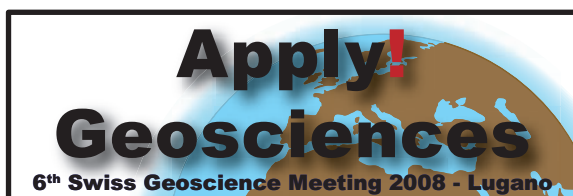




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# 13. Global change – lessons from the geological past

Helmut Weissert, Peter O. Baumgartner

- 13.1 Adatte, T.: Impacts, volcanism, sea-level and climate fluctuations: towards a multi-causal scenario for the Phanerozoic extinctions, a lesson from the past ?
- 13.2 Baumgartner P.O. & Tschudin P.: Eutrophication of marginal seas by river input: The Middle Jurassic Western Tethys compared to the Modern Caribbean
- 13.3 Dessauges A., Leuenberger M., Nicolussi K., Schlüchter C. : Glacial geology and paleoclimate: Stable isotope analysis in Holocene tree rings Mont Miné glacier (VS)
- 13.4 Erba E., Bottini C., Casellato C.E., De Bernardi B., Tiraboschi D.: A geological perspective on calcareous nannoplankton evolution: biotic response to global change and environmental perturbations?
- 13.5 Föllmi K.B., Godet A., Bodin S., Linder P., de Kaenel E., Adatte T., Stein M.: The rise and fall of the Urgonian empire
- 13.6 Giorgioni M., Weissert H., Bernasconi S. : Oceanic and climatic Changes during the Albian- Cenomanian: the World at the End of Pangea
- 13.7 Girault F.E., Weller A.F., Thierstein H.R. : Neogene global cooling and its impact on diatom size evolution
- 13.8 Godefroid F., Kindler P., Samankassou E. : Confirmation of an exceptional sea-level highstand at +20 m during MIS 11 (400'000 ka BP) from Bahamian sedimentary rocks: a credible scenario for future global warming?
- 13.9 Hermann E., Hochuli P.A., Bucher H., Brühwiler T., Goudemand N., Ghazala R.: Evidence for major climatic change at the Smithian-Spathian boundary from low palaeolatitudinal records
- 13.10 Jaccard S., Galbraith E., Haug G., Sigman D.: Reduced oxygen concentrations in the abyssal North Pacific during the last glacial period – implications for oceanic carbon storage
- 13.11 Keller C.E., Giorgioni M., Garcia T.I., Bernasconi S.M., Hochuli P.A., Weissert H. : Cretaceous carbon cycle and climate: The Barremian-Early Aptian C-cycle perturbation
- 13.12 Mehay S., Keller C.E., Bernasconi S.M., Weissert H., Erba E.: The initiation of OAE1a revealed by a high resolution biomarker carbon isotope record
- 13.13 Richoz S., Van De Schootbrugge B., Püttmann W., Heunisch C., Quan T.M., Fiebig J., Pross J.: Evidence of sulfidic marine environment after the Triassic-Jurassic mass-extinction event
- 13.14 Westermann S., Matera V., Fiet N., Adatte T., Föllmi K.B.: Paleoredox changes associated with the Early Aptian Oceanic Anoxic Event

## 13.1

### Impacts, volcanism, sea-level and climate fluctuations: towards a multi-causal scenario for the Phanerozoic extinctions, a lesson from the Past

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Mass extinctions in the Phanerozoic are closely related with severe climate changes and sea-level fluctuations. The consistent association of large magmatic provinces (LIPs and CFBPs) with all but one (end-Ordovician) of the five major Phanerozoic mass extinctions suggests that volcanism played a major role. Faunal and geochemical evidence from the end-Permian, end-Devonian, end-Cretaceous and Triassic/Jurassic transition suggests that the biotic stress was due to a lethal combination of tectonically induced hydrothermal and volcanic processes, leading to eutrophication in the oceans, global warming, sea level transgression and ocean anoxia. It must be concluded that major magmatic events and their long-term environmental consequences are major contributors, though not the sole causes of mass extinctions. Sudden mass extinctions, such as at the K/T boundary, may require the coincidence of major volcanism and a very large impact. Mass extinction is therefore the culmination of many factors which contributed to high-stress environmental conditions, including longterm perturbations (volcanism, e.g. Deccan traps for the end-Cretaceous, cooling, sea-level fluctuations) and short terms events (impacts). No single kill mechanism can really be identified. Whether studies into Earth's oceans and climate change are conducted in the present or the past, they remain of fundamental importance in predicting the future. A grasp of how climate has behaved and evolved in the past allows us to put into context what we see today and better understand what could lie ahead tomorrow. The mass extinction events that punctuate Earth's history are still enigmatic and therefore understanding their various causal mechanisms can provide us with a powerful tool in accessing future climate scenarios.

