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ORIGINAL PAPER

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Carbon isotope stratigraphy of Lochkovian to Eifelian limestones from the Devonian of central and southern Europe

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Abstract Lower to Middle Devonian carbonates of the Prague Syncline, the Carnic Alps, the Montagne Noire, and the Cantabrian Mountains were investigated for $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$. These values were measured on bulk rocks, selected components and cements. Many carbonates exhibit primary marine values, but some are altered by diagenesis. A $\delta^{13}C$ curve can be presented for the latest Pridolian to Emsian time interval. Several sharp or broad positive excursions are obvious in the *woschmidti-postwoschmidti, sulcatus, kitabicus,* Late *serotinus*, and *kockelianus* conodont zones. The excursion at the Silurian–Devonian boundary is known worldwide and therefore considered global in nature. 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 in other regions. Most excursions relate to and/or started during major regressions whereas sea-level highstands correspond to minimal $\delta^{13}C$ values. Similar relationships between sea-level changes and $\delta^{13}C$ have been observed from other early Palaeozoic intervals. The transgressive Choteč (?) and Kačák events are marked by positive isotope excursions, this type of combination is usually observed in late Palaeozoic to Cenozoic black shale events.

Keywords Carbon isotopes · Devonian · Event stratigraphy · Sea level · Prague Syncline · Carnic Alps · Montagne Noire · Cantabrian Mountains

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Introduction

Reliable $\delta^{13}C$ curves are usually based on analyses of brachiopod shells, which consist of low magnesium calcite and are therefore relative resistant against diagenetic alteration. But brachiopods are strongly dependent on environmental conditions and therefore their occurrence is restricted. In order to get a higher temporal resolution, whole-rock samples of carbonates were investigated for this paper, their availability is almost unlimited. Published data of carbon isotopes from whole-rock samples are concentrated at series and stage boundaries and certain "events" (e.g., Silurian Devonian boundary: Saltzmann 2002; Lower Devonian of the Prague Syncline: Hladíková et al. 1997). The aim of this paper is to present a complete high-resolution carbon isotope curve for Early to early Middle Devonian carbonate rocks from central and southern Europe.

Regional setting

At the end of the Silurian, the globe was divided into supercontinents and a superocean: most of the continental crust was assembled in Laurussia and Gondwana, the Panthalassa Ocean covered the other part of the globe (Fig. 1). Laurentia and Gondwana were separated by the Rheic and Proto-Tethys Oceans. Small Variscan terranes traveled northward from Northern Gondwana and collided with Laurussia during the Devonian and Carboniferous (Fig. 1B). The drift of the terranes was combined with the closure of oceanic basins like the Saxo-Thuringian Basin north of the Moldanubian Block or the Rheic Ocean north of the Cantabrian and Intra-Alpine Terranes (Ziegler 1988). All investigated carbonates were deposited on these isolated terranes (e.g. Cantabrian, Moldanubian and Intra-Alpine), which were situated between 10° and 35°S during the Early Devonian (Ziegler 1988; Scotese 2001). The following considerations apply to this restricted part of the tropical Devonian oceans.

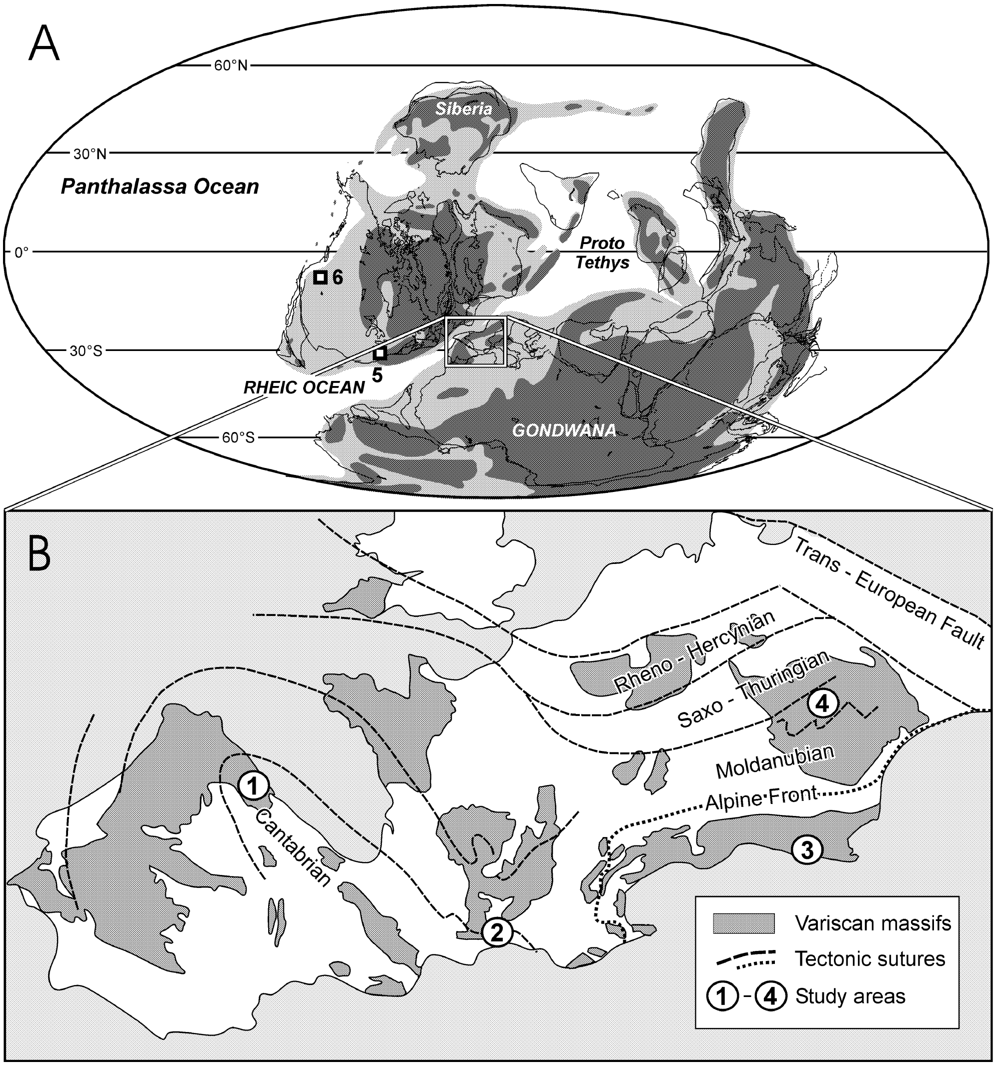


Fig. 1 A Paleogeographic reconstruction for the Early Devonian (Scotese 2001) and locations of selected sections of Saltzmann (2002) [*5*Virginia; *6* Nevada] **B** European Variscan terranes in a reconstruction of Franke (2002) with sample localities of this study: *1* Cantabrian Mountains; *2* Montagne Noire; *3* Carnic Alps; *4* Prague Syncline. Samples derived from a latitudinal band of 0° to 35°S

Rocks were collected for carbon isotope analyses from several sections in the Prague Syncline (Barrandian), the Carnic Alps, the Montagne Noire, and the Cantabrian Mountains (Table 1).

Prague Syncline

Palaeozoic rocks of the Barrandian occur in a large syncline in the vicinity of Prague. Above a marked Cadomian angular unconformity, the Palaeozoic sequence consists of weakly deformed, unmetamorphosed to very low grade metamorphic Cambrian to Devonian sediments (Chlupáč 1993, 1998b). The Silurian is characterized by Landoverian to Ludlovian black and grey graptolitic shales and volcanic rocks, which are composed of submarine basaltic lava flows and pyroclastic material. Bioclastic to micritic limestones and platy limestones with calcareous shale interbeds were deposited during the Pridolian. Sedimentation continued from Silurian into Devonian; the transition beds are exposed in several sections with rich faunas, which allow an exact biostratigraphic definition of the boundary. Therefore, the international stratotype for this boundary was chosen in the Prague Syncline (GSSP Klonk near Suchomasty; Chlupáč and Hladil 2000).

Early and lower Middle Devonian sediments can be divided into two different facies associations (Table 1):

Discontinuous shallow water deposits with bioclastic grainstones, rudstones and boundstones in the southwest.

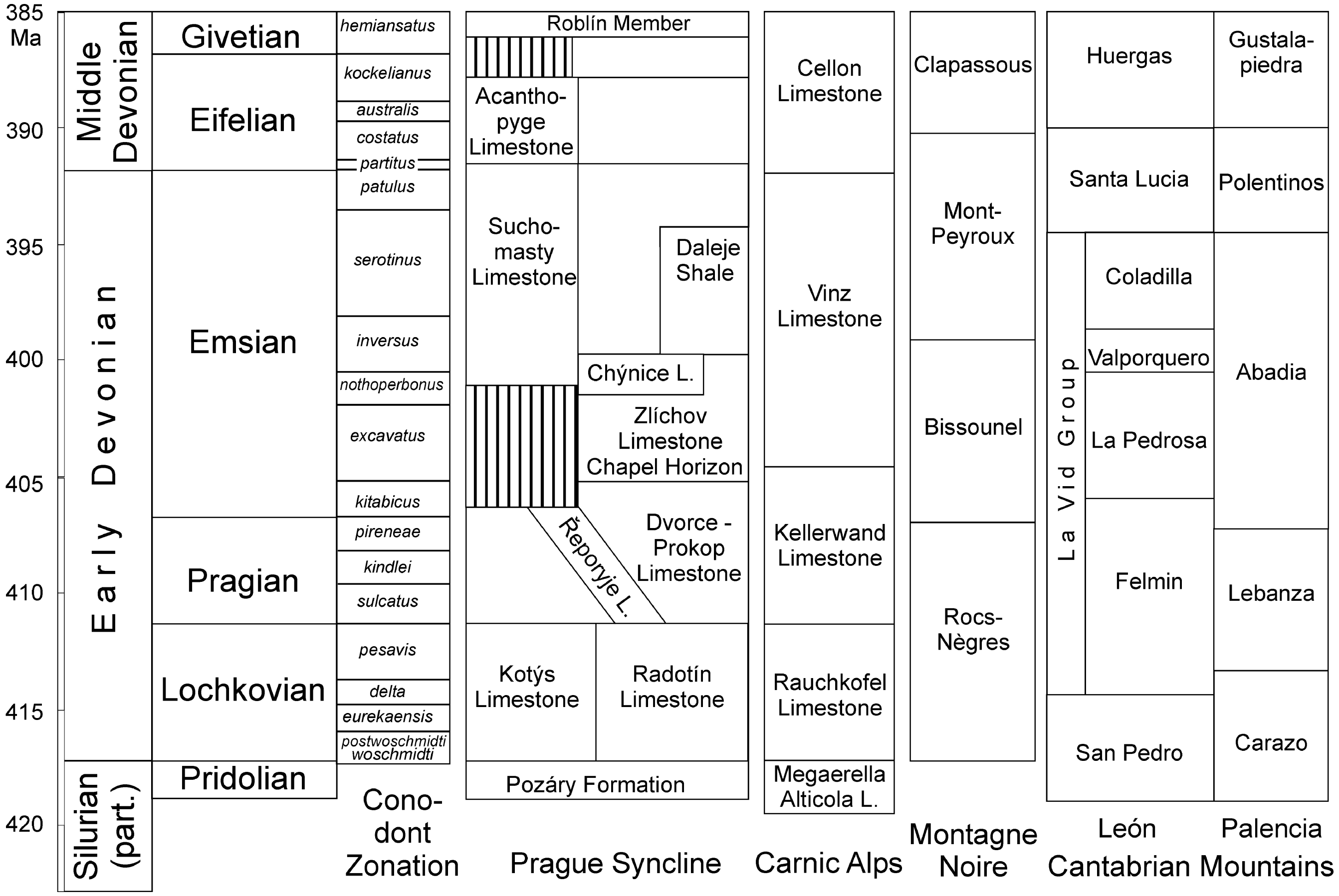
Continuous deeper water deposits with alternating wackestones and shales in the northeast.

Both facies realms interfinger and deeper water sediments lap on shallow water deposits. At the Eifelian–Givetian boundary, carbonates were abruptly replaced by black shales (Kačák event), which are overlain by flyschoid siliciclastic sediments (Roblín Member, see Table 1).

Carnic Alps

The Carnic Alps are situated south of the Periadriatic Lineament—an alpine plate boundary, which separates the allochthonous nappes of the eastern Alps in the north

Table 1 Stratigraphic correlation chart of the investigated sections (for references, see text)



from the autochtonous Southern Alps. In the Carnic Alps an almost continuous fossiliferous sedimentary sequence is exposed ranging from the Caradocian to the Late Carboniferous (Schönlaub 1980, 1998; Schönlaub et al. 1994). The Palaeozoic sediments are sliced and piled up into south dipping imbricates. The pre-Late Carboniferous rocks were affected by the Variscan deformation and very low grade to low-grade metamorphism.

