



Devonian climate and reef evolution: Insights from oxygen isotopes in apatite

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ABSTRACT

Conodonts, microfossils composed of carbonate-fluor apatite, are abundant in Palaeozoic–Triassic sediments and have a high potential to preserve primary oxygen isotope signals. In order to reconstruct the palaeotemperature history of the Devonian, the oxygen isotope composition of apatite phosphate was measured on 639 conodont samples from sequences in Europe, North America and Australia. The Early Devonian (Lochkovian; 416–411 Myr) was characterized by warm tropical temperatures of around 30 °C. A cooling trend started in the Pragian (410 Myr) with intermediate temperatures around 23 to 25 °C reconstructed for the Middle Devonian (397–385 Myr). During the Frasnian (383–375 Myr), temperatures increased again with temperatures to 30 °C calculated for the Frasnian–Famennian transition (375 Myr). During the Famennian (375–359 Myr), surface water temperatures slightly decreased. Reconstructed Devonian palaeotemperatures do not support earlier views suggesting the Middle Devonian was a supergreenhouse interval, an interpretation based partly on the development of extensive tropical coral–stromatoporoid communities during the Middle Devonian. Instead, the Devonian palaeotemperature record suggests that Middle Devonian coral–stromatoporoid reefs flourished during cooler time intervals whereas microbial reefs dominated during the warm to very warm Early and Late Devonian.

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1. Introduction

The Devonian Period was characterized by major changes in both the marine and terrestrial realms. On the continents, trees and seed plants evolved and the first multi-storied forests developed (Algeo and Scheckler, 1998). In the marine realm, coral–stromatoporoid reef complexes flourished in the late Early, Middle Devonian and early Late Devonian (Frasnian) forming the most extensive reef constructions in Earth history (Copper and Scotese, 2003). The successful coral–stromatoporoid reef ecosystem became extinct in the late Frasnian during the Frasnian–Famennian mass extinction event and was replaced by calcimicrobial reefs in the Famennian (Copper, 2002a). The Devonian reef history is generally seen as reflecting the palaeoclimate of the Devonian, which is interpreted to have been a warm greenhouse interval. High atmospheric CO₂ levels were modelled for the Early Devonian and decreasing CO₂ concentrations were predicted for the Middle and Late Devonian (Berner and Kothavala, 2001; Simon et al., 2007), potentially as a consequence of

land plant evolution and development of effective root systems favouring silicate weathering and low atmospheric pCO₂ (Algeo and Scheckler, 1998). There is no geological evidence for high-latitude ice sheets during most of the Devonian, except for the latest Devonian with glacial sediments documented from South America (Caputo et al., 2008).

Oxygen isotopes of calcitic biogenic hard parts have been used to reconstruct the palaeoclimatic history of the Phanerozoic. Preference has been given to brachiopods in the Palaeozoic since their shells consist of low-magnesium calcite, representing a relatively stable mineralogy with respect to diagenetic alteration. Comprehensive $\delta^{18}\text{O}$ datasets for the Devonian were published by Veizer et al. (1999) and Van Geldern et al. (2006). However, interpretation of the brachiopod $\delta^{18}\text{O}$ records concerning the palaeotemperature history of the Devonian is hampered by Palaeozoic brachiopods showing in general a trend towards lower oxygen isotope values with increasing age (Veizer et al., 1999). Veizer et al. (1999) interpreted this trend as a secular change in the oxygen isotope composition of seawater with the $\delta^{18}\text{O}$ of Palaeozoic seawater differing from modern seawater. This hypothesis initiated a debate on whether hydrothermal and weathering processes at mid-ocean ridges buffered seawater $\delta^{18}\text{O}$ at a value

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of $0 \pm 1\%$ or resulted in a secular change in seawater $\delta^{18}\text{O}$ (Land and Lynch, 1996; Muehlenbachs, 1998; Lécuyer and Allemand, 1999; Wallmann, 2001; Jaffres et al., 2007).

Biogenic apatite is considered as another mineralogical phase with a high potential for the preservation of the primordial oxygen isotope composition. Conodonts are phosphatic microfossils (0.5 mm up to approximately 2 mm in size) composed of carbonate–fluorapatite (francolite; Pietzner et al., 1968) with its oxygen isotope composition considered to be a reliable recorder of palaeotemperature (Wenzel et al., 2000; Joachimski and Buggisch, 2002; Joachimski et al., 2004; Bassett et al., 2007; Buggisch et al., 2008; Trotter et al., 2008). These tooth-like elements are the only skeletal remains of the marine conodont animal, assumed to have been one of the earliest jawless vertebrates (Sansom et al., 1992; Donoghue et al., 2000). These morphologically different elements, arranged in the head region of the conodont animal, are interpreted as a feeding or filtering apparatus. Each conodont element consists of an upper crown and a lower basal body, both constructed of concentric lamellae. Whereas the more densely packed lamellae of the crown consist of comparatively coarse prismatic apatite crystallites (typically 1–30 μm in length), those of the basal body are characterized by finer cuboidal crystallites with a higher organic matter content making them less resistant with respect to mechanical abrasion and post-depositional alteration.

This contribution presents a comprehensive oxygen isotope record for the Devonian based on analysis of conodont apatite; it considerably expands the record published by Joachimski et al. (2004). The composite oxygen isotope curve of conodont apatite will be discussed in the context of Devonian climatic evolution and development of tropical reef ecosystems.

2. Materials and methods

2.1. Studied sections

Conodonts were studied from several sections in Germany, the Czech Republic, France, the USA and Australia spanning the time

interval of latest Silurian (Pridoli) to Late Devonian (Famennian). According to palaeogeographic reconstructions of Golonka (2000), all studied locations were situated in tropical to subtropical palaeolatitudes between 10 and 30° southern latitude (Fig. 1). The stratigraphic ranges of the sampled intervals of the studied sections are shown in Fig. 2 (details concerning locations as well as references for the studied sections are given in the Supplementary Material).

2.2. Extraction of conodonts

Conodonts were extracted by dissolving carbonate rocks in 10% acetic or formic acid, heavy liquid separation using sodium–polytungstate and picking conodont elements from the heavy fraction under a binocular microscope. Only conodont elements without basal bodies were selected for further processing since the basal bodies have shown to be a potential source of contamination (Wenzel et al., 2000). Several mono-generic conodont samples were studied to test whether different conodont taxa vary in their oxygen isotope ratios. In most cases, we used multi-generic conodont assemblages for isotope analysis since the abundance of conodont elements was generally not sufficiently high to allow mono-specific or mono-generic analyses.

2.3. Silver phosphate precipitation

Conodont carbonate fluorapatite (Pietzner et al., 1968; Sweet, 1988) has the general formula $\text{Ca}_5\text{Na}_{0.14}(\text{CO}_3)_{0.16}(\text{PO}_4)_{3.01}(\text{H}_2\text{O})_{0.85}\text{F}_{0.73}$. Since oxygen is present in different sites in the apatite mineral, the PO_4^{3-} group was isolated and precipitated as Ag_3PO_4 (O'Neil et al., 1994; Wenzel et al., 2000). 0.5 to 1 mg of conodont apatite was weighed into small PE-beakers and dissolved by adding 5 ml 2 M HNO_3 . After neutralizing the solutions with 2 M KOH , Ca^{2+} was precipitated as CaF_2 by adding 2 M HF . The solutions were centrifuged and the supernatant transferred to a clean beaker. Silver amine solution (0.34 g AgNO_3 , 0.28 g NH_4NO_3 , 1 ml NH_4OH in 30 ml aqua dest.) was added in order to precipitate the phosphate as trisilverphosphate. The beakers were stored for 8 h in a drying oven at 60 °C. As NH_4 slowly evolves, the pH of the solution

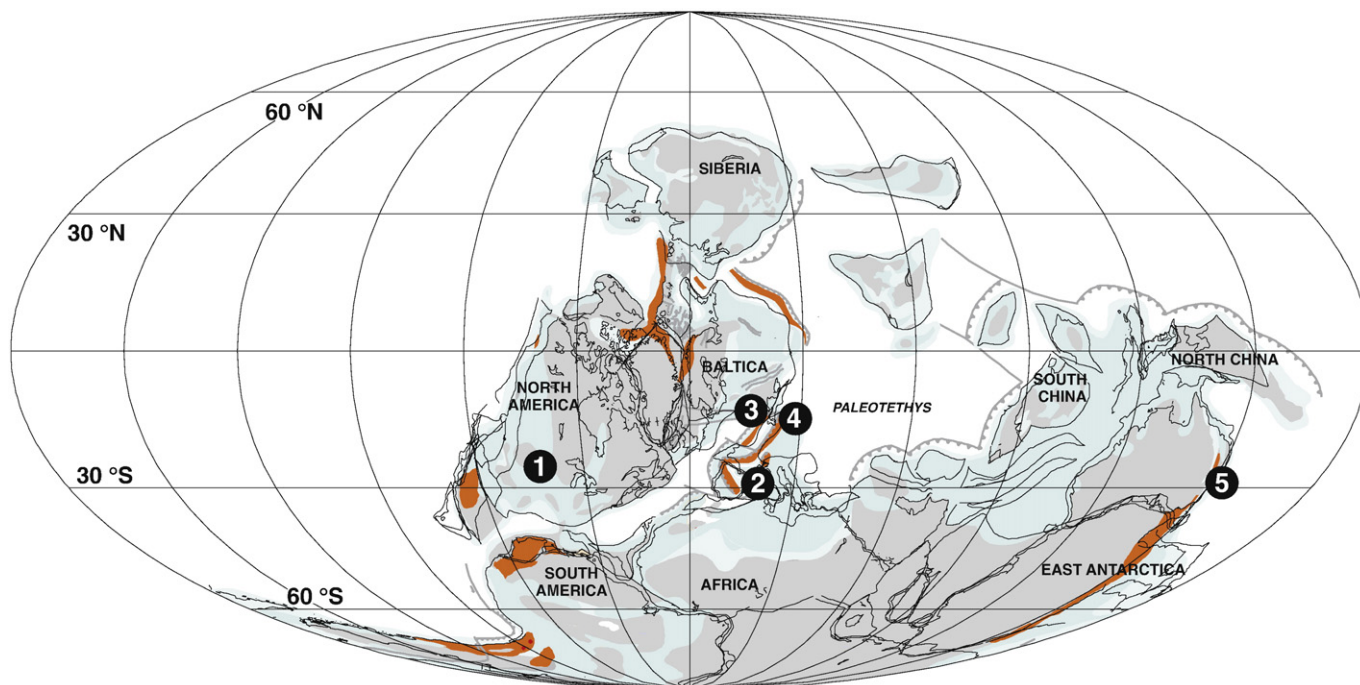


Fig. 1. Palaeogeographic reconstruction for the Middle/Late Devonian (Golonka, 2000) and location of studied sections. Gray = land, blue = continental shelf, white = open ocean, orange = collision belts. 1 – Iowa, 2 – France, 3 – Germany, 4 – Czech Republic, and 5 – Australia.

