

# Modelling the geochemical cycle of boron: Implications for the long-term $\delta^{11}\text{B}$ evolution of seawater and oceanic crust

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## Abstract

The boron geochemical cycle has been simulated using a time-dependent geochemical box model that was coupled to a one-dimension model of seawater–oceanic crust interactions. Boron elemental and isotopic compositions of oceanic rocks as a function of depth were calculated by mass balance, using the temperature and porosity profiles of the crust as well as the available experimental and empirical distribution coefficients and fractionation factors between mineral and water. Ranges of boron elemental and isotopic variations of seawater were calculated for crust–seawater interactions that take place from the ridge-axis to the off-axis closure of the hydrothermal system. The present-day  $\delta^{11}\text{B}$  of seawater (40‰) could represent a steady-state value. However, depending on crustal permeability, lifetime of water–rock interactions, and expansion rate of the oceanic ridge, the  $\delta^{11}\text{B}$  of seawater may vary from 30‰ to 50‰ at the 10 million year scale.

Some boron isotope compositions of Cretaceous biogenic carbonates and ophiolitic serpentinites from Oman are comparable to modern rock samples, suggesting that the  $\delta^{11}\text{B}$  of Cretaceous seawater was close to the present-day value. Low  $\delta^{11}\text{B}$  values of some biogenic carbonates cannot be attributed to low pH values of past seawater, but more probably to  $\delta^{11}\text{B}$  variations of seawater or diagenetic alteration by crustal aqueous fluids. Boron isotope composition of hydrothermally altered serpentines could be considered as a promising proxy of the seawater composition.

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## 1. Introduction

The knowledge of the evolution of the boron isotope composition of seawater is crucial to reconstruct the paleo-pH of the oceans from the analysis of the  $\delta^{11}\text{B}$  of ancient marine carbonates. The boron isotope fractionation between modern biogenic carbonates and seawater is a function of pH (Vengosh et al., 1991; Hemming and Hanson, 1992; Sanyal et al., 1995; Sanyal and

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Bijma, 1999; Lécuyer et al., 2002). Therefore, even if the boron isotope fractionation certainly also depends on temperature, boron isotope compositions of past marine carbonates have the potential to provide estimates of variations in the pH of seawater during the last million years (Spivack et al., 1993; Gaillardet and Allègre, 1995).

Some authors proposed that the  $\delta^{11}\text{B}$  of biogenic carbonates could constitute valuable proxies of atmospheric  $\text{CO}_2$  partial pressures (Pearson and Palmer, 1999; 2000). The estimate of marine paleo-pH of seawater from sediments older than a few million years requires to know whether the  $\delta^{11}\text{B}$  of seawater is sensitive to climate, continental erosion and chemical exchange at oceanic ridges. Measurements of boron isotope riverine fluxes (Rose et al., 2000; Lemarchand et al., 2000) have improved the knowledge of the global geochemical cycle of boron, for which only few mass balances have been proposed (You et al., 1993; Smith et al., 1995; Lemarchand et al., 2002; Park and Schlesinger, 2002). Using a box-modelling approach, Lemarchand et al. (2000, 2002) deduced that the composition of seawater is mainly controlled by the continental discharge and off-axis low-temperature interactions with the oceanic crust. From the inferred properties of their modelled boron geochemical cycle, the authors interpret the past 60 My evolution of foraminifera  $\delta^{11}\text{B}$  as the reflect of changes in seawater composition instead of the result of low pH values driven by higher  $p\text{CO}_2$  during the Eocene than nowadays as proposed by Pearson and Palmer (2000).

Besides riverine input, other sources of boron in seawater are hydrothermal fluids (Spivack and Edmond, 1987) and fluids expelled at convergent margins (You et al., 1995; Kopf et al., 2000; Deyhle and Kopf, 2002). The major competing sinks are the low-temperature alteration of oceanic crust (Spivack and Edmond, 1987; Smith et al., 1995), the adsorption on clay-rich sediments and boron adsorption on the products of continental erosion carried by rivers (Spivack et al., 1987). The strong  $^{10}\text{B}$  uptake by clay minerals, chlorites and serpentines at low temperature should be responsible for the  $^{11}\text{B}$ -enrichment of seawater (Spivack and Edmond, 1987; Spivack et al., 1987). Boron uptake from seawater also occurs during coprecipitation in marine carbonates (Vengosh et al., 1991), evaporites (Smith and Medrano, 1996), and biogenic silica (Ishikawa and Nakamura, 1993; Kolodny and Chaussidon, 2004).

Seawater is enriched in boron (4.5 ppm) relatively to fresh Mid Ocean Ridge basalts (<1 ppm) (Chaussidon

and Marty, 1995). During hydrothermal alteration of the oceanic crust, a large boron enrichment of oceanic rocks occurs, which is up to 150 ppm for serpentinites and commonly higher than 20 ppm for hydrothermally altered basalts and gabbros (Spivack and Edmond, 1987; Ishikawa and Nakamura, 1992; Smith et al., 1995; Benton et al., 2001). Seawater–crust interaction is also responsible for a boron isotope fractionation, leading to a  $^{11}\text{B}$ -enrichment of oceanic rocks. The  $\delta^{11}\text{B}$  of hydrothermally altered rocks ranges from  $-2\text{‰}$  to  $26\text{‰}$  (Spivack and Edmond, 1987; Ishikawa and Nakamura, 1992; Smith et al., 1995; Benton et al., 2001) in comparison to fresh mid-ocean ridge (MOR) basalts ( $\delta^{11}\text{B} \sim -3\text{‰}$ ) (Chaussidon and Jambon, 1994; Chaussidon and Marty, 1995). However, the boron isotope composition of the oceanic crust still remains poorly documented and the few boron isotope data obtained for gabbros and basalts cannot provide a good estimate of the whole oceanic crust. Such an undersampling potentially leads to a bias in the quantification of the global flux of boron isotope exchange with seawater that operates during hydrothermal and weathering alteration of the oceanic crust.

The aim of this study is to calculate the range of boron elemental and isotopic variations of seawater during crust–seawater interactions from the ridge-axis to the off-axis closure of the hydrothermal system. The boron cycle will be simulated at the My time scale using a time-dependent box model with first-order kinetics of mass transfer (Lasaga, 1980). Distribution coefficients and fractionation factors between output fluxes and boron reservoirs are calculated from experimental fractionation factors between mineral and water phases. The boron content and isotopic composition of the oceanic crust will be computed as a function of age and depth using a modified version of the model developed by Lécuyer and Allemand (1999) for oxygen isotopes. The evolution of the boron isotope composition of seawater will thus be obtained as a function of the rate of oceanic crust production, the closure time of the hydrothermal system, and the flux of seawater through the crust. Finally, the results of our model combined to new measurements of Cretaceous biogenic carbonates will be used to address three major aspects of the boron geochemical cycle that are:

- Does the boron exchange between oceanic crust and seawater play a major role for controlling the secular evolution of seawater?
- To what extent boron isotope compositions of biogenic carbonates can be used to estimate pH of past seawater?

- What can we propose as suitable proxies for the past boron isotope composition of seawater?

