<i>Campylotoxus</i>	366	5.20	0.1195	1.554
TAL 11	<i>Campylotoxus</i>	380	5.20	0.1239	1.611
TAL 13	<i>Campylotoxus</i>	511	5.20	0.1666	2.166
TAL 14	<i>Campylotoxus</i>	683	5.20	0.2229	2.898
TAL 15	<i>Campylotoxus</i>	447	5.20	0.1457	1.894
TAL 17	<i>Campylotoxus</i>	254	5.20	0.0828	1.076
TAL 18	<i>Campylotoxus</i>	6	5.20	0.0020	0.026
TAL 19	<i>Campylotoxus</i>	93	5.20	0.0304	0.395
TAL 23	<i>Campylotoxus</i>	43	5.20	0.0139	0.181
TAL 24	<i>Campylotoxus</i>	268	5.20	0.0876	1.138
TAL 25	<i>Campylotoxus</i>	144	5.20	0.0469	0.609
TAL 26	<i>Campylotoxus</i>	171	5.20	0.0559	0.726
TAL 27	<i>Campylotoxus</i>	171	5.20	0.0556	0.723
TAL 29	<i>Campylotoxus</i>	167	5.20	0.0544	0.707
TAL 30	<i>Campylotoxus</i>	213	5.20	0.0696	0.905
TAL 32	<i>Campylotoxus</i>	147	5.20	0.0480	0.625
TAL 34	<i>Campylotoxus</i>	216	5.20	0.0705	0.916
TAL 35	<i>Campylotoxus</i>	249	5.20	0.0812	1.055
TAL 37	<i>Campylotoxus</i>	155	5.20	0.0505	0.656
TAL 38	<i>Campylotoxus</i>	122	5.20	0.0399	0.519
TAL 39	<i>Campylotoxus</i>	328	5.20	0.1071	1.393
TAL 40	<i>Campylotoxus</i>	243	5.20	0.0791	1.029
TAL 42	<i>Campylotoxus</i>	96	5.20	0.0312	0.406
TAL 43	<i>Campylotoxus</i>	194	5.20	0.0633	0.822
TAL 44	<i>Radiatus-Nodosoplicatum</i>	129	4.62	0.0422	0.488
TAL 45	<i>Radiatus-Nodosoplicatum</i>	170	4.62	0.0556	0.642
TAL 46	<i>Radiatus-Nodosoplicatum</i>	105	4.62	0.0344	0.397
TAL 47	<i>Radiatus-Nodosoplicatum</i>	34	4.62	0.0112	0.129
TAL 48	<i>Radiatus-Nodosoplicatum</i>	364	4.62	0.1188	1.372
TAL 48	<i>Radiatus-Nodosoplicatum</i>	360	4.62	0.1174	1.356
TAL 50	<i>Radiatus-Nodosoplicatum</i>	191	4.62	0.0623	0.720
TAL 52	<i>Radiatus-Nodosoplicatum</i>	31	4.62	0.0101	0.117
TAL 53	<i>Radiatus-Nodosoplicatum</i>	416	4.62	0.1357	1.567
TAL 55	<i>Radiatus-Nodosoplicatum</i>	307	4.62	0.1002	1.157
TAL 56	<i>Radiatus-Nodosoplicatum</i>	313	4.62	0.1023	1.181
TAL 57	<i>Radiatus-Nodosoplicatum</i>	1124	4.62	0.3666	4.234
TAL 58	<i>Radiatus-Nodosoplicatum</i>	437	4.62	0.1427	1.648
TAL 63	<i>Radiatus-Nodosoplicatum</i>	1467	4.62	0.4785	5.527
TAL 64	<i>Radiatus-Nodosoplicatum</i>	10	4.62	0.0033	0.038
TAL 68	<i>Radiatus-Nodosoplicatum</i>	684	4.62	0.2232	2.578
TAL 71	<i>Radiatus-Nodosoplicatum</i>	524	4.62	0.1710	1.976
TAL 72	<i>Radiatus-Nodosoplicatum</i>	505	4.62	0.1646	1.901
TAL 74	<i>Radiatus-Nodosoplicatum</i>	798	4.62	0.2604	3.007

