Newsl. Stratigr.	**42 (3)**	145–179	15 Fig.	Berlin · Stuttgart, 30. 4. 2008

Chemostratigraphy

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with 15 figures

Abstract. Chemostratigraphy uses chemical fingerprints stored in sediments and sedimentary rocks for stratigraphic correlation. Stable isotope signatures fixed in sedimentary inorganic and organic matter are among the most powerful proxies used in chemostratigraphy. This contribution focuses on the use of oxygen and carbon isotope geochemistry in stratigraphy. The importance of oxygen isotope stratigraphy for paleoclimate research is documented in case study I. Oxygen isotope stratigraphy can be used to trace climate pulses through the last few million years. It serves also as a tool for reconstruction of multicentennial climate variations on a global scale. Case study II demonstrates how carbon isotope stratigraphy in Cretaceous successions is used for correlation between ammonite-dated sections and sections dated with magnetostratigraphy. Case study III focuses on the use of carbon isotope stratigraphy in the Palaeozoic. Carbon isotope studies have been intensively used in the Palaeozoic to unravel changes in the global carbon cycle and for chemostratigraphic correlation of sections from various palaeocontinents. However, diagenesis is a major concern since Palaeozoic carbonates may have been affected by recrystallisation and considerably higher temporal overprint in comparison to Mesozoic or Cenozoic carbonate sequences.

PART I: Concepts, methods, definitions

1 Introduction

Chemostratigraphy or chemical stratigraphy uses chemical fingerprints in sedimentary sequences for stratigraphic correlation. It is a very powerful stratigraphic tool if it is applied in combination with bio- and magnetostratigraphy. Geochemical proxies used for stratigraphy were originally developed and utilized as proxies for paleoenvironmental change. Many of these chemical proxies turned out to record – to different degrees – global changes in climate and oceanography. These changes left their signature in marine or terrestrial sedimentary records. Due to the geologically short mixing time of the ocean-atmosphere system, which is in the order of thousands of years, some signatures of global

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DOI: 10.1127/0078-0421/2008/0042-0145 0078-00421/08/0042-0145 $ 8.75

environmental change stored in the atmosphere and/or seawater will be mirrored in a variety of biotic geochemical proxies that can be used as accurate stratigraphic marker.

The most powerful method used in chemostratigraphy is stable isotope geochemistry. When Harold Urey and his research group started analyzing various minerals, rock types and shell material for their isotopic composition, they were interested in using stable-isotope geochemistry as a paleoenvironmental tool. The group indeed could establish a paleotemperature scale based on oxygen isotope analyses of shells (Epstein et al. 1953). Urey and his group also reported variations in the carbon isotope composition of various compounds and the possible use of carbon isotopes in Earth sciences (Craig 1953).

Cesare Emiliani (1955) demonstrated how the oxygen isotope composition in planktonic foraminifera in piston cores from the Caribbean varied through time. He interpreted the oscillations of the curve as a paleotemperature curve recording 7 glacial-interglacial cycles. Improved understanding of oxygen isotope geochemistry and of fractionation processes in the water cycle have later shown that oxygen isotope variations through time record changes in both temperature and isotopic composition of seawater, which was controlled by ice volume variations, thus producing a signal of global sea level variations (Shackleton & Opdyke 1973 and 1977). Oxygen isotope curves established on benthic foraminifera living at low temperature remaining largely constant through glacial-interglacial cycles were reinterpreted as accurate ice volume proxies. Oxygen isotope records provide most relevant information on the dynamics of ice ages but they also provided a chemostratigraphy to be employed for the reconstruction of marine environments on a global scale.

The importance of stable carbon isotope geochemistry for paleoceanography and for stratigraphy was recognized in the mid 1970s (e.g. Berger, et al. 1978, Duplessy et al. 1981, Weissert et al. 1979, Scholle & Arthur 1980). The findings of Craig (1953) formed the baseline for new investigations of carbon-isotope geochemistry in the oceanic reservoir. The growing knowledge of fractionation processes in water-carbonate systems facilitated the use of carbon isotopes as a tracer in paleoceanography.

2 Oxygen isotopes as stratigraphic tool

The two oxygen isotopes used in chemostratigraphy are ^{16}O and ^{18}O. 99.8 % of all the oxygen is in the form of ^{16}O, ^{18}O makes up most of the remaining 0.2 %. Absolute variations in the two stable isotopes are very small, therefore isotope geochemists measure departures of the $^{18}O/^{16}O$ ratio from a laboratory standard, today the Vienna Pee Dee Belemnite Standard (V-PDB). The results are expressed in the per mil notation.

The oxygen isotope composition of calcium carbonate is dependent on the isotopic composition of the ambient fluid and on the temperature of precipitation. In an ocean with constant isotopic composition of the water, an increase in temperature of little more than 4 °C corresponds to a decrease in $\delta^{18}O$ of about 1 ‰ (Shackleton 1987). At stable temperatures a change in $\delta^{18}O$ of -1 ‰ corresponds to a deglaciation-induced sea-level rise of about 110 m (e.g. Schrag et al. 2002), which can be explained by melting of isotopically light polar ice (−20 to −40 per mil). The best carriers of marine oxygen isotopic composition are planktonic and benthic foraminifera. Variations in deep-water benthic foraminifera living under constant bottom water temperatures (± 1 °C) record ice build-up and deglaciation through time. Planktonic foraminifera record a combined ice volume and temperature effect plus a local salinity record in their oxygen isotope signature.

The oxygen isotope record established over the last few million years provides a history of multiple glacial-interglacial cycles showing cyclicities of 20 ky and 40 ky and, over the last 800 ky of 100 ky. These cycles record the beat of orbital variations and climate change triggered by changes in insolation through time. Time control on the duration of the climate cycles identified in the marine oxygen isotope records was established by the combination of isotope stratigraphy with other stratigraphies. Shackleton & Opdyke (1973 and 1977) combined oxygen isotope curves with magnetostratigraphy and succeeded in establishing the first oxygen isotope stratigraphy of the last 700,000 years with 22 isotope stages. These isotope stages, today known as MIS (marine isotope stage) are numbered starting with the Holocene as MIS 1. For example, the base of the Gelasian stage (2.59 Ma), which closely coincides with the Matuyama/Gauss magnetic polarity chron boundary, corresponds to the peak of MIS 103. Power spectra analyses are used to extract any cyclic signal in the measured isotope curves. These analyses confirmed the hypothesis of Milankovitch (Hays et al. 1976). Thus, climate pulses preserved in the oxygen isotope records were established as precise chronostratigraphic tool and accordingly, provide an accurate astrochronological frame for the Neogene (e. g. Berggren et al. 1995; Lourens 2004).

Due to diagenesis, oxygen-isotope records from lithified pelagic sediments cannot be used as a reliable stratigraphic tool. Only pelagic sediments which escaped deep-burial diagenesis preserve oxygen isotope compositions which serve for paleotemperature reconstructions but, due to insufficient sampling density, not for high-resolution oxygen isotope stratigraphy (e. g. Wilson & Norris 2001).

3 C-isotopes and C-isotope stratigraphy

Of the two stable carbon isotopes, the abundance of ^{12}C in nature is given as 98.89 %, while ^{13}C forms the remaining 1.11 % (Craig 1953). Mass differences of the two isotope species lead to strong fractionation during photosynthetic incorporation of carbon into organic matter, while inorganic carbonate precipitates formed in the aquatic environment are less affected by fractionation processes as discussed and reviewed in a number of articles (e. g. Hayes et al. 1999).

The large carbon pool of the oceans controls the exogenic carbon cycle with reservoir residence time in the order of 10^5 years. The $\delta^{13}C$-value of modern ocean water varies between –1.5 ‰ in deep water and 2.0 ‰ in surface water (Kroopnick 1985). ^{13}C enrichment of surface water is caused by carbon isotope fractionation during organic matter production. Marine organic matter is strongly depleted in ^{13}C (ca. –25 ‰ $\delta^{13}C$). Isotopically light organic carbon is oxidized in intermediate and deep water and CO_2 enriched in ^{12}C is added to these waters. Calcium carbonate precipitating from ocean water has an enrichment factor of 0.2 ‰ up to + 2 ‰ at 25 °C, depending on carbonate mineralogy (e. g. Grossmann & Ku 1986, Romanek et al. 1992). However, this factor is only little affected by temperature (0.03 ‰/°C, Emrich & Vogel 1970). This small temperature-induced fractionation effect makes carbon isotopes in carbonate precipitates a powerful monitor of the carbon-isotope composition of the ambient water – if equilibrium conditions are reached.

Most accurate oxygen and carbon isotope stratigraphies are based on marine paired planktonic and benthic foraminifera records. The isotope curves across the Paleocene-Eocene Thermal Maximum (PETM), one of the most dramatic global warming events in Earth history, serve as a good example. Benthic and planktonic single specimen isotope curves across the PETM record how the warming event was triggered by a perturbation of the global carbon cycle possibly related to sudden and massive thermal dissociation of methane hydrate (Dickens et al. 1995). The stratigraphic resolution of planktonic isotope records is in the order of hundreds to thousands of years (e.g. Zachos et al. 2005). The sudden shift in both oxygen and carbon isotope curves therefore serves as an accurate marker of the Paleocene-Eocene boundary (e.g. Thomas et al. 2002; Zachos et al. 2005). In stratigraphically more extended sections, the isotope shift coincides with the base of the benthic extinction event, the base of the planktonic foraminiferal "excursion fauna" and with a marlstone unit marking the Paleocene-Eocene boundary (Dupuis et al. 2003). The PETM is also recorded in carbon isotope curves from terrestrial sedimentary sections and the carbon isotope curve serves as an accurate stratigraphic correlation tool between marine and terrestrial environments (e.g. Koch et al. 2003).

While diagenesis increasingly alters the oxygen-isotopic signature of deeply buried marine sediments, C-isotope geochemistry is less influenced by diagenesis in pelagic settings. This explains why lithified pelagic sedimentary successions store very good information for C-isotope stratigraphy. The most reliable carriers of pre-Cenozoic marine carbon isotope signatures are either individual fossils or pelagic bulk carbonate (e.g. Veizer et al. 1999, Weissert et al. 1985). The carbon isotope signature measured in bulk sediments of hemipelagic origin records the mixing of pelagic and neritic carbonate ooze. Analyses of hemipelagic sediments indicate that bulk carbonate can be used for C-isotope stratigraphy even if the measurements may differ in their absolute values from measurements in corresponding pelagic sediments. Neritic carbonates can preserve a global marine carbon isotope signature but marine and/or meteoric diagenesis can mask the original marine carbon isotope value (e.g. Hennig 2003).

Carbon isotope stratigraphy also serves as an important tool in ordering of Proterozoic time (Knoll 2000). Carriers of Proterozic carbon isotope signatures used in stratigraphy often are neritic carbonates including dolostones. Ling et al. (2007) argue that a primary marine carbon isotope signature is even preserved in dolomitized platform carbonates.

The isotopic composition of marine and/or terrestrial organic matter serves as excellent source of information on past environmental change (e.g. Hayes et al. 1999). Marine carbon isotope curves based on the analysis of organic matter and/or specific biomarkers record a complex history of changing ocean chemistry, productivity and $p\mathrm{CO}_2$. However, their use as a stratigraphic correlation tool is limited even if extreme events like the sudden addition of isotopically light carbon to the ocean and atmosphere is also recorded in marine organic matter (e.g. Triassic-Jurassic boundary event, Hesselbo et al. 2002). Sometimes marine carbonate and organic carbon isotope curves show contrasting trends which indicates that organic carbon isotope curves record peculiar environmental changes coinciding with perturbations of the global carbon cycle (e.g. Louis-Schmid et al. 2007). Variations in terrestrial organic carbon-isotope composition provide the possibility to use C-isotope stratigraphy as tool for correlating marine and terrestrial records (GRÖCKE et al. 1999).

