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doi:10.1016/j.gca.2004.11.017

## Boron isotope geochemistry of Paleozoic brachiopod calcite: Implications for a secular change in the boron isotope geochemistry of seawater over the Phanerozoic

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(Received June 17, 2004; accepted in revised form November 15, 2004)

**Abstract**—Boron isotope composition of marine carbonates has been proposed as a paleo-pH proxy and potential tool to reconstruct atmospheric  $p\text{CO}_2$ . The precise knowledge of the boron isotopic composition of ancient seawater represents the fundamental prerequisite for any paleo-pH reconstruction. This contribution presents boron isotope values for Silurian to Permian brachiopod calcite that might be used to reconstruct pH or boron isotope composition of past oceans. All brachiopod shells were screened for diagenetic recrystallization by means of cathodoluminescence microscopy, trace element geochemistry (B, Fe, Mn, Sr) as well as SEM. Only nonluminescent shells revealing well-preserved microstructures, high strontium and boron concentrations as well as low iron and manganese contents were accepted for boron isotope analysis. The boron isotope ratios of Silurian, Devonian, Pennsylvanian and Permian brachiopod calcite range from 6.8 to 11.0‰, 7.3 to 14.9‰, 12.4 to 15.8‰ and 10.1 to 11.7‰, respectively. These  $\delta^{11}\text{B}$  values are significantly lower in comparison to  $\delta^{11}\text{B}$  values of modern biogenic carbonates and indicate that the Paleozoic oceans were depleted in  $^{11}\text{B}$  by up to 10‰. Box modeling of the boron geochemical cycle suggests that the significant depletion of  $^{11}\text{B}$  in the oceanic reservoir may have been initiated by an enhanced continental boron discharge. Our data support the earlier made conclusion that boron isotopes may not be used in the geological past as reliable paleo-pH proxy unless the boron isotopic composition of ancient oceans can be constrained by further studies. Copyright © 2005 Elsevier Ltd

### 1. INTRODUCTION

The boron isotope composition of carbonates is of major interest as a potential proxy to reconstruct past oceanic pH and has been used to estimate atmospheric  $p\text{CO}_2$  (Spivack and Edmond, 1987; Hemming and Hanson, 1992; Pearson and Palmer, 2000). Boron dissolved in seawater occurs as  $\text{B}(\text{OH})_4^-$  and  $\text{B}(\text{OH})_3$  and the relative proportion of these species is determined by the pH of ambient seawater. The boron isotopic composition of the two species reveals a significant fractionation with  $\text{B}(\text{OH})_4^-$  being depleted in  $^{11}\text{B}$  by  $\sim 20\%$  with respect to  $\text{B}(\text{OH})_3$  (Kakihana et al., 1977). If pH changes, the relative proportion of the two species and the isotopic composition of  $\text{B}(\text{OH})_4^-$  and  $\text{B}(\text{OH})_3$  will change as well. Since it was generally assumed that the charged species  $\text{B}(\text{OH})_4^-$  is incorporated into carbonate minerals without any significant biogenic fractionation (Hemming and Hanson, 1992; Sanyal et al., 2000),  $\delta^{11}\text{B}$  of biogenic carbonate was used as a paleo-pH proxy (Spivack et al., 1993; Sanyal et al., 1995, 1997; Palmer et al., 1998; Pearson and Palmer, 1999). Pearson and Palmer (2000) used  $\delta^{11}\text{B}$  values of planktonic foraminifera to calculate pH and to reconstruct atmospheric carbon dioxide contents for the past 60 myr. The reconstruction of this long-term pH or atmospheric  $\text{CO}_2$  record requires the knowledge of the boron isotope composition of seawater. Pearson and Palmer (2000) assumed that the  $\delta^{11}\text{B}$  of seawater had a modern value of +39.5‰ and that  $\delta^{11}\text{B}$  of seawater did not change during the Cenozoic. This assumption was based on the relatively long

residence time of dissolved boron in the ocean (20 Myr; Spivack and Edmond, 1987) that according to Pearson and Palmer (2000) makes fluctuations in the  $\delta^{11}\text{B}$  of seawater unlikely.

The oceanic boron concentration as well as its isotopic composition are controlled by the input and output of boron. The main sources of boron to the oceans are continental weathering (Lemarchand et al., 2000, 2002; Rose et al., 2000), hydrothermal venting (Spivack and Edmond, 1987) as well as fluids expelled at convergent margins (You et al., 1995; Kopf and Deyhle, 2002). The main sinks of boron comprise uptake of boron during low-temperature weathering of oceanic crust (Spivack and Edmond, 1987), absorption on clastic sediments and marine clays (Schwarcz et al., 1969; Palmer et al., 1987; Spivack et al., 1987), as well as coprecipitation in carbonate. Measurements of the boron isotope riverine fluxes by Lemarchand et al. (2000) and Rose et al. (2000) and box modeling by Lemarchand et al. (2000, 2002) suggested that the present-day boron cycle is at steady state and that the residence time of boron in the oceans is only 14 myr. The calculation of the boron isotope composition of seawater for the past 120 myr suggested that the hypothesis of a constant  $\delta^{11}\text{B}$  value of seawater is not tenable for time periods longer than a few million years and that the variations in  $\delta^{11}\text{B}$  recorded by Pearson and Palmer (2000) for the past 60 myr may reflect changes in the marine boron isotope budget rather than changes in pH.

This study focuses on the boron isotopic composition of Silurian to Permian brachiopod calcite. Brachiopod shells are composed of low-magnesium calcite that has high potential to preserve its primary geochemical signals. As a consequence, brachiopod shells were intensively used to document changes in  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  in the geological past (e.g., Veizer

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Table 1. Brachiopod samples investigated in this study.

