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Carbon isotope stratigraphy of the Devonian of Central and Southern Europe

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Abstract

Carbonate rocks of the Rhenohercynian and Saxothuringian zones of the Variscan Mountains, Prague Syncline, Carnic Alps, Montagne Noire, Pyrenees, and Cantabrian Mountains were investigated for $\delta^{13}C_{carb}$. The values were measured on bulk carbonate, selected carbonate components and cements. Many of the studied carbonates are interpreted to exhibit primary marine $\delta^{13}C$ values with only some showing evidence of diagenetic alteration. A $\delta^{13}C$ curve is presented for the entire Devonian time interval. Positive $\delta^{13}C$ excursions are documented in the *woschmidti-postwoschmidti*, *sulcatus*, *kitabicus*, Upper *serotinus*, *kockelianus,* Middle *varcus*, *falsiovalis*, Upper *rhenana*, *linguiformis* to Middle *triangularis*, and Middle to Upper *praesulcata* conodont Zones. Some excursions are recorded worldwide and interpreted to be of global significance as e.g. at the Silurian–Devonian and Frasnian–Famennian boundaries. Some of the others are described for the first time from Central and Southern Europe, and their global nature has to be verified by further investigations. Most $\delta^{13}C$ excursions coincide with sea-level changes and the deposition of black shales. A coupling of changes in sea-level, weathering intensity, nutrient supply, organic carbon production, and climate is assumed as driving force of the carbon isotope excursions.

Keywords: Carbon isotopes; Bio-events; Black shale; Devonian; Rhenohercynian; Saxothuringian; Prague Syncline; Carnic Alps; Montagne Noire; Cantabrian Mountains

1. Introduction

Reliable $\delta^{13}C$ curves are usually based on the analysis of brachiopod shells which are composed of low-magnesium calcite and consequently relatively resistant against diagenetic alteration (Popp et al., 1986; Brand, 1989; Grossman et al., 1993; Wenzel and Joachimski, 1996; Mii et al., 1999; Veizer et al., 1999, among others). Carbon isotope data for Devonian brachiopods were presented by Popp et al. (1986), Brand (1989), Bates and Brand (1991), Gao (1993), Diener et al. (1996), Veizer et al. (1997, 1999), Brand et al. (2004) and van Geldern et al. (2006-this volume). However, the abundance of brachiopods is strongly dependent on facies and it is therefore difficult to reconstruct high-resolution isotope records based on the analysis of brachiopod calcite. A higher temporal resolution can be achieved by the analysis of bulk carbonate samples. However, whole rock carbon isotope data were until now only available for specific series and stage boundaries and for certain "events" (e.g. Silurian–Devonian boundary, Saltzman, 2002; Lower Devonian

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of the Prague Syncline, Hladíková et al., 1997; Frasnian–Famennian boundary, Buggisch, 1992; Joachimski et al., 2002).

This study aims to reconstruct the carbon isotope history of the Devonian time interval by presenting a composite carbon isotope curve based on the analysis of whole rock carbonates from Central and Southern Europe. The composite $\delta^{13}C$ curve will be discussed in the light of concomitant sea-level changes (Johnson et al., 1985), deposition of black shales and bio-events (Walliser, 1996; House, 2002).

2. Investigated sections

The investigated sections from Central and Southern Europe were located on isolated terranes (e.g. Rhenohercynian, Saxothuringian, Moldanubian, Cantabrian and Intra-Alpine) situated at latitudes of 10° to 35°S during the Devonian (Ziegler et al., 1988; Scotese, 2001). These small Variscan terranes were travelling northward from Northern Gondwana and colliding with Laurussia during the Devonian and Carboniferous (Fig. 1). The drift of the terranes was combined with the closure of small oceanic basins like the Rhenohercynian Ocean south of the Rhenohercynian Zone, the Saxothuringian Basin north of the Moldanubian Block or the Rheic Ocean north of the Cantabrian and Intra-Alpine Terranes (Ziegler et al., 1988; Franke, 2002).

2.1. Rhenohercynian Zone

The Rhenohercynian Zone represents the southern shelf of the Devonian Old Red continent. During the Middle Devonian, shallow water carbonates and siliciclastics were deposited in the northern Rheinische Schiefergebirge (Fig. 1), whereas volcanic rocks and shales are the predominant deposits in the basinal setting of the southern part of the Rheinische Schiefergebirge and Harz Mountains. Volcanic seamounts in part reached the photic zone or formed small islands within the basin. Some seamounts were settled or fringed by coral-stromatoporoid reefs. Carbonate mudstones and wackestones (cephalopod limestones) were deposited on the distal slopes of these seamounts and on submarine rises situated at greater water depths.

Most of the investigated sections from the Rhenohercynian Zone were situated in deep water settings below wave base (Fig. 1: 7, 8, 9 and 11). Although these sucessions are generally condensed, no major stratigraphic gaps are recorded by means of conodont biostratigraphy. The section of Beringhausen (Fig. 1: 10) represents a shallow water setting. Continuous carbonate sedimentation ended with the deposition of the late Famennian Hangenberg shale (Fig. 1: 12, 13, 14). During the Lower Carboniferous, carbonate production shifted northwards which is documented by the occurrence of Carboniferous limestones in Belgium, Great Britain and Ireland.

2.1.1. Section Blauer Bruch (N 51°06′47″, E 9°08′33″; Fig. 1: 8)

Emsian to Famennian carbonates are exposed in several dissected tectonic slices in the abandoned quarry Blauer Bruch. The outcrop is well-known for the exposure of the Lower and Upper *pumilio* horizons and the *Pharciceras* limestone (Walliser et al., 1988; Lottmann et al., 1988b; Lottmann, 1990).

2.1.2. Section Beringhausen (N 51°24′0″, E 8°42′ 36.33″; Fig. 1: 10)

The lower part of the Beringhausen section is characterized by Givetian volcanic rocks which are overlain by 100 m thick reefal limestones and rudstones composed of stromatoporoids, corals and echinoderms. Clausen et al. (1989a, 1991) reported conodonts of the Middle *varcus* Zone from the base of the limestone unit. The uppermost 5 m of the lower section are depicted in Fig. 3 which have been dated by means of conodonts to be of Upper *falsiovalis* Zone age. After almost 50 m without exposure, about 20 m of Upper Devonian wackestones (*punctata* to Lower *expansa* zone) are exposed in a trench in the upper part of the section (Schülke and Popp, 2005). The part of the section containing the Lower and Upper Kellwasser Horizons is shown in Fig. 4.

2.1.3. Section Benner (N 50°41′16″, E 8°23′54″; Fig. 1: 11)

More than 25 m of cephalopod limestones (upper Givetian–Famennian) are exposed in the abandoned quarry Benner (Wittekind, 1965). The lower part of the quarry is nowadays used as a fishpond, but the upper part of the section with both Kellwasser horizons being exposed, is still accessible (Buggisch, 1972, 1991; Schindler, 1990; Joachimski and Buggisch, 1993, 2002).

2.1.4. Section Hengstebeck (N 51°07′06.5″, E 8°00′ 56.2″; Fig. 1: 9)

The Hengstebeck section exposes about 7.5 m of Givetian and Frasnian cephalopod limestones that are underlain by Middle Devonian gray shales and siltstones and overlain by Famennian red shales (Clausen et al., 1979). Both *pumilio* horizons are