4 Sr-isotope stratigraphy

Among other isotopes used in stratigraphy, strontium isotopes are most widely used for correlation (e.g. VEIZER et al. 1999, MCARTHUR & HOWARTH 2004). Sr has a long ocean residence time of $\sim 2.4 \times 10^6$ years (JONES & JENKYNS 2001), therefore Sr isotope geochemistry has been of limited use for high-resolution stratigraphy (10^4–10^5 years). The Phanerozoic Sr-isotope composition is characterized by long-term fluctuations marked by major turning points in the Sr-isotope curve which can be used as stratigraphic marker levels, for example the turning point in the Mesozoic Sr-isotope curve in the Late Jurassic (Fig. 1) and the rapid change in Sr-isotope values during the Aptian (e.g. JONES & JENKYNS 2001, BRALOWER et al. 1997). STEUBER (2003) has documented how Sr-isotope stratigraphy can provide important information for biostratigraphy. He measured the Sr-isotope composition of Cretaceous rudists. Based on these analyses he succeeded in revising the stratigraphic ranges of chronospecies of hippurid rudists.

MCARTHUR & HOWARTH (2004) presented a global seawater strontium isotope curve of the Phanerozoic calibrated against numerical ages. The authors used a statistical regression method for the construction of a best-fit curve for the $^{87}Sr/^{86}Sr$ data as a function of time. Increasing accuracy in Sr-isotope analyses, the use of laser ablation combined with inductively coupled plasma mass-spectrometry (MC-ICPMS) results in improved and highly accurate Sr-isotope data sets which will contribute to a further improvement in the resolution of Sr-isotope stratigraphy (e.g. RAIS 2007).

5 Other chemostratigraphic tools

Changes in ocean chemistry over geological time controlled by fluctuating global weathering rates, by changes in volcanic and hydrothermal activity and by sedimentological and tectonic processes are also recorded in the sulfur isotopic composition of past seawater. The seawater $\delta^{34}S_{SO4}$ record is controlled by changes in riverine and/or hydrothermal and volcanic input sources and/or by environmentally controlled changes in partitioning of sulfur between the oxidized and reduced sedimentary sulfur sinks. PAYTAN et al. (1998, 2004) used marine barite, a mineral that shows to record seawater $\delta^{34}S_{SO4}$ for the establishment of a detailed Cretaceous and Cenozoic sulfur isotope curve (Fig. 2). Prominent fluctuations recorded in this curve can be used as stratigraphic marker levels which mirror global perturbations in ocean chemistry and in the global sulfur cycle.

New paleoceanographic proxies, including hafnium or osmium isotopes are of increasing importance for stratigraphy. Osmium isotopes have been successfully used as a stratigraphic or dating tools in condensed sediments. KLEMM et al. (2006) dated the growth pattern of hydromanganese crusts in the Pacific over the last 80 million years. Neodynium is of limited use for stratigraphy on a global scale because it varies through space and time. This makes neodymium isotope geochemistry a promising tool in paleoceanography (e.g. FRANK et al. 2006).

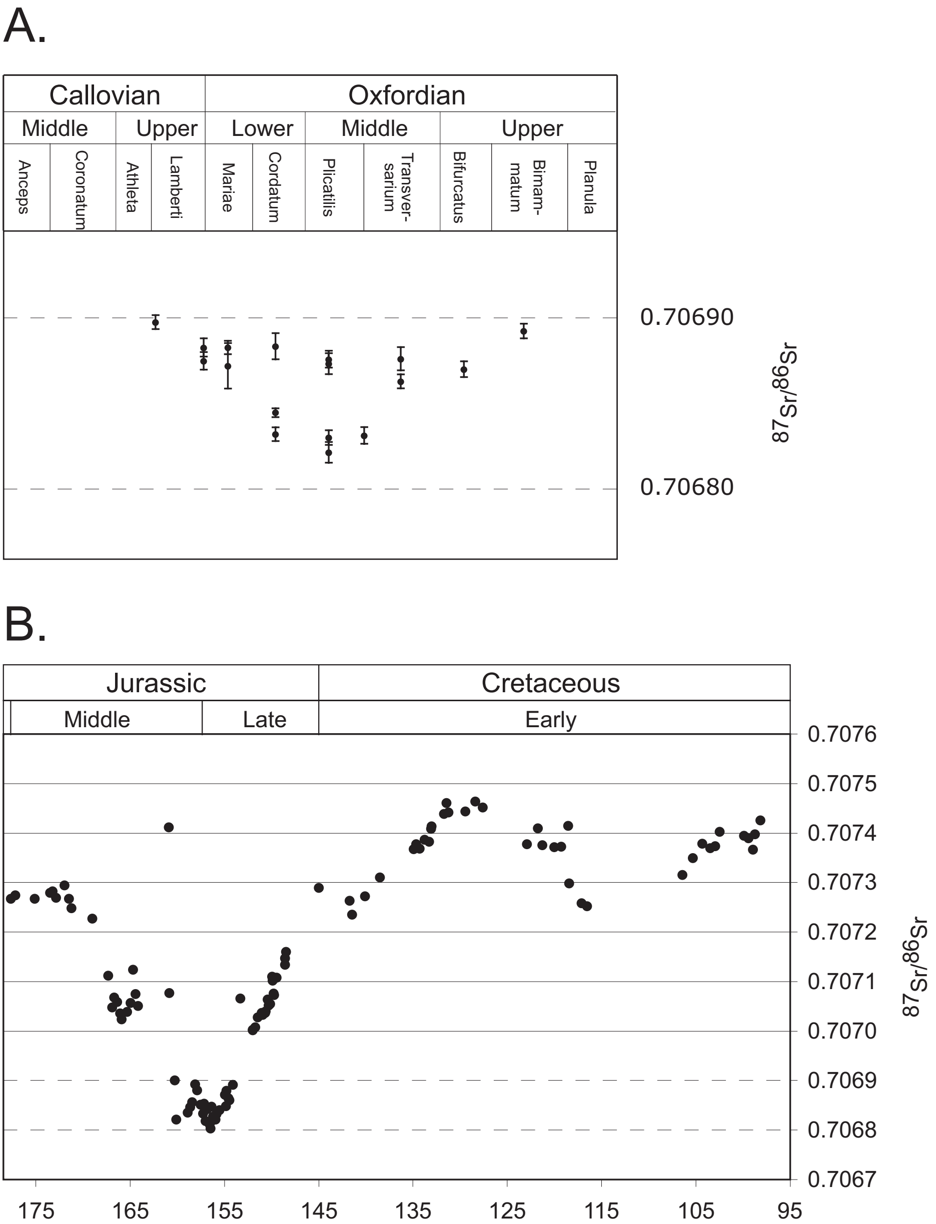

Fig. 1. A. High-resolution Sr-isotope stratigraphy across the major turning point in Late Jurassic Sr-isotope stratigraphy. Sr-isotope analyses were performed on belemnites from the northern Tethys (Jura Mountains, Switzerland). Sr-isotope compositions were measured using Laser Ablation ICPMS at ETH Zürich (Rais 2007).
B. 87Sr/86Sr variations for the Jurassic-Cretaceous (after Jones & Jenkyns 2001).

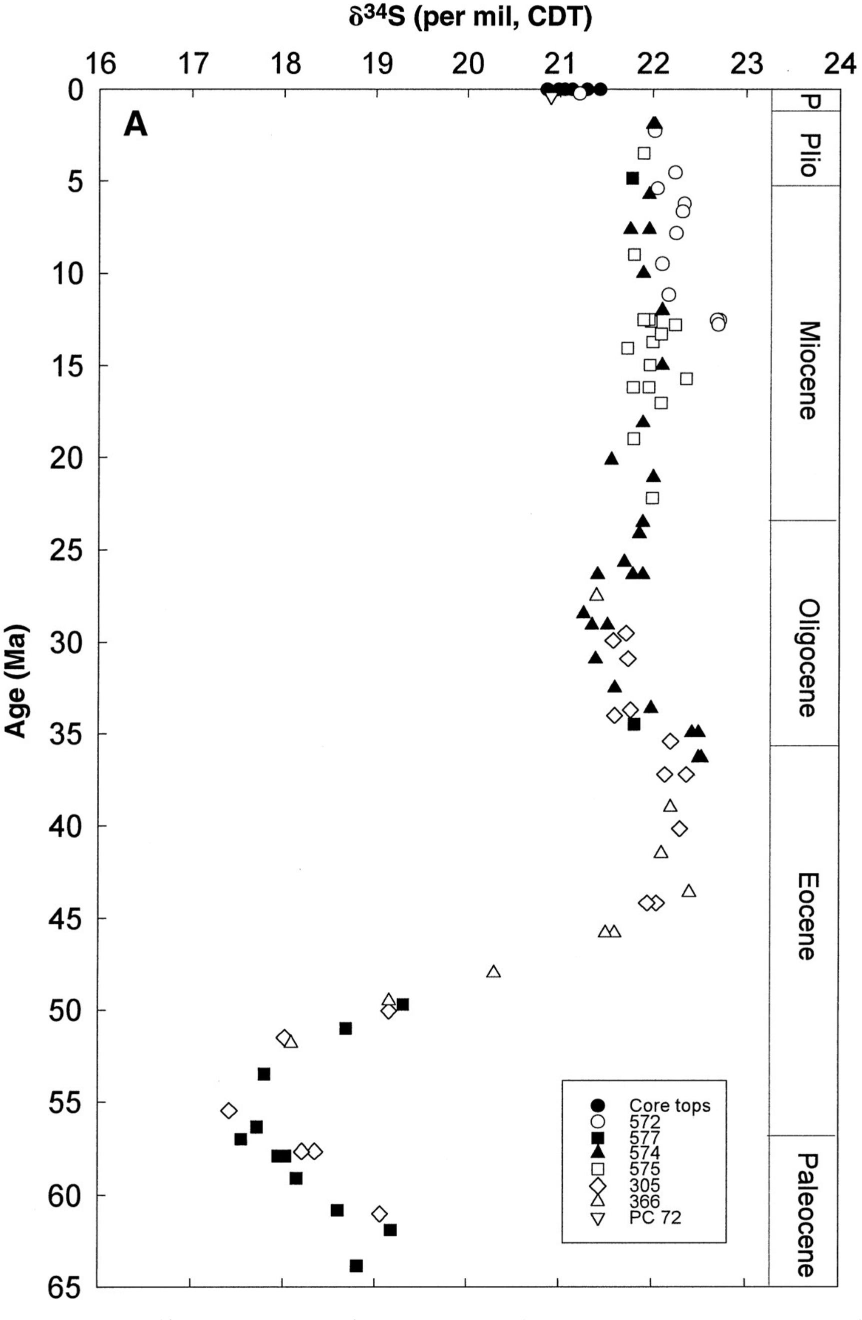

Fig. 2. Cenozoic sulfur isotope curve (from PAYTAN et al. 1998). S-isotopic composition of seawater sulfate over the past 65 million years measured on marine barite samples.

Other chemostratigraphic tools include the use of element distribution in sedimentary rocks. Trace element stratigraphy can provide relevant stratigraphic information in carbonate-poor sedimentary successions (e.g. Aldahan et al. 2000). Renard (1986) combined isotope stratigraphy with carbonate trace-element stratigraphy in a study of Mesozoic and Cenozoic pelagic carbonates. He proposed that fluctuations observed in Sr/Mg and Mg/Ca ratios record global paleoceanographic changes. A sudden increase in iridium contents in Cretaceous/Paleogene boundary clays was first measured by Alvarez et al. (1980) at the locality Gubbio in Italy. The authors related this spike to a meteorite impact. This iridium spike serves as an accurate boundary marker on a global scale (e.g. Ellwood et al. 2003).

PART II: Case Studies

6 Case Study I

Pliocene oxygen isotope records of the onset of Northern Hemisphere Glaciation and the origin of Quaternary-style climates

The Late Neogene, in particular the Pliocene is marked by a phase of rapid transition in Earth history, the onset of major Northern-Hemisphere Glaciation and Quaternary-style oscillations between glaciations and interglaciations, starting ~3.2 to 2.6 Ma. During this time, a reorganization of the global ocean-climate system took place toward a regime of marked glacials and interglacials that (1) continues until today and (2) strongly contrasts with a more uniform regime during most of the preceding Cenozoic and Mesozoic. (3) The new regime probably has strongly promoted the rapid evolution of men. Over the last two decades a highly demanding chronology was developed for these events by means of oxygen isotope ($\delta^{18}O$) stratigraphy and has contributed significantly to a better understanding of the origin of this paramount global change, its world-wide correlations, and the causal chains involved.