Sample	Brachiopod genus	Biostratigraphic age		Stratigraphic unit/location
OL 18-1	<i>Neospirifer</i> sp.	Permian	Late Sakmarian	Saiwan Fm. (Oman)
OL 18-2	<i>Neospirifer</i> sp.	Permian	Late Sakmarian	Saiwan Fm. (Oman)
OL 15-2	<i>Neospirifer</i> sp.	Permian	Late Sakmarian	Saiwan Fm. (Oman)
OL 15-1	<i>Neospirifer</i> sp.	Permian	Late Sakmarian	Saiwan Fm. (Oman)
OL 14	<i>Neospirifer</i> sp.	Permian	Late Sakmarian	Saiwan Fm. (Oman)
CV 1-1	<i>Composita</i> sp.	Permian	Early Sakmarian	Eiss Lst. (Kansas—USA)
CV 2-3	<i>Composita</i> sp.	Permian	Early Sakmarian	Eiss Lst. (Kansas—USA)
CV 2-4	<i>Composita</i> sp.	Permian	Early Sakmarian	Eiss Lst. (Kansas—USA)
TK 2-2	Undetermined	Carboniferous	Virgilian	Hughes Creek Sh. (Kansas—USA)
TK 2-1	Undetermined	Carboniferous	Virgilian	Hughes Creek Sh. (Kansas—USA)
LPM 1	Undetermined	Carboniferous	Gzhelian	Pseudoschwag. Lst. (Carnic Alps—Austria)
LPM 2	Undetermined	Carboniferous	Gzhelian	Pseudoschwag. Lst. (Carnic Alps—Austria)
LPM 4	Undetermined	Carboniferous	Gzhelian	Pseudoschwag. Lst. (Carnic Alps—Austria)
JIA 5-11	<i>Cyrtospirifer</i> sp.	Devonian	Frasnian	Jiangjiaqiao section (Hunan—China)
JIA 5-8	<i>Cyrtospirifer</i> sp.	Devonian	Frasnian	Jiangjiaqiao section (Hunan—China)
SY 5-1	<i>Tenticospirifer</i> sp.	Devonian	Frasnian	Shetianqiao section (Hunan—China)
HG 12-4	<i>Theodassia</i> sp.	Devonian	Frasnian	Lime Creek Fm. (Iowa—USA)
BQ 64-3	<i>Pseudoatrypa</i> sp.	Devonian	Givetian	Coralville Fm. (Iowa—USA)
BQ 46-3	<i>Orthospirifer</i> sp.	Devonian	Givetian	Little Cedar Fm. (Iowa—USA)
BQ 36-2	<i>Orthospirifer</i> sp.	Devonian	Givetian	Little Cedar Fm. (Iowa—USA)
BQ 35-2	<i>Orthospirifer</i> sp.	Devonian	Givetian	Little Cedar Fm. (Iowa—USA)
MRKI 25-1	<i>Cyrtinospis</i> sp.	Devonian	Givetian	Madène ei Mrakib (AntiAtlas—Morocco)
MRKI 19-1	<i>Cyrtinospis</i> sp.	Devonian	Eifelian	Madène ei Mrakib (AntiAtlas—Morocco)
STL 4-9	<i>Plicathyris</i> sp.	Devonian	Emsian	Santa Lucia Fm. (Cantabria—Spain)
ELM 11-2	<i>Gypidula</i> sp.	Devonian	Emsian	Jebel Maharch (AntiAtlas—Morocco)
MRKII 10-3	<i>Sieberella</i> sp.	Devonian	Emsian	Madène ei Mrakib (AntiAtlas—Morocco)
MRK II 10-4	<i>Sieberella</i> sp.	Devonian	Emsian	Madène ei Mrakib (AntiAtlas—Morocco)
ELM 1-2	<i>Gypidula</i> sp.	Devonian	Emsian	Jebel Maharch (AntiAtlas—Morocco)
VIN 4-5	Pentamerida	Devonian	Lochkovian	Abelgas Fm. (Cantabria, Spain)
VIN 4-4	Pentamerida	Devonian	Lochkovian	Abelgas Fm. (Cantabria, Spain)
Rivviken 2	<i>Atrypa</i> sp.	Silurian	Ludfordian	Hamra/Sundre Beds (Gotland—Sweden)
Näs 1	<i>Atrypa</i> sp.	Silurian	Ludfordian	Eke Beds (Gotland—Sweden)
Tomsarve 1	<i>Atrypa</i> sp.	Silurian	Ludfordian	Eke Beds (Gotland—Sweden)
Petsarve 8	<i>Atrypa</i> sp.	Silurian	Ludfordian	Eke Beds (Gotland—Sweden)
Havor 2	<i>Atrypa</i> sp.	Silurian	Gorstian	Hemse Beds (Gotland—Sweden)
Grogams 1	<i>Atrypa</i> sp.	Silurian	Gorstian	Hemse Beds (Gotland—Sweden)
Blåhäll 1	<i>Atrypa</i> sp.	Silurian	Homerian	Mulde Beds (Gotland—Sweden)
Blåhäll 1	<i>Atrypa</i> sp.	Silurian	Homerian	Mulde Beds (Gotland—Sweden)
Tjeldersholm 1	<i>Atrypa</i> sp.	Silurian	Homerian	Slite Beds (Gotland—Sweden)
Tjeldersholm 1	<i>Atrypa</i> sp.	Silurian	Homerian	Slite Beds (Gotland—Sweden)
Norderstrand 1	<i>Atrypa</i> sp.	Silurian	Sheinwoodian	Visby Beds (Gotland—Sweden)

et al., 1999). Lécuyer et al. (2002) investigated the boron isotopic composition of modern brachiopods. The authors observed a comparable dependence on  $\delta^{11}\text{B}$  and pH for brachiopods and cultured foraminifera which suggested that the boron isotopic composition of brachiopod calcite may be used to reconstruct  $\delta^{11}\text{B}$  of past oceans. The aim of this contribution is to document that pristine Paleozoic brachiopod shells preserved the boron isotope composition of ancient seawater and that the  $\delta^{11}\text{B}$  of Paleozoic seawater was significantly different in comparison to modern seawater.

## 2. METHODS AND SAMPLES

Silurian (Gotland/Sweden), Devonian (Morocco, China, USA), Pennsylvanian (USA) and Early Permian (Oman) brachiopod shells (Table 1) were investigated during this study. Before boron isotope analysis, the shells were carefully screened for diagenetic alteration. All shells were investigated using cathodoluminescence microscopy and only nonluminescent shells were accepted for further analysis. Trace element contents (B, Mn, Fe, Sr) of shell calcite were determined using a Spectroflame D inductively-coupled plasma (ICP-OES). The microscale preservation of the shell microstructures was investigated using SEM (Phillips XL 30).

The boron isotope measurements followed the procedure described by Lécuyer et al. (2002). A total of 150 to 450 mg of shell calcite were collected from individual thick-shelled brachiopods using a dental drill. Calcite powders were dissolved in  $\text{HNO}_3$  1 M and the solutions neutralized with KOH until pH reached 7. Dissolved boron was subsequently purified by adding an anion-exchange resin (Amberlite IRA 743). After shaking the reaction tubes for 4 h, the excess liquid was discarded and the resin rinsed 4 to 5 times with 40 mL of ultrapure water. Following, 10 mL  $\text{HNO}_3$  0.01 M were added to the resin to elute the borate. After shaking the reaction tubes for another 4 h, the solutions were carefully evaporated to 4 to 5 mL at room temperature (20°C). Mediterranean seawater was used as external standard and processed using the same chemical procedure. The boron isotope composition of Mediterranean seawater was determined by Vengosh et al. (1998) as 40.3‰ which is significantly higher than the  $\delta^{11}\text{B}$  value of Atlantic or Pacific sea surface waters (39.5‰). Vengosh et al. (1998) measured the boron isotope ratio with an analytical precision of only  $\pm 2\text{‰}$  ( $1\sigma$ ). However, the comparatively high  $\delta^{11}\text{B}$  value for Mediterranean seawater is not surprising considering the excess of evaporation over precipitation that characterizes Mediterranean seawater.

Boron isotope ratios were determined using a VG Elemental MC-ICP-MS Plasma 54 at the École Normale Supérieure de Lyon, France. The instrumental mass bias was corrected by bracketing samples with measurements of NIST SRM 951 standard solutions. Boron isotope ratios of both standard and sample solutions were obtained by running

Table 2. Trace element contents and boron isotope composition of Palaeozoic brachiopod shells.

Sample	Stratigraphy	Age (myr)	Sr (ppm)	Mn (ppm)	Fe (ppm)	B (ppm)	$\delta^{11}\text{B}$ (‰)
OL 18-1	Permian	285	556	1240	3570	96	10.7
OL 18-2	Permian	285	707	56	65	104	10.4
OL 15-2	Permian	285	615	31	38	60	10.3
OL 15-1	Permian	285	677	158	174	81	10.1
OL 14	Permian	285	646	34	25	88	11.7
CV 1-1 <sup>a</sup>	Permian	289	340	49	111	b.d.l. <sup>b</sup>	
CV 2-3 <sup>a</sup>	Permian	289	301	10	28	b.d.l.	
CV 2-4 <sup>a</sup>	Permian	289	316	9	131	b.d.l.	
TK 2-2	Carboniferous	297	587	19	61	29	12.4
TK 2-1	Carboniferous	297	585	20	44	24	15.8
LPM 1 <sup>a</sup>	Carboniferous	300	284	10	25	b.d.l.	
LPM 2 <sup>a</sup>	Carboniferous	300	299	11	28	b.d.l.	
LPM 4 <sup>a</sup>	Carboniferous	300	326	5	19	b.d.l.	
JIA 5-11	Devonian	371.9	1344	12	100	34	9.0
JIA 5-8	Devonian	371.9	1275	13	107	48	9.8
SY 5-1	Devonian	373.8	1467	19	79	37	6.7
HG 12-4	Devonian	375.8	1196	17	61	35	7.3
BQ 64-3	Devonian	381.4	686	12	44	16	10.9
BQ 46-3	Devonian	381.6	880	63	49	46	12.0
BQ 36-2	Devonian	381.7	890	220	165		11.4
BQ 35-2	Devonian	381.7	857	288	100	59	8.7
MRKI 25-1	Devonian	385.7	758	4	56	41	10.4
MRKI 19-1	Devonian	388.6	1036	13	86	19	14.0
STL 4-9	Devonian	392.1	1027	6	84	41	13.1
ELM 11-2	Devonian	396.9	833	16	43	36	12.6
MRK II 10-3	Devonian	398.3	785	24	170	40	14.5
MRK II 10-4	Devonian	398.3	848	21	145	35	13.3
ELM 1-2	Devonian	398.1	879	21	56	37	11.3
VIN 4-5	Devonian	412.5	1273	8	87	24	7.3
VIN 4-4	Devonian	412.5	1277	7	91	30	8.7
Rivviken 2	Silurian	419	1830	33	81		7.5
Näs 1	Silurian	420	1376	53	174	17	8.6
Tomsarve 1	Silurian	420	1411	32	409		9.6
Petsarve 8	Silurian	420	1358	426	106	40	10.7
Havor 2	Silurian	422	1485	87	155	32	8.4
Grogams 1	Silurian	421				27	7.3
Blåhäll 1	Silurian	424					11.0
Blåhäll 1	Silurian	424					8.0
Tjeldersholm 1	Silurian	426	1223	17	13	33	6.8
Tjeldersholm 1	Silurian	426	1211	13	2	33	7.4
Norderstrand 1	Silurian	427				32	7.2