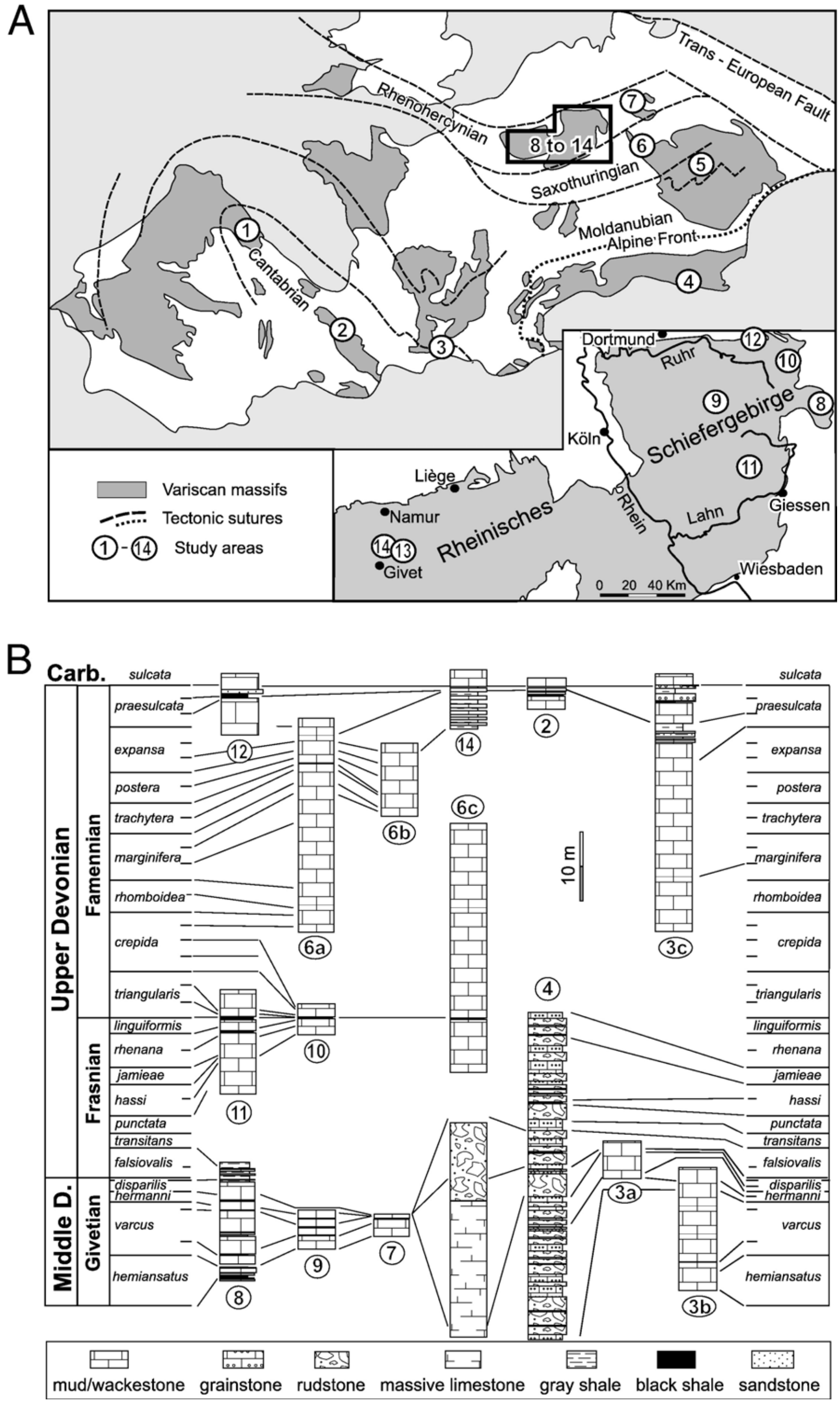

Fig. 1. A: European Variscan terranes according to reconstruction of Franke (2002) with sample localities of Buggisch and Mann (2004) and this study. B: Lithologic columns and stratigraphic range of studied sections. 1—Cantabrian Mountains, 2—Pyrenees, 3—Montagne Noire (3a—Puech de la Suque, 3b—Pic de Bissous, 3c—La Serre C), 4—Carnic Alps Timau, 5—Prague Syncline, 6—Saxothuringian (6a—Köstenhof, 6b—Kahlleite, 6c—Vogelsberg), 7—Harz Mountains (Hühnertal), 8 to 14—Rheinisches Schiefergebirge (8—Blauer Bruch, 9—Hengstebeck, 10—Beringhausen, 11—Benner, 12—Drever, 13—Anseremme, 14—Geron-Celles).

developed in this section with the Lower *pumilio* horizon being represented by 3 cm of dark shales and bituminous limestones. The Upper *pumilio* horizon is formed by several centimeters of dark grey limestones characterized by the mass occurrence of *Terebratula pumilio* (Lottmann, 1990).

2.1.5. Section Drever (N 51°30′08″, E 8°21′29″; Fig. 1: 12)

Famennian to Visean strata are exposed in the abandoned Drever quarry. The Upper Devonian part of section is composed of nodular limestones (Clausen et al., 1989b; Korn et al., 1994). The uppermost Devonian is made up of dark-grey nodular limestones of the Lower and Middle *praesulcata* Zone. Black shales, fine-grained sandstones, and nodular limestones were deposited during the Upper *praesulcata* Zone. Shales and nodular limestones formed during the lowermost Carboniferous *sulcata* Zone. The conodont stratigraphy of the section exposed in the NE quarry wall was studied by Ziegler and the section was proposed as a candidate for the stratotype of the D–C boundary (Ziegler et al., 1988).

2.1.6. Section Hühnertal (N 51°52′16″, E 10°21′17″, Fig. 1: 7)

The Givetian *Stringocephalus* limestone, the 10 m thick Büdesheim shale as well as the upper Frasnian to lower Famennian Adorf limestone are exposed along a forest road cut in the Grane valley (Harz mountains; Stoppel and Zscheked, 1971; Lottmann et al., 1988a). The lower part of the section that comprises the Lower and Middle *varcus* Zone was excavated and sampled for this study. The section includes both *pumilio* horizons, although only the Upper horizon is well developed. A hiatus is observed above the Upper *pumilio* horizon, comprising at least the uppermost Upper *varcus* and *hermanni-cristatus* Zones (Lottmann, 1990).

2.1.7. Anseremme (N 50°14′35″, E 4°54′30″; Fig. 1: 14)

Uppermost Devonian ("Strunian" Etroeungt limestone) and lower Carboniferous (Tournaisian) strata are exposed along the railway cut near Anseremme (Bouckaert et al., 1974). The D–C boundary coincides with the transition from the "Strunian" limestones and shales to the thick-bedded limestones of the Hasterian α. The Strunian limestones consist of wackestones with a diverse, open marine fauna (Van Steenwinkel, 1988). The increasing occurrence of grain- and packstones towards the D–C boundary indicates a shallowing of the depositional environment. Van Steenwinkel (1988) and Casier et al. (2004) demonstrated that bed 159 (Fig. 5) is bound by unconformities with the gaps spanning the Upper *expansa* to Middle *praesulcata* and *sulcata* Zones. Conodonts of the Upper *praesulcata* zone were identified in Bed 159.

2.1.8. Gendron-Celles (E 4°58′11″, N 50°12′53″; Fig. 1: 13)

Similar to the section near Anseremme, the uppermost Devonian ("Strunian") and lower Carboniferous (Tournaisian) strata are exposed along the railway cut (Conil et al., 1975).

2.2. Saxothuringian Zone (Germany)

In the Saxothuringian Zone, Devonian volcanism reached its climax during the lower Frasnian and created an up to 400 m high submarine relief which influenced the sedimentation in the Thuringian trough (Linnemann et al. 2004). Carbonate mud- and wackestones as well as nodular limestones (cephalopod limestone) were deposited during the upper Frasnian to uppermost Famennian on these volcanic swells.

2.2.1. Köstenhof section (N 50°15′29″, E 11°32′42″; Fig. 1: 6a)

About 36 m of Famennian cephalopod limestones are exposed in the abandoned Köstenhof quarry (Upper *crepida* to *praesulcata* zone). The mudstones and wackestones are interpreted to have been deposited on a submarine volcanic rise (Horstig and Stettner, 1976). Marker horizons like the *annulata* and Hangenberg shales are well developed (Hartenfels and Tragelehn, 2001).

2.2.2. Vogelsberg section (N 50°38′12″, E 11°52′28″; Fig. 1: 6c)

Frasnian volcanic rocks and upper Frasnian and Famennian nodular and platy limestones (mud- and wackestones) are exposed in the active Vogelsberg quarry. Two intercalated gray units correspond to the Lower and Upper Kellwasser horizons (Joachimski and Buggisch, 2002). The carbonate succession is characterized by numerous sheet cracks which are filled by several generations of cements and internal sediment. The sampled interval comprises the *rhenana* to *marginifera* Zones.

2.2.3. Kahlleite (N 50°37′32″, E 11°50′32″; Fig. 1: 6b)

Frasnian to uppermost Famennian nodular limestones overlying lower Frasnian volcanic rocks are exposed in the section Kahlleite (known as Kahlleite

East: Gereke, 2004). The approx. 40 m thick succession contains both Kellwasser horizons as well as the *annulata* and Hangenberg shales. The interval from the Upper *marginifera* to Middle *expansa* Zone was sampled during this study.

2.3. Carnic Alps (Austria and Italy)

The Carnic Alps are located south of the Periadriatic Lineament which separates the allochthonous nappes of the Eastern Alps in the north from the autochthonous Southern Alps. The Devonian rocks of the Carnic Alps are developed in four main facies (Kreuzer, 1992): shallow-water platform and reef limestones, proximal as well as distal slope limestones and basinal (siliceous) shales with isolated limestone intercalations. The carbon isotope record for the Lower Devonian to Eifelian carbonates was presented by Buggisch and Mann (2004). In this study, additional data are reported for two further sections.

2.3.1. Timau section (E 13°01′33″, N 46°35′40″; Fig. 1:4)

About 45 m of mainly rud- and grainstones with few mudstones layers are exposed in the Timau section (*hermanni-cristatus* to the Upper *rhenana* Zone; section Pramosio 327 of Spaletta and Perri, 1998). Breccias represent about 70% of the entire sequence with wackestone intraclasts floating in a grainstone matrix. Stromatoporoids and corals occur as bioclasts. The succession was deposited in a proximal slope setting.

2.3.2. Wolayer Glacier (E 12°52′33″, N 46°36′47″; Fig. 1: 4)

The section Wolayer Glacier ranges from the Eifelian into the Famennian. The youngest limestones are of *crepida* Zone age and are disconformably overlain by Carboniferous flysch deposits (Schönlaub, 1980; Schönlaub et al., 1994; Joachimski et al., 1994). Mud- and wackestones are the most prominent facies indicating an off-platform, distal slope depositional environment. 6 cm of black shales corresponds to the Lower Kellwasser horizon. Light-coloured bioturbated mudstones are developed at the Frasnian–Famennian (F–F) boundary and indicate well-aerated conditions during this specific time interval.

2.4. Montagne Noire (France)

In the Montagne Noire, carbonate deposition started with the Lochkovian transgression and ended with the sedimentation of late Lower Carboniferous flysch deposits. Late Visean to early Namurian Variscan tectogenesis resulted in the emplacement of olistostromes (Cabrière Klippen) and recumbent fold nappes. The Lower Devonian to Eifelian carbonate sequence as well as the carbon isotope record were described by Buggisch and Mann (2004) and will not be repeated here.