Samples	Biozones	PO4 ppm	Sed. rates cm/kyr	P mg/g	PAR mg/cm2/kyr
TAL 77	<i>Radiatus-Nodosoplicatum</i>	565	4.62	0.1842	2.127
TAL 77	<i>Radiatus-Nodosoplicatum</i>	552	4.62	0.1802	2.081
TAL 80	<i>Radiatus-Nodosoplicatum</i>	1701	4.62	0.5550	6.410
TAL 81	<i>Radiatus-Nodosoplicatum</i>	1332	4.62	0.4347	5.020
TAL 83	<i>Radiatus-Nodosoplicatum</i>	660	4.62	0.2153	2.487
TAL 85	<i>Nodosoplicatum-Ligatus</i>	3616	0.13	1.1797	0.393
TAL 88	<i>Ligatus-Angulicostata</i>	473	1.73	0.1544	0.668
TAL 89	<i>Ligatus-Angulicostata</i>	472	1.73	0.1539	0.666
TAL 91	<i>Ligatus-Angulicostata</i>	366	1.73	0.1195	0.517
TAL 92	<i>Ligatus-Angulicostata</i>	469	1.73	0.1530	0.662
TAL 100	<i>Ligatus-Angulicostata</i>	496	1.73	0.1619	0.700
TAL 101	<i>Ligatus-Angulicostata</i>	661	1.73	0.2155	0.932
TAL 102	<i>Ligatus-Angulicostata</i>	567	1.73	0.1849	0.800
TAL 102	<i>Ligatus-Angulicostata</i>	294	1.73	0.0960	0.415
TAL 104	<i>Ligatus-Angulicostata</i>	534	1.73	0.1744	0.754
TAL 107	<i>Ligatus-Angulicostata</i>	966	1.73	0.3150	1.362
TAL 108	<i>Ligatus-Angulicostata</i>	544	1.73	0.1773	0.767
TAL 109	<i>Ligatus-Angulicostata</i>	596	1.73	0.1944	0.841
TAL 115	<i>Angulicostata</i>	2077	2.17	0.6777	3.677
TAL 116	<i>Angulicostata</i>	464	2.17	0.1513	0.821

Table 25 – Phosphorus data Pilatus

Samples	Depth m	Biozones	PO4 ppm	Sed. rates cm/kyr	P mg/g	PAR mg/cm2/kyr
PIL 7	4.25	<i>Radiatus</i>	790	5.20	0.258	3.35
PIL 21	7.55	<i>Radiatus</i>	555	5.20	0.181	2.35
PIL 27	9.35	<i>Radiatus</i>	443	5.20	0.145	1.88
PIL 28	9.65	<i>Radiatus</i>	565	5.20	0.184	2.40
PIL 29	9.95	<i>Radiatus</i>	562	5.20	0.183	2.38
PIL 30	10.25	<i>Radiatus</i>	563	5.20	0.184	2.39
PIL 31	10.7	<i>Loryi</i>	342	5.20	0.111	1.45
PIL 32	10.9	<i>Loryi</i>	738	5.20	0.241	3.13
PIL 36	15.02	<i>Loryi</i>	520	5.20	0.170	2.21
PIL 42	17.87	<i>Loryi</i>	332	5.20	0.108	1.41
PIL 44	18.79	<i>Loryi</i>	386	5.20	0.126	1.64
PIL 47	20.6	<i>Loryi</i>	149	5.20	0.049	0.63
PIL 57	26.6	<i>Loryi</i>	166	5.20	0.054	0.70
PIL 58	27.8	<i>Loryi</i>	243	5.20	0.079	1.03
PIL 59	28.95	<i>Loryi</i>	363	5.20	0.118	1.54
PIL 60	29.2	<i>Loryi</i>	285	5.20	0.093	1.21
PIL 69	37.2	<i>Loryi</i>	231	5.20	0.075	0.98
PIL 73	41.55	<i>Loryi</i>	866	5.20	0.283	3.67
PIL 76	44.95	<i>Loryi</i>	353	5.20	0.115	1.50
PIL 78	46.75	<i>Loryi</i>	307	5.20	0.100	1.30
PIL 79	47.9	<i>Loryi</i>	477	5.20	0.156	2.03
PIL 82	50.25	<i>Loryi</i>	396	5.20	0.129	1.68
PIL 84	52.2	<i>Loryi</i>	343	5.20	0.112	1.46
PIL 85	52.65	<i>Loryi</i>	509	5.20	0.166	2.16
PIL 87	53.55	<i>Loryi</i>	275	5.20	0.090	1.16
PIL 89	56.05	<i>Loryi</i>	570	5.20	0.186	2.42
PIL 90	56.8	<i>Loryi</i>	159	5.20	0.052	0.67
PIL 91	58.1	<i>Loryi</i>	476	5.20	0.155	2.02
PIL 92	59.1	<i>Loryi</i>	246	5.20	0.080	1.04
PIL 93	60.15	<i>Loryi</i>	252	5.20	0.082	1.07
PIL 95	62.5	<i>Loryi</i>	248	5.20	0.081	1.05
PIL 96	63.45	<i>Loryi</i>	832	5.20	0.272	3.53
PIL 97	64.9	<i>Loryi</i>	738	5.20	0.241	3.13
PIL 98	65.9	<i>Loryi</i>	244	5.20	0.079	1.03
PIL 99	66.9	<i>Loryi</i>	528	5.20	0.172	2.24
PIL 100	67.9	<i>Loryi</i>	376	5.20	0.123	1.60
PIL 102	70.05	<i>Loryi</i>	561	5.20	0.183	2.38
PIL 103	71.05	<i>Loryi</i>	663	5.20	0.216	2.81
PIL 107	74.35	<i>Nodosoplicatum-Ligatus</i>	2427	0.02	0.792	0.04
PIL 109	74.55	<i>Nodosoplicatum-Ligatus</i>	3550	0.02	1.158	0.06
PIL 110	75.65	<i>Balearis-Angulicostata</i>	268	2.66	0.087	0.58
PIL 111	76.65	<i>Balearis-Angulicostata</i>	113	2.66	0.037	0.24
PIL 114	79.65	<i>Balearis-Angulicostata</i>	295	2.66	0.096	0.64