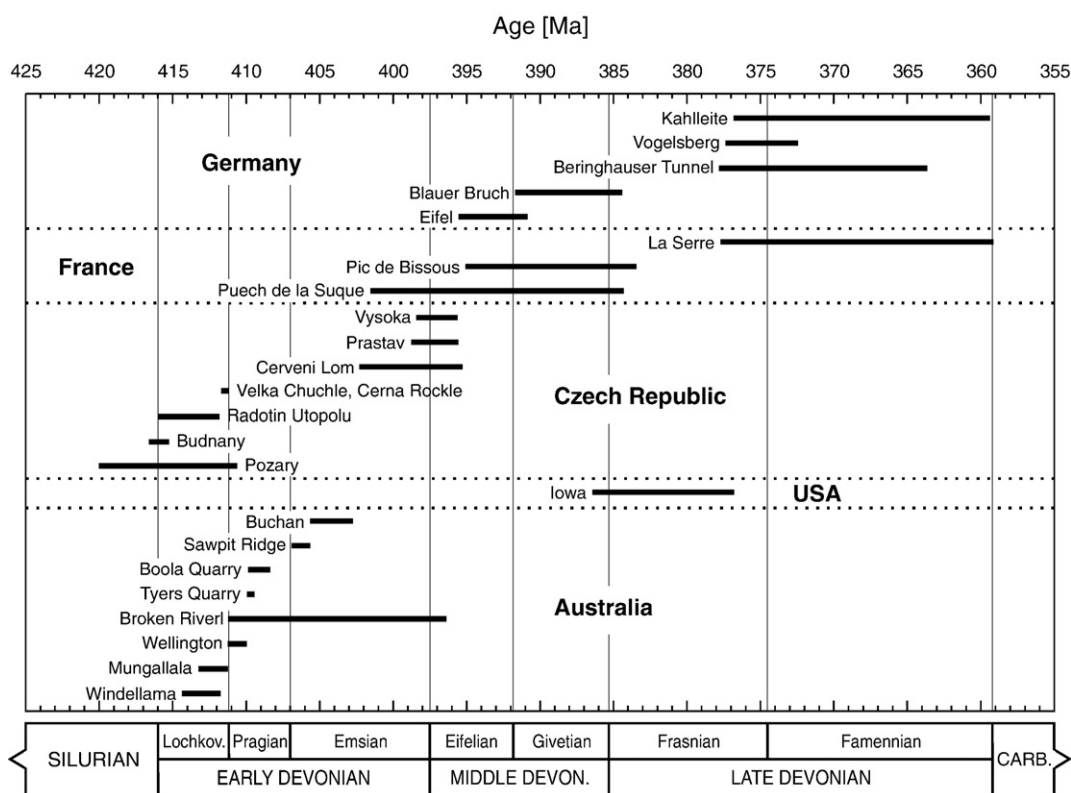


Fig. 2. Stratigraphic range of sampled intervals of studied sections in Germany, France, Czech Republic, USA and Australia. Absolute ages after Gradstein et al. (2004).

decreases and Ag_3PO_4 crystals start to precipitate (O'Neil et al., 1994). The Ag_3PO_4 crystals were extensively rinsed with deionised water, dried at 50 °C and homogenized using a small agate mortar. Weighing of Ag_3PO_4 yields allowed calculation of the PO_4^{3-} recovery rate, typically in the range of 92 to 99%. Processing of smaller conodont apatite samples (<0.5 mg) gave significantly lower PO_4^{3-} recovery rates and a poor external reproducibility of $\delta^{18}\text{O}$ measurements.

2.4. Oxygen isotope analysis

Oxygen isotope analyses were performed using a TC-EA (high temperature reduction furnace) coupled online to a ThermoFinnigan Delta Plus mass spectrometer. 0.2 to 0.3 mg Ag_3PO_4 was weighed into silver foil and transferred to the sample carousel of the TC-EA. Samples and internal standards were generally measured in triplicate (He flow rate is 80 ml/s, reactor temperature is set to 1450 °C, column temperature is 90 °C). At 1450 °C, the silver phosphate is reduced and CO forms as the analyte gas (Vennemann et al., 2002). CO was transferred in the helium stream through a gas chromatograph via a Conflo III interface to the mass spectrometer.

A yellowish-brown precipitate was observed during the early runs in the open split glass tube of the Conflo interface. Since this precipitate affected reproducibility of the measurements, disassembling and cleaning of the open split was required at regular intervals (Vennemann et al., 2002). We circumvented this problem by plunging the stainless steel capillary connecting the TC-EA with the Conflo III interface into a dewar filled with liquid nitrogen (LN_2). By this, volatilized phosphorus compounds (PH_3 ?) were completely retained in the trap and no contamination of the open split of the Conflo III interface occurred. At the end of each day, the capillary was taken out of the LN_2 dewar and the He-stream diverted to a vent by switching a 4-way valve introduced before the Conflo III interface. The yellowish viscous precipitate then concentrated at the end of the vent capillary. At the same time the Conflo III interface was flushed with helium.

All values are reported in ‰ relative to VSMOW. Reproducibility of triplicate sample measurements is generally $\pm 0.2\text{‰}$ (1 std. dev.). External reproducibility of replicate standard analysis is $\pm 0.15\text{‰}$ (1 std. dev.). Daily drifts in $\delta^{18}\text{O}$ values of the samples were corrected by analyzing laboratory standards with a known oxygen isotope composition (1 standard after 5 samples). The average oxygen isotope composition of the internationally distributed standards NBS 120c and YR-2 (Vennemann et al., 2002) were measured as $22.4 \pm 0.16\text{‰}$ ($n = 49$) and $13.2 \pm 0.08\text{‰}$ ($n = 6$), respectively. Vennemann et al. (2002) reported a $\delta^{18}\text{O}$ value of $22.58 \pm 0.09\text{‰}$ for NBS 120c and $13.1 \pm 0.21\text{‰}$ for YR-2 using conventional fluorination with BrF_5 .

2.5. Locfit regression analysis

Isotope trend lines were calculated using the nonparametric locally weighted regression method 'Locfit' (Loader, 1999) which produces a 'smoothed' curve retaining 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. All calculations were performed with the open source statistic software 'R' (version 1.5.1, Ihaka and Gentleman, 1996).

3. Results

Analyses of mono-generic conodont samples (*Icriodus* spp., *Polygnathus* spp., *Palmatolepis* spp.) extracted either from identical samples or from different depositional environments show no significant differences in $\delta^{18}\text{O}$ (Fig. 3, Table 1), taking into account an analytical precision of $\pm 0.2\text{‰}$ (1 std. dev.). Moreover, multi-generic conodont assemblages characteristic for specific environments show also comparable oxygen isotope ratios (Fig. 3; Famennian, Early *expansa* Zone). In addition, ramiform conodont elements do not differ in their $\delta^{18}\text{O}$ values from $\delta^{18}\text{O}$ values measured on individual taxa.

The composite oxygen isotope curve is based on total 639 individual measurements (Fig. 4) including 162 data points from

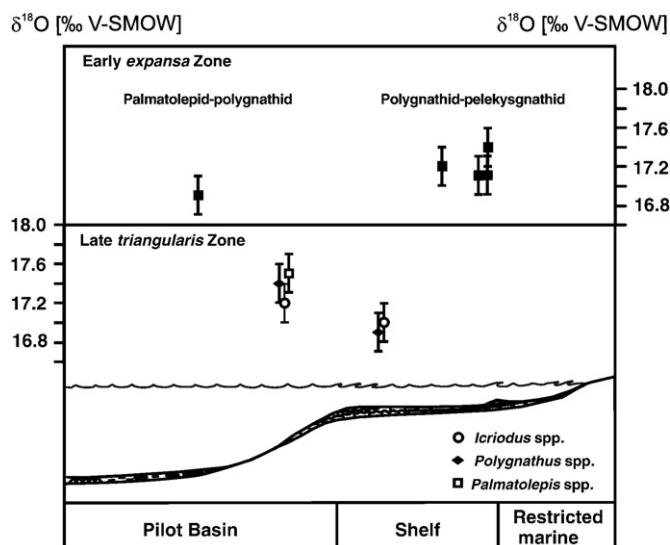


Fig. 3. Oxygen isotope ratios of conodont assemblages characteristic for specific environments (Famennian–Early *expansa* Zone) and of mono-specific samples from shelfal and deeper water environments (Famennian, Late *triangularis* Zone) of the western shelf of North America. Note that oxygen isotope ratios are comparable given an analytical precision of $\pm 0.2\%$ (1 std. dev.) suggesting that Devonian conodonts lived in surface waters. Palaeogeographic reconstructions from Sandberg and Dreesen (1984).

Joachimski et al. (2004). Isotope ratios of Late Silurian and Lochkovian conodonts are generally between 17 and 19‰. Lochkovian conodonts from Australia are slightly depleted in ^{18}O with values ranging from 16 to 18‰. An increase in $\delta^{18}\text{O}$ is observed in the Pragian and Emsian with values between 19 and 21‰ measured for conodonts from the Czech Republic. Pragian and Emsian conodonts from Australia also show an increase in $\delta^{18}\text{O}$ with ratios of 18 to 19.5‰ measured for late Emsian and early Eifelian conodonts.