## 2. Formulation of the model

### 2.1. Boron exchange between seawater and oceanic crust

The model of boron exchange between seawater and oceanic rocks consists of two parts (see [Lécuyer and Allemand, 1999](#)): (1) a thermal and hydraulic model, and (2) a model of boron exchange between minerals and seawater. The reactive crust, i.e. the part of the oceanic crust through which seawater circulation occurs, is divided into  $N$  equal-volume boxes characterised by their age and their thermal and porosity profiles. At each step time  $\Delta t$ , a new box with fresh crust properties is created at the ridge axis and the box older than the closure time  $T_c$ , no more reactive, is removed from the model. The boron isotopic exchange model is then computed into each box, and calculations are iterated for each  $t=t+\Delta t$ .

#### 2.1.1. Thermal and hydraulic model

We use the following equation ([Turcotte and Schubert, 1982](#)) to calculate the thermal profile of the oceanic crust with time ( $t$ ) and depth ( $z$ ):

$$T_{z,n\Delta t} = T_0 \operatorname{erf}\left(\frac{z}{2\sqrt{\kappa n\Delta t}}\right) \quad (1)$$

with  $T_0$  the temperature of the crust at  $t=0$  and  $z>0$ ,  $\kappa$  the thermal diffusivity (set to  $10^{-6} \text{ m}^2 \text{ s}^{-1}$ ) and  $n\Delta t$  the age of each box.

In the hydraulic model, we do not consider convective water circulation in the crust. Only the porosity of the oceanic crust (i.e. water–rock ratio) is calculated, using an equation in which the water–rock ratio decreases exponentially with depth ([David et al., 1994](#)) and as the square root of time according to the decrease of the oceanic heat flow:

$$\left(\frac{W}{R}\right)_z^{n\Delta t} = \left(\frac{W}{R}\right)_0 \frac{1}{1 + c_1 \sqrt{n\Delta t}} \exp\left(\frac{-z}{z_0}\right) - c_2 \sqrt{n\Delta t}. \quad (2)$$

Coefficients  $c_1$  and  $c_2$  are adjusted in order to close the porosity at 6 km at the ridge axis,  $t=0$ , to decrease the water–rock ratio at  $z=0$  from the initial value  $\left(\frac{W}{R}\right)_0^0$  to 0 at the closure time  $T_c$  of the hydrothermal system, and to decrease the depth of closure of porosity from 6 km at  $t=0$  to the surface of the oceanic crust at the

closure time  $T_c$ . This model describes the documented thinning of the porous layer with age ([Carlson and Herrick, 1990](#)), due to the oceanic crust cooling and to the increase of the sedimentary thickness. Initial water–rock ratios between 1 and 10 were considered in the model and correspond to the range estimated from both heat fluxes ([Corlis et al., 1979](#); [Sclater et al., 1980](#)) and geochemical measurements based on Sr isotopes and Mg elemental fluxes ([Albarède et al., 1981](#); [Alt and Emmermann, 1985](#); [Alt et al., 1986](#)). Closure time of the oceanic crust porosity has been selected between 10 and 50 My.

#### 2.1.2. Boron exchange between seawater and oceanic crust

The behaviour of boron through exchange between seawater and silicates of the oceanic crust is a delicate issue to handle. Most of the experimental data related to the elemental and isotopic partitioning of boron have been obtained from hydrothermal experiments involving clay minerals ([Palmer et al., 1987](#); [You et al., 1995](#); [Williams et al., 2001](#)) and from high-temperature melt experiments ([Hervig et al., 2002](#)).

Shales and marine sediments are enriched in B at the expense of seawater because of the preferential uptake of B by clay minerals. At temperature lower than  $\sim 120^\circ \text{C}$ , the enrichment of B in clay minerals occurs through B adsorption on clay surfaces ([Schwarcz et al., 1969](#); [You et al., 1995](#)). During diagenesis and metamorphism, smectite reaction to illite results in the incorporation of B into the silicates by substitution for Si. During low-temperature recrystallization of smectite ( $\sim 60^\circ \text{C}$ ), B may be adsorbed on clay surface or substituted to Si ([Williams et al., 2001](#)). Although several experiments have led to the determination of the B adsorption partition coefficient ([Spivack et al., 1987](#); [Palmer et al., 1987](#); [You et al., 1995](#)), there is no experimental determination of the B partition coefficient between “non-exchangeable-B” in silicates and aqueous solutions.

The B enrichment of the oceanic crust is the result of secondary mineral formation, mainly smectites, chlorites and serpentines, during low-temperature alteration ([Spivack and Edmond, 1987](#)). Both adsorption on mineral surfaces and substitution for Si into silicates should be involved as B enrichment mechanisms of altered oceanic rocks. Because of the lack of data and of the complexity of the mechanism of B exchange between seawater and silicates, we used an empirical method to calculate a bulk equilibrium distribution coefficient ( $D$ ) of B between oceanic rocks and water.  $D$ , which depends on the temperature of alteration, is calculated by using the linear correlation between the B content

and the  $\delta^{18}\text{O}$  of smectites precipitated from unevolved seawater (Donnelly et al., 1979; Spivack and Edmond, 1987; Smith et al., 1995). The B concentration of altered oceanic rocks in equilibrium with seawater,  $[\text{B}]_{\text{eq}}$ , is then calculated by using the following mass balance equation describing mass exchange in an open system (Spivack and Edmond, 1987), which is related to the amount of circulating water as following:

$$\frac{d[\text{B}]_{\text{eq}}}{dW/R} = - \left( \frac{[\text{B}]_{\text{eq}}}{D} - [\text{B}]_{\text{sw}} \right) \quad (3)$$

where  $[\text{B}]_{\text{sw}}$  is the boron content of seawater. At the crust scale, the boron content of the circulating aqueous fluid, initially unevolved seawater on the ocean floor, is calculated by mass balance as a function of increasing depth, leading to a progressive boron depletion of the circulating water.

Isotopic fractionation factors  $\alpha$  have been experimentally determined for B exchange between clay minerals and water. B adsorption on clays leads to a preferential  $^{10}\text{B}$  uptake from water at low temperature (Palmer et al., 1987). This isotopic fractionation is related to the coordination change of B from trigonal to tetrahedral on the clay surfaces, and may be a good proxy for the value of the fractionation factor associated to other trigonal to tetrahedral coordination changes (Palmer and Swihart, 1996), for example during B incorporation in silicon tetrahedra (Williams et al., 2001). Assuming that B isotope fractionation depends mainly on coordination changes rather than on mineral properties, Williams et al. (2001) proposed a general isotope fractionation equation for B between mineral and water ( $\Delta_{\text{mineral-water}} = -10.12 \times 1/T + 2.44$ ). The magnitude of this temperature dependence is different from that determined by Kakhana et al. (1977) between the dissolved species  $\text{B}(\text{OH})_3$  (trigonal) and  $\text{B}(\text{OH})_4^-$  (tetragonal). This pioneering work was based on theoretical calculations of partition functions and adsorption experiments using ion exchange resins, however the reliability of this fractionation equation has recently been questioned by Pagani et al. (2003).