Samples	Depth m	Biozones	PO4 ppm	Sed. rates cm/kyr	P mg/g	PAR mg/cm2/kyr
PIL 115	80.65	<i>Balearis-Angulicostata</i>	315	2.66	0.103	0.68
PIL 116	81.55	<i>Balearis-Angulicostata</i>	365	2.66	0.119	0.79
PIL 118	87.8	<i>Balearis-Angulicostata</i>	279	2.66	0.091	0.61
PIL 119	88.8	<i>Balearis-Angulicostata</i>	247	2.66	0.081	0.54
PIL 121	91.25	<i>Balearis-Angulicostata</i>	108	2.66	0.035	0.23
PIL 123	92.7	<i>Balearis-Angulicostata</i>	359	2.66	0.117	0.78
PIL 125	95.2	<i>Balearis-Angulicostata</i>	79	2.66	0.026	0.17
PIL 127	97.35	<i>Balearis-Angulicostata</i>	86	2.66	0.028	0.19
PIL 129	100.45	<i>Balearis-Angulicostata</i>	214	2.66	0.070	0.46
PIL 130	101.65	<i>Balearis-Angulicostata</i>	481	2.66	0.157	1.04
PIL 134	106	<i>Balearis-Angulicostata</i>	165	2.66	0.054	0.36
PIL 135	108	<i>Balearis-Angulicostata</i>	370	2.66	0.121	0.80
PIL 136	110	<i>Balearis-Angulicostata</i>	181	2.66	0.059	0.39
PIL 137	112.2	<i>Balearis-Angulicostata</i>	174	2.66	0.057	0.38
PIL 138	115.1	<i>Balearis-Angulicostata</i>	342	2.66	0.111	0.74
PIL 138	115.1	<i>Balearis-Angulicostata</i>	334	2.66	0.109	0.72
PIL 140	118.65	<i>Balearis-Angulicostata</i>	212	2.66	0.069	0.46
PIL 143	125	<i>Balearis-Angulicostata</i>	210	2.66	0.069	0.46
PIL 145	131	<i>Balearis-Angulicostata</i>	195	2.66	0.064	0.42