The person who has been most influential in creating a framework of Quaternary and Neogene $\delta^{18}O$ stratigraphy over the last 30–40 years has been Nicholas Shackleton. Almost 25 yr ago he established a first $\delta^{18}O$ record of the Late Pliocene from Site 552A on the Gardar Drift (Fig. 3), with a sampling resolution that almost reached orbital resolution (± 5,000 yr). On this basis he provided first evidence for the onset in the deposition of ice-rafted debris (IRD), that occurred in the northern North Atlantic close to the Gauss-Matuyama boundary (Shackleton et al. 1984), today dated near 2.6 Ma.

Subsequently, a few $\delta^{18}O$ stratigraphies were published with similar resolution, still insufficient for orbital tuning. Only Tiedemann et al. (1994) established major progress in $\delta^{18}O$ stratigraphy by generating and comparing two benthic (monospecific) foraminiferal $\delta^{18}O$ records from the northeast Atlantic Site 659 and equatorial East Pacific Site 846 (details documented in Shackleton et al. 1995a; locations in Fig. 3), each of them showing a sampling density of 1,000–3,000 yr and better and well constrained by magneto- and biostratigraphic datums. Thus these records were sufficient for an identification of marine isotope stages (MIS). Below MIS 104, Tiedemann et al. (1994) introduced the

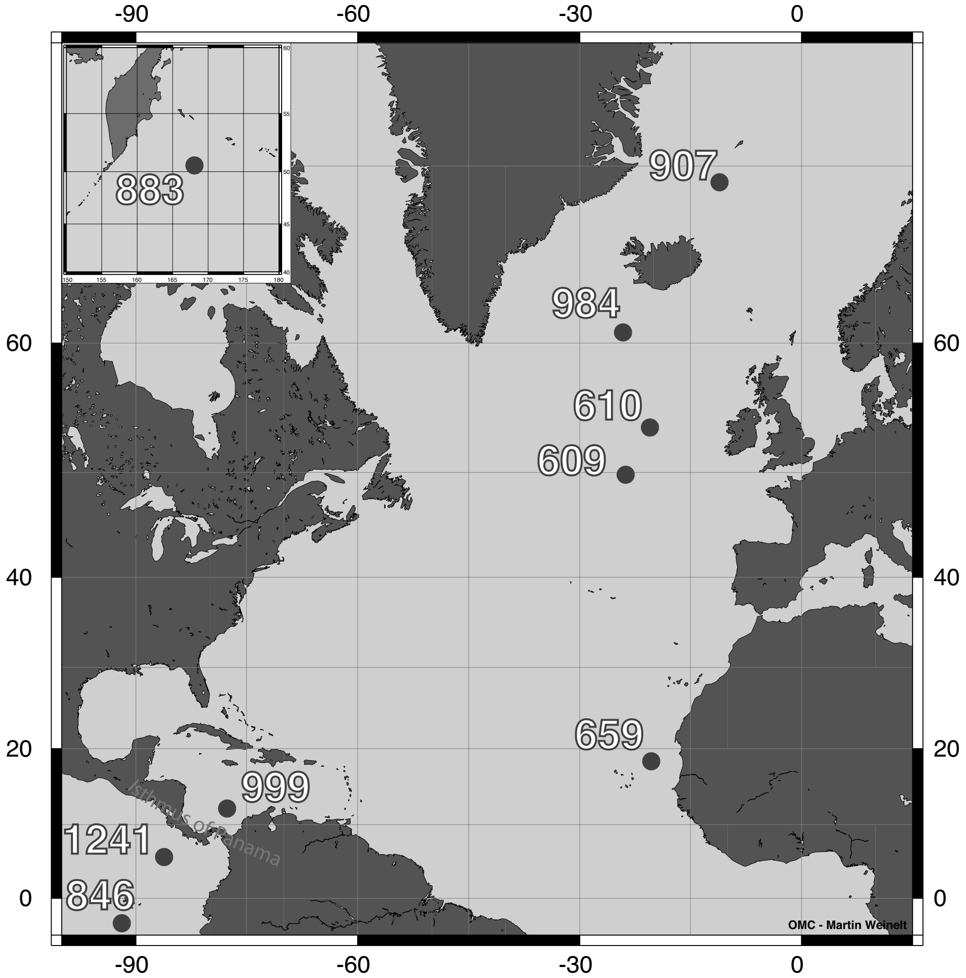

Fig. 3. Locations of Atlantic and North Pacific DSDP/ODP sites mentioned in Case Study 1.

principle of numbering MIS separately for each geomagnetic chron (e. g., G1–G20 for the upper Gauss). Most important, they first generated an orbitally tuned Pliocene time scale for the interval from 2.5 to 5.0 Ma (Fig. 4), which equally applied to the Atlantic and Pacific oceans. Both the Atlantic and Pacific $\delta^{18}O$ records document a fairly uniform mid-Pliocene climatic "Golden Age" and subsequently, after short-lasting precursor events near 3.3 and 3.15 Ma, a major long-term increase in continental ice volume from ~3.0 to 2.65 Ma, thus a massive climatic deterioration leading to Quaternary-style conditions.

Tiedemann et al. (1994) still employed an insolation record for June at 65° N published by Berger & Loutre (1991) as tuning target for $\delta^{18}O$-based ice volume changes. Later-

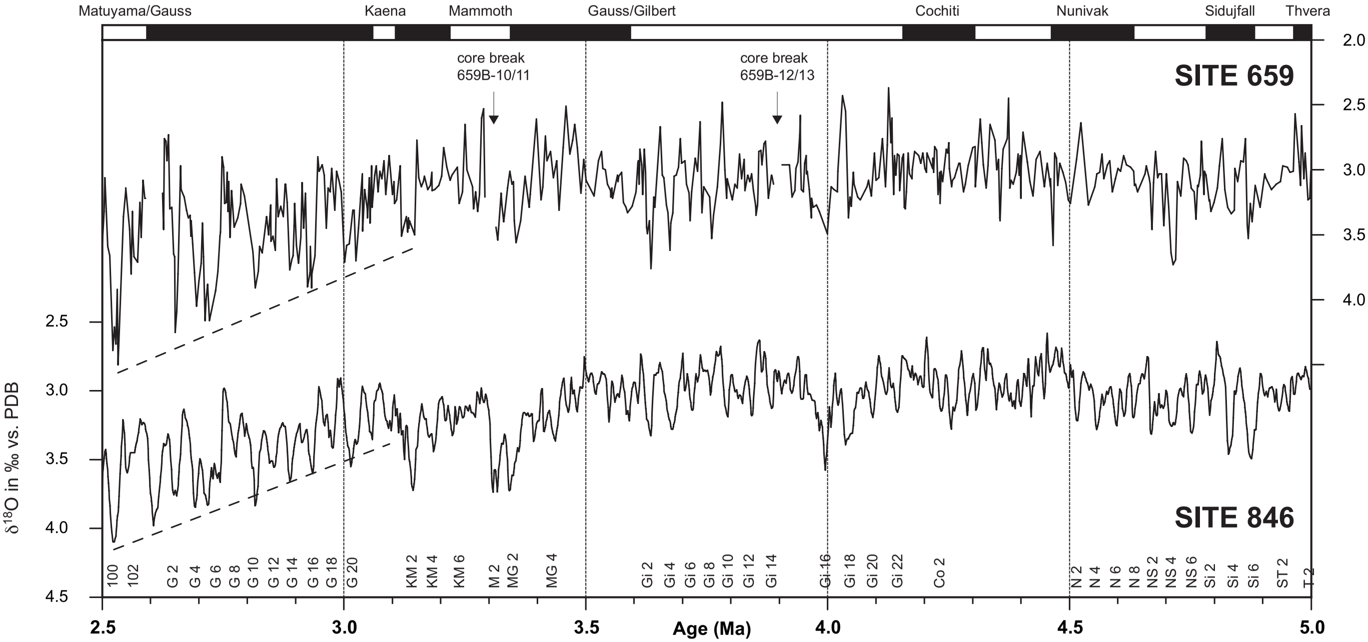

Fig. 4. Comparison of benthic δ^{18}O records from Atlantic site 659 and Pacific site 846 on independently tuned time scales. Isotope stages and geomagnetic chrons are labelled (from TIEDEMANN et al. 1994).

on orbital calculations were refined by Laskar et al. (1993), which led to minor age shifts (Shackleton et al. 1995b) and an astronomic record still accepted today (Lisiecki & Raymo 2005). In these orbital age models the non-linearity constant b and mean time constant T_m of the ice model form partially unknown variables. Estimates for T_m vary between 5 kyr for small mid-Pliocene ice volumes and 15 kyr for large ice volumes over the last 3.0 Myr.

Over the last decade a great number of planktonic and benthic $\delta^{18}O$ records were generated from all oceans at orbital-scale resolution (e. g., Mix et al. 1995; Kleiven et al. 2002). On the basis of 57 carefully stacked benthic foraminiferal $\delta^{18}O$ curves Lisiecki & Raymo (2005) published the stable-isotope stratigraphic synthesis record "LR04" for the last 5.5 Myr (Fig. 5), that now forms a chronostratigraphic backbone for Plio-Pleistocene times. The authors distinguished two additional MIS slightly shifting some MIS boundaries in the Pliocene, however, by no more than 10 kyr. Over the complete time span studied, in particular over the last 900 ky, the LR04 $\delta^{18}O$ record, a clear chronicle of global ice

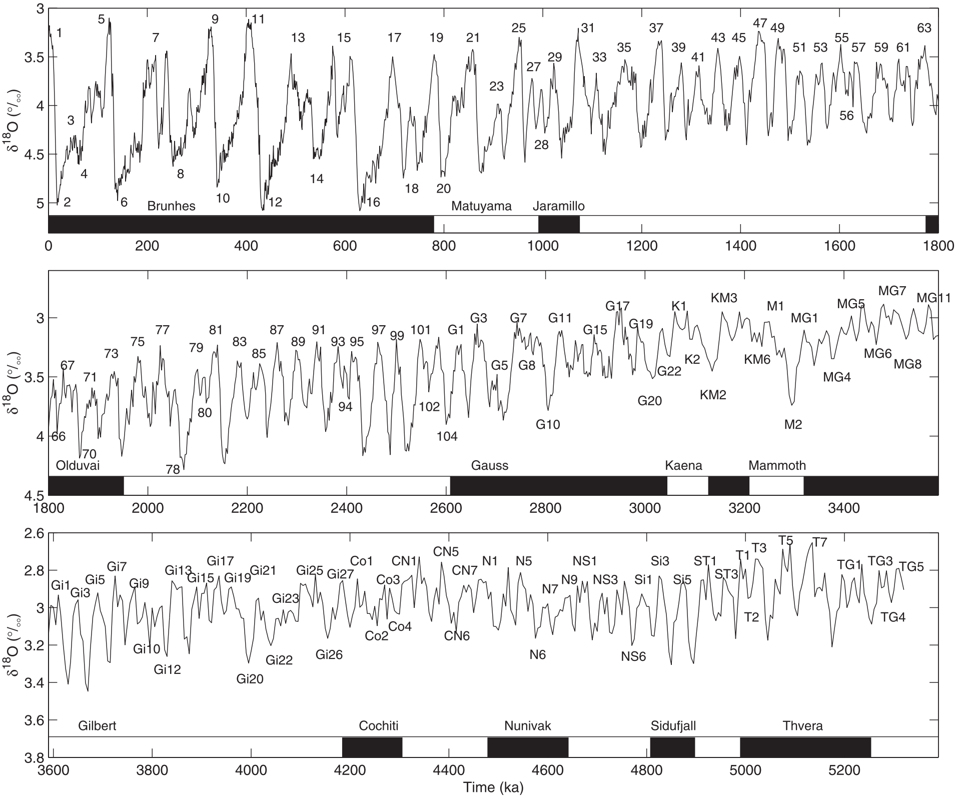

Fig. 5. The LH04 stack benthic $\delta^{18}O$ stack constructed by graphic correlation of 57 globally distributed benthic $\delta^{18}O$ records. Scale of the vertical axis is changing across panels; geomagnetic chrons are labelled (from Lisiecki & Raymo 2005).

volume changes, contains a clear signal of orbital periodicities. Recently, Kawamura et al. (2007) have proven that both benthic $\delta^{18}O$ records and changes in Antarctic temperature have been mainly controlled summer insolation in the Northern Hemisphere (65° N), as originally proposed by Milankovitch.