As indicated above, several uncertainties are associated with the knowledge of B behaviour in the oceanic crust also including the dependence of the B isotope fractionation on the mineral chemistry which is not known so far. However, a major change in B fractionation has been documented as a function of temperature. At low temperatures (lower than 150 °C), the mineral–water partition coefficients for dissolved boron are larger than 1 and  $^{10}\text{B}$  incorporates preferentially hydrous minerals such as clays and chlorites (Palmer et al.,

1987; You et al., 1995). At temperatures of hydrothermal fluids discharged on axis (over 300 °C), boron is released from silicates and no or slight isotopic fractionation occurs (Spivack et al., 1987). The  $^{11}\text{B}/^{10}\text{B}$  ratio of oceanic rocks that completely reacted with seawater ( $R_{\text{eq}}$ ) is calculated by using the following equation, a generalisation of the mass balance equation for open systems (Taylor, 1977; Gregory and Taylor, 1981; Criss, 1999):

$$\frac{d}{dW/R} \left( R_{\text{eq}} \cdot [\text{B}]_{\text{eq}} \right) = R_{\text{sw}} \cdot [\text{B}]_{\text{sw}} - \frac{[\text{B}]_{\text{eq}}}{D} \frac{R_{\text{eq}}}{\alpha} \quad (4)$$

where  $R_{\text{sw}}$  is the boron isotope ratio of seawater. The fractionation factor  $\alpha$  between the altered mineral phases and water is equal to 0.968 at 25 °C as proposed by Spivack and Edmond (1987). This value is close to the fractionation factor experimentally determined by Palmer et al. (1987) between clay and water at low temperatures (5–40 °C). Therefore, the B isotope fractionation equation from Williams et al. (2001) was selected as it includes the data from Palmer et al. (1987).

The boron concentration and  $\delta^{11}\text{B}$  of seawater (sw subscript) reacting with oceanic crust are calculated for each time step  $\Delta t$  by using simple mass balance equations:

$$[\text{B}]_{\text{sw}}^t = [\text{B}]_{\text{sw}}^{t-\Delta t} + \frac{M_{\text{hw}} \cdot [\text{B}]_{\text{hw}}}{M_{\text{sw}}} \quad (5)$$

$$[\text{B}]_{\text{sw}}^t \cdot \delta^{11}\text{B}_{\text{sw}}^t = [\text{B}]_{\text{sw}}^{t-\Delta t} \cdot \delta^{11}\text{B}_{\text{sw}}^{t-\Delta t} + \frac{M_{\text{hw}} \cdot [\text{B}]_{\text{hw}} \cdot \delta^{11}\text{B}_{\text{hw}}}{M_{\text{sw}}} \quad (6)$$

where  $M_{\text{hw}}$  is the total mass of hydrothermal water circulating into the oceanic crust for an increment of time  $\Delta t$ , with the mean boron concentration  $[\text{B}]_{\text{hw}}$  and isotopic composition  $\delta^{11}\text{B}_{\text{hw}}$ .  $M_{\text{sw}}$  is the mass of the ocean. Given shifts in the B concentration and  $\delta^{11}\text{B}$  of the oceanic crust lead to corresponding shifts in the boron elemental and isotopic compositions of seawater which depend on the amount and composition of hydrothermal fluids released to the ocean.

### 2.1.3. Kinetics

The amplitude of boron exchange between rocks and seawater is limited by the kinetics of reaction. Kinetic data for boron exchange between rock-forming minerals and water are not available so far. Since boron is carried by minerals neofomed during crust hydration, we assume that the kinetics of boron exchange between seawater and oceanic crust follows the zero-order kinetic heterogeneous reaction of silicate dissolution during crust hydration (Wood and Walther, 1983).

The fraction  $f$  of boron exchanged with time between rocks and water is then:

$$f = k \cdot t \quad (7)$$

with the rate constant  $k$ :

$$\log k = -\frac{2900}{T} - 6.85 \quad (8)$$

where  $k$  is expressed in moles of oxygen per square-centimeter per second. The rate constant  $k$  depends on the reactive surface area,  $A_\theta$ , that could be approximated as follows according to Lasaga (1998):

$$A_\theta = \frac{4 \cdot x_\theta}{100 \cdot r_{\max}} \quad (9)$$

with  $r_{\max}$  is the mean radius of minerals in centimeter and  $x_\theta$  is their percentage in volume assuming spherical grains. The ranges of values used for  $r_{\max}$  and  $x_\theta$  are 0.1–1 mm and 20–80%, respectively, which describe the average mineral mode and size of oceanic basalts and gabbros. After reaction with seawater, the resulting boron elemental and isotopic profiles of the oceanic crust are computed with the two following equations:

$$[B]_r^t = [B]_r^{t-\Delta t}(1-f) + [B]_{\text{eq}}^t \cdot f \quad (10)$$

$$\delta^{11}[B]_r^t = \delta^{11}B_r^{t-\Delta t}(1-f) + \delta^{11}B_{\text{eq}}^t \cdot f \quad (11)$$

in which the mass balance equations Eqs. (3) and (4) and the kinetic law Eq. (7) are substituted, and temperature and water–rock ratios calculated in Eqs. (1) and (2) are also substituted in Eqs. (3), (4) and (8).

This kinetic model is obviously an oversimplification of what really operates at the mineral scale. It does not represent the complexity of the various processes (diffusion, adsorption, mineral recrystallization) that globally result in B uptake by silicates. For example, B adsorption, strongly dependent on pH and temperature, and which can be reversible, is not taken into account in this study. Williams et al. (2001) notice however that the kinetics of B exchange during recrystallization of smectite and neoformation of illite crystals follow the mineralogical changes.

#### 2.1.4. Channelised fluid flow

In the frame of the above model, the permeability structure of the oceanic crust does not take into account fluid flows channelised through the fracture networks. These fluid flows could be responsible for localised high water–rock interactions, leading to the formation of veins with high boron contents. Hydrothermal veins represent probably less than 10% in mass of the global

oceanic crust (Lécuyer and Reynard, 1996), and about 5% according to the estimate of vein density based on field studies led in the Oman ophiolite (Nehlig, 1989). Veins in the oceanic crust do not affect geochemical mass balances of major elements such as oxygen (Lécuyer and Allemand, 1999), however they could significantly contribute to increase the amount of boron taken up by the oceanic crust during low-temperature water interactions. Boron contents in veins may be of two orders of magnitude higher in vein minerals than in wall rocks, especially within the gabbroic section of the crust characterised by chlorite and amphibole-bearing veins (Spivack and Edmond, 1987). The “vein contribution” to the bulk boron composition of the oceanic crust is calculated by considering a portion of the crust (5 to 10 wt.%) that reacts with seawater under infinite water–rock ratios.

#### 2.2. Box-model modelling of the boron geochemical cycle

The evolutions of boron concentration and isotopic composition of seawater are calculated by connecting our oceanic crust–seawater exchange model to the global boron cycle involving the continental crust and marine sediment reservoirs. The various boron fluxes are presented in Table 1. Besides the low-temperature crust alteration, the main sinks of marine boron are clays and shales (Spivack et al., 1987) and biogenic carbonates (Vengosh et al., 1991). Evaporites can contain up to a few % of boron (Smith and Medrano, 1996) and should be taken into account as a mechanism of boron uptake. Another flux of B uptake from seawater is the biogenic silica precipitation (Ishikawa and Nakamura, 1993). The  $\delta^{11}\text{B}$  of biogenic silica ranges between 0‰ and 5‰, with a mean B content of about 75 ppm (Kolodny and Chausidon, 2004). The net burial flux of Si is close to  $1.7 \times 10^{11}$  kg year<sup>-1</sup> (Tréguer et al., 1995), leading to a B removal flux of  $1.3 \times 10^7$  kg year<sup>-1</sup>.