## 13.2

### Eutrophication of marginal seas by river input: The Middle Jurassic Western Tethys compared to the Modern Caribbean

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The Caribbean - Gulf of Mexico marginal sea (15-30° N) is discussed here in terms of a potential circulation model for the Middle Jurassic Western Tethys. Both seas share a similar size, latitude, lie W of a large ocean and are characterized by a system of complicated sub-basins, shelves and islands. High nutrient input in the Caribbean results from direct river input (Mississippi, Orinoco) and indirect transfer of nutrient-rich freshwater transported by ocean currents – the subject discussed here in detail.

The Amazon and Orinoco Rivers shed together approximately 8000 km<sup>3</sup> yr<sup>-1</sup> freshwater into the tropical Atlantic Ocean and the Caribbean Sea. This corresponds to 20% of the global continental runoff at a rate of ≈0.2 Sv. Undisturbed river systems carry ≈20µg of dissolved P and >40µg of total dissolved N per L of water [3] resulting in a minimal flux of 1.6 \* 10<sup>11</sup> g yr<sup>-1</sup> P and >3.2 \* 10<sup>11</sup> g yr<sup>-1</sup> N. Particulate transport may be a multiple of the above values. Taking a C/P ratio of 500-1000 in Caribbean marine organisms implies that this water-mass is capable of fixing 80-160 Tg of organic carbon and (assuming a K/Si ratio of 1) >0.32 Tg of Si annually. The Amazon and Orinoco river inputs form large plumes that are carried into the Southern Caribbean by the North Brazil Current (NBC ≈20 Sv). In the Southern Caribbean surface water salinity, temperature and nutrient availability vary seasonally with the variation of freshwater input from the rivers and the position of the Intertropical Convergence Zone (ITCZ) that determines the oceanic current pattern. During summer and fall NBC rings (around 400 km in overall diameter, average ≈9 Sv) separate from the main current, translate northwestward toward the Caribbean Sea, stall around 14-18°N and decay shedding important amounts of nutrient laden, low salinity water into the area of the Windward Antilles.

While the physical oceanography of the system is now well described, its impact on Caribbean ecosystems is poorly documented. There are reports of increasing and rapid demise of coral reefs in the Windward Antilles from areas devoid of local pollution, but no relationship with declining Amazon and Orinoco water quality has been established. We suspect that the



rapidly increasing deforestation of the last 20-30 years in the catchment areas of the two large S-American rivers may have increased the nutrient load of their waters, due to increased erosion of organic top soils. The area most affected by such a change must be the SE-Caribbean, where the freshwater pulses are most evident.

The Middle Jurassic (or more exactly the Toarcian to middle Oxfordian) is a time interval of important fluctuations of  $\delta^{13}\text{C}$  with long lasting highs in the Aalenian - early Bajocian and the Middle Callovian to Middle Oxfordian intervals. These fluctuations have been interpreted in terms of high  $C_{\text{org}}$  cycling and low  $C_{\text{carb}}$  production during positive peak times. While the N-Tethyan margin is swamped by detrital material washed off the Eurasian continent, southern Tethyan sediments of this time are characterized by meso- to eutrophic biogenic facies: green radiolarites in basins and monotonous, grey, microbial, often siliceous limestones on platforms such as the High Karst and the Pelagonian. Both pelagic and shelf areas of S-Tethys were beyond the reach of detrital input, but experienced increased nutrient levels throughout most of the Middle Jurassic.

Radiolarite occurrences in Tethyan basins have been explained by upwelling either in a peri-equatorial ocean basin or in monsoonal circulation system. However, the more elaborate reconstructions of the middle Jurassic Tethys show a complicated system of poorly interconnected oceanic basins with often deeply submerged margins separated by submerged shelves on micro-continents. To produce upwelling in all these relatively narrow basins, especially the Alpine Tethys, seems very difficult. An equatorial current system cannot be made responsible either, because palaeolatitudes of the mid Jurassic Tethyan basins are between  $20^\circ$  and  $40^\circ$  N. Another fact speaks clearly against an equatorial current system: The Jurassic Central Atlantic is devoid of biosiliceous sediments. The presence of pelagic carbonates (above the CCD) throughout the Jurassic must be interpreted as the consequence of surface waters that are more oligotrophic than those of the adjacent Tethys and Paleopacific. The Jurassic Atlantic was a "mediterranean" ocean basin such as the Modern Red Sea. Important bottlenecks (Paleo-Gibraltar, S-Florida-Bahamas) exist through the middle and late Jurassic and must have prevented a voluminous (10-20 Sv) water exchange between the Atlantic and its neighbouring basins.