The refined Pliocene chronostratigraphy was both a key and incentive for various authors, so Haug et al. (1999) and Bartoli et al. (2005), to tackle the age-old quest for the origin of the fairly abrupt onset of major Northern Hemisphere glaciation and Quaternary-style glacial cycles and for the various linkages controlling large-scale climate change on a global scale. These objectives also are important in the context of potential future men-made rapid melt of the Greenland ice sheet. The onset of ice-rafted debris deposition in both the North Atlantic and North Pacific (Site 883; Fig. 3) is almost coeval near MIS G6 (2.73 Ma) to MIS 104 (2.6 Ma) (Shackleton & Hall 1984; Haug et al. 1999). This finding and the partly preceding, partly coeval well-dated massive $\delta^{18}O$ shift shortly prior to and close to the basis of the Gelasian also formed the prime arguments for many INQUA colleagues to plea for shifting the basis of the Quaternary back to the Gauss-Matuyama geomagnetic boundary (Pillans & Naish 2004).

New insights into the processes of general North Atlantic climate deterioration (Bartoli et al. 2005; Fig. 6) came from various proxy techniques, (1) from strongly increased resolution of Pliocene benthic stable-isotope records up to Late-Pleistocene-style multicentennial scale records (Bartoli et al. 2006) as basis for a proper definition of the amplitude of most positive $\delta^{18}O$ excursions, that is for defining most closely the actual ice volume of the earliest glacial stages, (2) from paired Mg/Ca-based sea surface and deep-water temperature records (Sites 609 and 984; Fig. 3), (3) also, from a revised radiometric chronology for IRD deposition at Greenland Sea Site 907, crucial for the understanding of the timing of earlymost Greenland ice outbreaks. (4) Coeval major changes in the paleoceanography of the subarctic North Pacific (correlated by $\delta^{18}O$ stratigraphy) were deduced from biomarker- and $\delta^{15}N$-based paleoproductivity records at North Pacific Site 883 (Haug et al. 1999). (5) On the basis of detailed $\delta^{18}O$ stratigraphy it became possible to reconstruct the gradual and/or stepwise increase of the sea surface salinity gradient between the Caribbean and Equatorial East Pacific (Sites 999 and 1241; Fig. 3 and 6, top). The evolution of this gradient provided key evidence for establishing a precise record for the final closure of the Central American Seaways (Steph et al. 2006), a record also confirmed by various land-based evidence from Panama. Various ocean models (e. g., Schneider & Schmittner 2006) display that in turn, the final closure of the Panama Isthmus led to a major increase in Caribbean sea surface salinity and thus to a strenghened poleward transport of heat and salt and more vigorous meridional overturning in the northern North Atlantic, and finally, to an increased moisture transport to northern high latitudes.

Accordingly, the final closure of the Central American Seaways (i. e., the closure of seaways with 100 m water depth and less, that are crucial for a transfer of low-salinity surface waters) started with a short-lasting precursor event at MIS KM4 to KM3 (~3.15 Ma) (Fig. 5). A second closure event ocurred from MIS G16 to G10 (2.81 Ma). Later-on, the seaways were probably reopened only for short interglacial time spans of high sealevel. After MIS G6 (~2,72 Ma), the seaways were probably closed for ever. The three closing phases of the Isthmus each were followed by a massive increase in the deposition of ice-

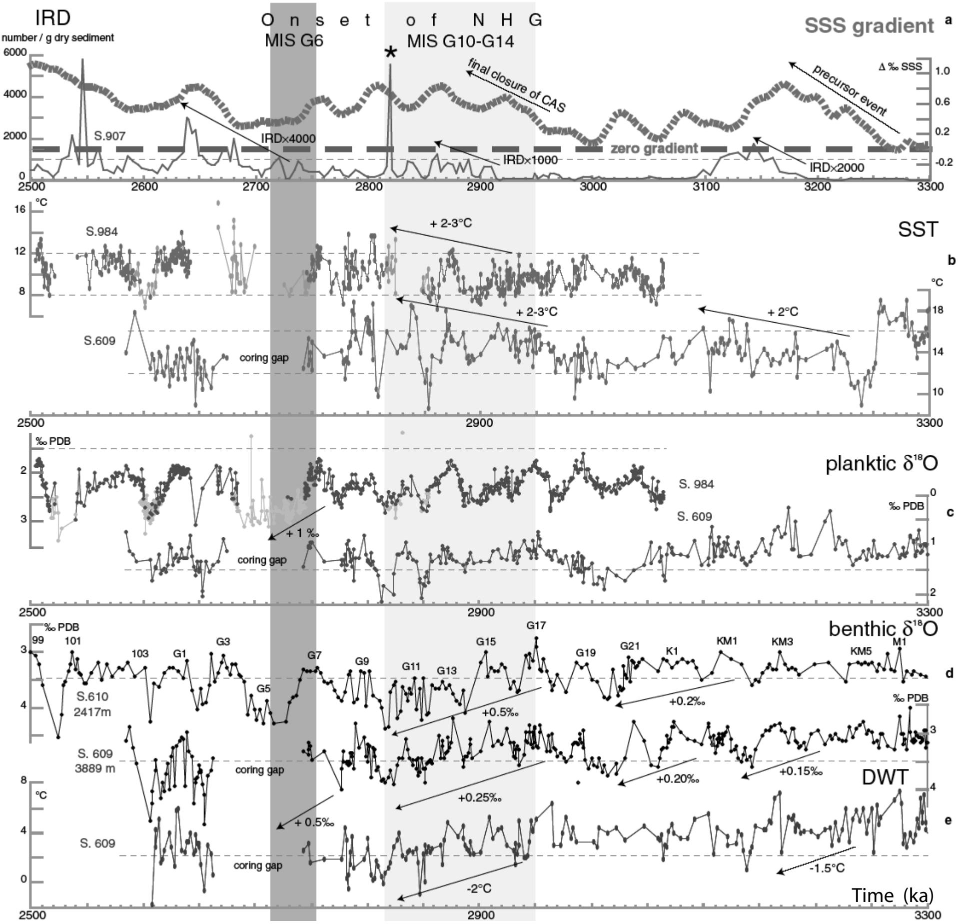

Fig. 6. Paleoclimatic records for the Pliocene North Atlantic for Marine Isotope Stages (MIS) 99 – M2 (time resolution = 300–600 yr). (a) Caribbean-to-East Pacific sea surface salinity (SSS) anomalies recording the final closure of the Central American Seaways (CAS) (Groeneveld et al. 2006) and ice-rafted debris (IRD) record of Northern Hemisphere Glaciation (NHG) from ODP Site 907 (with new age model); (b) Mg/Ca-based sea surface temperature (SST) records from northeast ODP sites 984 and 609, (c) Planktonic δ^{18}O curves from ODP sites 984 and 609, (d) Benthic δ^{18}O records from DSDP sites 610 and 609. Numbers 101, 103, G1, G13, etc. are interglacial MIS, (e) Mg/Ca-based deep-water temperatures (DWT) from Site 609 (from Bartoli et al. 2005).

rafted debris from East Greenland, with a lag of no more than 40 to 60 kyr (Fig. 5, panel a). Thus we may conclude on close linkages between geodynamic processes leading to the closure of the seaways in Central America and general climatic deterioration to Quaternary-style conditions both in the Northern Hemisphere and on global scales. Coeval phases of pronounced rise in sea surface temperatures by 2° to 3 °C in the northeastern

North Atlantic further corroborate the proposed climate linkage (Fig. 5, panel b). Moreover, the coeval onset of dominating surface water stratification in the subarctic North Pacific may have led to long-term reduced atmospheric CO_2 pressure at the main "climate crash" approximately 2.72 Ma (Haug et al. 1999). $\delta^{18}O$ records of multicentennial-scale resolution show that millennial-scale climate cyclicities such as Dansgaard-Oeschger and Heinrich events have first appeared only during this transitional interval, near MIS G14 (Bartoli et al. 2006).

7 Case Study II

Carbon isotope stratigraphy of the Early Cretaceous: The Valanginian-Hauterivian carbon isotope excursion

Paleoceanographers investigating conditions and causes of Oceanic Anoxic Events began to use carbon isotope geochemistry as a tracer of the global carbon cycle in the late 1970ties (e. g. Weissert et al. 1979; Scholle & Arthur 1980). They analyzed the carbon isotopic composition of bulk carbonate from pelagic limestone successions and were able to show how Oceanic Anoxic Events were coupled with perturbations of the global carbon cycle reflected in "positive carbon isotope excursions". Remarkable was the observation that the first of the Cretaceous carbon isotope anomalies, identified in sediments of Valanginian and Hauterivian age did not coincide with one of the prominent oceanic anoxic events. Detailed investigations of this carbon isotope anomaly showed that it coincides with only minor black shale episodes but that it is indeed of global extent. This explains why the Valanginian-Hauterivian carbon isotope anomaly not only serves as a proxy of global carbon cycling but also as an excellent stratigraphic marker.

An informal reference curve

Pelagic limestones of Early Cretaceous Maiolica Formation are exposed along the Southern Alps of northern Italy. Four sections (Breggia, Pusiano, Capriolo, Polaveno) located in the Lombardy Basin and one section (Valle del Mis) situated in the Belluno Basin were chosen for the establishment of a pelagic carbonate carbon isotope curve through the Valanginian and Hauterivian (Fig. 7). The Maiolica Formation chosen for the isotope study consists of a continuous succession of white to grey pelagic nannofossil limestones with chert nodules and bands. A remarkable change in pelagic facies from whitish to light-grey, mainly thick-bedded limestones to grey, thin bedded limestones with marly interlayers and centrimetric black-shale interlayers occurs within the Valanginian (Weissert et al. 1985). The studied sediments were deposited along the southern continental margin of the Tethys ocean in water depths of thousand meters or more (Bernoulli & Jenkyns 1974). This margin was characterized by a number of platforms and basins bound by approximately N-S trending palaeotectonic normal faults.

Bulk carbonate samples were analyzed for their oxygen and carbon isotope composition. All carbon isotopic analyses were performed on samples with a carbonate content varying between 85 % and 97 % and a TOC concentration between 0.1 % and 0.5 %. The

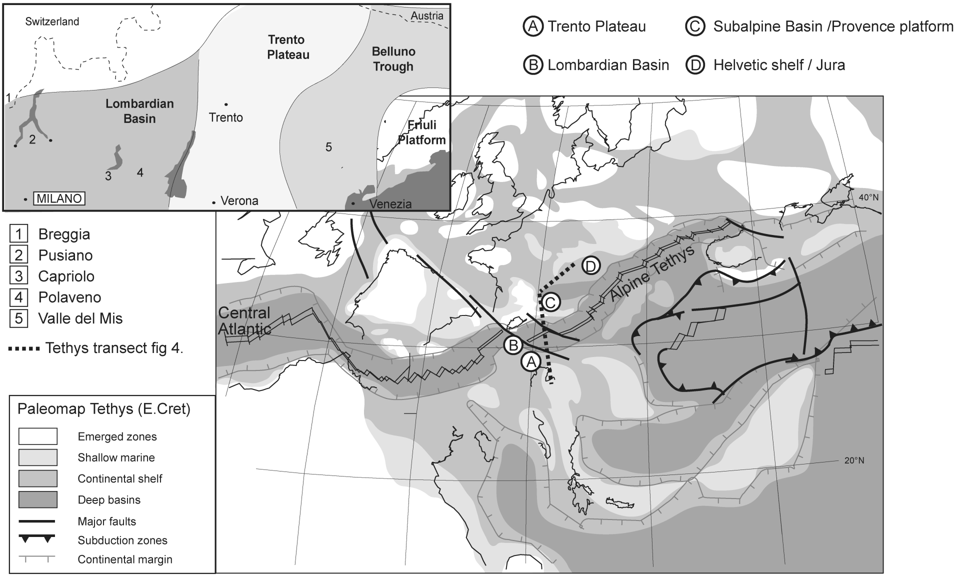

Fig. 7. Paleogeographic reconstruction of the alpine Tethys in the Early Cretaceous, with sections studied.

sections have been dated with bio- and magnetostratigraphy (Channell et al. 1993). The results of carbon isotopic analyses plotted against bio- and magnetostratigraphy are displayed in composite figure 8 (Channell et al. 1993). The data clearly show a remarkable excursion to positive $\delta^{13}C$ values in the carbonate $\delta^{13}C$ record during the Late Valanginian. Although the absolute isotopic values differ slightly from section to section, the relative pattern of fluctuations is consistent. Low $\delta^{13}C$ values near 1.3–1.5‰ analyzed in Berriasian and early Valanginian sediments (*Cretarhabdus angustiforatus* nannofossil zone) were replaced by positive $\delta^{13}C$ values near 3‰ in the Late Valanginian (*Calcicalathina oblongata* nannofossil zone). The carbonate C-isotope excursion ends in the Early Hauterivian (*Lithraphidites bollii* nannofossil zone) with values fluctuating between 1.5 and 2‰.