The major source of dissolved boron to the oceans is the continental weathering (Rose et al., 2000; Lemarchand et al., 2000), discharging a flux of  $3.8 \times 10^8$  kg year<sup>-1</sup> (Lemarchand et al., 2002). Other boron sources include on-axis hydrothermal activity (Spivack and Edmond, 1987) and fluids expelled from accretionary prisms (You et al., 1993). Boron-enriched fluids are also released at erosional convergent margins (Kopf et al., 2000; Deyhle and Kopf, 2002), but no quantification of the B flux has been proposed so far. The main source of this flux is the B desorption of clay-rich marine sediments (Deyhle and Kopf, 2002). It seems reasonable to propose that this flux is of the same order

Table 1

Boron present-day fluxes, isotopic compositions and fractionation factor between output and seawater ( $\alpha_{\text{out-sw}}$ )

Flux	B ( $10^7$ kg year $^{-1}$ )	$\delta^{11}\text{B}$ (‰)	$\alpha_{\text{out-sw}}$	Ref.
<i>Ocean inputs</i>				
Hydrothermal fluids				This model
Rivers	38	10		a
Fluids expelled at convergent margins	4	$20 \pm 5$		b
<i>Ocean outputs</i>				
Oceanic crust alteration				This model
Coprecipitation				
in carbonates and evaporites	6		$0.980 \pm 0.005$	c; d; e
in biogenic silica	1.3		0.960	f
Adsorption on clay	1.3		0.976	a; g

(a) Lemarchand et al. (2002).

(b) You et al. (1995) and Deyhle and Kopf (2002).

(c) Vengosh et al. (1991).

(d) Smith and Medrano (1996).

(e) Blanc (2000).

(f) Ishikawa and Nakamura (1993) and Kolodny and Chaussidon (2004).

(g) Spivack and Edmond (1987).

of magnitude than the B expelled from accretionary prisms.

The rate of boron transfer between seawater, continental crust and sediments (mainly carbonates and evaporites) are computed using a time-dependent box model (Lasaga, 1980). The boron content of each reservoir is obtained according to the following mass balance equation:

$$\frac{dM_i}{dt} = \sum_{j \neq i} Q_{j \rightarrow i} - \sum_{j \neq i} Q_{i \rightarrow j}, \quad (12)$$

where  $M_i$  is the boron mass in the reservoir  $i$  and  $Q_{i \rightarrow j}$  the boron mass flux from reservoir  $i$  to reservoir  $j$ . The evolution of the boron isotope composition is computed by solving:

$$\frac{dC_i}{dt} = \frac{\sum_{j \neq i} Q_{j \rightarrow i} K_{j \rightarrow i}}{M_i} C_j - \left( \frac{\sum_{j \neq i} Q_{i \rightarrow j} K_{i \rightarrow j}}{M_i} + \frac{\sum_{j \neq i} Q_{j \rightarrow i} - Q_{i \rightarrow j}}{M_i} \right) C_i \quad (13)$$

where  $C_i$  is the  $^{11}\text{B}$  concentration in reservoir  $i$  and  $K_{i \rightarrow j}$  the fractionation coefficient of  $^{11}\text{B}$  upon transfer between reservoirs  $i$  and  $j$ .

### 3. Boron isotope composition of carbonates

Boron isotope compositions of shells from Jurassic and Cretaceous carbonate-secreting marine inverte-

brates have been measured according to the method developed by Lécuyer et al. (2002). Carbonate powders (300–400 mg) are dissolved in  $\text{HNO}_3$  1 M and the solution is partly neutralised with KOH 1 M until the pH reaches 6. Dissolved boron is subsequently purified on an anion-exchange resin, Amberlite IRA 743, using a batch technique. To elute the borate,  $\text{HNO}_3$  0.05 M is added to the resin and the solution is gently shaken for 4 h. The boron isotope compositions were measured with a MC-ICP-MS Plasma 54 developed by VG Elemental (Lécuyer et al., 2002). Normalisation of sample isotopic ratios was made against NIST reference NBS 951 with an external reproducibility of  $\pm 0.3\delta$  unit at 95% confidence level. Ionisation yield was about 1 V of signal per ppm of B. Isotopic ratios were corrected from the instrumental mass bias by bracketing samples with measurements of NBS 951 standard solutions. The  $\delta^{11}\text{B}$  of the marine carbonates are presented in Table 2.

A *Placentieras*, ammonoid from the Valanginian of the Western Interiors (USA), has a  $\delta^{11}\text{B}$  of 0.9‰. Jurassic and Cretaceous brachiopods have  $\delta^{11}\text{B}$  ranging from 7‰ to 19‰. Limestone matrices have  $\delta^{11}\text{B}$  ranging from 3‰ to 15‰, at least 4‰ lower than the isotopic compositions of the associated invertebrate samples.

### 4. Results of the model

#### 4.1. $\delta^{11}\text{B}$ of altered oceanic crust

Profiles of boron concentrations and isotopic compositions of the oceanic crust were computed for a 1

Table 2  
Boron isotope compositions of present-day, Cretaceous and Jurassic marine carbonates

Sample	Taxon	Stratigraphic age	Location	Environment	$\delta^{11}\text{B}$
DJ-113	<i>Terebratula carnea</i>	Campanian	Meudon, France	Offshore	17.6
DJ-110	<i>Terebratula emiglobosa</i>	Late Turonian	Armeau, France	Offshore	15.9
DJ-109	<i>Terebratula biplicata</i>	Lower Cenomanian	Villers s/Mer, France	Offshore	18.4
DJ-105	<i>Terebratula sella</i>	Lower Barremian	Saint Dizier, France	Littoral, variable salinity	16.8
DJ-103	<i>Terebratula acuta</i>	Lower Hauterivian	Bettancourt, France	Upper offshore	17.5
SEP/CAL	<i>Septaliphoria</i> sp.	Upper Callovian	Vesaignes, France	Offshore	16.8
TOR/AAL	<i>Torquirhynchia</i> sp.	Aalenian	Jamprestes, Portugal	Offshore	15.0
SEP/OXF	<i>Septaliphoria pinguis</i>	Upper Oxfordian	La Charités/Loire, France	Shoreface	19.0
SEP/OXF mat	Limestone matrix	Upper Oxfordian	La Charités/Loire, France	Shoreface	15.4
SEP/OXF	<i>Septaliphoria pinguis</i>	Upper Oxfordian	La Charités/Loire, France	Shoreface	18.7
SEP/OXF mat	Limestone matrix	Upper Oxfordian	La Charités/Loire, France	Shoreface	14.5
PLA/VAL	<i>Placenticerus placenta</i>	Senonian	Dakota, USA	Epicontinental	0.9
CRA/MAN	<i>Crassostrea virginica</i>	Modern	Pointe Jean-Claude, Martinique, France	Mangrove	17.4
CFL 1	<i>Ceratostreon abellatum</i>	Upper Cenomanian	Ile Madame, France	Shoreface/upper offshore	11.9
CFL 2	<i>Ceratostreon abellatum</i>	Lower Cenomanian	Archingeay, France	Shoreface	6.7
AH1-5a inf	<i>Aetostreon</i> sp.	Lower Valanginian	Aït Hamouch, Morocco	Shoreface/upper offshore	13.1
AH1-MAT	Limestone matrix	Lower Valanginian	Aït Hamouch, Morocco	Shoreface/upper offshore	8.2
SYOS-E106	<i>Aetostreon</i> sp.	Valanginian	Sidi Yahia, Agadir, Morocco	Upper offshore	13.5
SYOS-E106-MAT	Limestone matrix	Valanginian	Sidi Yahia, Agadir, Morocco	Upper offshore	3.4
AH1-3b	<i>Aetostreon</i> sp.	Upper Berriasien	Aït Hamouch, Morocco	Upper offshore	13.8