While the mid Jurassic global setting is right for meso- to eutrophic (low  $C_{\text{carb}}$ ) sedimentation, we need a mechanism to continuously supply nutrients to the Western Tethys. In analogy with the Caribbean-Gulf of Mexico we can imagine that the Tethyan N-Equatorial Current struck the Arabian Platform, was deviated to the N and may have entered the Jurassic Eastern Mediterranean. On its way, it interacted with freshwater plumes of large rivers draining tropical N-Africa. While the suspended load sedimented in the deep Eastern Mediterranean, freshwater plumes rich in dissolved nutrients were carried into the entire S-Tethyan realm providing a constant nutrient input. This input allowed for high accumulation rates of biosiliceous sediments, caused deep water anoxia during peak intervals and microbial carbonates on platforms.

Modern anthropogenic changes in the Amazon - Orinoco - Caribbean system may represent a turning point from  $C_{\text{carb}}$  rich to  $C_{\text{carb}}$  poor sedimentation. Global Change can be a lesson for the interpretation of the Past.

### 13.3

## Glacial geology and paleoclimate: Stable isotope analysis in Holocene tree rings Mont Miné glacier (VS)

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The goal of this study is to reconstruct regional-scale climate variability in the Val d'Hérens in Valais. The period we are investigating is the Holocene. It is known that the early Holocene climate was unstable and characterized by a cool event around 8.2 ka BP (Before Present).

This work was motivated by the recent found of *Pinus cembra* and *Larix decidua* trees during the summer 2006 at the front of the tongue of the Mont Miné glacier, found thanks to the present-day melting of the glacier.

We first reconstructed the environment characteristics and properties where the trees were found and where they lived with a glacial geomorphological map and with a georadar investigation. The reconstruction of the Mont Miné glacier movements helped to show the different phases of advances and retreats of the glacier with time. This analysis of tree's local environment was then completed by a temporal climate analysis made accessible with the oxygen and carbon tracers measured on cellulose extracted from rings of the found trees. Dendrochronology (Nicolussi 2006) shows that they originate from the early Holocene.

During the investigated period our results show significant changes in the value of  $\delta^{18}\text{O}$ , indicating that the climate already was unstable with warmer and colder periods. We suggest that these signatures indicate that between the years 6450 and 6180 BC the Mont Miné glacier was smaller than today. Climatic conditions during the Holocene were warm enough to allow the vegetation to grow at an altitude that is currently recovered by the glacier.

The hypothetical advance of the Mont Miné glacier that followed seems to be contemporaneous with the « 8.2 event ». We speculate that before this date the glacier was smaller. During the warmer period the glacier could most likely not advance. It is even possible that the ice was melting during this warmer period. The  $\delta^{18}\text{O}$  values reach a minimum, which indicates that a cool event occurred and implied the death of the trees.

## 13.4

### A geological perspective on calcareous nannoplankton evolution: biotic response to global change and environmental perturbations?

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Recent environmental changes and climate instabilities pose urgent questions regarding biota ability to keep pace with concurrent excess  $\text{CO}_2$ , global warming and ocean acidification. Major concerns are addressed to the possibility of near future extinctions causing a biodiversity loss and revealing a biota failure in sustaining rapid and progressive environmental changes accelerated by anthropogenic impacts. However, the findings of new organisms in various ecosystems raise the possibility that global change might stimulate biota speciation and/or innovation: novel life forms might represent temporary adaptation to environmental stress or might be real new species evolved in response to global change.

The ocean, the oldest and largest ecosystem on Earth, best recorded global changes in climate and oceanic physical, chemical and trophic parameters. Within the oceanic biosphere, calcareous phytoplankton plays a special role as: (1) is common and widespread and consists of cosmopolitan and endemic taxa; (2) has a 220 My-long evolutionary history; (3) is one of the most effective calcite producers of the planet since the Jurassic; (4) is relevant for both the inorganic and organic carbon cycle; (5) is extremely sensitive to environmental variations; (6) may directly climate change by altering albedo and absorption/emission of  $\text{atm-CO}_2$  at large scale.

The Phanerozoic geological record of global change unambiguously indicates that the Earth system already experienced conditions of (super)greenhouse and (super)icehouse. Diversity pulses of calcareous nannoplankton are grossly coeval with major events such as climate and sea-level changes, large magmatic episodes and variations in ocean structure and composition, suggesting that evolutionary patterns are intimately linked to environmental modifications.

Our study aims at reconstruction of both tempo and mode of nannoplankton evolution and the causal/casual role of environmental pressure. We explored time-intervals of (1) evolutionary acceleration in absence of coeval environmental change, during a period of presumed climatic stability (Tithonian, latest Jurassic), and (2) global change marked by calcareous phytoplankton adaptation/evolution (Early Aptian Oceanic Anoxic Event 1a; PETM). For each case history calcareous nannofossils have been investigated in sections from different oceans in order to discriminate among local, regional or global causes, and to verify possible diachroneity in calcareous phytoplankton evolution and/or in response to global changes. Calcareous nannofossil species richness, first and last occurrences and abundance (relative and absolute) have been achieved. Morphometric analyses of selected taxa have been performed to separate malformation, under-calcification, over-calcification, and real ultrastructure changes.