<sup>a</sup> Diagenetically overprinted samples.<sup>b</sup> b.d.l. = below the limit of detection.

3 blocks of 20 measurements. The cleaning procedure following every sample or standard run consisted of the sequential use of HF 0.3%, HNO<sub>3</sub> 0.65 N, and finally HNO<sub>3</sub> 0.05 N at a flow rate of 3 mL/min for ~30 min. The boron isotopic composition is expressed in the conventional  $\delta$ -notation as the relative deviation of the <sup>11</sup>B/<sup>10</sup>B ratio in the sample relative to the <sup>11</sup>B/<sup>10</sup>B ratio of NIST SRM 951 in permil:

$$\delta^{11}\text{B} (\text{‰}) = \left[ \left( \frac{{}^{11}\text{B}/{}^{10}\text{B}_{\text{sample}}}{{}^{11}\text{B}/{}^{10}\text{B}_{\text{SRM 951}}} \right) - 1 \right] \times 1000 \quad (1)$$

Precision and reproducibility of the measurements were monitored by replicate analysis of Mediterranean seawater. Reproducibility was better than  $\pm 0.25\text{‰}$  ( $1\sigma$ ;  $n = 17$ ).

### 3. RESULTS

#### 3.1. Trace Element Contents

The strontium contents of Silurian, Devonian and Pennsylvanian to Early Permian brachiopod shells are in the ranges 1211–1830 ppm, 686–1467 ppm and 284–707 ppm, respectively (Table 2; Fig. 1). Manganese contents of the shells from the respective time intervals range from 13–426 ppm, 4–288

ppm and 5–1240 ppm, whereas iron contents range from 2–409 ppm, 43–170 ppm, and 19–3570 ppm, respectively. The boron contents of the Silurian, Devonian and Pennsylvanian to Early Permian brachiopod shells are 17–40 ppm, 16–59 ppm and 24–104 ppm, respectively. In comparison, modern brachiopod shells investigated during this study reveal boron concentrations of 19 to 40 ppm.

#### 3.2. Shell Microstructure

SEM micrographs of brachiopod shells cut perpendicular to growth axis were used to document the preservation state of the shell microstructure (Fig. 2). An almost perfect preservation of individual calcite fibers of the secondary fibrous shell layer is observed for shells that are nonluminescent (Fig. 2b). In contrast, luminescent shells clearly reveal the imprint of diagenetic recrystallization with individual calcite fibers amalgamating to larger calcite crystals (Fig. 2c)

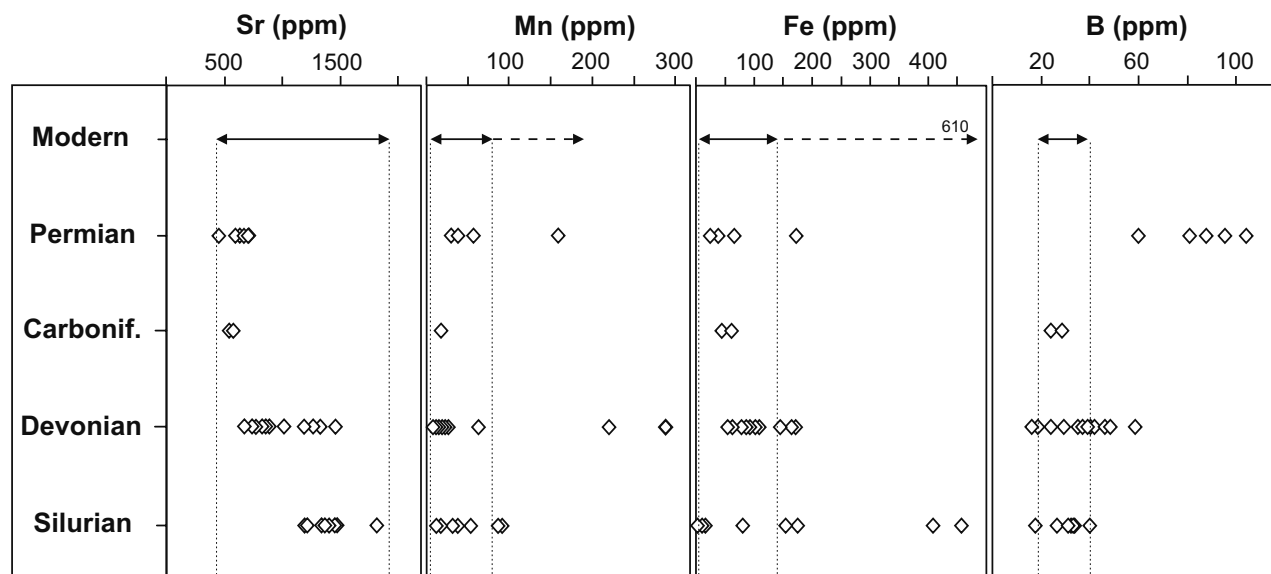


Fig. 1. Strontium, manganese, iron and boron concentrations of well-preserved Silurian to Permian brachiopod shells. Strontium, manganese, iron (Brand et al., 2003) and boron concentrations (Hemming and Hanson, 1992; this study) are provided for comparison.

### 3.3. Boron Isotopes

The  $\delta^{11}\text{B}$  values of the Silurian brachiopod shells from Gotland (Sweden) range from 6.8 to 11.0‰ (Table 2). Two Lochkovian shells show comparable values of 7.3 and 8.7‰. Emsian to Givetian brachiopod shells have higher  $\delta^{11}\text{B}$  values between 10.4 to 14.5‰, except shell BQ 35–2 that has a  $\delta^{11}\text{B}$  value of 8.7‰. Late Devonian (Frasnian) brachiopod shells have  $\delta^{11}\text{B}$  values comparable to those of the Silurian brachiopods ranging from 7.3 to 9.8‰. Pennsylvanian and Early Permian brachiopod shells have  $\delta^{11}\text{B}$  values from 12.4 to 15.8‰ and 10.1 to 11.7‰, respectively (Fig. 3).

## 4. DISCUSSION

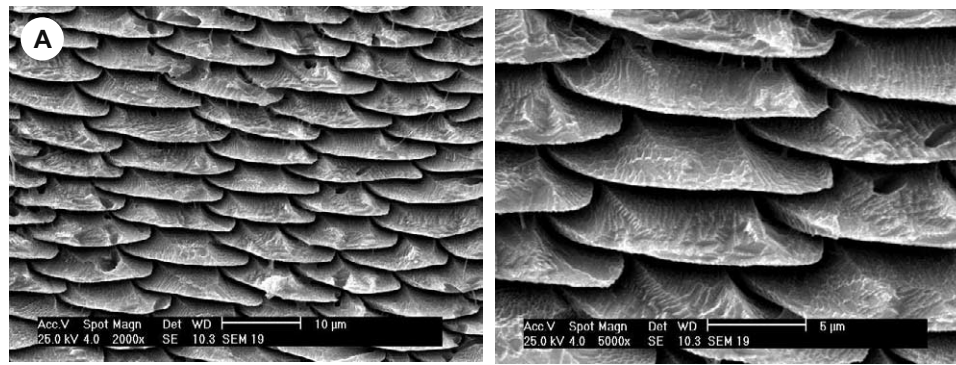
Boron is considered as a highly mobile element and diagenetic recrystallization is expected to alter boron contents as well as the primary boron isotope composition of shell calcite. Any interpretation of the measured boron isotope values with respect to  $\delta^{11}\text{B}$  or pH of ancient oceans requires that a diagenetic recrystallization of the shells must be ruled out. Cathodoluminescence microscopy, trace element concentrations as well as preservation of shell microstructures were used as criteria for the preservation state of the studied brachiopod shells.