The Givetian to Tournaisian sediments of the nappe successions are represented by pelagic shales and “Griotte”-limestones. Contemporaneous sediments of the Klippen of the Cabrière Zone were generally deposited in a more proximal position to the shoreline (Feist, 2002). Nevertheless, pelagic conditions prevailed during the Givetian. During the Frasnian and lower Famennian, restricted and oxygen-depleted conditions spread over the proximal platform (Tribovillard et al. 2004). The upper Famennian is represented by “Griotte”-limestones shallowing-upward into laminated siltstones with plant fragments and oolithes at the D–C transition (Flajs and Feist, 1988).

2.4.1. Puech de la Suque (N 43°30′15,1″ E 3°05′15,1″; Fig. 1: 3a)

The 4 m thick section exposed at Puech de La Suque represents the Global Stratotype Section and Point (GSSP) of the Givetian/Frasnian stage boundary (House et al., 2000). The well bedded grey and reddish mud- and wackestones comprise the Upper *hermanni-cristatus* to Upper *falsiovalis* zones.

2.4.2. Pic de Bissous, Marble Quarry (N 43°36′10.0″, E 3°21′28.9″; Fig. 1: 3b)

The 23.5 m thick section in the Marble quarry at Pic de Bissous exposes well-oxygenated mud- and wackestones (Feist, 2002). Fossiliferous beds about 20 m above the base of the section may correspond to the *pumilio* Horizons (House, 1995). The upper Eifelian to middle Givetian interval was sampled during this study (Fig. 2).

2.4.3. La Serre Trench C, new (N 43°33′22.8″, E 3°21′40.4″) and Trench E′ (N 43°33′20.0″, E 3°21′35.7″; Fig. 1: 3c)

The rocks exposed at La Serre hill are part of a chaotic set of olistolithes of the Cabrière Klippen, emplaced in the Lower Carboniferous flysch basin (Engel et al., 1978). Several trenches give access to the Frasnian to Tournaisian succession. Samples from the Lower and Middle Griotte Formation were sampled in the new trench C, which exposes nodular mudstones and wackestones of the Upper *rhomboidea* to Lower *praesulcata* Zones (Feist, 2002). The Upper Griotte

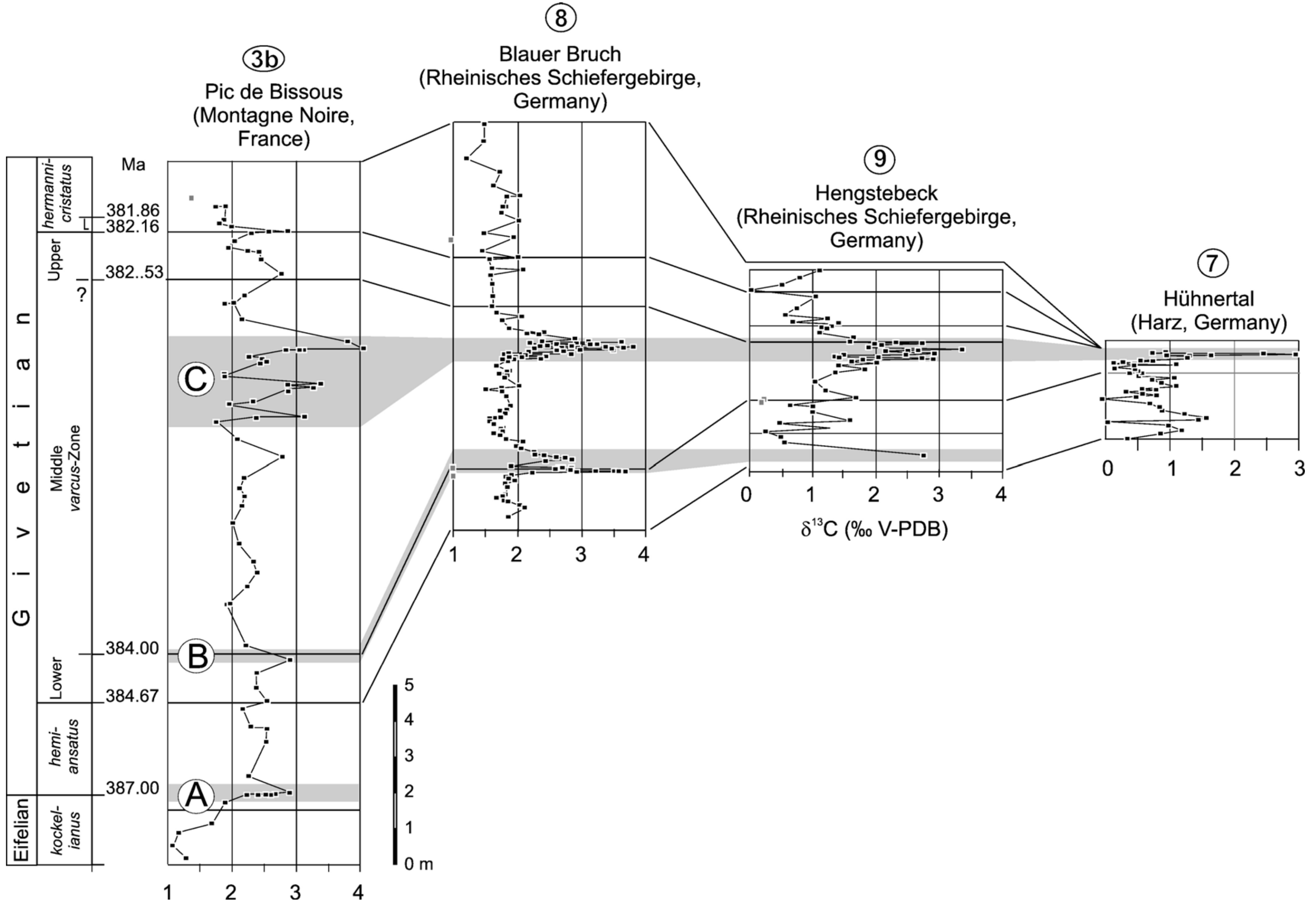

Fig. 2. δ^{13}C of uppermost Eifelian to upper Givetian carbonates. Sections are arranged according to depositional environment from shallow-water below wave base (Pic de Bissous) to deeper water (Hühnertal). Gray shaded bars highlight major excursions (A: Kaèák Event, B: Lower *pumilio* Event, C: Upper *pumilio* Event).

Formation was sampled in Trench C (new) and in Trench E′, which represents the D–C boundary stratotype (Flajs and Feist, 1988; Feist et al., 2000).

2.5. Pyrenees (France)

The Variscan High Chain (Aller et al., 2002) represents the external zone of the Iberian Variscan belt. A general trend from siliciclastic to carbonate deposits is observed in the Lower and Middle Devonian, culminating in the growth of vast carbonate platforms during the Famennian. Upper Devonian deep water carbonates ("Griotte" and "Supragriotte") are overlain by Tournaisian limestones with a considerable unconformity developed in most sections. The uppermost to entire Famennian and the lowermost Tournaisian strata are missing in several sections. Samples were collected from an almost complete D–C boundary section in the Northern Pyrenees at Milles.

2.5.1. Milles (N 42°58′42.2″; E 1°18′07.0″; Fig. 1: 2)

About 100 m of Frasnian Griotte and Famennian Supragriotte deep water limestones are exposed along a road cut at Milles. The upper few meters of the section have been dated to be of *praesulcata* Zone age, of which the uppermost 80 cm belong to the Upper *praesulcata* Zone. The *sulcata* Zone is represented by 60 cm of wackestones deposited above a 3 to 5 cm thick shale interval (Cygan and Perret, 2002). The D–C boundary interval is highly condensed and characterized by the occurrence of several hardgrounds.

3. Methods

A total of 2532 samples were collected from the various sections in Central and Southern Europe (Fig. 1). Hand specimens were cut and polished in order to describe lithology and facies. Calcite powders (<0.5 mg) for isotope analysis were drilled from fresh surfaces or from polished slabs using a microdrill. Mud- and wackestones were preferentially sampled, but analyses were also performed on grainstones, individual carbonate components and marine carbonate cements.

Carbonate powders were reacted with phosphoric acid in an on-line carbonate preparation system (Carbo III) connected on-line to a ThermoFinnigan 252 mass spectrometer. All values are reported in ‰ relative to V-PDB by assigning a $\delta^{13}C$ value of +1.95‰ and a $\delta^{18}O$ value of −2.20‰ to NSB 19. Accuracy and precision was controlled by replicate measurements of laboratory standards and was better than ±0.06‰ (1σ).

In order to correlate $\delta^{13}C$ records of time-equivalent sections, an absolute age was assigned to each carbon isotope data point. Absolute ages were calculated by using the biostratigraphic zonation given by the authors describing the various sections, by the absolute ages given for the biozone boundaries by the Stratigraphic Table of Germany 2002 timescale (STG 2002) and by interpolating between these datum points according to sediment thickness and facies. The validity of this method is dependent on the precision of the biostratigraphic dating and on the assumption of continuous deposition and constant sedimentation rate. Problems for correlation emerged due to the ongoing refinement of conodont taxonomy and the resulting changes in the biozonation used by the various biostratigraphers. Major carbon isotope excursions were used for chemostratigraphic correlation. Isotope trend lines were calculated using the nonparametric locally weighted regression method "Locfit" (Loader, 1997, 1999). All calculations were performed with the open source statistic software "R" (version 1.5.1, Ihaka and Gentleman, 1996).