The sediment successions are characterized by different facies realms grading from shallow water to deep basin environments at least since the Silurian. According to Kreutzer (1992) and Kreutzer et al. (2000), the Lower Devonian to Frasnian sediments were deposited in four depositional environments: shallow water facies (Kellerwand nappe), transitional facies (Cellon nappe), pelagic carbonate facies (Rauchkofel nappe), and basinal facies (Bischofalm nappe). Sections from slope to basin environments (Cellon, Rauchkofelboden, Oberbuchach II) are suitable for carbon isotope investigations (see Table 1).

Montagne Noire

Cambrian through Early Carboniferous marine deposits outcrop in the Montagne Noire at the southern margin of the French Massif Central (Feist 1985, 2002). A nearly continuous carbonate succession started with the Lochkovian transgression and ended with the late Early Carboniferous flysch deposits. The late Visean to early Namurian Variscan tectogenesis resulted in the emplacement of olistostromes (Cabrière Klippen) and recumbent fold nappes.

Olistoliths of the Cabrière Klippen exhibit late Early to Middle Devonian neritic carbonates. In contrast, several sedimentary environments can be recognized in the nappe sequences: After the Lochkovian transgression, supra- to intertidal dolomites, followed by neritic limestones, pelagic carbonates with mud mounds, and stylionid- and cephalopod-bearing wackestones were deposited during Early to Middle Devonian times. Carbonates from sections of the nappe units were sampled for carbon isotope analyses (see Table 1).

Cantabrian Mountains

The Cantabrian Zone is the external zone of the Iberian Variscan belt in the northwestern Iberian Peninsula (Aller et al. 2002). Almost complete Palaeozoic successions of sediments are exposed in the Cantabrian Mountains. Siliciclastic sediments dominated in Early Palaeozoic times up to the Silurian. The siliciclastics were replaced by carbonates during the Lochkovian. Uplift in the NE (the later Central Coal Basin) led to widespread erosion and return to siliciclastic sedimentation during the Devonian. The Variscan Orogeny resulted in thin skinned tectonics and imbricates of Palaeozoic sediments, whereas metamorphism was usually restricted to very low grade conditions in the Cantabrian Zone.

The Lochkovian transgression led to the deposition of lagoonal dolomites, followed by Pragian to Emsian shallow water carbonates, shales and reefal limestones, Eifelian shales, and Givetian to early Frasnian reefs in most of the thrust sheets of the Cantabrian Zone. Sediments of the Palentine Nappe of the Cantabrian Zone exhibit deposits of a relatively deep but still neritic environment. Samples for carbon isotope analyses were collected from several sections of the Cantabrian Zone (see Table 1).

Sampling and laboratory procedures

A total of more than 1,500 samples were collected for carbon and oxygen isotope analyses from carbonate successions. Most sampled sections have been described in the literature on which the lithologic descriptions of the present study are based. Hand specimens were cut and polished to control lithology and facies of the sampled rocks. A few milligrams of rock powder were taken from the polished slabs with a dental drill. Mudstones and wackestones were preferentially sampled, but analyses were also performed on grainstones, individual carbonate components and cements.

Carbonate powders were reacted with phosphoric acid in an on-line carbonate preparation system (Carbo-Kiel) connected to a ThermoFinnigan 252 mass spectrometer. All values are reported in ‰ relative to V-PDB by assigning a δ^{13}C value of +1.95‰ and a δ^{18}O value of −2.20‰ to NSB 19. Accuracy and precision was controlled by replicate measurements of laboratory standards and was better than ±0.1‰ for both carbon and oxygen isotopes. In order to control the effects of diagenesis, δ^{13}C of total organic carbon (TOC) was analyzed. Samples were decarbonatized with 10% HCl at 40 °C for several hours. Carbon isotopes of total organic carbon were measured from samples yielding >1% organic matter by combusting samples with a CE 1110 elemental analyzer connected on-line to a ThermoFinnigan Delta plus mass-spectrometer. Accuracy and precision was checked by replicate analysis of graphite standard USGS 24 and laboratory standards. Reproducibility is better than ±0.1‰ (1σ).

Evaluation of data

In order to interpret carbon isotope signals of whole-rock samples, the question whether the δ^{13}C values mirror the composition of the ancient sea water in which the carbonates formed or whether they were altered by diagenesis has to be addressed. The temperature dependent fractionation of carbon isotopes during formation of carbonates is small (Hudson 1977; Romanek et al. 1992). The effect of vital (Wefer and Berger 1991; Brand et al. 2003) or mineralogical (calcite versus aragonite; Romanek et al. 1992) fractionation on Palaeozoic carbonate rocks is difficult to estimate particularly because sediments contain a mixture of different carbonate components which are mostly recrystallized. Early cements are precipitated from pore waters which are similar in chemical composition to seawater (Marshall 1992) or only up to 1‰ lighter in δ^{13}C (McCorkle et al. 1985). Due to oxygen exchange with pore water during recrystallization, δ^{18}O values of all whole-rock samples show more or less effects of alteration (Brand 2004). Alteration of $\delta^{13}C_{carb}$ is most effective under the influence of meteoric water and re-mineralized organic carbon during early diagenesis (Irvin et al. 1977; Allen and Matthews 1982). In contrast to oxygen, late diagenesis of carbonates usually occurs in a closed system for carbon and even dolomitization sometimes does not significantly alter δ^{13}C (Holser 1997; Buggisch et al. 2003; Brand 2004). Therefore, δ^{13}C values of whole-rock samples are regarded as almost primary signals, when the rock-forming components of the carbonates were cemented early in marine porewaters or later in a diagenetically closed system.

Which criteria are available to discriminate between primary and altered δ^{13}C signals?

1. Subtidal carbonates without thick interbeds of shales or marlstones are most suitable for preserving primary signals. Whether these carbonates are mudstones, wackestones, packstones, or grainstones with marine cements does not influence the preservation potential significantly.
2. δ^{13}C values of intertidal and supratidal carbonates may be affected by meteoric diagenesis. The influence of meteoric water can reach several metres below emersion surfaces. This process is most effective during rapid glacio-eustatic sea level falls and lowstands.
3. Carbonates rich in organic matter or intercalated between shales and marlstones rich in organic carbon interact with CO_2 produced by the decay of isotopically light organic carbon through bacteria in the oxic or sulfate reduction zone (Irwin et al. 1977).
4. In sections with varying lithologies, δ^{13}C values probably reflect primary signals, when the values between different beds are similar or gradually increasing or decreasing, independent of lithology.
5. A big scatter of data and erratic changes of δ^{13}C-values are indicative of diagenetic overprinting.
6. Similar stratigraphical trends of δ^{13}C values in different sections of the same age are a strong argument for regional or global variations in the carbon isotope composition (Holser et al. 1988; Holser 1997).
7. A positive correlation between $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ gives evidence of a change in the oceanic carbon reservoir from which carbonates and organic matter

were produced (Holser et al. 1988; Magaritz et al. 1992; Holser 1997).

Consequently, it is assumed that early meteoric diagenesis did not affect the deep-subtidal carbonates, which were preferentially analyzed for this study. However, carbonates with shale interbeds are often altered during diagenesis and exhibit light $\delta^{13}C_{carb}$ values.

Results

$\delta^{13}C$ values are plotted against lithostratigraphy or thickness of the individual sections. Biostratigraphic correlation is based on conodont zones wherever possible; sometimes, especially at the Pridolian—Pragian and Pragian—Lochkovian transitions graptolites and tentaculites were considered to define the boundaries. The biostratigraphy is adopted from literature which was published between 1978 and 2002. During this time span, the concept of the Early Devonian timescale changed significantly. Originally, two parallel scales were available: (1) the Bohemian scale with subdivision into Lochkovian, Pragian, Zlichovian, and Dalejan and (2) the Rhenohercynian zonation with Gedinnian, Siegenian and Emsian. Finally, the International Commission on Stratigraphy decided to subdivide the Early Devonian into the Lochkovian, Pragian and Emsian. Unfortunately no section exists in which “traditional Pragian” rocks are overlain by rocks of the “traditional Emsian” realm. Therefore, the base of the new Emsian was defined in Uzbekistan (Yolkin et al. 2000), where the base of the Emsian is older than the traditional Siegenian—Emsian or the traditional Pragian—Zlichovian boundaries, respectively, (Carls and Valenzuela-Ríos 2002).

A second problem for correlation based on literature data emerges from the progress in conodont work and resulting zonations. Table 2 shows the development and use of Pragian and Emsian conodont zones from 1977 to 1994 (Yolkin et al. 1994). The biostratigraphic correlation is hampered by the time-dependent use of names of the conodont zones.

Table 2 Development of Early Devonian conodont zonation from 1977 to 1994 (based on Yolkin et al.1994)

Weddige (1977)	Klapper (1977)	Yolkin & Izokh (1988)	Yolkin et al. 1994		
serotinus	*serotinus*	*serotinus*	*serotinus*	EMSIAN	DALEJAN
laticostatus	*inversus*	*inversus*	*inversus*		
	gronbergi	*nothoperbonus*	*nothoperbonus*		ZLICHOV.
gronbergi		*gronbergi*	*excavatus*		
dehiscens	*dehiscens*	*dehiscens*	*kitabicus*		PRAGIAN
	sulcatus	*pireneae*	*pireneae*	PRAGIAN	
		kindlei			

Prague Syncline

Samples were collected from 16 sections, which are described in the literature. The following descriptions of the lithology and stratigraphy are based on Chlupáč et al. (1985), Chlupáč (1993, 1998a), and Chlupáč and Lukeš (1999); otherwise references are given for the individual outcrops. The results of 12 sections are reported here in detail:

Požáry Quarries

Stratigraphy: Pridolian to Zlichovian (Late Silurian to Early Devonian). The Silurian–Devonian boundary is exposed at the entrance to the northern abandoned quarry which is connected with the southern quarry by a tunnel. No detailed biostratigraphy of the Early Devonian strata of this section is published (Fig. 2).

Carbon isotopes: Early Pridolian $\delta^{13}C_{carb}$ values are around 0±0.5‰. Values increase during Late Pridolian to 3.5‰ at the Silurian–Devonian boundary and decline again to 0‰ during early Lochkovian. From late Lochkovian to early Pragian a gentle rise of 2.5‰ is observed reaching a maximum at about 17 m above the boundary.

Parallel to the inorganic record, $\delta^{13}C_{org}$ values increase from about −30.0 to −26.5‰ in the Pridolian. Middle to late Lochkovian samples gave $\delta^{13}C_{org}$ values around 29.0‰. Organic and inorganic carbon exhibit a significant positive correlation (r^2=0.81).

Klonk Borehole

Stratigraphy (Chlupáč and Hladil 2000): The international Silurian–Devonian boundary stratotype is situated in the Klonk section NE of the village Suchomasty. The uppermost Silurian Přídolí Formation consists of dark calcareous shales with intercalated fine-grained bituminous limestones. This lithology continues into the lowermost Devonian Lochkov Formation (Hladil 1992). Limestone interbeds become more abundant in the Lochkov Formation than in the Přídolí Formation. The Silurian–Devonian boundary is well defined by graptolites of the *Monograptus transgrediens* Zone and the *M. uniformis* Zone. *Scyphocrinites* occur already in the uppermost Silurian strata but are not concentrated in dense *Scyphocrinites* beds, which are observed in many other boundary sections. The Klonk borehole recovered sediments from the lower Lochkov and the whole Přídolí Formations, and ended in the uppermost Ludlowian Kopanina Formation. The core was compared with the stratotype section and