### 4.1. Preservation of Boron Isotopic Composition

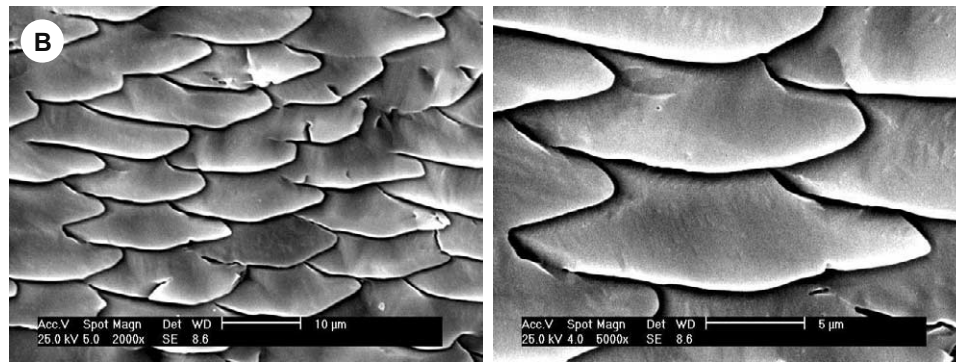
Cathodoluminescence microscopy is extensively used to identify diagenetically altered shell material (e.g., Popp et al., 1986; Grossman et al., 1993; Wenzel, 2000).  $\text{Mn}^{2+}$  is considered as the main activator of an orange-colored luminescence, whereas  $\text{Fe}^{2+}$  acts as an inhibitor resulting in a dark red (dull) or no luminescence (Savard et al., 1995; Machel et al., 1991). Substitution of  $\text{Ca}^{2+}$  by  $\text{Mn}^{2+}$  or  $\text{Fe}^{2+}$  is indicative of reducing conditions during calcite precipitation since  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$

are only stable in solutions with a negative  $E_{\text{H}}$ . Brachiopods live in well-aerated waters and as a consequence any luminescence observed in shell calcite is indicative of incorporation of  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  during diagenesis. However, if the diagenetic solutions had low manganese or iron contents, or if diagenetic recrystallization occurred in solution with a positive  $E_{\text{H}}$ , manganese and or iron will not be available for incorporation into the calcite lattice. Under these conditions the imprint of diagenetic recrystallization can not be identified by means of cathodoluminescence microscopy. In conclusion, luminescent shell calcite can be classified as diagenetically altered, whereas non-luminescent shell calcite may have been recrystallized if diagenetic recrystallization occurred under oxidizing conditions. As a consequence, additional investigations were performed to document that the nonluminescent shells preserved their primary geochemical information.

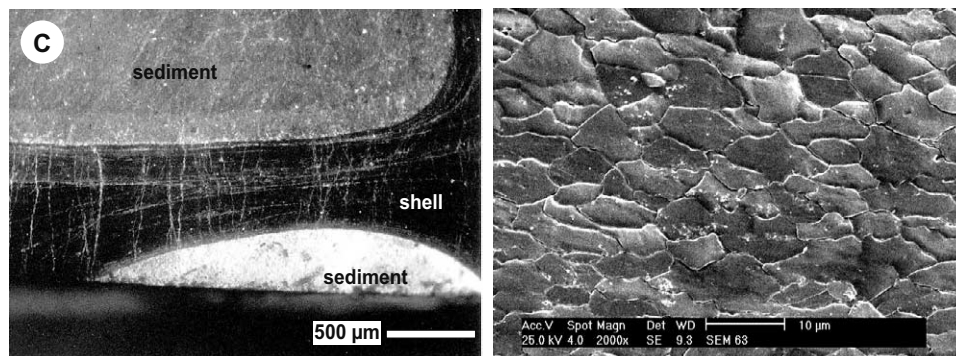
The strontium, manganese, iron and boron contents of the investigated shells as well as the concentrations measured in modern shells (Brand et al., 2003) are shown in Figure 1. The strontium contents of the Paleozoic brachiopods are well within the range of modern brachiopods (450 to 1928 ppm Sr). However, Silurian brachiopods show the highest concentrations (1211–1830 ppm Sr), whereas Devonian (758 to 1467 ppm Sr), Carboniferous (585 ppm Sr) and Permian brachiopods (556 to 707 ppm Sr) reveal significantly lower strontium concentrations (Fig. 1). Diagenetic recrystallization of calcite generally results in a depletion of strontium, but manganese and iron are preferentially incorporated into the diagenetically formed calcite (e.g., Brand and Veizer, 1980). The lower strontium contents of the Carboniferous and Permian shells could indicate a diagenetic loss of strontium if the relatively high strontium contents of the Silurian shells are taken as concentrations typical for brachiopod calcite. Interestingly, the compilation of Sr/Ca ratios of Phanerozoic biogenic low-Mg calcite (LMC)



***Notosaria nigricans* (modern, New Zealand)**



***Plicathyris alejensis* (Emsian, sample STL 4-9)**



***Tenticospirifer martellii* (Frasnian, sample SY 05-13)**

Fig. 2. SEM micrographs of polished and slightly etched modern and fossil brachiopod shells: (a) secondary fibrous shell layer of modern brachiopod *Notosaria nigricans* (New Zealand) showing stacking pattern of calcite fibers. (b) Early Devonian (Emsian) brachiopod *Plicathyris alejensis* with well-preserved calcite fibers. (c) Cathodoluminescence micrograph (left) of Late Devonian (Frasnian) brachiopod shell *Tenticospirifer martellii* with bright luminescent linings. SEM micrograph (right) shows amalgamation of calcite fibers to larger calcite crystals as result of diagenetic recrystallization.

shows a comparable pattern with high Sr/Ca ratios measured for Silurian LMC, intermediate Sr/Ca ratios for Devonian LMC and low Sr/Ca ratios for Carboniferous and Permian LMC (Steuber and Veizer, 2003). Steuber and Veizer (2003) explained this trend by the transition of the Ordovician to Mississippian calcite episode to the Pennsylvanian to Jurassic aragonite episode. Strontium-rich calcite was the predominant carbonate phase during the calcite episode that resulted in high

Sr/Ca ratios in oceanic waters. In contrast, Sr/Ca ratios of seawater were interpreted to have been low during the Pennsylvanian to Jurassic aragonite episode when strontium-rich aragonite was preferentially precipitated (Steuber and Veizer, 2003). Consequently, the low strontium contents of Carboniferous and Permian brachiopod calcites are interpreted not to be the effect of a diagenetic overprint but to represent precipitation of shell calcite from seawater with low Sr/Ca ratios.

