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Carbon, oxygen and strontium isotope records of Devonian brachiopod shell calcite

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Abstract

Devonian brachiopod shells from North America, Spain, Morocco, Siberia, China and Germany were analysed for δ^{13}C, δ^{18}O and ^{87}Sr/^{86}Sr. The samples were screened for diagenetic alteration by means of cathodoluminescence, trace element chemistry (Sr, Mn, Fe) and scanning electron microscopy. 409 out of 1678 shells ranging from the middle Emsian to the middle Famennian were accepted as well-preserved.

^{87}Sr/^{86}Sr ratios start with values of 0.70860 in the Lochkovian and decline continuously to 0.70782 at the Emsian–Eifelian boundary. This decrease is attributed to a reduced riverine strontium flux caused by the termination of the Caledonian orogeny. For the Eifelian and Givetian, relatively uniform values between 0.70782 and 0.70784 are observed. ^{87}Sr/^{86}Sr ratios start to rise again in the late Givetian and reach a value of 0.70807 in the early Famennian. An enhanced continental delivery of strontium as consequence of tectonic uplift due to the Eovariscan orogeny, in combination with climatic warming, as suggested by the δ^{18}O record, is interpreted to be responsible for the shift to more radiogenic strontium isotope values. The carbon isotope curve shows four positive δ^{13}C excursions with amplitudes ranging from +2.0‰ and +3.5‰. The positive excursion observed in the *australis* Zone coincides with the deposition of the Bakoven black shale in New York state. The δ^{13}C excursion near the Eifelian–Givetian boundary is correlated with the Kacàk event while the two positive excursions in the late Frasnian and at the Frasnian–Fammenian transition are contemporaneous with the deposition of the Kellwasser horizons. All carbon isotope excursions are interpreted to be the result of increased burial of organic carbon.

The oxygen isotope record reveals short-term excursions in the late Givetian, late Frasnian and at the Frasnian–Famennian transition which are interpreted to result from changes in surface water temperature. The long-term evolution in δ^{18}O shows values of −2.8‰ to −3.5‰ in the Early and Middle Devonian to generally lower δ^{18}O values between −4.3‰ and −6.1‰ in the latest Givetian and Late Devonian. Assuming a δ^{18}O of Devonian seawater of −1‰ V-SMOW, Early and Middle Devonian δ^{18}O values translate into realistic palaeotemperatures (24 to 27 °C) for tropical to subtropical latitudes. In contrast, the δ^{18}O values of Late Devonian brachiopods indicate a shift to unrealistically warm palaeotemperatures (31 to 41 °C). The change in δ^{18}O of brachiopod calcite cannot be explained solely by a change in temperature, pH or by a secular decrease in δ^{18}O of seawater. A combination of

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climatic warming and a moderate decrease in δ^{18}O of seawater from the Middle to Late Devonian may account for the observed decrease in δ^{18}O of brachiopod calcite. However, this tentative interpretation is not confirmed by conodont apatite δ^{18}O data that translate into warm but realistic Late Devonian palaeotemperatures.

Keywords: Devonian; Carbon isotopes; Oxygen isotopes; Strontium isotopes; Brachiopods

1. Introduction

Carbon, oxygen and strontium isotopes have been intensively used to study secular isotopic variations of ancient ocean water. Oxygen isotope ratios of foraminiferal calcite were used to reconstruct the palaeotemperature history as well as the onset of the modern glaciations in the northern and southern hemispheres (Zachos et al., 1999). Carbon isotopes of benthic and planktonic foraminifera served as a proxy for the fertility of past oceans as well as an indicator for changes in the global carbon cycle (Holser, 1997; Kump and Arthur, 1999). Secular variations in ^{87}Sr/^{86}Sr of biogenic carbonate were interpreted to represent changes in the strontium fluxes (continental weathering vs. hydrothermal activity) that determine the strontium isotope ratio of the oceans (Veizer et al., 1997b) and were used as a correlation and dating tool (McArthur et al., 2001).

Low-magnesium calcite (LMC) marine cements (Carpenter et al., 1991) and especially shells of articulate brachiopods (Popp et al., 1986a; Brand, 1989; Grossman et al., 1993; Wenzel and Joachimski, 1996; Mii et al., 1999; Veizer et al., 1999) are the most commonly used fossil material in Palaeozoic isotope studies. Brachiopods are abundant in Palaeozoic shallow water sediments and secrete multi-layered shells composed of low-magnesium calcite that are resistant to diagenetic resetting of the primordial isotopic signatures. Isotope data for Devonian brachiopods were presented by Popp et al. (1986b), Veizer et al. (1986), Brand (1989), Bates and Brand (1991), Gao (1993), Diener et al. (1996) and Veizer et al. (1997a, 1999). The oxygen isotope data reported by the various authors show a large variance with δ^{18}O values ranging from −2‰ to −10‰. This variance cannot be explained by changes in palaeotemperature nor can a secular change in the oxygen isotope composition of seawater account for this significant spread.

The primary objective of this study is to present new isotope data for Devonian brachiopods that were carefully screened for diagenetic alteration. The strontium, oxygen and carbon isotope data will be used to constrain the Devonian isotope curves. Oxygen and

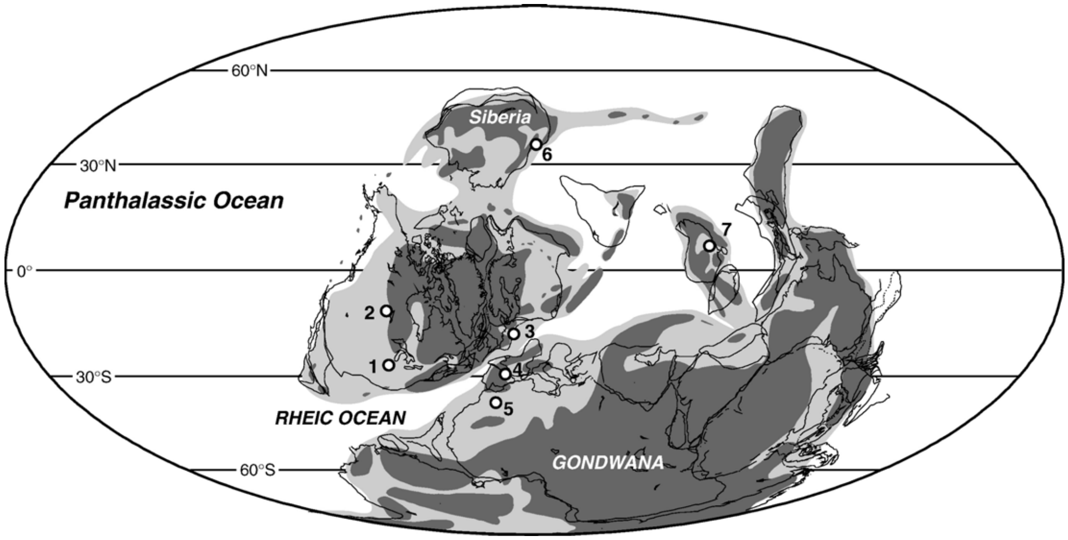


Fig. 1. Early Devonian palaeogeography after Scotese (1997). Sample locations are marked by circles: (1) Iowa (USA), (2) Manitoba (Canada), (3) Eifel Mts. (Germany), (4) Cantabrian Mts. (Spain), (5) Anti-Atlas (Morocco), (6) Altai-Salair (Siberia/Russia), (7) South China. Additional samples derived from Missouri (USA) and New York state (USA). Dark grey:landmass, light grey:shelf.

carbon isotope data will be discussed in the light of the palaeoclimatic evolution of the Devonian and with respect to potential changes in the Devonian carbon cycle.

2. Materials and methods

Brachiopods were collected from various sections in Morocco (Anti-Atlas), Spain (Cantabrian Mts.), Germany (Eifel Mts.), North America (Iowa, Manitoba), Siberia (Altai Mts./Salair area) and South China (Figs. 1 and 2). All shells ($n=1678$) were cut parallel to the plane of symmetry (longitudinal section) and cut slabs were slightly polished. The state of preservation of the brachiopod shells was assessed using cathodoluminescence microscopy (Technosyn 8200 MK II). Non-luminescent shells were further investigated by means of trace element analysis (Sr, Mn, Fe) and scanning electron microscopy (SEM). Recent brachiopods *Terebratella* and *Notosaria* (from New Zealand) and *Terbratalia* (from San Juan archipelago, USA) were analyzed for comparison.

Calcite powders for trace element and isotope analysis were collected using a microdrill (0.4 mm) from the secondary or prismatic tertiary layer of non-luminescent parts of the shells. For trace element analysis, 1 to 2 mg of shell calcite were dissolved with 1 ml 0.5 N HCl and brought to a final volume of 5 ml with distilled water after complete reaction. Strontium, manganese and iron concentrations were determined for 551 samples using ICP-AES (Spectroflame, University of Erlangen; Zeiss Plasmaquant, University of Halle). Reproducibility was calculated on replicate analyses of standards and was better than ±5% (1σ) for Sr, Mn and Fe.

For SEM analysis, transverse sections perpendicular to the plane of symmetry were carried out on selected shells ($n=86$). Longitudinal sections proved to be unsuitable for the characterisation of the shell ultrastructure, since the convex-concave shape of the secondary layer fibres can not be investigated. After polishing, the cut slabs were etched with 0.1 N HCl for 90 to 120 s, sputtered with gold and investigated using a Philips XL 30 scanning electron microscope. Recent brachiopods were etched for 50 s. Based on cathodoluminescence microscopy, trace element contents and preservation of the shell ultrastructure (SEM), 409 out of 1678 brachiopod shells were identified as diagenetically unaltered and accepted for oxygen, carbon and strontium isotope analysis.