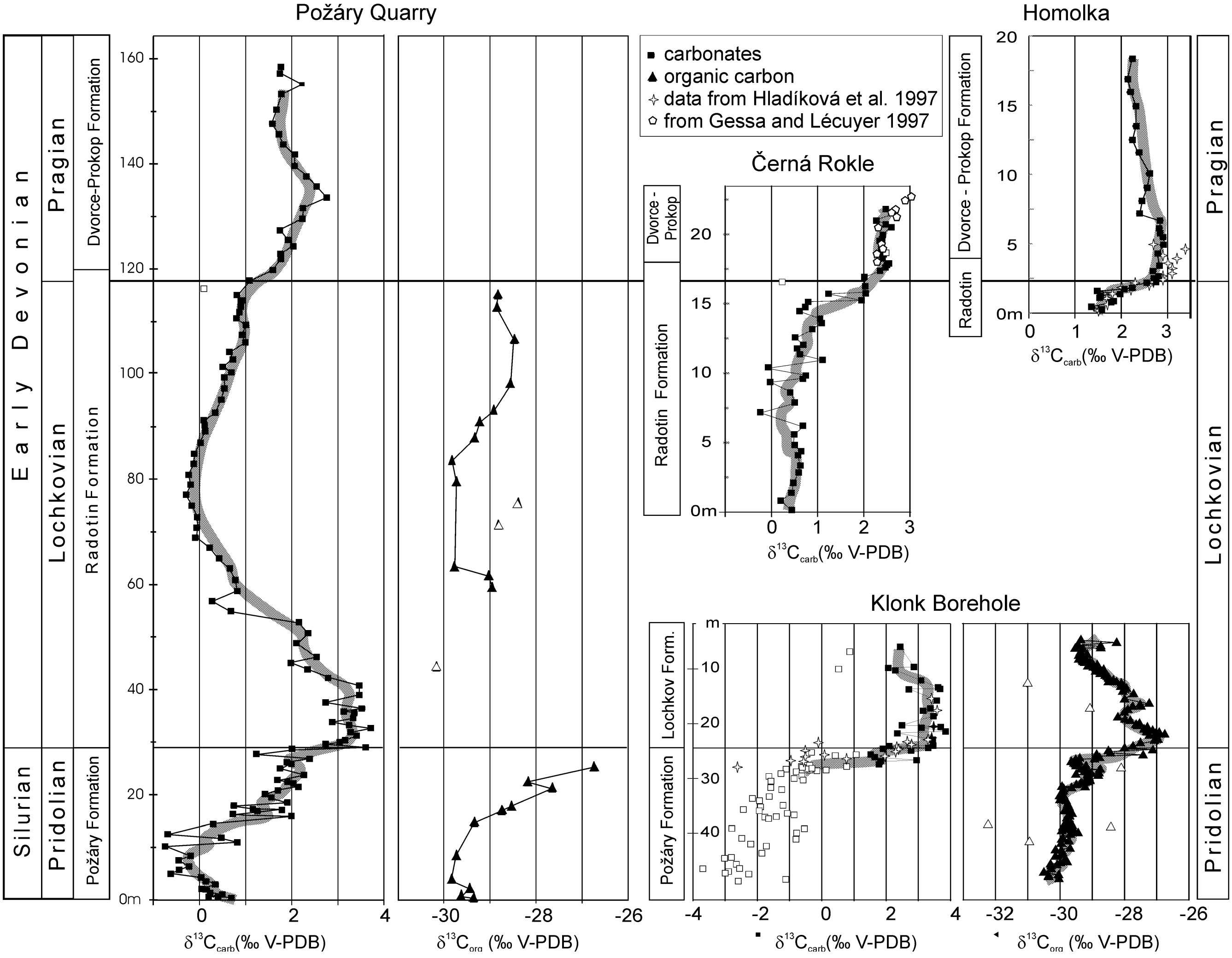


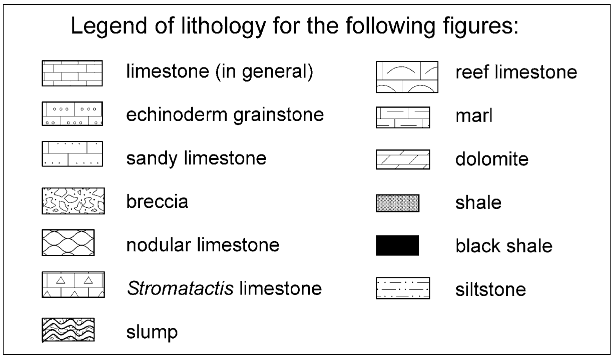
Fig. 2 δ^{13}C of inorganic and organic carbon of Pridolian to Pragian sections of the Prague Syncline (Požáry Quarry, Černá Rokle, Praha-Velká Chuchle [Homoloka section], Klonk borehole). Stratigraphy after Chlupáč et al. (1985), Chlupáč (1993, 1998a) and Chlupáč and Hladil (2000). *Gray shaded line;* running mean of five values. *Open symbols*; Data from literature and from diagenetically altered limestones, which are not used for running mean calculations

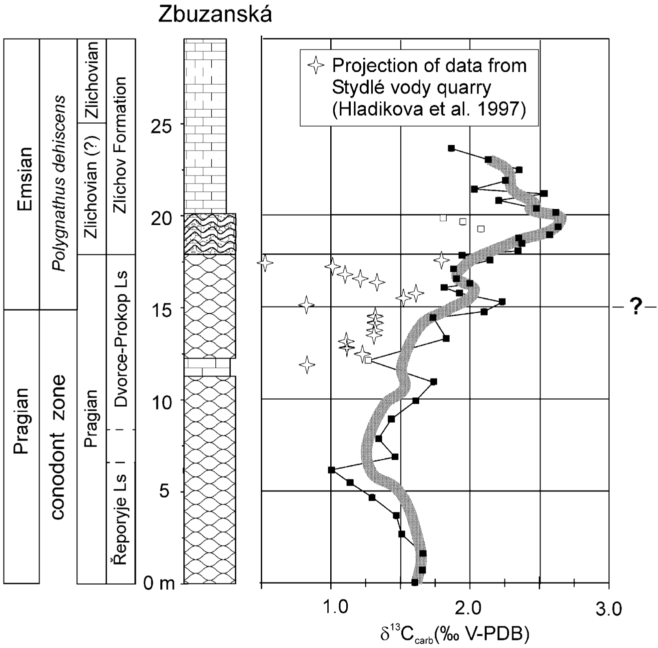
the Silurian–Devonian boundary was drawn at about 25 m. Analysed samples from the outcrop and the core exhibit the same trends in $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ in both sections. In this paper, only data from the more densely sampled core are reported (Fig. 2).

Carbon isotopes: The isotope ratios of inorganic and organic carbon were measured in core samples collected by Herten (2000), Kranendonck (2000) and Fröhlich (2000). $\delta^{13}C_{carb}$ values of samples from Pridolian limestones exhibit a large scatter between −4.0 and 0‰. Values rise in the uppermost Požáry Formation and reach +4.0‰ immediately above the Silurian–Devonian boundary of the stratotype. They start to drop again about 10 m above the boundary. $\delta^{13}C_{org}$ values are all around −30.0‰ in the lower and middle Požáry Formation. The positive excursion, seen also in the inorganic carbon record, starts in the uppermost Požáry Formation and reaches its maximum of more than −27.0‰ in the lowermost Lochkov Formation. After a short second, maximum values decrease to about −29.5‰, approximately 20 m above the boundary.

Černá Rokle

Stratigraphy: Late Lochkovian to early Pragian (Fig. 2). The Lochkovian–Pragian boundary was defined in this section in 1958. Later, the boundary was redefined and the Praha-Velká Chuchle section (see there) was chosen as stratotype. Platy limestones of the Radotín Formation with intercalated shales were deposited during the Late Lochkovian according to the occurrence of zonal index fossils (*Monograptus hercynicus, M. kayseri*). The amount of limestone beds increases from the base to the top in the sampled section. The Lochkovian–Pragian boundary, which is defined by the first appearance of *Eognathodus sulcatus* is situated in the uppermost Radotín Formation about 175 cm below the base of the





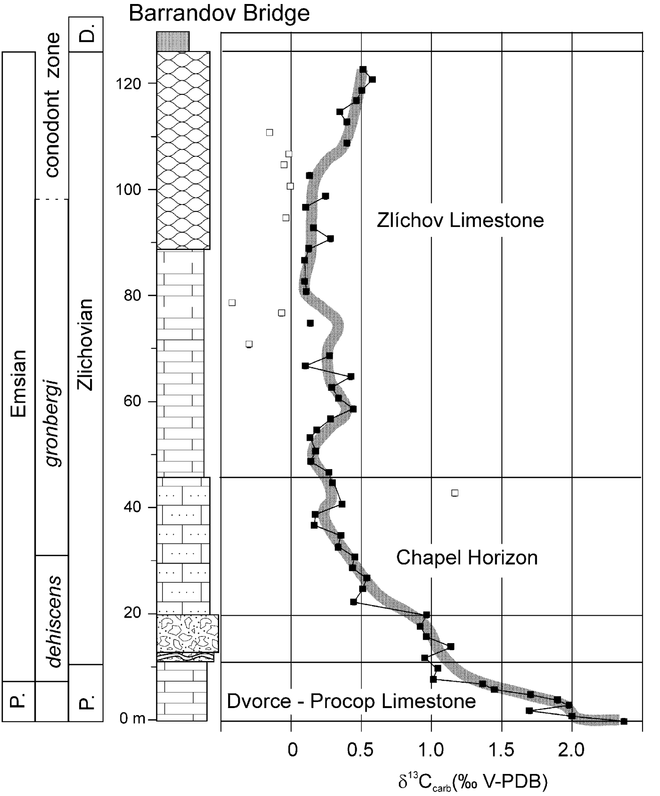


Fig. 3 δ^{13}C of inorganic carbon of Pragian to Emsian sections of the Prague Syncline (Zbuzanská Marble Quarry and section north of Chapel Quarry below Barrandov highway bridge). Stratigraphy after Chlupáč et al. (1980) and Chlupáč and Lukes (1999). Symbols as in Fig. 2

Dvorce–Procop Limestone. The Dvorce–Procop Limestone consists of nodular wackestones rich in fossils. Samples were collected from the first 5 m of this up to 170 m thick sequence.

Carbon isotopes: $\delta^{13}C_{carb}$ values of the late Lochkovian limestones are mainly around 0.5‰. A sharp rise is observed within the uppermost Radotin Limestone about 1 m below the Lochkovian–Pragian boundary and values reach +2.5‰ already within the Radotin Limestone. $\delta^{13}C_{carb}$ values stay at this level in the lowermost Dvorce–Procop Limestone.

Praha–Velká Chuchle, Homoloka Section (N 50° 00’ 55’’; E 14° 22’ 24’’.)

Stratigraphy (Chlupáč 2000): Stratotype of the Lochkovian–Pragian boundary (Fig. 2). About 4 m of platy grey limestones with few intercalations of calcareous shales are exposed at the base of the abandoned quarry. The Lochkovian/Pragian boundary is drawn at the base of bed no. 12, which coincides with the first appearance of *Eognathodus sulcatus praesulcatus* within the Radotín Limestone at about 140 cm below the onset of the typical nodular wackestones of the Dvorce–Prokop Limestone.

Carbon isotopes: Uppermost Lochkovian samples exhibit $\delta^{13}C_{carb}$ values increasing from about 1.5‰ to almost 3.0‰. $\delta^{13}C_{carb}$ values stay at this level during earliest Pragian and decrease within the basal nodular Dvorce–Prokop Limestones.

Zbuzanská Marble Quarry near Chýnice (N 50° 00’ 17,3’’; E 14° 16’ 14’’.)

Stratigraphy (Chlupáč and Lukes 1999): Late Pragian to early Emsian (Fig. 3). Samples were taken from the NW part of the quarry, were the section starts with red nodular wackestones of the late Pragian Řeporyje Limestone. A change in colour from red to grey nodular wackestones indicates the transition to the Dvorce–Procop Limestone, which is overlain by distorted dark grey wackestones and finally by platy grey limestones of the Zlíchov Formation. The Pragian–Emsian boundary is defined by the first appearance of *Polygnathus dehiscens* within the upper part of the Dvorce–Procop Limestone. The position of the traditional Pragian–Zlichovian boundary is not well established. Zlichovian trilobites were found about 10 m above the base of the contorted limestones. Tentaculites diagnostic for the upper part of the Lower Zlichovian occur about 5 m upsection.

Carbon isotopes: $\delta^{13}C_{carb}$ values fluctuate around 1.5±0.5‰ during the Late Pragian and increase to more than 2.5‰ during the Early Emsian. Maximal values of this positive excursion are measured in the distorted dark grey wackestones which are possibly attributed to the basal Zlichovian.

Section North of Chapel Quarry below Barrandov highway bridge (N 50° 02' 22''; E 14° 24' 21''.)

Stratigraphy (Chlupáč et al. 1980): Uppermost Pragian and almost complete Zlichovian (Fig. 3). The rocks exposed in the abandoned "Chapel Quarry" and at the base of the continuing road cut belong to the Dvorce–Procop Limestone which consists of platy wackestones. The following beds of the basal Zlichovian were contorted by slumping. They are discontinuously overlain by more than 6 m thick massive limestone breccias and about 39 m of bedded limestones with grainstones and rudstones of the Chapel Coral Horizon that characterizes the base of the Zlichovian in this area. Upsection about 80 m of platy limestones and nodular wackestones with cherts are exposed. The Pragian–Emsian boundary is defined by the first appearance of *Polygnathus dehiscens* indicative for the *P. kitabicus* Zone 3.8 m below the traditional Pragian–Zlichovian boundary. *P. gronbergi* was found about 25 m above the base of the Zlichovian indicating the *P. excavatus* Zone.

