

Chemostratigraphy

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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 methods used in chemostratigraphy. This study focuses on the use of oxygen and carbon isotope geochemistry in stratigraphy. The importance of oxygen isotope stratigraphy for paleoclimatic research is documented in case study I. Oxygen isotope stratigraphy can be used to trace climate pulse 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 section and sections dated with magnetostratigraphy. Case study III focuses on the use of carbon isotope stratigraphy in the Paleozoic. Carbon isotope studies have been intensively used in the Paleozoic 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 temporal overprint in comparison to Mesozoic or Cenozoic carbonate sequences. Reliable Paleozoic carbon isotope curves are generally based on the analysis of brachiopod shells.

1 Introduction

Chemostratigraphy or chemical stratigraphy uses chemical fingerprints in sedimentary sequences for stratigraphic correlation. 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, any signature of global environmental change stored in the atmosphere and/or seawater and mirrored in a variety of biotic geochemical proxies 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 about variations in the carbon isotope composition of various compounds and the possible use of carbon isotopes in earth science (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 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 and 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 1970ties (e.g. Berger, et al., 1978, Duplessy et al., 1981, Weissert et al., 1979, Scholle and 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 , ^{16}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 $^{18}\text{O}/^{16}\text{O}$ 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 $\delta^{18}\text{O}$ of about 1‰ (Shackleton, 1987). At stable temperatures a change in $\delta^{18}\text{O}$ of -1‰ corresponds to a deglaciation induced sea-level rise of about 110 m, which can be explained by melting of isotopically light polar ice (-20 to -40 per mil). Best carriers of marine oxygen isotopic composition are planktic and benthic foraminifera. Variations in deep-water benthic foraminifera living under constant bottom water temperatures ($\pm 1^\circ\text{C}$) record ice build-up and deglaciation through time. Planktic foraminifera record a combined glacial and temperature effect plus a local salinity record in their oxygen isotope signature (Berger, 1979).

The oxygen isotope record established over the last few million years provides a history of multiple glacial-interglacial cycles showing cyclicities of 20ky and 40ky 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 and 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).

3 C-isotopes and C-isotope stratigraphy

Of the two stable carbon isotopes, the abundance of C-12 in nature is given as 98.89%, while C-13 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. Berger, 1979, Anderson and Arthur, 1983).

The large carbon pool of the oceans controls the exogenic carbon cycle, with reservoirs having residence times in the order of 10^4 - 10^5 years. The $\delta^{13}\text{C}$ -value of modern ocean water varies between -1.5‰ and 2.0‰ which is the result of mere physical fractionation between the atmosphere and the ocean (Kroopnick, 1985; Alternbach and Sarnthein, 1989). Calcium carbonate precipitating from ocean water has an enrichment factor of 0.2‰ up to $+2\text{‰}$ at 25°C , depending on carbonate mineralogy (e.g. Grossmann and Ku, 1986, Romanek et al. 1992). However, this factor is only little affected by temperature ($\Delta 0.03\text{‰}/\Delta^\circ\text{C}$, Emrich and Vogel, 1970). This small temperature-induced fractionation effect makes carbon isotopes in carbonate precipitates a most 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 planktic and benthic foraminifera records. The Paleocene-Eocene Thermal Maximum (PETM), one of the most dramatic global warming in Earth history, is accurately recorded in oxygen and carbon isotope records of benthic and planktic foraminifera. Benthic and planktic single specimen isotope records 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 planktic 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, it coincides with the base of the benthic extinction event and with a marlstone unit marking the Paleocene-Eocene boundary (Giusberti et al., 2006). 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).

In pre-Cenozoic sediments a variety of methods are used for reconstructing paleotemperatures. While these investigations are of great importance for paleoceanographic and paleoclimatic reconstructions, they are not yet of importance for stratigraphy. By contrast, C-isotope geochemistry of pre-Cenozoic sedimentary successions provides the most powerful stratigraphic information. The carriers of pre-Cenozoic marine carbon isotope signatures are either individual fossils or bulk carbonate often of pelagic or neritic origin. 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 $p\text{CO}_2$. 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 Other chemostratigraphic tools

Among other isotopes used in stratigraphy, strontium isotopes are most widely used for correlation. Sr has a long ocean residence time of up to several million years, therefore Sr isotope geochemistry is not used for high-resolution stratigraphy but Sr

isotope signatures in marine carbonates provide essential information that are useful for of stratigraphy. The Sr-isotope composition is characterized by long-term fluctuations. Major turning points in the Sr-isotope curve can be used as stratigraphic marker levels, for example the turning point in the Mesozoic Sr-isotope curve in the upper Jurassic and the rapid change in Sr-isotope values during the Aptian, (e.g. Jones et al., 2001, Bralower et al., 1997). Steuber et al. (2003) measured the Sr-isotope composition of Cretaceous rudists. Based on these analyses they succeeded in revising the stratigraphic ranges of chronospecies of hippurid rudists.