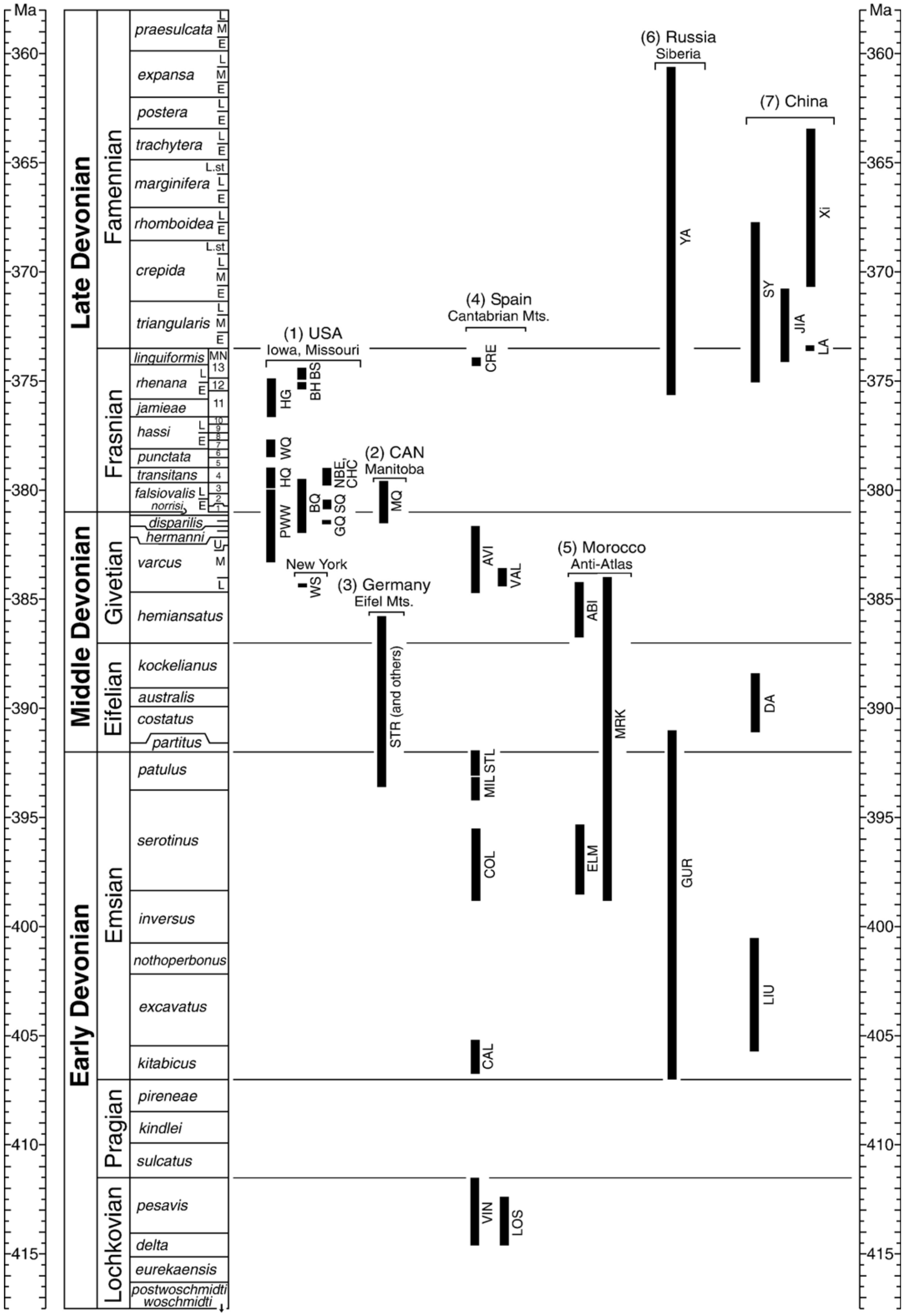
Oxygen and carbon isotope analyses were performed with a carbonate preparation line (Kiel device) connected online to a ThermoFinnigan 252 mass spectrometer. Oxygen and carbon isotope values are reported in ‰ relative to V-PDB by assigning a δ^{18}O value of −2.20‰ and a δ^{13}C value of +1.95‰ to NBS 19. Reproducibility of the isotope measurements was controlled by replicate analyses of laboratory standards and NBS 19 and was ±0.03‰ (1σ) for δ^{13}C and ±0.05‰ (1σ) for δ^{18}O. Palaeotemperatures were calculated using the equation given by O'Neil et al. (1969) and modified by Friedmann and O'Neil (1977):

$$10^3 \ln\alpha_{\mathrm{c-w}} = 2.78\frac{10^6}{T^2} - 2.89 \tag{1}$$

with $\alpha_{\mathrm{c-w}}$ being the fractionation factor between calcite and water and T the temperature in K. The exact function $10^3 \ln\alpha$ instead of the approximation via the permil fractionation was used in all calculations (see O'Neil, 1986).

For strontium isotope analysis, 5 to 10 mg of calcite powder were milled from the valves with a microdrill. All analysis were performed at the Department of Geology, Mineralogy and Geophysics of the Ruhr-University in Bochum (Germany) using a ThermoFinnigan 262 mass spectrometer. Analytical details concerning strontium extraction as well as strontium isotope analysis are given in Diener et al. (1996). Accuracy and reproducibility was monitored by replicate analysis of standards NIST (SRM) 987 and USGS EN-1. The mean ^{87}Sr/^{86}Sr value for NIST 987 and USGS EN-1 was $0.710228 \pm 12 \times 10^{-6}$ ($\pm 2\sigma$, $n=9$) and $0.709141 \pm 12 \times 10^{-6}$ ($\pm 2\sigma$, $n=10$), respectively. The ^{87}Sr/^{86}Sr values were normalized to a value of 0.710248 for NIST 987 and 0.709175 for EN-1 by adding $+31 \times 10^{-6}$ to the measured values (McArthur et al., 2001). The typical $2\sigma_{\mathrm{mean}}$ (standard error) for a single sample was better than $\pm 8 \times 10^{-6}$.

Isotope trend lines were calculated using the nonparametric locally weighted regression method "Locfit" (Loader, 1997, 1999). Locfit is the latest development of the ideas behind the locally weighted regression methods Lowess (Cleveland, 1979) and Loess (Cleveland and Devlin, 1988) which were used, e.g., by Howarth and McArthur (1997) and McArthur et al. (2001) for the calculation of the Phanerozoic strontium isotope curve. The output of the Locfit procedure is a "smoothed" curve, which keeps the local minima and maxima. Compared to other smoothing methods (e.g. running average) the locally weighted regression methods yield good results even with unevenly spaced data points. The carbon and oxygen isotope Locfits were calculated by dividing the data set into six and three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410
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Famennian
Frasnian
Givetian
Eifelian
Emsian
Pragian
Lochkovian
praesulcata
expansa
postera
trachytera
marginifera
rhomboidea
crepida
triangularis
linguiformis
rhenana
jamieae
hassi
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falsiovalis
norrisi
disparilis
hermanni
varcus
hemiansatus
kockelianus
australis
costatus
partitus
patulus
serotinus
inversus
nothoperbonus
excavatus
kitabicus
pireneae
kindlei
sulcatus
pesavis
delta
eurekaensis
postwoschmidti
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BQ
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NBE,
CHC
New York
WS
(2) CAN
Manitoba
MQ
(3) Germany
Eifel Mts.
STR (and others)
(4) Spain
Cantabrian Mts.
CRE
AVI
VAL
MIL
STL
COL
CAL
VIN
LOS
(5) Morocco
Anti-Atlas
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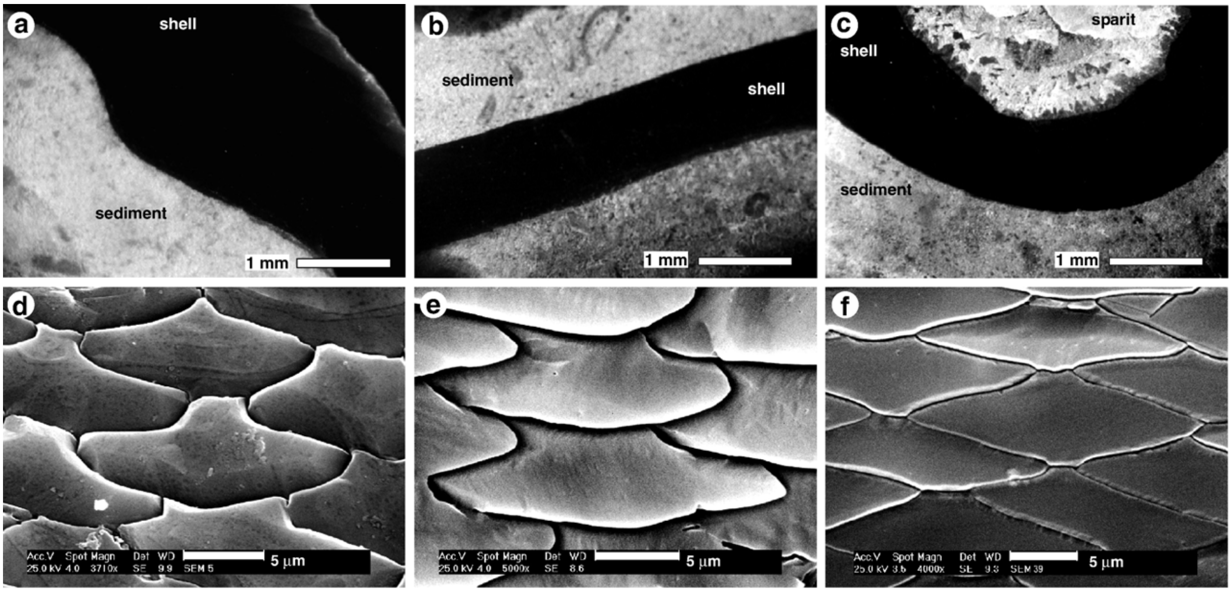

Fig. 3. (a–c) Cathodoluminescence photomicrographs of non-luminescent brachiopod shells. (a) Iowa, *Pseudoatrypa* sp. (sample BQ 78-2). (b) Russia, *Cyrtospirifer* sp. (sample YA 33-1). (c) Morocco, Pentamerida (sample MRK 19-3). (d–f): SEM photomicrographs of non-luminescent shells with well preserved microstructure of the rounded, convex-concave shaped calcite fibres forming the secondary shell layer (d) Iowa, *Rigauxia orestes* (sample from Bird Hill, BH). (e) Spain, *Plicathyris alejensis* (sample STL 4-7). (f) Morocco, *Atrypa* sp. (sample ABI 11-3).

overlapping segments, respectively. Individual Locfits were calculated for each of the segments and connected in the overlapping parts for the final curve. The strontium isotope Locfit was calculated in one step using all data points. All calculations were performed with the open source statistic software "R" (version 1.5.1, Ihaka and Gentleman, 1996).

3. Results

3.1. Preservation of brachiopod shells

3.1.1. Cathodoluminescence and scanning electron microscopy

CL microscopy was used as a first method for the identification of diagenetic recrystallisation of brachiopod calcite (e.g. Popp et al., 1986a; Grossman et al., 1993; Mii et al., 1999; Wenzel, 2000). Mn^{2+} is considered to be the main activator of an orange-coloured luminescence in calcite, whereas the incorporation of Fe^{2+} induces a dark red (dull) luminescence. Since Mn^{2+} and Fe^{2+} are only soluble under reducing conditions, an orange-coloured or dull luminescence is indicative for a diagenetic recrystallisation of brachiopod shell calcite. Fossil punctate shells and samples showing a bright yellow to dull luminescence were discarded. Examples of well-preserved, nonluminescent shells are shown in Fig. 3. Recent shells did not show any luminescence.