My time interval from 1 to 20 My, firstly considering equilibrium with seawater (Fig. 1). Both [B] and  $\delta^{11}\text{B}$  of seawater are assumed to be constant and equal to the present-day values of 4.5 ppm and 39.5‰. The sequence of curves (Fig. 1a) depicts a rapid decrease of the B content of the oceanic crust with depth, driven by the increase of temperature and the decrease of permeability. With aging, the crust becomes enriched in B as the result of prevailing low-temperature interactions. The maximal boron enrichment of the oceanic crust is located within the altered basalts of the crustal layer 2A (0–500 m), in good agreement with the measured B profiles (Ishikawa and Nakamura, 1992; Smith et al., 1995). Layer 3 of the oceanic crust (gabbros, from 1500 m to the bottom of the 6000-m-thick crust) is characterised by low boron concentrations, close to 1 ppm, as a consequence of both weak permeability of the lower crust and high temperatures of water–rock interactions.

The calculated  $\delta^{11}\text{B}$  profiles (Fig. 1b) show a global  $^{11}\text{B}$  enrichment with time of the oceanic crust relatively to the fresh MORB and gabbros. The upper 500 m of the crust (layer 2A) are progressively enriched in  $^{11}\text{B}$ , from  $\delta^{11}\text{B}$  values about 5‰ at the surface to a maximum of 15‰ at 500 to 1500 m depth (layer 2B), in a relatively good agreement with the available range of rock data from ODP sites (Spivack and Edmond, 1987; Ishikawa and Nakamura, 1992; Smith et al., 1995) and ophiolites (Smith et al., 1995). The computed  $\delta^{11}\text{B}$  values of the deeper part of the oceanic crust (gabbros below 2000 m) decrease and progressively tend to the

value of fresh oceanic rocks (–3‰). This pattern results from the progressive decrease of crustal permeability with increasing depth and time. The boron isotope composition of the lower crust appears to be mainly controlled by the density of hydrothermal veins. For example,  $\delta^{11}\text{B}$  values of +5‰ are computed at depths below 3000 m (Fig. 1b).

Computed curves presented in Figs. 1 and 2 neglect kinetics of boron exchange between mineral and water, thus overestimating the boron content of the hydrothermally altered oceanic crust. Assuming that equilibrium is reached between phases, the calculated average crustal contents that range from 5 to 25 ppm (Fig. 2) are much higher than the average boron concentration (5.2 ppm) estimated from rocks of DSPD/ODP Holes and ophiolites (Smith et al., 1995). Kinetic effects could explain this discrepancy for the upper part of the crust that is mainly controlled by low-temperature alteration processes. Boron concentration profiles from 1 to 20 My are computed with our kinetic model of boron exchange between seawater and basalts (Fig. 3). In this case, lower B contents between 2 and 20 ppm are obtained for the bulk altered crust, depending on the initial water–rock ratio and the closure time of the hydrothermal system (Fig. 4). As expected, the concentration of boron in the crust increases with the amount of water reacting at low temperatures (Fig. 4). Hydrothermal veins constitute a large contribution to the boron budget of the oceanic crust with a boron enrichment of about 3 ppm (Fig. 4).

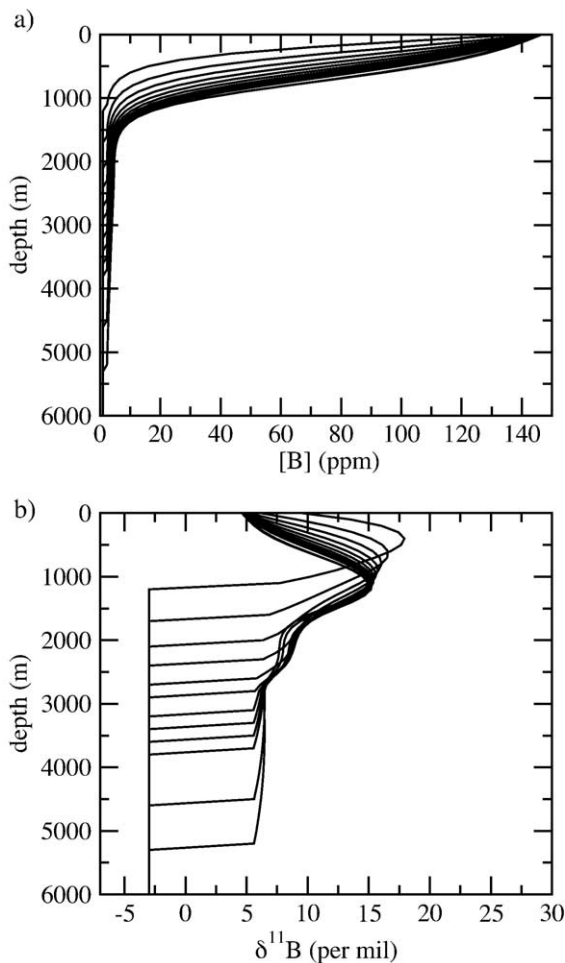


Fig. 1. Evolution of boron elemental (a) and isotopic (b) compositions of the oceanic crust from 1 to 20 My (curves each My) assuming that equilibrium is reached between rocks and seawater.

The boron isotope composition of the oceanic crust was also computed for various water–rock ratios and closure times of the hydrothermal system (Fig. 5). The average  $\delta^{11}\text{B}$  of the oceanic rocks ranges between  $-2\text{‰}$  for a water–rock ratio of 1 and a closure time of 10 Ma, and about  $3\text{‰}$  for a water–rock ratio of 10 and a closure time of 50 My (Fig. 5). The larger the water–rock ratios, the larger is the  $^{11}\text{B}$  enrichment of the crust at the expense of seawater. The primordial role of the hydrothermal veins is emphasised in Fig. 5, which depicts how the  $\delta^{11}\text{B}$  value of the crust is highly dominated by the composition of veins resulting from the filling in of thermal cracks. The average boron isotope composition of the crust at steady state ranges from  $6\text{‰}$  to  $8\text{‰}$  when considering 5 wt.% of hydrothermal veins (Fig. 5).

Despite some basic assumptions presented in Section 4.1, our crust–seawater model shows its capability

to reproduce both documented boron elemental and isotopic compositions of rocks sampled from the oceanic crust and ophiolites. Computed average values of boron contents ( $2\text{--}20$  ppm) and  $\delta^{11}\text{B}$  ( $-2\text{‰}$  to  $8\text{‰}$ ) are consistent with the “composites” proposed by Smith et al. (1995) ( $[\text{B}] = 5.2 \pm 1.7$  ppm and  $\delta^{11}\text{B} = 3.7 \pm 1.1\text{‰}$ ), and bracket the averaged values from other measured profiles, ranging from about 2 ppm (Ishikawa and Nakamura, 1992) to 25 ppm (Spivack and Edmond, 1987). Comparison of computed depth profiles with boron contents and  $\delta^{11}\text{B}$  values of samples from DSDP site 504B (Ishikawa and Nakamura, 1992), from ODP/DSDP sites 417 and 735B, and from ophiolites (Smith et al., 1995) reveals similar evolutions with depth: (1) maximal B enrichment and low  $\delta^{11}\text{B}$  in the uppermost 500 m of the oceanic crust, (2) below 500 m,