Table 26 – Phosphorus data Monte Acuto

Sample	Depth	Biozones	PO4 ppm	Sed. rates cm/kyr	P mg/g	PAR (mg/cm2/kyr)
MA 0	0	<i>Loryi-Nodosoplicatum</i>	257	2.66	0.084	0.558
MA 3	3	<i>Loryi-Nodosoplicatum</i>	249	2.66	0.081	0.541
MA 6.8	6.8	<i>Loryi-Nodosoplicatum</i>	226	2.66	0.074	0.491
MA 10.75	10.75	<i>Loryi-Nodosoplicatum</i>	155	2.66	0.051	0.336
MA 11.5	11.5	<i>Loryi-Nodosoplicatum</i>	219	2.66	0.071	0.475
MA 14	14	<i>Loryi-Nodosoplicatum</i>	296	2.66	0.097	0.642
MA 16	16	<i>Loryi-Nodosoplicatum</i>	206	2.66	0.067	0.446
MA 18	18	<i>Loryi-Nodosoplicatum</i>	282	2.66	0.092	0.612
MA 20	20	<i>Loryi-Nodosoplicatum</i>	59	2.66	0.019	0.129
MA 22	22	<i>Loryi-Nodosoplicatum</i>	285	2.66	0.093	0.617
MA 24	24	<i>Loryi-Nodosoplicatum</i>	219	2.66	0.071	0.475
MA 26	26	<i>Loryi-Nodosoplicatum</i>	224	2.66	0.073	0.486
MA 27	27	<i>Loryi-Nodosoplicatum</i>	290	2.66	0.095	0.629
MA 29	29	<i>Loryi-Nodosoplicatum</i>	241	2.66	0.079	0.524
MA 31	31	<i>Loryi-Nodosoplicatum</i>	498	2.66	0.162	1.080
MA 33	33	<i>Loryi-Nodosoplicatum</i>	334	2.66	0.109	0.725
MA 35	35	<i>Loryi-Nodosoplicatum</i>	425	2.66	0.139	0.921
MA 37	37	<i>Loryi-Nodosoplicatum</i>	334	2.66	0.109	0.724
MA 41	41	<i>Radiatus</i>	231	1.33	0.075	0.251
MA 43.3	43.3	<i>Radiatus</i>	208	1.33	0.068	0.225
MA 45	45	<i>Radiatus</i>	255	1.33	0.083	0.277
MA 47	47	<i>Radiatus</i>	401	1.33	0.131	0.435
MA 49	49	<i>Radiatus</i>	405	1.33	0.132	0.440
MA 51	51	<i>Verrucosum-Callidiscus</i>	275	1.82	0.090	0.408
MA 54	54	<i>Verrucosum-Callidiscus</i>	330	1.82	0.108	0.490
MA 56	56	<i>Verrucosum-Callidiscus</i>	342	1.82	0.112	0.508
MA 58	58	<i>Verrucosum-Callidiscus</i>	181	1.82	0.059	0.269
MA 61	61	<i>Verrucosum-Callidiscus</i>	357	1.82	0.117	0.530
MA 62	62	<i>Verrucosum-Callidiscus</i>	240	1.82	0.078	0.357
MA 64	64	<i>Verrucosum-Callidiscus</i>	162	1.82	0.053	0.240
MA 66	66	<i>Verrucosum-Callidiscus</i>	156	1.82	0.051	0.231
MA 68	68	<i>Verrucosum-Callidiscus</i>	259	1.82	0.084	0.384
MA 71	71	<i>Verrucosum-Callidiscus</i>	195	1.82	0.063	0.289
MA 73	73	<i>Verrucosum-Callidiscus</i>	217	1.82	0.071	0.323
MA 75	75	<i>Verrucosum-Callidiscus</i>	220	1.82	0.072	0.327
MA 76	76	<i>Verrucosum-Callidiscus</i>	187	1.82	0.061	0.278
MA 78	78	<i>Verrucosum-Callidiscus</i>	145	1.82	0.047	0.215
MA 80	80	<i>Verrucosum-Callidiscus</i>	289	1.82	0.094	0.428
MA 82	82	<i>Verrucosum-Callidiscus</i>	286	1.82	0.093	0.424
MA 84	84	<i>Verrucosum-Callidiscus</i>	160	1.82	0.052	0.238
MA 86	86	<i>Verrucosum-Callidiscus</i>	300	1.82	0.098	0.445