Selected non-luminescent shells from each sample locality were studied with SEM. The calcite fibres forming the secondary layer of well-preserved Devonian brachiopod shells show a convex-concave shape with rounded surfaces comparable to the ultrastructure of recent brachiopods (Fig. 3). This convex-concave structure is destroyed during diagenetic recrystallisation. The rounded surface of the calcite fibres is replaced by an angular shape and individual fibres amalgamate to larger,

Fig. 2. Stratigraphic range of sections sampled for brachiopod shells. Absolute age after STG (2002), relative length of standard conodont Zones from Weddige (1996), correlation of standard conodont Zones and Montagne Noire Zonation (MN) after Klapper and Becker (1998). Locations (alphabetical): ABI—Jebel Abiir, AVI—Aviados, BH—Bird Hill East, BQ—Buffalo Quarry, BS—Buseman Quarry, CAL—Caldas de Luna, CHC—Craghead Creek Quarry, COL—Colle, CRE—Crémenes Limestone (Esla area), DA—Dale, ELM—Jebel Maharch, GQ—Glory Quarry, GUR—Gur'evsk town, HG—Hackberry Grove, HQ—Hanneman Quarry, JIA—Jiangjiaqiao, LA—Laojiangchong of Xikuangshan, LIU—Liujing, LOS—Los Barrios de Luna, MIL—El Millar, MQ—Mafeking Quarry, MRK—Madène el Mrakib, NBE—New Bloomfield East, PPW—IPSCO well, SQ—State Quarry, STL—St. Lucia Village, STR—Collection Struve, SY—Shetianqiao, VAL—Valdoré, VIN—Viñayo, WQ—Williams Quarry, WS—Eighteen Mile Creek, Xi—Xikuangshan, YA—Yaya-Petropavalovskoye Village.

Table 1
Trace element chemistry of recent brachiopods and selection criteria for shells analyzed for stable isotopes in this study

	Sr (ppm)	Mn (ppm)	Fe (ppm)
Morrison and Brand (1986)	200–1400	4–450	20–700
Lepzelter et al. (data in Popp et al., 1986b)	739–2150	10–47	80–276
Brand et al. (2003)	450–1928	1–80 (max. 199)[a]	1–140 (max. 610)[a]
This study (n=9)	952–1373	3–48	30–382
Criteria for well-preserved brachiopod shells used in this study	≥500 ppm (≥325 ppm for ^{87}Sr/^{86}Sr)[b]	≤100 ppm	≤400 ppm

[a] Only very few samples in Brand et al. (2003) show concentrations of Mn>80 ppm and Fe>140 ppm.

[b] 10 out of 72 ^{87}Sr/^{86}Sr analysis were carried out with shells of Sr concentrations between 325 ppm and 500 ppm. Oxygen and carbon isotope ratios of these samples were discarded.

irregular packages of two or more fibres. In this case, individual fibres are only recognized as relics (see also Popp et al., 1986b; Samtleben et al., 2001). Some brachiopod groups, as for example Pentamerida, secrete a third shell layer composed of larger, prismatic calcite crystals. SEM cannot be used to identify diagenetic recrystallisation of these shells since the calcite prisms have no clearly distinguishable microstructure (Samtleben et al., 2001). Instead, growth bands frequently observed within the calcite prisms were taken as an indicator for a good preservation of the pentamerid shells.

3.1.2. Trace element contents

Most published studies on the isotope geochemistry of brachiopod shells used strontium, iron and manganese contents for the identification of diagenetic alteration (e.g. Popp et al., 1986b; Grossman et al., 1996; Veizer et al., 1999, among others). Recent brachiopod shells typically show low concentrations of Mn and Fe and high concentrations of Sr (Table 1). Diagenetic recrystallisation is expected to result in a decrease in Sr and increase in Mn and Fe (for theory see Brand and Veizer, 1980; Veizer, 1983a,b).

During this study, shells with Mn, Fe and Sr contents <100 ppm, <400 ppm and >500 ppm, respectively, were classified as well-preserved. Seventy-eight percent of the samples have Sr concentrations higher than 750 ppm and 90% of the samples have Mn contents below 50 ppm (Fig. 4). Ten out of 72 shells that were analysed for strontium isotopes show Sr concentrations ranging from 325 to 500 ppm (hatched area in Fig. 4a). The shells with low Sr concentrations belong to the genera *Pseudoatrypa* (Atrypida) and *Gypidula* (Pentamerida). Since strontium contents of other shells of these genera were up to 1230 ppm (*Pseudoatrypa*) and 1070 ppm (*Gypidula*), we exclude taxonomic differences in the Sr/Ca ratio as explanation for the low strontium contents. Additionally, the shells do not differ in their ^{87}Sr/^{86}Sr ratios in comparison to contemporaneous shells with strontium contents above 500 ppm. Since a diagenetic loss of strontium is expected to result in a change in ^{87}Sr/^{86}Sr, these low strontium contents are interpreted as primary values and the ^{87}Sr/^{87}Sr value of these shells were included in the final strontium isotope data set.

3.2. Strontium isotopes

The ^{87}Sr/^{86}Sr ratios of the brachiopod shells as well as the calculated Locfit curve are shown in Fig. 5. Samples from the Lochkovian have ^{87}Sr/^{86}Sr ratios

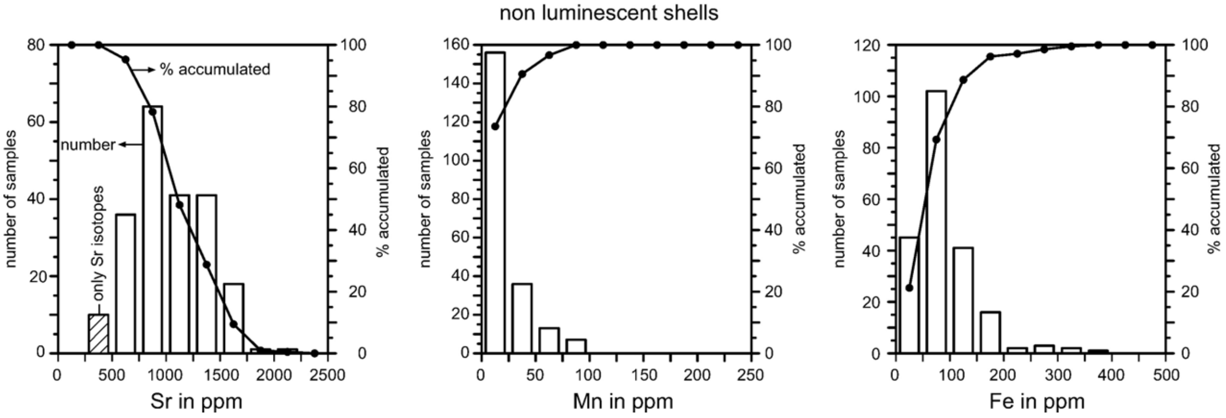

Fig. 4. Trace element contents (Sr, Mn and Fe) of non-luminescent brachiopod shells (n=212). Left axis is number of samples; right axis gives accumulated percentage (curve). The hatched bar corresponds to samples only investigated for strontium isotopes (see text for details).

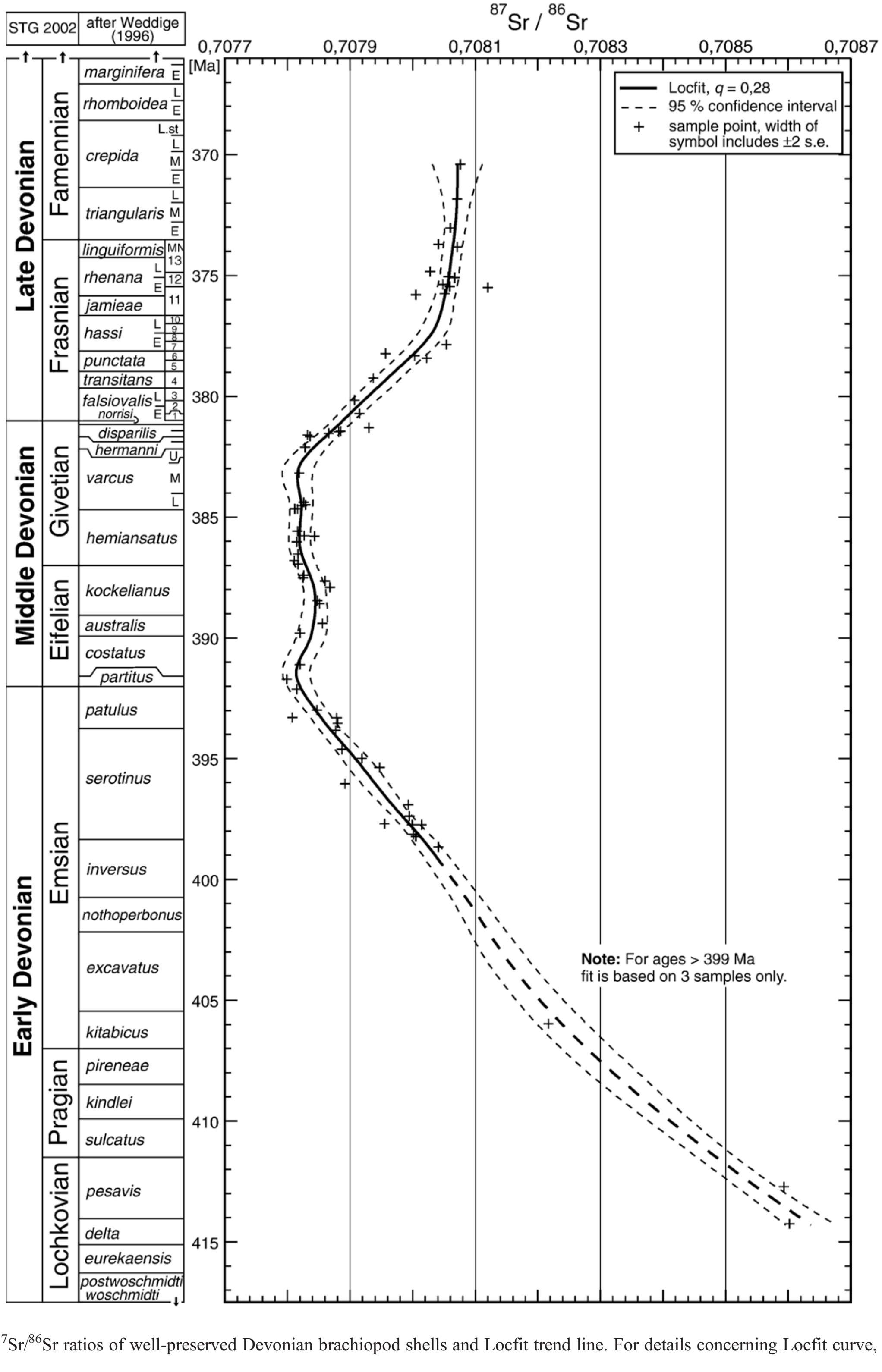

Fig. 5. ^{87}Sr/^{86}Sr ratios of well-preserved Devonian brachiopod shells and Locfit trend line. For details concerning Locfit curve, see text.

around 0.70860. Brachiopod shells from the Emsian are less radiogenic and indicate a continuous decrease in $^{87}Sr/^{86}Sr$ during the Early Devonian. Relatively uniform $^{87}Sr/^{86}Sr$ values around 0.70782 are measured from the early Eifelian up to the Middle *varcus* conodont Zone. $^{87}Sr/^{86}Sr$ starts to increase in the Upper *varcus* Zone and reaches values around 0.70807 in the early Famennian. The $^{87}Sr/^{86}Sr$ data presented in this study correspond to the lowest $^{87}Sr/^{86}Sr$ values reported by Veizer et al. (1999) and the Locfit curve is similar to the Lowess curve of McArthur et al. (2001).