Three speciation models were proposed: phyletic gradualism, punctuated equilibrium and punctuated gradualism. Phyletic gradualism holds that new species arise from slow and steady transformation of populations providing gradational fossil series linking separate phylogenetic species. Punctuated equilibrium explains the appearance of new species by rapid speciation occurring in small peripheral isolated populations, followed by migration to other areas where the fossil sequence usually shows a series of sharp morphological breaks. Punctuated gradualism implies long-lasting evolutionary stasis interrupted by rapid, gradual phyletic transformation without lineage splitting.

The Jurassic-Paleogene case-histories investigated provide examples of all evolutionary patterns in calcareous nannoplankton. Preliminary results suggest: (1) potentially different speciation styles of coccoliths versus nannoliths; (2) that punctuated gradualism prevails in intra-generic speciation, whereas punctuated equilibrium dominates inter-generic speciation; (3) that most new morphotypes associated with extreme, global change represent ephemeral adaptations rather than true species. Although climate and environmental changes have been instrumental for directing nannoplankton evolution, epi-

sodes of major innovation occurred during times of ecosystem stability suggesting very successful diversification and adaptations to steady conditions. Contrary to general models, extreme events such as OAE1a and PETM did not cause extinctions among calcareous nannoplankton.

## 13.5

### The rise and fall of the Urgonian empire

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Urgonian-type shallow-water carbonates of late early Cretaceous age exhibit a typical facies characterized by the presence of large benthic foraminifera, green calcareous algae, calcareous sponges, chaetetids, stromatoporoids, and the co-occurrence of corals and rudists. Urgonian carbonates occur on a global scale in shallow-waters of tropical and subtropical regions and represent a photozoan, oligotrophic community of carbonate producers, which was unique for the Cretaceous - a time of otherwise frequent eutrophic episodes, which translated into oceanic anoxic events and platform-drowning episodes.

The onset and demise of the Urgonian regime is controversially dated, which is for a large part related to different calibration schemes for large benthic foraminifera used by different research groups. We present new ammonite and nannofossil-based data from the helvetic Alps and the western Swiss Jura, which suggest that the onset of the Urgonian did not occur before the late Barremian, after a long period of erosion, condensation and phosphogenesis related to the drowning of the Hauterivian carbonate platform, for which its onset is related to the Faraoni anoxic episode. The demise of the Urgonian platform appears synchronous on a world-wide scale and is dated as middle early Aptian, just before the unfolding of the Selli anoxic episode.

The exact timing of the Urgonian period allows us to tie the evolution of Urgonian platforms and especially their demise to environmental and paleoceanographic change in a way, which resembles the actual development of so-called "dead zones" in shallow-water areas and the progressive loss of reefs on a world-wide scale.

## 13.6

### Oceanic and climatic Changes during the Albian- Cenomanian: the World at the End of Pangea

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The mid-Cretaceous is renowned for being a period in Earth's history when the global conditions differed drastically from those of today. There were exceptionally high temperatures, an absence of permanent polar ice sheets, very high sea level and strong greenhouse effect. The behavior of Earth's climate system and its ruling factors in such warm conditions are still poorly understood and represent a tantalizing topic in Earth and climate sciences.

New paleotemperature and CO<sub>2</sub> estimates reveal that the period from the Albian to the Turonian was the warmest of the all Cretaceous and that this warming cannot be explained by enhanced greenhouse effect only. Quantitative models show a relationship between the thermal maximum and a major re-arrangement of oceanic circulation due to the opening of the Equatorial Atlantic Gateway (EAG) that brought the definitive break-up of the super-continent Pangea.

During the Albian deep-water sediments in the Western Tethys are characterized by more or less alternating varicolored facies testifying to very unstable conditions at the bottom of the ocean, punctuated by three organic matter rich intervals, identified as minor Oceanic Anoxic Events (OAE 1b, OAE 1c, OAE 1d). In the uppermost Albian, after the end of the OAE 1d, this sedimentation pattern is replaced by more homogeneous facies that span the Cenomanian interval until the last major Cretaceous Oceanic Anoxic Event (OAE 2).

This work provides stratigraphical, sedimentological, and geochemical data of Albian-Cenomanian sections from Lusitanian Basin (Portugal) and Southern Alps (Northern Italy). During the Albian-Cenomanian these areas were part of the North

Atlantic and the Western Tethyan realms respectively and they must have been particularly susceptible to the changes induced by the opening of the EAG. We present correlation between the two regions and possible evidences of the major climate changes that took place at that time. The aim is to test whether these changes can be related to the opening of the EAG, supporting the prediction of the models, or other factors played a significant role on the mid-Cretaceous oceanic-climatic system.