Carbon isotopes: $\delta^{13}C_{carb}$ values decrease sharply from about 2.5‰ to 1.0‰ in the uppermost Pragian beds of the Dvorce–Prokop limestone. The $\delta^{13}C_{carb}$ ratios stay at about 1.0‰ in the lowermost Emsian Dvorce–Prokop Limestone, in the slumped beds and the massive breccia of the basal Zlichovian. $\delta^{13}C_{carb}$ values of the following Zlichovian beds are mainly between 0 and 0.5‰ with a gentle rise to the base of the Dalejan shales.

Červený Lom

Stratigraphy (Klapper et al. 1978): Emsian to early Eifelian (Fig. 4). Pragian reef limestones (Koněprusy Limestone) are disconformably covered by Emsian crinoidal wackestones and grainstones of the Suchomasty Limestone. Most of the Zlichovian is missing in this section. The 23-m-thick Suchomasty Limestone is overlain by crinoidal grainstones and rudstones of the *Acanthopyge* Limestone with reworked corals and stromatoporids. The conodont biostratigraphy was investigated in detail by Klapper et al. (1978) who gave evidence for all conodont zones from the *P. laticostatus* to the *P. costatus costatus* Zone.

Carbon isotopes: $\delta^{13}C_{carb}$ values of samples from the *laticostatus* Zone decrease from about 1.6 to 0.8‰. A positive excursion up to maximum values of 2.5‰ is observed in the Early *P. serotinus* Zone. Values vary between 1.5 and 2.0‰ in the Late *P. serotinus* Zone up to the *P. costatus costatus* Zone.

Prastav Quarry (N 50° 02' 03''; E 14° 21' 20''.)

Stratigraphy (Klapper et al. 1978; Chlupáč et al. 1980; Ziegler 2000): Parastratotype of the Early–Middle Devonian boundary (Fig. 4). Exposed are light grey wackestones of the upper Třepotov Limestone overlain by darker grey limestones of the Choteč Formation. *Polygnathus serotinus* occurs already at the base of the exposed section. *P. costatus patulus* appears about 6 m below the top of the Třepotov Limestone. The Emsian–Eifelian boundary is defined by the first appearance of *P. costatus partitus* about 3 m below the base of the Choteč Limestone. The index fossil of the *P. costatus costatus* Zone was found 1.8 m above the base of the Choteč Limestone.

Carbon isotopes: $\delta^{13}C_{carb}$ values are constant around 1.5‰ in the *P. serotinus* Zone, decrease to about 1.0‰ within the *P. patulus* Zone and rise again to more than 2.0‰ in the *P. partitus* and *P. costatus costatus* Zones.

Škrábek (N 49° 59' 23''; E 14° 16' 48''.)

Stratigraphy (Chlupáč 1998b): Late Emsian to Eifelian (Fig. 4). The outcrop represents the stratotype of the Choteč Formation. Diabases and tuffs are followed by 10.5 m of bedded limestones of the upper Třepotov Limestone. The overlying 0.9-m-thick dark thin bedded limestones exhibit the effect of the Choteč event. The following lower Choteč Formation consists of medium bedded fine grained limestones with mm thick shale interbeds.

Carbon isotopes: $\delta^{13}C_{carb}$ values decrease from 1.5‰ to almost 1.0‰ within the late Emsian Třepotov Limestone. An increase is observed in the early Eifelian uppermost Třepotov Limestone. Maximal values of more than 2.0‰ are registered in the lowermost Choteč Limestone. $\delta^{13}C_{carb}$ decline to values between 1.0 and 1.5‰ 7 m above the base of the Choteč Limestone.

Mostim, Kačák Valley (N 49° 57' 27''; E 14° 09' 05''.) and Hlubočepy (N 50° 02' 24''; E 14° 23' 48''.)

Stratigraphy (Budil 1995; Chlupáč 1993): Late Eifelian (Fig. 5). The upper part of the Choteč Limestone is ex-

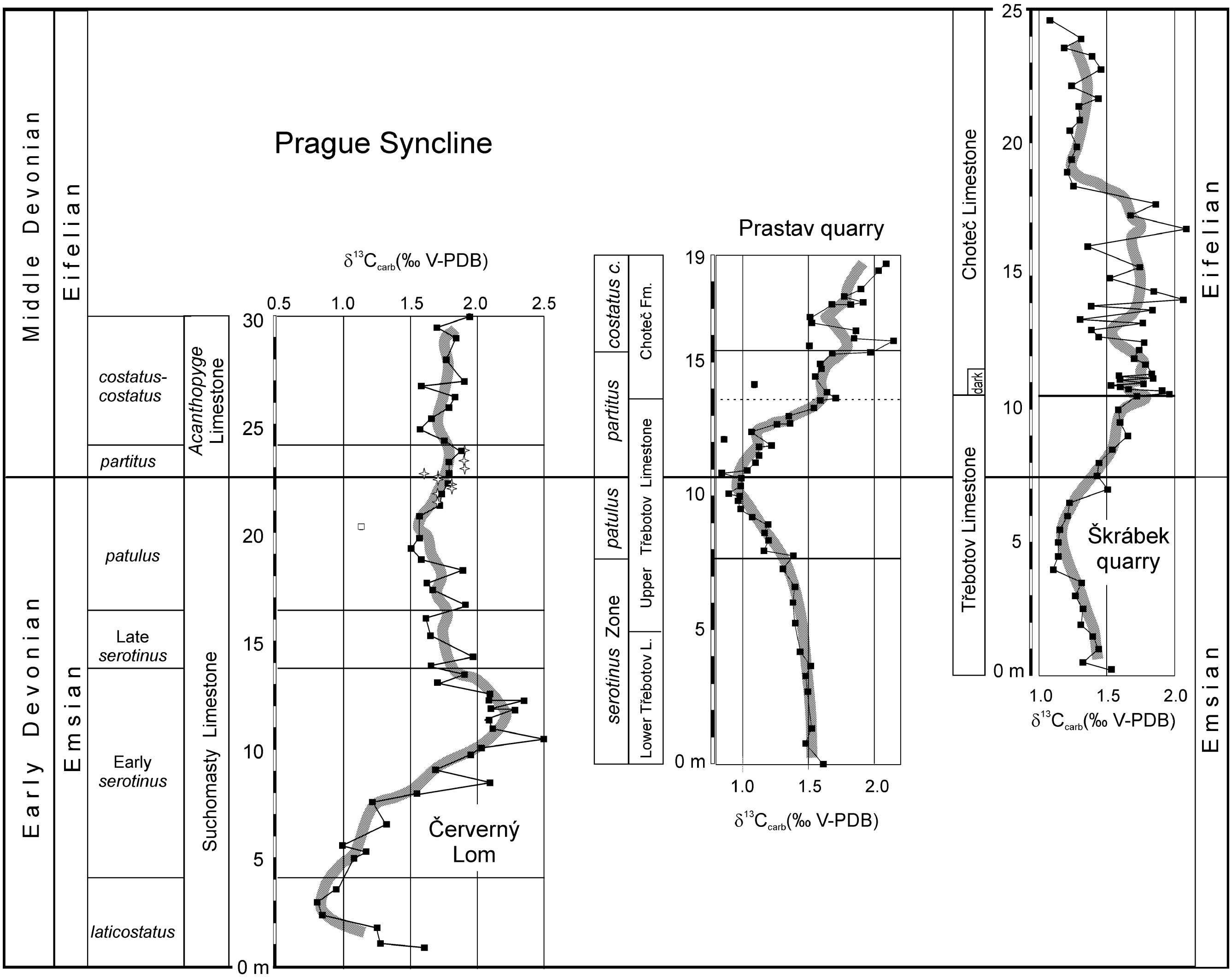


Fig. 4 δ^{13}C of inorganic carbon of Emsian to Eifelian sections of the Prague Syncline (Červený Lom, Prastav Quarry, Škrábek Quarry). Stratigraphy after Klapper et al. (1978) Chlupáč et al. (1980), Chlupáč (1998b) and Ziegler (2000). *Symbols* as in Fig. 2

posed in some cliffs above the Kačák valley near Mostim. The outcrop on the SE side of the Hlubocepy railway cut provides a section in which the transition from the Choteč Limestone to the Kačák Member is exposed. The uppermost Choteč Limestone consists mainly of thin bedded, often nodular wackestones with some intercalations of thicker grainstone beds. The uppermost Choteč Limestone belongs to the *T. kockelianus* conodont Zone and the dacryoconarid *Nowakia chlupaciana* Zone. It is sharply overlain by black shales and cherts of the Kačák Member in which *Nowakia otomari* was found about 1 m above the base.

Carbon isotopes: $\delta^{13}C_{carb}$ values vary around 2.0‰.

Jirásek

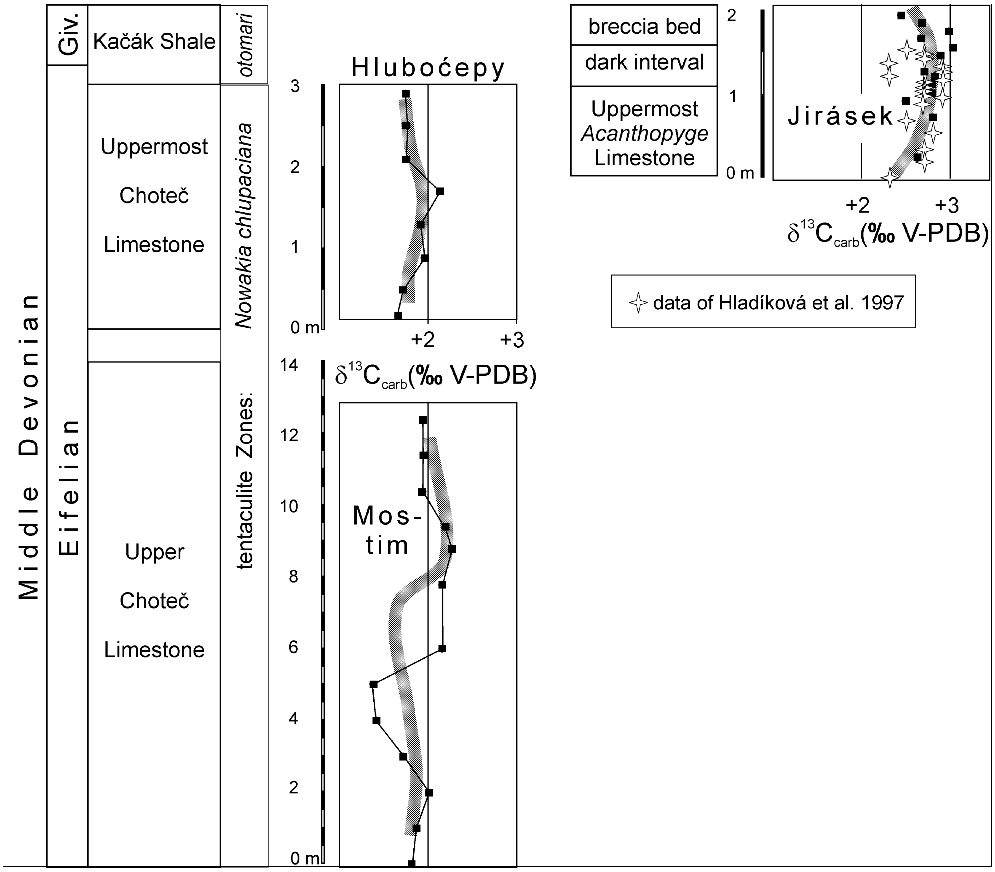
Stratigraphy (Budil 1995; Hladíková et al. 1997): Late Eifelian (Fig. 5). A few meters of biodetridal and peloidal grainstones are exposed at the eastern wall of the abandoned quarry. The section starts in coarse grainstones of the uppermost part of the *Acanthopyge* Limestone, which are followed by dark, thin-bedded peloidal grainstones of the "dark interval" that in turn are overlain by rudstones with large intraclasts, fragments of corals and stromatoporids. The fauna of the dark interval is very poor, but the tentaculite *Nowakia* ex. gr. *otomari* is abundant. *N. otomari* is recorded from the basal Kačák Member in many other sections but was not found in the Choteć Limestone. Therefore, the dark interval is regarded as equivalent to the Kačák Member.

Carbon isotopes: $\delta^{13}C_{carb}$ values of our own samples and from Hladíková et al. (1997) are mostly above 2.5‰ and reach up to 3.0‰ in the "dark interval".

Carnic Alps

In the Carnic Alps, Palaeozoic rocks range from the Ordovician up to the Permian with only a short interruption

Fig. 5 $\delta^{13}C$ of inorganic carbon of Eifelian to earliest Givetian sections of the Prague Syncline (Mostim, Hlubоćepy and Jirásek sections). Stratigraphy after Chlupáč (1993) and Budil (1995). *Symbols* as in Fig. 2



during the Late Carboniferous due to the Variscan Orogeny. The first reliable conodont stratigraphy was established by Walliser (1964) in the Cellon section. Our current knowledge of the Palaeozoic stratigraphy of the Carnic Alps is mainly due to the studies of H.P. Schönlaub who mapped large areas, described many sections and investigated the conodonts (e.g., Schönlaub 1979, 1980, 1985; Schönlaub et al. 1994; Kreutzer et al. 2000).