Middle Devonian conodonts exhibit the highest oxygen isotope ratios independent of provenance of the elements. Eifelian, Givetian and early Frasnian conodonts from the Prague Basin (Czech Republic), Montagne Noire (France) and Rheinische Schiefergebirge (Germany) show $\delta^{18}\text{O}$ values ranging from 19 to 21‰ VSMOW. Givetian conodonts from Iowa (USA) reveal a relatively large spread in $\delta^{18}\text{O}$ from 17.7 to 19.5‰.

$\delta^{18}\text{O}$ values of early Frasnian conodonts from Iowa are 19 to 20.2‰. Late Frasnian and early Famennian $\delta^{18}\text{O}$ values of conodonts from the Rheinische Schiefergebirge, Montagne Noire and Iowa are between 17 and 19‰ and thus lower compared to Middle Devonian values. $\delta^{18}\text{O}$ values increase slightly in the late Famennian.

4. Discussion

Interpretation of the oxygen isotope values with respect to the climatic evolution of the Devonian requires knowledge concerning the life habitat of Devonian conodonts. Whereas some workers suggested that conodonts lived nektonic (Barnes and Fahraeus, 1975) others favoured a nektonic lifestyle within the water column (e.g. Sweet, 1988). Conodonts thriving in surface waters would record surface water temperature (SST), whereas conodonts living deeper in the water column would record cooler temperatures that would not be helpful deciphering climatic changes. In order to constrain the life habitat of Devonian conodonts, we studied mono-generic conodont assemblages and multi-generic Late Devonian assemblages from the western United States, France and Germany.

4.1. Palaeoecology of Devonian conodonts

The conodont biofacies concept is based on the observation that specific conodont taxa preferentially occur in certain lithofacies,

which are used as a proxy of palaeoenvironment. For example, Sandberg (1976) proposed five Late Devonian conodont biofacies belts ranging from pelagic to shallow-water settings. This concept was extended, *inter alia*, by Sandberg and Dreesen (1984), Klapper and Lane (1988) and Sandberg et al. (1989) who discriminated 11 laterally coexisting biofacies representing inner shelf to offshore basinal environments. Three offshore biofacies –the palmatolepid-bispathoid, palmatolepid-polygnathid and polygnathid-icriodid biofacies – were recognized. Based on the offshore–onshore conodont element distributions, either a pelagic, free-swimming mode of life or a benthic to nektonic lifestyle (Schülke, 2003) were favoured for Devonian conodonts. For example, representatives of *Palmatolepis* are generally interpreted to have lived in offshore, pelagic environments, whereas *Polygnathus* and *Icriodus* are considered to have lived in more shallow waters. Though shallow-water taxa are assumed to have lived in the upper water column and thus recorded SST, the lifestyle of pelagic conodonts is more difficult to constrain: these forms lived either in near-surface waters, within the water column or near the sediment–water interface.

We compared the oxygen isotope composition of icriodid, polygnathid and palmatolepid Pa elements as well as of ramiform elements isolated from multi-generic conodont assemblages (Table 1). Different genera showed no significant differences in their $\delta^{18}\text{O}$ values suggesting that conodont apatite was precipitated in waters of comparable temperature. In addition, we analysed mono-specific samples of *Icriodus alternatus* and *Polygnathus brevilaminus* and multi-specific samples of *Palmatolepis* spp. (Late *triangularis* Zone) from middle platform and basinal settings (Table 1, Fig. 3). The $\delta^{18}\text{O}$ values of all taxa are comparable within analytical reproducibility suggesting that all taxa precipitated conodont apatite at comparable water temperatures and thus at comparable water depth. Calculated palaeotemperatures (assuming a $\delta^{18}\text{O}$ value for Devonian sea water of -1% VSMOW) range from 32 to 35 °C. Although these temperatures are slightly higher than modern tropical SSTs, they accord with all taxa having thrived in surface waters.

The comparison of the oxygen isotope ratios of Late Famennian (Early *expansa* Zone) conodont assemblages from inner-shelf and basinal environments confirms an upper water-column habitat. Assemblages

Table 1

Oxygen isotope composition for individual conodont taxa or conodont assemblages characteristic for specific environments.

Sample	Conodont genera	Age	Unit/location	$\delta^{18}\text{O}$ (‰ VSMOW)
US 5	Polygnathid– pelekysgnathid	Famennian (Early <i>expansa</i> Zone)	Glenwood Canyon (Colorado)	17.4
US 6				17.1
US 8				17.1
US 9–13			Rockwood Quarry (Colorado)	17.2
US 17	Palmatolepid– polygnathid		Confusion Range (Utah)	16.9
Nev 1	<i>Icriodus</i> spp.	Famennian (Late <i>triangularis</i> Zone)	Middle/outer shelf (Nevada)	17.0
Nev 2	<i>Polygnathus</i> spp.			16.8
Nev 3	<i>Icriodus</i> spp.		Pilot Basin (Nevada)	17.2
Nev 4	<i>Polygnathus</i> spp.			17.4
Nev 5	<i>Palmatolepis</i> spp.			17.5
BT 1a	<i>Icriodus</i> spp.	Frasnian (Late <i>rhenana</i> Zone)	Beringhauser Tunnel (Germany)	17.6
BT 1a	<i>Palmatolepis</i> spp.			17.6
LSC	<i>Polygnathus</i> spp.	Frasnian (Late <i>rhenana</i> Zone)	La Serre C (France)	17.1
13a2				
LSC	<i>Palmatolepis</i> spp.			17.5
13a2				
LSC	Ramiform elements			17.3
13a2				
UQ 26b	<i>Icriodus</i> spp.	Frasnian (Late <i>rhenana</i> Zone)	Coumiac (France)	19.1
UQ 26b	<i>Polygnathus</i> spp.			18.9
UQ 26b	<i>Palmatolepis</i> spp.			18.9
UQ 26b	Ramiform elements			19.1

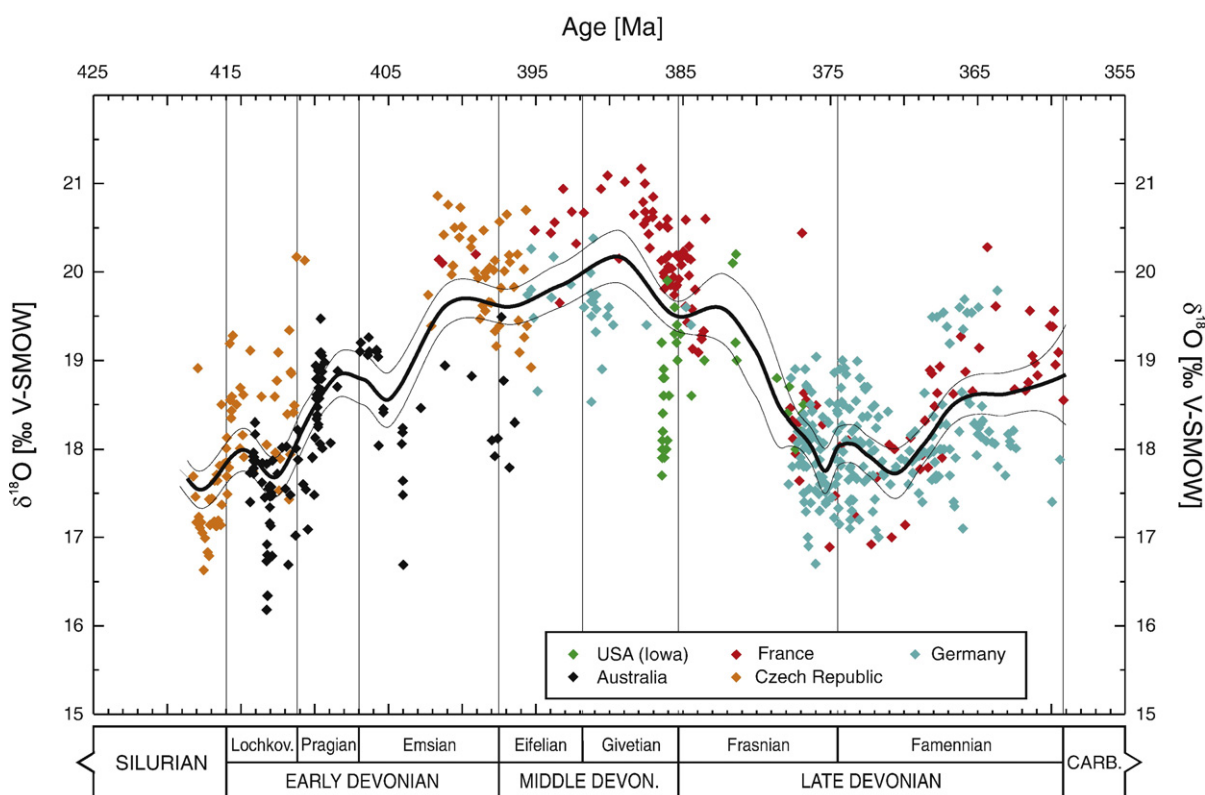


Fig. 4. Composite oxygen isotope curve ($n = 693$) based on analysis of conodont apatite from sections in Germany, France, Czech Republic, USA and Australia. Bold line represents locfit regression, thin lines give the 95% confidence interval.

from the inner shelf facies are represented preferentially by *Polygnathus* and *Pelekygnathus* (polygnathid-pelekygnathid conodont biofacies), whereas the basinal association is dominated by *Palmatolepis* and subordinately by *Polygnathus* (palmatolepid-polygnathid conodont biofacies of Sandberg and Dreesen, 1984). The oxygen isotope ratios of assemblages from both environments are closely comparable with calculated palaeotemperatures between 32 and 34 °C. These temperatures correspond to those reconstructed for the early Famennian and, moreover, indicate that different conodont taxa were thriving in surface waters. Based on these findings, we argue that Devonian conodonts were thriving in surface waters and can be used to reconstruct SST.