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## 13.7

### Neogene global cooling and its impact on diatom size evolution

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A major characteristic among skeletonized phytoplankton in the ocean is that they depend on the availability of bio-limiting nutrients in the photic zone. Competition (inter- and intra-group) for these bio-limiting nutrients together with present and past changes in oceanic conditions are potential dominant drivers of the adaptation and resulting evolution of these micro-organisms. Over the Cenozoic and particularly since the Neogene, diatoms have become the most efficient group for nutrient uptake, by far outcompeting the coccolithophores in nutrient-rich areas and assuming dominance in the oceanic cycling of dissolved silica.

Here we explore the utility of a quantitative measure, mean test sizes of centric diatoms and their variability, to characterize the macro-ecological patterns in today's oceans and the evolutionary response of this group in the past. Size and morphological characteristics of the centric diatom frustules (diameter >20 µm) were collected using recently developed automated light microscopy and image analysis techniques for a statistically representative number of specimens (i.e. 250-700) per sample. We present initial results of these size analyses by comparing our macro-ecological calibration in 46 Holocene core-top samples from tropical to polar environments with the macro-evolutionary patterns observed in DSDP/ODP sites from the Southern Ocean, the Equatorial and the North Pacific over the past 20 million years at a temporal sampling resolution of 0.3-2 m.y.

Although our Holocene sample set shows large variability in environmental conditions, changes in the mean size of centric diatom assemblages are rather small. In contrast, during the Neogene mean sizes of centric diatoms show large variability through time with regional shifts occurring during well-known climatic and oceanic events (i.e. onset of northern hemisphere glaciation). These patterns imply an evolutionary trend possibly related to Neogene global cooling and related reorganizations of water masses and their dissolved silica pools. Since diatoms are the primary competitors of coccolithophores for nutrients among the skeletonized phytoplankton, their evolutionary emergence to dominance would imply coeval consequences for the evolution of the coccolithophores.

## 13.8

### Confirmation of an exceptional sea-level highstand at +20 m during MIS 11 (400'000 ka BP) from Bahamian sedimentary rocks: a credible scenario for future global warming?

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The discovery of elevated marine and lacustrine deposits near Glass Window (North Eleuthera, Bahamas) validates the controversial sea-level highstand at about +20 m during Marine Isotope Stage (MIS) 11. Considered as the longest interglacial of the past half million years, MIS 11 is an excellent candidate for providing a credible scenario for a future, human-induced, global warming.

Two stratigraphic sections (GW1 and GW2) including five carbonate units were logged near Glass Window in North Eleuthera Island. Sedimentological, petrographic and geochronological (amino-acid racemization dating) analyses were performed.

On both sections, which form high cliffs about 18 and 22 m high, Unit 1 consists of cross-stratified biopeloidal limestone showing a late generation of fibrous rim cement of marine origin. This late cementation entirely affects this first unit. The boundary between Units 1 and 2 is represented by a planar erosional surface. Unit 2 displays well-defined planar bedding at both sites, whereas faint cross-stratifications are also visible at GW 1. It consists of laminated biopeloidal grainstone containing *Halimeda* fragments and rounded lithoclasts derived from Unit 1, and is further characterized by an early generation of isopachous fibrous cement. The upper part of Unit 2 shows one thick laminated crust including numerous spherulites of cyanobacterial origin, and is capped by a reddish paleosol. The top of the GW 2 section is represented by an oolitic/peloidal grainstone (Unit 3), whereas the upper part of GW 1 includes one bioclastic (Unit 4) and one oolitic (Unit 5) unit, separated by a paleosol.

The values of alioisoleucine/isoleucine (A/I) ratios average at 0.740, 0.737, 0.652, 0.467, and 0.371 for Units 1 to 5, respectively.

Based on these analyses, Units 1, 3, 4 and 5 can be identified as eolianites dating from MIS 11 (A/I = 0.740), MIS 9 (A/I = 0.652), MIS 7 (A/I = 0.467) and MIS 5e (A/I = 0.371), respectively. Exposed between +12 and +14.5 m, the basal part of Unit 2 can be interpreted as subtidal and beach deposits, whereas its upper part, at +15 m, likely corresponds to lacustrine (pond) sediments, both dating from MIS 11 (A/I = 0.737). The presence of spherulites of cyanobacterial origin shows that the thick laminated crust at the top of Unit 2 was formed at the surface, and not within a soil profile. Considering the subsidence affecting Eleuthera Island (1 m/100 kyr), the beach and pond deposits of Unit 2 and the marine cements present in Unit 1 indicate that sea level reached an elevation of about +20 m during MIS 11, implying the collapse of both the Greenland and the West-Antarctic ice-sheets, and the partial melting of the East-Antarctic ice-sheet.