Based on the available biostratigraphic resolution the positive carbonate C-isotope excursion observed in the studied Tethyan sections can be considered as a synchronous event falling within the middle and upper part of the *C. oblongata* nannofossil zone. The paleomagnetic data allow a calibration of the C-isotope stratigraphy established in the five sections with magnetostratigraphy. As shown in figure 8, the positive C-isotope excursion begins during the upper part of CM12 (today M11A) and reaches its maximum during CM11. From CM10N to CM8 the $\delta^{13}C$ ratios return to normal pre-excursion values.

Comparison with a carbon isotope curve from the ammonite stratotype section

The southern alpine pelagic limestones used for the carbon isotope investigation are of limited use for ammonite stratigraphy because of rather poor preservation of ammonite

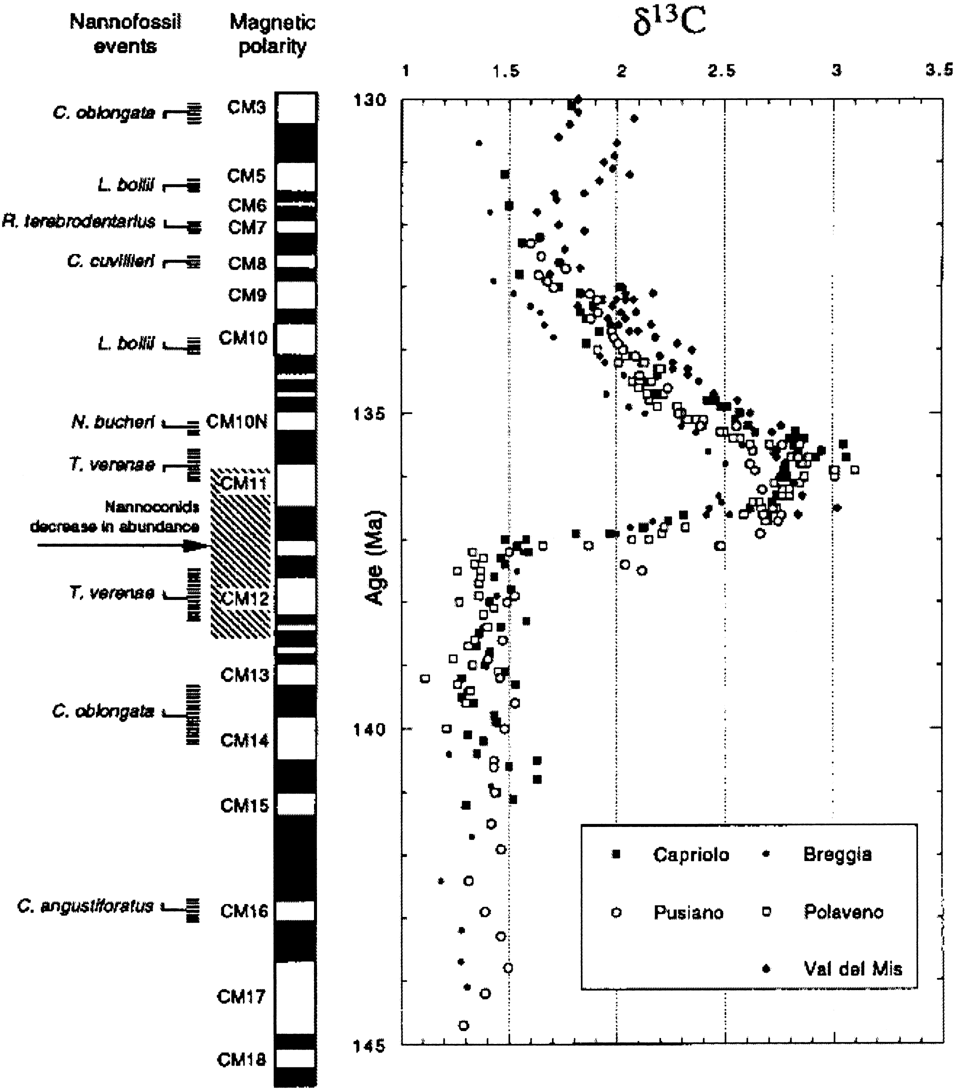

Fig. 8. Composite C-isotope stratigraphy, Valanginian-Hauterivian, Southern Alps (N. Italy) correlated to magneto- and biostatigraphy (from CHANNELL et al. 1993).

faunas in the nannofossil limestones (CECCA 1998). Better suitable for ammonite stratigraphy are hemipleagic sections today outcropping in Southern France. The ammonite-rich section La Charce in the basinal part of the Vocontian domain is described in BULOT et al. (1993). It is now used as the stratotype for the Late Valanginian to Early Hauterivian ammonite zonation (MUTTERLOSE 1996). Its lithology consists of hemipelagic, fos-

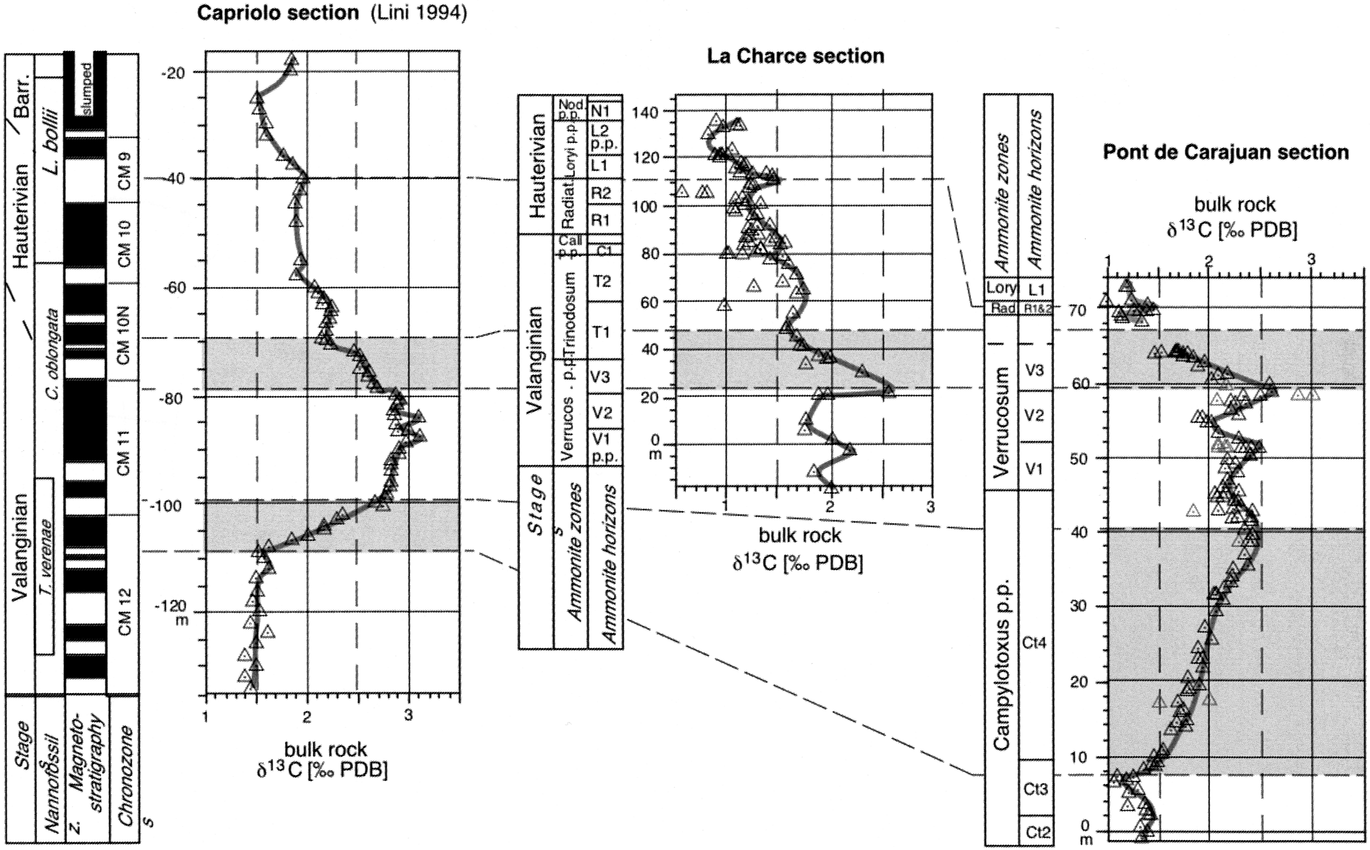

Fig. 9. Valanginian-Hauterivan carbon isotope stratigraphy from Provence (S-France) and Southern Alps. Ammonite stratigraphy from Provence sections can be correlated to magnetostratigraphy by means of C-isotope stratigraphy (from HENNIG et al. 1999).

siliferous, cyclic marl-limestone alternations. The Early Valanginian and the Early Hauterivian parts of the section are more calcareous than the Upper Valanginian interval, where marls predominate. The section Pont de Carajuan has been studied previously by various authors (e.g. ATROPS & REBOULET 1995). It is located within the "réserve géologique de Haute Provence", in the Verdon valley near Castellane. The section is paleogeographically situated at the transition of the Provence platform to the Vocontian domain. The sequence consists of fossiliferous shallow water limestones and marls. HENNIG et al. (1999) and HENNIG (2003) present carbon isotope curves from the two sections, La Charce and Pont de Carajuan (Fig. 9). The isotope curves established by HENNING et al. (1999) cover the Late Valanginian and Early Hauterivian and they can be correlated with the pelagic curves from the Southern Alps even if detailed biostratigraphic data indicate that several hiatues are present in both studied sections (JANSSEN & CLEMENT 2002). HENNIG et al. (1999) identified several distinct changes in their carbon isotope record:

(1) A minor negative δ^{13}C-event within the *Campylotoxus* Ammonite Horizon (Ct3) marks the base of the Valanginian C-isotope excursion. The positive shift of +1.3‰ to the first maximum in the δ^{13}C-record falls within the upper part of the *Aampylotoxus* Zone. The first maximum is measured in the upper part of *the Inostranzewi* Subzone (Ct4).

(2) An interval of positive δ^{13}C-values of up to 2.6‰ extends from the uppermost *Campylotoxus* to the lower to middle *Verrucosum* Zones. The second positive peak (+2.5‰) occurs within the *Verrucosum* horizon (V1) and the highest peak is measured at the base of the *Peregrinus* horizon (V3).

(3) The δ13C-values decrease rapidly by 1‰ within the upper *Verrucosum* and lower *Trinodosum* Zones. Then, they decrease consistently and finally reach pre-excursion values in the *Loryi* Zone.