3.3. Carbon isotopes

Carbon isotope values as well as the calculated Locfit curve are shown in Fig. 6. The $\delta^{13}C$ curve for the early part of the Emsian (older than late *inversus* Zone) is based on five data points. Therefore, this part of the

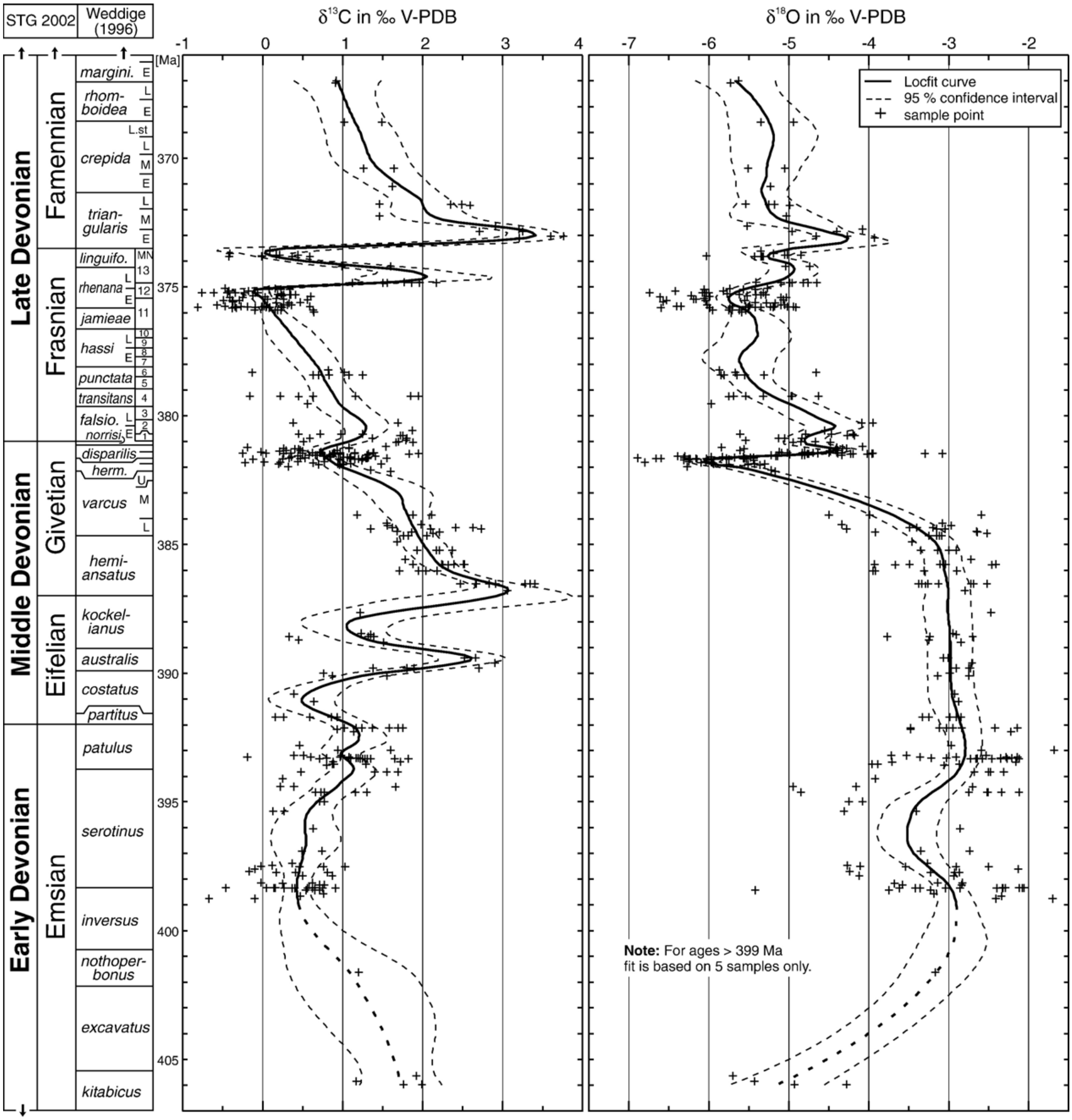

Fig. 6. $\delta^{13}C$ and $\delta^{18}O$ data of well-preserved Devonian brachiopod shells. For explanation, see text.

curve will not be discussed in detail. In the late Emsian, the $\delta^{13}C$ Locfit curve starts around +0.5‰. A minor increase to +1.0‰ is observed in the latest Emsian with a subsequent decrease to +0.5‰ in the earliest Eifelian. In the *australis* Zone, a positive excursion to values of +2.6‰ occurs. A second positive excursion with maximum $\delta^{13}C$ values around +3.0‰ is observed near the Eifelian–Givetian boundary. During the Givetian and early Frasnian, the curve declines gradually. The minor negative excursion in the latest Givetian is not a real excursion. The shape of the curve is influenced by the high density of data points in this time period. Since the density of data points in the middle Givetian and early Frasnian is very sparse, this negative excursion is rather an artifact from the Locfit calculation than an event in the carbon cycle. In the late *rhenana* Zone, the $\delta^{13}C$ curve rises to +2.0‰ followed by a decrease to values around 0‰ in the *linguiformis* Zone. A fourth positive excursion with a maximum at +3.5‰ occurs immediately above the Frasnian–Famennian (F-F) boundary. During the early Famennian, carbon isotope ratios decrease and reach values around +1.0‰ in the *marginifera* Zone.

Except for the excursion in the late Frasnian, all excursions were measured on brachiopod shells taken from continuous sections. The $\delta^{13}C$ excursions observed in the late Frasnian are based on the analysis of shells from several sections. Since the biostratigraphic dating of these sections is reasonably good, it is unlikely that the positive excursion in $\delta^{13}C$ is an artifact of sample origin or from the fit calculation. All sampled successions indicate an open marine depositional environment, as indicated by a diverse fauna composed of corals, crinoids, bryozoans, bivalves, gastropods, stromatoporoids and brachiopods. In addition, we observed no systematic difference in the $\delta^{13}C$ values of shells of different genera.

3.4. Oxygen isotopes

The $\delta^{18}O$ Locfit curve starts with values between −2.8‰ and −3.5‰ in the late Emsian. From the base of the *patulus* Zone to the Lower *varcus* Zone, the Locfit curve shows relatively uniform values around −3.0‰ with the absolute $\delta^{18}O$ values ranging from −2.1‰ to −4.0‰ (Fig. 6). At the base of the Lower *varcus* Zone, the $\delta^{18}O$ curve declines until a minimum value of −6.1‰ is reached in the *hermanni* Zone. In the *disparilis* Zone, the curve rises to values around −4.5‰ and decreases to about −5.5‰ during the Frasnian. A positive excursion with a maximum at −4.9‰ and a subsequent decrease to −5.3‰ is observed in the Late *rhenana* Zone. Across the F-F boundary, the Locfit curve shows another positive excursion with an amplitude of about 1‰. The Locfit curve reaches a maximum value at −4.3‰. Following, $\delta^{18}O$ decreases to values between −5.2‰ and −5.6‰ in the early Famennian.

4. Discussion

4.1. Strontium isotopes

The $^{87}Sr/^{86}Sr$ ratio of the ocean is driven mainly by (i) continental runoff and ground-water runout which supplies radiogenic ^{87}Sr to the ocean, and (ii) seawater–oceanic crust interaction particularly at mid ocean ridges that depletes seawater in ^{87}Sr due to the low $^{87}Sr/^{86}Sr$ ratio of fresh basalts. Additional factors influencing the $^{87}Sr/^{86}Sr$ of seawater are co-precipitation of strontium in sedimentary minerals, reflux of strontium during carbonate diagenesis, enrichment of ^{87}Sr in carbonates during metamorphism, and subduction of sediments and entrapped marine waters (cf. Veizer, 1983b; François et al., 1993; Jones and Jenkyns, 2001). The $^{87}Sr/^{86}Sr$ ratio of present-day seawater is 0.709175 (McArthur, 1994) and appears to be homogenous throughout the World's oceans due to the long residence time of strontium in the oceanic reservoir (2.4×10^6 years, Jones and Jenkyns, 2001). Since the $^{87}Sr/^{86}Sr$ ratio of seawater is incorporated into brachiopod calcite without any significant isotope fractionation (Brand et al., 2003), the strontium isotope record derived from brachiopod calcite can be used to reconstruct the $^{87}Sr/^{86}Sr$ of past oceans.

The shape of the Devonian $^{87}Sr/^{86}Sr$ curve can be interpreted as the result of one or a combination of the processes mentioned above. In most studies, the marine strontium isotope ratio is related to the riverine strontium flux (e.g. Raymo, 1991; François et al., 1993; Bruckschen et al., 1999; Korte et al., 2003). Short-term (5 to 13 Ma) negative excursions in $^{87}Sr/^{86}Sr$ have been attributed to enhanced hydrothermal activity (Jones and Jenkyns, 2001).

The final closure of the Iapetus Ocean and the formation of Euramerica occurred in the Pridoli as consequence of continent–continent collisions between Laurentia, Avalonia and Baltica (Golonka, 2000). The final phase of Caledonian tectonic activities is dated into the Early Devonian (Pragian and Emsian, "Acadian Phase" after McKerrow et al., 2000). The equatorial position of this newly formed mountain range will have favoured intense chemical weathering, since weathering is more intensive in warm and humid climates (White and Blum, 1995). This is expressed by a maximum in the

^{87}Sr/^{86}Sr curve at the Silurian–Devonian boundary. The decrease in ^{87}Sr/^{86}Sr during the Early Devonian correlates relatively well with the end of the Caledonian orogeny (Figs. 5 and 7) and can be explained by decreasing exposure and weathering of ^{87}Sr-rich crustal rocks.