The boron concentration of the shells is used as a further indicator to identify a diagenetic overprint. Boron is a highly mobile element and any diagenetic recrystallization is expected to result in a significant loss of boron from calcite (Gaillardet and Allègre, 1995; Spivack and You, 1997). This is clearly documented by some nonluminescent Pennsylvanian and early Permian brachiopod shells that have low manganese (5–50 ppm) and iron concentrations (19–131 ppm; Table 2) which seem apparently to indicate a good preservation state of the shells. However, strontium contents are below 400 ppm and thin section microscopy reveals the replacement of primary shell calcite by sparry calcite. Both observations suggest that these nonluminescent shells recrystallized despite the fact that manganese and iron contents are low. Most important, boron contents are below analytical detection limit which demonstrates significant boron loss during diagenetic recrystallization. In contrast, brachiopod shells classified as well-preserved based on cathodoluminescence and trace element contents have boron contents comparable to modern biogenic calcite. Boron contents of Silurian to Carboniferous brachiopods range from 17 to 59 ppm. Early Permian brachiopods reflect concentrations of 60 to 104 ppm. In comparison, boron concentrations of modern brachiopod calcite are in the ranges 26–49 ppm ( $n = 2$ ; Hemming and Hanson, 1992) and 19–40 ppm ( $n = 4$ ; this study). Boron contents of modern biogenic carbonate range from 20 to 80 ppm (Vengosh et al., 1991; Hemming and Hanson, 1992; Spivack et al., 1993; Sanyal et al., 1995). In addition, we observe no correlation of  $\delta^{11}\text{B}$  with  $1/[\text{B}]$  ( $r^2 = 0$ ). This is in contrast to investigations made by Gaillardet and Allègre (1995) on aragonitic corals and Spivack and You (1997) on whole rock carbonates. These authors observed a significant correlation between  $\delta^{11}\text{B}$  and  $1/[\text{B}]$  which was interpreted as the imprint of diagenetic recrystallization lowering boron contents and depleting shell calcite in  $^{11}\text{B}$ .

In conclusion, preserved shell microstructures, high strontium contents, as well as manganese, iron and boron contents comparable to concentrations measured on modern brachiopod calcite argue against recrystallization and diagenetic alteration of the shells. Consequently, the boron isotope ratios of the pristine brachiopod shells are interpreted as the primary boron isotope ratios that may allow to reconstruct pH or  $\delta^{11}\text{B}$  of Paleozoic oceans.

#### 4.2. Boron Isotopic Composition of Paleozoic Oceans

The boron isotope values of Silurian to Permian brachiopod shells range from 6.8 to 15.8‰ and are significantly depleted in  $^{11}\text{B}$  in comparison to modern brachiopod shells with  $\delta^{11}\text{B}$  values between 16.8 and 19.7‰ (Lécuyer et al., 2002). The low  $\delta^{11}\text{B}$  values may be attributed either to precipitation of calcite at low pH or from seawater that was significantly depleted in  $^{11}\text{B}$ . High atmospheric  $\text{CO}_2$  concentrations are assumed for the early Paleozoic and may have had an effect on oceanic pH although variation in the pH of open surface seawater is limited because the carbonate systems acts as a buffer for pH. Pearson and Palmer (1999) calculated a pH of 8.4 to 7.8 for atmospheric  $\text{CO}_2$  contents ranging from 300 to 2000 ppm. Atmospheric  $\text{CO}_2$  concentrations for the Silurian are modeled around 3000 ppm and expected to have decreased to 300 ppm in the Permian (Berner and Kothavala, 2001). High Silurian atmospheric  $p\text{CO}_2$

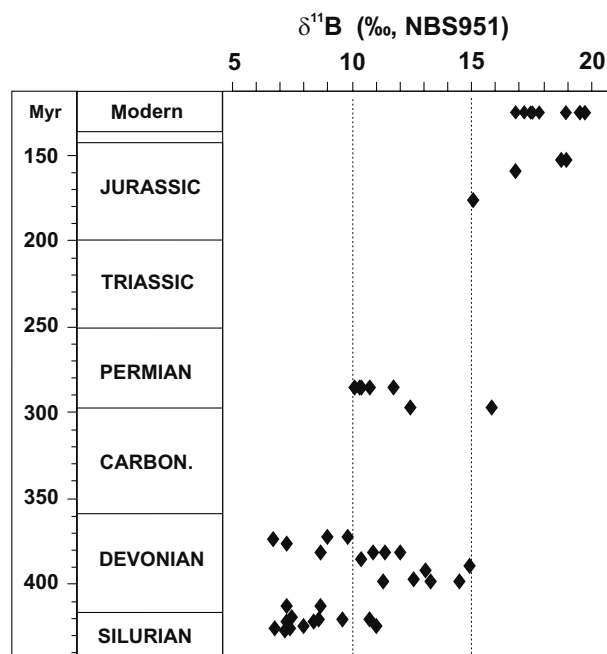


Fig. 3. Boron isotope values of Paleozoic (this study), Jurassic and modern brachiopod calcite (Lécuyer et al., 2002).

and the significant decrease in  $p\text{CO}_2$  during the Devonian and Carboniferous may have affected surface water pH and have the potential to be recorded in the boron isotope ratio of Silurian to Permian brachiopod calcite.

Hemming and Hanson (1992) calculated the lowest possible boron isotope ratio for marine carbonate at around 18.5‰ taking into account a boron isotope ratio of modern seawater of +39.5‰, a pH range for seawater of 7.5 to 8.4 and the fractionation factor for the isotope partitioning between the dissolved boron species. Kakihana et al. (1977) gave a theoretical fractionation factor for equilibrium isotope exchange between  $\text{B}(\text{OH})_3$  and  $\text{B}(\text{OH})_4^-$  of 1.0194 (25°C). The reliability of this theoretically determined value has recently been questioned by Pagani et al. (2005). Sanyal et al. (2000) showed that  $\delta^{11}\text{B}$  of inorganically precipitated calcite is 2–3‰ lower than  $\delta^{11}\text{B}$  values calculated for  $\text{B}(\text{OH})_4^-$  by Hemming and Hanson (1992). Species-dependent offsets in  $\delta^{11}\text{B}$  of foraminiferal calcite as well as coral aragonite relative to calculated equilibrium values were observed by several studies (Sanyal et al., 1995; Sanyal et al., 1996; Hoenisch et al., 2003; Hoenisch et al., 2004). Hoenisch et al. (2003) showed that photosynthesis and respiration of the foraminifer-symbiont association may modify the pH of the calcifying microenvironment in foraminifera and result in an offset in  $\delta^{11}\text{B}$  of foraminiferal calcite in comparison to calculated equilibrium values. Species-specific vital effects are considered to result in a constant offset in  $\delta^{11}\text{B}$  relative to the theoretical  $\text{B}(\text{OH})_4^-$  curve and do not compromise the use of  $\delta^{11}\text{B}$  as a proxy for pH (Hoenisch et al., 2003). However, the absolute  $\delta^{11}\text{B}$  value of biogenic carbonate will be affected by any vital fractionation effect. As a consequence, we use the empirically determined pH-dependent relation between  $\delta^{11}\text{B}$  of seawater and  $\delta^{11}\text{B}$  of modern brachiopod calcite given by Lécuyer et al. (2002). With this relation and assuming a low but potentially still realistic pH of 7.5 for Silurian seawater, Silu-

Table 3. Mass, isotopic composition and boron isotope fractionation between output and seawater ( $\alpha_{\text{out-sw}}$ ) of main boron fluxes.<sup>a</sup>

	Boron flux ( $10^9\text{kg} \times \text{yr}^{-1}$ )	$\delta^{11}\text{B}$ (‰)	$\alpha_{\text{out-sw}}$	Ref. <sup>a</sup>
<b>Sinks</b>				
Low-T oceanic crust alteration	27		0.966	a
Adsorption on clays	13		0.976	b, c
Coprecipitation in carbonates	6		0.977–0.981	d, e
<b>Sources</b>				
Rivers	38	10.1		c
High-T hydrothermal	1–4	–3 to +10		f, g
Fluid expelled at convergent margins	2	25		h

<sup>a</sup> References: (a) Smith et al. (1995); (b) Spivack et al. (1987); (c) Lemarchand et al. (2002); (d) Vengosh et al. (1991); (e) Lécuyer et al. (2002); (f) Spivack and Edmond (1987); (g) You et al. (1993); (h) You et al. (1995).

rian brachiopod calcite is expected to have a boron isotopic composition of 15.5 to 16.0‰. However, Silurian brachiopod calcite is depleted in  $^{11}\text{B}$  by up to 8‰ in comparison to this minimum value of 15.5‰. These low  $\delta^{11}\text{B}$  values cannot be explained by a change in seawater pH alone because the slope of the  $\delta^{11}\text{B}$  of  $\text{B}(\text{OH})_4$  vs. pH curve is almost zero at lower pH and no further significant change in the boron isotopic composition of  $\text{B}(\text{OH})_4^-$  is possible. As a consequence, the low  $\delta^{11}\text{B}$  values of the Paleozoic brachiopods cannot be explained by a significant change in seawater pH but indicate that the boron isotope ratio of Paleozoic seawater was significantly different from the modern value of +39.5‰.