4. Results

4.1. Carbon isotope record

The major features of the Devonian carbon isotope record will be described in the following paragraphs with the Lochkovian to Eifelian $\delta^{13}C$ record being summarized briefly (for details see Buggisch and Mann, 2004).

4.1.1. Lochkovian to Eifelian

A major positive excursion in $\delta^{13}C$ with an amplitude of +3.8‰ was observed at the Silurian–Devonian boundary in several sections from the Prague syncline and the Carnic Alps (Fig. 6). $\delta^{13}C$ values increase from around +0.5‰ in the Pridoli to maximum values around +3.8‰ at the Silurian–Devonian boundary and are followed by a gradual decrease to values around 0‰ during the lower Lochkovian. A second increase in $\delta^{13}C$ starts in the upper Lochkovian with maximum values around +3.5‰ recorded in the lower Pragian. During the Pragian and Emsian $\delta^{13}C$ values gradually decrease to +1‰ and subsequently show an increase with values reaching +1.5‰ in the Eifelian. The Eifelian–Givetian boundary is characterized by a distinct positive $\delta^{13}C$ excursion with an amplitude of +2‰.

4.1.2. Givetian

Carbon isotope data for the Givetian time interval derive from analysis of upper slope (Timau, Carnia and

Beringhausen, Rheinisches Schiefergebirge), lower slope and submarine rise (Pic de Bissous and Puech de la Suque, Montagne Noire; Blauer Bruch, Rheinisches Schiefergebirge; McWhae Ridge, Canning Basin) and basinal carbonate sections (Hengstebeck, Rheinisches Schiefergebirge; Hühnertal, Harz; Figs. 2 and 3). Base line $\delta^{13}C$ values are between +2‰ and +3‰ at Timau, around +2‰ at Beringhausen and Pic de Bissous, between +1‰ and +2‰ at Blauer Bruch and Puech de la Suque and below +1‰ at Hengstebeck and Hühnertal. In general, a trend to lighter values in the order of 2‰ is observed from upper slope to basinal settings.

A positive excursion is evident at the Eifelian–Givetian boundary in the Pic de Bissou section (Fig. 2), in which lower Givetian carbonates of the *hemiansatus* and Lower *varcus* Zones are about 0.5‰ heavier than those of the Middle *varcus* to Upper *hermanni-cristatus* Zones. Further, positive $\delta^{13}C$ excursions are observed at the transition of the Lower to Middle *varcus* Zones, and in the upper part of the Middle *varcus* Zone. The amplitude of the excursions is about +2‰. Whereas the excursion at the transition Lower to Middle *varcus* Zone is not documented in all studied localities, the excursion in the upper part of the Middle *varcus* Zone was recognized in all investigated sections.

4.1.3. Frasnian

A prominent positive excursion in $\delta^{13}C$ with values increasing by +1.5‰ to +3.0‰ is observed in the lowermost Frasnian *falsiovalis* Zone. Peak values reach +4.4‰ in the Beringhausen section (Fig. 3). Minimum $\delta^{13}C$ values are found in carbonates of the *jamieae* and Lower *rhenana* Zone. The prominent excursions in the Upper *rhenana* and *linguiformis* Zones (Fig. 4) correspond to the Lower and Upper Kellwasser horizons (Joachimski and Buggisch 1993; Joachimski et al. 2002).

4.1.4. Famennian

The carbon isotope excursion that starts with the onset of the Upper Kellwasser horizon lasts into the Middle *triangularis* Zone. Lower Famennian $\delta^{13}C$ values starting from the Upper *triangularis* Zone are relatively uniform ranging from +1‰ to +2‰ and increase by about +1‰ in the *marginifera* zone. Prominent excursions are not observed within the Famennian except in the *praesulcata* Zone. Several sections were examined spanning the D–C boundary interval. A decrease in $\delta^{13}C$ by 0.5‰ to 1.0‰ was observed in the Drever quarry and Milles section (Fig. 4). A positive excursion within the Upper *praesulcata* Zone is indicated by some data points in the Belgium sections Anseremme and Geron-Celles (Fig. 5). $\delta^{13}C$ values measured at the D–C boundary in the La Serre section show values up to +5‰ for brachiopods and up to +4‰ for ooids. $\delta^{13}C$ values of echinoderms, matrix samples and granular cements range generally from +1‰ to +2‰, but may be as low as −4‰.

5. Discussion

The carbon isotope composition of marine carbonate is generally interpreted to reflect $\delta^{13}C$ of oceanic dissolved inorganic carbon (DIC). However, the primary mineralogy (aragonite vs. low-magnesium calcite) may have major control on the carbon isotope composition since the thermodynamic carbon isotope fractionation between DIC and low-magnesium calcite is smaller than the fractionation between DIC and aragonite (Romanek et al. 1992). As a consequence, aragonite dominated carbonates will have a higher $\delta^{13}C$ value than calcite dominated carbonates.

The carbon isotope composition of DIC is dependent on the fluxes and the isotopic composition of carbon entering and leaving the oceanic reservoir. The input flux comprises mantel derived (volcanic) CO_2 and carbon derived from weathering of carbonate and organic carbon. The carbon isotope composition of the riverine carbon flux depends on the proportion of inorganic (carbonate) and organic carbon being weathered on the continents. The carbon isotope composition of the total output flux is a function of the burial ratio of organic vs. inorganic carbon as well as of the photosynthetic carbon isotope fractionation (Kump, 1991; Kump and Arthur, 1999).

5.1. Diagenetic evaluation of the carbon isotope data

In order to interpret the carbon isotope signals of whole rock samples with respect to changes in the carbon isotope composition of the oceanic reservoir, it has to be made sure that the measured $\delta^{13}C$ values mirror the primary isotope composition and were not reset during the diagenetic stabilisation of the carbonates. Whole rock carbonate samples have a high potential to preserve their initial carbon isotope ratio as long as the stabilization or recrystallisation proceeds in a diagenetically closed system. However, the primary carbon isotope composition may be altered in case that the stabilization occurs in system open for CO_2 derived from the remineralisation of organic carbon. This may either be the case in meteoric waters enriched in ^{13}C-depleted soil-derived CO_2 (Allen and Matthews, 1982;

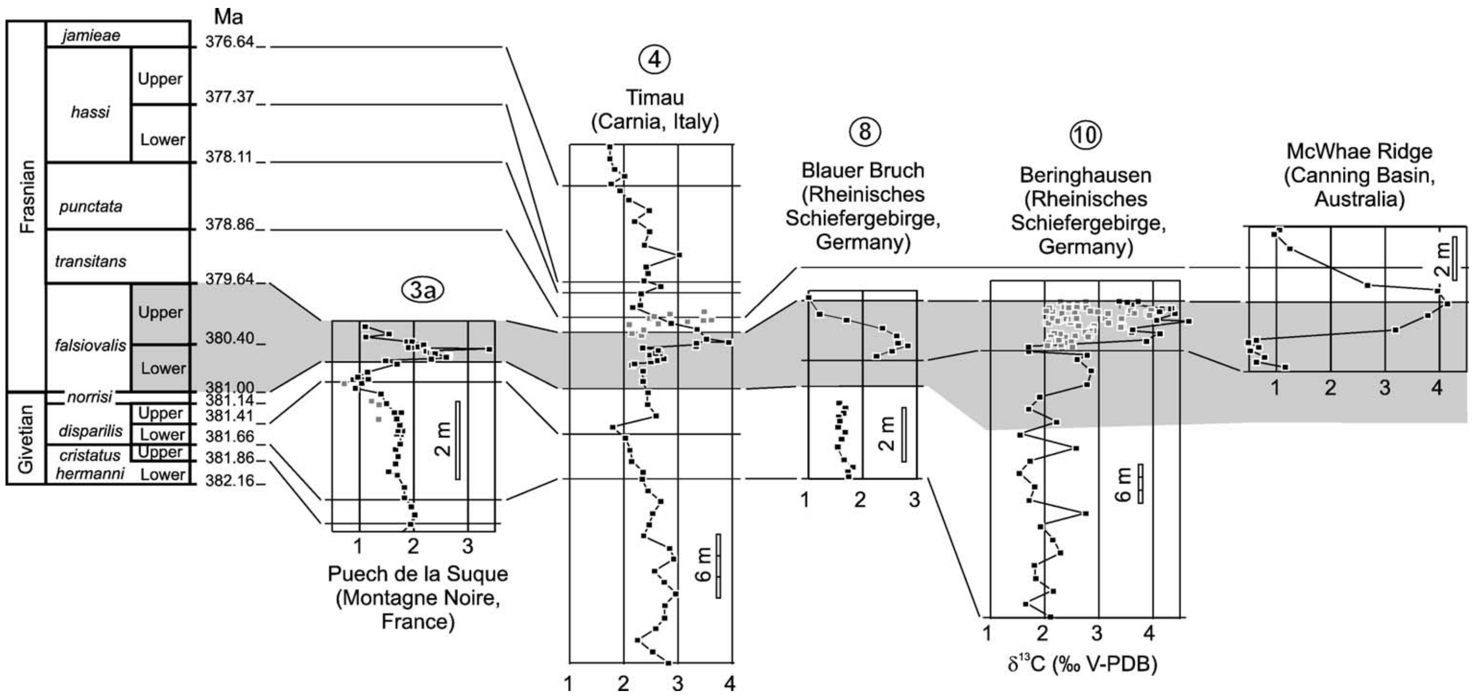

Fig. 3. δ^{13}C of upper Givetian to lower Frasnian carbonates. Grey squares represent diagenetically overprinted samples. Sections 4 and 10 were deposited in shallow water environments, Sections 3a and 8 represent deep water facies below wave base. Gray shaded bar indicates carbon isotope excursion in the *falsiovalis* Zone.