The Earth's orbital parameters were about the same during MIS 11 than today (i.e. MIS 1). Climatic conditions and climate evolution during these two interglacials can, therefore, be compared. The prominent melting of polar ice-sheets and the associated sea-level fluctuation at +20 m occurred at the end of MIS 11, and were probably linked to its exceptional duration (20-35'000 yrs). Stage 1 began only 12'000 years ago and, thus, the prospect of a 20 m rise in sea level appears rather remote in time. However, the present-day, human-induced increase in atmospheric greenhouse gases may drastically accelerate the disintegration of polar ice-sheets, triggering a catastrophic elevation of sea level in the next decades or centuries. The MIS 11 stratigraphic record from the Bahamas shows that this is possible.



## 13.9

### Evidence for major climatic change at the Smithian-Spathian boundary from low palaeolatitudinal records

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The delayed recovery of marine and terrestrial ecosystems after the end-Permian extinction event is still up for debate. Focusing on the Smithian-Spathian boundary, palaeoecological changes are reflected by a significant global faunal turnover as indicated by ammonoids (Brayard et al. 2006) and conodonts (Orchard 2007) as well as a change in the palynological associations of the Boreal realm. There, the Smithian-Spathian transition is marked by a conspicuous change from spore dominated assemblages in the Smithian to gymnosperm dominated assemblages in the Spathian (Galfetti et al. 2007a).

Here, we present the composition of the Early Triassic microfloras of Nammal, Salt Range, Pakistan. Ammonoids and conodonts provide the high resolution age control of the studied section (Brühwiler et al. 2007).

The late Smithian palynological assemblages are characterized by a general dominance of hygrophytic elements. Slightly below the Smithian-Spathian boundary, between the *Anasibirites* beds and the *Glyptophiceras* beds, the composition changes dramatically with a drastically increasing proportion of xerophytic elements. This event coincides with the onset of a positive shift in the  $\delta^{13}\text{C}$  record marking the Smithian-Spathian boundary (Galfetti et al. 2007b). Preliminary results from southern Tibet also indicate a similar trend from hygrophyte-dominated to xerophyte-dominated assemblages across the boundary.

Thus, there is evidence for the Smithian-Spathian boundary climatic event from high as well as from low palaeolatitudes, demonstrating its global significance.

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## 13.10

### Reduced oxygen concentrations in the abyssal North Pacific during the last glacial period – implications for oceanic carbon storage

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The deep North Pacific represents an end-member of the modern circulation regime. It is far from sites of deep-water renewal, and so is enriched in  $\text{CO}_2$  and dissolved nutrients due to the accumulation of the products of remineralised organic matter along the path of global deep-water circulation. For the same reasons, deep North Pacific waters show a depletion in dissolved oxygen.

Reconstructions of  $\delta^{13}\text{C}$  distribution for the glacial Pacific Ocean show that deep water below 2000 - 2500 m was depleted in  $\delta^{13}\text{C}$  when compared with mid-depth and upper ocean waters. Below 2000 m, the deep waters were enriched in nutrients and metabolic  $\text{CO}_2$ , while nutrient concentrations in the intermediate depth Pacific were apparently lower. Partition of  $\text{CO}_2$  in favor of the deep ocean would have contributed to decrease atmospheric  $\rho\text{CO}_2$  during cold periods.

This hypothesis has been tested by studying the sedimentary distribution of redox-sensitive trace metals (Mo & U) in two sediment cores spanning the abyssal subarctic Pacific. The fundamental control on sediment redox state is the balance between the flux of organic matter to the seafloor and the flux of oxidants to the sediment from overlying seawater. Thus, variations in sedimentary redox state are linked to changes in the magnitude of biological export and the role of ocean circulation. Comparison of redox-sensitive trace metals abundance with reconstruction of biogenic flux to the sediment will yield inferences about relative changes of oxygen concentrations at the water-sediment interface.

Sediments deposited during the last ice age are enriched in authigenic U when compared to the Holocene. Here, the export production proxies Ba/Al and biogenic opal indicate that the local flux of biogenic detritus to the seafloor was generally reduced during the last glacial period. Given this evidence, the enhanced U accumulation must have been a response to substantially lower bottom water  $\text{O}_2$  and, by inference, the glacial North Pacific contained a higher concentration of respired carbon than today. Although the absence of Mo enrichments argues that anoxia did not develop in the vicinity of our core sites, oxygen concentrations may have dropped far below their current concentrations during the last ice age. If this elevated respired carbon burden is representative of the deep glacial Indo-Pacific Ocean, it could represent the primary reservoir of glacial  $\text{CO}_2$  sequestration. It results, that a significant fraction of  $\text{CO}_2$  has been sequestered into the deep ocean during glacial periods leading to a large reduction of atmospheric  $\rho\text{CO}_2$ , that is widely documented in Antarctic ice cores.