Oberbuchach II

Stratigraphy: Late Silurian to late Middle Devonian rocks are exposed in the Oberbuchach II section (Schönlaub 1985) (Fig. 6). The Lochkovian–Pragian boundary is defined by the first appearance of the tentaculite *Nowakia acuraria*. Conodonts are scarce in the basal Pragian beds, the index fossil *Polygnathus pireneae* was found in the upper part. The Pragian–Emsian boundary is drawn at the appearance of *P. dehiscens*. The traditional Pragian–Zlichovian boundary coincides approximately with the first findings of *P. gronbergi*. Conodont faunas suggest a stratigraphic gap between the Findinig Limestone and the limestone breccia which is regarded as the base of the Zlichovian. Index conodonts of all zones from *P. gronbergi* to *P. costatus patulus* are present. The Early–Middle Devonian boundary is drawn at the first appearance of *P. costatus partitus*. Grainstones and rudstones occur in the upper *P. c. costatus* and *T. australis* Zones. Platy limestones with shales and cherts of the *T. kockelianus* Zone indicate a deepening which culminated in black bedded cherts of the lower *P. ensis* Zone. Cherty limestones, marlstones, calcareous shales with interbedded echinoderm grainstones and finally rudstones with corals and stromatoporids are the typical sediments of the upper *P. ensis* to middle *P. varcus* Zones (Givetian).

Carbon isotopes: $\delta^{13}C_{carb}$ values of early Lochkovian carbonates show a large scatter between –0.5 and +2.5‰. In contrast, $\delta^{13}C_{org}$ values exhibit the known positive $\delta^{13}C$ excursion at Silurian–Devonian boundary reaching from –28.5 to almost –26.0‰. With the onset of continuous limestone deposition during late Lochkovian, $\delta^{13}C_{carb}$ values increase from about 1.0 to 2.0‰ at the Lochkovian–Pragian boundary and reach a maximum with 3.5‰ in the *E. sulcatus* Zone. Interrupted by a short positive excursion, values decrease from the *P. dehiscens* Zone to a minimum in the late *gronbergi* and *laticostatus* Zone. $\delta^{13}C_{carb}$ values are around 1.5‰ from the late Emsian *P. serotinus* Zone up to the Eifelian *P. australis* Zone, increase in the early *kockelianus* Zone and decrease from the late *ensis* Zone to the *P. varcus* Zone. $\delta^{13}C_{carb}$ values of carbonates intercalated in cherts and black shales vary between 1.0 and 2.0‰ at the Eifelian–Givetian boundary.

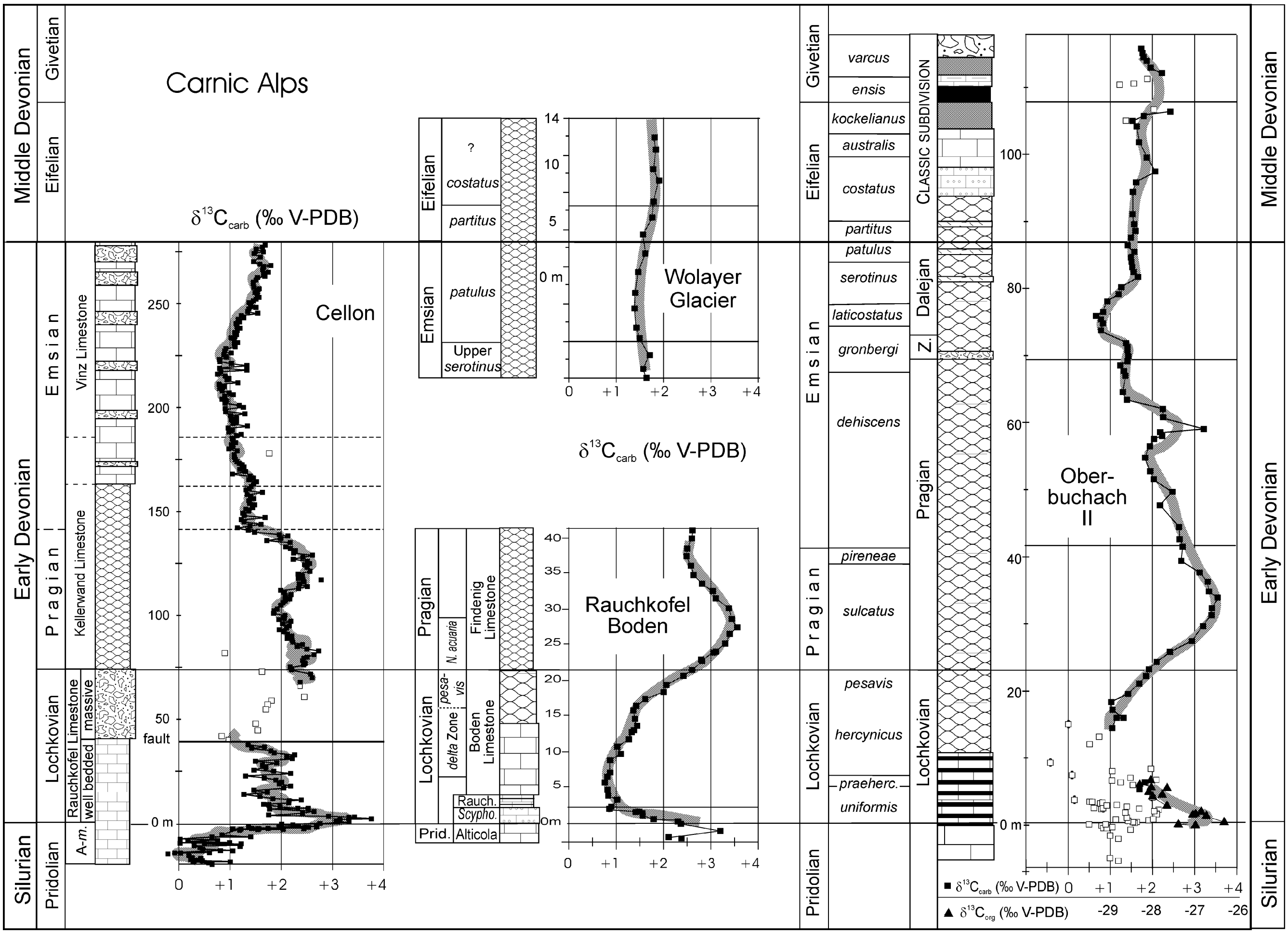


Fig. 6 $\delta^{13}C$ of inorganic and organic carbon of Pridolian to Givetian sections of the Carnic Alps (Cellon, Rauchkofelboden, Wolayer Glacier, Oberbuchach II). Stratigraphy after Walliser (1964), Schönlaub (1980, 1985) Kreutzer (1990). *Symbols* as in Fig. 2

Rauchkofelboden–Wolayer Glacier

Stratigraphy (Schönlaub 1980): Strata from the Late Ordovician to the Middle Devonian are continuously exposed in the Rauchkofelboden section (Fig. 6). *Scyphocrinites* beds mark the Silurian–Devonian boundary. The thin limestone beds with shale intercalations of the Rauchkofel Limestone contain *I. woschmidti* ssp. and *I. eolatericrescens,* which are associated with *Monograptus uniformis* in other sections. *Ozarkodina delta* was found in wackestones of the "Orthoceras Limestone" and *Pedavis pesavis* occurs in the middle part of the grey nodular limestones. The Lochkovian–Pragian boundary is defined by the first appearance of *Nowakia* aff. *acuraria*. The conodont fauna of the Findenig Limestone is very poor, but several elements have been found which prove a Pragian age. The Rauchkofelboden section is terminated by a fault.

Emsian and Eifelian beds are exposed in the condensed Wolayer Glacier section, where conodonts of the Late *P. serotinus* Zone up to the *P. c. costatus* Zone were recovered from red nodular limestones.

Carbon isotopes: $\delta^{13}C_{carb}$ values of the *Scyphocrinits* beds decrease from 2.5 to 0.8‰. Signals are below 1.0‰ in samples from the lower "Orthoceras Limestone", increase during late Lochkovian and early Pragian to 3.5‰ and decrease to about 2.5‰ in the upper Findenig Limestone forming a broad positive excursion with maximal values in the *Nowakia acuraria* Zone. Emsian and Eifelian limestones of the Wolayer Glacier section show $\delta^{13}C_{carb}$ values between 1.4 and 1.8‰.

Cellon

Stratigraphy (Walliser 1964; Kreutzer 1990): An almost complete section spanning the Late Ordovician to Late Devonian is exposed in the avalanche ravine of the Cellon (Fig. 6). The Pridolian–Lochkovian boundary is defined by the first occurrence of *I. woschmidti* within echinoderm grainstones of bed 47. Unfortunately, the middle part of the Lochkovian is disturbed by faulting. The following late Lochkovian massive limestone unit is strongly

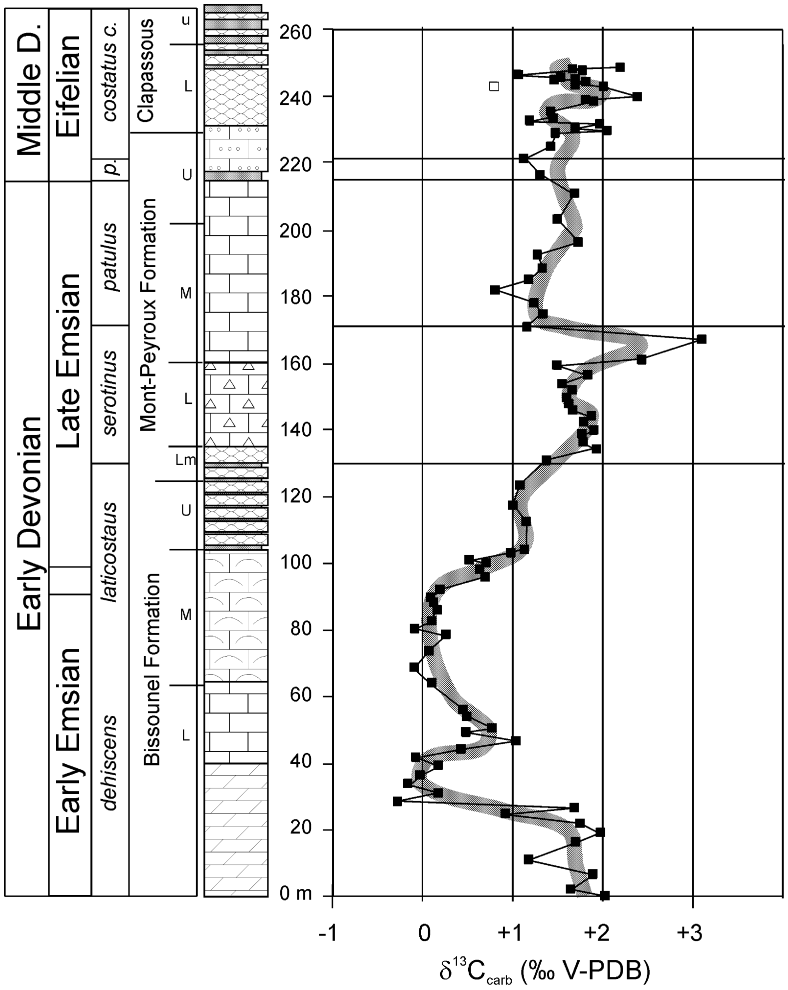


Fig. 7 δ^{13}C of inorganic carbon of the Puech de la Suque section (Montagne Noire, Southern France). Stratigraphy after Feist (1985, 2002). *Symbols* as in Fig. 2

recrystallized. No detailed biostratigraphic data are available for the Pragian and Emsian part of the section.

Carbon isotopes: $\delta^{13}C_{carb}$ values are ±0.5‰ in the Pridolian and exhibit a positive excursion at the Silurian–Devonian boundary reaching 2.0‰ in the early Lochkovian Rauchkofel Limestones. The rise of $\delta^{13}C_{carb}$ values during late Lochkovian–early Pragian is obscured due to faulting and reworking. Two maxima reaching more than 2.5‰ occur in the Pragian Kellerwand Limestone. A sharp drop followed by a gentle decline in $\delta^{13}C_{carb}$ forms a broad minimum around 1.0‰ in the Emsian Lower Vinz Limestone.

Montagne Noire

Palaeozoic rocks are widely exposed in the Montagne Noire and several Middle and Late Devonian stratotypes were defined in this area. Lower Devonian rocks are best exposed in the Mont Peyroux nappe unit. The stratigraphic framework was elaborated by Feist, Schönlaub, Klapper and others (see Feist 1985, 2002).