Modeling of the boron geochemical cycle was used to test whether variations in the main boron fluxes might result in a significantly lower  $\delta^{11}\text{B}$  ratio of Paleozoic seawater which is suggested by the low  $\delta^{11}\text{B}$  values of Paleozoic brachiopod calcite. The modeling of the boron elemental and isotopic composition of seawater through time was performed using time-dependent box-models (Lasaga, 1980; Albarède, 1995) with a first-order kinetic of the transfers between the involved reservoirs. A comparable model was used by Lemarchand et al. (2000, 2002) to propose a secular evolution of  $\delta^{11}\text{B}$  of seawater during the last 120 Ma. The mass and isotopic composition of seawater boron is determined by the input and output of boron into and from the oceanic reservoir (Table 3). Boron is removed from seawater by low temperature alteration of the oceanic crust (Spivack and Edmond, 1987; Smith et al., 1995), adsorption of boron on clay-rich sediments (Spivack et al., 1987) and coprecipitation in biogenic carbonates (Vengosh et al., 1991). All these processes are characterized by a preferential  $^{10}\text{B}$  removal and tend to enrich seawater in  $^{11}\text{B}$ . Lemarchand et al. (2002) estimated that the isotopic fractionation associated with total boron uptake from seawater is about –30‰. The main sources of boron to the ocean are hydrothermal venting (Spivack and Edmond, 1987), fluids being expelled from accretionary prisms (Kopf and Deyhle, 2002), and continental weathering (Lemarchand et al., 2000, 2002; Rose et al., 2000). Lemarchand et al. (2002) proposed that the continental boron flux to the oceans represents the major input flux with a modern mean isotopic composition of +10‰. An increasing input of boron from the continents would tend to lower the  $\delta^{11}\text{B}$  of seawater.

The boron concentration and isotopic composition of seawater were calculated using the following mass-balance equations

$$\frac{dB_i}{dt} = \sum^{j \neq i} Q_{j \rightarrow i} - \sum^{i \neq j} Q_{i \rightarrow j} \quad (2)$$

and

$$\frac{dR_i}{dt} = \frac{\sum^{j \neq i} Q_{j \rightarrow i} K_{j \rightarrow i}}{B_j} R_i - \left( \frac{\sum^{i \neq j} Q_{i \rightarrow j} K_{i \rightarrow j}}{B_i} + \frac{\sum^{i \neq j} Q_{j \rightarrow ij} - Q_{j \rightarrow i}}{B_i} \right) R_i \quad (3)$$

where  $B_i$  is the boron concentration of the reservoir  $i$ ,  $R_i$  the boron isotope ratio,  $Q_{i \rightarrow j}$  the boron mass flux from reservoir  $i$  to reservoir  $j$ , and,  $K_{i \rightarrow j}$  the boron fractionation coefficient upon transfer from  $i$  to  $j$ .

We choose to perform two simulations to test whether significant changes in the above described fluxes may result in a significant change in the boron isotope ratio of seawater. The first simulation assumed variations in oceanic spreading rate and a constant supply of continental boron to the oceans. During the second simulation, we introduced a variable riverine boron flux. During both simulations, the  $\delta^{11}\text{B}$  of riverine input was kept constant at the present-day value of 10‰ (Lemarchand et al., 2002). In addition, partition coefficients and isotopic fractionation factors were assumed not to have changed during Earth history. The model was calibrated using the modern boron fluxes reported by Lemarchand et al. (2002), a present-day seawater boron content of 4.5 ppm and a  $\delta^{11}\text{B}$  value for seawater of 39.5‰ (Tab. 3). The boron isotopic composition of biogenic calcite was calculated using the pH-dependent relationship between  $\delta^{11}\text{B}$  of seawater and  $\delta^{11}\text{B}$  of brachiopod calcite given by Lécuyer et al. (2002).

In the first simulation (assuming a constant boron flux from the continents), the evolution of the boron isotopic ratio of seawater is mainly dependent on the exchange of boron between seawater and the oceanic crust. The processes that control boron concentration as well as isotopic composition of seawater are boron uptake during low temperature alteration of the oceanic crust, boron input by high temperature hydrothermal venting and continental boron input. The latter was held constant at a modern value of  $3.8 \times 10^8 \text{ kg B/yr}$  (Lemarchand et al., 2002). Following the model of Lemarchand et al. (2002), the amount of boron trapped in altered oceanic crust was set to be proportional to the oceanic crust spreading rate. A comparable relationship is expected for high temperature hydrothermal venting as well as fluids expelled from accretion prisms

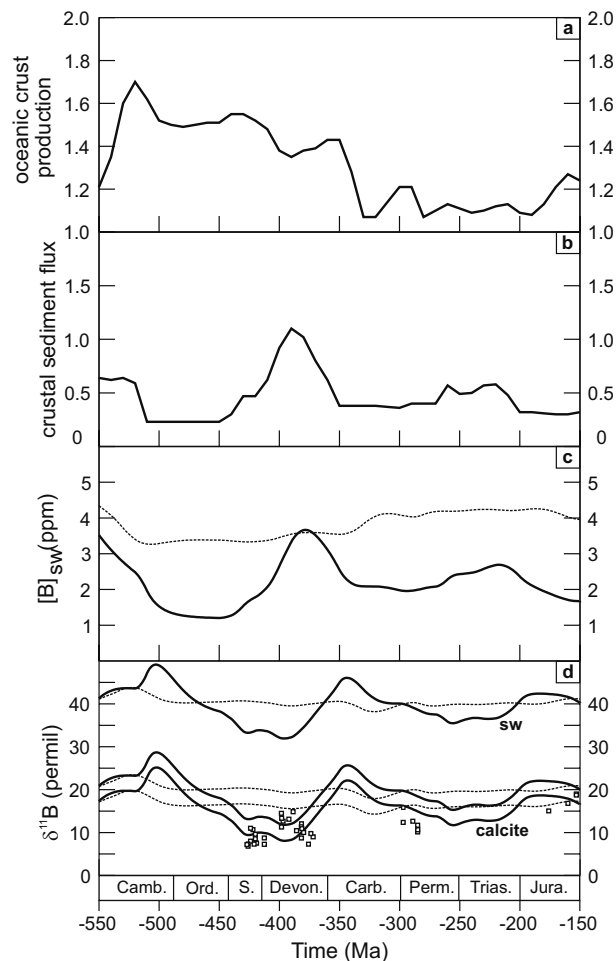


Fig. 4. Evolution of boron isotope composition of seawater and calcite (Cambrian to Jurassic) as function of major processes controlling oceanic boron budget: (a) oceanic crust production rate (Gaffin, 1987) relative to modern production rate; (b) crustal sediment flux (Hay et al., 2002) normalized to modern flux rate; (c) boron concentration of seawater assuming constant continental boron flux (dashed line) and variable continental boron flux proportional to crustal sediment flux (solid line); (d) modeled  $\delta^{11}\text{B}$  of seawater (sw) and marine calcite (calcite) for constant continental boron flux (dashed line) and variable continental boron flux (solid line). Maximum and minimum  $\delta^{11}\text{B}$  for calcite calculated assuming minimum and maximum fractionation as function of pH. Squares indicate  $\delta^{11}\text{B}$  values of Silurian to Permian (this study) and Jurassic brachiopod calcite (Lécuyer et al., 2002).

with both fluxes of boron increasing as consequence of enhanced spreading. In the lack of more recent data for Paleozoic spreading rates, we used the oceanic crust production rates given by Gaffin (1987, Fig. 4) that were reconstructed by inverting the long-term sea level record. Assuming a comparable ratio between high (on-axis) and low temperature (off-axis) hydrothermal activity than today, the boron isotope ratio of seawater did not show a prominent change through time although oceanic crust production rate varied (Fig. 4). Increasing the high temperature hydrothermal activity relative to the low temperature oceanic crust alteration (e.g., by lowering the closure time of the hydrothermal system, see Lécuyer and Allemand, 1999) resulted in a lower  $\delta^{11}\text{B}$  value of the oceans because in this case the  $^{11}\text{B}$  depleted flux from hydrothermal

vents dominates the  $^{11}\text{B}$  enrichment as consequence of low-temperature alteration of oceanic crust. The response of the boron isotope ratio of seawater to a shorter lifetime of the oceanic hydrothermal systems was estimated using the seawater-oceanic crust exchange model of Lécuyer and Allemand (1999) adapted for B exchange. A lifetime of the oceanic hydrothermal systems shorter than 5 Ma resulted in a decrease of the  $\delta^{11}\text{B}$  of seawater to values  $<33\%$ . However, this assumption seems not realistic given the compilation of marine heat flow data that suggests closure times for modern oceanic crust in the range of 50 to 65 ma (Johnson and Pruis, 2003).