Other chemostratigraphic tools include the use of element distribution in sediments. Trace element stratigraphy can provide relevant stratigraphic information in carbonate-poor sedimentary successions (e.g. Aladhan 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-Tertiary 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).

5 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 ($d^{18}O$) 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 $\delta^{18}\text{O}$ stratigraphy over the last 30-40 years has been Nicholas Shackleton. Almost 25 yr ago he established a first $\delta^{18}\text{O}$ record of the upper Pliocene from Site 552A on the Gardar Drift, with a sampling resolution that almost reached orbital resolution (± 5000 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 $\delta^{18}\text{O}$ stratigraphies were published with similar resolution, still insufficient for orbital tuning. Only Tiedemann et al. (1994) established major progress in $\delta^{18}\text{O}$ stratigraphy by generating and comparing two benthic $\delta^{18}\text{O}$ records from the northeast Atlantic Site 659 and equatorial East Pacific Site 846 (details documented in Shackleton et al., 1995a), each of them showing a sampling density of 1000-3000 yr and better. Thus these records were sufficient for an identification of marine isotope stages (MIS). Below MIS 104, Tiedemann et al. (1994) introduced the 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 (Figure 1), which equally applied to the Atlantic and Pacific oceans. Both the Atlantic and Pacific $\delta^{18}\text{O}$ 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 and Loutre (1991) as tuning target for $\delta^{18}\text{O}$ -based ice volume changes. Later-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 and 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 planktic and benthic $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ curves Lisiecki and Raymo (2005) published the chemostratigraphic synthesis record “LR04” for the last 5.5 Myr, that now forms a chronostratigraphic backbone for Plio-Pleistocene times, finding two further MIS and slightly shifting some MIS boundaries, however, by no more than 10 kyr.

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 man-made rapid melt of the Greenland ice sheet. The almost coeval onset of ice-rafted debris deposition in both the North Atlantic and North Pacific near MIS G6 (2.73 Ma) to MIS 104 (2.6 Ma) (Shackleton and Hall, 1984; Haug et al., 1999) and the partly preceding, partly coeval well-dated massive $\delta^{18}\text{O}$ shift shortly prior to and close to the basis of the Gelasian also formed the prime argument for many INQUA colleagues to plea for shifting the basis of the Quaternary back to the Gauss-Matuyama geomagnetic boundary (Pillans and Naish, 2004).

New insights into the processes of general North Atlantic climate deterioration (Bartoli et al., 2005) came from various proxy techniques, (1) from strongly increased resolution of Pliocene benthic stable-isotope records up to Late-Pleistocene-style multi-centennial scale records (Bartoli et al. 2006) as basis for a proper definition of the amplitude of most positive $\delta^{18}\text{O}$ 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, (3) also, from a revised radiometric chronology for IRD deposition at Greenland Sea Site 907, crucial for the understanding of the timing of earliest Greenland ice outbreaks. (4) Coeval major changes in the paleoceanography of the subarctic North Pacific (correlated by $\delta^{18}\text{O}$ stratigraphy) were deduced from biomarker- and $\delta^{15}\text{N}$ -based paleoproductivity records (Haug et al., 1999). (5) On the basis of detailed $\delta^{18}\text{O}$ 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 (Figure 3, top). This gradient provided key evidence for establishing a precise record for the final closure of the Central American Seaways (Groeneveld et al., 2006), a record also confirmed by various land-based evidence from Panama. Various ocean models

(e.g., Schneider and 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 strengthened poleward transport of heat and salt and more vigorous meridional overturning in the northern North Atlantic.

