



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

PALAEO

Palaeogeography, Palaeoclimatology, Palaeoecology 205 (2004) 337–357

www.elsevier.com/locate/palaeo

Biochemostratigraphy of the Devonian–Carboniferous boundary global stratotype section and point, Griotte Formation, La Serre, Montagne Noire, France

Uwe Brand^{a,*}, Marie Legrand-Blain^b, Maurice Streef^c

^a Department of Earth Sciences, Brock University, 500 Glenridge Avenue, St. Catharines, ON, Canada L2S 3A1

^b Institut EGID, Université de Bordeaux 3, Allée Daguin, F-33607 Pessac, France

^c Université de Liège, Paléobotanique et Paléopalynologie, Sart-Tilman Bât. B 18, B-4000 Liège 1, Belgium

Received 21 February 2003; received in revised form 12 December 2003; accepted 22 December 2003

Abstract

The Griotte Formation and the base of Bed 89 exposed at La Serre, Montagne Noire, France represent the Global Stratotype Section and Point (GSSP) for the Devonian–Carboniferous (D–C) boundary. This study represents the geochemical work on brachiopods and matrix covering the *Siphonodella praesulcata* to *Siphonodella sulcata* Zones at the GSSP. Values of $^{87}\text{Sr}/^{86}\text{Sr}$ of unaltered brachiopods provide the most powerful biochemostratigraphic tool in recognizing and correlating the Devonian–Carboniferous boundary on a global scale. The frequency and variations of the latest Devonian $^{87}\text{Sr}/^{86}\text{Sr}$ trend (0.708167 ± 0.000042) are invariant but the population means are similar ($p = 1.000$) to the essentially pronounced trend for the post-boundary Carboniferous (0.708165 ± 0.000054) brachiopods from the GSSP and supplementary sections. The Devonian–Carboniferous boundary $^{87}\text{Sr}/^{86}\text{Sr}$ value based on unaltered brachiopod samples from within 0.2 m of either side of the boundary is 0.708231 ± 0.000021 (NBS 987 = 0.710240). Oxygen isotope values of unaltered brachiopods from the Devonian side of the boundary are $-1.99 \pm 2.29\%$ (PDB) and those from the Carboniferous side are $-3.08 \pm 0.51\%$ (PDB, $p = 0.229$), which are from within to outside the range recorded in Recent low-latitude counterparts. Carbon isotope values for the Devonian brachiopods with $+4.37 \pm 1.69\%$ (PDB) are dissimilar to those from the Carboniferous side of the boundary with $+1.93 \pm 0.49\%$ (PDB; $p = 0.0001$), but both mostly overlap with the range observed in Recent low-latitude brachiopods. The large positive excursions in $\delta^{13}\text{C}$ ($\Delta 5.5\%$) and $\delta^{18}\text{O}$ ($\Delta 6.9\%$) of the unaltered brachiopods reflect changing oceanographic conditions of the La Serre Sea and possibly of the global oceans during the uppermost Middle and Upper *S. praesulcata* Subzones. Oxygen isotope trend may reflect, in part, a climatic response of a rapid, short and distinct glacial event during the upper Middle *S. praesulcata* Subzone. This cryogenic event of a larger oceanographic/climatic shift correlates, in part, to the Hangenberg Event sensu lato. Excursions in the seawater– ^{87}Sr bracket the onset and offset of the glacial event, reflecting changes in continental weathering patterns and processes and with it changes in riverine fluxes. In contrast, the carbon isotope shift although related to the cooling trend is probably associated with a drawdown of atmospheric CO_2 and/or burial of organic matter. The biochemostratigraphic values/contents and trends presented in this study, in conjunction with biostratigraphic observations, facilitate the

* Corresponding author. Tel.: +1-905-688-5550; fax: +1-905-682-9020.

E-mail address: uwe.brand@brocku.ca (U. Brand).

correlation of sequences at Hasselbachtal and Wocklum (Germany), Nانبiancun (China) and Starks Road and Hannibal (Missouri, USA).

© 2004 Elsevier B.V. All rights reserved.

Keywords: Devonian–Carboniferous GSSP; La Serre; Carbon; Oxygen and strontium isotopes; Hangenberg Event; Glaciation; Global correlation

1. Introduction

The search for a Devonian–Carboniferous boundary stratotype began in earnest in 1978 after the Working Group was organized in 1976. Its work culminated in 1988, when the IUGS Working Group selected the La Serre section to represent the Global Stratotype Section and Point (GSSP) for the Devonian–Carboniferous boundary. The first appearance of the conodont *Siphonodella sulcata* characterizes the Devonian–Carboniferous (D–C) boundary and global stratotype point. This selection was ratified by the International Stratigraphic Commission (ICS) in 1991 (Paproth et al., 1991).

This biochemostratigraphic study of the boundary beds (LS-E') at the La Serre Devonian–Carboniferous GSSP has three major objectives. The first objective is to present biochemostratigraphic trends (St, O, C isotopes) at the GSSP and other boundary sequences using unaltered brachiopod material. The second objective is to evaluate the geochemical trends across the D–C boundary with respect to the Hangenberg Event sensu lato and other terminal Devonian oceanographic-climatic-atmospheric events. By Hangenberg Event sensu lato, we mean the Hangenberg Event sensu stricto post-event (see Streeel et al., 2000, p. 160 for detailed explanation and discussion). The Hangenberg Event sensu stricto (Walliser, 1984) corresponds to the transgressive Hangenberg Black Shale (HBS) in Germany, which highlights the disappearance of many marine taxa and is an equivalent of Bed 69 at La Serre. The post-event corresponds to the Hangenberg shales and sandstones in Germany, which underline the changes in the terrestrial flora, and are an equivalent of the regressive succession starting with Bed 70 at La Serre. The last objective is to compare the biochemostratigraphic data from other boundary sections, including auxiliary stratotype sections (AS) to the Devonian–Carboniferous GSSP trend, and thus assess their chemocorrelation potential.

La Serre located at the southeastern end of the Massif Central is about 43 km west of Montpellier (Fig. 1; cf. Flajs and Feist, 1988). The Devonian–Carboniferous boundary occurs in a shallowing upward carbonate sequence with a deepening in the lower Middle *Siphonodella praesulcata* Subzone in the Griotte Formation (Fig. 2; Trench LS-E', cf. Legrand-Blain and Martinez Chacon, 1988; Feist et al., 2000; Feist, 2002). The Griotte Formation consists of fossiliferous limestones and shales with a preponderance of conodonts, brachiopods, plants, trilobites, ostracods, bryozoans, rugose corals, ammonoids and ooids (Brauckmann et al., 1993; Legrand-Blain, 1995). The global stratotype point defining the Devonian–Carboniferous boundary is set at the first appearance of the conodont *S. sulcata* at the base of Bed 89 of a continuous sequence in Trench LS-E' at La Serre (Paproth and Streeel, 1984). Fig. 2 represents the ranges of important fossils (conodonts, trilobites and brachiopods) recovered and observed in the sequence of Trench LS-E'. Additional litho-, bio- and sequence stratigraphic and paleontologic information of the boundary section has been reviewed, described and presented in detail by Feist (1985), Flajs and Feist (1988), Legrand-Blain and Martinez Chacon (1988), Semenoff-Tian-Chansky (1988), Vachard (1988), Brand and Legrand-Blain (1993), Girard (1994), Feist et al. (2000) and Feist (2002). The reader is referred to these studies and references therein for further information about the Devonian–Carboniferous GSSP at La Serre. It is far from an ideal GSSP since it lacks palynomorphs and about 80% of the conodont fauna is reworked (Feist et al., 2000). Consequently Auxiliary Stratotype sections (AS) have been designated at Hasselbachtal, Germany (Becker and Paproth, 1993) and Nانبiancun, China (Wang, 1993) to serve as supplementary regional sections (Streeel et al., 2000).

For this study, additional brachiopod material from sections at Starks Road-Hannibal, Missouri (Louisiana Limestone and Glen Park Formation,

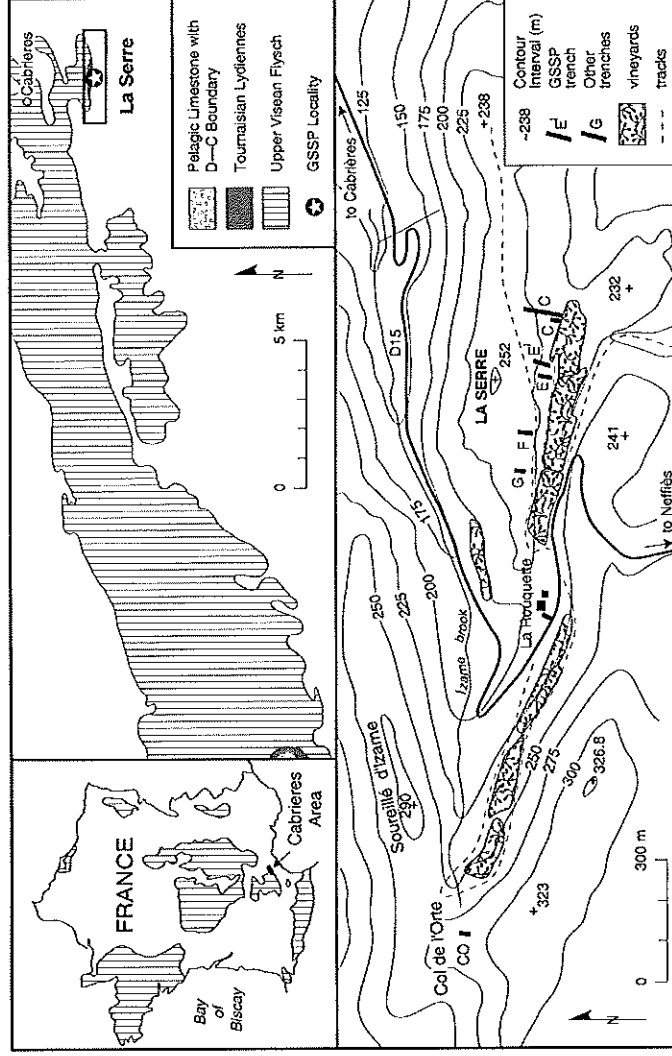


Fig. 1. Locality diagram of La Serre, Griotte Formation and the Global Stratotype Section and Point (GSSP) for the Devonian - Carboniferous boundary in southern France. The insets show details of the Cabrières region and the trenches excavated in the La Serre area to expose the Griotte Formation about the boundary (modified after Flajs and Feist, 1988, and Galtier et al., 1988).

respectively), and at Wocklum (Wocklum Limestone), Germany are helpful in establishing more definitive biochemostratigraphic trends about the D-C boundary. Further comparison with other material from the auxiliary stratotype sections at Haselbachtal and Nambiancum, from the section at the Grüne Schneid (Austria), as well as whole rock isotope chemistry from numerous latest Devonian/earliest Carboniferous units completes the assessment of this study (Fig. 3).