4.2. Preservation of the $\delta^{18}\text{O}$ signal in conodont apatite

Preservation of the primary oxygen isotope signals in conodont apatite depends on the influence of diagenetic recrystallisation and exchange of the phosphate-bound oxygen as a consequence of dissolution and reprecipitation processes. The crown tissues of conodont elements are composed of crystals ranging in size from $<1\ \mu\text{m}$ to $>30\ \mu\text{m}$ (hyaline tissue) to several hundred micrometers (albid tissue; Donoghue, 1998; Trotter et al., 2007). Although porosity has been recognized in both conodont crown tissues, permeability is considered to have been relatively low, especially in the hyaline crown tissue (Trotter et al., 2007). The low permeability is interpreted as inhibiting interaction and chemical exchange of phosphate-bound oxygen with oxygen from pore fluids. Experimental studies by Blake et al. (1997) and Zazzo et al. (2004) showed that the phosphate component of bioapatite is very resistant to inorganic exchange with water at low temperatures. However, at higher temperatures as well as under microbially mediated conditions (Blake et al., 1997), the oxygen isotope exchange between apatite and water proceeds faster and may affect the oxygen isotope composition of biogenic apatite.

With increasing temperature during burial of the sediments, and depending on the duration of burial, the colour of conodont elements

changes from pale yellow to black and finally to white as a consequence of thermal maturation of organic material trapped in conodont apatite. Epstein et al. (1977) introduced the conodont colour alteration index (CAI) ranging from CAI 1 (thermally immature) to CAI 5 (low-grade metamorphism), which was later extended to CAI 8 by Rejebian et al. (1987). Studies on the textural alteration of conodont apatite have demonstrated that recrystallisation of apatite crystallites may occur either on the surface or in the interior of conodonts. Königshof (1992) described an increase in crystallite size by contact metamorphism of conodonts with a CAI of 5 to 7, but did not observe any signs of recrystallisation in conodonts with a CAI of 1 to 4.5. Nöth (1998), however, showed syntaxial recrystallisation on conodont surfaces starting at CAI 1.5, though crystallisation in the interior of conodonts occurred only at CAI 5. Recrystallisation of low-CAI conodonts was explained by Nöth (1998) as reflecting long-term heating that promoted aggrading crystallization of crystallites at relatively low temperatures.

In contrast to studies on biogenic calcite, diagenetic recrystallisation and potential alteration of the oxygen isotope signal of fossil bioapatite are difficult to identify by other methods. Pucéat et al. (2004) demonstrated that the crystallinity of biogenic apatite, a proxy initially proposed by Shemesh (1990) as a tool to identify diagenetic overprint of apatite, is a poor criterion for identifying diagenetic alteration. Cathodoluminescence (CL) is generally used to identify diagenetic recrystallisation of biogenic carbonates. CL intensities in apatite are positively correlated with REE concentrations (Habermann et al., 2000). REEs become concentrated in biogenic apatite post-mortem (Grandjean-Lécuyer et al., 1993), but adsorption of REEs is not necessarily related to recrystallisation and/or diagenetic exchange of oxygen in the phosphate group of biogenic apatite. Consequently, neither REE patterns nor CL characteristics will help to identify diagenetic exchange of oxygen in apatite phosphate.

In order to evaluate a potential imprint on the oxygen isotope composition of conodont apatite from thermal maturation and

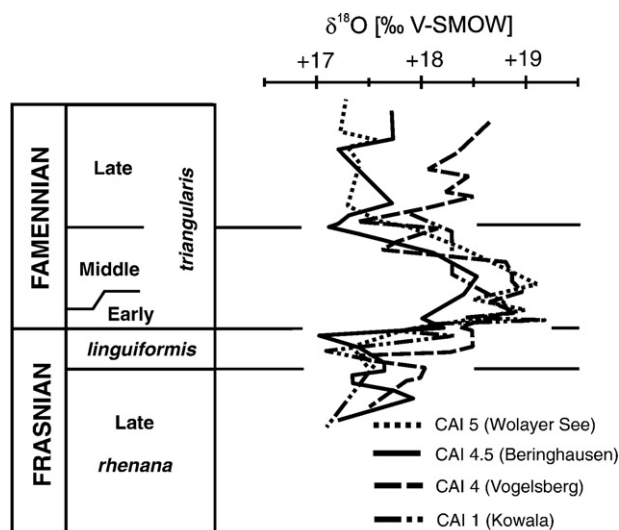


Fig. 5. Oxygen isotope ratios of conodonts with different conodont colour alteration indices (CAI) from Frasnian–Famennian boundary sections. Kowala–Holy Cross Mountains, Poland, Vogelsberg–Rheinisches Schiefergebirge, Germany, Beringhausen–Rheinisches Schiefergebirge, Germany, Wolayer See – Carnic Alps, Austria. Records show comparable trends independent of the thermal maturation (for further details see text).

concomitant recrystallisation, we compared $\delta^{18}\text{O}$ records of conodonts from four Frasnian–Famennian boundary sections (Fig. 5). Conodonts from the Kowala section (Holy Cross Mountains, Poland) have a CAI of 1 indicating a minor thermal overprint below 75 °C (Joachimski et al., 2001). Conodonts from the Vogelsberg (Thuringia, Germany), Beringhausen (Rheinisches Schiefergebirge, Germany) and Wolayer See sections (Carnic Alps, Austria) show higher CAI values of 4, 4.5 and 5, respectively. Thermal overprint in the latter

sections is estimated to have been at least between 200 and 300 °C. All four oxygen isotope records show a positive excursion in $\delta^{18}\text{O}$ in the earliest Famennian with an amplitude of around +1.5‰. Conodonts from the latest Frasnian as well as the Late *triangularis* Zone show no major difference in $\delta^{18}\text{O}$ taking into account an analytical reproducibility of $\pm 0.2\text{‰}$ and potentially slightly different SSTs in the various regions. This positive excursion was interpreted by Joachimski and Buggisch (2002) as reflecting a short-term cooling episode resulting from enhanced burial of organic carbon (Kellwasser horizons) and concomitant lowering of atmospheric $p\text{CO}_2$. The good accordance of the four records as well as the observation that conodonts from other time periods with different CAI values generally show no major differences in their $\delta^{18}\text{O}$ values suggest that enhanced thermal overprinting up to a CAI value of 5 and potential recrystallisation of conodont apatite did not result in oxygen isotope exchange in apatite phosphate. We thus interpret conodont apatite $\delta^{18}\text{O}$ values as a reliable proxy for reconstruction of Devonian sea surface temperatures.

4.3. Comparison of conodont apatite and brachiopod calcite $\delta^{18}\text{O}$ records

Given the equations of Kolodny et al. (1983) and O'Neil et al. (1969), calcite is expected to be enriched in ^{18}O relative to apatite. For the temperature range of 20–40 °C, the offset is 8.6 to 9.0‰ and increases by almost 0.5‰ over the 20 °C temperature range. This calculated offset was confirmed by measurements of Iacumin et al. (1996) who observed an offset in $\delta^{18}\text{O}$ of mammalian bone carbonate and apatite of 8.6 to 9.0‰. In order to compare the $\delta^{18}\text{O}$ values of conodont apatite and brachiopod calcite, the brachiopod calcite $\delta^{18}\text{O}$ VPDB values were converted to the VSMOW scale and a value of 8.7‰ was subtracted from the calcite $\delta^{18}\text{O}$ values (Fig. 6).

Comparison with the brachiopod $\delta^{18}\text{O}$ dataset published by Veizer et al. (1999) shows that calcite $\delta^{18}\text{O}$ values are in general depleted in

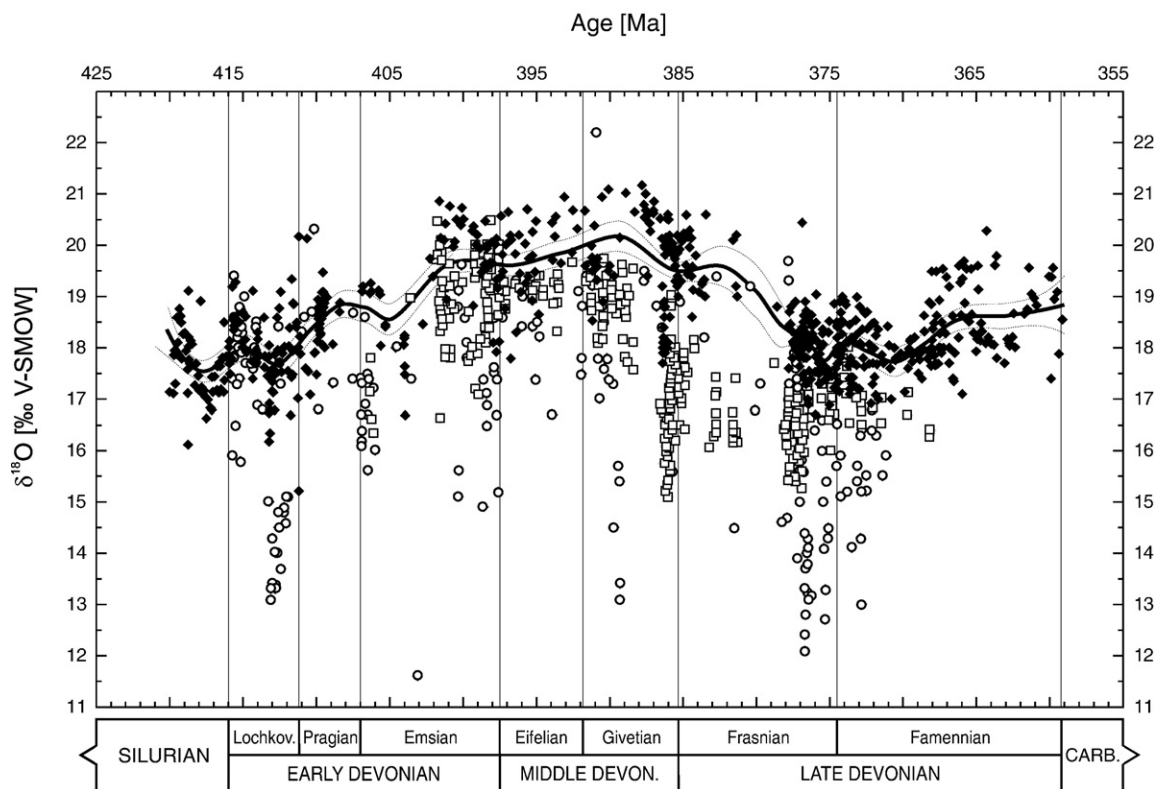


Fig. 6. Comparison of conodont $\delta^{18}\text{O}$ record (filled diamonds) with published $\delta^{18}\text{O}$ data for brachiopod calcite. Brachiopod calcite $\delta^{18}\text{O}$ V – PDB values were converted to the V – SMOW scale and a value of 8.7‰ was subtracted from the calcite $\delta^{18}\text{O}$ values in order to account for different thermodynamic oxygen isotope fractionations of calcite and apatite. Brachiopod $\delta^{18}\text{O}$ values: open circles – Veizer et al. (1999), open squares – van Geldern et al. (2006). Locfit regression for conodont apatite $\delta^{18}\text{O}$ as in Fig. 4.