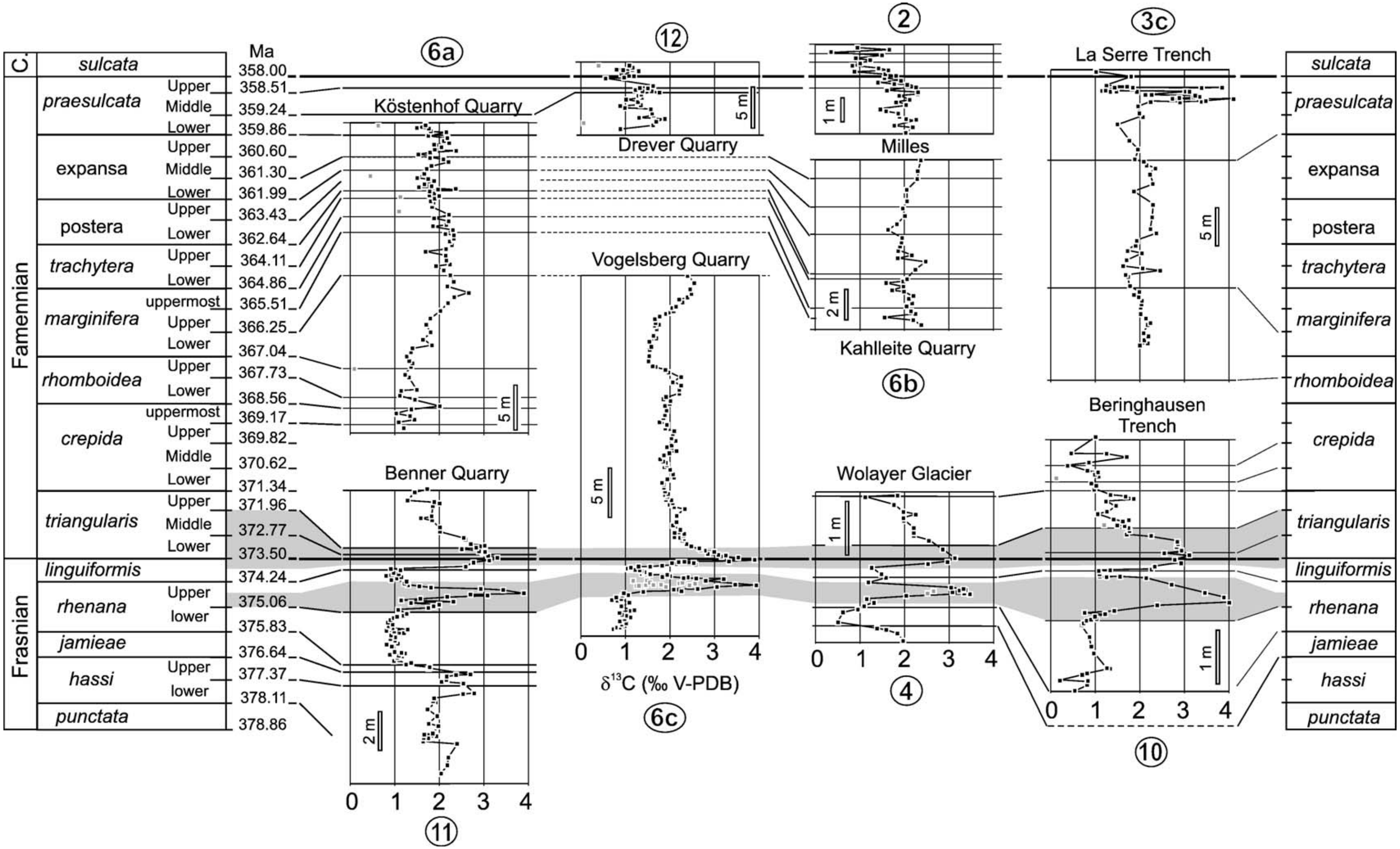

Fig. 4. δ^{13}C of Upper Frasnian and Famennian carbonates. Gray squares represent diagenetically overprinted samples.

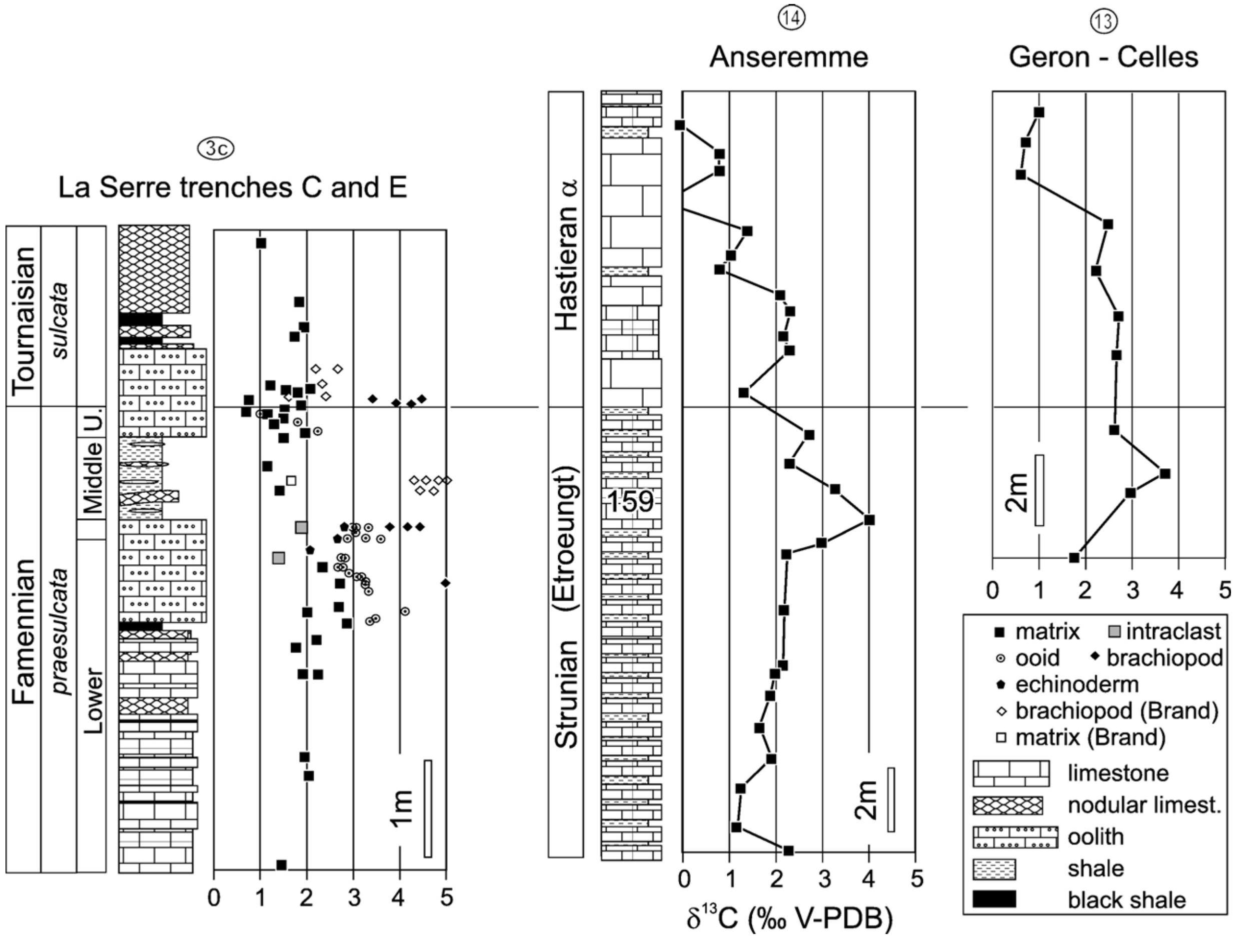

Fig. 5. $\delta^{13}C$ of carbonate rocks at the Devonian–Carboniferous transition (bed 159 is marked in the Anseremme section).

Lohmann, 1988; Joachimski, 1994) or in organic carbon rich sediments (e.g. black shales). In both cases, the contribution of ^{13}C-depleted CO_2 will shift the carbon isotope composition to lower $\delta^{13}C$ values. Hence, the carbon isotope values of carbonates with shaly and organic-carbon rich interbeds have to be interpreted with caution. In contrast, late diagenesis usually occurs in a system closed for carbon and even dolomitization may not alter the primary $\delta^{13}C$ values significantly (Holser, 1997; Buggisch et al., 2003; Brand, 2004).

A systematic difference in $\delta^{13}C$ is observed for time-equivalent samples from shallow-water, slope and basinal sections with deep water carbonates being depleted in ^{13}C relative to shallow water carbonates (Figs. 2 and 3). However, $\delta^{13}C$ excursions with comparable amplitudes are observed in all sections. This difference can be explained either by (1) a higher contribution of aragonite to shallow-water sediments, or, (2) carbonate precipitation/early cementation of deep-water carbonates in marine bottom waters depleted in 13C. Aragonite is enriched in ^{13}C relative to low-magnesium calcite (Romanek et al. 1992). Swart and Eberli (2005) showed that $\delta^{13}C$ of modern periplatform carbonates of the Great Bahama Platform is strongly correlated with the percentage of aragonite and significantly higher in comparison to deep water limestones dominated by low-magnesium calcite. Higher $\delta^{13}C$ values of shallow-water carbonates will be preserved after recrystallisation of metastable aragonite as long as the diagenetic stabilization proceeds in diagenetic system closed for carbon.