## 13.11

### Cretaceous carbon cycle and climate: The Barremian-Early Aptian C-cycle perturbation

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Late Early Cretaceous marine sediments feature a fascinating succession of repeated greenhouse pulses interrupted by episodes of cool climate, which is indicated by the several important positive carbon isotope anomalies documented in the sedimentary record.

The Ontong-Java volcanism is thought to be the trigger of the major positive carbon isotope excursion in the Aptian (Larson & Erba 1999). However, this volcanic activity predates the isotope excursion considerably (Tejada et al. 2002). This led to the hypothesis that the "Aptian greenhouse pulse" already began in the Barremian (Weissert & Erba 2004; Coccioni et al. 2004) with a first  $\text{CO}_2$  pulse initiating climate warming and a first perturbation of the global carbon cycle. This is evidenced by deposition of black shales and a positive carbon isotope excursion during the mid-Barremian (mid-Barremian event of Coccioni et al. 2004). Accelerated organic carbon burial caused a decrease of the atmospheric  $\text{CO}_2$  levels and induced a cooling event, which is thought to have resulted in a renewed carbonate-dominated sedimentation in the Late Barremian/Early Aptian oceans.

In this study, a composite Late Hauterivian-Early Aptian Tethyan record is presented combining carbonate carbon isotope values with magnetostratigraphic and biostratigraphic data. From the Late Hauterivian to the early Early Aptian, the carbonate carbon isotope values fluctuate essentially between 1.6‰ and 2.4‰. The most positive values are reached during the early Aptian pre-OAE 1a excursion with carbonate carbon isotope values of up to 3‰.

The different sections feature extremely variable thicknesses, which seems to be due to frequent sedimentary hiatus, a pattern that is well-known from Barremian-Aptian successions and is interpreted to result from increased current intensities.

The distribution pattern of black shales combined with the carbon isotopes allows to assign the black shales to the known over-regional events such as the Faraoni Event in the Late Hauterivian or the OAE 1a in the Early Aptian.

The studied sections highlight the variability and complexity of sedimentary deposits at various positions in the different basins at the southern margin of the Tethyan Ocean and allow a varied insight into the ocean-atmospheric evolution of the Early Cretaceous.

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## 13.12

## The initiation of OAE1a revealed by a high resolution biomarker carbon isotope record

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Oceanic anoxic events (OAEs) are time envelopes in the Cretaceous when ocean conditions favoured the episodic deposition of organic-rich sediments on a global scale. The first Cretaceous oceanic anoxic event (OAE1a, Early Aptian, ≈120 million years ago) is marked by an enigmatic negative carbon isotope ( $\delta^{13}\text{C}$ ) spike of up to 3‰ in marine carbonates and of 4 to 5‰ in the organic carbon at its base (Schlanger & Jenkyns, 1976; Menegatti et al., 1998). This carbon-cycle perturbation is believed to reflect a massive release of  $^{13}\text{C}$  depleted carbon into the ocean and the atmosphere. Because the Early Aptian is known as a period of greenhouse conditions, this light carbon has been proposed to derive from the dissociation of methane hydrates (Dickens, 2003). The aim of our study is to elucidate the initiation of OAE1a in an attempt to anticipate the possible evolutions of both atmospheric and oceanic ecosystems on Earth, under warmer climate than today.

Because exchanges between ocean and atmosphere pools are faster than the resolution of the carbon isotope records available so far for the OAE1a and bulk  $\delta^{13}\text{C}$  combines effects of a whole ecosystem, a higher resolution carbon isotope study on specific biomarkers is essential. Bulk and biomarkers  $\delta^{13}\text{C}$  were therefore measured at sampling intervals of 2000 to 6000 years on samples from the Cismon core (Southern Alps, Italy), showing one of the best stratigraphic resolution for the OAE1a interval at low latitudes (Li et al., 2008).

The new carbon isotope record shows a stepwise initiation of OAE1a which was divided into five intervals, covering ≈70 kyr. They successively describe a massive outgassing of mantle CO<sub>2</sub>, a temperature rise, an increase in carbon-isotope fractionation and partial methane hydrates dissolution. This evidences that the negative carbon isotope spike recorded at the onset of OAE1a was probably caused by a combination of different processes affecting the carbon-cycle and primarily triggered by an intense volcanic activity, linked to the Ontong-Java Plateau large igneous province.