The correlation of the Southern France composite δ^{13}C-stratigraphy with the reference δ^{13}C stratigraphy in the Southern Alps offers the opportunity to link ammonite stratigraphy with magnetostratigraphy. The new correlation differs by about one magnetozone from earlier published correlations. CHANNELL et al. (1993) placed the top of the *Campylotoxus* Zone into CM12A. With the new correlation, the boundary between *Campylotoxus* and *Verrucosum* Zone can be placed into CM11 (M11–M11A) and the *Verrucosum* Zone falls within M11, which agrees with the ammonite stratigraphy-magnetostratigraphy correlation proposed by CECCA (1998). The base of the *Radiatus* Zone is proposed as the stage boundary between the Valanginian and the Hauterivian (BULOT & THIEULOY 1993; MUTTERLOSE 1996). According to the isotope-based correlation, this boundary falls into the normally magnetised reversal of M10, while CHANNELL et al. (1995) and GRADSTEIN et al. (2004) placed it into M11.

A global carbon isotope anomaly

HENNIG (2003) traced the carbon isotope excursion of the Valanginian along a northwest-southeast trending transect through the alpine Tethys Ocean (Fig. 10). She was able to recognize the trend to more positive carbon isotope values in a northern Tethyan coastal succession (Lamoura, French Jura; see HENNIG 2003). The upper part of the curve is missing

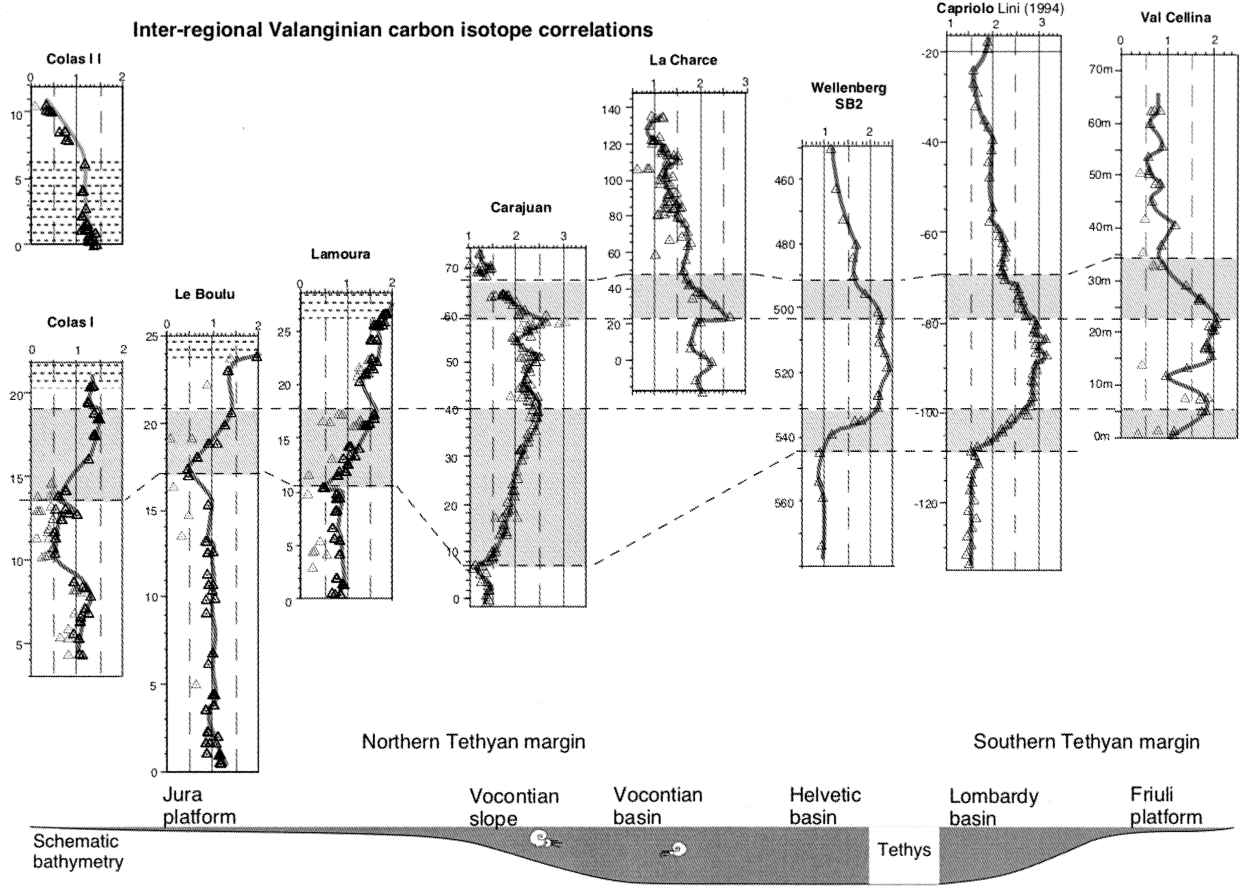

Fig. 10. Interregional C-isotope stratigraphy correlation along an NW-SE transect through the alpine Tethys Ocean (from HENNIG 2003).

due a stratigraphic gap recording a prominent sea-level lowstand at the Valanginian-Hauterivan transition. The other neritic successions provide carbon isotope data which do not record any clear carbon isotope anomaly (e. g. section Salève, HENNING 2003). This confirms that a carbon isotope anomaly may not be stored in neritic limestones due to local seawater chemistry (PATTERSON & WALTER 1994), due to impact of marine and meteoric

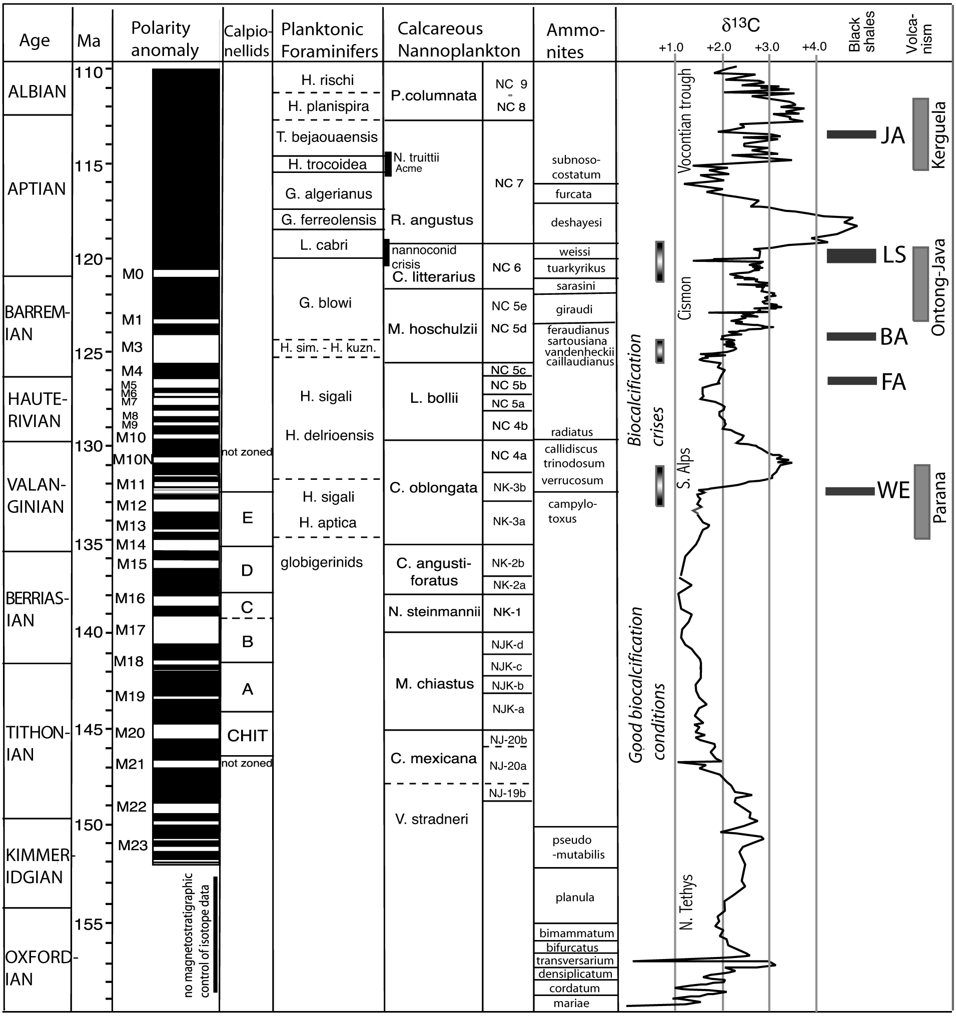

Fig. 11. Composite carbonate carbon isotope stratigraphy through Late Jurasssic and Early Cretaceous (modified after WEISSERT & ERBA 2004). Combined ammonite- carbon isotope stratigraphy: Barremian-Aptian data from WISSLER et al. (2003); Valanginian-Hauterivian data from HENNIG et al. (1999). JA: Niveau Jacob, LS: Livello selli, BA: Mid-Barremian Event, Fa: Faraoni Level, We: Weissert Anoxic Event.

diagenesis (Allan & Matthews 1982) and variations in precursor mineralogy (Swart & Eberli 2005), or due to sedimentary gaps as documented by Gréselle (2007). Despite of these obvious problems, Henning (2003) succeeded in tracing a carbon isotope excursion across the alpine Tethys Ocean from coastal into pelagic environments at a time of a major carbon isotope anomaly (Fig. 10).

The carbon isotope excursion spanning the Late Valanginian and the earliest Hauterivian has also been identified in pelagic successions of other oceans (Erba et al. 2004), in other neritic environments (Gréselle 2007) and in continental successions (Gröcke et al. 2005). These findings confirm that the Valanginian carbon isotope excursion is of global extent and that it serves as an accurate stratigraphic marker. The Valanginian carbon isotope excursion records the fist major carbon cycle perturbation in the Early Cretaceous. The composite carbonate-carbon isotope stratigraphy (Weissert & Erba 2004; Fig. 11) of the Late Jurassic and Early Cretaceous shows that the Valanginian carbon isotope anomaly marks the end of a long period of low and stable carbon isotope values characterizing the Tithonian and Berriasian and that it serves as a prominent stratigraphic marker level in the Early Cretaceous. The composite carbon isotope stratigraphy displayed in figure 11 is based on numerous detailed carbon isotope studies in magneto- and biostratigraphically dated sections. The studies by Hennig et al. (1999, Valangnian-Hauterivian) and Wissler et al. (2003, Barremian – Early Aptian) provide examples how ammonite stratotypes with no magnetostratigraphic information can be correlated to magnetostratigraphy with the help of carbon isotope stratigraphy (Fig. 11).

8 Case Study III

Carbon isotope stratigraphy of the Palaeozoic

Carbon isotope studies have been intensively used in the Palaeozoic to unravel changes in the global carbon cycle and for chemostratigraphic correlation of sections from various palaeocontinents. However, diagenesis is a major concern since Palaeozoic carbonates may have been affected by intense recrystallisation and considerably higher overprint in comparison to Mesozoic or Cenozoic carbonate sequences. Reliable Palaeozoic carbon isotope curves are generally based on the analysis of brachiopod shells (e. g. Popp et al. 1986; Brand 1989; Grossman et al. 1993; Wenzel & Joachimski 1996; Mii et al. 1997; Veizer et al. 1999, van Geldern et al. 2006, among others) which are composed of low-magnesium calcite. In contrast to metastable aragonite and high-magnesium calcite, low-magnesium calcite is a stable modification of calcium carbonate and has a relatively high potential to preserve the primary geochemical signature. However, the occurrence of Palaeozoic brachiopods is facies-dependent and it is generally difficult to construct high-resolution carbon isotope records based on the analysis of brachiopod calcite. A much higher temporal resolution can be achieved by analysis of whole-rock, preferentially micritic carbonates. Although carbonates will recrystallize (dissolution of aragonite and high-magnesium calcite and reprecipitation of low-magnesium calcite) and be cemented during diagenesis, the initial carbon isotope ratios have a fair chance to be preserved as long as diagenesis proceeds in a system closed for carbon. The carbon isotopic composition of stabilized carbonate minerals and cements is dependent on the carbon isotopic composition of dissolved inorganic carbon (DIC) of the diagenetic solution which in case of a closed diagenetic system is determined by the $\delta^{13}C$ of the dissolving precursor carbonate minerals. However, in an open diagenetic system, carbon derived from the remineralization of organic carbon depleted in ^{12}C or from soil-gas CO_2 may contribute to the dissolved inorganic carbon pool. In this case, the initial carbon isotope ratio will not be preserved in the fossil carbonate. Consequently, analyses of carbonates rich in organic carbon or embedded in organic carbon-rich shales may not provide reliable carbon isotope records due to the contribution of isotopically light carbon from the remineralization of organic carbon.