2. Methodology

A total of 53 samples (45 brachiopods and 8 matrix) were analyzed for trace elements, stable and radiogenic isotopes to establish parameters for biochemostratigraphy and chemocorrelation of the Devonian-Carboniferous GSSP at La Serre, Montagne Noire (Appendix A; supplementing the data of Brand and Legrand-Blain, 1993). Additional data from the Glen Park Formation and Louisiana Limestone of Missouri

and from the Wocklum Limestone at Wocklum, Germany complete the database (Appendix A). Special care in preparation of brachiopod material is of utmost importance in acquiring geochemical signatures of original seawater (cf. Brand and Veizer, 1980; Wenzel, 2000). All shell fragments must be extricated from the rock, which involved the removal of adhering matrix and visibly altered shell material (e.g., primary layer) from brachiopod fragments with dental and other tools. Subsequently, brachiopod fragments were immersed and leached in 10% HCl (suprapure) for 30 s (or longer as needed) and rinsed in copious amounts of deionized water and left to air-dry. The physical and chemical etching processes removed all extraneous material as well as the primary layer of the brachiopod shell. Matrix samples were cleaned of fossil fragments and weathered rinds to obtain the least cross-contaminated sample as possible. These too were etched in acid solution and rinsed with water to assure cleanliness of the specimens. Macro- and microtextural (structures) preservation of brachiopods was further examined under binocular microscope, by

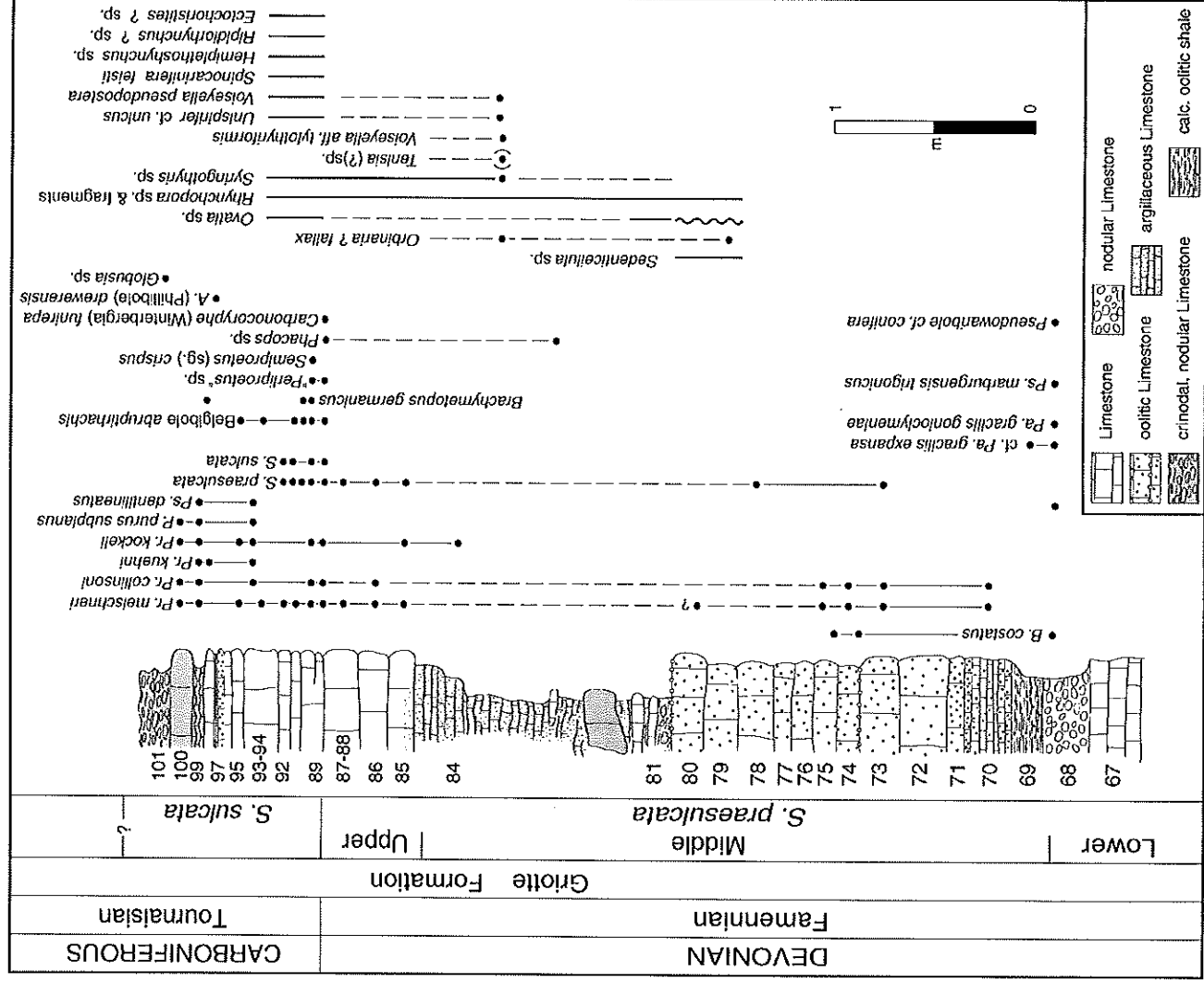


Fig. 2. Ranges of important conodonts, trilobites, and brachiopods for the bed interval LS-E' 68-101 of the Griotte Formation in the global stratotype section (modified from Flajs and Feist, 1988; LeGrand-Blain and Martinez Chacon, 1988; Feist et al., 2000) and lithostratigraphy of the boundary beds. Conodont zones (*S. praesulcata* and *S. sulcata*) and subzones (Lower, Middle and Upper *S. praesulcata*) are based on information gleaned from Flajs and Feist (1988) and new zonation espoused by Ziegler and Sandberg (1984b).

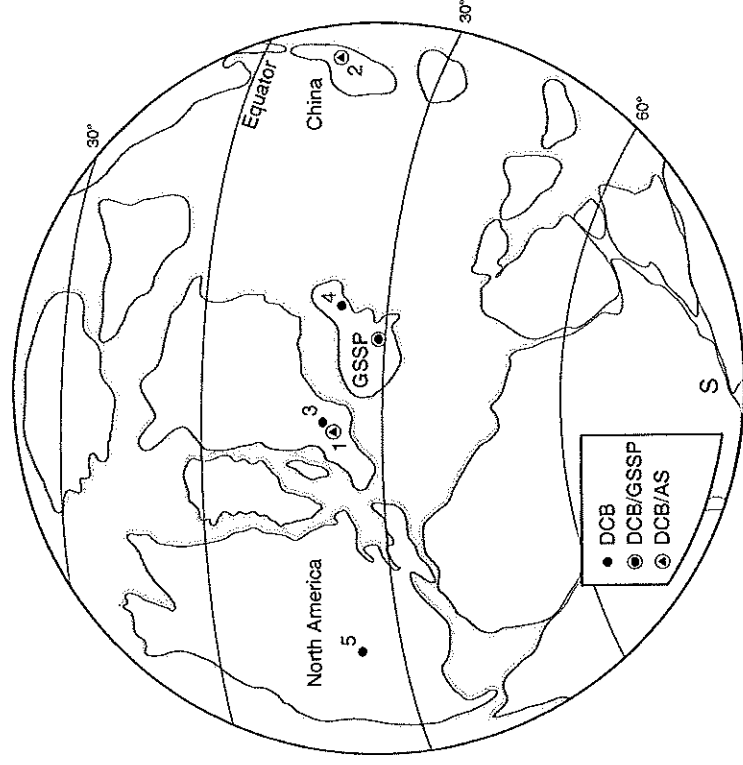


Fig. 3. Paleogeographic reconstruction of late Devonian–early Carboniferous continental plates (after Street et al., 2000 modified from Heckel and Witzke, 1979). Devonian – Carboniferous boundary material (brachiopods and conodonts) is from the Global Stratotype Section and Point (GSSP) at La Serre, France, Auxiliary Stratotypes at Hasselbachthal, Germany (AS-1) and at Nanbiancun, Guilin, China (AS-2), and from other sections such as Wocklum, Germany (3), Grüne Schneid, Austria (4) and Starks Roadcut and Hannibal, Missouri, USA. (5).

cathode luminescence (CL) and scanning electron microscope (SEM). Cleaned fragments were sputter coated with gold/palladium, and microstructures were evaluated with an ISI scanning electron microscope. Luminescence of carbonates and allochems was investigated with a Nuclide ELM-2B Luminescope. Microtextural preservation (SEM), luminescence patterns (CL) and trace element contents are the primary selection tools used in identifying unaltered brachiopod material (e.g., Brand and Veizer, 1980; Brand and Legrand-Blain, 1993). Up to 60 mg of sample powder of each sample, weighed to four decimal places, was digested in 10 ml of 5% (v/v) of suprapure HNO_3 for about 1 h. After volumetric filtration of liquid, the weight of the noncarbonate portion was determined thermogravimetrically by incinerating the ashless filter paper (Whatman #40) at 400 °C for 1 h. All glassware and plasticware were aqua regia cleaned to assure cleanliness of sample containers. N.I.S.T. (formerly

N.B.S.) and U.S.G.S. SRMs (standard reference materials; 636, 633, 19-1AEA, 987, EN-1), sample duplicates and blanks were routinely analyzed with the samples to assure sample solution integrity, and data precision and accuracy. All samples, brachiopod fragments and matrix, were tested for insoluble residue (I.R.) content, and Ca, Mg, Sr, Mn, and Fe (Appendix A). Elemental analyses were carried out on a Varian 400P atomic absorption spectrophotometer with digital sampling preparation station. Precision and accuracy of elemental analyses of the standard reference material (SRM) powders are within 3% of the recommended values for Ca, Mg, Sr, Mn, and Fe specified by the National Institute of Standards and Technology, Washington, DC (NIST-SRMs #636, 633; cf. Brand and Veizer, 1980).

A subset of the samples (brachiopods and matrix) was further analyzed for carbon, oxygen and strontium isotope compositions (Appendix A). Aliquots of about

5 mg of each sample were reacted with 100% phosphoric acid at 50 °C for 30 min. The carbon and oxygen isotope analyses were performed on a VG SIRA-12 triple collector mass spectrometer with soft seat micro-inlet, results calibrated to PDB, corrected to a temperature of 25 °C, and reported in the standard δ notation (Appendix A). The precision and accuracy of the isotopic analyses are better than: 0.05‰ and 0.02‰ for carbon, and 0.10‰ and 0.05‰ for oxygen, respectively (NBS 19-IAEA; cf. Brand and Veizer, 1981).

For strontium isotope analyses, about 1 mg of select unaltered brachiopod and matrix samples were digested in 2.5 N suprapure HCl for about 24 h at room temperature. This was followed by separation with 4.5 ml of AGW 50X8 (Biorad) cation exchange resin in quartz glass columns to obtain purified Sr. Samples were analyzed at Ruhr University (Bochum) on a Finnigan MAT 262 5-collector solid source mass spectrometer with single Ta filament (cf. Brand, 1991). Loading blank was below 5 pg, column blank was less than 1 ng, and reagent blank was below 0.01 ppb. The mean for 6 analyses of the SRM in this run was 0.710230 ± 0.000004 (2σ), and the mean of 20 analyses of ocean water off Norway and France was 0.709149 ± 0.000020 (2σ). Precision of duplicate analyses was better than 0.000008 (cf. Brand, 1991). Strontium isotope analyses of this and referenced studies were all corrected to a nominal NBS 987 value of 0.710240.

3. Results

Prior to using geochemical data and trends for correlation and as original seawater proxies, the diagenetic integrity must be assured through rigorous testing of the studied carbonate allochem(s) (cf. Brand and Veizer, 1980; Brand, 2004). Without this important step, the geochemical composition of some or all carbonate allochems may reflect postdepositional alteration or admixtures of diagenetic-original signatures. Brand and Veizer (1980, 1981) clearly laid out the concept of selecting unaltered material with pristine geochemical composition. In general, geochemical compositions of carbonates will approach the values/composition of the diagenetic reaction system. Diagenesis leads to increases in Mn and Fe and to

more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ and to concomitant, but not necessarily to the same degree, decreases in Sr, Na, Mg, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (Brand and Veizer, 1980, 1981; Brand, 1991; Banner and Kaufman, 1994). The combined careful evaluation of geochemical trends and physical observations (visual, microscope, scanning electron microscope and cathode luminescence) should lead to the selection of material that contains original depositional signals (cf. Marshall, 1992; Brand, 2004).