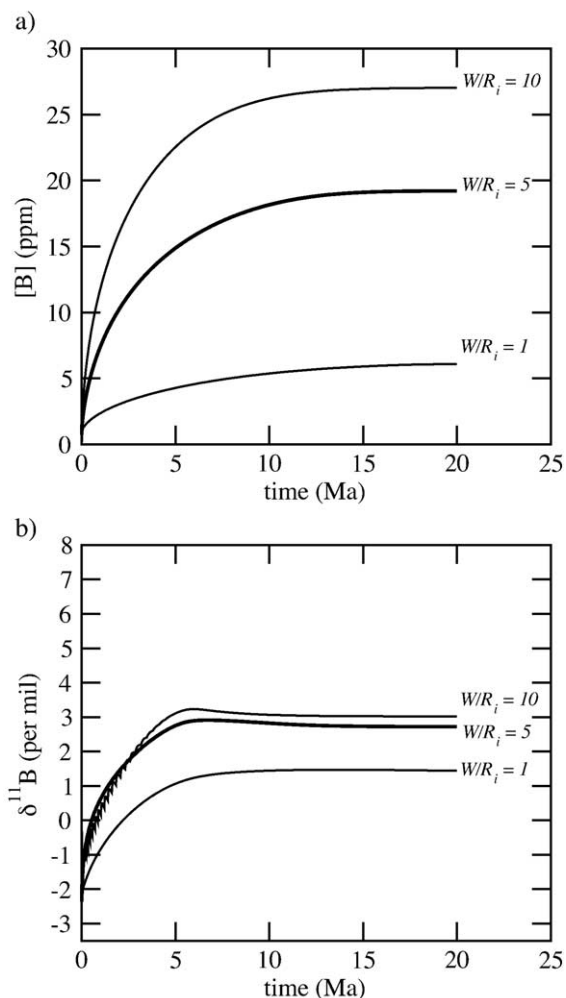


Fig. 2. Evolution of the average boron elemental (a) and isotopic (b) compositions of the oceanic crust over 20 My assuming that equilibrium is reached between rocks and seawater.



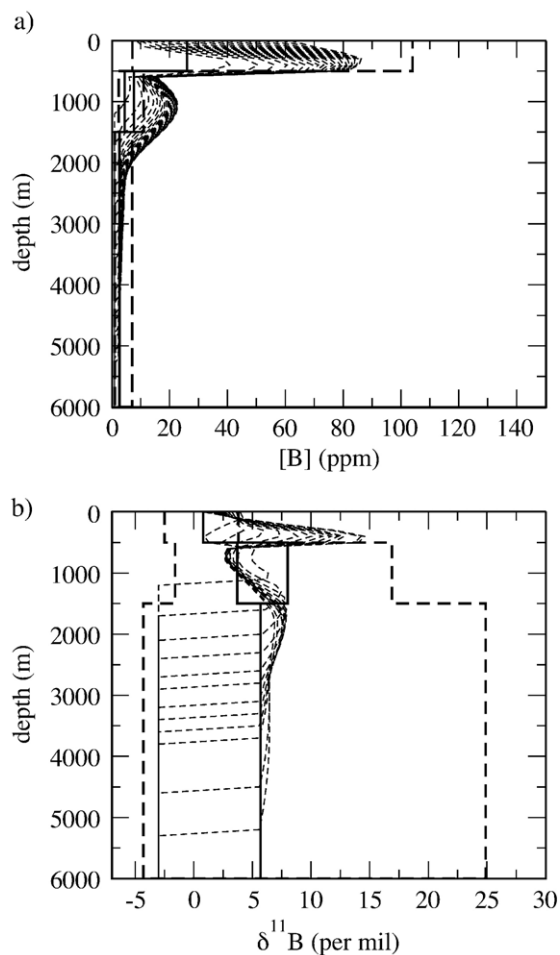


Fig. 3. Evolution of boron elemental (a) and isotopic (b) compositions of the oceanic crust from 1 to 20 My (curves each My) with the kinetic rate of boron exchange according to our model (see Section 2.1). The dashed vertical black lines delimit the range of observed values, the plain lines represent the average values for each crustal layer (Smith et al., 1995).

rapid decrease of the B content down to the B concentration of fresh MORB, and (3) maximal  $^{11}\text{B}$  enrichment between 500 and 1500 m depth (Fig. 3).

#### 4.2. Box-model computation results and $\delta^{11}\text{B}$ budget of seawater

Boron elemental and isotopic evolutions of seawater have been computed (Figs. 6 and 7) as a function of the oceanic expansion rate (1, 3 and 10  $\text{cm year}^{-1}$ ), the crustal permeability ( $W/R=1, 3$  and 10), and the abundance of hydrothermal veins. At steady-state, low boron concentrations of seawater (Fig. 6) correspond to long-lived hydrothermal systems and high water–crust ratios. Indeed, the circulation at low temperatures

of large amounts of seawater favours a net B enrichment of the oceanic crust at the expense of seawater. The time required to reach a new steady state is inversely proportional to the initial water–rock ratio (Fig. 6) and to the expansion rate of the oceanic crust (Fig. 8a). The boron concentration of seawater decreases by a few ppm when taking into account hydrothermal veins. For example, with a closure time set at 20 Ma and for a given initial water–rock ratio of 1 and an expansion rate of 3  $\text{cm year}^{-1}$ , the steady state boron concentration of the oceans is 4 ppm instead of 5 ppm when the oceanic crust contains 5 wt.% of hydrothermal veins located in the gabbroic section (Fig. 9a). The  $\delta^{11}\text{B}$  of seawater varies from +34‰ to +44‰ for closure times of crust–water interactions varying between 10 and 50 My and considering a constant expansion rate of 3  $\text{cm year}^{-1}$ . Note also that an increase of the  $\delta^{11}\text{B}$  of seawater of about 2‰ results from the formation of 5% of chlorite-rich veins in the oceanic crust (Fig. 9b).

The boron isotope composition of seawater is also highly sensitive to the expansion rate of the oceanic crust (Fig. 8b). High expansion rates cause a boron depletion of the hydrosphere relatively to oceanic rocks and lead to shorter response times of the boron composition of seawater. As the rate of boron exchange between the crust and seawater increases with expansion rates,  $\delta^{11}\text{B}$  of seawater vary from +44‰ down to +33‰ for expansion rates decreasing from 10  $\text{cm year}^{-1}$  down to 1  $\text{cm year}^{-1}$ .