The Eifelian and early Givetian time intervals are characterised by relatively uniform ^{87}Sr/^{86}Sr values which are explained by a balance of the riverine- and mantle-derived strontium flux. The strontium isotope curve presented by McArthur et al. (2001) shows an abrupt shift in the slope of the ^{87}Sr/^{86}Sr curve near the Emsian–Eifelian boundary which was attributed by McArthur et al. (2001) to problems with the Devonian time model (Young, 1996). Our data show a more gradual change in the slope, which in part may be related to the different time model used in this study (STG, 2002). The observed change in the slope of the strontium isotope curve could be related to an increase of the mantle strontium flux. Indications of increased sea-floor spreading and hydrothermal activity can be inferred from the sea-level curve (see Fig. 8b) which shows significant transgressions in the late Emsian and early Eifelian (T-R cycles Ic and Id, Johnson et al., 1985; Johnson and Sandberg, 1988). The sea-level rises are interpreted to have reduced the continental areas exposed to weathering which may have reduced the riverine strontium flux. Rowley (2002) presumed a constant production rate of oceanic crust and hydrothermal activity for the last 180 Ma. If this assumption is valid, other processes must have been responsible for the recorded changes in the sea level, pCO$_2$ and ^{87}Sr/^{86}Sr of seawater. Since no data are available concerning the nature of such processes, this issue will not be discussed further.

An increase in the ^{87}Sr/^{86}Sr Locfit curve starts in the Middle *varcus* conodont Zone. According to Johnson et al. (1985), a prominent, long-term rise in sea level (Taghanic transgression) started in the upper part of Middle *varcus* Zone (base of T-R cycle IIa, Johnson et al., 1985), which was interpreted to be the result of enhanced spreading. Intensified spreading should have resulted in an increased flux of low radiogenic, mantle-derived strontium. Consequently, a decrease in the marine strontium isotope ratio is expected which is opposite to the observed trend in ^{87}Sr/^{86}Sr. On the other hand, the Eovariscan orogeny may have uplifted ^{87}Sr-rich continental crust and exposed it to weathering. This collisional event is dated to have occurred in late Frasnian to Famennian times and led to the formation of mountain chains including the Ellesmerian Fold Belt, the Antler orogen, part of the Appalachian orogen as well as parts of the Hercynian (Variscan) Belt in Europe and northern Africa (Piqué et al., 1993; Murphy and Keppie, 1998; Golonka, 2000; Matte, 2001; Echarfaoui et al., 2002). The comparison of the ^{87}Sr/^{86}Sr curve with the δ^{18}O curve shows that the shift in ^{87}Sr/^{86}Sr occurs in the Middle *varcus* Zone, shortly after a major decrease in the oxygen isotope ratios. As will be discussed below, the lower δ^{18}O values in the late Givetian and Late Devonian are in

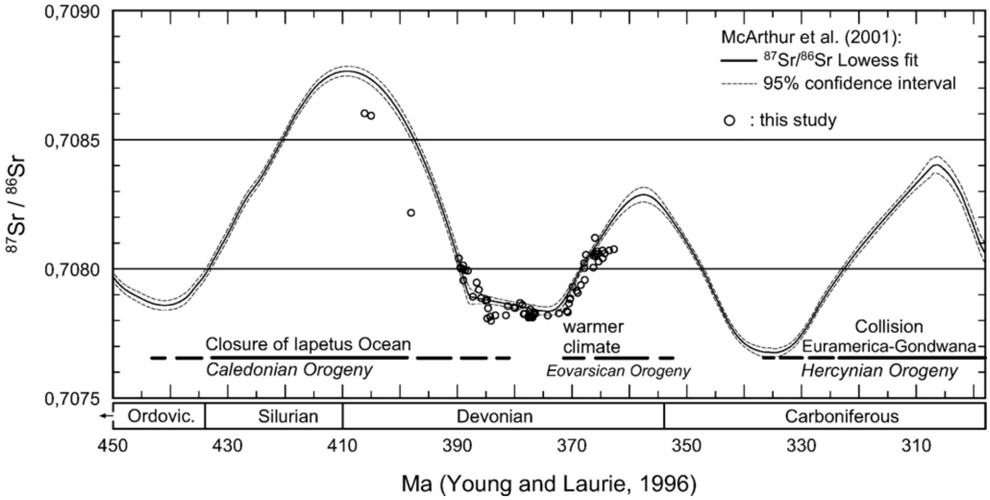

Fig. 7. ^{87}Sr/^{86}Sr values (this study) compared with ^{87}Sr/^{86}Sr curve of McArthur et al. (2001). Major plate tectonic events after McKerrow et al. (2000) and Golonka (2000). Note that time chart used in this figure is from Young and Laurie (1996). Conversion of STG (2002) to Young and Laurie (1996) was performed by linear interpolation between stage boundaries taking into account the differences in length of conodont Zones used in both charts (Weddige, 1996; Young, 1996).

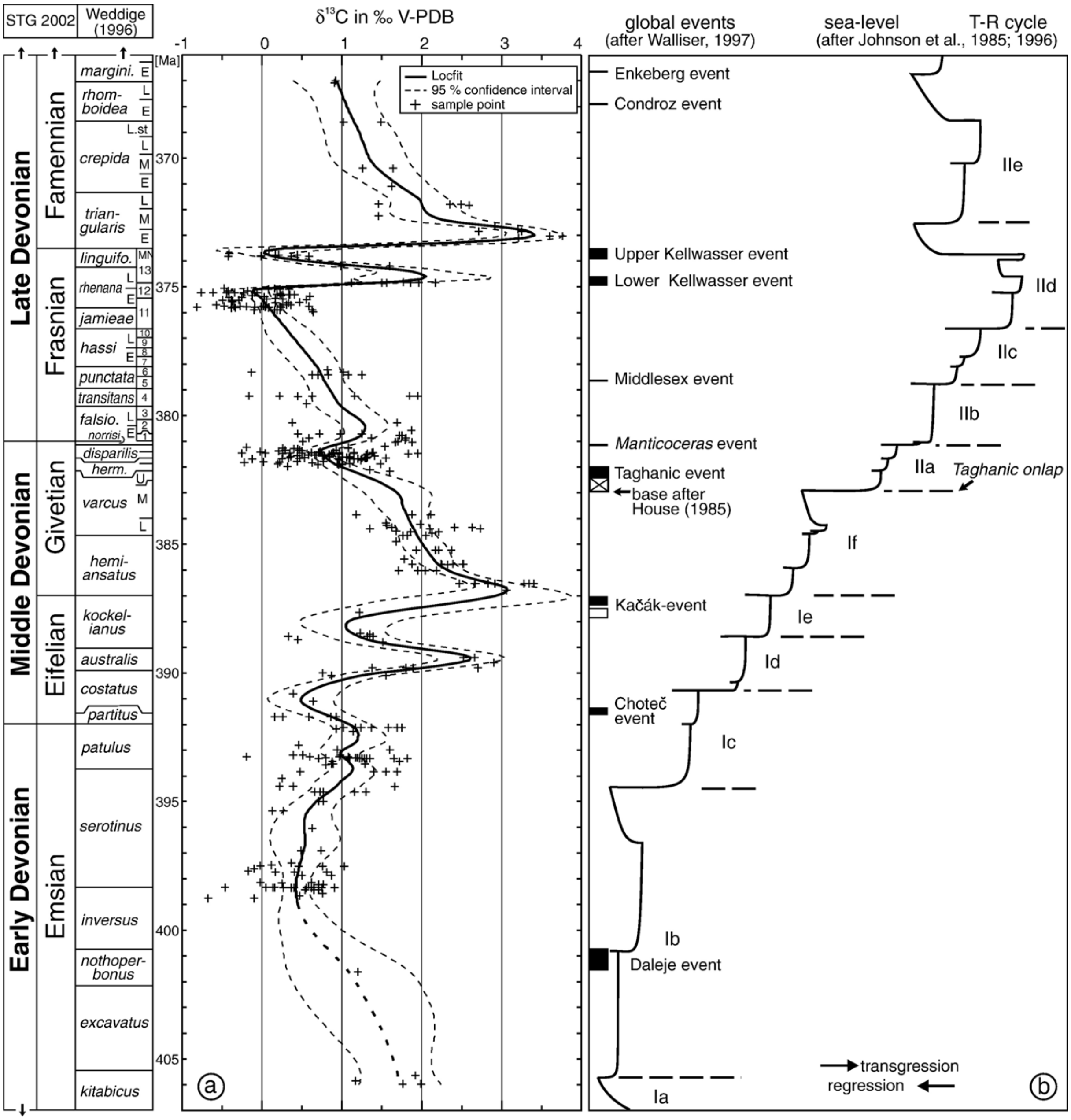

Fig. 8. (a) δ^{13}C Locfit curve, (b) Devonian sea-level curve and global events (Walliser, 1997). Sea-level curve (Johnson et al., 1985; Johnson and Sandberg, 1988) was adjusted to the STG (2002) time scale and the relative length of conodont Zones (Weddige, 1996). Revisions of the sea-level curve (Johnson et al., 1986; Johnson and Klapper, 1992; Johnson et al., 1996) were considered. Note that timing of some events differs between different authors (e.g. base of the Taghanic event).

part interpreted as indicative of higher palaeotemperatures. A warmer climate is interpreted to have intensified enhanced chemical weathering increasing the flux of ^{87}Sr to the oceans. This was probably enhanced by the continuous northern drift of Gondwana (Scotese, 1997) which gradually exposed larger areas to warmer temperatures in low latitudes.

4.2. Carbon isotopes

Brachiopods are generally assumed to secrete shell calcite in carbon isotopic equilibrium with seawater. However, studies on the isotopic fractionation between the carbon isotope composition of seawater ($\delta^{13}C_{DIC}$) and δ^{13}C of the brachiopod calcite are ambiguous.

While some studies suggest that shell calcite is secreted in near-isotopic equilibrium with seawater (Carpenter and Lohmann, 1995; Rahimpour-Bonab et al., 1997; Brand et al., 2003), others observed a significant kinetic fractionation effect (Auclair et al., 2003) or do not provide unambiguous results (Buening and Spero, 1996). The only study which determined $\delta^{13}C_{DIC}$ of ambient marine waters as well as $\delta^{13}C$ of brachiopod calcite (Rahimpour-Bonab et al., 1997) suggests equilibrium fractionation during secretion of brachiopod calcite. In general, the majority of the published studies suggest that recent brachiopods secrete calcite in carbon isotopic equilibrium with ambient seawater and that the $\delta^{13}C$ of fossil shells can be used to trace changes in the carbon isotope ratio of the oceanic carbon reservoir. Four carbon isotope excursions are observed in the $\delta^{13}C$ Locfit curve (Figs. 6 and 8) and these will be discussed in chronological order in the following paragraphs.