Microstructural evaluation shows that for the most part the brachiopods from the Griotte, Glen Park and Louisiana Formations are well preserved (Fig. 4A–C). Trabecular fibers of the secondary layer are microstructurally preserved showing no signs of diagenetic change in the preserved specimens. In contrast, in a few specimens, the fibers show evidence of diagenetic alteration by fusion (Fig. 4D) or replacement by secondary calcite cement (Fig. 1D; Brand and Legrand-Blain, 1993). The microstructural evaluation was followed by a detailed comparison of trace element and isotope trends. Fig. 5 is a detailed geochemical analysis of sample sets from specific horizons of the Griotte (A–C) and Louisiana (D–F) Formations. The preserved brachiopod material from Bed 93 of the Griotte Formation has the highest Sr and lowest Mn contents (Fig. 5A) that are complemented by heavier $\delta^{18}\text{O}$ and invariant $\delta^{13}\text{C}$ values than of its altered counterpart and enclosing whole rock material (Fig. 5B). This is confirmed by the difference in $^{87}\text{Sr}/^{86}\text{Sr}$ values between what is deemed a preserved specimen (thus containing an original seawater signature) and what is a diagenetically altered one (Fig. 5C; cf. Brand, 1991, 2004). Their values and ranges do not overlap as observed in modern brachiopod material as required for material from the same spatial and temporal oceanographic setting (Brand et al., 2003). Thus the more radiogenic sample is deemed altered and not representative of original seawater conditions. The samples (brachiopods and whole rock-micrite) from the uppermost horizon of the Louisiana Limestone follow the expected trends for Sr, Mn (Fig. 5D), $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ (Fig. 5E) with progressive postdepositional alteration (cf. Brand and Veizer, 1980, 1981). The Louisiana brachiopods deemed preserved have the highest Sr, lowest Mn, heaviest $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, an interpretation complemented by the $^{87}\text{Sr}/^{86}\text{Sr}$ values (Fig. 5F). Furthermore, the ranges of the two brachiopod specimens

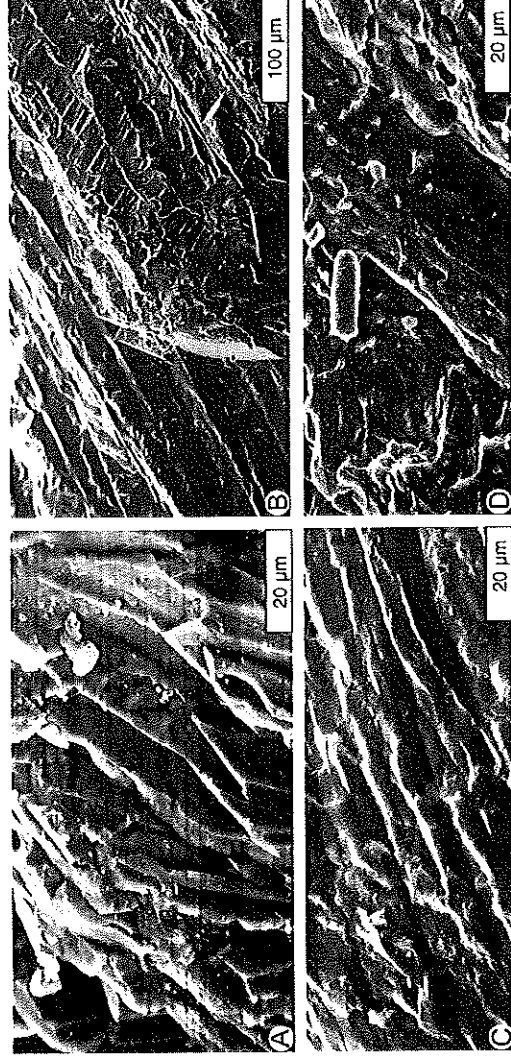


Fig. 4. Photomicrographs of microstructures in brachiopods from the Griotte Formation (GSSP), Glen Park Formation and Louisiana Limestone. A shows well preserved trabecular fibers (secondary layer) in specimen LSF-04 from the Griotte Formation. B shows well-preserved secondary layer fibers of specimen GP-03 from the Glen Park Formation. C shows preserved fibers of the secondary layer in specimen LL-02 from the Louisiana Limestone, whereas D depicts fusion and disgenetic alteration of the fibers in specimen LL-05.

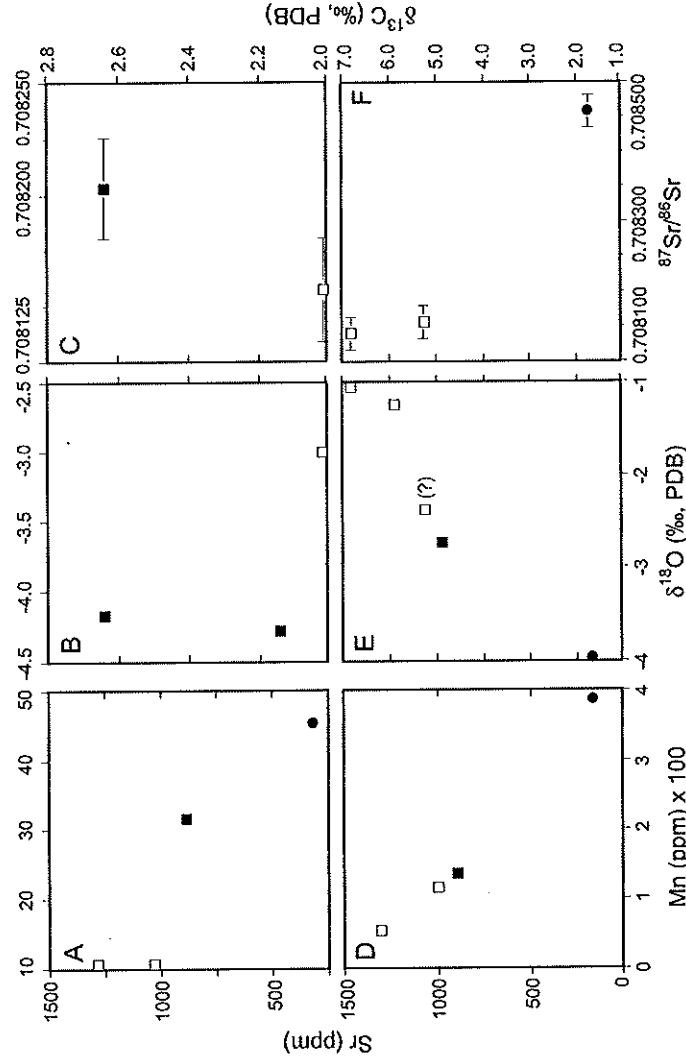


Fig. 5. Diagenetic evaluation of brachiopods and matrix (whole rock) from the Griotte Formation (sample set from LS-E' bed 93; A, B and C) and Louisiana Limestone (sample set ULL; D, E and F; Appendix A). A and D show the Sr versus Mn distribution of brachiopods (preserved [open square] and altered [solid square]) and corresponding matrix (altered [solid circle]). B and E show the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ distribution of the various allochems from the two horizons (Griotte and Louisiana Formations, respectively). C and F show the $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ isotope distributions of preserved and altered specimens/material from the respective formations and horizons.

with original seawater— ^{87}Sr values fulfill the criterion for spatial and temporal uniformity set by their modern counterparts (Brand et al., 2003). This horizon-specific diagenetic evaluation process was carried out for all sample sets from the Griotte, Glen Park and Louisiana Formations (Appendix A).

Material of this study and that of other authors (Brand and Legrand-Blain, 1993; Bruckschen et al., 1995, 1999; Bruckschen and Veizer, 1997) was carefully evaluated as to their pristine state and reliability as proxies of original seawater chemistry (Brand, 2004). In general, if any of their samples are considered altered, they have been excluded from the database (the only exception is the data for whole rock material). All diagenetically altered material and values are excluded from the following presentation and discussion, except for Fig. 9, which includes all data including those deemed altered (?) of brachiopods, conodonts and whole rock-based data from other studies.

3.1. Biochemostratigraphic trends

The following diagrams (Figs. 6–9) depict the geochemical trends of unaltered brachiopods during the Devonian–Carboniferous boundary interval at the GSSP, several AS's and other important boundary sections. The size of the symbol includes the stratigraphic uncertainty unless indicated by error bars (y -axis), whereas the error bars (x -axis) on the unaltered brachiopod(s) from each horizon/bed represent the range observed in modern counterparts (Brand et al., 2003). Sr isotopes are the correlation tool/proxy of choice for high-resolution biochemostratigraphic work (e.g., Veizer et al., 1997; Brand and Brenckle, 2001; Brand and Bruckschen, 2002; Brand, 2004).

Oxygen and carbon isotope compositions of carbonate material should reflect the temperature and composition of the ambient fluid provided the material was precipitated or formed in isotopic equilibrium and was subsequently not diagenetically altered (cf. Epstein et al., 1953; Brand and Veizer, 1980, 1981; Veizer, 1983; Brand et al., 2003). This applies to brachiopods that precipitate multi-layered low-Mg calcite shells formed in isotopic equilibrium with their surrounding seawater (e.g., Lowenstam, 1961; Brand and Veizer, 1981; Bates and Brand, 1991). Thus these carbonate components, if unaltered, should contain

essentially invariant isotopic compositions and should be able to serve as proxies of seawater isotopic composition (Lowenstam, 1961; James et al., 1997). Furthermore, if the water composition is known or can be modeled (Broecker, 1986; Lécuyer and Allemand, 1999), then the oxygen isotopic compositions of the carbonate constituents may reflect combinations of climatic variations in temperature and composition of the ambient seawater.

3.2. Strontium isotope biochemostratigraphy

Strontium isotopes of unaltered brachiopods form the basis of the trend depicted for the Devonian–Carboniferous boundary interval (Fig. 6). The brachiopod data from the GSSP define tie lines and points for the D–C interval from the *S. praesulcata* to *S. sulcata* conodont Zones of the La Serre section. Supplementary brachiopod material from specific stratigraphic horizons of the Hasselbachtal, Louisiana and Glen Park sections were superimposed on the GSSP– ^{87}Sr trend using the information gleaned from various sources (cf. Kürschner et al., 1993; Bruckschen et al., 1995, 1999; Bruckschen and Veizer, 1997). This suggests that the two brachiopod data from the Hasselbachtal section define the Lower *S. praesulcata* Subzone, with sample Ha18B from the base of the subzone (and of the *S. praesulcata* Zone) and sample Ha44B about 0.9 m higher up in the section (Kürschner et al., 1993).

Placement of the brachiopod data from the Glen Park Formation and Louisiana Limestone (Koenig et al., 1961; Scott and Collinson, 1961) from the North American Midcontinent is more complicated due to some stratigraphic uncertainty within their respective *S. sulcata* and *S. praesulcata* Zones (Collinson et al., 1971; Ziegler and Sandberg, 1984a). Ultimately their placement in Fig. 6 was guided by the trend established by the material from the GSSP and the Hasselbachtal AS, biostratigraphic information and field sampling information. This information suggests the placement of the Glen Park data into the upper part of the *S. sulcata* Zone, and the Louisiana data into the upper part of the Middle *S. praesulcata* Subzone (Fig. 6). These seem reasonable placements with respect to all factors considered in the process (fit with adjacent geochemical data, relative field position and biostratigraphic information). Consequently, the Sr isotope trend