The second simulation assumed variations in the oceanic spreading rate (Gaffin, 1987) and a variable input of boron from the continents. The continental boron flux to the oceans was assumed to be proportional to the clastic sediment input. This assumption is based on the positive correlations between continental runoff and clastic sediment yield (Ludwig et al., 1996) as well as between mechanical erosion and chemical weathering (Millot et al., 2002). We used reconstructions of the clastic sediment flux to the oceans for the past 600 Ma (Wold and Hay, 1990; Hay et al., 2002) and calculated the boron input into the oceanic reservoir as well as the boron uptake from seawater by absorption on clay minerals. Figure 4 shows the evolution of the oceanic boron concentration and boron isotopic composition. The boron concentration varies as a function of the crustal sediment flux with contents varying from 1.2 to almost 4 ppm. The  $\delta^{11}\text{B}$  of seawater shows significant changes with values ranging from 31 to 42‰. Assuming a boron isotope fractionation factor between seawater and biogenic calcite between 0.977 (low pH) to 0.981 (high pH), minimum  $\delta^{11}\text{B}$  values for Silurian and Devonian calcite are expected in the range of 8 to 12‰. Maximum  $\delta^{11}\text{B}$  values were calculated to range from 13 to 17‰ for the early Silurian and from 17 to 20‰ for the late Devonian. The modeled  $\delta^{11}\text{B}$  values are in accordance with the measured  $\delta^{11}\text{B}$  values of Silurian to Devonian brachiopod shells. The modeled  $\delta^{11}\text{B}$  values for Permian and Jurassic calcite are slightly higher than the measured  $\delta^{11}\text{B}$  values (Fig. 4). Given the uncertainties in the reconstructed clastic sediment flux (Wold and Hay, 1990; Hay et al., 2002), we argue that the modeled and measured  $\delta^{11}\text{B}$  values agree reasonably well.

In conclusion, we suggest that an enhanced riverine boron flux may have been responsible for a significant lowering of the boron isotopic composition of the Paleozoic oceans. We are aware that an enhanced continental discharge during the Silurian to Devonian is speculative at the current state of knowledge and that there are no proxy data to support this suggestion. However, climate modeling (Otto-Bliesner, 1995) as well as the reconstruction of the global water cycle (Tardy et al., 1989) indicate a significant increase in continental runoff during the Silurian to Devonian time periods. Since neither the oceanic crust production rate nor the clastic sedimental flux are well constrained for the Paleozoic, the modeled  $\delta^{11}\text{B}$  curve should be only considered as indicative of possible  $\delta^{11}\text{B}$  fluctuations of seawater during the Paleozoic.

## 5. CONCLUSIONS

The boron isotopic compositions of Paleozoic brachiopod calcite are significantly depleted in comparison to modern brachiopod or biogenic calcite. These low  $\delta^{11}\text{B}$  values cannot

be explained by a loss of boron or exchange of boron isotopes during diagenesis because the shells are well-preserved and reflect boron contents comparable to modern biogenic carbonate. High boron contents are taken as additional argument for a preservation of the geochemical signals since the high mobility of boron suggests a significant loss of boron if recrystallization would have occurred. Diagenetically altered shell calcite reflects boron contents below analytical detection limit which points to a significant boron loss during diagenesis. The  $\delta^{11}\text{B}$  values of Silurian to Permian brachiopod calcite are interpreted as primary isotope signals and suggest that the boron isotope ratio of the Paleozoic oceans was up to 10‰ lower in comparison to the modern ratio. Numeric modeling of the boron geochemical cycle indicates that the low oceanic  $\delta^{11}\text{B}$  values may preferentially be explained by an enhanced riverine flux of boron from the continents to the oceanic reservoir. The outcome of this study together with the modeling results of Lemarchand et al. (2002) suggest that the boron isotope ratio of seawater may have varied during the Phanerozoic as a consequence of a variable boron exchange with the oceanic crust and changes in the boron delivery from the continents. This study suggests that boron isotopes cannot be used as a paleo-pH proxy on longer timescales (>14 ma) until the secular evolution of the boron isotope composition of seawater is constrained by further data.

*Acknowledgments*—We thank Philippe Telouk (École Normale Supérieure de Lyon) for helpful support during the boron isotope analysis at the ENS at Lyon. Lucia Angiolini (University of Milano) is thanked for providing Permian brachiopods from Oman. Axel Munnecke (University of Erlangen) kindly provided Silurian brachiopods from Gotland. The constructive comments by three anonymous reviewer and by GCA associate editor Tim Lowenstein greatly improved the manuscript. This study was financially supported by the German Science Foundation DFG (Project Jo 219/7-1 within SPP Evolution of System Earth during the Devonian to Permian).