Accordingly, the final closure of the Central American Seaways (i.e., the closure of seaways with 100 m water depth and less) started with a short-lasting precursor event at MIS KM4 to KM3 (~3.15 Ma) (Figure 3). A second closure event occurred 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-rafted debris from East Greenland, with a lag of no more than 40 to 60 kyr (Figure 3, 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 (Figure 3, panel b). Moreover, the coeval onset of dominating surface water stratification in the subarctic North Pacific may have led to long-term reduced atmospheric CO₂ pressure (Haug et al., 1999). $\delta^{18}\text{O}$ 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).

6 Case Study II

The Valanginian-Hauterivian carbon isotope excursion

Paleoceanographers investigating conditions and causes of Oceanic Anoxic Events started to use carbon isotope geochemistry as a tracer of the global carbon cycle in the late 1970ties (e.g. Weissert et al., 1979; Scholle and Arthur, 1980). They analyzed the carbon isotopic composition of bulk carbonate from pelagic limestone successions and could 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 as well as an excellent stratigraphic marker.

An informal reference curve

Pelagic carbonates of Early Cretaceous age exposed along the Southern Alps of northern Italy were chosen for the establishment of a pelagic carbonate carbon isotope curve through the Valanginian and Hauterivian. The studied sediments were deposited along the southern continental margin of the Tethys ocean in water depths of thousand meters or more (Bernoulli and Jenkyns, 1974). This margin was characterized by a number of platforms and basins bound by approximately N-S trending paleotectonic normal faults (Winterer and Bosellini, 1981). Four of the studied sections (Breggia, Rio Corna, Capriolo, Polaveno) are located in the Lombardy Basin. The remaining section (Valle Aviana) is situated on the Trento Plateau (Fig. 1).

The limestones of the Maiolica Formation consist of a continuous succession of white to grey pelagic nanofossil 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 results of carbon isotopic analyses of bulk carbonate for the studied sections are summarized in composite figure 2 (Channell et al, 1993). 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% (Lini, 1994). The sections have been dated with bio- and magnetostratigraphy (Channell et al., 1993). The data clearly show a remarkable excursion to positive $\delta^{13}\text{C}$ values in the carbonate $\delta^{13}\text{C}$ record during the late Valanginian. Although the absolute isotopic values differ slightly from section to section, the relative pattern of fluctuations is consistent. Low $\delta^{13}\text{C}$ values near 1.3-1.5 ‰ analyzed in Berriasian and early Valanginian sediments (*Cretarhabdus angustiforatus* nanofossil zone) were replaced by positive $\delta^{13}\text{C}$ values near 3‰ in the Upper Valanginian (*Calcicalathina oblongata* nanofossil

zone). The carbonate C-isotope excursion ends in the Lower 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 section with magnetostratigraphy. As shown in figure 2 , the positive C-isotope excursion begins during CM12 and reaches its maximum during CM11. From CM10N to CM8 the $\delta^{13}\text{C}$ ratios return to normal pre-excursion values.

Comparison with a carbon isotope curve from the ammonite stratotype

Hennig et al. (1999) and Hennig (2003) present carbon isotope curves from two sections, La Charce and Pont de Carajuan, both located in Southern France ((Fig. 1 in Hennig et al., 1999). The ammonite-rich section La Charce in the basinal part of the Vocontian domain is described in Bulot et al. (1992). It is now used as the stratotype for the Upper Valanginian to Lower Hauterivian ammonite zonation (Mutterlose 1996). Its lithology consists of hemipelagic, fossiliferous, cyclic marl-limestone alternations. The Lower Valanginian and the Lower Hauterivian parts of the section are more calcareous than the Upper Valanginian interval, where marls predominate. The section used for C-isotope stratigraphy covers the Late Valanginian and Early Hauterivian (Verrucosum zone - Loryi zone, fig. 3).

The section Pont de Carajuan has been studied previously by various authors (e.g. Walter 1991). 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. The detailed ammonite stratigraphy for the Pont de Carajuan section is published in Arnaud and Bulot et al. (1993). The isotope curves established by Henning et al. (1999) at these localities can be correlated with the pelagic curves from the Southern Alps:

(1) A minor negative $\delta^{13}\text{C}$ -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 $\delta^{13}\text{C}$ -record falls within the upper part of the *campylotoxus*

zone. The first maximum is measured in the upper part of *the inostranzewi* subzone (Ct4).