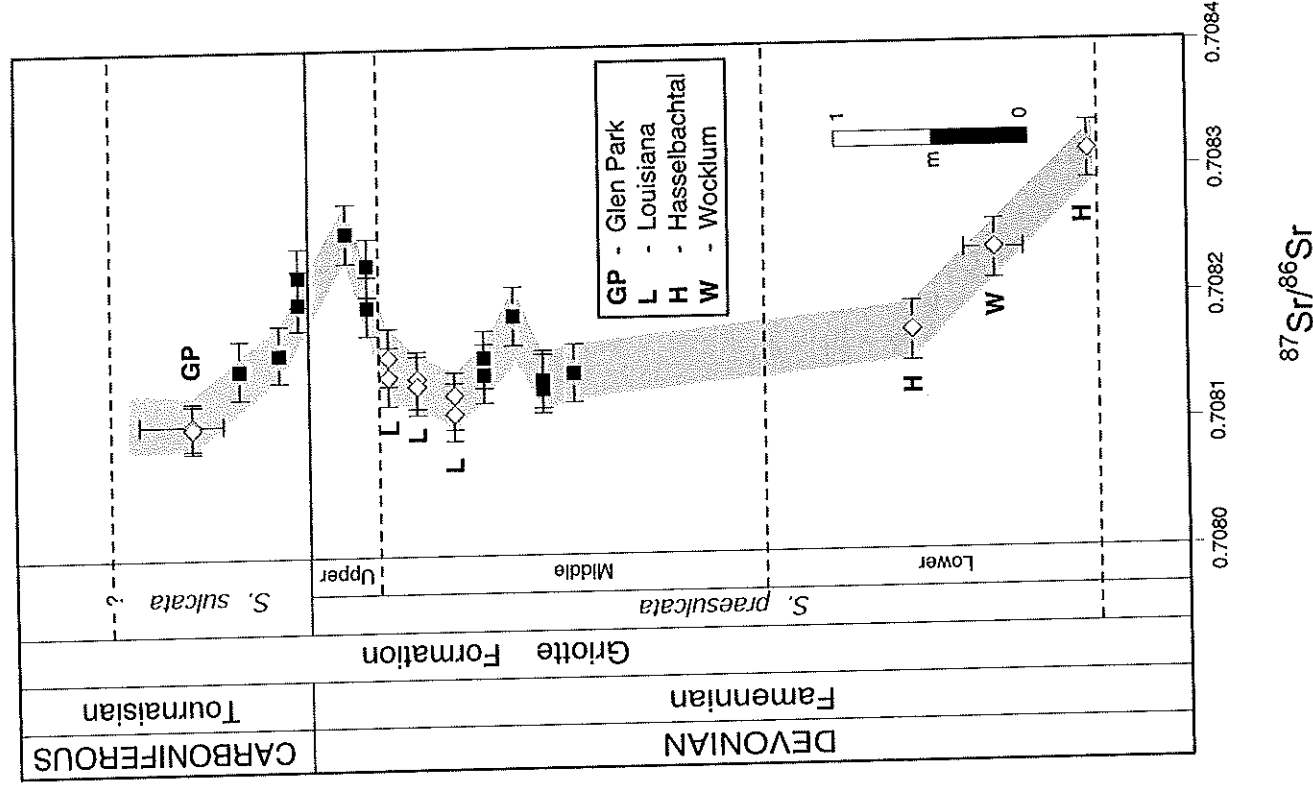


Fig. 6. Strontium isotope biochemostratigraphic trend for Griotte Formation brachiopods from La Serre (GSSP), and supplemented by data (brachiopod-based) from Starks Roadcut-Hannibal (L&GP; Koenig et al., 1961; Ziegler and Sandberg, 1984a,b), Wocklum (W; Korn, 1984) and Hasselbachtal sections (H; Kürschner et al., 1993). Error bars (x-axis) represent the range observed in modern brachiopods (Brand et al., 2003), whereas y-axis bars represent stratigraphic uncertainty. Conodont zonation as in Fig. 2.

depicted in Fig. 6 is a biochemostratigraphically sound presentation for the *S. praesulcata* Zone of the uppermost Devonian and *S. sulcata* Zone of the lowermost Carboniferous.

The $^{87}\text{Sr}/^{86}\text{Sr}$ values for the Devonian and Carboniferous intervals are 0.708167 ± 0.000042 and 0.708165 ± 0.000054 , respectively ($p = 1.000$). Based on samples from within 0.2 m of the D–C boundary, one from the Devonian and two from the Carboniferous, a $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.708231 ± 0.000021 (adjusted to NBS = 0.710240) is assigned to the D–C GSSP boundary. The Devonian–Carboniferous boundary trend with its distinct peaks in the upper Middle *S. praesulcata* and mid Upper *S. praesulcata* Subzones should facilitate comparison with data from other sections spanning this interval.

3.3. Carbon isotope biochemostratigraphy

Devonian–Carboniferous $\delta^{13}\text{C}$ brachiopod-based data are placed in spatial and temporal positions as defined by the strontium isotopes of samples from the GSSP and supplementary sections (Fig. 6; Bruckschen and Veizer, 1997). The most interesting feature is the drastic and sudden excursion of the curve to heavier $\delta^{13}\text{C}$ values during the uppermost Middle *S. praesulcata* Subzone followed subsequently by a return to more 'normal' values (Fig. 7). Some uncertainty in the trend characterizes the *S. sulcata* Zone; however, brachiopod $\delta^{13}\text{C}$ data of the Lower *S. praesulcata* Subzone and *S. sulcata* Zone are in general agreement with those recorded by modern low-latitude counterparts (Fig. 7).

Some difference exists between the Lower *S. praesulcata* Subzone ($\delta^{13}\text{C}$, $+1.67 \pm 0.14\text{‰}$) and *S. sulcata* Zone ($\delta^{13}\text{C}$, $+1.93 \pm 0.49\text{‰}$) brachiopod data ($p = 0.026$), where the data of the Middle *S. praesulcata* Subzone ($\delta^{13}\text{C}$, $+4.90 \pm 1.13\text{‰}$) are significantly different to those of its sub- ($p = 0.0001$) and superjacent ($p = 0.0001$) units at the 95% confidence level. The difference in $\delta^{13}\text{C}$ of about 3‰ between brachiopods from the Lower *S. praesulcata* and Middle *S. praesulcata* Subzones is large enough to suggest a major temporal shift in the carbon reservoir during the latest Famennian. Temporal shifts in $\delta^{13}\text{C}$ values of similar magnitude have been observed for the latest Ordovician (Brenchley et al., 1994; Marshall et al., 1997) and Late Cambrian

(Brasier, 1993; Saltzman et al., 2000). Lacking supportive evidence, the nature of the $\delta^{13}\text{C}$ shift for the Late Cambrian is uncertain, but in contrast the temporal shift in $\delta^{13}\text{C}$ for the latest Ordovician has been clearly ascribed to a glacial episode.

A global sea-level fall has been recognized in many sections during the search over the years for a D–C GSSP. This event is related to a global biotic event and deposition of the Hangenberg Shale. Lately this sea-level low stand of the latest Famennian has been interpreted to reflect the rapid development of glaciers in several basins during the terminal Devonian (e.g., Johnson et al., 1985; Dickens, 1996; Streef et al., 2000). The carbon isotope trend spanning the *S. praesulcata* to *S. sulcata* Zones support some drastic change in seawater chemistry with possible links to changes in atmospheric composition (CO_2), climate and terrestrial biomass (cf. Arthur et al., 1988; Berner, 1990; Caputo, 1995; Algeo et al., 1995; Mii et al., 1999).

3.4. Oxygen isotope biochemostratigraphy

Placement of the $\delta^{18}\text{O}$ values follows the principles and parameters used to construct the strontium isotope curve for the Devonian–Carboniferous boundary interval (Fig. 6). The oxygen isotope values depict a complicated scenario for the uppermost Devonian and lowermost Carboniferous (Fig. 8). Lower *S. praesulcata* Subzone is characterized by light $\delta^{18}\text{O}$ values of about -7.06‰ , which suddenly rise to about -2‰ by the middle of the Middle *S. praesulcata* Subzone and climax at $+0.27\text{‰}$ by the uppermost Middle *S. praesulcata* Subzone. The uppermost Upper *S. praesulcata* Subzone documents a reversal in the shift towards lighter $\delta^{18}\text{O}$ values, a trend that continues across the Devonian–Carboniferous boundary and during the *S. sulcata* Zone (lowermost Carboniferous; Fig. 8).

Although Devonian $\delta^{18}\text{O}$ values ($-2.00 \pm 2.29\text{‰}$) are statistically not different ($p = 0.229$) from lowermost Carboniferous ones ($-3.08 \pm 0.50\text{‰}$), there are nonetheless variations in the $\delta^{18}\text{O}$ curves between the *S. praesulcata* and *S. sulcata* Zones, which underline the importance of horizon-by-horizon evaluations. A distinct shift may be recognized for the $\delta^{18}\text{O}$ values, mirrored by the $\delta^{13}\text{C}$ values, spanning *S. praesulcata* to *S. sulcata* Zones. The Lower *S. praesulcata*

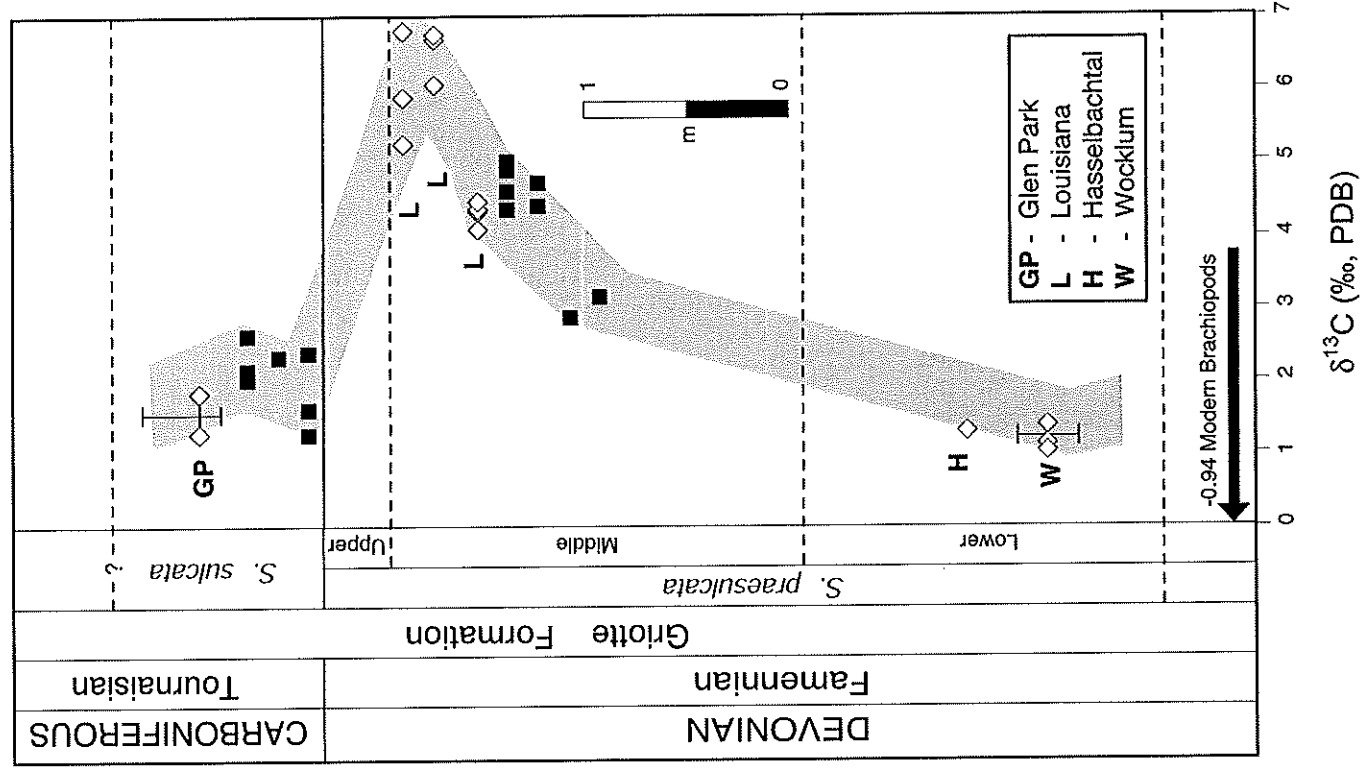


Fig. 7. Carbon isotope biochemostratigraphic trend for Griotte Formation brachiopods from La Serre (GSSP), Starks Roadcut-Hannibal (L&GP), Wocklum (W) and Hasselbachtal (H; Bruckschen and Veizer, 1997) sections. The $\delta^{13}C$ range of modern low-latitude brachiopods is from Carpenter and Lohmann (1995) and Brand et al. (2003). Other information and symbols as in Fig. 6.