4.2.1. Eifelian (australis Zone)

The first excursion starts with a $\delta^{13}C$ value of +0.5‰ at the end of the *costatus* Zone and reaches a maximum at +2.6‰ in the *australis* Zone. Since this increase in $\delta^{13}C$ was measured only on brachiopods from the Eifelian Hills (Germany), the question arises whether this excursion represents a global signal. An isolation of the epicontinental sea bordering the Old Red continent to the South could account for the positive excursion in $\delta^{13}C$. A higher nutrient input from continental areas could have stimulated enhanced productivity which would have enriched ^{13}C in surface waters due to the export of isotopically light organic carbon to the lower water column and sediments. However, there is no palaeogeographic evidence to support such a scenario. The depositional environment of the Middle Devonian of the Eifelian Hills is interpreted as an outer shelf setting with the deposition of platform margin carbonates (Struve et al., 1997, p. 132). In addition, no time-equivalent organic carbon-rich deposits are known from this area that could give evidence for enhanced burial of organic carbon. Black shales of *australis* Zone age (Bakoven Shale, Marcellus Subgroup) are developed in western New York state that are interpreted to have been deposited under dysoxic to anoxic conditions (Klapper, 1981). The coincidence of black shale deposition in New York state and the positive $\delta^{13}C$ excursion let us assume that the excursion could be of global significance.

This positive $\delta^{13}C_{carb}$ excursion zone has an estimated duration of around 1 Ma. For longer time intervals (>0.1 Ma), the carbon isotopic composition of the ocean is controlled by the isotopic composition of the weathering flux ($\delta^{13}C_w$), the organic carbon burial fraction (f_{org}), and the isotopic difference between organic and inorganic carbon ($\Delta_B = \delta^{13}C_{org} - \delta^{13}C_{carb}$) (Kump, 1991; Kump and Arthur, 1999). According to Kump (1991), the organic carbon burial fraction on total carbon burial can be calculated by

$$f_{org} = \frac{(\delta^{13}C_w - \delta^{13}C_{carb})}{\Delta_B} \qquad (2)$$

Assuming $\Delta_B = -30$‰ and $\delta^{13}C_w = -5$‰ (cf. Joachimski et al., 2002), the increase in $\delta^{13}C_{carb}$ from +0.5‰ to a maximum of +2.6‰ indicates an increase of the organic carbon burial fraction from 0.18 to 0.25 (+36%).

4.2.2. Eifelian–Givetian boundary

A +2‰ excursion in $\delta^{13}C_{carb}$ was measured at the Eifelian–Givetian transition on brachiopods from the Anti-Atlas in southern Morocco (Section Madène el Mrakib). The $\delta^{13}C$ maximum occurs just above the “*Drotops*” horizon, a level which is characterized by a mass occurrence of the trilobite *Drotops megalomanicus*. Only one *Drotops* horizon is developed at the studied section at Jebel el Mrakib. However, two *Drotops* horizons are observed in the vicinity around Jebel Issimour. Conodonts from a sample taken 14 m below the *Drotops* horizon at Jebel el Mrakib indicate a *kockelianus* Zone age (K. Weddige, pers. comm.). Brachiopods (*Quiringites* cf. *elegans* and *Cyrtinopsis* sp.) from above the $\delta^{13}C$ maximum suggest an Eifelian age (U. Jansen, pers. comm.). According to Struve (1995, p. 99), the *Drotops* horizons are dated as middle to late Eifelian in age (*australis* to *kockelianus* Zone). In a section 8 km east from Madène el Mrakib (Aferdou el Mrakib), the *Drotops* horizon was dated as early Givetian with the Eifelian–Givetian boundary placed immediately below the horizon (Fig. 10 in Kaufmann, 1998). Based on these various age assignments, the excursion in $\delta^{13}C$ occurs either in the latest Eifelian or earliest Givetian. This carbon isotope excursion has been confirmed by other studies (Pawellek and Veizer, 1992; cited in Holser et al., 1996, p. 70; Hladikova et al., 1997; Buggisch and Joachimski, this volume).

A facies change from light grey coloured grainstones to black, fine grained mud and wackestones is observed 4 m below the *Drotops* level in section Madène el Mrakib. Contemporaneous facies changes and the occurrence of black shales are reported from many localities in Morroco (cf. Kaufmann, 1998; Bultynck and Walliser, 2000), Bohemia (Chlupac and Kukal, 1986), Spain (Truyols-Massoni et al., 1990), New York (Oatka Creek Shale, Kirchgasser et al., 1997) and Germany (Odershausen Kalk, Walliser, 1985; Struve et al., 1997).

This event has been named the Kacàk event (House, 1985) and been dated at the end of the Eifelian (Walliser, 1997; House, 2002). The Kacàk event is often interpreted in context with a eustatic sea-level rise (T-R cycle Ie, Johnson et al., 1985). During the transgression, dysoxic to anoxic conditions favoured the enhanced sedimentation of organic carbon in the deeper waters which is documented by the recorded positive excursion in δ^{13}C. By assuming $\Delta_B = -30‰$ and $\delta^{13}C_w = -5‰$, the positive shift in δ^{13}C indicates an increase of organic carbon burial on total carbon burial from 0.20 to 0.27 (+33%).

4.2.3. Frasnian–Famennian transition

The Locfit curve shows two positive δ^{13}C excursions in the late Frasnian (Late *rhenana* Zone) and across the F-F boundary with amplitudes of +2.5‰ and +3.5‰, respectively. These excursions correspond to carbon isotope excursions measured on whole rock samples that were shown to occur globally in conjunction with the sedimentation of the Lower and Upper Kellwasser horizons (Joachimski and Buggisch, 1993; Joachimski et al., 2002; Stephens and Sumner, 2003). An increase in the organic carbon burial fraction from 0.17 to 0.23 (+40%) is calculated for the +2‰ excursion in the late Frasnian. The +3.5‰ excursion observed across the F-F boundary requires an increase in the organic carbon burial fraction from 0.17 to 0.28 (+70% increase). According to Joachimski and Buggisch (2002), the enhanced burial of organic carbon resulted in a decrease of atmospheric $p\text{CO}_2$ that was interpreted to have culminated in global climatic cooling. Using numeric modelling, Goddéris and Joachimski (2004) suggested that enhanced organic carbon burial could only be achieved by a higher phosphate flux to the oceans as consequence of intensified continental weathering.

4.3. Oxygen isotopes

The oxygen isotope record shows a long-term trend with high δ^{18}O values around −3‰ encountered in the Early Devonian, Eifelian and early Givetian, a significant decrease in δ^{18}O in the late Givetian to early Frasnian and low δ^{18}O values around −4.5‰ to −6‰ in the late Frasnian and Famennian. Superimposed are a negative δ^{18}O excursion in the late Givetian and two positive δ^{18}O excursions in the late Frasnian and at the F-F boundary (Fig. 6). The oxygen isotope record can be used to reconstruct the palaeotemperature history of the Devonian in case that brachiopod calcite was secreted in thermodynamic isotope equilibrium with seawater and in case that the oxygen isotopic composition of Devonian seawater can be constrained.

The issue whether brachiopod calcite is secreted in oxygen isotopic equilibrium with seawater has been addressed by several studies. Lowenstam (1961), Buening and Spero (1996), James et al. (1997) and Brand et al. (2003) conclude that brachiopod calcite is secreted in thermodynamic equilibrium with seawater. Carpenter and Lohmann (1995) observed that the secondary shell layer is secreted in near-isotopic equilibrium but that large intra-specimen variability in δ^{18}O may limit the use of brachiopod shells as a precise temperature indicator. Comparable observations were made by Curry and Fallick (2002). Rahimpour-Bonab et al. (1997) observed that brachiopod δ^{18}O values were mostly heavier than equilibrium values. A significant kinetic fractionation effect on the oxygen isotope composition of the recent brachiopod *Terebratalia transversa* was reported by Auclair et al. (2003). Temperatures calculated from δ^{18}O values of recent brachiopods investigated in this study (for details see Table 2) show a good agreement with mean annual water temperature suggesting that shell calcite was secreted in isotopic equilibrium. In conclusion, although there are controversial results with respect to equilibrium secretion of brachiopod shell calcite, we assume that the shells of the Devonian brachiopods were secreted in isotopic equilibrium. This assumption is supported by the study of Lee and Wan (2000) that observed no species-specific differences in δ^{18}O of several Middle Devonian brachiopod species.

Table 2
Stable isotopic composition of recent brachiopods from offshore Christchurch/Dunedin (New Zealand)

Sample	Species	$\delta^{18}O_{carb}$ (‰ V-PDB)	$\delta^{18}O_w$ (‰ V-SMOW)	T_{calc} (°C)	T_{mean} (°C) (Stephens et al., 2002)
FC 1(1)	*Terebratella sanguinea* (endopunc.)	0.97	0	11.5	10 to 11
FC 1(2)	*Terebratella sanguinea* (endopunc.)	0.95	0	11.6	
F 1(1)	*Notosaria nigricans*	1.33	0	10.0	
F 1(2)	*Notosaria nigricans*	1.35	0	10.0	

Water temperatures (T_{calc}) calculated from $\delta^{18}O_{carb}$ using the equation given by O'Neil et al. (1969). Mean annual water temperature (T_{mean}) from Stephens et al. (2002); $\delta^{18}O_w$ of seawater offshore Christchurch from Schmidt et al. (1999). endopunc.: endopunctate.