(2) An interval of positive $\delta^{13}\text{C}$ -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 $\delta^{13}\text{C}$ -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 $\delta^{13}\text{C}$ stratigraphy with the reference $\delta^{13}\text{C}$ 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. (1995) 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. The *verrucosum* zone placed by Channell et al (1995) and by Gradstein et al. (2004) into CM12A-CM11A. Our data document that the *verrucosum* Zone falls within CM11, and possibly the lower part of CM 10N. Channell et al. (1995) and Mutterlose (1996) place the *acanthodiscus radiatus* Zone into CM11-CM10N. The *radiatus* Zone falls into CM10 to CM9. The Loryi Zone is shifted from a CM10N position (Channell et al. 1995; Mutterlose 1996) into CM 9. The base of the *radiatus* zone is proposed as the stage boundary between the Valanginian and the Hauterivian (Bulot and Thieuloy 1993; Busnardo et al. 1979; Mutterlose 1996). According to the isotope-based correlation, this boundary falls into the normally magnetised reversal of CM10, while Channell et al. (1995) and Gradstein et al. (2004) placed it into CM11.

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. 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 due a stratigraphic gap recording a prominent sea-level lowstand at the Valanginian-Hauterivian transition. The other neritic successions provide carbon isotope data which do not record any clear carbon isotope anomaly (e.g. section Salève, Hennig 2003). This confirms that a carbon isotope anomaly

may not be stored in neritic limestones due to local seawater chemistry, variations in mineralogy or diagenesis. Parts of carbon isotope excursions can also be missing due to sedimentary gaps. Despite of this, Henning (2003) succeeded in tracing a carbon isotope excursion across an ocean transect and was able to correlate changes in coastal environments with the trends in pelagic environments during the Valanginian-Hauterivian carbon-isotope excursion. 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 neritic environments 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.

7 Case Study III

Carbon isotope stratigraphy of the Devonian

Carbon isotope studies have been intensively used in the Paleozoic 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 temporal overprint in comparison to Mesozoic or Cenozoic carbonate sequences. Reliable Paleozoic 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 and Joachimski, 1996; Mii et al., 1999; 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 isotope 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 $\delta^{13}\text{C}$ 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

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

The Devonian whole rock carbon isotope record (Buggisch & Mann 2004, Buggisch & Joachimski 2006) shows several positive excursions (Fig. 1) 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 $\delta^{13}\text{C}_{\text{DIC}}$ that is documented in higher $\delta^{13}\text{C}_{\text{carb}}$ values. The brachiopod $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ record and from the fact that whole rock carbonate $\delta^{13}\text{C}$ records may have been affected by diagenesis. While the brachiopod $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ values than carbonates composed exclusively of low-magnesium calcite. This was documented by Swart & Eberli (2005) who showed that $\delta^{13}\text{C}$ of modern peri-platform carbonates is strongly correlated with the percentage of aragonite with aragonite-rich limestones revealing significantly

higher $\delta^{13}\text{C}$ values in comparison to limestones dominated by low-magnesium calcite. Following, carbonates that initially had a significant aragonite proportion are expected to have higher $\delta^{13}\text{C}$ values in comparison to e.g. shells composed of low-magnesium calcite.

In order to construct composite carbon isotopes curve 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 epeiric seas may be different in their chemical properties than the open ocean (e.g. Holmden et al. 1998, Immenhauser et al. 2002, Panchuk et al. 2005, Melchin and Holmden 2006). This may be relevant especially for the Palaeozoic since the Palaeozoic shelves were more expanded than during modern times. Differences in the carbon isotope ratios of dissolved inorganic carbon 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 the shallow water sediments and diagenetic overprinting (Allan & Matthews 1982, Joachimski 1994).

Examples for the comparison of Early to Middle Devonian as well as Late Devonian carbon isotope records are given in figures 2 and 3. Figure 2 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). The general pattern is well comparable in all sections (Fig. 2). However, the absolute values as well the amplitudes of the excursions in $\delta^{13}\text{C}$ may be different. Buggisch and Mann (2004) observed that samples from basinal settings have generally lower $\delta^{13}\text{C}$ values in comparison to samples from shallow water carbonates. The lower $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ of dissolved inorganic carbon of surface and deeper marine waters (vertical gradient in $\delta^{13}\text{C}$ of DIC), which will represent the diagenetic solutions in which the respective carbonates will stabilize. The different amplitudes in $\delta^{13}\text{C}$ may either be explained by the imprint of diagenesis or by the fact that global changes in $\delta^{13}\text{C}$ of DIC are recorded slightly differently in various parts of the World's oceans due to differences

in $\delta^{13}\text{C}$ of DIC in shallow epeiric seas. Figure 2 shows as well that the $\delta^{13}\text{C}$ excursion measured on inorganic carbon across the Silurian-Devonian boundary is well reproduced in the carbon isotopic composition of organic carbon.