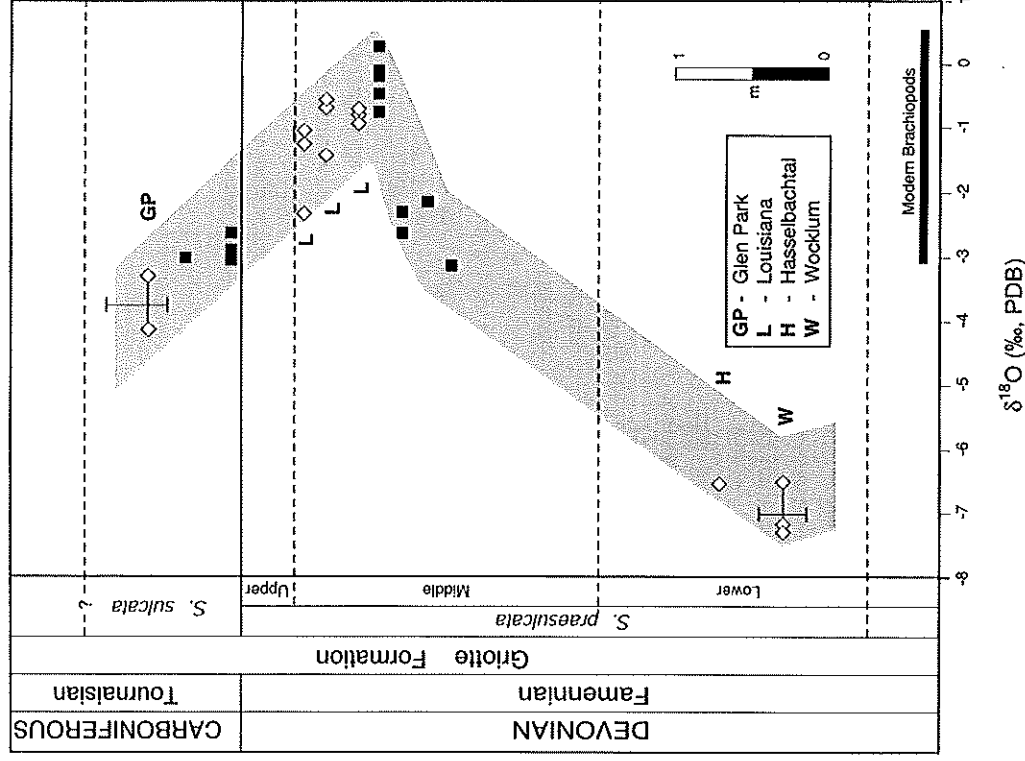


Fig. 8. Oxygen isotope biochemostratigraphic trend for Griotte Formation brachiopods from La Serre (GSSP), Starks Roadcut-Hannibal (L&GP), Wocklum (W) and Hasselbachtal (H) sections. The $\delta^{18}\text{O}$ range of modern low-latitude brachiopods is from Lowenstein (1961), Carpenter and Lohmann (1995) and Brand et al. (2003). Other information and symbols as in Figs. 6 and 7.

sulcata Subzone with an average value of -7.06‰ . This $\delta^{18}\text{O}$ is significantly different ($p=0.0001$) from that of the Middle *S. praesulcata* Subzone with -1.15‰ , and that in turn is also significantly different ($p=0.0001$) from its successor zone (*S. sulcata*) with a value of -3.08‰ (Fig. 8).

$\delta^{18}\text{O}$ values for the *S. praesulcata*–*S. sulcata* Zones range from a low of -7.35‰ , to a transitional maximum of $+0.27\text{‰}$ during the upper-mid Middle *S. praesulcata* Subzone, with a minimum of

-4.11‰ during the *S. sulcata* Zone (Fig. 8). This range covers all, but for the most part it is well outside the range exhibited by modern low-latitude ($>30^\circ$) brachiopods (Carpenter and Lohmann, 1995; Brand et al., 2003). Thompson and Newton (1988) evaluated and summarized thermal regime ranges and their affects on marine invertebrates. In conjunction with paleoceanographic, climatic and tectonic influences (Broecker, 1986; Lécuyer and Allemand, 1999), these factors have been considered in the

calculation of 'acceptable' ambient temperatures for the $\delta^{18}\text{O}$ of the studied brachiopods. Temperatures calculated using modern seawater parameters (Tu) are unacceptable except for mid Middle and upper Middle *S. prae sulcata* brachiopod databases (Table 1). To obtain ambient water temperatures amenable to low-latitude marine invertebrates, an adjustment in seawater- ^{18}O composition of -2.2% and slight shift in oceanic salinity of ~ 5.5 ppt (reflecting water temperature and ice volume effects) is required for those specimens from the mid Lower *S. prae sulcata* Subzone. At the other end of the spectrum, an adjustment in seawater- ^{18}O composition of $+1.2\%$ and ~ 3 ppt in salinity is required for mid Middle *S. prae sulcata* Subzone brachiopod specimens to obtain 'reasonable' paleotemperatures.

Table 1
Temperatures ($^{\circ}\text{C}$) of ambient conditions calculated with average oxygen isotope values ($\%$, PDB) from unaltered brachiopods from about the Devonian–Carboniferous boundary (zones–subzones as per Fig. 2)

Unit/(sub) zones	$\delta^{18}\text{O}$	T_0	T_1	T_2	T_3	T_4
Glen Park mid-upper	-3.70	35	–	–	–	29
<i>S. sulcata</i> Griotte (GSSP)	-2.97	31	–	–	–	25
lower <i>S. sulcata</i> Louisiana upper Middle	-1.14	22	–	–	–	26
<i>S. prae sulcata</i> Griotte (GSSP) mid Middle	-0.01	17	–	–	–	26
<i>S. prae sulcata</i> Griotte (GSSP) lower Middle	-3.14	32	–	26	–	–
<i>S. prae sulcata</i> Wocklum mid Lower	-6.57	51	29	–	–	–
<i>S. prae sulcata</i>						

Thermal ranges considered are for Optimal Growth ($24\text{--}28\text{ }^{\circ}\text{C}$), Reproduction ($21\text{--}29.5\text{ }^{\circ}\text{C}$) and Instantaneous Lethal (<9 or $>33\text{ }^{\circ}\text{C}$) in marine organisms (Thompson and Newton, 1988), acceptable (optimal) calculated temperatures after seawater adjustments are highlighted in bold, with ameliorate temperatures in the tropics (cf. Broecker, 1986).

Adjustment parameters for seawater: $T_0 = 0.0\%$, 34.8 ppt; $T_1 = -2.2\%$, 29 ppt; $T_2 = -1.2\%$, 34.8 ppt; $T_3 = +1.2\%$, 37 ppt; $T_4 = +0.8\%$, 34.8 ppt; (considering changing cryospheric, oceanographic and climatic conditions; cf. Lécuyer and Allemand, 1999).

The modeled temperatures using appropriate adjustment factors become reasonable and realistic for subtropical seas and for low-latitude seawater conditions during the uppermost Devonian–lowermost Carboniferous (17 to $29\text{ }^{\circ}\text{C}$; Table 1).

4. Devonian–Carboniferous oceanography and biochemostratigraphy

Important biochemostratigraphic trends and with it biotic, oceanographic and cryospheric events mark the terminal phase of the Devonian and its transition into the Carboniferous. Specifically, the end Devonian culminates in a significant extinction, the Hagenberg Event sensu Walliser (1984), which was succeeded by glacioeustatic sea-level fall (regression), drastic climatic oscillations, expansion and recession of polar icecaps/glaciers and atmospheric changes in oxygen and carbon dioxide (e.g., Streef et al., 2000). According to Sandberg et al. (1988, p. 211), this regression was "worldwide, even in basinal areas, the fall was first recognized by a brief interruption of a deep water... conodont biofacies...", which "... initiated a Famennian global mass extinction, and ultimately ended the Devonian Period". Isotopic information of unaltered brachiopods presented from the Global Stratotype Section and Point (GSSP) at La Serre (France; Paproth et al., 1991), from the Auxiliary Stratotype (AS) section at Hasselbachtal (Germany) and from boundary sections in Germany and North America support these changes and events (Fig. 9).

4.1. D–C boundary-event biochemostratigraphy

The strontium trend based on unaltered brachiopods from the GSSP and AS sections, Glen Park and Louisiana Formations from North America about the Devonian–Carboniferous boundary is relatively invariant spanning the Middle *S. prae sulcata* Subzone to lowermost *S. sulcata* Zone, except for radiogenic excursions during the mid-upper Middle and Upper *S. prae sulcata* Subzones (Fig. 9a). A slight radiogenic contribution is witnessed in the strontium trend during the lowermost Lower *S. prae sulcata* Subzone, although the paucity of data limits its reliability factor. The first two mentioned excursions exhibit

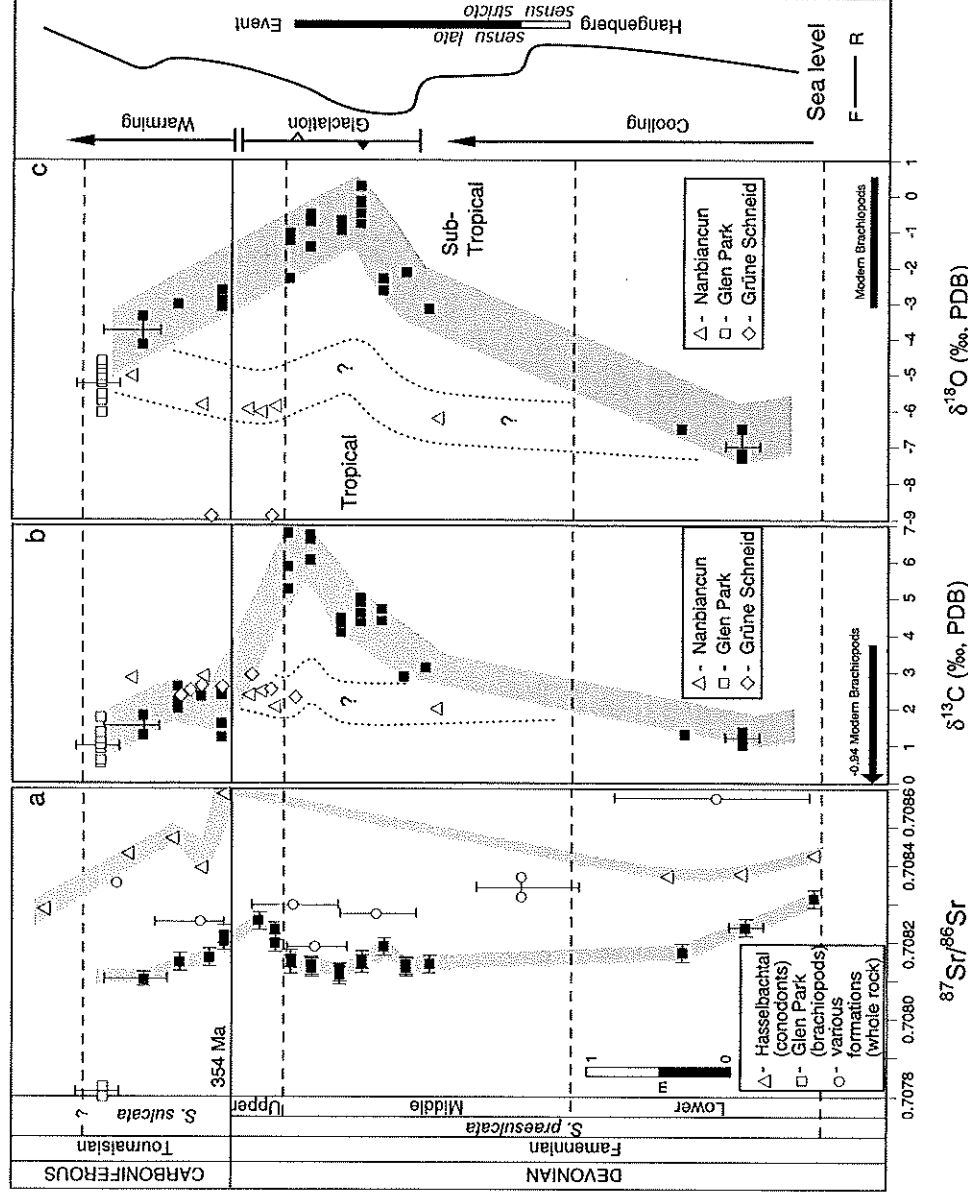


Fig. 9. Strontium, carbon and oxygen isotope biochemostratigraphic summary diagrams. (a) shows the Sr isotope trend established for the Devonian – Carboniferous boundary interval with other data superimposed from the Glen Park Formation (brachiopods-Illinois, Mii et al., 1999), various formations and localities (whole rock, Denison et al., 1994, 1997, in ascending order: Pilot, Holt Summit, Palliser, Louisiana, Pilton and New Albany, Yang et al., 1988, Nambiancun, China), and from Hasselbachthal (conodonts, Kürschner et al., 1995). The age of the D – C boundary is based on information from Claoüé-Long et al. (1992). (b) depicts the C isotope trend for the Devonian – Carboniferous boundary interval with other brachiopod isotope data from the Glen Park Formation (Mii et al., 1999), Nambiancun Formation (Huang et al., 1988), and matrix (whole rock) data from the Grüne Schneid section (Schönlauß et al., 1992). Tropical trend inferred from brachiopod isotope data from Nambiancun of southern China. (c) shows the O isotope trend and data for the Devonian – Carboniferous boundary interval from this and Nambiancun studies (Huang et al., 1988). Duration of the Hangenberg Event (sensu stricto Walliser, 1984 open and solid part of bar, sensu lato solid part of bar only), general climatic information from Streef et al. (2000), and paleoceanographic information (sea level, F—fall, R—rise) from Feist et al. (2000). Solid triangle on 'glaciation' bar indicates glacial maximum, whereas the open triangle indicates the CO_2 min drawdown/organic matter burial maximum.