^{18}O compared with conodont apatite. In addition, brachiopod $\delta^{18}\text{O}$ values reveal a significantly higher variance compared with the values of conodont apatite. The variance in $\delta^{18}\text{O}$ of conodonts from specific time intervals is generally in the range of 2‰ and is explained by regional short-term variations in SST and/or salinity. Elrick et al. (2009) suggest that variations in $\delta^{18}\text{O}$ of Early to Middle Devonian conodonts reflect climatic changes and the formation and melting of continental ice masses.

Instead, brachiopod $\delta^{18}\text{O}$ values vary by 6 and 8‰ in the Lochkovian and Frasnian, respectively (Fig. 6). This large variance cannot be explained by differences in water temperature and/or salinity: it suggests that brachiopod shells with low $\delta^{18}\text{O}$ values were probably affected by diagenetic recrystallisation. This interpretation is supported by the comparison of different brachiopod $\delta^{18}\text{O}$ records; brachiopod $\delta^{18}\text{O}$ values of Van Geldern et al. (2006) are generally higher and show minor variance compared with the brachiopod $\delta^{18}\text{O}$ values of Veizer et al. (1999).

Interestingly, the conodont $\delta^{18}\text{O}$ record (this study) and the brachiopod $\delta^{18}\text{O}$ record of Van Geldern et al. (2006) show comparable trends with relatively high values in the late Emsian to Givetian, a decrease in the Frasnian and relatively low values in the late Frasnian to Famennian (Fig. 6). However, the brachiopod $\delta^{18}\text{O}$ values are generally lower and result in unrealistically high palaeotemperatures especially in the Frasnian and Famennian (assuming an oxygen isotope composition of Devonian sea water of -1‰ VSMOW). Different life habitats of benthic brachiopods and nektonic conodonts cannot account for this offset (Joachimski et al., 2004). Further, diagenetic recrystallisation of the brachiopod shells studied by Van Geldern et al. (2006) seems unlikely since the shells were screened for a diagenetic overprint using cathodoluminescence microscopy, secondary electron microscopy and trace element analysis. Non-equilibrium fractionation presents another potential explanation for the observed offset. However, a kinetic oxygen isotope fractionation during apatite precipitation would result in a depletion in ^{18}O and lower $\delta^{18}\text{O}$ values: it cannot explain the generally higher $\delta^{18}\text{O}$ values

of conodont apatite (for detailed discussion see Joachimski et al., 2004).

The observation that the highest brachiopod $\delta^{18}\text{O}$ values agree relatively well with the conodont $\delta^{18}\text{O}$ values suggests that these samples may represent the best-preserved shells and that all other shells showing significantly lower $\delta^{18}\text{O}$ values were affected by diagenesis. This interpretation underlines our earlier conclusion that oxygen isotopes of conodont apatite are a more reliable palaeotemperature proxy than oxygen isotopes of Palaeozoic biogenic calcite.

4.4. Palaeotemperature of the Devonian

The oxygen isotope composition of biogenic apatite is dependent on the temperature during apatite precipitation and the $\delta^{18}\text{O}$ of seawater from which the apatite is precipitated (Kolodny et al., 1983). The latter depends on salinity and ice volume. Since almost all of the Devonian is generally considered a non-glaciated time interval, a value of -1‰ VSMOW is a realistic estimate for the $\delta^{18}\text{O}$ of Devonian open-ocean water (Savin, 1977). However, the oxygen isotope composition of surface waters in epeiric seas may be influenced by higher evaporation or enhanced freshwater input. Whereas enhanced evaporation will result in higher salinities and $\delta^{18}\text{O}$ values, freshwater input will lower salinity and $\delta^{18}\text{O}$ of surface waters.

Assuming a $\delta^{18}\text{O}$ value for Devonian seawater of -1‰ VSMOW, Late Silurian to Lochkovian average low-latitude SSTs are calculated to have been between 30 and 32 °C (Fig. 7). Average SSTs start to decrease in the early Pragian and show minimum values around 22 °C in the late Emsian to Givetian. Temperatures reconstructed for the middle to late Frasnian and early Famennian were again significantly warmer with average temperatures ranging between 30 and 32 °C; this accords with the low latitudes warming considerably during the Frasnian. During the middle to late Famennian a moderate cooling trend is apparent culminating in the short-term glaciation at the Devonian–Carboniferous boundary, documented by a positive $\delta^{18}\text{O}$

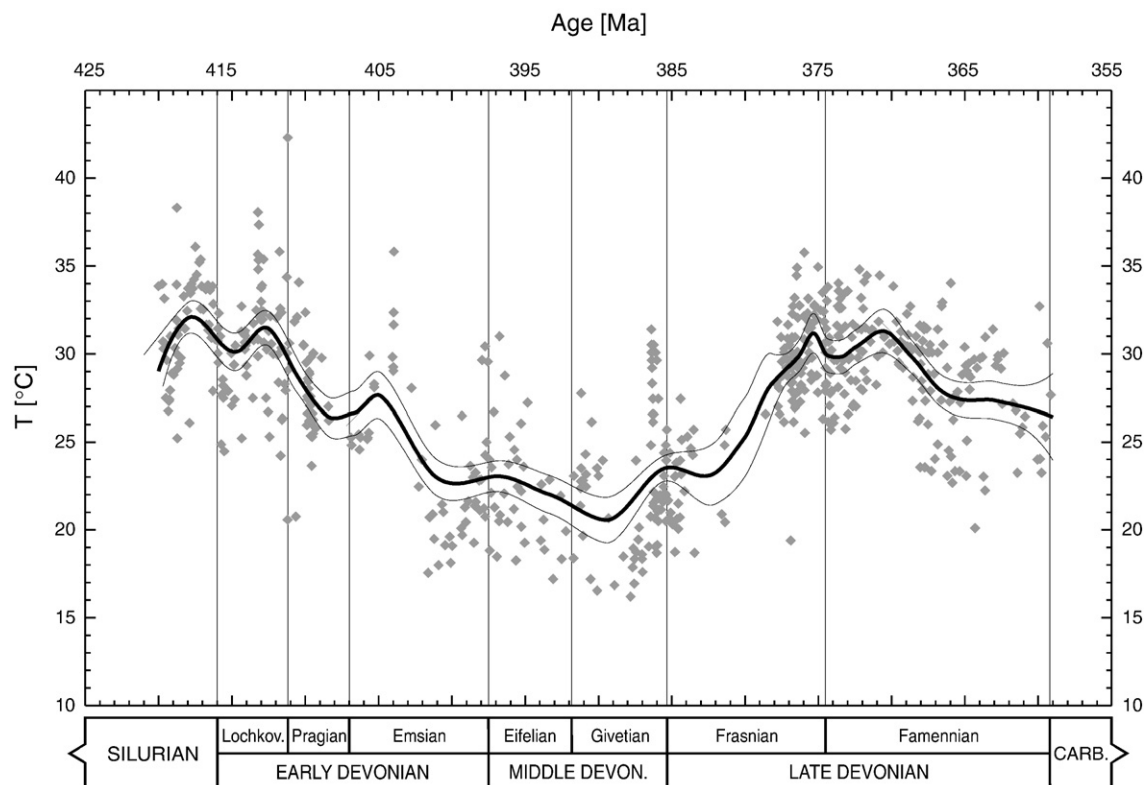


Fig. 7. Palaeotemperature record for the latest Silurian and Devonian calculated from $\delta^{18}\text{O}$ of conodont apatite assuming a $\delta^{18}\text{O}$ value for Devonian sea water of -1‰ VSMOW.

excursion in conodont apatite (Kaiser et al., 2006; Buggisch et al., 2008).

Regional differences in SST and/or salinity become obvious when comparing the $\delta^{18}\text{O}$ data sets from Australia, North America and Europe. High SSTs and/or lower salinities are reflected in the $\delta^{18}\text{O}$ data of conodonts from the epicontinental seas in southeastern Australia and the US Midcontinent (Iowa). In comparison, $\delta^{18}\text{O}$ values of conodonts from shelfal seas bordering the western Palaeotethys (France, Germany and Czech Republic) indicate lower SSTs and/or higher salinities (higher $\delta^{18}\text{O}$ values in comparison to $\delta^{18}\text{O}$ values of conodonts from Australia and Iowa). However, since the same long-term $\delta^{18}\text{O}$ trend is recognized in $\delta^{18}\text{O}$ datasets measured on conodonts from different palaeocontinents, we argue that the reconstructed long-term temperature record represents global climatic change within the Devonian.

By assuming an oxygen isotope composition for Devonian seawater of -1% VSMOW, the $\delta^{18}\text{O}$ values of Devonian conodont apatite translate into temperatures fully consistent with modern tropical to subtropical SSTs. This observation clearly contradicts the idea that the oxygen isotope composition of seawater has changed through time (Veizer et al., 1999; Wallmann 2001; Jaffres et al., 2007) but agrees well with studies on the oxygen isotope composition of ancient ophiolites which indicate that the $\delta^{18}\text{O}$ of Palaeozoic seawater was near $0 \pm 1\%$ VSMOW (Gregory, 1991; Muehlenbachs et al., 2003).

4.5. Devonian climate and reef evolution

Palaeotemperatures calculated from the conodont $\delta^{18}\text{O}$ record suggest that the earliest Devonian as well as the late Frasnian and most of the Famennian were relatively warm climatic periods, whereas the Middle Devonian represented a cooler interval. We suggest that these climatic changes resulted from variations in Devonian atmospheric CO_2 levels. For example, the GEOCARB III model (Berner and Kothavala, 2001) indicates a continuous decrease in $p\text{CO}_2$ during the Devonian. Simon et al. (2007) suggested that CO_2 concentrations decreased from about 2000 ppmv in the Early Devonian to 900 ppmv in the Middle Devonian. These predictions agree well with climatic cooling indicated by the conodont $\delta^{18}\text{O}$ record. However, both models do not show an increase in $p\text{CO}_2$ during the Frasnian that might be expected in context with the inferred climatic warming. In addition, CO_2 proxy data (e.g. soil carbonate $\delta^{13}\text{C}$) are too sparse to reconstruct shorter-term variations in atmospheric CO_2 during the Middle to Late Devonian.