## 5. Discussion

### 5.1. Implications on seawater $\delta^{11}\text{B}$ variations

Using the data set given in Table 1, the modelling of the boron cycle suggests that the elemental content and isotopic composition of boron in seawater could correspond to steady-state values for an average expansion rate of oceanic crust close to 3  $\text{cm year}^{-1}$  and a crust–water rock ratio between 1 and 3. The residence time of boron in seawater is thus estimated close to 10 My. Similarly to other chemical elements, the abundance and isotopic composition of boron in seawater are sensitive to variations in the fluvial discharge, chemical exchange with the oceanic crust, and mass changes of chemical (evaporites) and biogenic (carbonates) sediments. For example, the  $7.88 \times 10^{18}$  kg of Messinian evaporites (Blanc, 2000) trapped into the deep sediments of the Mediterranean Sea could modify the boron budget of the global ocean. We can assume that these evaporites contain an average B

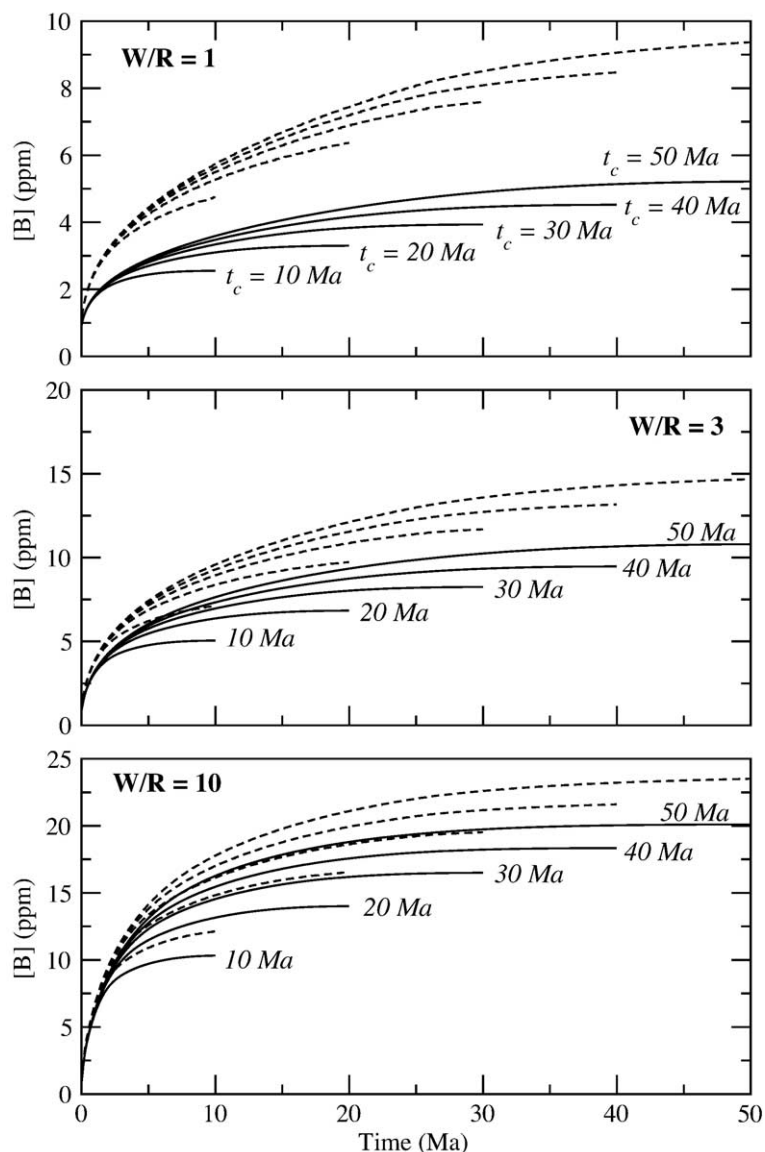


Fig. 4. Average boron content of the oceanic crust for closure times ( $t_c$ ) between 10 and 50 My, for three water–rock ratios of 1, 3 and 10, and taking into account the absence of hydrothermal veins (plain curves) and 5 wt.% of hydrothermal veins (dashed curves).

content of 100 ppm with a  $\delta^{11}\text{B}$  value of 20‰ (Smith and Medrano, 1996). Dissolving this boron and mixing it with the world ocean would lead to an increase of its boron content from 4.5 up to 5.1 ppm and to decrease its isotopic composition from 40‰ down to 37.8‰.

According to this study and Lemarchand et al. (2002), the  $\delta^{11}\text{B}$  of seawater may largely fluctuate through time (up to 10‰) in response to either changes in runoff or oceanic expansion rates. However, based on  $\delta^{11}\text{B}$  measurements of pore fluids in

oceanic sediments, Spivack et al. (1993) proposed that the boron isotope composition of seawater remained roughly constant over the past 21 My. Analysing pH profiles in the upper water column and using the property of planktonic foraminifera species that precipitate calcium carbonate at a given pH and depth, Pearson and Palmer (2000) have presented a model of  $\delta^{11}\text{B}$  secular evolution of seawater over the past 60 Ma. These authors interpreted the measured variation through time of the  $\delta^{11}\text{B}$  of biogenic carbonates as pH changes in seawater, down to 7.4 during

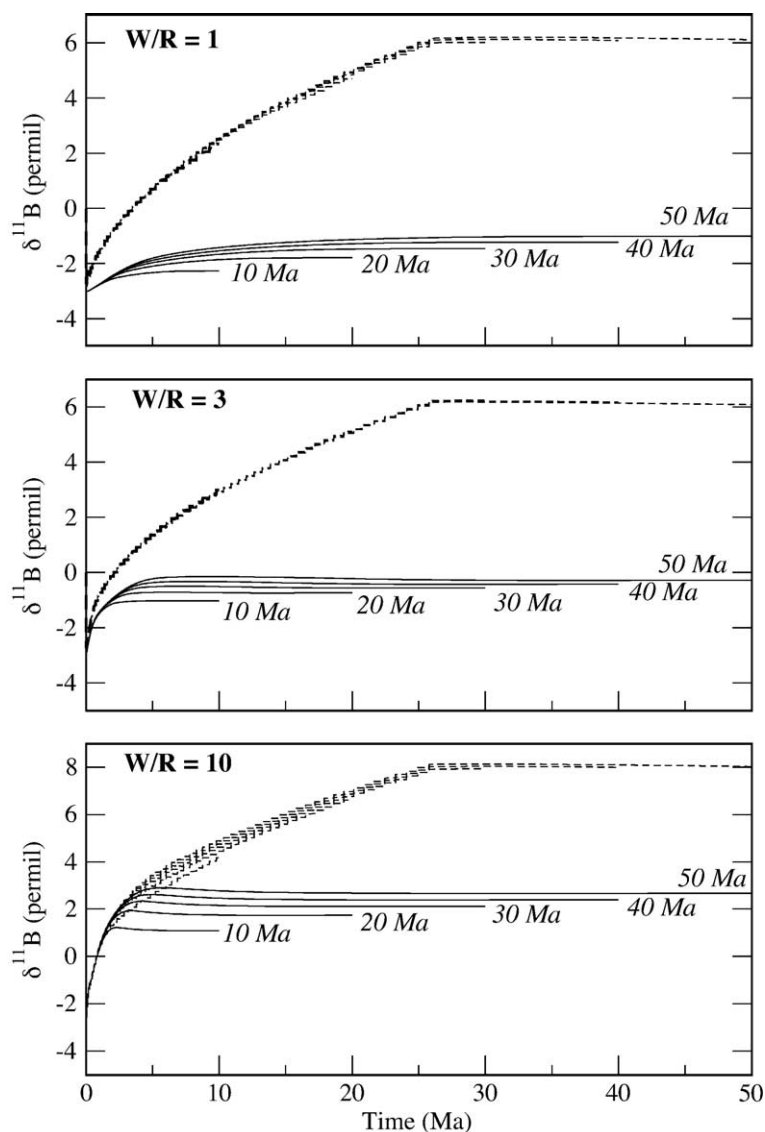


Fig. 5. Average  $\delta^{11}\text{B}$  of the oceanic crust (same legend as Fig. 4).

the early Paleogene. However, according to Lemarchand et al. (2000, 2002), low  $\delta^{11}\text{B}$  of foraminifera could record low  $\delta^{11}\text{B}$  of seawater without involving variations in the pH of seawater. Because of marine calcium carbonate acting as a pH buffer, the range of variations in the pH of open surface seawater is very limited, from 8.4 to 7.8 for  $p\text{CO}_2$  ranging from 300 to 2000 ppmv (Pearson and Palmer, 1999). Even during the warmest period of the Cretaceous, about 90 My ago, characterised by  $p\text{CO}_2$  4 to 5 times present-day values (Berner, 1994; Berner and Kothavala, 2001) and sea surface temperatures at least 10 °C higher (Frakes, 1999; Puc at et al., 2003), the pH of seawater likely remained close to 8.