seawater- ^{87}Sr changes of 0.000052 and 0.000105, respectively and relatively to their subjacent data points. Similar observations of small and sudden

excursions in seawater- ^{87}Sr during the Cenozoic have been attributed to changes in the magnitude of dissolved Sr flux delivered to the oceans by river

water (Capo and DePaolo, 1990). More importantly, increased fluvial Sr fluxes of about 0.000100 have been linked to high periodicity in glacioeustatic oscillations, with exceptionally high rates of change during glacial–interglacial transitions (Clemens et al., 1993). The Sr isotope excursions documented by the GSSP brachiopod data and those from supplementary sections during the Middle *S. praesulcata* and Upper *S. praesulcata* Subzones appear to correspond to the dramatic change to heavier and lighter $\delta^{18}\text{O}$ values of the GSSP trend, respectively (Fig. 9a,c). This change in $\delta^{18}\text{O}$ values has been interpreted to reflect a sudden and strong glacial episode during the latest Devonian (see below). The *S. praesulcata* Zone- ^{87}Sr excursions agree with interglacial–glacial and glacial–interglacial transition models and to corresponding changes in fluxes of fluvial- ^{87}Sr coupled to changes in continental weathering patterns and processes (Clemens et al., 1993; Banner and Kaufman, 1994).

At the same time, the trend depicted by strontium data obtained from conodonts at Hasselbachtal follows a significantly more radiogenic pattern (Fig. 9a). The differences between the unaltered brachiopod data (GSSP and supplementary sections) and that of the conodonts are well outside the range acceptable for contemporaneous seawater as observed in modern shallow and deep water brachiopods (Brand et al., 2003). This variance in databases supports the assertion that conodont-based strontium isotopes from Hasselbachtal, supported by XRD and trace element data, represent diagenetically altered material (cf. Kürschner et al., 1993). Some additional data of brachiopods from the Glen Park Formation of Illinois are less radiogenic than that of ‘contemporaneous’ material from Missouri (Fig. 9a). These samples are deemed problematic (by virtue of stratigraphic uncertainty) since they do not fit the Sr-isotope trend nor strict preservation criteria of the original authors (Mii et al., 1999). The few available results based on whole-rock samples do not fare much better, in that the data are not only significantly different from but are also stratigraphically poorly constrained (except for the Nambiancun datum) relative to the unaltered brachiopods of this and other studies (Fig. 9a). For these reasons, the more radiogenic results of the whole rock material probably reflect mostly diagenetic

signals, and thus they are not suitable for describing the original seawater Sr-isotope trend spanning the Devonian–Carboniferous boundary (Brand, 2004).

$\delta^{13}\text{C}$ values exhibit a significant change during the uppermost Lower *S. praesulcata* Subzone from about +1.32‰ to +4.31‰ by the mid Middle *S. praesulcata* Subzone, which is followed by a drastic decline to +1.70‰ during the *S. sulcata* Zone (Fig. 9b). The onset of this change corresponds well to the postulated biotic crisis noted for the Hangenberg Event sensu lato and the change in the cryosphere (Fig. 9b). This global cooling event was probably related to a massive increase in terrestrial plant biomass, which in conjunction with the deposition of worldwide anoxic shales sequestered large volumes of atmospheric CO_2 (e.g., Algeo and Scheckler, 1998; Berner, 1990; Caputo, 1995). Another variation for the change in global climate may be due to a decrease in CO_2 atm related to an increase in burial of organic matter (e.g., Walter, 1984; Arthur et al., 1988). The heavy $\delta^{13}\text{C}$ values noted for the duration of the glacial period of the latest Devonian Hangenberg Event sensu lato (Fig. 9b) are in accord with trends observed for other glacial events of the Paleozoic (e.g., late Ordovician, Marshall et al., 1997).

$\delta^{13}\text{C}$ values of whole rock samples from the Grüne Schneid section overlap, in part, with those that define the D–C GSSP trend, except for the one from the upper Middle *S. praesulcata* Subzone (Fig. 9b). Diagenetic alteration of the material may be a factor of these diverging trends and values. The $\delta^{13}\text{C}$ values of the brachiopods from the Glen Park of Illinois are in agreement with the trend for the uppermost *S. sulcata* Zone, and are deemed to represent original seawater values (cf. Mii et al., 1999). In contrast, the $\delta^{13}\text{C}$ values of the brachiopods from the Nambiancun AS in China follow a systematically ‘straight’ trend (Fig. 9b), and by virtue of this deviate from that exhibited by the GSSP trend. The deviation is most pronounced during the Middle *S. praesulcata* Subzone and may reflect local oceanographic–environmental variations. This may be a reasonable explanation especially since Nambiancun occupied a lower latitudinal position open to the eastern oceanic body during the latest Devonian/earliest Carboniferous (Fig. 3) and consequently was probably less impacted

by cryogenic event effects of higher latitudes (cf. Broecker, 1986). Another possibility, which cannot be discounted at this time, is that some of the Nanbiancun brachiopod material may be diagenetically altered as is reflected in the lighter $\delta^{13}\text{C}$ values (Fig. 9b).

Oxygen isotope values of unaltered brachiopods from the GSSP, Hasselbachtal-AS, Louisiana, Glen Park and Wocklum define a trend that seems to mimic that described by the carbon values (Fig. 9b,c). Pre-Hangenberg Event was characterized by light $\delta^{18}\text{O}$ values (-7.35 to -3.14‰) indicative of warm equitable climatic conditions, followed by a dramatic and sudden shift towards heavier values ($+0.27\text{‰}$) and colder conditions during the upper Middle *S. praesulcata* Subzone (Fig. 9c). A reversal to lighter $\delta^{18}\text{O}$ values (-2.64‰ to -4.11‰), as dramatic and sudden across the Devonian–Carboniferous boundary, was noted in material from the lowermost *S. sulcata* Zone and consequently an amelioration of climatic conditions for the earliest Carboniferous. Except for Lower *S. praesulcata* and uppermost *S. sulcata* data, all others are similar to those recorded in modern low-latitude brachiopods (Fig. 9c). This shift in isotopic values from light to heavy to light appears to parallel the Hangenberg Event defining the end-Famennian biotic crisis, which occurred over a period of about 100,000 years (sensu Walliser, 1984; Sandberg and Ziegler, 1992). The presented cooling trend for the upper Middle *S. praesulcata* Subzone supports the terminal Devonian sea-level fall and its corresponding global low stand (Ross and Ross, 1988; Feist et al., 2000), with the development of glaciers in high latitudes and icecaps reaching coastal regions (Steele et al., 2000). This was followed in turn by nonglacial conditions during the earliest Carboniferous (Dickins, 1996). A number of causes for these cryogenic and climatic changes have been presented and the reader is referred to Caplan and Bustin (1999), Steele et al. (2000) and Wang et al. (1993) for further discussion.

Extensive and rapid onset of glaciation is postulated for, during and beyond, Hangenberg Event time and adjustments in seawater $-\delta^{18}\text{O}$ of $+0.8\text{‰}$ to $+1.2\text{‰}$ (for ice-volume effects) are reasonable parameters to use in temperature calculations. These suggest sea level drops of between 80 to 120 m (Fairbanks and Matthews, 1978), and by the beginning of the Carboniferous, glaciers had disappeared and oceanic condi-

tions were back to those resembling nonglacial conditions. Consequently, adjustments in seawater $-\delta^{18}\text{O}$ for *S. sulcata*-based $\delta^{18}\text{O}$ values were set to range from $+1.2\text{‰}$ to -2.2‰ , with an additional adjustment for salinity. The observed shift in oxygen isotope values and calculated temperatures supports climatic cooling during the Hangenberg Event sensu lato and subsequent recovery by the uppermost Upper *S. praesulcata* Subzone (Fig. 9b).

The $\delta^{18}\text{O}$ values of the brachiopods from the Glen Park of Illinois appear to satisfy the trend depicted for the uppermost *S. sulcata* Zone (Fig. 9c); however, its authors discounted these values as altered because they did not pass strict preservation criteria (Mii et al., 1999). The brachiopod $\delta^{18}\text{O}$ data from the Nanbiancun AS of China deviate from the GSSP- $\delta^{18}\text{O}$ trend of the Middle to middle Upper *S. praesulcata* Subzones (Fig. 9c). A diagenetic impact on these values cannot be discounted with certainty. If this condition eventually may be discounted, then they may reflect truly tropical and open ocean conditions during the latest Devonian. Modern counterparts from low and mid latitudes exhibit a $\delta^{18}\text{O}$ range of about 6.5‰ , which is similar to the range differential between the GSSP trend and those depicted by the brachiopods from Nanbiancun. Detailed isotope geochemistry investigation of the brachiopods from Nanbiancun may resolve some of the outstanding issues concerning the current database.

As previously espoused during the discussion of $\delta^{13}\text{C}$ values, the impact of global climatic changes on lower latitude localities was less dramatic than those from higher ones such as the GSSP and other localities (cf. Broecker, 1986). Nevertheless, the isotope biogeostratigraphic data support warm and wet climatic conditions until the onset of the glaciation event during the uppermost Middle *S. praesulcata* Subzone triggering an event (Hangenberg sensu lato) in the marine biosphere. As sudden as this event manifested itself, it dissipated by the end of the Upper *S. praesulcata* Subzone and with it the restoration of more amicable climatic conditions for the onset of the Carboniferous.

Another interesting observation is the lag between the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ maxima (Fig. 9b,c). The heaviest $\delta^{18}\text{O}$ values precede $\delta^{13}\text{C}$ ones by a quarter duration of the Middle *S. praesulcata* Sub-

zone. The $\delta^{18}\text{O}$ maximum appears to correspond to the mid Hangenberg Event *sensu lato*, whereas the $\delta^{13}\text{C}$ maximum appears to signal the end of this biotic, mostly marine event. At the same time, it might possibly highlight the terrestrial floral crisis of the end-Famennian (cf. Algeo et al., 1995; Streel et al., 2000).

5. Conclusions

Stratigraphically well-characterized and pristine brachiopods were used to delineate the biochemostratigraphy of the Devonian–Carboniferous GSSP at La Serre, France and supplementary-auxiliary boundary sections. On this basis, the following conclusions about the brachiopods geochemical potential as important biochemostratigraphic tools and paleoceanographic/climatologic proxies of the Devonian–Carboniferous boundary and events may be reached:

- (1) Biochemostratigraphic trends of stable and radiogenic isotopes reveal a varied history of seawater chemistry changes for the latest Devonian–earliest Carboniferous. The $^{87}\text{Sr}/^{86}\text{Sr}$ trend for the latest Devonian is relatively invariant (0.708167 ± 0.000042) and not significantly different from that of the earliest Carboniferous (0.708165 ± 0.000054). The $^{87}\text{Sr}/^{86}\text{Sr}$ value assigned to the Devonian–Carboniferous boundary, based on unaltered brachiopods from within 0.2 m of either side, is 0.708231 ± 0.000021 . Correlation of GSSP horizon-data with material from other sections is complicated, in some instances, by either diagenetic influences/overprinting of the chemistry and/or uncertainties of stratigraphic assignment of samples. Seawater– ^{87}Sr excursions during the *S. praevalcata* Zone reflecting changes in continental weathering patterns and processes.
- (2) Carbon isotopes show a significant excursion towards heavier values (increase of about +3‰) for most of the Middle *S. praevalcata* Subzone. $\delta^{13}\text{C}$ values from below and above this specific

interval are significantly more negative (+1.7‰ and +1.9‰, respectively), but those are in relative agreement with those of their modern counterparts.