Table 27 – Palynofacies data Pilatus

	Opaque-eq	Opaque-Blade shaped	Translucent	Bisaccates	Non-Saccates	Spores	Dinoflagellates	Algae	Foraminifera	Acritarchs	Total	Continental flux	Marine flux
Pil 4	33	54	3	2	0	3	107	0	1	4	207	95	112
Pil 6	59	63	0	3	0	4	73	0	0	3	205	129	76
Pil 8	59	50	0	8	0	6	54	0	6	3	186	123	63
Pil 10	75	63	4	8	0	1	40	0	0	3	194	151	43
Pil 12	42	36	3	2	0	1	120	0	0	2	206	84	122
Pil 20	48	34	1	0	0	0	108	0	6	3	200	83	117
Pil 23	16	24	0	39	2	3	85	0	3	4	176	84	92
Pil 34	73	68	15	0	0	3	17	0	15	4	195	159	36
Pil 38	67	61	3	0	0	0	31	0	34	4	200	131	69
Pil 40	75	90	5	0	0	0	14	0	12	3	199	170	29
Pil 43	92	72	10	2	0	4	16	0	6	0	202	180	22
Pil 63	83	98	3	0	1	1	13	0	3	0	202	186	16
Pil 67	82	76	10	0	0	2	26	0	4	0	200	170	30
Pil 77	57	68	10	2	0	2	35	0	15	2	191	139	52
Pil 81	64	66	0	4	0	8	60	0	0	0	202	142	60
Pil 86	64	64	14	8	0	6	30	0	10	0	196	156	40
Pil 101	12	10	9	0	0	0	103	10	30	27	201	31	170
Pil 106	58	76	0	2	0	4	54	2	11	26	233	140	93
Pil 112	49	83	1	2	0	6	53		5	2	201	141	60
Pil 113	36	78	2	1	0	4	55	0	44	0	220	121	99
Pil 117	36	31	0	4	0	7	88	5	29	3	203	78	125
Pil 122	60	47	0	2	0	2	56	0	37	5	209	111	98
Pil 128	28	29	0	2	11	4	79	0	54	2	209	74	135
Pil 132	56	39	0	0	0	0	46	0	75	3	219	95	124
Pil 133	72	110	12	0	0	0	27	0	14	1	236	194	42
	%	%	%	%	%	%	%	%	%	%	%	%	%
Pil 4	15.9	26.1	1.4	1.0	0.0	1.4	51.7	0.0	0.5	1.9	100.0	45.9	54.1
Pil 6	28.8	30.7	0.0	1.5	0.0	2.0	35.6	0.0	0.0	1.5	100.0	62.9	37.1
Pil 8	31.7	26.9	0.0	4.3	0.0	3.2	29.0	0.0	3.2	1.6	100.0	66.1	33.9
Pil 10	38.7	32.5	2.1	4.1	0.0	0.5	20.6	0.0	0.0	1.5	100.0	77.8	22.2
Pil 12	20.4	17.5	1.5	1.0	0.0	0.5	58.3	0.0	0.0	1.0	100.0	40.8	59.2
Pil 20	24.0	17.0	0.5	0.0	0.0	0.0	54.0	0.0	3.0	1.5	100.0	41.5	58.5
Pil 23	9.1	13.6	0.0	22.2	1.1	1.7	48.3	0.0	1.7	2.3	100.0	47.7	52.3
Pil 34	37.4	34.9	7.7	0.0	0.0	1.5	8.7	0.0	7.7	2.1	100.0	81.5	18.5
Pil 38	33.5	30.5	1.5	0.0	0.0	0.0	15.5	0.0	17.0	2.0	100.0	65.5	34.5
Pil 40	37.7	45.2	2.5	0.0	0.0	0.0	7.0	0.0	6.0	1.5	100.0	85.4	14.6
Pil 43	45.5	35.6	5.0	1.0	0.0	2.0	7.9	0.0	3.0	0.0	100.0	89.1	10.9
Pil 63	41.1	48.5	1.5	0.0	0.5	0.5	6.4	0.0	1.5	0.0	100.0	92.1	7.9
Pil 67	41.0	38.0	5.0	0.0	0.0	1.0	13.0	0.0	2.0	0.0	100.0	85.0	15.0
Pil 77	29.8	35.6	5.2	1.0	0.0	1.0	18.3	0.0	7.9	1.0	100.0	72.8	27.2
Pil 81	31.7	32.7	0.0	2.0	0.0	4.0	29.7	0.0	0.0	0.0	100.0	70.3	29.7
Pil 86	32.7	32.7	7.1	4.1	0.0	3.1	15.3	0.0	5.1	0.0	100.0	79.6	20.4
Pil 101	6.0	5.0	4.5	0.0	0.0	0.0	51.2	5.0	14.9	13.4	100.0	15.4	84.6
Pil 106	24.9	32.6	0.0	0.9	0.0	1.7	23.2	0.9	4.7	11.2	100.0	60.1	39.9

	Opaque-eq	Opaque-Blade shaped	Translucent	Bisaccates	Non-Saccates	Spores	Dinoflagellates	Algae	Foraminifera	Acritarchs	Total	Continental flux	Marine flux
Pil 112	24.4	41.3	0.5	1.0	0.0	3.0	26.4	0.0	2.5	1.0	100.0	70.1	29.9
Pil 113	16.4	35.5	0.9	0.5	0.0	1.8	25.0	0.0	20.0	0.0	100.0	55.0	45.0
Pil 117	17.7	15.3	0.0	2.0	0.0	3.4	43.3	2.5	14.3	1.5	100.0	38.4	61.6
Pil 122	28.7	22.5	0.0	1.0	0.0	1.0	26.8	0.0	17.7	2.4	100.0	53.1	46.9
Pil 128	13.4	13.9	0.0	1.0	5.3	1.9	37.8	0.0	25.8	1.0	100.0	35.4	64.6
Pil 132	25.6	17.8	0.0	0.0	0.0	0.0	21.0	0.0	34.2	1.4	100.0	43.4	56.6
Pil 133	30.5	46.6	5.1	0.0	0.0	0.0	11.4	0.0	5.9	0.4	100.0	82.2	17.8