Most of the $\delta^{13}C$ values generated in this study derive from the analysis of deep water lime mudstones which to our understanding have a high potential to preserve the primary carbon isotope values. The observation that comparable isotope patterns were observed in sections with different facies and from different palaeogeographic settings is another argument in favour of a preservation of the primary oceanic signal.

Positive δ^{13}C excursions are often associated with the deposition of black shales. In the Devonian, this applies to the Klonk, *pumilio*, and Kellwasser events. The isotopic composition of carbonate samples from black shale horizons may have been lowered by the contribution of remineralized organic carbon during diagenesis recrystallisation (see Coniglio 1989 and Joachimski et al. 2002 for details). However, besides methanogenesis, no diagenetic process is known to result in an enrichment of ^{13}C during recrystallisation. Consequently, the positive δ^{13}C excursions are considered to reflect the primary isotopic signal, whereas lower δ^{13}C observed during the increase in δ^{13}C are interpreted as diagenetically altered.

Some of the Devonian carbon isotope events are recorded in sediments composed of grain- and rudstones with frequent intra- and extraclasts (e.g. *falsiovalis* and Hangenberg events). In case of a short-term positive carbon isotope excursion, carbonates which were deposited before the onset of the excursion may have been reworked. On the other hand, limestones formed during the excursion may have been incorporated into younger sediments. This uncertainty may be responsible for the poor stratigraphic definition of the *falsiovalis* event and the scatter in the data from the Timau and Beringhausen sections (Fig. 3).

5.2. Devonian carbon isotope record

All measured δ^{13}C values including published data from Brand and Legrand-Blain (1993) and Brand et al. (2004) and δ^{13}C values of pristine brachiopod shells (van Geldern et al., 2006-this volume) are plotted in Fig. 6. The locfit curves shown in Fig. 6 were calculated based on all whole rock δ^{13}C data including (grey line) and excluding the brachiopod shell δ^{13}C values (white line) of van Geldern et al. (2006-this volume). Carbon isotope values classified as diagenetically altered or measured on reworked clasts are given as well (Fig. 6). Fig. 7 shows running mean and locfit curves based on δ^{13}C values of all diagenetically unaltered and non-redeposited samples. The calculation of the locfit or running mean curves becomes difficult in case that data from basinal sections (generally lower δ^{13}C values) are combined with data from contemporaneous shallow-water sections (higher δ^{13}C values) since the quantity of data deriving from basinal, slope or shallow water successions will influence the calculated average of the locfit and running mean trend lines. However, the locfit and running mean curves exhibit the same pattern in Fig. 6 (incorporating all data) and Fig. 7 (using only selected data) in which the δ^{13}C excursions are more pronounced. In the following, we will discuss the most significant carbon isotope excursions in relation to the co-occurrence of black shales, sea-level changes and bio-events (House, 2002).

5.2.1. Klonk Event (Pridoli–Lochkovian)

The Pridoli–Lochkovian boundary is characterized by a significant faunal change (Chlupáč and Hladil, 2000). Close to the boundary two blooming events of floating *Scyphocrinites* occurred that resulted in the widespread deposition of coarse-grained echinoderm limestones (Scyphocrinus–Limestone of Bohemia and Carnic Alps). The biotic event can be correlated with a major positive δ^{13}C excursion that has been named the Klonk isotope event. The carbon isotope excursion was previously reported from Europe (Schönlaub et al., 1994; Hladikova et al., 1997; Buggisch, 2001; Buggisch and Mann 2004), Australia (Andrew et al., 1994), and Laurentia (Saltzman, 2002). A sea-level rise was assumed to have occurred in conjunction with the contemporaneous deposition of organic carbon-rich sediments in the Prague Syncline and Carnic Alps (Hladiková et al., 1997). In contrast, most Silurian sea-level curves of Laurentia and Baltica indicate a regression and sea-level lowstand for the latest Silurian (Ross and Ross 1996, Witzke and Bunker 1996). This sea-level fall can be interpreted as the consequence of the final Caledonian collision which led to the erosion of large Silurian carbonate platforms and initiated the deposition of the wide-spread predominantly continental "Old Red" sandstones. The increased erosion of continental crust is also documented in the increase in the ^{87}Sr/^{86}Sr ratio during the late Silurian and Early Devonian (Veizer et al. 1999). In North America, the Silurian–Devonian transition is marked as well by a sea-level fall (Saltzman, 2002) indicated by the widespread sedimentation of peritidal to supratidal carbonates in the Appalachian Basin, the formation of discontinuities in the Oklahoma Basin and the progradation of shallow-water limestones in central Nevada. Saltzman (2002) argued that lagoonal carbonates at the Silurian–Devonian boundary in Laurentian sections indicate a global eustatic sea level drop.

5.2.2. Lochkov–Prag Event

The Lochkov–Prag isotope event is characterized by a rapid increase in δ^{13}C starting in the late Lochkovian and high values oberserved in the Lower Pragian (*E. sulcatus* to early *P. kindlei* Zone transition; Fig. 6).The coeval bio-event that was defined by Walliser (1996) is associated with a facies change in the Prague syncline, where dark Lochkovian shales and limestones are

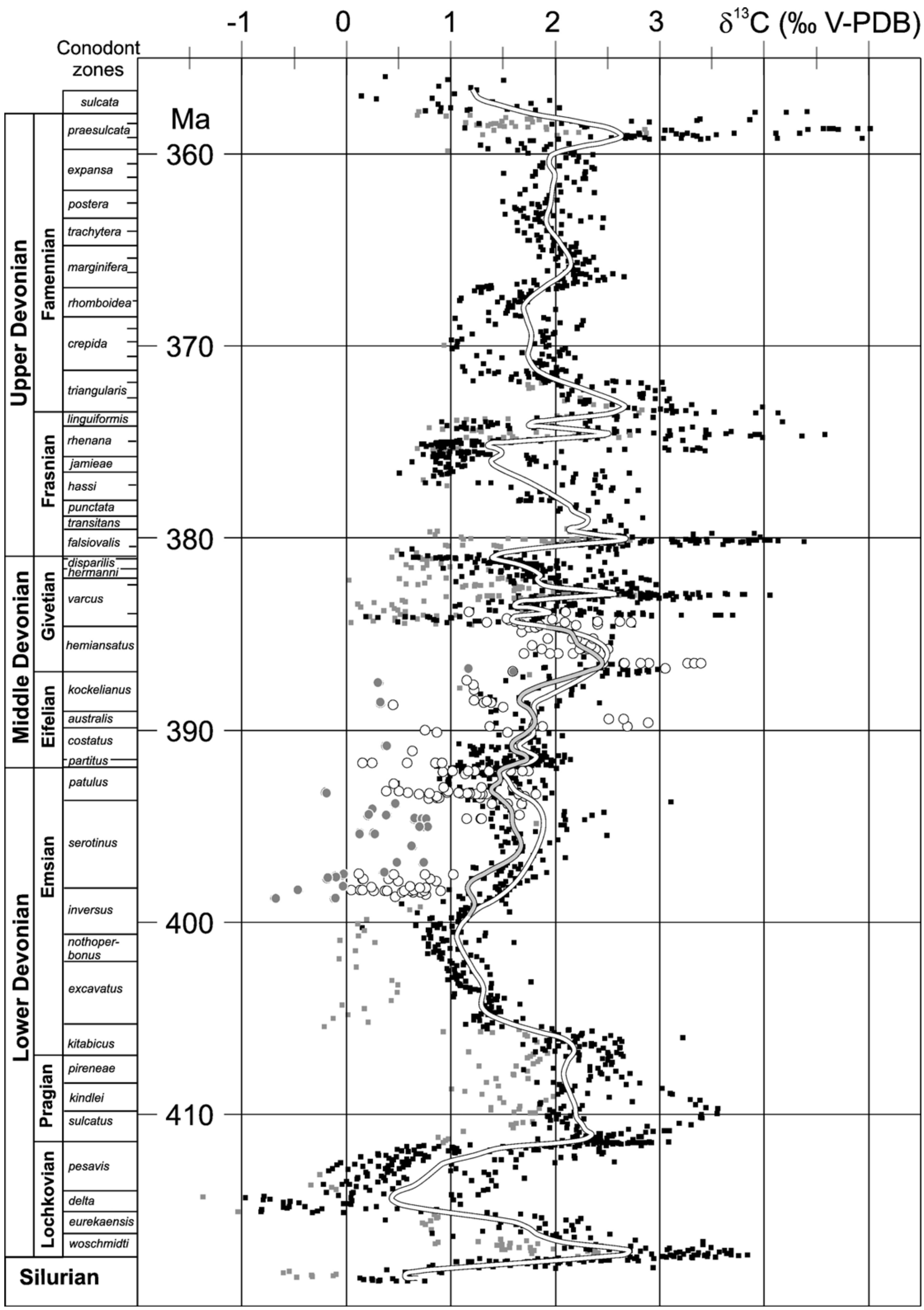

Fig. 6. Compilation of Devonian $\delta^{13}C$ values. Black squares—whole rock carbonate samples; gray squares—diagenetically overprinted and reworked samples; circles: European and North African brachiopod shell data from van Geldern et al. (2006-this volume). Locfit curves were calculated using all data with (white curve) and without (grey curve) the brachiopod shell $\delta^{13}C$ values of van Geldern et al. (2006-this volume). Data of black squares and circles were used to calculate locfit and running mean curves in Fig. 7.