- (3) The oxygen isotopes and trend mimic that of the carbon isotopes exhibiting a large positive excursion lasting for most of the upper Middle *S. praevalcata* Subzone. The positive shift is significant (about 7‰) and overall is different from the values of the sub- (–7.1‰) and superjacent (–3.1‰) intervals. The strontium, carbon and oxygen isotope trends support the suggestion of a rapid, short and distinct glacial event during the upper Middle *S. praevalcata* Subzone. The onset and duration of this glacial event may correspond to the terminal Devonian Hangenberg Event *sensu lato*, and may have been a trigger for the end-Famennian terrestrial floral crisis.

- (4) The carbon, oxygen and strontium isotopes of brachiopods, conodonts and whole rock from other locations (Glen Park, Hasselbachtal, Nambiancun, and Grüne Schneid) concur in some instances with those of the GSSP trends. Some material, however, shows definite evidence of diagenetic overprinting and with it diminished correlation potential.

Acknowledgements

We appreciate Professor E. Poty's (Université de Liege) helpful comments and suggestions on an early draft of this paper. Special thanks to M. Lozon (Brock University) for computer drafting of the figures, and Dr. D. Buhl (Ruhr-Universität Bochum) for facilitating the Sr isotope analyses. The reviewers Dr. R.E. Denison (University of Texas, Dallas), Dr. P.B. Wignall (University of Leeds) and especially the editor Dr. F. Surlyk (University of Copenhagen) are acknowledged for their insightful and helpful reviews of the manuscript. This study was supported by Natural Sciences and Engineering Research Council of Canada Discovery operating grants (#7961) to UB.

Appendix A. Geochemistry of Devonian–Carboniferous brachiopods and matrix from the Griotte Formation at La Serre (GSSP), and from regional sections (questionable and/or altered data in bold; all Sr isotope data adjusted to a nominal value for NBS 987 of 0.710240)

No.	Bed	Conodont zone/material	Strat unit	Ca	Mg	Sr	Mn	Fe	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	$^{87}\text{Sr}/^{86}\text{Sr}$
LSF-5	93	<i>S. sulcata</i>	Griotte	369120	2048	1283	1025	216	-4.29	2.14	
LSF-8	93			348684	2789	880	3156	53			
LSF-9	93								-4.16	2.64	0.708203
LSF-10	93			359710	2222	1029	1025	228	-2.99	2.01	0.708157
LSF-27m	93	matrix		339286	3418	317	4535	572			
LSF-22	92	<i>S. sulcata</i>	Griotte						-5.74	2.32	
LSF-23m	92	matrix		357287	2915	418	2341	529	-3.31	1.11	0.708169
LSF-6	91	<i>S. sulcata</i>	Griotte	348791	1692	1011	689	176			
LSF-11	89	<i>S. sulcata</i>	Griotte						-2.65	-1.63	
LSF-12	89								-2.64	-3.70	0.708229
LSF-13	89			352147	1999	979	1582	535	-2.99	1.27	0.708211
LSF-19	89								-4.05	1.55	
LSF-20	89								-2.92	2.36	
LSF-24m	89			358048	2807	356	2086	711			
GP-03		<i>S. sulcata</i>	Glen Park	407115	942	1036	248	288	-4.11	1.31	0.708115
GP-04				340328	967	679	363	395			
GP-05				412600	980	1244	239	267	-3.28	1.76	0.708113
ML-1129	87–85	Upper <i>S. praesulcata</i>	Griotte								0.708163
ML-1128	87–85	Upper <i>S. praesulcata</i>	Griotte								0.708253
ML-1128A	87–85										0.708227
ML-1128B	87–85	matrix									0.708196
ML-1128C	87–85										0.708286
LSF-1A	82u	Middle <i>S. praesulcata</i>	Griotte	366901	936	994	137	22	-0.11	5.02	0.708163
LSF-1B	82u			359761	1235	916	301	142	-0.49	4.47	
LSF-2	82u			365899	93	1071	197	20	-0.75	4.90	
LSF-15A	82u			365542	1022	1306	105	57	0.27	4.66	
LSF-16	82u	Middle <i>S. praesulcata</i>	Griotte	368801	864	1300	77	68			0.708152
LSF-17	82u			374556	986	1104	194	110	-0.18	4.63	
LSF-3	82l	Middle <i>S. praesulcata</i>	Griotte	370459	1169	962	438	285	-2.34	4.42	
LSF-4	82l			354149	3527	996	213	145	-2.65	4.71	0.708199
LSF-14	81	Middle <i>S. praesulcata</i>	Griotte	347548	2045	787	1142	178	-2.18	2.86	
LSF-18	81			371937	662	1063	127	115			0.708148
LSF-21	81			388900	601	1148	35	51			0.708145
LSF-28m	81	matrix		316267	2754	280	1364	672	-2.94	1.59	
LSF-7	79	Middle <i>S. praesulcata</i>	Griotte	359333	1289	1177	300	204	-3.14	3.16	0.708152
LSF-26m	79	matrix		307377	2684	301	970	968			
ULL-03	top of unit	Middle <i>S. praesulcata</i>	Louisiana	405967	545	1305	51	89	-1.03	6.80	0.708140
ULL-04	top								-1.22	5.88	
ULL-05	top			377909	1921	890	134	431	-1.22	5.88	
ULL-05w	top			409681	2580	996	113	298	-2.73	4.87	
ULL-6m	top	matrix		1715	166	385	637		-2.37	5.24	0.708156
MLL-01	below	Middle <i>S. praesulcata</i>	Louisiana	383058	1418	1131	29	40	-3.97	1.68	0.708458
MLL-02	below			347994	1061	1228	13	10	-1.42	6.04	0.708137
MLL-02d	below			381531	1037	1162	13	5	-0.68	6.67	0.708133
MLL-7m	below	matrix		2207	381	130	488		-0.59	6.72	
LL-01		Middle <i>S. praesulcata</i>	Louisiana	423302	557	2002	51	52	-4.15	4.88	0.708285
LL-02				411522	630	2198	63	48	-0.71	4.45	0.708122
LL-03				395874	1056	1847	63	67	-1.75	4.35	0.708122
									-0.81	4.33	

Appendix A (continued)

No.	Bed	Conodont zone/material	Strat unit	Ca	Mg	Sr	Mn	Fe	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	$^{87}\text{Sr}/^{86}\text{Sr}$
LL-04				432037	954	1461	188	370	-0.95	4.11	0.708131
LL-05				432203	534	1610	51	38			
St-07		Lower <i>S. praesulcata</i>	Wocklum	332990	1250	1350	50	110	-6.57	1.32	0.708242
St-08				380620	1130	1350	105	175	-7.35	1.05	
St-08b									-7.25	1.13	

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. London B* 353, 113–130.
- Algeo, T.J., Berner, R.A., Maynard, J.B., Scheckler, S.E., 1995. Late Devonian oceanic anoxic events and biotic crises: "rooted" in the evolution of vascular land plants? *Geol. Soc. Am. Today* 5, 63–66.
- Arthur, M.A., Dean, W.A., Pratt, L.M., 1988. Geochemical and climatic effects of increased marine organic carbon burial at the Cenomanian/Turonian boundary. *Nature* 335, 714–717.
- Banner, J.L., Kaufman, J., 1994. The isotopic record of ocean chemistry and diagenesis preserved in non-luminescent brachiopods from Mississippian carbonate rocks, Illinois and Missouri. *Geol. Soc. Am. Bull.* 106, 1074–1082.
- Bates, N.R., Brand, U., 1991. Environmental and physiological influences on isotopic and elemental compositions of brachiopod shell calcite: implications for the isotopic evolution of Paleozoic oceans. *Chem. Geol., Isot. Geosci. Sect.* 94, 67–78.
- Becker, R.T., Paproth, E., 1993. Auxiliary stratotype sections for the global stratotype section and point (GSSP) for the Devonian–Carboniferous boundary: Hasselbaachtal. *Ann. Soc. Geol. Belg.* 115, 703–706.
- Berner, R.A., 1990. Atmospheric carbon dioxide levels over Phanerozoic time. *Science* 249, 1382–1386.
- Brand, U., 1991. Strontium isotope diagenesis of biogenic aragonite and low-Mg calcite. *Geochim. Cosmochim. Acta* 55, 505–513.
- Brand, U., 2004. Carbon, oxygen and strontium isotopes in Paleozoic carbonate components: an evaluation of original seawater-chemistry proxies. *Chem. Geol.* 204, 23–44.
- Brand, U., Brackley, P., 2001. Chemostratigraphy of the Mid-Carboniferous boundary global stratotype section and point (GSSP), Bird Spring Formation, Arrow Canyon, Nevada, USA. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 165, 321–347.
- Brand, U., Bruckschen, P., 2002. Correlation of the Askyn River section, southern Urals, Russia, with the Mid-Carboniferous boundary GSSP, Bird Spring Formation, Arrow Canyon, Nevada, USA: implications for global paleoceanography. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 184, 177–193.
- Brand, U., Legrand-Blain, M., 1993. Paleogeology and biogeochemistry of brachiopods from the Devonian–Carboniferous boundary interval of the Griotte Formation, La Serre, Montagne Noire, France. *Ann. Soc. Geol. Belg.* 115, 497–505.
- Brand, U., Veizer, J., 1980. Chemical diagenesis of a multicomponent carbonate system: 1. Trace elements. *J. Sediment. Petrol.* 50, 1219–1236.
- Brand, U., Veizer, J., 1981. Chemical diagenesis of a multicomponent carbonate system: 2. Stable isotopes. *J. Sediment. Petrol.* 51, 987–997.
- Brand, U., Logan, A., Hiller, N., Richardson, J., 2003. Geochemistry of modern brachiopods: applications and implications for oceanography and paleoceanography. *Chem. Geol.* 198, 305–334.
- Brasier, M.D., 1993. Towards a carbon isotope stratigraphy of the Cambrian System: potential of the Great Basin succession. *Geol. Soc. London, Spec. Publ.* 70, 341–350.
- Brauckmann, C., Chlupac, I., Feist, R., 1993. Trilobites at the Devonian–Carboniferous boundary. *Ann. Soc. Geol. Belg.* 115, 507–518.
- Branchley, P.J., Marshall, J.D., Carden, G.A.F., Robertson, D.B.R., Long, D.G.F., Meidla, T., Hints, L., Anderson, T.F., 1994. Bathymetric and isotopic evidence for a short-lived Late Ordovician glaciation in a greenhouse period. *Geology* 22, 295–298.
- Broecker, W.S., 1986. Oxygen isotope constraints on surface ocean temperatures. *Quat. Res.* 26, 121–134.
- Bruckschen, P., Veizer, J., 1997. Oxygen and carbon isotopic composition of Dinantian brachiopods: paleoenvironmental Palaeogeogr. Palaeoclimatol. 132, 243–264.
- Bruckschen, P., Bruhn, F., Veizer, J., Buhl, D., 1995. $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic evolution of lower Carboniferous seawater: Dinantian of western Europe. *Sediment. Geol.* 100, 63–81.
- Bruckschen, P., Oesmann, S., Veizer, J., 1999. Isotope stratigraphy of the European Carboniferous: proxy signals for ocean chemistry, climate and tectonics. *Chem. Geol.* 161, 127–163.
- Caplan, M.L., Bustin, R.M., 1999. Devonian–Carboniferous Hangenberg mass extinction event, widespread organic-rich mudrock and anoxia: causes and consequences. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 148, 187–207.
- Capo, R.C., DePaolo, J.D., 1990. Seawater strontium isotopic variations from 2.5 million years ago to the present. *Science* 249, 51–55.
- Caputo, M.V., 1995. Anti-greenhouse effect as a glaciation and biotic crisis triggering agent: the Late Devonian and Early Carboniferous glacial cases. *Acad. Bras. Cienc. (Rio de Janeiro) Resumo. Comm.* 67 (3), 390.
- Carpenter, S.C., Lohmann, K.C., 1995. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of modern brachiopod shells. *Geochim. Cosmochim. Acta* 59, 3749–3764.