Col du Puech de la Suque (N 43° 30’ 17’’; W 3° 05’’ 20’’.)

Stratigraphy (Feist 1985, 2002): Emsian to Eifelian (Fig. 7). Sampling started in secondary dolomites and subtidal wackestones of the Lower Bissounel Formation in which *P. dehiscens* was found. The overlying marly shales and gray marly limestones lack conodonts. An age of the *inversus/laticostatus* Zone is assigned by conodonts for the Upper Bissounel Formation.

The Mont Peyroux Formation starts with 6 m of red nodular limestones of the *P. serotinus* Zone. The index fossil *P. costatus patulus* appears 12.30 m above the base of the Middle Mont Peyroux Formation. *P. c. patulus* has been recorded from the base of the Upper Mont Peyroux Formation, the first appearance of *P. c. costatus* is documented 13.30 m above the base. The Emsian–Eifelian boundary has to be drawn between these two points of reference.

Nodular limestones developed at the base of the Clapassous Formation. Upsection, intercalated shales become more frequent and dominate the Upper Member of the Clapassous Formation. Most conodonts are indicative for the *P. c.costatus* Zone, the uppermost part of the Lower

Clapassous Formation may already reach into the P. *australis* Zone.

Carbon isotopes: $\delta^{13}C_{carb}$ values decrease from about 2.0 to 0‰ in the dolomites of the Lower Bissounel Formation. Signals increase during the late *P. laticostatus* – early *P. serotinus* interval to almost 2.0‰. Samples from the Lower Mont–Peyroux to Lower Clapassous Formations give scattered values between 1.0 and 2.0‰ with a positive excursion reaching 3.0‰ at the boundary of the *P. serotinus* and *P. patulus* Zones.

Cantabrian Mountains

Rocks of the Cantabrian Mountains have been studied since the end of the 19th century (Barrois 1882). An excellent field trip guidebook was published for the 8th international conodont symposium held in Europe ECOS VIII (García-López and Bastida 2002). If not mentioned otherwise, the following biostratigraphic and lithologic descriptions of the sections are based on this guidebook.

Araúz (N 42° 59' 57''; W 4° 35' 50''.)

Stratigraphy (Jahnke et al. 1983; García-López et al. 2002): An almost complete succession from the late Pridolian to Early Devonian is exposed in the Araúz section (Fig. 8). Conodonts represent typical shallow water assemblages with dominant Icriodid–Ozarkodinid faunas. A correlation to the global conodont standard zones is given by Weddige (1996) and Carls and Weddige (1996).

Carbon isotopes: $\delta^{13}C_{carb}$ data of the Lebanza Formation exhibit a scatter of ±0.5‰ around a mean value of –0.5‰ in the *Icriodus rectangularis lotzei* Zone of the lower Member A and around 0 to +0.5‰ in the upper Member A and B (Fig. 8). A positive excursion is observed in Member C that started during the late Lochkovian with maximal values above 3.0‰ measured immediately above the Lochkovian–Pragian boundary. Samples from Member D and E gave values of about 2.0‰.

Lebanza (N 42° 58' 08''; W 04° 31' 41''.)

Stratigraphy and carbon isotopes: Type section of the Lebanza Formation (Fig. 8). The middle and upper part is well exposed but biostratigraphy is better defined in the Araúz section. $\delta^{13}C_{carb}$ values from Lebanza match well with $\delta^{13}C_{carb}$ values of the Araúz section.

La Vid (N 42° 50' 49''; W 05° 07' 25''.)

Stratigraphy (Keller 1988; García-López and Sanz-López 2002): Conodonts from the base of the Felmin Formation belong to the middle Lochkovian *Lanea omoalpha-Ancyrodelloides trigonicus* Zone (Fig. 9). Conodonts from the uppermost Felmin Formation contain *Icriodus curvicaudatus* and *Ozarkodina* ex. gr. *excavatus* which are indicative for the late Pragian *P. pireneae* to early Emsian *P. kitabicus* Zone. An Early Emsian to early Late Emsian age can be assigned to the La Pedrosa Formation.

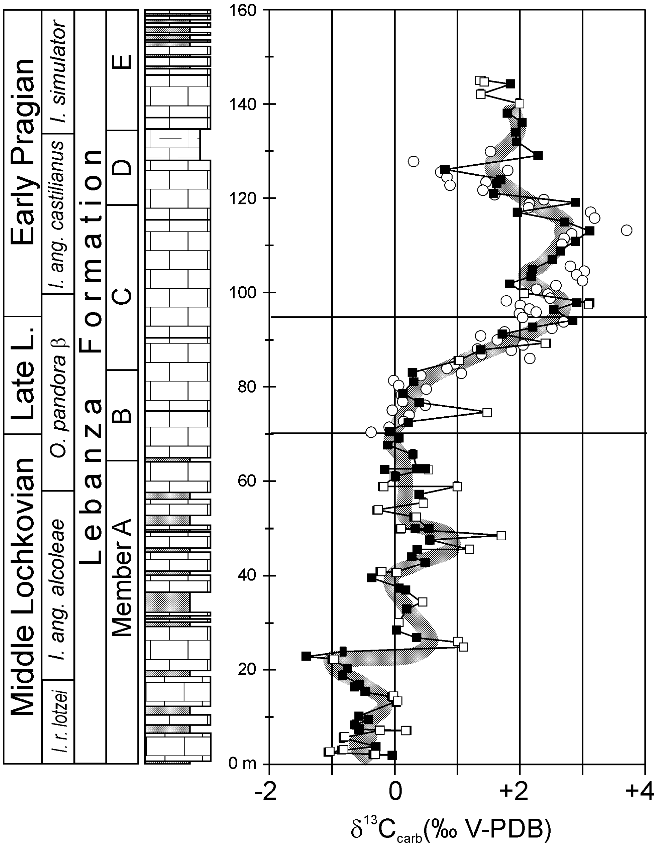


Fig. 8 $\delta^{13}C$ of inorganic carbon of the Araúz and Lebanza sections (Cantabrian Mountains, North Spain). *Rectangles* Araúz (*closed*: sediment, *open:* brachiopods); *open circles*; data from Lebanza. Stratigraphy after Jahnke et al. (1983) and García-López et al. (2002)

Carbon isotopes: $\delta^{13}C_{carb}$ values increase from about 0‰ to more than 3.0‰ and decline to 1.3‰ in the dolomites of the Felmin Formation. They are in the range of 1.0 to 2.0‰ in lower La Pedrosa Formation and exhibit a distinct positive excursion of more than 3.0‰ during the *I. celtiberius* Zone.

Santa Lucia (N 42° 52' 23''; W 05° 07' 45'.)

Stratigraphy (García-López and Sanz-López 2002): With few Icriodids in the section at Santa Lucia, it allows only a tentative correlation with conodont zones (Fig. 10). The appearance of *Icriodus retrodepressus* is correlated with the onset of the *P. c. partitus* Zone. A rich Icriodid-Polygnathid fauna at the Santa Lucia–Huergas Formation boundary is assigned to the *P. c. costatus* Zone.

Carbon isotopes: Also scattered, the $\delta^{13}C$ values show a distinct pattern with maximum $\delta^{13}C_{carb}$ values of >2.5‰ observed in the massive reef limestone of Member II and

Fig. 9 δ^{13}C of inorganic carbon of the La Vid section (Cantabrian Mountains, North Spain). Stratigraphy after Keller (1988) and García-López and Sanz-López (2002)

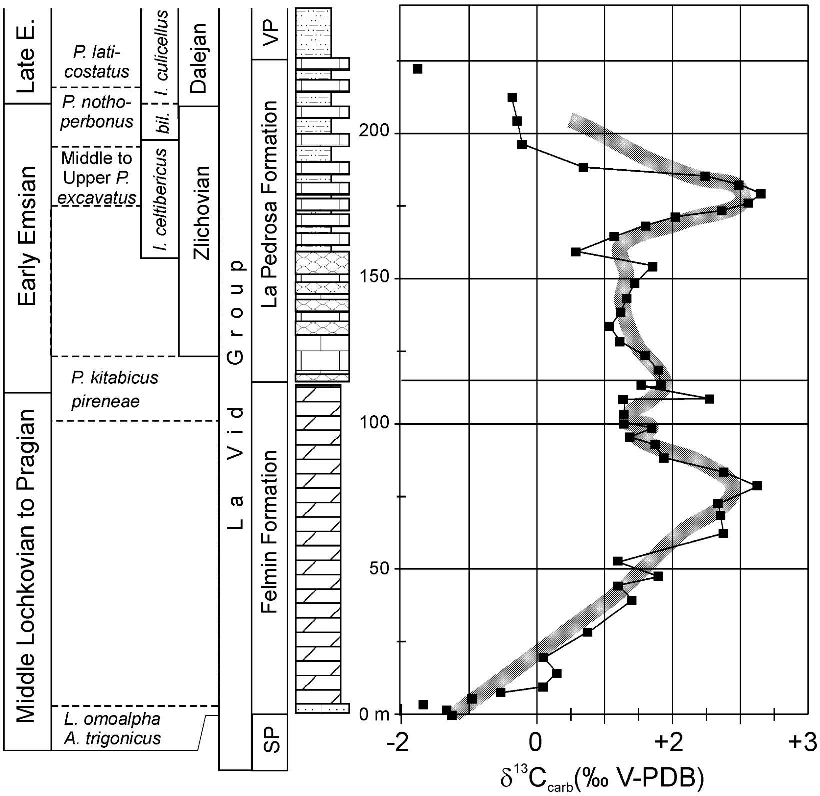
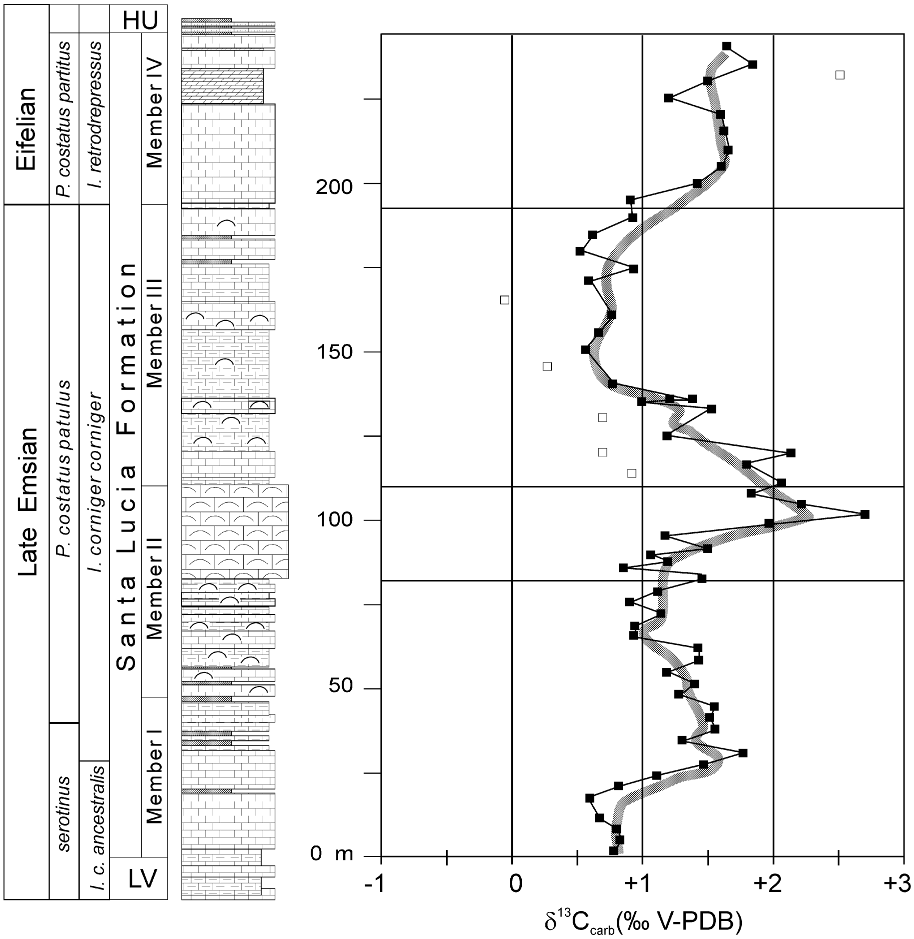


Fig. 10 δ^{13}C of inorganic carbon of the Santa Lucia section (Cantabrian Mountains, North Spain). Stratigraphy after García-López and Sanz-López (2002). *Symbols* as in Fig. 2



minimal values around 0.5‰ represented at the base of Member I and in the upper Member III. Data of the Eifelian Member IV are around 1.5‰.