In order to construct composite carbon isotope curves as the standard isotope curves for a certain time interval, the carbon isotope records of several sections representing either different paleoenvironmental settings and/or from different palaeocontinents should be studied and compared. This requirement results from the potential problems outlined above and from the fact that several studies suggested that especially shallow waters in epeiric seas may be different in their carbon isotope composition than open ocean waters (e. g. HOLMDEN et al. 1998, IMMENHAUSER et al. 2002, PANCHUK et al. 2005, MELCHIN & HOLMDEN 2006). This may be relevant especially for the Palaeozoic since Palaeozoic shelves were more extensive than during modern times. Differences in $\delta^{13}C$ of dissolved inorganic carbon (DIC) of shallow epeiric seas and the open ocean may be due to stronger land-derived inputs of freshwater (HOLMDEN et al. 1998; PANCHUK et al. 2005), remineralisation of organic carbon to CO_2 forming bicarbonate in sea water (PATTERSON & WALTER 1994), or fluctuating sea level leading to subaerial exposure of shallow water sediments and diagenetic overprinting (ALLAN & MATTHEWS 1982; JOACHIMSKI 1994).

The carbon isotope composition of organic carbon may be used to constrain inorganic carbon isotope records because both the $\delta^{13}C$ of organic carbon as well as $\delta^{13}C$ of inorganic carbon are dependent on $\delta^{13}C$ of DIC. Any change in the carbon isotopic composition of carbonates should thus be mirrored in a parallel change in the carbon isotope composition of organic carbon. However, the amplitudes of the changes in $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ may be different due to dependence of the photosynthetic carbon isotope fractionation on the dissolved CO_2 concentration.

A carbon isotope record based on the analysis of Cambrian to Carboniferous whole rock carbonates was presented by SALTZMAN & YOUNG (2005). Prominent positive excursions in $\delta^{13}C$ with amplitudes of up 6‰ are observed in the Upper Cambrian, Late Ordovician to Silurian and Late Devonian to Mississippian. Most of these carbon isotope excursions have been measured in several sections from various palaeocontinents indicating that the excursions are of global and not only of regional significance. The amplitude of a positive carbon isotope excursion may vary from section to section. Interestingly, the Paleozoic $\delta^{13}C$ excursions are significantly larger than the excursions observed in the Mesozoic/Cenozoic, but lower than the +10‰ excursions observed in Neoproterozoic. The Palaeozoic carbon isotope excursions have proven to be a reliable tool for the correlation of the individual sections (e. g. KALJO et al. 1997, SALTZMAN et al. 1998, JOACHIMSKI et al. 2002, SALTZMAN 2002, BUGGISCH & MANN 2004, MELCHIN & HOLMDEN 2006).

However, during time periods with no major changes in the carbon isotope ratios, carbon isotopes will not be useful for chemostratigraphic correlation (e.g. Ordovician, see Fig. 12).

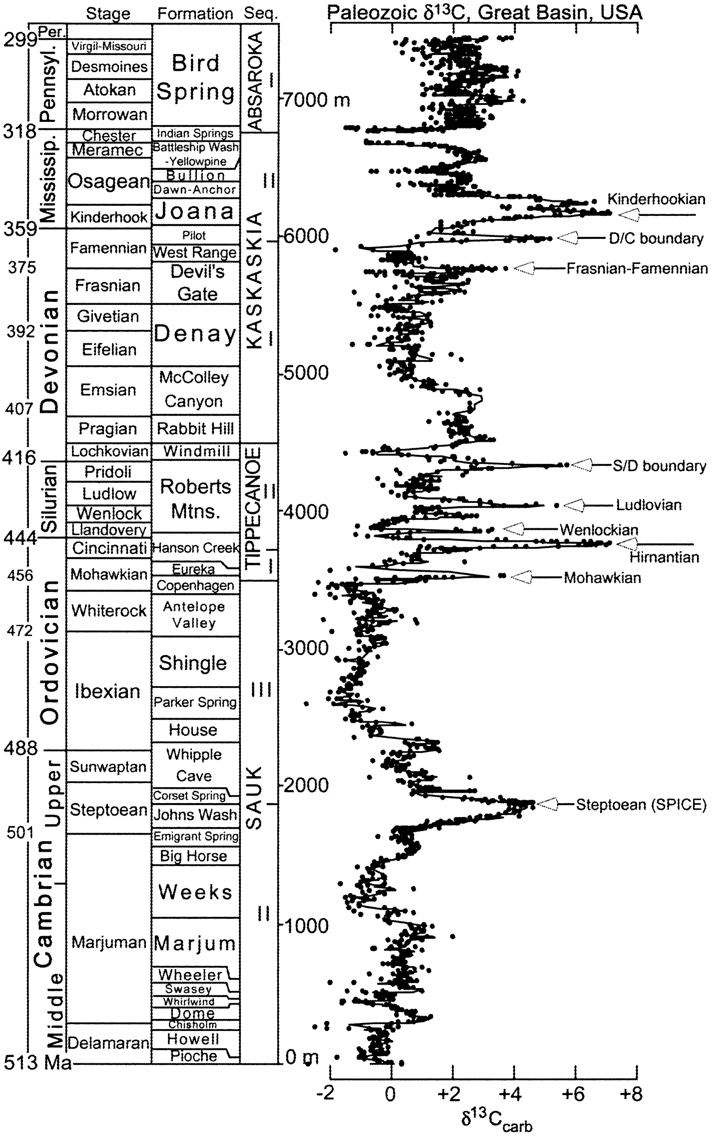

Fig. 12. Carbon isotope composite for the Middle Cambrian to Pennsylvanian time interval showing major carbon isotope exursions in the Upper Cambrian, Late Ordovician to Silurian and Late Devonian to Mississippian (from SALTZMAN & YOUNG 2005).

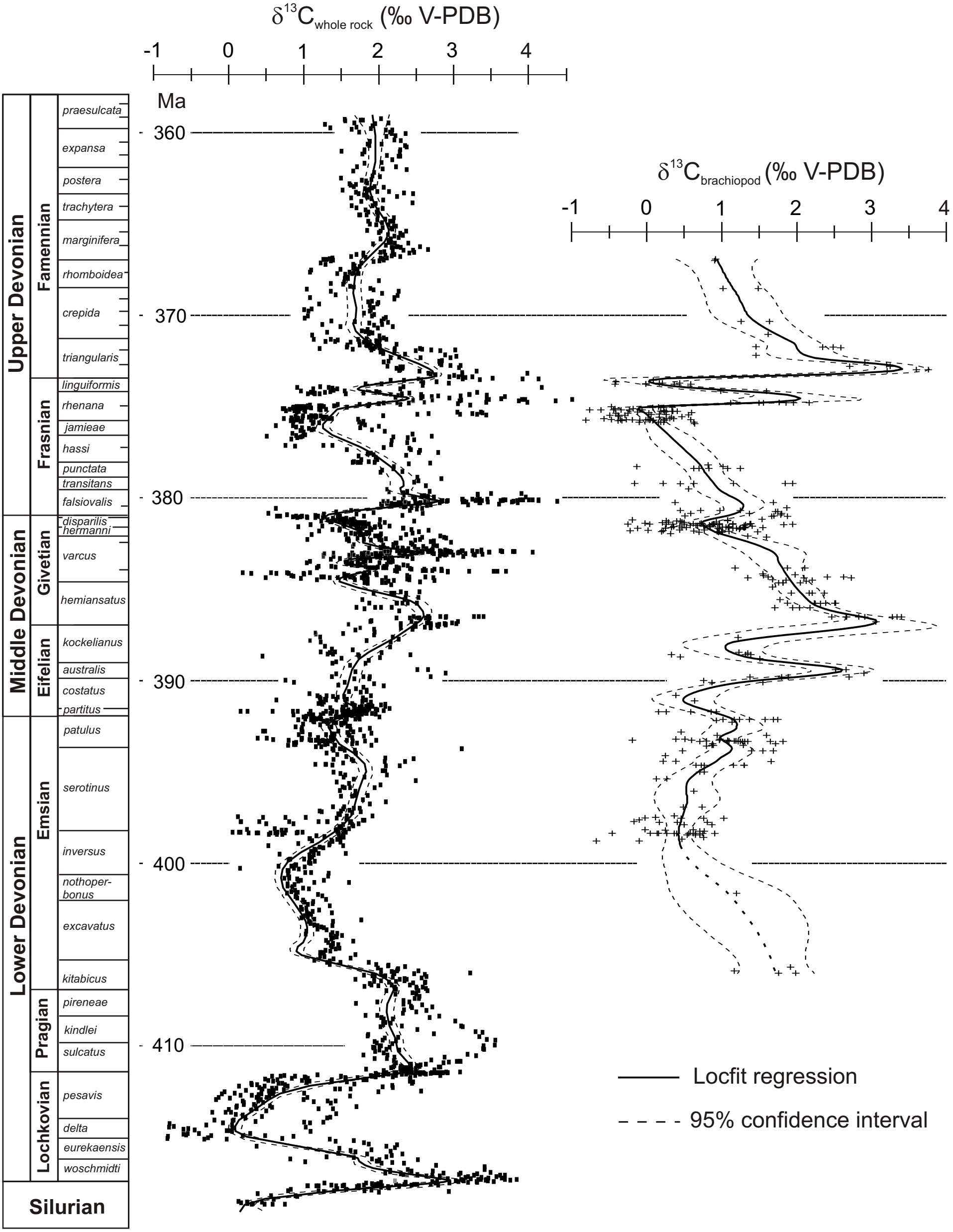

Fig. 13. Comparison of composite carbon isotope records for the Devonian based on analyses of whole rock samples (BUGGISCH & JOACHIMSKI 2006) and pristine brachiopod shells (VAN GELDERN et al. 2006).

As an example, the carbon isotope record of the Devonian is presented in greater detail. The Devonian whole rock carbon isotope record (Buggisch & Mann 2004, Saltzman & Young, 2005, Buggisch & Joachimski 2006) shows several positive excursions (Fig. 13) which in most cases coincide with sea-level changes, black shale deposition and in part with bio-events. The correlation of positive carbon isotope excursion with the deposition of black shales argues that enhanced burial of organic carbon depleted in ^{12}C resulted in a positive shift in $\delta^{13}C_{DIC}$ that is documented in higher $\delta^{13}C_{carb}$ values. The brachiopod $\delta^{13}C$ record (van Geldern et al. 2006), which, in comparison to the whole rock carbon isotope curve (n = 2000), is based on less data points (n = 403), shows a comparable pattern to the whole rock $\delta^{13}C$ record in the Givetian and Late Devonian, but in part different trends in the Emsian and Eifelian. The differences in the two records may result from the much lower sample density in case of the brachiopod $\delta^{13}C$ record and from the fact that whole rock carbonate $\delta^{13}C$ records may have been affected by diagenesis. While the brachiopod $\delta^{13}C$ record is based on the analysis of well-preserved low-magnesium calcitic shells, whole rock carbonates may have been initially composed of different proportions of aragonite, high- and low-magnesium calcite. Aragonite is enriched in ^{13}C by 1.6 ‰ relative to low-magnesium calcite (Romanek et al. 1992). As a consequence, carbonates that initially had a significant proportion of aragonite, will show higher $\delta^{13}C$ values than carbonates composed exclusively of low-magnesium calcite. This was documented by Swart & Eberli (2005) who showed that $\delta^{13}C$ of modern peri-platform carbonates is strongly correlated with the percentage of aragonite with aragonite-rich limestones revealing significantly higher $\delta^{13}C$ values in comparison to limestones dominated by low-magnesium calcite. Following, carbonates that initially had a significant aragonite proportion are expected to have higher $\delta^{13}C$ values in comparison to e. g. shells composed of low-magnesium calcite.