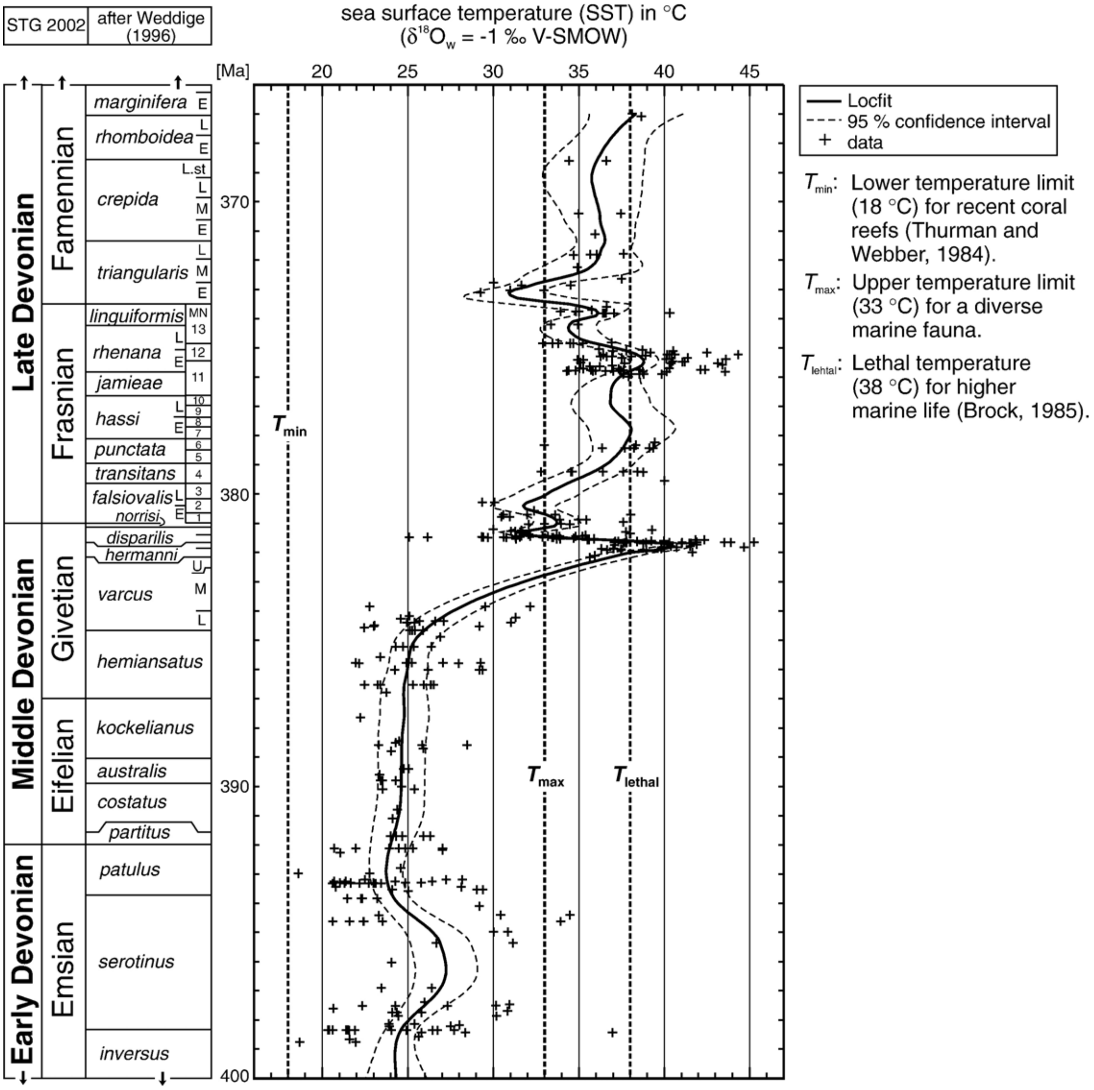

Fig. 9. Sea surface temperature (SST) calculated from $\delta^{18}O$ data of the brachiopod calcite assuming a $\delta^{18}O_w$ value of −1‰ V-SMOW. Temperature minima and maxima according to Thurman and Webber (1984) and Brock (1985).

The Devonian time interval is generally considered as an ice-free period (Frakes et al., 1994) with high-latitude ice-caps only reported from the latest Famennian (Streel et al., 2000). We therefore assume as a working hypothesis a $\delta^{18}O$ value for Devonian seawater of −1‰ V-SMOW (Shackleton and Kennett, 1975). Palaeotemperatures calculated from the $\delta^{18}O$ of brachiopod calcite are shown in Fig. 9. For the Emsian, Eifelian and the early Givetian, mean temperatures are around 25 °C, temperatures which correspond relatively well to the temperature range of 23 to 29 °C typical for modern tropical to subtropical surface waters (Stephens et al., 2002). In contrast, sea surface temperatures (SSTs) calculated for the latest Givetian, Frasnian and early Famennian are warmer by 6 to 14 °C and in part above 38 °C, which is considered as the lethal temperature limit for higher marine life (Brock, 1985). Since the investigated successions reveal a diverse and normal marine fauna, we argue that an upper temperature limit of 33 °C may represent a more realistic threshold for Devonian surface waters. With this estimate, palaeotemperatures calculated for the late Givetian to Famennian are far too warm (Fig. 9).

Veizer et al. (1997a) and Veizer et al. (1999) proposed that the oxygen isotope composition of Palaeozoic oceans was significantly lower in comparison to the modern ocean. This hypothesis is based on the observation that Palaeozoic brachiopod calcite as well as Precambrian carbonates (Shields and Veizer, 2002) become gradually depleted in ^{18}O with increasing age. Using the oxygen isotope data of Veizer et al. (1999), Wallmann (2001) presented a modelling study suggesting that the oxygen isotopic composition of seawater may have changed from a value of −8‰ V-SMOW in the Cambrian to a value of 0‰ V-SMOW in the modern. However, the hypothesis of a secular change in the oxygen isotope composition of seawater is in contradiction to studies which claim that the oceanic $\delta^{18}O$ was buffered at a value of 0 ± 2‰ V-SMOW (Muehlenbachs, 1986; Land and Lynch, 1996; Muehlenbachs, 1998; Lécuyer and Allemand, 1999).

The model of Wallmann (2001) predicts a $\delta^{18}O_w$ of −3‰ V-SMOW for the Early Devonian and a $\delta^{18}O_w$ of −2‰ V-SMOW for the Late Devonian. With these estimates, SSTs calculated for the Early and Middle Devonian are around 18 °C and palaeotemperatures for Late Devonian oceans range from 25 to 32 °C. While Late Devonian palaeotemperatures seem reasonable for tropical latitudes, temperature estimates for the Middle Devonian to Frasnian are too low. The Middle Devonian and Frasnian period is characterized by the development of vast stromatoporoid-coral reefs reaching 45°N in the middle Frasnian (Copper, 2002). Reconstructed palaeotemperatures are significantly lower than the optimum temperature for the growth of recent coral reefs (23 to 29 °C, James and Bourque, 1992; Duxbury and Duxbury, 1997). In addition, Late Devonian SSTs are 7 to 14 °C higher than SSTs calculated for the Eifelian and early Givetian. To our understanding, warming of low latitude surface waters by 7 to 14 °C seems unrealistic.

A change in pH of ocean surface waters is an additional factor that may have affected the oxygen isotope composition of brachiopod calcite. Spero et al. (1997) and Bijma et al. (1999) showed that the $\delta^{18}O$ of foraminiferal calcite is dependent on the pH or on the CO_3^{2-} concentration of seawater. Zeebe (1999) suggested that the oxygen isotopic composition of total dissolved inorganic carbon decreases with increasing pH since HCO_3^- (the dominant species at intermediate pH) is enriched in ^{18}O relative to CO_3^{2-} (the dominant species at high pH). If calcite is formed from a mixture of bicarbonate and carbonate ions in proportion to their relative contribution to total dissolved inorganic carbon, the $\delta^{18}O$ of brachiopod calcite is expected to decrease with increasing pH. The change in the oxygen isotope composition is −1.42‰ per pH unit increase (Zeebe, 2001).

The CO_2 concentration of the ocean–atmosphere system exerts a major control on the pH of sea-surface water. We used two pCO_2 predictions for the Devonian in order to test for the effect on the change in pH on $\delta^{18}O$. The GEOCARB III model of Berner and Kothavala (2001) predicts high CO_2 concentrations (15 times pre-industrial atmospheric CO_2 level [PAL]) for the Middle Devonian, whereas Rothman (2002) propose only a slightly increased CO_2 level (2 to 3 PAL). Other models (e.g. François et al., 1993) predict PALs between these limits. It should be noted that these estimates were criticized as inadequate for atmospheric CO_2 estimation by Boucot and Gray (2001) and Boucot et al. (2004). With these pCO_2 estimates, the expected decrease in the pH of Devonian surface oceans is calculated not to exceed 0.6 pH units (for details see Table 3). Nevertheless, any change in pH is supposed to affect the oxygen isotopic composition of calcite. The pH effect on the $\delta^{18}O$ of brachiopod calcite was calculated according to

$$\delta^{18}O_{\text{pH-corrected}} = \delta^{18}O_{\text{carb}} + 1.42 \times \Delta\text{pH} \qquad (3)$$

The pH-corrected $\delta^{18}O$ values translate into palaeotemperatures that are 1.6 °C (2 to 3 PAL) and 4.1 °C (15 PAL) higher in comparison to non-corrected $\delta^{18}O$ values (Fig. 10). With this correction, Late Devonian SSTs become even more unrealistic.

In summary, no single factor controlling $\delta^{18}O$ of brachiopod calcite (T, $\delta^{18}O_w$, pH) seems able to account for the recorded secular change in $\delta^{18}O$. The only possible explanation seems to be a combination of global warming and a decrease in $\delta^{18}O$ of seawater during the transition from the late Givetian into the Famennian. Assuming an upper thermal limit of 33 °C for tropical surface waters, the $\delta^{18}O$ values of Late Devonian brachiopods suggest that $\delta^{18}O_w$ must have been lower than −2.4‰ V-SMOW. Taking into account the effect of a lower pH (due to higher atmospheric

Table 3
pH of surface waters depending on changes in atmospheric pCO_2

pCO_2 (ppmV)	PAL	pH	ΔpH
300	1	8.12	0.00
365 (today)	1.2	8.08	0.04
600	2	7.97	0.15
900	3	7.88	0.24
1500	5	7.77	0.35
3000	10	7.62	0.50
4500	15	7.54	0.59

$pK_0 = 1.547$, $pK_1 = 5.847$, $pK_2 = 8.915$ (after Millero, 1996, $T = 25$ °C, salinity 35‰).
A constant $[CO_3^{2-}] \approx 260$ μmol kg^{-1} is assumed, which is controlled by the position of the CCD (cf. Sundquist, 1986; Zeebe, 2001). A pCO_2 of 300 ppmV is assumed as the pre-industrial value (PAL = 1) to be consistent with other models (Berner and Kothavala, 2001). Total alkalinity is set equal to carbonate alkalinity. For formulas, see DOE (1994).