Table 28 – All AAS and isotope data used in Chapter 4

Sample #	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	T°C	Species	Sr ppm	Fe ppm	Mg ppm	Mn ppm	Zone
LC 256c	-0.05	0.30	10.1	<i>Indet.</i>	1638	51	4883	<10	<i>Radiatus</i>
LC 257c	0.97	-0.08	11.5	<i>Hibolites spp.</i>	1427	13	3692	<10	<i>Radiatus</i>
LC 258c-1	0.14	-0.15	11.8	<i>Duvalia spp.</i>	1215	10	2381	19	<i>Radiatus</i>
LC 258c-2	0.17	-0.28	-	<i>Pseudobelus brevis</i>	1196	355	2614	19	<i>Radiatus</i>
LC 262c	0.25	-0.19	-	<i>Duvalia spp.</i>	1210	1375	2549	49	<i>Radiatus</i>
LC 264c	0.08	0.08	-	<i>Indet.</i>	-	-	-	-	<i>Radiatus</i>
LC 272c	0.16	0.09	10.9	<i>Indet.</i>	1599	59	3719	12	<i>Radiatus</i>
LC 276c	0.32	0.36	9.9	<i>Indet.</i>	956	127	2990	14	<i>Loryi</i>
LC 284c	0.05	0.59	9.0	<i>Pseudobelus brevis</i>	770	102	2810	18	<i>Loryi</i>
LC 286c	-0.56	0.05	-	<i>Indet.</i>	1310	838	3044	58	<i>Loryi</i>
LC 293c	-0.30	-0.09	11.6	<i>Hibolites spp.</i>	1466	30	3948	<10	<i>Loryi</i>
LC 294c	0.33	0.02	11.1	<i>Pseudobelus brevis</i>	709	72	2573	12	<i>Nodosoplicatum</i>
LC 299c	0.72	0.32	-	<i>Indet.</i>	-	-	-	-	<i>Nodosoplicatum</i>
LC 300c	0.51	0.15	-	<i>Hibolites spp.</i>	1047	856	2718	18	<i>Nodosoplicatum</i>
LC 301c	0.31	0.10	-	<i>Indet.</i>	1129	404	2988	21	<i>Nodosoplicatum</i>
LC 303c	0.08	-0.46	-	<i>Hibolites spp.</i>	-	-	-	-	<i>Nodosoplicatum</i>
LC 313c	-0.27	0.33	10.0	<i>Hibolites spp.</i>	1407	64	3907	64	<i>Nodosoplicatum</i>
LC 315c	0.11	0.02	11.1	<i>Hibolites spp.</i>	1377	46	3277	11	<i>Nodosoplicatum</i>
LC 316c	-0.09	0.11	-	<i>Indet.</i>	1194	725	3162	73	<i>Nodosoplicatum</i>
LC 326c	0.32	0.03	-	<i>Indet.</i>	-	-	-	-	<i>Sayni</i>
LC 329c	-0.62	-0.07	-	<i>Pseudobelus brevis</i>	1212	1434	2525	44	<i>Sayni</i>
LC 338c	-0.42	0.47	9.5	<i>Hibolites spp.</i>	790	99	3258	12	<i>Sayni</i>
LC 339c	-0.58	-0.31	12.4	<i>Hibolites spp.</i>	1402	1	3606	<10	<i>Sayni</i>
LC 342c	-0.18	-0.10	11.6	<i>Hibolites spp.</i>	1380	1	3890	<10	<i>Sayni</i>
LC 346c	0.37	-0.22	-	<i>Indet.</i>	-	-	-	-	<i>Sayni</i>
LC 348c	-0.25	-0.41	-	<i>Indet.</i>	-	-	-	-	<i>Sayni</i>
LC 350c	-0.02	-0.52	-	<i>Hibolites spp.</i>	-	-	-	-	<i>Sayni</i>
VG 69c	-0.41	-0.21	12.0	<i>Duvalia spp.</i>	1203	75	2961	11	<i>Sayni</i>
VG 76c	0.38	-0.20	12.0	<i>Hibolites spp.</i>	1078	150	2630	12	<i>Sayni</i>
VG 78c	0.50	-1.19	-	<i>Pseudobelus brevis</i>	1429	1429	3968	66	<i>Sayni</i>
VG 79c	-0.01	-0.15	11.8	<i>Indet.</i>	1724	70	3952	13	<i>Sayni</i>
VG 82c	-0.32	-0.53	13.3	<i>Indet.</i>	1314	121	2727	<10	<i>Sayni</i>
VG 91c	0.07	-0.53	-	<i>Indet.</i>	1446	1031	4284	135	<i>Sayni</i>
VG 99c	-0.53	-0.63	13.7	<i>Hibolites spp.</i>	1353	106	3515	23	<i>Sayni</i>
VG 108c	-0.40	-0.83	-	<i>Duvalia spp.</i>	1627	730	5296	<10	<i>Ligatus</i>
VG 109c	-0.24	-1.90	-	<i>Indet.</i>	1359	6496	4239	<10	<i>Ligatus</i>
VG 117c	-0.59	-0.38	12.7	<i>Indet.</i>	1574	41	3718	<10	<i>Ligatus</i>
VG 128c	-0.07	-0.47	13.0	<i>Indet.</i>	1514	294	3729	11	<i>Ligatus</i>
VG 130c	-0.33	-0.24	-	<i>Hibolites spp.</i>	-	-	-	-	<i>Ligatus</i>
VG 133c	-0.59	-0.16	11.8	<i>Hibolites spp.</i>	1393	71	3676	15	<i>Ligatus</i>
VG 150c	-0.31	-0.24	-	<i>Hibolites spp.</i>	-	-	-	-	<i>Ligatus</i>
VG 155c	0.18	-0.13	-	<i>Indet.</i>	1297	685	4227	15	<i>Balearis</i>
AN 8c	-0.17	-0.40	12.8	<i>Hibolites spp.</i>	1490	98	3943	<10	<i>Balearis</i>
AN 9c	0.73	-0.28	12.3	<i>Hibolites spp.</i>	1588	67	4405	<10	<i>Balearis</i>