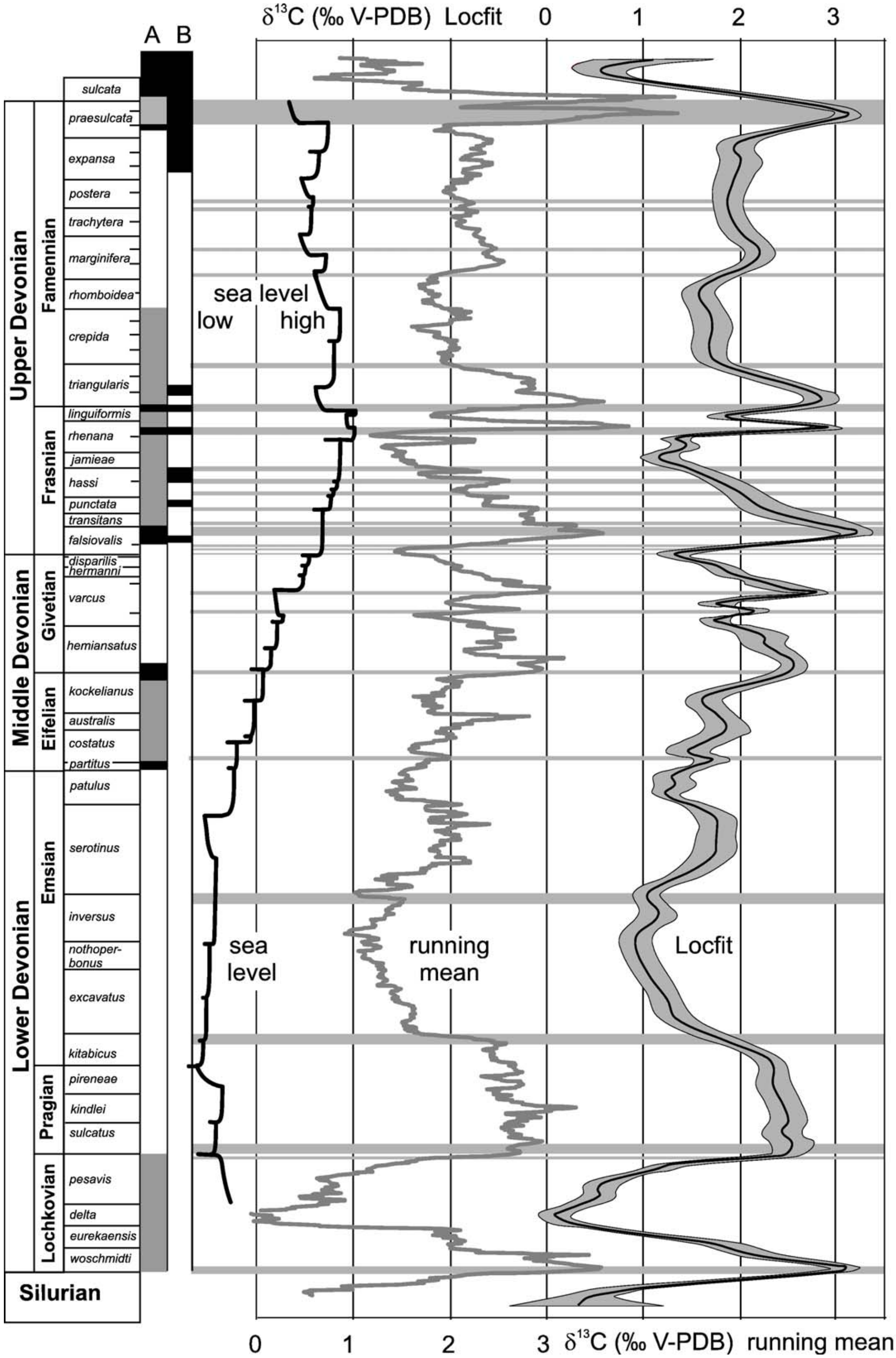

Fig. 7. Comparison of running mean (time window of 0.3 Ma), locfit curve (with 90% confidence interval), sea-level changes (Johnson et al., 1985, 1996) and occurrence of black shale deposits (black shales in black, dark grey shales in grey) in Europe/North Africa (A) and Laurentia (B). Events according to House (2002).

overlain by light-coloured Pragian nodular lime mudstones at the Lochkovian–Pragian GSSP. In other sections of the Prague syncline, reef and reef detritus limestones of Pragian age are found on top of Lochkovian sediments. This facies change was interpreted to have been caused by “a fairly rapid but not very large lowering of sea level” (Chlupáè and Kukal, 1988), but not as a deepening, as stated by House (2002). In contrast to the sea-level interpretation derived from the Bohemian sections, the sea-level curve of Johnson et al. (1985) records a transgression (T–R cycle Ia) at this stratigraphic level.

5.2.3. Kačák Event (Eifelian–Givetian)

Black shales are common in most European Eifelian–Givetian boundary sections spanning the upper *kockelianus* to lower *P. hemiansatus* Zones. The Kačák Event (Budil, 1995; House, 2002) marks one of the sharpest stratigraphical boundaries in the Prague Syncline (Chlupáč and Kukal, 1988) with black siliceous shales overlying the Choteč limestone. The Jirásek section represents the only section in the Prague syncline from which carbonates of this age are reported. The exposed limestones of the “dark interval” can be correlated with the black shales of the Kačák Member (Budil, 1995; Hladíková et al., 1997). The limestones are about 1‰ higher in δ^{13}C than the underlying Choteč limestone (Hladíková et al., 1997; Buggisch and Mann, 2004). In the Pic de Bissous section (Montagne Noire, Fig. 2), δ^{13}C values increase by about 2‰ at the Eifelian–Givetian boundary and reach maximum values of around +3‰. The Kačák Event is a typical black shale event that was interpreted to coincide with a eustatic rise of sea-level (base of T–R cycle Ie of Johnson et al. 1985).

5.2.4. Lower and Upper pumilio Events (Givetian)

The positive carbon isotope excursions observed in the *varcus* Zone coinicide with the *pumilio* Events that have been named after two dark gray limestone beds characterized by the mass occurrence of the brachiopod *T. pumilio* and have been traced from Germany to Northern Africa (Lottmann, 1990). No faunal extinction is associated with these events (Walliser, 1996). The matrix consists of dark to black micritic carbonate or shale and *T. pumilio* is abundant in distinct layers. Besides complete shells, disarticulated and broken valves are common. The *pumilio* beds are often graded and the matrix is sometimes partly winnowed which indicates short-lived current activities. The brachiopod lumachelles have been interpreted as tsunami deposits by Lottmann (1990). However, this interpretation is not consistent with occurrence of two positive carbon isotope excursions which probably lasted several 100,000 a. House (2002) stated that the nature of the deposits suggests a transgressive pulse, but no sedimentological feature is indicative for a deepening. Alternatively, we propose that the mass accumulation of brachiopod shells represents distal tempestites that were deposited below storm-wave base. With this interpretation, the *pumilio* beds were deposited during a lower sea-level.

5.2.5. Falsiovalis Event (early Frasnian)

The carbon isotope excursion observed in the early Frasnian shows maximum values around +4‰ and represents one of the most prominent δ^{13}C excursions during the Devonian. The excursion is observed in upper slope deposits (Timau, Beringhausen, Fig. 3), and deep-water limestones (Blauer Bruch, Puech de la Suque, Fig. 3) in Europe, but was also measured in deep water limestones deposited on a reef slope in Australia (Canning Basin, McWhae Ridge, Fig. 3). The stratigraphic position of the excursion is not very well constrained. It correlates most probably with the Upper *falsiovalis* Zone, but an onset in the Lower *falsiovalis* Zone and a continuation into the lower part of the *transitans* Zone cannot be excluded. The positive excursion in δ^{13}C coincides with the deposition of black shales in NE America (House, 2002), Morocco and Algeria. In the Antiatlas of Morocco, a prolonged episode with dysoxic conditions started in the *falsiovalis* zone (Belka and Wendt, 1992). Widespread deposition of black shales during the *falsiovalis* to lower *transitans* zone was reported from the Algerian Ahnet Basin (Lüning et al., 2004). Local occurrences of “Kellwasser-like” black limestones of the same age were described by Buggisch (1972) from the Northern Rheinische Schiefergebirge.

The interpretation with respect to coincident sea-level changes is ambiguous. The drowning of carbonate platforms precedes the δ^{13}C excursion in the Canning Basin but postdates it in the Timau and Beringhausen sections, where the excursion is documented in breccias and rudstones. Racki et al. (2004) described a positive δ^{13}C excursion from the uppermost Lower Frasnian and lowermost Middle Frasnian of Poland (*transitans* to *punctata* Zones). The δ^{13}C excursion with maximum values of +5‰ was further reported from the Ardennes (Yans et al. in Racki et al., 2004, Fig. 12). This excursion, which is not documented in our data set, is distinctly younger than the above described *falsiovalis* Event. Interestingly, the excursion coincides with intercalations of grainstones and flat-pebble conglomerates in deep-water carbonates in Poland, which may point to shallowing of the depositional environment and to a eustatic sea-level fall.