Discussion

In the previous chapter and figures, isotope data were plotted against thickness and lithology. In order to compare the $\delta^{13}C$ curves from different sections with each other and with data from literature, data were converted to time-dependent curves. This was performed by using the biostratigraphic data known from literature as datum points, and interpolating between these datum points according to sediment facies and thickness. The validity of this method depends obviously on the amount and precision of available biostratigraphic data and on the assumption of continuous deposition and sedimentation rates between the biostratigraphic datum points.

$\delta^{13}C$ values of all analysed sections exhibit a large positive excursion in inorganic and organic carbon at the Silurian–Devonian boundary (Fig. 11). The heaviest values reach almost 4.0‰ for C_{carb} and −26.0‰ for C_{org} in the Požáry, Klonk, Cellon, and Oberbuchach sections. This excursion was previously reported from Europe (Schönlaub et al. 1994; Hladikova et al. 1997; Buggisch 2001a) and Australia (Andrew et al. 1994). Saltzmann (2002) described three sections from Laurentia with peak values as heavy as 5.8‰. Many Pridolian–Lochkovian boundary sections exhibit alternations of dark to black shales and limestones (Klonk, Oberbuchach). Due to the oxidation of organic matter in the black shales during diagenesis, $\delta^{13}C_{carb}$ values are often altered in these sections. In limestone dominated sections (Požáry, Cellon), the Pridolian baseline is situated between 0 and 1.0‰ $\delta^{13}C_{carb}$. Similar $\delta^{13}C_{carb}$ values were reported by Saltzmann (2002) from the Roberts (Nevada) and Arbuckle Mountains (Oklahoma). The Pridolian baseline of $\delta^{13}C_{org}$ is between −30.0 to −29.0‰ (Požáry, Klonk).The positive correlation of $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ in the Požáry section corroborates, that these values reflect more or less the primary carbon isotope ratios. Middle Lochkovian $\delta^{13}C_{carb}$ values are in the range of 0 to 1.0‰. On average, the excursion at the Silurian–Devonian boundary shows an amplitude of 2.5 to 3.0‰ (max. 4.0‰) in Europe and up to 5.0‰ in Laurentia.

After the pronounced positive excursion during the *I. woschmidti-postwoschmidti* conodont Zone, a broad minimum with $\delta^{13}C_{carb}$ values between 0 and 1.5‰ is observed in the time interval spanning the *O. eurekaensis, A. delta* and early *P. pesavis* Zone. $\delta^{13}C$ values start to rise during the late Lochkovian and show a broad maximum with average values around 3.0‰ and peak values of 3.5‰ (Rauchkofelboden, Oberbuchach II, Fig. 6) in the Early Pragian *E. sulcatus* to early *P. kindlei* Zone. Values decline slightly during the late *E. kindlei*–early *P. pireneae* Zone and reach a second maximum in the earliest Emsian *P. kitabicus* Zone. Only the data from the Barrandov section (Fig. 3) are not in accordance with this observation and show a strong decline in $\delta^{13}C$ values during the *P. dehiscens* Zone which is equivalent to the *P. kitabicus* Zone (see Table 2). This discrepancy may be due to stratigraphic correlation. Walliser (1985; p. 230) pointed out the stratigraphic correlation problem between the earlier used Siegenian–Emsian boundary and the newly defined Pragian–Zlichovian boundary. In the Barrandov section, slumps and breccias mark the base of the Zlichovian. Therefore, a stratigraphic gap comprising most of the *P. kitabicus* Zone is assumed in the Barrandov section.

$\delta^{13}C$ values are between 0 and 1.0‰ during the time span of the Emsian *P. excavatus* to *P. inversus* zones with

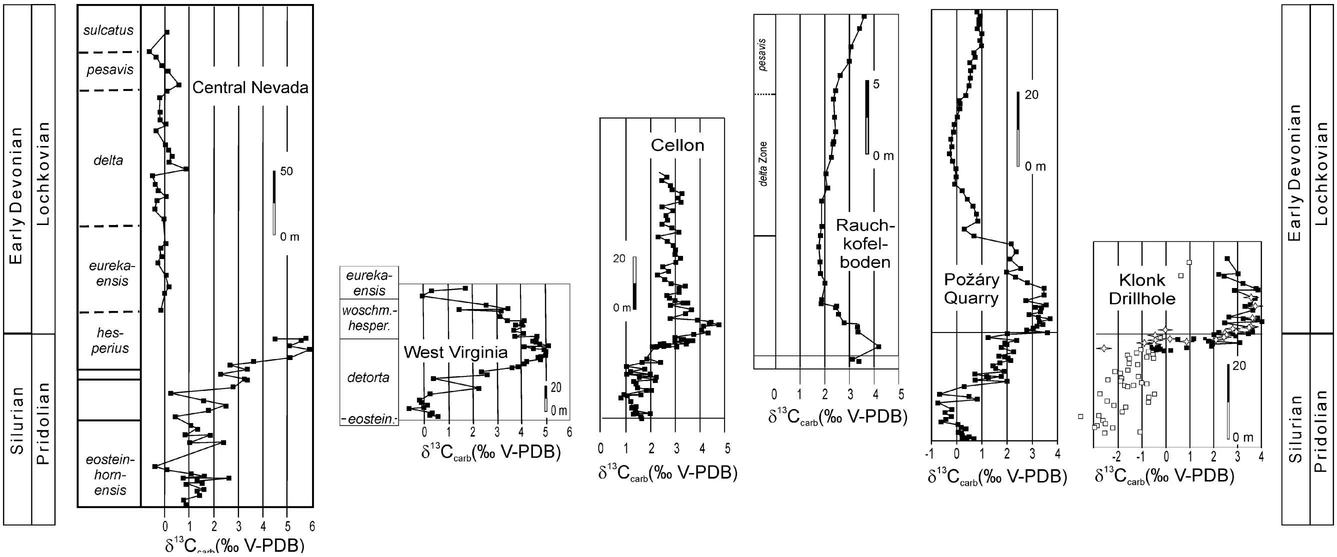


Fig. 11 The positive $\delta^{13}C$ excursion at the Silurian/Devonian boundary. Comparison of data from Laurentia (West Virginia and Central Nevada (Saltzmann 2002) and Europe (this paper). *Symbols* as in Fig. 2

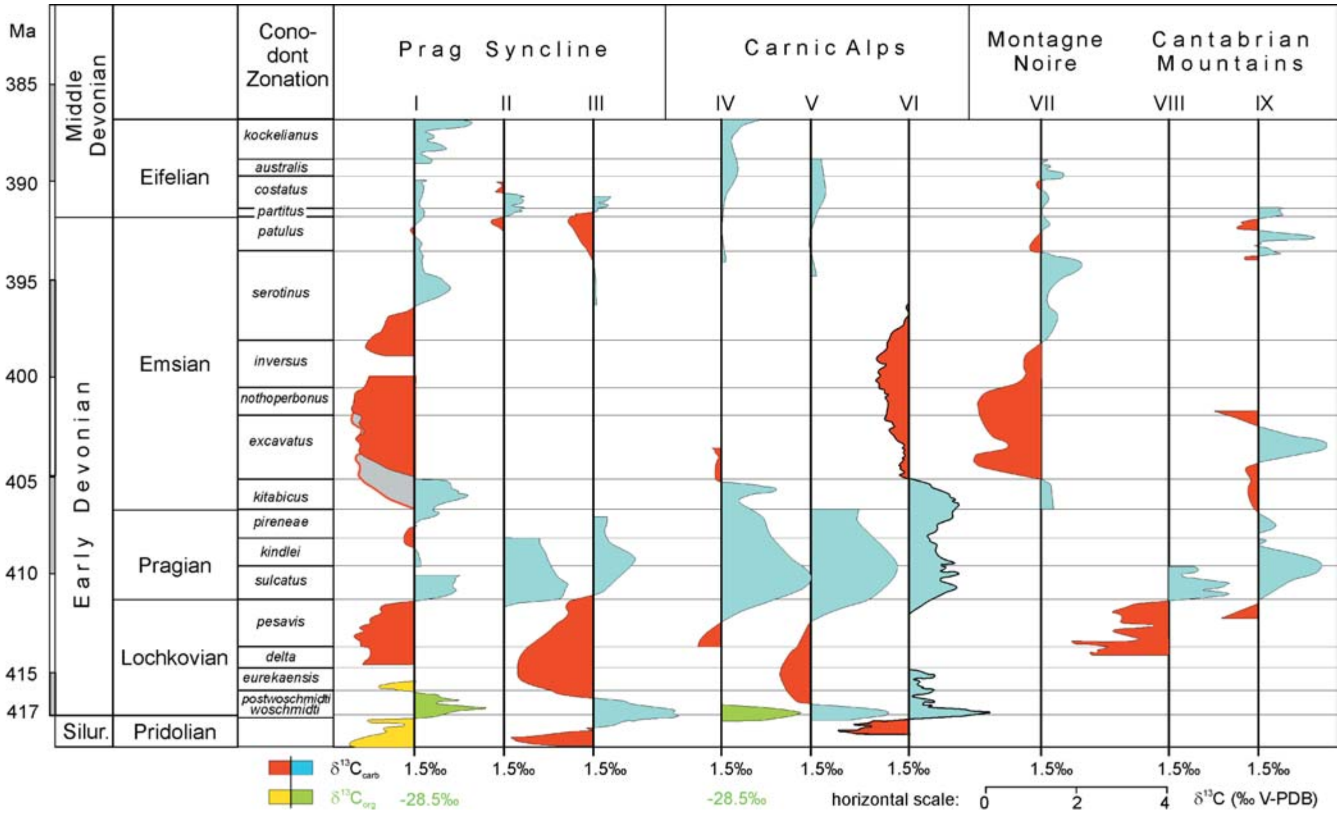


Fig. 12 Compilation of the inorganic and organic δ^{13}C record of all described sections. The running mean (five values) *curves* are plotted against the stratigraphic time table (German Stratigraphic Commission 2002). The 1.5‰ axes for inorganic and –28.5‰ for organic carbon are chosen for optical reasons. The following sections are incorporated: (*I*) Klonk, Černá Rokle; Zbuzanská, Barrandov, Červený Lom, Mostim, Hlubočepy, Jirásek; (*II*) Velká Chuchle, Škrábek; (*III*) Požáry, Prastav Quarry; (*IV*) Oberbuchach; (*V*) Rauchkofelboden, Wolayer Glacier; (*VI*) Cellon; (*VII*) Puech de la Suque; (*VIII*) Araúz Lebanza; (*IX*) La Vid, Santa Lucia

exception of the La Vid section in the Cantabrian Mountains. There, a distinct positive excursion with peak values as high as 2.6‰ is observed in the *I. celtibericus* Zone which correlates with the *P. excavatus* Zone (Fig. 9). It is a matter of debate whether this exception is due to stratigraphic correlation problems or it is caused by local isotopic variations.

δ^{13}C values increase by about 1‰ during the *P. serotinus* Zone (Fig. 4 and 10). Probably both peaks in the Červený Lom section (Prague, Fig. 4) and in the Col du Puech de la Suque section (Montagne Noire, Fig. 7) coincide to one single positive excursion within the *P. serotinus* Zone (Fig. 12). Peak values above 3.0‰ are observed in the Montagne Noire (Fig. 7).

δ^{13}C values of the late Emsian to Eifelian *P. patulus* to early T. *kockelianus* zones are between 1.0 and 2.0‰. Only in the Santa Lucia section of the Cantabrian Mountains a short positive excursion up to 2.7‰ is observed in massive reef limestones of the *P. patulus* Zone. Another small shift to heavier values occurs in the Prague Syncline during the *P. partitus* Zone (Figs. 12, 13).

Black shales of the late *kockelianus* to early *P. hemiansatus* Zone mark the Eifelian–Givetian boundary in most European sections. Therefore, only few unaltered $\delta^{13}C_{carb}$ data are available. A positive excursion is indicated in the Carnic Alps (Oberbuchach section, Fig. 6). In the Prague Syncline, limestones of the "dark interval" of the Jirásek section (Budil 1995; Hladíková et al. 1997) probably correspond to the black shales of the Kačák Member. $\delta^{13}C_{carb}$ data of own samples and from Hladíková et al. (1997) reach up to peak values of 3.0‰ in the "dark interval".