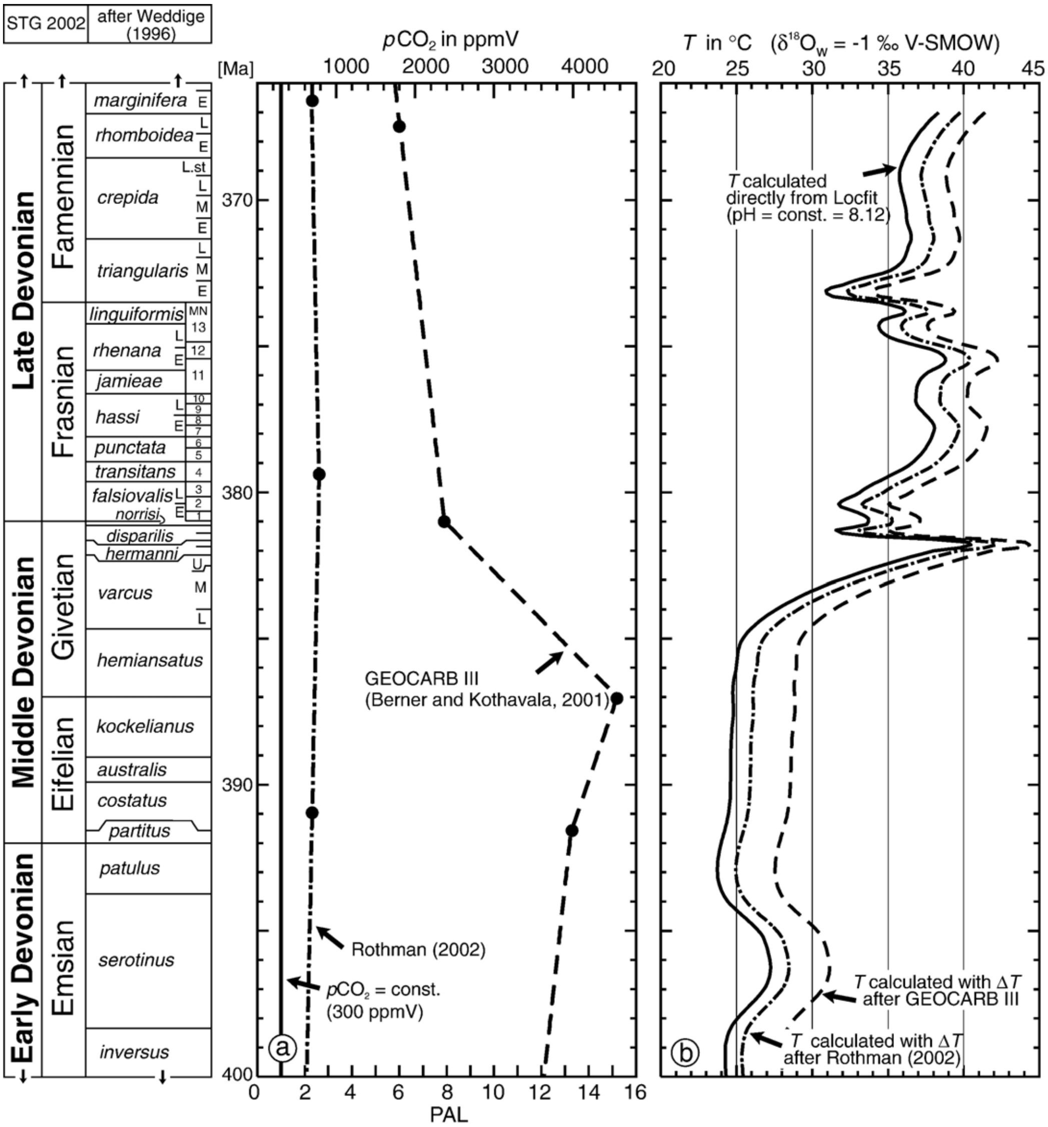

Fig. 10. (a) $p\mathrm{CO}_2$ of the Devonian atmosphere after the models of Berner and Kothavala (2001) and Rothman (2002). Solid line: PAL = 1. Time scales used in these models (Harland et al., 1990; Gradstein and Ogg, 1996) were converted to the STG (2002) time scale. (b) Sea surface temperature (SST) curves calculated from the Locfit curve ($\delta^{18}\mathrm{O}_\mathrm{w} = -1$‰ V-SMOW). Temperature correction, which compensates for the pH effect is given by: $\Delta T = T_{(\Delta\mathrm{pH}=0)} - T_{(\Delta\mathrm{pH})}$.

$p\mathrm{CO}_2$) on δ^{18}O of calcite, $\delta^{18}\mathrm{O}_\mathrm{w}$ would have been −3‰ V-SMOW. Interestingly, a lower δ^{18}O value for Late Devonian (Frasnian) seawater was suggested independently by the study of well-preserved marine radiaxial fibrous cements ($\delta^{18}\mathrm{O} = -4.8 \pm 0.5$‰, Carpenter and Lohmann, 1989; Carpenter et al., 1991). By assuming water temperatures between 21 and 31 °C, Carpenter et al. (1991) estimated a δ^{18}O value for Frasnian seawater of −2‰ to −3‰ V-SMOW. In conclusion, if $\delta^{18}\mathrm{O}_\mathrm{w}$ decreased from −1‰ V-SMOW in the Middle Devonian to −3‰ during the Late Devonian, the secular increase in tropical surface water temperatures would be reduced to 8 °C.

The oxygen isotopic composition of the ocean is controlled by the balance of high-temperature processes at mid ocean ridges and off-axis, low-temperature alteration of oceanic crust. Enhanced hydrothermal activity will raise $\delta^{18}\mathrm{O}_\mathrm{w}$, since hydrothermal fluids expelled from mid ocean ridges are enriched in ^{18}O relatively to seawater. Low-temperature off-axis alteration processes produce fluids depleted in ^{18}O that may balance the isotopic flux of hot hydrothermal fluids

(Muehlenbachs, 1998; Wallmann, 2001). The model of Lécuyer and Allemand (1999) predicts that $\delta^{18}O_w$ may have varied by ±2‰ in the geological past. During time periods without significant ice-caps, the oceanic $\delta^{18}O$ may have been as much as 3‰ lower than at present-day. In order to obtain a world ocean with a negative $\delta^{18}O_w$, closure times (i.e., the expected life of the hydrothermal system) of the oceanic crust of at least 30 Ma, a low water–rock ratio and a slowly decreasing permeability of the ocean crust are required (Lécuyer and Allemand, 1999). In addition, continental silicate weathering is an important sink for ^{18}O and may lower the $\delta^{18}O$ of the oceanic reservoir since the products of continental silicate weathering (clay minerals and other H_2O-bearing minerals) are enriched in ^{18}O. If continental weathering increased during the Givetian–Frasnian transition, as indicated by the $^{87}Sr/^{86}Sr$ record, it may have had an impact on the oxygen isotope composition of oceanic reservoir.

However, since none of these factors can be constrained, the suggestion of a relatively short-term change in $\delta^{18}O_w$ from the Middle to Late Devonian remains speculative. In addition, the oxygen isotope record based on the analysis of conodont apatite does not support this potential interpretation (Joachimski et al., 2004). $\delta^{18}O$ values of Eifelian to early Givetian conodonts translate into palaeotemperatures comparable to those derived from $\delta^{18}O$ of brachiopod calcite. Conodont $\delta^{18}O$ decreases as well during the late Givetian and Frasnian, but the magnitude of the shift is only −2% in comparison to the −3% observed for brachiopod calcite. Late Devonian palaeotemperatures calculated from $\delta^{18}O_{apatite}$ by assuming $\delta^{18}O_w = -1\%$ V-SMOW are around 30 to 34 °C and do not indicate a moderate change in $\delta^{18}O$ of Devonian seawater (Joachimski et al., 2004).

4.3.1. Short-term excursions in $\delta^{18}O$

The superimposed short-term excursions in $\delta^{18}O$ are interpreted to reflect temperature changes. The significant drop in $\delta^{18}O$ during the Givetian (*hermanni* Zone) has yet been recorded only from sections from Iowa (this study, Joachimski et al., 2004). A highly diverse, open marine fauna with brachiopods, crinoids, bryozoans, solitary and colonial corals, and stromatoporoids is observed in the Rapid Member of the Cedar Valley Group (Witzke et al., 1988, p. 232). Thus, it is difficult to imagine that an increased influx of ^{18}O-depleted meteoric waters and thus a change in salinity may have contributed to the significant shift in $\delta^{18}O$ (for a detailed discussion see Joachimski et al., 2004).

The two positive excursions in the latest Frasnian and near the F-F boundary correlate with two positive $\delta^{13}C$ excursions, which are interpreted to be the result of an increase in the organic carbon burial rate. Enhanced burial of organic carbon will result in lower atmospheric CO_2 concentrations, which in turn would cause climatic cooling. The amplitude of the $\delta^{18}O$ excursion in the late Frasnian and at the Frasnian–Famennian transition are +0.8‰ and +1.3‰, respectively, which translates into cooling of about 4 °C and 6 °C. A short-term pH increase due to the lower pCO_2 would lower the amplitudes slightly. The positive excursions in $\delta^{18}O$ of brachiopod calcite are in agreement with conodont $\delta^{18}O$ data measured by Joachimski and Buggisch (2002) which supports their interpretation that short-term cooling pulses may be responsible for the mass extinction in the late Frasnian.

5. Conclusions

The evaluation of the Devonian strontium isotope record indicates that the $^{87}Sr/^{86}Sr$ ratio of the ocean was mainly controlled by the continental weathering flux. While the decrease in $^{87}Sr/^{86}Sr$ during the Early Devonian is attributed to a decrease in the continental strontium delivery at end of the Caledonian orogeny, the rise in $^{87}Sr/^{86}Sr$ during the late Middle Devonian is considered to be the result of an enhanced weathering flux of strontium as consequence of climatic warming in the Late Devonian, potentially in combination with tectonic uplift due to the Eovariscan orogeny. The long-term rise of sea level during the late Middle Devonian and Frasnian is interpreted as a consequence of enhanced seafloor spreading. Enhanced hydrothermal activity coincides with intensified CO_2 outgassing at mid ocean ridges (Marty and Tolstikhin, 1998; Berner and Kothavala, 2001), which in combination with CO_2 contributions from island arc volcanism (cf. Jones and Jenkyns, 2001) may have caused Late Devonian greenhouse warming. The late Middle Devonian and Late Devonian are considered as a time interval with a minor climatic gradient between low and high latitudes (Boucot and Gray, 2001). For example, miospores typical for middle and higher latitudes disappeared at the end of the Givetian and equatorial and (sub)tropical forms spread in subpolar areas during the Frasnian (Streel et al., 2000). Climatic warming may have intensified continental weathering in the tropics, which according to our interpretation is documented in the contemporaneous increase in $^{87}Sr/^{86}Sr$ (Fig. 5).

Climatic warming is suggested also by the brachiopod oxygen isotope record. However, the decrease in

$\delta^{18}O$ across the Middle/Late Devonian boundary is considered to be too large to be explained exclusively by a temperature increase. Evaluation of the parameters determining $\delta^{18}O$ of shell calcite suggests that neither a secular decrease in $\delta^{18}O_w$ of seawater (Veizer et al., 1999) nor a change in surface water pH can explain the $\delta^{18}O$ trend reported in this study. Therefore, we propose the combination of a temperature rise and a moderate decrease in $\delta^{18}O_w$ from the Middle to Late Devonian to explain the lower $\delta^{18}O$ values of Late Devonian brachiopods. However, this interpretation is speculative at the current state of knowledge and not confirmed by the oxygen isotope record of conodont apatite (Joachimski et al., 2004).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.palaeo.2006.03.045.

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