- Claoué-Long, J.C., Jones, P.J., Roberts, J., Maxwell, S., 1992. The numerical age of the Devonian–Carboniferous boundary. *Geol. Mag.* 129, 281–291.
- Clemens, S.C., Farrell, J.W., Gromet, L.P., 1993. Synchronous changes in seawater strontium isotope composition and global climate. *Nature* 363, 607–610.
- Collinson, C., Rexroad, C.B., Thompson, T.L., 1971. Conodont zonation of the north American Mississippian. In: Sweet, W.C., Bergstrom, S.M. (Eds.), *Symposium on Conodont Biostratigraphy*. *Geol. Soc. Mem.*, vol. 127, pp. 353–394.
- Denison, R.E., Koepnick, R.B., Burke, W.H., Hetherington, E.A., Fletcher, A., 1994. Construction of the Mississippian, Pennsylvanian and Permian seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve. *Chem. Geol., Isot. Geosci. Sect.* 112, 145–167.
- Denison, R.E., Koepnick, R.B., Burke, W.H., Hetherington, E.A., Fletcher, A., 1997. Construction of the Silurian and Devonian seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve. *Chem. Geol.* 140, 109–121.
- Dickins, J.M., 1996. Climate of the Late Devonian to Triassic. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 100, 89–94.
- Epstein, S., Buchsbaum, R., Lowenstam, H.A., Urey, H.C., 1953. Revised carbonate–water isotopic temperature scale. *Geol. Soc. Am. Bull.* 62, 417–425.
- Fairbanks, R.G., Matthews, R.K., 1978. The marine oxygen isotope record in Pleistocene coral, Barbados, West Indies. *Quat. Res.* 10, 181–196.
- Feist, R., 1985. Devonian Stratigraphy of the southeastern Montagne Noire (France). *Cour. Forschungsinst. Senckenberg* 75, 331–352.
- Feist, R., 2002. Montagne Noire 25–28 June 2002. *IGCP* 421: North Gondwana mid-Paleozoic biodynamics and ECOS VIII: 8th European Conodont Symposium—Guidebook of the Field Excursion. Institut des Sciences de l'Évolution, University of Montpellier II, Montpellier, pp. 1–85.
- Feist, R., Flajs, G., Girard, C., 2000. The stratotype section of the Devonian–Carboniferous boundary. *Cour. Forschungsinst. Senckenberg* 225, 77–82.
- Flajs, G., Feist, R., 1988. Index conodonts, trilobites and environment of the Devonian–Carboniferous boundary beds at La Serre (Montagne Noire, France). *Cour. Forschungsinst. Senckenberg* 100, 53–107.
- Galtier, J., Meyer-Berthaud, B., Rowe, N.P., 1988. Tournaisian plants from the “Lydiennes”. Formation of the Montagne Noire (France). *Cour. Forschungsinst. Senckenberg* 100, 109–117.
- Girard, C., 1994. Conodont biofacies and event stratigraphy across the D/C boundary in the stratotype area (Montagne Noire, France). In: Königshof, P., Werner, R. (Eds.), *Willi Ziegler Festschrift*. *Cour. Forschungsinst. Senckenberg*, vol. 168, pp. 199–309.
- Heckel, P.H., Witzke, B.J., 1979. Devonian world palaeogeography determined from distribution of carbonates and related lithic and palaeoclimatic indicators. In: House, M.R., Scrutton, C.T., Bassett, M.G. (Eds.), *The Devonian System*. *Spec. Pap. Palaeontol.*, vol. 23, pp. 99–123.
- Huang, Z.-C., Zhu, S.-Z., Zhang, Y.-E., 1988. Microfacies analysis and sedimentary environment interpretation. In: Yu, C.M. (Ed.), *Devonian–Carboniferous Boundary in Nanbiancun, Guilin, China—Aspects and Records*. Science Press, Beijing, pp. 37–57.
- James, N.P., Bone, Y., Kyser, T.K., 1997. Brachiopod $\delta^{18}\text{O}$ values do reflect ambient oceanography, Laceyde Shelf, southern Australia. *Geology* 25, 551–554.
- Johnson, J.C., Klapper, G., Sandberg, C., 1985. Devonian eustatic fluctuations in Euramerica. *Geol. Soc. Am. Bull.* 96, 567–587.
- Koenig, J.W., Martin, J.A., Collinson, C.W., 1961. 26th Regional Field Conference: Northeastern Missouri and West–Central Illinois. *Guide Book*. *Rep. Invest.*, vol. 27, 255 p.
- Korn, D., 1984. Die Goniaten der Stockum Imotercras-Kalklinien (Ammonoidea; Devon/Karbon-Grenze). *Cour. Forschungsinst. Senckenberg* 67, 71–89.
- Kürschner, W., Becker, R.T., Buhl, D., Veizer, J., 1993. Strontium isotopes in conodonts: Devonian–Carboniferous transition, the northern Rhenish Slate Mountains Germany. *Ann. Soc. Geol. Belg.* 115, 595–621.
- Léouyer, C., Allemand, P., 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.
- Legrand-Blain, M., 1995. Relations entre les domaines d'Europe occidentale, d'Europe méridionale (Montagne Noire) et d'Afrique du Nord à la limite Dévonien–Carbonifère: les données des brachiopodes. *Bull. Soc. Belge Geol.* 103, 77–97.
- Legrand-Blain, M., Martínez Chacon, M.-L., 1988. Brachiopods at the Devonian–Carboniferous boundary, La Serre (Montagne Noire; Hérault, France): preliminary report. *Cour. Forschungsinst. Senckenberg* 100, 119–127.
- Lowenstam, H.A., 1961. Mineralogy, $^{18}\text{O}/^{16}\text{O}$ ratios, and strontium and magnesium contents of recent and fossil brachiopods and their bearing on the history of the ocean. *J. Geol.* 69, 341–360.
- Marshall, J.D., 1992. Climatic and oceanographic isotopic signals from the carbonate rock record and their preservation. *Geol. Mag.* 129, 143–160.
- Marshall, J.D., Brechley, P.J., Mason, P., Wolff, G.A., Astini, R.A., Hinds, L., Meidla, T., 1997. Global carbon isotopic events associated with mass extinction and glaciation in the late Ordovician. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 132, 195–210.
- Mii, H.-S., Grossman, E.L., Yancey, T.E., 1999. Carboniferous isotope stratigraphies of North America: implications for Carboniferous paleoceanography and Mississippian glaciation. *Geol. Soc. Am. Bull.* 111, 960–973.
- Paprot, E., Streel, M. (Eds.), 1984. *The Devonian–Carboniferous Boundary*. *Cour. Forschungsinst. Senckenberg*, vol. 67, pp. 1–258.
- Paprot, E., Feist, R., Flajs, G., 1991. Decision on the Devonian–Carboniferous boundary stratotype. *Episodes* 14, 331–335.
- Ross, C.A., Ross, J.R., 1988. Late Paleozoic transgressive–regressive deposition. In: Wilgus, C.K., Hastings, B.S., Kendall, C.G.-St.C., Posamentier, H.W., Ross, C.A., van Wagoner, J.C. (Eds.), *Sea-Level Changes: An Integrated Approach*. *Soc. Econ. Paleontol. Mineral., Spec. Publ.*, vol. 42, pp. 227–247.
- Salzman, M.R., Ripperdan, R.L., Brasier, M.D., Lohmann, K.C., Robison, R.A., Chang, W.T., Peng, S., Ergaliev, E.K., Runnegar, B., 2000. A global carbon isotope excursion (SPICE) during the Late Cambrian: relation to trilobite extinctions, organic-matter

- burial and sea level. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 162, 211–223.
- Sandberg, C.A., Ziegler, W., 1992. Devonian conodont biochronology in geologic time calibration. *Senckenb. Lethaea* 76, 259–265.
- Sandberg, C.A., Ziegler, W., Dreesen, R., Butler, N., 1988. Late Frasnian mass extinction: conodont event stratigraphy, global changes, and possible causes. *Cour. Forschungsinst. Senckenberg* 102, 263–307.
- Schönlaut, H.P., Atrep, M., Boeckelmann, K., Dreesen, R., Feist, R., Fenninger, A., Hahn, G., Klein, P., Korn, D., Kratz, R., Magaritz, M., Orth, C.H., Schramm, J.-M., 1992. The Devonian/Carboniferous boundary in the Carnic Alps (Austria)—a multidisciplinary approach. *Jb. Geol. B.-A.* 135, 57–98.
- Scott, A.J., Collinson, C., 1961. Conodont faunas from the Louisiana and McCraney Formations of Illinois, Iowa and Missouri. In: Koenig, J.W., Martin, J.A., Collinson, C.W. (Eds.), 26th Regional Field Conference: Northeastern Missouri and West-Central Illinois, Guide Book. *Rep. Invest.*, vol. 27, pp. 110–141.
- Semenoff-Tian-Chansky, P., 1988. Corals from the Devonian–Carboniferous boundary at La Serre (Montagne Noire, France). *Cour. Forschungsinst. Senckenberg* 100, 129–138.
- Strel, M., Caputo, M.V., Loboziak, S., Melo, J.H.G., 2000. Late Frasnian–Famernian climates based on palynomorph analyses and the question of the Late Devonian glaciations. *Earth-Sci. Rev.* 52, 121–173.
- Thompson, J.B., Newton, C.R., 1988. Late Devonian mass extinction: episodic climatic cooling or warming? In: McMillan, N.J., Embry, A.F., Glass, D.J. (Eds.), *Devonian of the World*. Paleontol. Paleocool. Biostratigr. Can. Soc. *Pet. Geol.*, vol. III, pp. 29–34.
- Vachard, D., 1988. Calcareous microfossils (algae, pseudo-algae, and foraminifera) from La Serre, Montagne Noire, France. *Cour. Forschungsinst. Senckenberg* 100, 139–147.
- Veizer, J., 1983. Trace elements and stable isotopes in sedimentary carbonates. In: Reeder, R.J. (Ed.), *Carbonates: Mineralogy and Chemistry*. *Rev. Miner.*, vol. 11, pp. 265–299.
- Veizer, J., Buhl, D., Dicner, A., Ebneth, S., Podlaha, O.G., Bruck-schen, P., Jasper, T., Korte, C., Schaaf, M., Ala, D., Azmy, K., 1997. Strontium isotope stratigraphy: potential resolution and event correlation. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 132, 65–77.
- Walliser, O.H., 1984. Pleading for a natural D/C boundary. *Cour. Forschungsinst. Senckenberg* 67, 241–246.
- Walter, H., 1984. *Vegetation und klimazonen-Grundriss der globalen Ökologie Engen Ulmer*. Stuttgart. 230 p.
- Wang, C.-Y., 1993. Auxiliary stratotype sections for the global stratotype section and point (GSSP) for the Devonian–Carboniferous boundary: Nanbiancun. *Ann. Soc. Geol. Belg.* 115, 707–708.
- Wang, K., Atrep Jr., M., Orth, C.J., 1993. Global iridium anomaly, mass extinction, and redox change at the Devonian–Carboniferous boundary. *Geology* 21, 1071–1074.
- Weizel, B., 2000. Differential preservation of primary isotopic signatures in Silurian brachiopods from northern Europe. *J. Sediment. Res.* 70, 194–209.
- Yang, J.-D., Wang, Y.-X., Wang, Z.-Z., 1988. Rb–Sr dating of clay minerals. In: Yu, C.M. (Ed.), *Devonian–Carboniferous Boundary in Nanbiancun, Guilin, China—Aspects and Records*. Science Press, Beijing, pp. 58–67.
- Ziegler, W., Sandberg, C.A., 1984a. Palmatolepis-based revision of upper part of standard Late Devonian conodont zonation. *Geol. Soc. Am., Spec. Pap.* 196, 179–194.
- Ziegler, W., Sandberg, C.A., 1984b. Important candidate sections for stratotype of conodont-based Devonian–Carboniferous boundary. *Cour. Forschungsinst. Senckenberg* 67, 231–239.