The correlation of carbon isotope patterns from various sections across the Frasnian-Famennian boundary is shown in Figure 3. The carbon isotope records have been plotted against absolute time using estimates for the duration of individual conodont zones of Sandberg & Ziegler (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 $\delta^{13}\text{C}$ 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. $\delta^{13}\text{C}$ 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. $\delta^{13}\text{C}$ 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 carbonates, 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 derive from different palaeocontinents.

8 Isotope stratigraphy: problems and limitations

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, Schrag and Stoll, 1996). This results in a modification of the original seawater composition. Carbonates that underwent considerable lithification are not reliable carriers of an original marine oxygen isotope composition. The use of oxygen isotope geochemistry in stratigraphy is clearly 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 (e.g. Wilson and Norris, 2001) for paleotemperature studies but not for stratigraphic purposes. In contrast, the oxygen isotope composition of shallow water carbonates is often strongly altered by meteoric or mixed meteoric-marine diagenesis which makes these carbonates as unreliable carriers of an original marine oxygen isotope composition.

Carbon isotope composition of pelagic carbonate is most reliable for chemostratigraphy. 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, C-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. Shallow-water limestones are affected by the local seawater isotope signature, by varying isotopic composition of biogenic and/or non biogenic fraction of the measured bulk samples or by meteoric diagenesis (e.g. Immenhauser et al., 2002).

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) split their isotope curve across the Aptian OAE 1a into 12 segments C1 –C12 where C stands for the section Cismon. Wissler et al. (2002) chose a different approach in their stratigraphic nomenclature. They split their Barremian C-isotope curve into 5 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 section is dated with magneto- and biostratigraphy. Pre-Mesozoic type stratigraphies will be based on brachiopod curves and/or on bulk carbon isotope stratigraphy.

Acknowledgements

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Figure captions (Quaternary case study)

Figure Q 1. Comparison of benthic $\delta^{18}\text{O}$ 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)

Figure Q 2. The LH04 stack benthic $\delta^{18}\text{O}$ stack constructed by graphic correlation of 57 globally distributed benthic $\delta^{18}\text{O}$ records. Scale of the vertical axis is changing across panels (from Lisiecki & Ramo, 2005).

Figure Q 3. Paleoclimatic records for the Pliocene North Atlantic. (a) Caribbean-to-East Pacific sea surface salinity anomalies recording the final closure of the Central American Seaways (CAS) (Groeneveld et al., 2006) and ice-rafted debris record of Northern Hemisphere Glaciation from ODP Site 907 (with new age model); (b) Mg/Ca-based sea surface temperature records from northeast ODP sites 984 and 609, (c) Planktic $\delta^{18}\text{O}$ curves from ODP sites 984 and 609, (d) Benthic $\delta^{18}\text{O}$ records from DSDP sites 610 and 609. Numbers 101, 103, G1, G13, etc. are interglacial MIS, (e) Mg/Ca-based deep-water temperatures from site 609 (from Bartoli et al., 2005).

Figure captions (Valanginian case study)

Fig. Val 1: Paleogeographic reconstruction of the alpine Tethys in the Early Cretaceous, with sections studied.

Fig. Val 2: Composite C-isotope stratigraphy, Valanginian-Hauterivian, Southern Alps (N. Italy) correlated to magneto- and biostratigraphy (from Channell et al., 1993).

Fig. Val 3: Valanginian-Hauterivian 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).

Fig. Val 4: Interegional C-isotope stratigraphy correlation along an NW-SE transect through the alpine Tethys Ocean (from Hennig, 2003).

Figure captions (Devonian case study)

Fig. Dev 1: 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).

Fig. Dev 2: 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).

Fig. Dev 3: 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 Sandberg & Ziegler (1996). Data from Joachimski et al. (2002).