Interestingly, the reconstructed temperature record is mirrored in the Devonian $^{87}\text{Sr}/^{86}\text{Sr}$ record. A continuous decrease in $^{87}\text{Sr}/^{86}\text{Sr}$ is observed in the Early Devonian. Relative uniform unradiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ values are observed in the Eifelian and early Givetian. $^{87}\text{Sr}/^{86}\text{Sr}$ values start to increase in the late Givetian with most radiogenic values observed at the Devonian–Carboniferous boundary (McArthur et al., 2001; Van Geldern et al., 2006). The increase in $^{87}\text{Sr}/^{86}\text{Sr}$ during the late Middle Devonian and Frasnian was interpreted to result from intensified continental weathering as consequence of the Eovariscan orogeny, enhanced volcanic CO_2 degassing and climatic warming (Van Geldern et al., 2006). Global warming in the Frasnian is supported by palaeontological data. According to Streel et al. (2000), tropical (non-equatorial) floras were spreading into higher latitudes during the Frasnian. Miospores reached their maximum latitudinal distribution in the latest Frasnian consistent with warm to very warm climatic conditions during the Frasnian–Famennian transition (Streel et al., 2000). Léthiers and Raymond (1991) suggested that Late Frasnian benthic ostracods were adapted to very warm temperatures. In conclusion, although modelled atmospheric CO_2 concentrations and sparse CO_2 proxy data are not in accord with climatic warming in the Frasnian, palaeontological as well as geochemical data support the reconstructed Late Devonian palaeotemperature record.

Our climate reconstruction contradicts the classical view that the Middle Devonian was characterized by a supergreenhouse climate (Copper, 2002b; Copper and Scotese, 2003) based partly in latitudinal increase in coral–stromatoporoid reefs in the Middle Devonian. Instead, during the Early Devonian, coral–stromatoporoid reefs occurred only rarely as small patch reefs. During the middle Emsian to Givetian, reef expansion was rapid, culminating in development of coral–stromatoporoid mega-reef complexes (Flügel and Flügel-Kahler, 1992; Copper, 2002b; Kiessling, 2002). For example, the Middle Devonian coral–stromatoporoid reef belts of Western Canada, the Urals and the Russian Platform extended over 3,100, 3,000 and 2,600 km, respectively (Copper and Scotese, 2003). These reefal build-ups are considered to be among the most extensive reef constructions in Earth history with a surface area up to 10 times those in the modern ocean (Copper, 1994).

In the Frasnian, coral–stromatoporoid reefs became more restricted and finally disappeared globally during the Frasnian–Famennian crisis. Almost no coral–stromatoporoid reefs are known for the following 15 million years. Instead, microbial reefs started to flourish during the Frasnian and were widespread in the Famennian (Tsien, 1988; George et al., 1995; Wood, 2000; Whalen et al., 2002). Early Devonian (late Lochkovian to early Emsian) reefs in the Urals consist mainly of algal and microbial communities with low-diversity metazoan assemblages (Antoshkina and Königshof, 2008). These reefs extend from Novaya Zemlya to the southern Urals over a distance of 2,500 km. Thus, Early Devonian (Lochkovian–Pragian) and Late Devonian (Famennian) reefs seem to have been dominated by microbial (cyanobacterial) communities whereas corals and stromatoporoids were the main reef builders of the Middle Devonian mega-reefs. Comparison of Devonian reef history with the palaeotemperature record suggests that the microbial reefs predominated during periods characterized by warm to very warm tropical SSTs, whereas coral–stromatoporoid mega-reefs flourished during the cooler Middle Devonian time interval. As shown in Fig. 8, the percentage of autotrophic reefs was relatively high in the Lochkovian–Pragian and in the Famennian (Kiessling, 2002). At the same time, the diversity of tropical reefs was relatively low (Flügel and Kiessling, 2002). Paralleling low-latitude cooling in the Pragian–Eifelian, the percentage of autotrophic reefs decreased whereas diversity of coral–stromatoporoid reefs increased. With increase in tropical SSTs in the Frasnian, the percentage of autotrophic reefs increased again whereas the diversity of tropical reefs decreased. Although the PalaeoReef database (Kiessling et al., 1999; Flügel and Kiessling, 2002) gives only a low-resolution record of Devonian reef evolution, the correlation between tropical SST, reef diversity and reef type suggests that temperature may have been a controlling factor in the development of the Devonian reefs.

That Middle Devonian reefs extended to very high palaeolatitudes of 40 to 50° was taken as another argument for warm climatic conditions during the Middle Devonian (Copper, 2002b). However, as noted by Kiessling (2002), the palaeolatitude of the northernmost Middle Devonian reefs in Siberia seems to be too high given the great volume of co-occurring evaporites (Witzke and Heckel, 1988) according with a position of Siberia in the subtropics. Accepting a corrected palaeolatitude of 40°N for Devonian Siberia (Kiessling, 2002), the Early Devonian tropical reef zone (Lochkovian) stretched from 46°S to 40°N , whereas the Emsian and Givetian to Early Famennian tropical reef zones ranged from 43°S to 45°N and 38°S to 45°N , respectively (Kiessling, 2002). Although the Early and Middle Devonian were characterized by a large percentage of reefs occurring in high latitudes ($>35^\circ$), the estimated latitudinal ranges for tropical reefs do not indicate that Middle Devonian reefs were spreading into higher latitudes compared with Early Devonian tropical reefs.

Riding (1992) suggested that cyanobacterial calcification episodes (e.g., Late Devonian) reflect periods of enhanced carbonate precipitation and that temperature was a main controlling factor for formation of microbial reef carbonates. In contrast, high tropical SSTs may not have been favourable for growth of coral–stromatoporoid reefs. Interestingly, coral–stromatoporoid reefs declined during the Frasnian, and finally

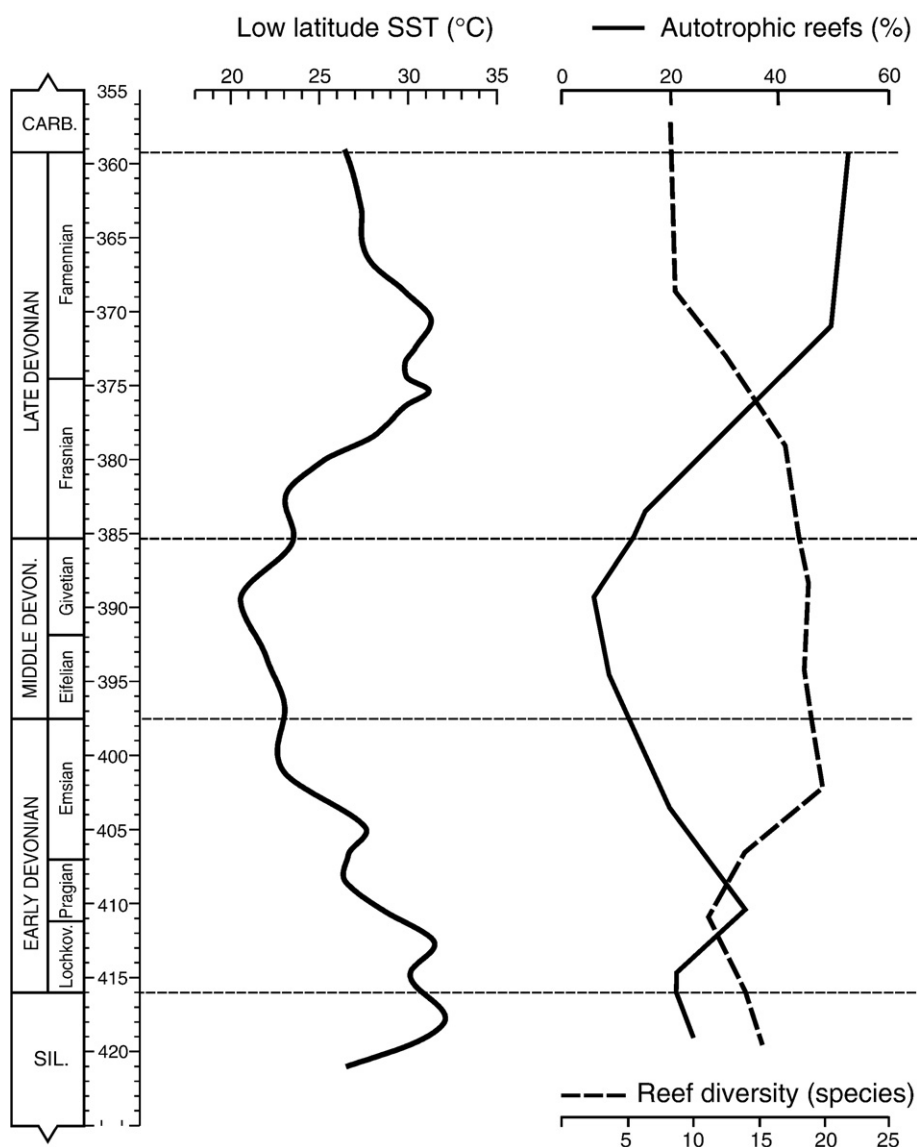


Fig. 8. Comparison of the Devonian palaeotemperature record with the percentage of autotrophic reefs on the total number of reefs (Kiessling, 2002) and the diversity of coral–stromatoporoid reefs in the Devonian (Flügel and Kiessling, 2002).

became extinct during the Frasnian–Famennian mass extinction event. However, it is an open question whether climatic warming during the Frasnian in conjunction with short-term cooling pulses in the latest Frasnian and at the Frasnian–Famennian boundary (Joachimski and Buggisch, 2002) were the ultimate cause of the extinction of many Devonian reef builders and the decline of the Devonian reef ecosystem.