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## 13.13

### Evidence of sulfidic marine environment after the Triassic-Jurassic mass-extinction event

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The Triassic-Jurassic boundary (T-J; 201 Ma) marks one of the so called Big Five mass-extinction events that may have led to the extinction of more than 80% of all marine invertebrates. The extinction of marine and terrestrial biota is increasingly linked to the outgassing of large volumes of CO<sub>2</sub> and SO<sub>2</sub> during the emplacement of the Central Atlantic Magmatic Province, however the exact kill mechanisms and the long-term effects of this large igneous province remain to be elucidated. Here, we present multi-disciplinary data, including organic geochemical, isotope (C, N) and microfossil data, from 3 cores in Luxemburg (Rosswinkel), and northern (Mariental) and southern Germany (Mingolsheim) that provide evidence for prolonged environmental instability during the earliest Jurassic. Organic geochemical analyses show elevated quantities of the biomarker isorenieratane in the lowermost Hettangian following a major overturn of terrestrial vegetation (fern spike) as documented by palynological analyses. Isorenieratane derives from the brown strains of photosynthetic green sulphur bacteria (Chlorobiaceae) that require both light and free hydrogen sulfide in the water column. The presence of abundant aryl isoprenoids (isorenieratane and its diagenetic products) in Luxemburg and N Germany suggests that marginal marine basins in NW Europe became salinity stratified and developed intense Photic Zone Euxinia (PZE) after the mass extinction event. This excludes euxinia as kill mechanism. Nitrogen and carbon isotope data from organic matter support the development of shallow marine anoxia in NW Europe. Our observations are consistent with the long-term effects of CO<sub>2</sub> release and greenhouse warming. Repeated and prolonged PZE in the Tethys Ocean may have contributed to the slow recovery of shallow marine ecosystems after the Triassic-Jurassic boundary.

## 13.14

### Paleoredox changes associated with the Early Aptian Oceanic Anoxic Event

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The Cretaceous is characterized by short periods during which widespread oceanic anoxic conditions developed, documented by the extensive deposition of organic carbon-rich sediments (Schlanger and Jenkyns, 1976). The early Aptian OAE, labeled OAE 1a, corresponds to one of the most studied anoxic event within the Cretaceous. This event is characterized by a positive excursion in δ<sup>13</sup>C, preceded by a pronounced negative spike, which was interpreted as the result of a pulse of methane release from clathrates from the ocean to the atmosphere (Weissert and Erba, 2004). In our study, we aim at improving our understanding of palaeoceanographic change leading to this event and test the proposed models by investigating phosphorus (P) and redox-sensitive trace-metals (TM) contents in sections through lower Aptian sediments along a basin-shelf transect in the western Tethys. We complement our geochemical analysis by the analyses of organic matter contents.

We selected three representative sections: Gorgo a Cerbara (central Italy) in the Umbria Marche basin, Glaise l'Ermitage (SE France) located in the Vocontian trough and Cassis/La Bédoule (SE France) located along the Provencal platform.



The general trend in P accumulation shows an increase at the onset of the early Aptian event followed by a rapid decrease. This suggests an increase in nutrient input, whereas the return to lower values through the first part of the anoxic event may be related to a weakened capacity to retain P in the sedimentary reservoir due to bottom water oxygen depletion. This general pattern is contrasted by the data of Gorgo a Cerbara which also show P-enrichments at the top of the Livello Selli. We compared these enrichments to the total organic carbon (TOC) values. The shales with the maximum TOC values also correspond to those with the highest P content. We also calculated  $C_{org}:P_{tot}$  ratios and observed that the highest values corresponds to the top of the Selli level. This is interpreted as a reflection of the decreased capacity of storing and preserving phosphorus in oxygen-depleted sediments.

TM exhibit comparable variations in the basinal settings. In the section of Gorgo a Cerbara, the data for U, V, Mo, Co, As show a low background level, contrasted by different maxima in concentrations near the top of the Selli level. Conversely, in the section of Glaise l'Ermitage and Cassis/La Bédoule, no significant enrichments have been observed in sediments equivalent to the Selli level. The different behaviour of the TM in the studied sections may be related to the palaeogeographic setting of the studied sections. These data seem to indicate anoxic conditions in the basin. In shallower-water environments, conditions may have been less reducing. Moreover, in Gorgo a Cerbara, three distinct enrichments have been observed. This seems to indicate fluctuations in the intensity of water column anoxia during the shift in  $\delta^{13}C$ .

Our results show that the expression of the OAE 1a is different following the palaeogeographic setting. The evolution of the P trend suggests an increase in nutrient input at the onset of the anoxic event, just after the negative spike in  $\delta^{13}C$ . TM and high C:P values may indicate anoxia conditions in the deep environment characterized by several anoxic phases with intermittent return to less oxygen-depleted conditions.

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