Examples for the comparison of Early to Middle Devonian as well as Late Devonian carbon isotope records are given in figures 14 and 15. Figure 14 shows the correlation of Early Devonian to Eifelian carbon isotope records measured in several sections from the Prague Basin (Czech Republic), Carnic Alps (Austria), Montagne Noire (France) and the Cantabrian Mountains (Spain; from Buggisch & Mann 2004). Figure 14 shows as well that the $\delta^{13}C$ excursion measured on inorganic carbon across the Silurian-Devonian boundary is well reproduced in the carbon isotopic composition of organic carbon. The general pattern is well comparable in all sections (Fig. 14). However, the absolute values as well the amplitudes of the excursions in $\delta^{13}C$ are different. Buggisch & Mann (2004) observed that samples from basinal settings have generally lower $\delta^{13}C$ values in comparison to samples from shallow water carbonates. The lower $\delta^{13}C$ values of samples from basinal environments potentially derive from a lower initial aragonite contribution in comparison to shallow-water sediments or by a difference in $\delta^{13}C$ of dissolved inorganic carbon of surface and deeper marine waters (vertical gradient in $\delta^{13}C$ of DIC), which will represent the diagenetic solutions in which the respective carbonates will stabilize. The different amplitudes in $\delta^{13}C$ may either be explained by the imprint of diagenesis or by the fact that global changes in $\delta^{13}C$ of DIC are recorded slightly differently in various parts of the World's oceans due to differences in $\delta^{13}C$ of DIC in shallow epeiric seas.

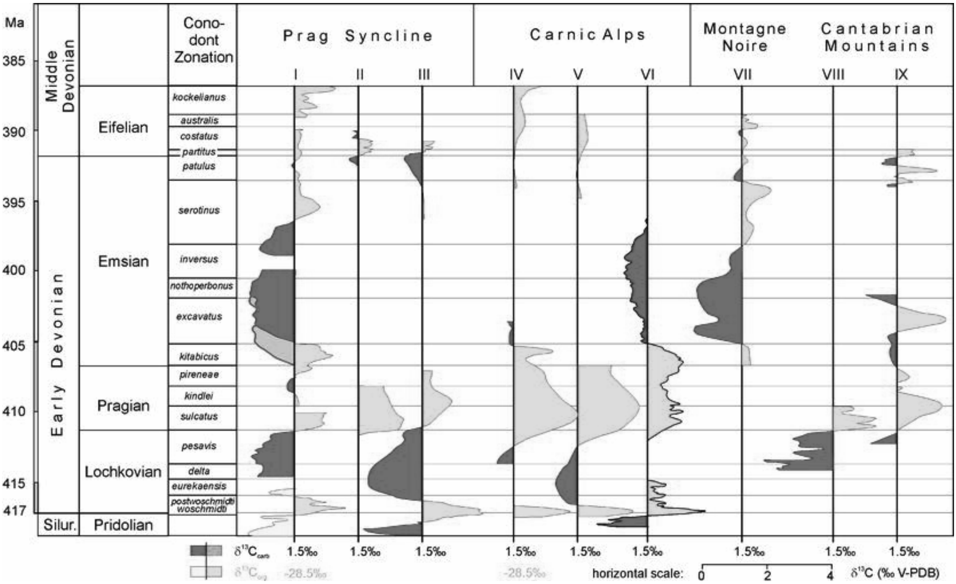

Fig. 14. Comparison of Early Devonian carbon isotope records measured on sections from the Prague Syncline (Czech Republic), Carnic Alps (Austria), Montagne Noire (France) and the Cantabrian Mountains (Spain). From Buggisch & Mann (2004).

The correlation of carbon isotope patterns from various sections across the Frasnian-Famennian boundary is shown in Figure 15. The carbon isotope records have been plotted against absolute time using estimates for the duration of individual conodont zones of Ziegler & Sandberg (1996) and the Devonian time scale of Tucker et al. (1998). The carbon isotope records have been calibrated against time assuming constant sedimentation rates and neglecting any effect of compaction. With these simplified assumptions, the $\delta^{13}C$ records from basinal (organic carbon), submarine swell and outer shelf (inorganic carbon) settings show an almost perfect match. A first positive excursion is observed in conjunction with the lower Kellwasser-Horizon which generally is represented by black, organic carbon-rich carbonates to marly shales that in most cases lack any evidence for bioturbation or benthonic life. $\delta^{13}C$ values decrease during the latest Frasnian and show a second positive shift which coincides with the onset of the deposition of the Upper Kellwasser Horizon marking the Frasnian-Famennian boundary. $\delta^{13}C$ values stay at a relatively high level during the earliest Famennian and start to decrease in the Late *triangularis* Zone. This example documents the expected correlation between inorganic carbon isotope records derived from whole rock carbonate analyses and organic carbon isotope records measured on organic carbon-rich basinal sediments.

The Devonian carbon isotope record documents that inorganic as well organic carbon isotope records have a high potential for the stratigraphic correlation of Palaeozoic sequences. However, in contrast to comparable studies on Mesozoic and Cenozoic car-

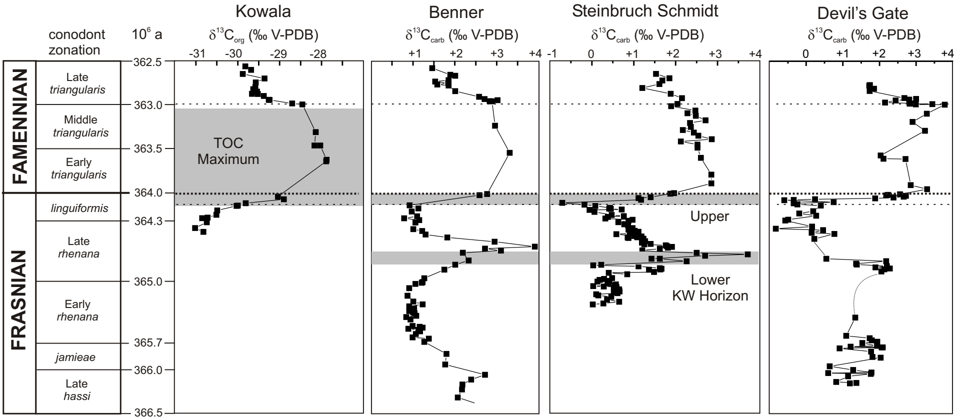

Fig. 15. Carbon isotope stratigraphy of the Frasnian-Famennian time interval for sections from Poland (Kowala), Germany (Benner, Steinbruch Schmidt) and USA (Devils Gate). Carbon isotopes are plotted relative to absolute time given the estimates for individual conodont zones by Ziegler & Sandberg (1996). Data from Joachimski et al. (2002).

bonates, diagenesis may have had a more pronounced influence on the carbon isotope signals. Consequently, any carbon isotope reference curve should be based on the analysis of several sections reflecting different depositional environments and derived from different palaeocontinents.

PART III: Discussion

9 Isotope stratigraphy: problems and limitations

Chemostratigraphy is, in most cases, based on "wiggle matching". If two records show similar fluctuations, it is inferred that the fluctuations can be correlated within a dating uncertainty. The amplitude of change in Neogene oxygen isotope serves as a proxy for combined ice volume and temperature fluctuations. Oxygen isotope stratigraphy is based on the assumption that marine oxygen isotope compositions are preserved in measured calcite and that early differential dissolution on the seafloor and diagenesis did not alter the original isotope composition. Burial of pelagic sediments results in sediment compaction and cementation. New diagenetic calcite added as overgrowth or cement to marine particles has an isotopic signature which is controlled by the temperature of cementation (Weissert et al. 1985, Stoll & Schrag 1996). In contrast, the oxygen isotope composition of shallow water carbonates is often strongly altered by meteoric or mixed meteoric-marine diagenesis. These processes result in a modification of the original oxygen isotope composition. Consequently, carbonates that underwent considerable lithification are no reliable carriers of the original marine oxygen isotope signal. The use of oxygen isotope geochemistry in stratigraphy is currently limited to young, mostly

Cenozoic pelagic sediments from the deep sea, where foraminiferal tests can still be obtained from washed sediment samples. Some pre-Neogene sediments may be excellent for paleotemperature studies, but not for stratigraphic purposes (e. g. Wilson & Norris, 2001). Oxygen isotope records derived from analysis of well-preserved Mesozoic/Paleozoic biogenic calcites (e. g. Veizer et al. 1999) or apatites (Pucéat et al. 2003, Joachimski et al. 2004) are currently not satisfactorily well-constrained to be applied for chemostratigraphic correlation.

The carbon isotope composition of pelagic carbonate is most reliable for chemostatigraphy. Numerous studies have demonstrated that carbon isotope curves established in pelagic sections are also reproducible in shallow water carbonate succession and in continental organic carbon records. However, carbon isotope curves may differ considerably in their absolute values. In pelagic sediments, variable contents of organic carbon may contribute to isotopically depleted cements that can shift bulk values towards lower numbers. The carbon isotope ratio of shallow-water limestones may be affected by the local seawater isotope signature, by originally varying contributions of aragonite and calcite or by meteoric diagenesis (e.g. Immenhauser et al. 2002). This is especially relevant for Palaeozoic carbon isotope records that are based on analysis of epeiric carbonate sequences. Therefore, absolute values and amplitudes of carbon isotope excursions can vary considerably from one locality to the other.

'Wiggle matching' between records differing in their absolute values and in the amplitude of excursions is difficult and can result in controversial interpretations of the carbon isotope curves. For example, Wissler et al. (2003) constructed a carbon isotope curve in hemipelagic sediments at the locality Angles (S. France), the stratotype for the Barremian. Based on a carbon isotope correlation with the informal pelagic references section (Cismon section/Northern Italy), the authors concluded that part of the Late Barremian is missing at Angles due to a major sedimentary gap. Föllmi et al. (2006) contradict this interpretation since the authors do not accept the pelagic carbon isotope curves as informal reference curves and conclude that the Barremian stratotype at Angles is continuous.

While the MIS numbering system in oxygen isotope stratigraphy is well established, C-isotope stratigraphers did not yet succeed in establishing an internationally accepted numbering system for their stratigraphies. Some authors introduced informal numbering of carbon isotope anomalies into the literature. Menegatti et al. (1998) drew lines between corresponding maxima or minima in a curve and split the curve into segments of increasing or decreasing trends. For example, the isotope curve across the Aptian OAE 1a was subdivided into 12 segments C1–C12 where C stands for the section Cismon. Wissler et al. (2003) chose a slightly different approach by subdividing the Barremian carbon isotope curve into segments B1–B5 (B stands for Barremian). A future chemostratigraphy working group will have to decide about a nomenclature for the carbon isotope stratigraphy. This decision will be related to the problem of chemostratigraphic type sections. We propose that the chosen sections in the Mesozoic should be of pelagic origin that the sections have to be dated by magneto- and biostratigraphy. Pre-Mesozic type stratigraphies will have to be based on carbon isotope records of pure carbonates sequences from stratigraphically well-dated sections that can be shown to be not affected by diagenesis.

Acknowledgements. First of all we like to thank the chairwoman of the ISSC, Maria Bianca Cita for inviting us to write this contribution on chemostratigraphy for the International Stratigraphic Guide. Chemostratigraphy was long not considered as a subdiscipline of stratigraphy, but the international research developments in the last few decades demonstrate that chemical proxies in sediments and sedimentary rocks serve as powerful source of information for stratigraphy. This contribution benefited from constructive comments by Jan Zalasiewicz, Brian Pratt, André Strasser, Bill Berggren, Jacques Thierry, Geza Csaszar, Bruce Waterhouse, Yokichi Takayanagi, Wout Bleeker, Nicol Morton, Ashton Embry, Yuri Gladenkov, Gilles Odin, Ki-Hong Chan, Henk Winter and Maria Cita. Helmut Weissert thanks for continuous support by the Swiss Science Foundation.

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