Table 28 – Continued

Sample #	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	T°C	Species	Sr ppm	Fe ppm	Mg ppm	Mn ppm	Zone
AN 11c	0.59	-0.23	12.1	<i>Hibolites spp.</i>	1373	17	3890	<10	<i>Balearis</i>
AN 15c									
AN 20c	0.28	-0.32	-	<i>Indet.</i>	1199	346	2931	12	<i>Balearis</i>
AN 24c	0.22	-0.51	-	<i>Hibolites spp.</i>	-	-	-	-	<i>Balearis</i>
AN 34c	0.34	-0.19	11.9	<i>Indet.</i>	1297	56	2961	11	<i>Balearis</i>
AN 40c	0.91	-1.29	-	<i>Indet.</i>	1968	440	5093	12	<i>Balearis</i>
AN 50c	0.56	-0.25	12.2	<i>Hibolites spp.</i>	1309	77	3643	12	<i>Angulicostata</i>
VG 181c	0.49	-1.02	15.3	<i>Pseudobelus brevis</i>	1464	29	3636	<10	<i>Angulicostata</i>
VG 191c	0.37	-0.28	-	<i>Indet.</i>	-	-	-	-	<i>Angulicostata</i>
VG 195c	-0.76	0.47	-	<i>Duvalia spp.</i>	846	862	3846	58	<i>Angulicostata</i>
VG 197c	-0.83	-0.63	13.7	<i>Indet.</i>	1175	76	2951	13	<i>Angulicostata</i>
TM 113c	0.43	-0.47	13.1	<i>Hibolites spp.</i>	1336	267	3609	11	<i>Loryi</i>
TM 116c	0.05	-0.80	14.4	<i>Hibolites spp.</i>	1420	310	3582	32	<i>Loryi</i>
TM 117c	0.39	-0.37	-	<i>Hibolites spp.</i>	1316	795	4235	29	<i>Loryi</i>
TM 119c	0.83	-0.37	-	<i>Hibolites spp.</i>	1499	1011	4484	12	<i>Loryi</i>
TM 121c	0.41	-0.48	13.1	<i>Indet.</i>	885	50	1888	16	<i>Loryi</i>
TM 122c	0.78	-0.36	-	<i>Hibolites spp.</i>	1322	818	4306	13	<i>Loryi</i>
TM 124c	0.42	-0.33	-	<i>Indet.</i>	1383	2742	5449	25	<i>Loryi</i>
TM 125c-1	0.12	-0.78	-	<i>Indet.</i>	1503	609	3524	25	<i>Loryi</i>
TM 125c-2	-0.22	-0.69	13.9	<i>Hibolites spp.</i>	1396	137	1495	<10	<i>Loryi</i>
TM 126c-1	0.60	-0.57	-	<i>Hibolites spp.</i>	573	761	3674	94	<i>Nodosoplicatum</i>
TM 126c-2	0.28	-0.67	-	<i>Hibolites spp.</i>	469	444	4008	94	<i>Nodosoplicatum</i>
TM 128c-1	-0.04	-0.76	-	<i>Hibolites spp.</i>	1365	741	4021	13	<i>Nodosoplicatum</i>
TM 128c-2	0.64	-0.65	-	<i>Hibolites spp.</i>	1444	698	3263	<10	<i>Nodosoplicatum</i>
TM 129c	0.41	-0.30	12.4	<i>Hibolites spp.</i>	1506	92	3477	10	<i>Nodosoplicatum</i>
TM 132c	0.45	0.09	-	<i>Indet.</i>	697	509	1717	27	<i>Nodosoplicatum</i>
TM 133c	0.78	-1.31	16.5	<i>Hibolites spp.</i>	1360	66	3343	12	<i>Nodosoplicatum</i>
TM 136c	0.50	-0.48	-	<i>Hibolites spp.</i>	1421	750	4346	15	<i>Nodosoplicatum</i>
TM 144c	-0.01	-0.81	14.4	<i>Hibolites spp.</i>	1347	247	3166	22	<i>Nodosoplicatum</i>
TM 145c-1	0.69	-2.16	-	<i>Hibolites spp.</i>	1436	710	4268	<10	<i>Nodosoplicatum</i>
TM 145c-2	0.34	-2.04	-	<i>Hibolites spp.</i>	1640	611	3090	<10	<i>Nodosoplicatum</i>
TM 146c	-0.23	-1.35	16.6	<i>Hibolites spp.</i>	1325	58	3779	30	<i>Nodosoplicatum</i>
TM 147c	-0.00	-0.55	13.3	<i>Hibolites spp.</i>	1355	108	3131	12	<i>Nodosoplicatum</i>
TM 150c	-0.30	-0.54	13.3	<i>Hibolites spp.</i>	1343	264	3461	20	<i>Nodosoplicatum</i>