In comparison, modern scleractinians are highly sensitive to increasing SSTs, this being one of the reasons for coral bleaching and mass mortality (Brown, 1997; Pockley, 2000). It is debatable, however, whether mid-Palaeozoic corals had symbionts and were as sensitive to higher SSTs as modern corals. Whereas Wood (1999) assumes that only modern scleractinians had symbionts, Talent (1988) and Copper (2002b) believe that probably all hermatypic tabulate and rugose corals were zooxanthellate. Most important and independent of this issue, Palaeozoic corals and stromatoporoids are expected to have had an upper thermal limit and may have suffered from high tropical SSTs in the Early and Late Devonian.

5. Conclusions

The conodont apatite oxygen isotope record is interpreted as reflecting the palaeotemperature of Devonian tropical to subtropical sea surface

waters. Salinity variations that might have affected $\delta^{18}\text{O}$ of sea-surface waters are unlikely to have contributed to the observed secular trend since the composite oxygen isotope curve based on analyses of conodonts from different palaeocontinents shows a consistent pattern. Comparison of the conodont $\delta^{18}\text{O}$ record with published $\delta^{18}\text{O}$ records measured on brachiopod calcite reveals that some of the $\delta^{18}\text{O}$ values of brachiopod calcite are in part significantly depleted in ^{18}O compared with conodont apatite. The brachiopod calcite record shows much greater variations not explicable by temperature variations.

Assuming an oxygen isotope composition of -1‰ VSMOW (non-glaciated world) for Devonian sea water, conodont $\delta^{18}\text{O}$ values provide realistic temperatures for tropical to subtropical surface waters. The generally lower $\delta^{18}\text{O}$ values of brachiopod shell calcite give unrealistically high palaeotemperatures. This discrepancy, plus the large variance in the brachiopod calcite $\delta^{18}\text{O}$ values can only be explained by diagenetic resetting of the oxygen isotope ratios of brachiopod calcite. Most importantly, the data presented in this study suggest that the oxygen isotope composition of Devonian seawater $\delta^{18}\text{O}$ was not significantly different from modern sea water.

The reconstructed Devonian palaeotemperature record contradicts earlier views that the Devonian represented a supergreenhouse

interval. Our data suggest that the Early Devonian (Lochkovian; 416–411 Myr) and Late Devonian (late Frasnian and Famennian; 377–359 Myr) were very warm intervals, whereas the late Early and Middle Devonian (405–385 Myr) were characterized by cooler climatic conditions. The climax of coral–stromatoporoid reef development was during the Middle Devonian, an interval characterized by cool to intermediate tropical SSTs. Coral–stromatoporoid reefs were rare in the Early Devonian, finally becoming extinct in the latest Frasnian. Microbial reefs were abundant in the Early and Late Devonian suggesting that warm to very warm SSTs in the Early and Late Devonian were unfavourable for the development of coral–stromatoporoid reefs, but promoted growth of autotrophic reefs that were abundant during these time intervals. Our data suggest that SST exerted a control on Devonian reef development and that climatic warming in the Late Frasnian in conjunction with short-term cooling pulses may have contributed to the extinction of coral–stromatoporoid reef ecosystems during the Frasnian–Famennian life crisis.

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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.epsl.2009.05.028.

References

- Algeo, T.J., Scheckler, S.E., 1998. Terrestrial-marine teleconnections in the Devonian: links between the evolution of land plants, weathering processes, and marine anoxic events. *Philos. Trans. R. Soc. Lond., B Biol. Sci.* 353, 113–130.
- Antoshkina, A., Königshof, P., 2008. Lower Devonian reef structures in Russia: an example from the Urals. *Facies* 54, 233–251.
- Barnes, C.R., Fahraeus, L.E., 1975. Provinces, communities, and the proposed necto-benthic habit of Ordovician conodontophorids. *Lethaia* 8, 133–149.
- Bassett, D., Macleod, K.G., Miller, J.L., Ethington, R.L., 2007. Oxygen isotope composition of biogenic phosphate and the temperature of Early Ordovician seawater. *Palaios* 22, 98–103.
- Berner, R.A., Kothavala, Z., 2001. GEOCARB III: a revised model of atmospheric CO₂ over Phanerozoic time. *Am. J. Sci.* 301, 182–204.
- Blake, R.E., O'Neil, J.R., Garcia, G., 1997. Oxygen isotope systematics of biologically mediated reactions of phosphate; I. Microbial degradation of organophosphorus compounds. *Geochim. Cosmochim. Acta* 61, 4411–4422.
- Brown, B.E., 1997. Coral bleaching: causes and consequences. *Coral Reefs* 16, 129–138.
- Buggisch, W., Joachimski, M.M., Sevastopulo, G., Morrow, J., 2008. Mississippian $\delta^{13}\text{C}_{\text{carb}}$ and conodont apatite $\delta^{18}\text{O}$ records? Their relation to the Late Palaeozoic glaciation. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 268, 273–292.
- Caputo, M.V., Melo, J.H.G., de Streel, M., Isbell, J., 2008. Late Devonian and Early Carboniferous glacial records of South America. *Spec. Pap. - Geol. Soc. Am.* 441, 161–173.
- Copper, P., 1994. Ancient reef ecosystem expansion and collapse. *Coral Reefs* 13, 3–11.
- Copper, P., 2002a. Reef development at the Frasnian/Famennian mass extinction boundary. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 181, 27–65.
- Copper, P., 2002b. Silurian and Devonian reefs: 80 million years of greenhouse between two ice ages. In: Kiessling, W., Flügel, E., Golonka, J. (Eds.), *Phanerozoic Reef Patterns: SEPM Special publication*, vol. 72, pp. 181–238.
- Copper, P., Scotese, C.R., 2003. Megareefs in Middle Devonian supergreenhouse climates. *Spec. Publ. - Geol. Soc. Am.* 370, 209–230.
- Donoghue, P.C.J., 1998. Growth and patterning in the conodont skeleton. *Philos. Trans. R. Soc. Lond., Ser. B Biol. Sci.* 353, 633–666.
- Donoghue, P.C., Forey, P.L., Aldridge, R., 2000. Conodont affinity and chordate phylogeny. *Biol. Rev.* 75, 191–249.
- Elrick, M., Berkow, S., Klapper, G., Sharp, Z., Joachimski, M., Fryda, J., 2009. Stratigraphic and oxygen isotope evidence for My-scale glaciation driving eustasy in the Early–Middle Devonian greenhouse world. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 276, 170–181.
- Epstein, A.G., Epstein, J.B., Harris, L.D., 1977. Conodont color alteration — an index to organic metamorphism. *U.S. Geol. Surv. Prof. Papers* 995, 1–27.
- Flügel, E., Flügel-Kahler, E., 1992. Phanerozoic reef evolution: basic questions and data base. *Facies* 26, 167–278.
- Flügel, E., Kiessling, W., 2002. Patterns of Phanerozoic reef crises. In: Kiessling, W., Flügel, E., Golonka, J. (Eds.), *Phanerozoic Reef Patterns: SEPM Spec. Pub.*, vol. 72, pp. 691–733.
- George, A.D., Playford, P.E., Powell, C.M., 1995. Platform-margin collapse during Famennian reef evolution, Canning Basin, Western Australia. *Geology* 23, 691–694.
- Golonka, J. (2000): Cambrian–Neogene Plate Tectonic Maps. — Wyd 1., Kraków b Wydawn. Uniwersytetu Jagiellońskiego, 125 pp, 36 plates. (Rozprawy habilitacyjne/Uniwersytet Jagielloński, ISSN 0239– 782X; 350): ISBN 83-233-1042-0. (<http://www.dinodata.org/Golonka/Golonka.htm>).
- Gradstein, F.M., Ogg, J.G., Smith, A.G., 2004. A geologic time scale 2004. Cambridge University Press, Cambridge.
- Grandjean-Lécuyer, P., Feist, R., Albarède, F., 1993. Rare earth elements I old biogenic apatites. *Geochim. Cosmochim. Acta* 57, 2507–2514.
- Gregory, R.T., 1991. Oxygen isotope history of seawater revisited: timescales for boundary event changes in the oxygen isotope composition of seawater. In: Taylor, H.P., O'Neil, O.R., Kaplan, I.R. (Eds.), *Stable Isotope Geochemistry: A Tribute to Samuel Epstein*. *Geochim. Spec. Pub.*, vol. 3, pp. 65–76.
- Habermann, D., Götze, T., Meijer, J., Stephan, A., Richter, D.K., Niklas, J.R., 2000. High-resolution rare-earth elements analyses of natural apatite and its application in geo-sciences: combined micro-PIXE, quantitative CL spectroscopy and electron spin resonance analyses. *Nuclear. Instrum. Methods Phys. Res. B* 161–163, 846–851.
- Iacumin, P., Bocherens, H., Mariotti, A., Longinelli, A., 1996. Oxygen isotope analysis of co-existing carbonate and phosphate in biogenic apatite: a way to monitor diagenetic alteration of bone phosphate? *Earth Planet. Sci. Lett.* 142, 1–6.
- Ihaka, R., Gentleman, R., 1996. R: a language for data analysis and graphics. *J. Comput. Graph. Stat.* 5, 299–314 (Software available from: <http://cran.r-project.org/>).
- Jaffres, J.B.D., Shields, G., Wallmann, K., 2007. The oxygen isotope evolution of seawater: a critical review of a long-standing controversy and an improved geological water cycle model for the past 3.4 billion years. *Earth-Sci. Rev.* 83, 83–122.
- Joachimski, M.M., Buggisch, W., 2002. Conodont apatite $\delta^{18}\text{O}$ signatures indicate climatic cooling as a trigger of the Late Devonian (F–F) mass extinction. *Geology* 30, 711–714.
- Joachimski, M., Ostertag-Neuning, C., Pancost, R.D., Strauss, H., Freeman, K.H., Littke, R., Sinninghe Damsté, J., Racki, G., 2001. Water column anoxia, enhanced productivity and concomitant changes in $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ across the Frasnian–Famennian boundary (Kowala–Holy Cross Mountains/Poland). *Chem. Geol.* 175, 109–131.
- Joachimski, M.M., van Geldern, R., Breisig, S., Day, J., Buggisch, W., 2004. Oxygen isotope evolution of biogenic calcite and apatite during the Middle and Upper Devonian. *Int. J. Earth Sci.* 93, 542–553.
- Kaiser, S., Steuber, T., Becker, B., Joachimski, M.M., 2006. Geochemical evidence for major environmental change at the Devonian–Carboniferous boundary in the Carnic Alps and the Rhenish Massif. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 240, 146–160.
- Kiessling, W., 2002. Secular variations in the Phanerozoic reef ecosystem. *Spec. Publ. - Soc. Econ. Paleontol. Mineral.* 72, 625–690.
- Kiessling, W., Flügel, E., Golonka, J., 1999. Paleoreef maps: evaluation of a comprehensive database on Phanerozoic reefs. *Am. Assoc. Pet. Geol. Bull.* 183, 1552–1587.
- Klapper, G., Lane, H.R., 1988. Frasnian (Upper Devonian) conodont sequence at Luscar Mountain and Mount Haultain, Alberta Rocky Mountains. *Can. Soc. Pet. Geol. Mem.* 14, 469–478.
- Kolodny, Y., Luz, B., Navon, O., 1983. Oxygen isotope variations in phosphate of biogenic apatites. I. Fish bone apatite — rechecking the rules of the game. *Earth Planet. Sci. Lett.* 64, 398–404.
- Königshof, P., 1992. Der Farbänderungsindex (CAI) von Conodonten in paläozoischen Gesteinen (Mitteldevon bis Unterkarbon) des Rheinischen Schiefergebirges — eine Ergänzung zur Vitriniteflexion. *Cour. Forsch.-Inst. Senckenberg*. 168, 255–265.
- Land, L.S., Lynch, F.L., 1996. $\delta^{18}\text{O}$ values of mudrocks: more evidence for an ^{18}O -buffered ocean. *Geochim. Cosmochim. Acta* 60, 3347–3352.
- Lécuyer, C., Allemand, P.A., 1999. Modelling of the oxygen isotope evolution of seawater: implications for the climate interpretation of the $\delta^{18}\text{O}$ of marine sediments. *Geochim. Cosmochim. Acta* 63, 351–361.
- Léthiers, F., Raymond, D., 1991. Les crises du Dévonien supérieur par l'étude des faunes d'ostracodes dans leurs cadres paléogéographiques. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 88, 133–146.
- Loader, C.R., 1999. Local Regression and Likelihood. Springer, Berlin. 290 pp.
- McArthur, J.M., Howard, R.J., Bailey, T.R., 2001. Strontium isotope stratigraphy: LOWESS version 3: best fit to the marine Sr-isotope curve for 0–509 Ma and accompanying look-up table for deriving numerical age. *J. Geol.* 109, 155–170.
- Muehlenbachs, K., 1998. The oxygen isotopic composition of the oceans, sediments and the seafloor. *Chem. Geol.* 145, 263–273.
- Muehlenbachs, K., Furnes, H., Fonneland, H.C., Hellevang, B., 2003. Ophiolites as faithful records of the oxygen isotope ratio of ancient seawater: the Solund-Stavfjord ophiolite complex as a Late Ordovician example. In: Dilek, Y., Robinson, P.T. (Eds.), *Ophiolites in Earth History*. *Geol. Soc. London Spec. Pub.*, vol. 218, pp. 401–414.
- Nöth, S., 1998. Conodont color (CAI) versus microcrystalline and textural changes in Upper Triassic conodonts from northwest Germany. *Facies* 38, 165–174.
- O'Neil, J.R., Clayton, R.N., Meyeda, T.K., 1969. Oxygen isotope fractionation in divalent metal carbonate. *J. Chem. Phys.* 51, 5547–5558.
- O'Neil, J.R., Roe, J.L., Reinhardt, E., Blake, R.E., 1994. A rapid and precise method of oxygen isotope analysis of biogenic phosphate. *Isr. J. Earth-Sci.* 43, 203–212.
- Pietzner, H., Vahl, J., Werner, H., Ziegler, W., 1968. Zur chemischen Zusammensetzung und Mikromorphologie der Conodonten. *Palaeontogr. Abt. A* 128, 115–152.
- Pockley, P., 2000. Global warming identified as a main threat to coral reefs. *Nature* 407, 932.