5.2.6. Kellwasser Events (late Frasnian—early Famennian)

The Kellwasser horizons comprise two black shale and limestone horizons that are dated into into the Late *rhenana* and *linguiformis* Zones. The Upper Kellwasser horizon marks the F–F boundary. The Kellwasser horizons were described from Central Europe and Morocco (Buggisch, 1972; Schindler, 1990; Belka and Wendt, 1992). The carbon isotope geochemistry of the F–F transition has been studied intensively during the last decade (e.g. Joachimski and Buggisch, 1993; Joachimski et al., 2001, 2002; Murphy et al., 2000; Stephens and Sumner, 2003, Chen et al. 2005). Two positive excursions in $\delta^{13}C$ with maximum amplitudes of +3‰ were reported from sections from various palaeocontinents. The first excursion coincides with Lower Kellwasser horizon. The second excursion starts in the *linguiformis* Zone simultaneously with the deposition of the Upper Kellwasser horizon. $\delta^{13}C$ values stay high during the Lower *triangularis* Zone and decrease to values around +1.5‰ in the Middle to Upper *triangularis* Zone.

The onset of the late Frasnian faunal crisis ("Kellwasser Crisis" of Schindler, 1990) correlates with the Lower Kellwasser Event. According to Johnson et al. (1985, 1996) the black shales and limestones of the Lower Kellwasser horizon were deposited during a sea-level highstand.

The F–F boundary is marked by a mass extinction event (Schindler, 1990; Buggisch, 1991; Walliser, 1996; Racki, 1999; House et al., 2000; Bond et al., 2004; and others) that is interpreted to represent a stepwise extinction of tropical shallow-water organisms. Impact(s), sea-level and climatic changes were claimed to be responsible for the faunal decline. The F–F boundary is marked by an unconformity in the Oscar Range (Low Stand System Tract) and by the occurrence of large allochthonous reef blocks at Dingo Gap and Windjana Gorge the Canning Basin, Australia (Stephens and Sumner, 2003). Stephens and Sumner interpreted this drop in sea level as a short-termed event superimposed on a long-term transgression. According to Johnson et al. (1985), the deposition of the Upper Kellwasser horizon started during the sea-level highstand of T–R cycle IId, but most of the positive carbon isotope excursion correlates with the regressive upper part of cycle IId. ε_{Nd} values exhibit a positive excursion below the Kellwasser horizons whereas values of the Kellwasser horizons are low (Dopieralska et al., 2006-this volume). The positive ε_{Nd} excursion is interpreted by Dopieralska et al. (2006-this volume) as indicative of a major transgression (*semichatovae* transgression), which is dated into the *jamiae* to lowermost *rhenana* Zones. However, ε_{Nd} values give no evidence for a transgression during the deposition of the Upper Kellwasser horizon. The oxygen isotope record across the F–F boundary documents a significant cooling (Joachimski and Buggisch, 2002). Although glaciogenic sediments of this age have not yet been described, several authors speculated about an early Famennian glaciation (Buggisch, 1991; Isaacson et al., 1999; Sandberg et al. 2002; Averbuch et al., 2005), which would have lowered sea level and may have culminated in the observed cooling.

5.2.7. Hangenberg Event and D–C boundary

The Hangenberg Event is marked by the deposition of gray or black shales in many areas of Europe, China and North America (Walliser, 1996). The onset of shale sedimentation varies. In the D–C GSSP at La Serre, dark shales have been dated at the transition Lower to Middle *praesulcata* Zone (Feist, 1985, 2002; Flajs and Feist, 1988; Feist et al., 2000). The overlying oolithic grain- to rudstones with intercalated sandy marls are of Middle *praesulcata* to *sulcata* Zone age. In the Rheinische Schiefergebirge, the Hangenberg shale starts in the Upper *praesulcata* zone (Oberrödinghausen section: Walliser, 1996; Drever section: Clausen et al., 1989b). Sandstones (Hangenberg Sandstone) are developed in several sections in the upper part of the Upper *praesulcata* Zone.

Conodont assemblages from sections in the northern Rheinisches Schiefergebirge suggest lowering of sea-level in the Middle and Upper *praesulcata* Zones with two successive regressive pulses occurring in at least one section (Rüthen-Nuttlar: Clausen et al., 1989). A change in conodont biofacies was observed as well by Girard (1994) in the Puech de la Suque section (Montagne Noire) and interpreted as being caused by a sea-level fall. Non-deposition observed in several sections from Belgium (Anseremme, Geron-Celles) gives further evidence for a lowering of sea-level during this time interval. Glacio-marine sediments in the Upper Curiri Formation of the Amazon Basin (Brasil) were dated by miospores into the Lower to Upper *praesulcata* Zones (Streel et al., 2000) suggesting that the glaciation in South America (Caputo, 1985) caused the sea-level fall. However, the bathymetric conditions during the deposition of the black Hangenberg shales are a matter of debate. Bless et al. (1993) assumed a short-lived sea-level rise at the base of the Hangenberg Event, whereas

Walliser (1996) considered that the black shales were deposited during the glacio-eustatic sea-level fall. A sharp regression at the base of the Middle *praesulcata* Zone is also evident in the sea-level curve of Johnson et al. (1985).

Several D–C boundary sections were analyzed during this study, but a positive $\delta^{13}C$ excursion was only observed in the La Serre (Montagne Noire), Anseremme and Gendron-Celles (Belgium) sections (Fig. 5). An increase in $\delta^{13}C$ at the D–C boundary was as well reported by Brand and Legrand-Blain (1993) and Brand et al. (2004) by analyzing brachiopod shells from the La Serre trench E. In this section, intraclasts, ooids and brachiopods are concentrated in 2-m-thick grain- to rudstone layers that are separated by about 1 m of silty shales and marls. $\delta^{13}C$ values of brachiopod shells studied in this study are around +5‰. Ooids have $\delta^{13}C$ values up to +4‰, whereas $\delta^{13}C$ of the matrix can be as low as −4‰. Assuming that brachiopod shells preserved the primary carbon isotope signal, the lower $\delta^{13}C$ values of the matrix are interpreted to have been reset by diagenesis.

In the Belgium sections, the positive $\delta^{13}C$ excursion is documented only by a few data points. This may be explained by the circumstance that sediments of the Lower and Middle *praesulcata* Zone as well as of the *sulcata* Zone are not preserved in the studied Belgium sections and that limestones of Upper *praesulcata* Zone age are restricted to one bed. The lack of the positive $\delta^{13}C$ excursion in the Milles and Drever sections is interpreted by a stratigraphic gap (Milles section) or by the circumstance that no carbonates were deposited during the respective time-interval (Drever section). A positive ε_{Nd} excursion is observed in the Lower *praesulcata* Zone of Poland (Dopieralska et al., 2006-this volume) that indicates a transgression which is followed by a regression spanning the upper part of the Lower to the Upper *praesulcata* Zone.

6. Conclusions

The major positive carbon isotope excursions of the Devonian coincide with sea-level changes, the deposition of black shales and in part with bio-events. The Kačák Event at the Eifelian–Givetian boundary is the only event that is clearly related to a rise in sea-level. According to the sea-level curve of Johnson et al. (1985, 1996) the Lower Kellwasser Event coincides with an eustatic highstand (Fig. 7). All other carbon isotope excursions seem to coincide with a sea-level fall, even if not all regressions are evident from the Johnson et al. curve. Most important, all Devonian carbon isotope excursions are correlated with the occurrence of organic carbon-rich sediments. This is in contrast to carbon isotope excursion observed in the early Palaeozoic. For example, $\delta^{13}C$ excursion in the late Cambrian (SPICE Event; Saltzman, 2000), Hirnantian (Marshall et al. 1997; Finney et al. 1999; Kump et al. 1999) and Lutfordian (Samtleben et al. 1996, 2000; Wenzel and Joachimski 1996) coincide as well with a major sea-level fall, but are not associated with the deposition of black shales. Instead, the positive $\delta^{13}C$ shifts coincide with a change from black shale sedimentation to the deposition of well-aerated sediments. The coincidence of positive carbon isotope excursions and better ventilated conditions on epicontinental shelves was interpreted by Bickert et al. (1997) and Munecke et al. (2003) to document a shift from an estuarine to an anti-estuarine oceanic circulation. Water column stratification and euxinic conditions in the deeper ocean during times with an anti-estuarine circulation (arid period) were thought to enrich surface waters in ^{13}C and to result in a positive carbon isotope shift. Instead, upwelling of deeper waters rich in ^{12}C during humid climatic periods was interpreted to induce an estuarine circulation with lower $\delta^{13}C$ of epicontinental waters.

The correlation of the Devonian positive $\delta^{13}C$ excursions with the deposition of black shales does not support such a scenario but suggests that burial of isotopically depleted organic carbon is the most important mechanism that shifted $\delta^{13}C$ of the oceanic reservoir to higher values. Two models are generally put forward as explanation for an enhanced burial of organic carbon (Desmaison and Moore 1980; Pederson and Calvert, 1990). The preservation model postulates better preservation of organic matter in stagnant oceans. The productivity model favours enhanced primary productivity to result in an elevated flux of organic carbon into the sediment. A higher productivity requires an additional nutrient flux either through enhanced upwelling or intensified continental weathering. A eustatic sea-level fall–as inferred for some of the Devonian carbon isotope excursions–will result in a lower base level and enhanced physical weathering that may have resulted in an enhanced continental nutrient flux. Numerical modelling suggested that significantly enhanced continental nutrient delivery may have been the major driving mechanism of the two +3‰ excursions observed in the late Frasnian (Goddéris and Joachimski, 2004). Consequently, we propose that some of the Devonian positive $\delta^{13}C$ excursions were initiated by eustatic sea-level falls, which led to enhanced weathering, higher nutrient supply to the oceans, elevated primary productivity which finally may have resulted in oxygen-deficient conditions and the deposition of organic carbon-rich black shales.

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