Table 28– Continued

Sample #	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	T°C	Species	Sr ppm	Fe ppm	Mg ppm	Mn ppm	Zone
LC 246c	0.45	-0.00	12.0	<i>Indet.</i>	1202	316	2946	26	<i>Callidiscus</i>
LC 249c	0.83	0.33	-	<i>Indet.</i>	-	-	-	-	<i>Callidiscus</i>
LC 223	1.37	-0.23	12.9	<i>B. extingtorus</i>	1539	33	2345	<10	<i>Trinodosum</i>
BSR 364	0.31	-0.75	15.0	<i>C. orbygnianus</i>	1464	130	2777	<10	<i>Verrucosum</i>
BSR 338	-1.90	-0.63	14.5	<i>B. extingtorus</i>	1570	68	3107	16	<i>Campylotoxus</i>
BSR 331d	-0.92	-0.79	15.1	<i>Duvalia conica</i>	1427	193	3598	16	<i>Campylotoxus</i>
BSR 331c	-2.27	-0.48	13.9	<i>Duvalia conica</i>	1189	49	2495	10	<i>Campylotoxus</i>
BSR 331b	-2.41	-1.36	17.5	<i>Duvalia conica</i>	1185	90	2457	<10	<i>Campylotoxus</i>
BSR 239b	-0.83	-0.59	14.3	<i>Indet.</i>	1415	86	3243	<10	<i>Campylotoxus</i>
BSR 237	-0.86	-0.95	15.8	<i>Duvalia lata</i>	1423	307	3881	<10	<i>Campylotoxus</i>
BLB 21	-1.47	-0.55	14.1	<i>B. extingtorus</i>	1820	201	2690	<10	<i>Pertransiens</i>
BLB 23	-1.39	-0.47	13.8	<i>B. extingtorus</i>	1650	56	3586	<10	<i>Pertransiens</i>
BLB 25	-0.62	-0.09	12.3	<i>Indet.</i>	1290	10	1397	<10	<i>Pertransiens</i>
BLB 26	-1.17	-0.66	14.6	<i>Indet.</i>	1299	10	2885	<10	<i>Pertransiens</i>
BLB 28	-0.54	-0.00	-	<i>Indet.</i>	899	405	3080	23	<i>Pertransiens</i>
BLB 36	-0.38	-0.08	12.3	<i>Indet.</i>	1471	75	1304	<10	<i>Pertransiens</i>
BLB 37b	-0.97	-0.47	13.8	<i>Duvalia lata</i>	1481	10	3860	<10	<i>Pertransiens</i>
BLB 37c	-0.13	-1.21	-	<i>Indet.</i>	1219	3418	1957	33	<i>Pertransiens</i>
BLB 38a	-1.41	-0.38	13.5	<i>Indet.</i>	1390	175	2884	<10	<i>Pertransiens</i>
BLB 38b	-0.11	-0.64	14.5	<i>Indet.</i>	-	-	-	-	<i>Pertransiens</i>
BLB 42	-1.54	-0.48	13.9	<i>B. extingtorus</i>	1555	273	3100	<10	<i>Pertransiens</i>
BLB 49	-1.49	-0.40	13.6	<i>C. orbygnianus</i>	1299	128	2438	25	<i>Pertransiens</i>
BLB 52a	-0.77	-0.20	12.8	<i>Indet.</i>	1406	10	2253	<10	<i>Pertransiens</i>
BLB 52b	-1.41	-0.36	-	<i>Indet.</i>	1561	141	4178	60	<i>Pertransiens</i>