- Pucéat, E., Reynard, B., Lécuyer, C., 2004. Can crystallinity be used to determine the degree of chemical alteration of biogenic apatites? *Chem. Geol.* 205, 83–97.
- Rejebian, V.A., Harris, A.G., Huebner, J.S., 1987. Conodont colour and textural alteration: An index to regional metamorphism, contact metamorphism and hydrothermal alteration. *Geol. Soc. Am. Bull.* 99, 471–497.
- Riding, R., 1992. Temporal variation in calcification in marine cyanobacteria. *J. Geol. Soc. (Lond.)* 149, 979–989.
- Sandberg, C., 1976. Conodont biofacies of Late Devonian *Polygnathus styriacus* Zone in western United States. In: Barnes, C.R. (Ed.), *Conodont paleoecology*: Geol. Assoc. Canada Spec. Pap., vol. 15, pp. 171–186.
- Sandberg, C., Dreesen, R., 1984. Late Devonian icriodontid biofacies models and alternate shallow-water conodont zonation. *Spec. Pap. - Geol. Soc. Am.* 196, 143–169.
- Sandberg, C.A., Ziegler, W., Bultynck, P., 1989. New standard conodont zones and early *Ancyrodella* phylogeny across Middle–Upper Devonian boundary. *Cour. Forsch.-Inst. Senckenberg* 110, 195–230.
- Sansom, I.J., Smith, M.P., Armstrong, H.A., Smith, M.M., 1992. Presence of the earliest vertebrate hard tissues in conodonts. *Science* 256, 1308–1311.
- Savin, S.M., 1977. The history of the earth's surface temperature during the past 100 million years. *Annu. Rev. Earth Planet. Sci.* 5, 319–355.
- Schülke, I., 2003. Famennian conodont biodiversity cycles. *Cour. Forsch.-Inst. Senckenberg* 242, 225–237.
- Shemesh, A., 1990. Crystallinity and diagenesis of sedimentary apatites. *Geochim. Cosmochim. Acta* 54, 2433–2438.
- Simon, L., Godderis, Y., Buggisch, W., Strauss, H., Joachimski, M., 2007. Modeling the carbon and sulphur isotope composition of marine sediments: climate evolution during the Devonian. *Chem. Geol.* 146, 19–38.
- Streel, M., Caputo, M.V., Loboziak, S., Melo, J.H.G., 2000. Late Frasnian–Famennian climates based on palynomorph analyses and the question of the Late Devonian glaciations. *Earth Sci. Rev.* 52, 121e–173e.
- Sweet, W.C., 1988. The conodonts: morphology, taxonomy, paleoecology and evolutionary history of a long-extinct-animal phylum. *Oxford Monographs Geol. Geophys.*, vol. 10. Clarendon Press, Oxford, pp. 2–212.
- Talent, J.A., 1988. Organic reef building: episodes of extinction and symbiosis. *Senckenb. Lethaea* 69, 315–368.
- Trotter, J.A., Fitz Gerald, J.D., Kokkonen, H., Barnes, C., 2007. New insights into the ultra-structure, permeability, and integrity of conodont apatite determined by transmission electron microscopy. *Lethaea* 97–110. doi:10.1111/j.1502-3931.2007.00024x.40.
- Trotter, J.A., Williams, I.S., Barnes, C.R., Lécuyer, C., Nicoll, R.S., 2008. Did cooling oceans trigger Ordovician biodiversification? Evidence from conodont thermometry. *Science* 321, 550–554.
- Tsien, H.H., 1988. Devonian paleogeography and reef development of northwestern and central Europe. In: McMillan, M.J., Embry, A.F., Glass, D.J. (Eds.), *Devonian of the World*, vol. 1: Can. Soc. Petrol. Geol. Mem., vol. 14, pp. 341–358.
- Van Geldern, R., Joachimski, M.M., Day, J., Jansen, U., Alvarez, F., Yolkina, E.A., Ma, X.P., 2006. Carbon, oxygen and strontium isotope records of Devonian brachiopod shell calcite. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 240, 47–67.
- Veizer, J., Ala, D., Azmy, K., Bruckschen, P., Buhl, D., Bruhn, F., Carden, G.A.F., Diener, A., Ebner, S., Godderis, Y., Jasper, T., Korte, C., Pawellek, F., Podlaha, O.G., Strauss, H., 1999. $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ evolution of Phanerozoic seawater. *Chem. Geol.* 161, 59–88.
- Vennemann, T.W., Fricke, H.C., Blake, R.E., O'Neil, J.R., Colman, A., 2002. Oxygen isotope analysis of phosphates: a comparison of techniques for analysis of Ag_3PO_4 . *Chem. Geol.* 185, 321–336.
- Wallmann, K., 2001. The geological water cycle and the evolution of marine $\delta^{18}\text{O}$ values. *Geochim. Cosmochim. Acta* 65, 2469–2485.
- Wenzel, B., Lécuyer, C., Joachimski, M.M., 2000. Comparing calcite and phosphate oxygen isotope paleothermometers — $\delta^{18}\text{O}$ of Silurian brachiopods and conodonts. *Geochim. Cosmochim. Acta* 64, 1859–1872.
- Whalen, M.T., Day, J., Eberli, G.P., Homewood, P.W., 2002. Microbial carbonates as indicators of environmental change and biotic crises in carbonate systems: examples from the Upper Devonian, Alberta basin, Canada. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 181, 127–151.
- Witzke, B.J., Heckel, P.H., 1988. Paleoclimatic indicators and inferred Devonian paleolatitudes of Euramerica. In: McMillan, M.J., Embry, A.F., Glass, D.J. (Eds.), *Devonian of the World*, vol. 1: Regional syntheses. Can. Soc. Petrol. Geol. Mem., vol. 14, pp. 49–63.
- Wood, R., 1999. Reef evolution. Oxford University Press, Oxford. 414 pp.
- Wood, R., 2000. Paleocology of a Late Devonian back reef, Canning Basin, Australia. *Palaeontology* 43, 671–703.
- Zazzo, A., Lécuyer, C., Mariotti, A., 2004. Experimentally-controlled carbon and oxygen isotope exchange between bioapatites and water under inorganic and microbially-mediated conditions. *Geochim. Cosmochim. Acta* 68, 1–12.