*Associate editor:* T. Lowenstein

## REFERENCES

- Albarède F. (1995) *An Introduction to Geochemical Modeling*. Cambridge University Press.
- Berner R. A. and Kothavala Z. (2001) Geocarb III: A revised model of atmospheric  $\text{CO}_2$  over Phanerozoic time. *Am. J. Sci.* **301**, 182–204.
- Brand U. and Veizer J. (1980) Chemical diagenesis of a multi-component carbonate system—I. Trace elements. *J. Sediment. Petrol.* **50**, 1219–1236.
- Brand U., Logan A., Hiller N., and Richardson J. (2003) Geochemistry of modern brachiopods: Applications and implications for oceanography and paleoceanography. *Chem. Geol.* **198**, 305–334.
- Gaffin S. (1987) Ridge volume dependence on sea-floor generation rate and inversion using long-term sea-level change. *Am. J. Sci.* **287**, 596–611.
- Gaillardet J. and Allègre C. J. (1995) Boron isotopic composition of corals: Seawater or diagenesis record? *Earth Planet. Sci. Lett.* **136**, 665–676.
- Grossman E. L., Mii H.-S., and Yancey T. E. (1993) Stable isotopes in late Pennsylvanian brachiopods from the United States. *Geol. Soc. Am. Bull.* **105**, 1284–1296.
- Hay W. W., Soeding E., DeConto R. M., and Wold C. N. (2002) The Late Cenozoic uplift—Climate change paradox. *Int. J. Earth Sci.* **91**, 746–774.
- Hemming N. G. and Hanson G. N. (1992) Boron isotopic composition and concentration in modern marine carbonates. *Geochim. Cosmochim. Acta* **56**, 537–543.
- Hoenisch B., Bijma J., Russell A. D., Spero H. J., Palmer M., Zeebe R., and Eisenhauer A. (2003) The influence of symbiont photosynthesis on the boron isotopic composition of foraminifera shells. *Mar. Micropaleont.* **49**, 87–96.
- Hoenisch B., Hemming N. G., Grottoli A. G., Amat A., Hanson G. N., and Bijma J. (2004) Assessing scleractinian corals as recorders for paleo-pH: Empirical calibration and vital effects. *Geochim. Cosmochim. Acta* **68**, 3675–3685.
- Johnson H. P. and Pruis M. J. (2003) Fluxes of fluid and heat from the oceanic crustal reservoir. *Earth Planet. Sci. Lett.* **216**, 565–574.
- Kakihana H., Kotaka M., Satoh S., Nomura M., and Okamoto M. (1977) Fundamental studies on the ion exchange separation of boron isotopes. *Bull. Chem. Soc. Jap.* **50**, 158–163.
- Kopf A. and Deyhle A. (2002) Back to the roots: Boron geochemistry of mud volcanoes and its implications for mobilization depth and global B cycling. *Chem. Geol.* **192**, 195–210.
- Lasaga A. C. (1980) The kinetic treatment of geochemical cycles. *Geochim. Cosmochim. Acta* **44**, 815–828.
- Lécuyer C. and Allemand P. (1999) Modelling of the evolution of the oxygen isotope composition of seawater: Implications for the climatic interpretation of the  $\delta^{18}\text{O}$  of marine sediments. *Geochim. Cosmochim. Acta* **63**, 351–361.
- Lécuyer C., Grandjean P., Reynard B., Albarède F., and Telouk Ph. (2002)  $^{11}\text{B}/^{10}\text{B}$  analysis of geological materials by ICP-MS plasma. *Chem. Geol.* **186**, 45–55.
- Lemarchand D., Gaillardet J., Lewin É., and Allègre C. J. (2000) The influence of rivers on marine boron isotopes and implications for reconstructing past ocean pH. *Nature* **408**, 951–954.
- Lemarchand D., Gaillardet J., Lewin É., and Allègre C. J. (2002) Boron isotope systematics in large rivers: Implications for the marine boron budget and palaeo-pH reconstruction over the Cenozoic. *Chem. Geol.* **190**, 123–140.
- Ludwig W., Probst J.-L., and Kempe S. (1996) Predicting the oceanic input of organic carbon by continental erosion. *Global Biogeochem. Cycles* **10**, 23–41.
- Machel H. G., Mason R. A., Mariano A. N. and Mucci A. (1991) Causes and emission of luminescence in calcite and dolomite. In *Luminescence Microscopy: Quantitative and Qualitative Aspects* (eds. C. E. Barker and D. C. Kopp), pp. 9–25. Short Course 25. SEPM.
- Millot R., Gaillardet J., Dupré B., and Allègre C. J. (2002) The global control of silicate weathering rates and the coupling with physical erosion: New insights from rivers of the Canadian Shield. *Earth Planet. Sci. Lett.* **196**, 83–98.
- Otto-Bliesner B. L. (1995) Continental drift, runoff and weathering feedbacks: Implications from climate model experiments. *J. Geophys. Res.* **100** (D6), 11537–11548.
- Pagani M., Lemarchand D., Spivack A., and Gaillardet J. (2005) A critical evaluation of the boron-pH proxy: The accuracy of ancient ocean pH estimates. *Geochim. Cosmochim. Acta* **69**, 953–961.
- Palmer M. R., Spivack A. J., Edmond J. M. (1987) Temperature and pH controls over isotopic fractionation during absorption of boron on marine clay. *Geochim. Cosmochim. Acta* **51**, 2319–2323.
- Palmer M. R., Pearson P. N., and Cobb S. J. (1998) Reconstructing past ocean pH-depth profiles. *Science* **282**, 1468–1473.
- Pearson P. N. and Palmer M. R. (1999) Middle Eocene seawater pH and atmospheric carbon dioxide concentrations. *Science* **284**, 1824–1826.
- Pearson P. N. and Palmer M. R. (2000) Atmospheric carbon dioxide concentrations over the past 60 million years. *Nature* **406**, 695–699.
- Popp B. N., Anderson T. F., and Sandberg P. A. (1986) Textural, elemental and isotopic variations among constituents in Middle Devonian limestones, North America. *J. Sediment. Petrol.* **56**, 715–727.
- Rose E., Chaussidon M., and France-Lanord C. (2000) Fractionation of boron isotopes during erosion processes; the example of Himalayan rivers. *Geochim. Cosmochim. Acta* **64**, 397–408.
- Sanyal A., Hemming N. G., Hanson G. N., and Broecker W. S. (1995) Evidence for a higher pH in the glacial ocean from boron isotopes in foraminifera. *Nature* **373**, 234–236.
- Sanyal A., Hemming N. G., Broecker W. S., Lea D. W., Spero H. J., and Hanson G. N. (1996) Oceanic pH control on the boron isotopic

- composition of Foraminifera; evidence from culture experiments. *Paleoceanography* **11**, 513–517.
- Sanyal A., Hemming N. G., Broecker W. S., and Hanson G. N. (1997) Changes in pH in the easter equatorial Pacific across stage 5–6 boundary based on boron isotopes in foraminifera. *Global Biogeochem. Cycles* **11**, 125–134.
- Sanyal A., Nugent M., Reeder R. L., and Bijma J. (2000) Seawater pH control on the boron isotopic composition of calcite; evidence from inorganic calcite precipitation experiments. *Geochim. Cosmochim. Acta* **64**, 1551–1555.
- Savard M. M., Veizer J., and Hinton R. H. (1995) Cathodoluminescence at low Fe and Mn concentrations: A SIMS study of zones in natural calcites. *J. Sed. Res.* **A65**, 208–213.
- Schwarcz H. P., Agyei E. K., and McMullen C. C. (1969) Boron isotope fractionation during clay absorption from seawater. *Earth Planet. Sci. Lett.* **6**, 1–5.
- Smith H. J., Spivack A. J., Staudigel H., and Hart S. R. (1995) The boron isotopic composition of altered oceanic crust. *Chem. Geol.* **126**, 119–135.
- Spivack A. J. and You C. F. (1997) Boron isotopic geochemistry of carbonates and pore waters, Ocean Drilling Program Site 851. *Earth Planet. Sci. Lett.* **152**, 113–122.
- Spivack A. J. and Edmond J. M. (1987) Boron isotope exchange between seawater and the oceanic crust. *Geochim. Cosmochim. Acta* **51**, 1033–1043.
- Spivack A. J., Palmer M. R., and Edmond J. M. (1987) The sedimentary cycle of the boron isotopes. *Geochim. Cosmochim. Acta* **51**, 1939–1949.
- Spivack A. J., You C. F., and Smith J. (1993) Foraminiferal boron isotope ratios as a proxy for surface ocean pH over the past 21 Myr. *Nature* **363**, 149–151.
- Steuber T. and Veizer J. (2003) Phanerozoic record of plate tectonic control of seawater chemistry and carbonate sedimentation. *Geology* **30**, 1123–1126.
- Tardy Y., N’Kounkou R., and Probst J. L. (1989) The global water cycle and continental erosion during Phanerozoic time (570 my). *Am. J. Sci.* **289**, 455–483.
- 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., and 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.
- Vengosh A., Kolodny Y., Starinsky A., Chivas A. R., and McCulloch M. T. (1991) Coprecipitation and isotope fractionation of boron in modern biogenic carbonates. *Geochim. Cosmochim. Acta* **55**, 2901–2910.
- Vengosh A., De Lange G. J., Starinsky A. (1998) Boron isotope and geochemical evidence for the origin of Urania and Bannock brines at the eastern Mediterranean: Effect of water rock interaction. *Geochim. Cosmochim. Acta* **62**, 3221–3228.
- Wenzel B. (2000) Differential preservation of primary isotopic signatures in Silurian brachiopods from Northern Europe. *J. Sediment. Res.* **70**, 194–209.
- Wold C. N. and Hay W. W. (1990) Estimating ancient sediment fluxes. *Am. J. Sci.* **290**, 1069–1089.
- You C. F., Spivack A. J., Smith J. H., and Gieskes J. M. (1993) Mobilization of boron in convergent margins: Implications for the boron geochemical cycle. *Geology* **21**, 207–210.
- You C. F., Spivack A. J., Gieskes J. M., Rosenbauer R., and Bishoff J. L. (1995) Experimental study of boron geochemistry: Implications for fluid processes in subduction zones. *Geochim. Cosmochim. Acta* **59**, 2435–2442.