Causes for fluctuations in δ^{13}C during Pridolian to Eifelian

At steady-state, the weathering carbon input is balanced by the sum of organic carbon and carbonate burial (Kump and Arthur 1999). The organic fraction (f_{org}) of the total carbon burial flux can be calculated as:

$$f_{org} = (\delta_w - \delta_{carb})/\Delta_B$$

with $\delta_w = \delta^{13}C$ of riverine weathering flux, $\delta_{carb} = \delta^{13}C_{carb}$ of marine carbonates, Δ_B=isotopic difference between organic matter and carbonate deposited in the ocean. The significant positive correlation of $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ in the Požáry section corroborates that Δ_B is constant and close to 30‰ at the Silurian–Devonian boundary. This value was already used by Kump and Arthur (1999) and

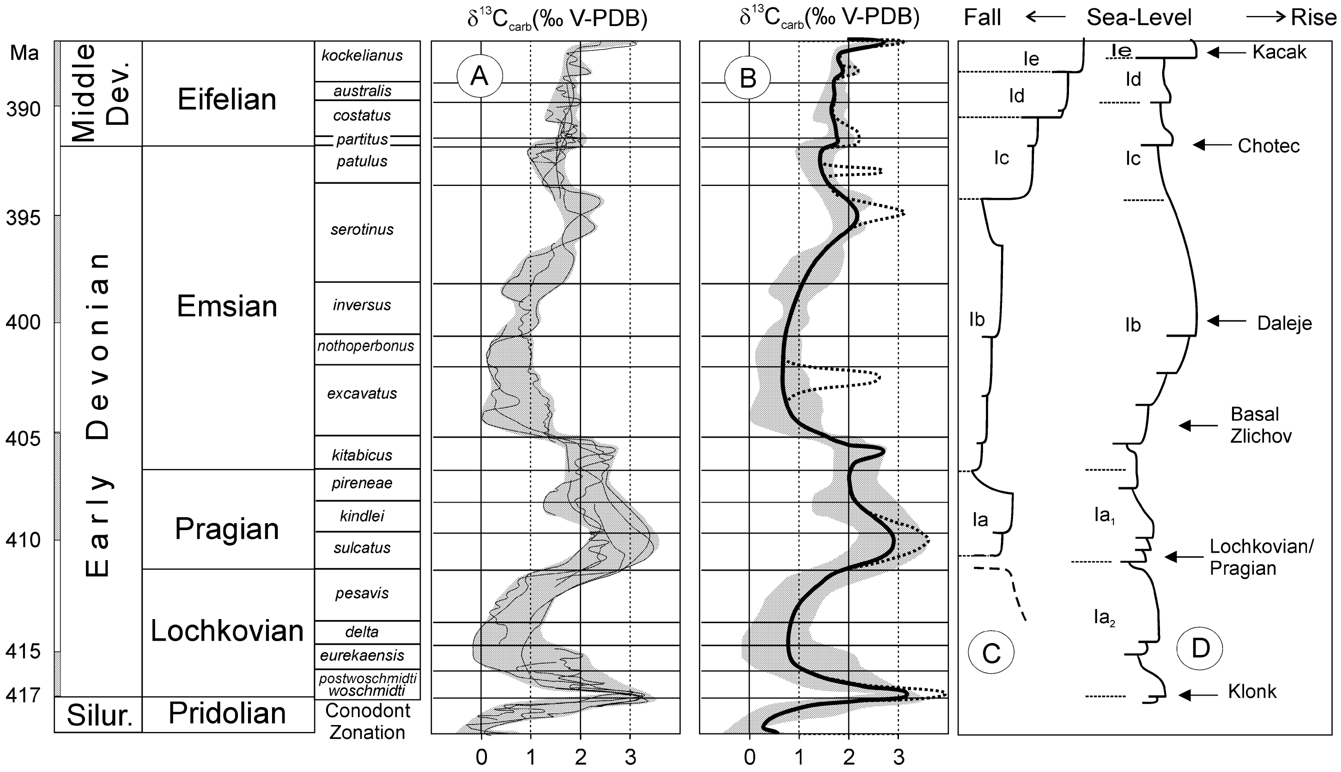


Fig. 13 Compilation of data and interpretation: *A* plot of all curves of Fig. 12, *shaded*: area covered by these curves; *B* resulting general isotope curve (*solid line*: mean values of all curves, *dotted line* maximum values and local excursions). *C* Sea level after Johnson et al. (1985, 1996). *D* Johnson's curve and events in the interpretation of Walliser (1996) and House (2002)

Saltzmann (2002), who calculated the amount of excess organic carbon burial needed for the 5‰ excursion at the Silurian–Devonian boundary. Besides changing burial rates of organic carbon and carbonates, the δ^{13}C value of the riverine input can be altered by the intensity of weathering and by the ratio of weathered carbonates versus black shales and silicate rocks (Kump et al. 1999).

Munnecke et al. (2003) proposed a model based on changing climate and its effect on oceanic surface currents, ocean stratification and deep water circulation. The authors pointed out, that planktic micro-organisms with calcareous tests were present in Palaeozoic times, but were of little significance for carbonate sedimentation compared with the Mesozoic and Cenozoic foraminifera and coccolithophorids. Most of the carbonate particles were produced by benthic organisms during Early Devonian. Therefore, Devonian carbonate particles probably mirror δ^{13}C ratios of the bottom water and not of oceanic surface waters. Additionally, early marine cements grew in pore water in contact with the bottom water.

Interestingly, samples from a basin setting are usually about >1‰ lighter in $\delta^{13}C_{carb}$ than shallow water derived carbonates of the same age (e.g. from "deep" to "shallow": Požáry, Rauchkofelboden and Cellon; Fig. 11). Obviously a vertical isotopic gradient of DIC (=dissolved inorganic carbon) is responsible for this difference.

Large bio-events are often combined with distinct excursions or shifts in δ^{13}C (end–Ordovician, Frasnian–Famennian, Permian–Triassic, Cretaceous–Tertiary) even if the causal connections are not always well understood. During the time span considered in this paper, several minor bio-events (Walliser 1996; House 2002) are documented (Fig. 13) some of which correlate to carbon isotope excursions (e.g., Klonk, Lochkovian/Pragian, Choteč [only locally], and Kačák) whereas others do not (Basal Zlichov, Daleje).

Another parameter of significance and often connected with the carbon cycle is sea level. The original Johnson curve (Johnson et al. 1985, 1996) and the interpretation of Walliser (1996) is depicted in Fig. 13. The Silurian/Devonian Boundary Event (Walliser 1985), which was named Klonk Event by House (2002), is defined at the type locality within a monotonous sequence of dark-gray platy limestones and interbedded calcareous shales (Haldil 1992), which indicate a sea-level highstand in the upper Pozary Formation close to the Silurian–Devonian boundary (Herten 2000). A rise of sea level is also documented in the Rhenohercynian and Saxothuringian zones of the European Variscids (Walliser 1985), in the Carnic Alps, in Sardinia and the Moroccan Meseta, where fine-grained dark platy limestones were deposited at the base of the Lochkovian. This transgression is also known from New South Wales, Australia, and SW Sibiria (Talent and Yolkin 1987).

Most Silurian sea level curves of Laurentia and Baltica show a regression and sea-level lowstand for the latest Silurian (Ross and Ross 1996; Witzke and Bunker 1996).This is the consequence of the final Caledonian collision which led to 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).

The Silurian–Devonian transition is marked by regressions in North America (Saltzmann 2002): widespread peritidal to supratidal carbonates in the Appalachian Basin, discontinuities in the Oklahoma Basin and progradation of shallow water limestones in central Nevada.

Significant faunal changes are documented for the Prague Syncline (for summary see Chlupáč and Hladil 2000), although faunistically the Silurian–Devonian transition appears to be gradual (Walliser 1985). Close to the boundary two blooming events of floating *Scyphocrinites* occurred, resulting in wide spread deposits of coarse grained echinoderm limestones.

The interpretation of the marked positive $\delta^{13}C$ excursion at the Silurian/Devonian boundary is ambiguous. The trend in sea level is ambivalent. Saltzmann (2002) assumed a global eustatic drop which exposed older Silurian carbonates and led to increased $\delta^{13}C$ values of the riverine flux δ_w. In contrast, a sea level rise is documented in several sections in Europe and Gondwana with organic rich sediments in the Prague Syncline and Carnic Alps region (Hladiková et al. 1997). A possible explanation for the $\delta^{13}C$ excursion is a combination of enhanced erosion of carbonates (changing δ_w), the erosion of the Caledonian Orogen, which is documented in Sr isotopes and lead to an increased nutrient flux and increased primary organic production (Saltzmann 2002).

The Lochkov/Prag Event (Walliser 1996) or Basal Prag Event (House 2002) is marked by a change in fauna and facies in the Prague Syncline (Chlupáč et al. 2000). Dark platy limestones and shales of the Radotin Formation are succeeded by light gray and red nodular Dvorce–Procop limestones or bioclastic grainstones and reef limestones (Koněpruy Ls.). This reflects a "rapid but not very large lowering of sea level", which is demonstrated to be globally well documented by Chlupáč and Kukal (1988). The marked broad positive $\delta^{13}C$ excursion started already in the uppermost Radotin Formation of the Prague Syncline and in the Late Lochkovian of the Carnic Alps and the Cantabrian Mountains and culminated during the Early Pragian. Obviously, the beginning of the $\delta^{13}C$ excursion corresponds with the onset of the regressive Lochkov/Prag Event (Hladíková et al. 1997).

The Pragian/Emsian boundary at the GSSP in Zinzil'ban Gorge, Uzbekistan was defined by the first appearance of *Polygnathus dehiscens* or *P. Kitabicus* (Yolkin et al. 2000). It corresponds to a global sea-level rise in the type area and is assumed to correlate with the base of Cycle Ib of Johnson et al. (1985). A correlation of the GSSP with sections in the Prague Syncline is still uncertain (Walliser 1996), where the first appearance datum (FAD) of *P. dehiscens* is not well established. The traditional Pragian/Zlíchovian boundary is significantly younger and corresponds to the Basal Zlíchov Event (Chlupáč and Kukal 1988; House 2002), which is marked by the onset of slumping and coarse grained bioclastic limestones and breccias in the south-eastern Prague Syncline and in the Carnic Alps (Oberbuchach II section). Due to litho- and biostratigraphical problems, the correlation of the $\delta^{13}C$ values between different sections and with the Pragian/Emsian boundary or the Basal Zlíchovian Event remains difficult.

The Daleje Event (Chlupáč and Kukal 1988), which is related to a gradual sea-level rise during the *P. inversus* Zone, does not affect the $\delta^{13}C$ record. The sea-level highstand which culminates during the deposition of the Daleje shales corresponds to a broad minimum in the $\delta^{13}C$ record. The positive excursion of the late P. serotinus Zone observed in the Prague Syncline and the Montagne Noire southern France might be correlated with the sea-level fall at the end of Cycle Ib (Johnson et al. 1985). Only minor local positive $\delta^{13}C$ excursions are observed in the Prague Syncline and the Cantabrian Mountains during the Choteč Event, which marks the onset of the Middle Devonian transgression. According to House (2000), the Choteč Event "has the first clear characters of many of the later Devonian events", such as deposition of dark micrites rich in planctonic or nektonic faunas suggestive of sea floor dysoxia or anoxia.

The Kačák Event (Budil 1995; House 2002) caused one of the sharpest stratigraphical boundaries in the Prague Syncline (Chlupáč and Kukal 1988), where the Choteč limestone is overlain by black siliceous shales. It is a typical black shale event that is connected with the global rise in sea-level at the base of Cycle Ie (curve of Johnson modified by Walliser 1996). Unfortunately, no limestones of this time interval are available from most of the sections in the Prague Syncline, except the Jirásek section, where limestones of the "dark interval" probably correlate with the Kačák shale (Budil 1995). $\delta^{13}C$ values reach 3.0‰ in the dark interval and at the base of the overlying breccia bed (Fig. 5). Black shales of the *ensis* Zone mark the Kačák event in the Carnic Alps (Fig. 6: Oberbuchach II), where $\delta^{13}C$ values increase in the limestones beds below the black shales and decrease immediately above them. Hence, the Kačák event corresponds probably to a distinct positive $\delta^{13}C$ excursion, but further studies are required.

Conclusion

The most interesting aspect is the obvious different behaviour of carbon isotopes during early Palaeozoic and late Palaeozoic to Cenozoic times. Black shales are the characteristic sediments during the Ordovician and Silurian. Positive excursions in $\delta^{13}C$ are observed, when grey and more coarse grained sediments were deposited, indicating a better ventilation of the oceans (Wenzel 1997; Marshall et al. 1997; Munecke et al. 2003). Later, in contrast, positive carbon isotope excursions usually correlate to sea-level highstands and deposition of organic rich sediments (Devonian: Buggisch 1991; Tournaisian: Buggisch 2001b, Cretaceous: Weissert et al. 1998; Tertiary: Berger and Vincent 1986).

The Pridolian to Eifelian is the time interval when this important change occurred. Most of the studied Early Devonian carbonates exhibit positive δ^{13}C excursions, which started already during regressions and are therefore not caused by the following transgression. A minor positive excursion (?) may be related to the Choteč transgression . Obviously, the positive δ^{13}C excursion of the transgressive Kačák event is in accordance with other late Palaeozoic carbon isotope trends.

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