### 5.2. Can seawater carbonates constrain seawater $\delta^{11}\text{B}$ variations?

Some Jurassic and Cretaceous brachiopods have  $\delta^{11}\text{B}$  (16.8‰ to 19‰) similar to present-day living species (L ecuyer et al., 2002), other specimens have values from 7‰ to 16‰ (Table 2). Using the empirically determined equation that links the  $\delta^{11}\text{B}$  of the brachiopod calcite to the  $\delta^{11}\text{B}$  of seawater (L ecuyer et al., 2002), pH lower than 7.6 leads to a minimal boron isotope composition of calcite of 16‰. Values lower than 16‰ thus cannot be explained by low seawater pH values only. Species-specific effects were observed in foraminifera and corals (Sanyal et al., 1995; 1996;

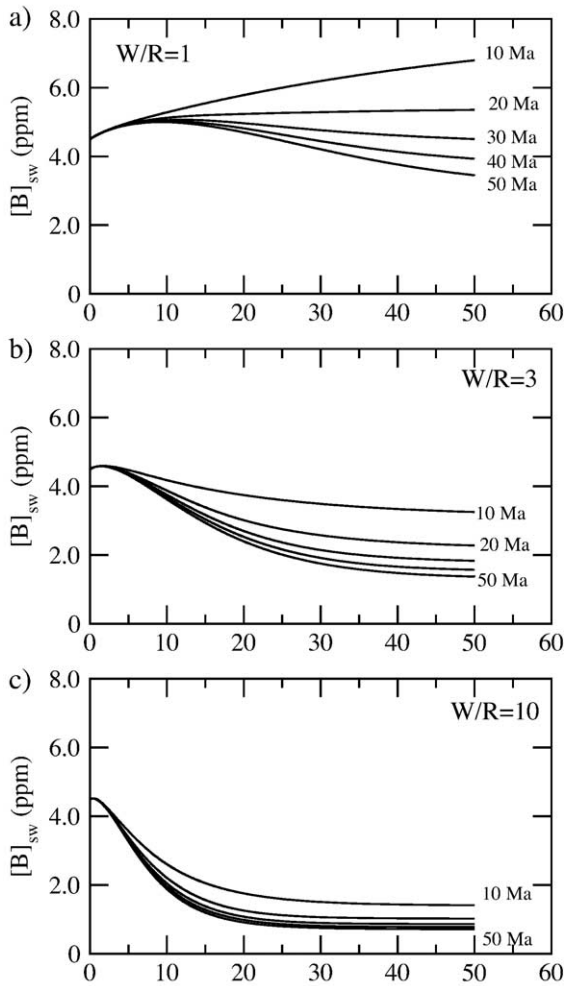


Fig. 6. Boron concentration of the ocean calculated for closure times ranging from 10 to 50 My, with initial water–rock ratio of: (a) 1; (b) 3; (c) 10. The expansion rate of the oceanic crust is set to  $3 \text{ cm year}^{-1}$ .

Hoensch et al., 2003; 2004) and differences in calcium carbonate mineralogy are suspected to result in offsets in the  $\delta^{11}\text{B}$  of shell carbonate (Deyhle et al., 2001). Nevertheless, these effects cannot explain the low  $\delta^{11}\text{B}$  values of brachiopod calcite and  $\delta^{11}\text{B}$  variations of seawater through time have to be involved (Joachimski et al., 2005).

Independently of the knowledge of past seawater  $\delta^{11}\text{B}$ , we highlight the fact that subtle variations in the pH of the global ocean through time may be very difficult to document from the boron composition of carbonates for several reasons. A *Placentieras*, ammonoid from the Valanginian of the Western Interiors (USA), has a  $\delta^{11}\text{B}$  of  $0.9\text{‰}$  despite the preservation of the original aragonite secreted by the cephalopod. Such an extreme low value for a marine biogenic carbonate can be only explained by a post-depositional boron

exchange with crustal-derived aqueous fluids. We thus cannot completely rule out processes of boron isotopic exchange with an aqueous fluid, since calcium carbonates are highly sensitive to dissolution and boron has a great affinity for aqueous fluids (Gaillardet and Allègre, 1995; Spivack and You, 1997).

Moreover, present-day littoral marine and brackish waters are characterised by varying pH depending on carbon dioxide solubility or fresh water inputs. In tropical littoral environments, organic-rich waters that are present in mangrove swamps have pH lower than those of open seawaters. The local increasing acidity of seawater-dominated solutions results from the degradation of organic matter that releases humic and fulvic acids. For example, a present-day oyster from

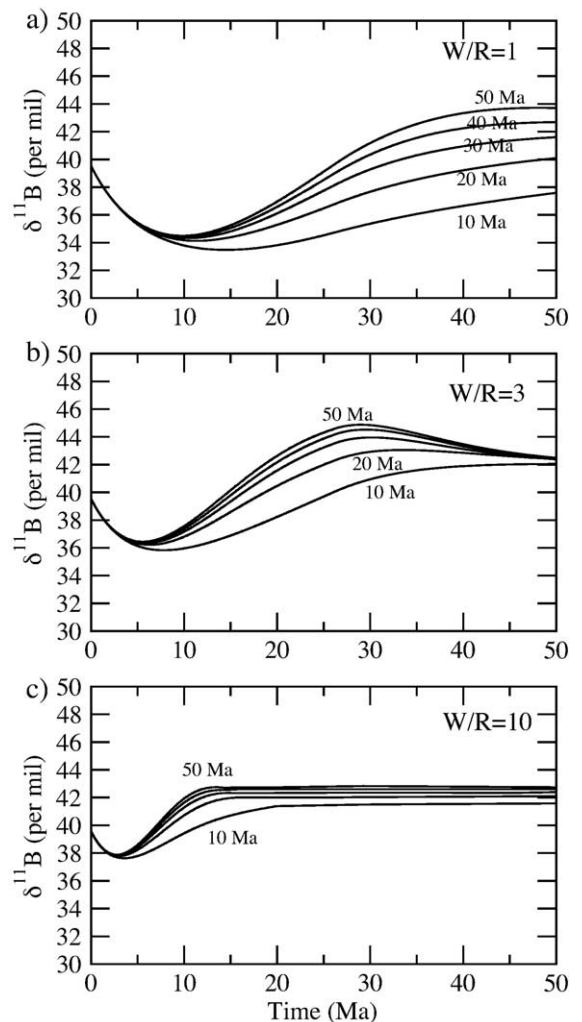


Fig. 7.  $\delta^{11}\text{B}$  of the ocean calculated for closure times ranging from 10 to 50 My, with initial water–rock ratio of: (a) 1; (b) 3; (c) 10. The expansion rate of the oceanic crust is set to  $3 \text{ cm year}^{-1}$ .

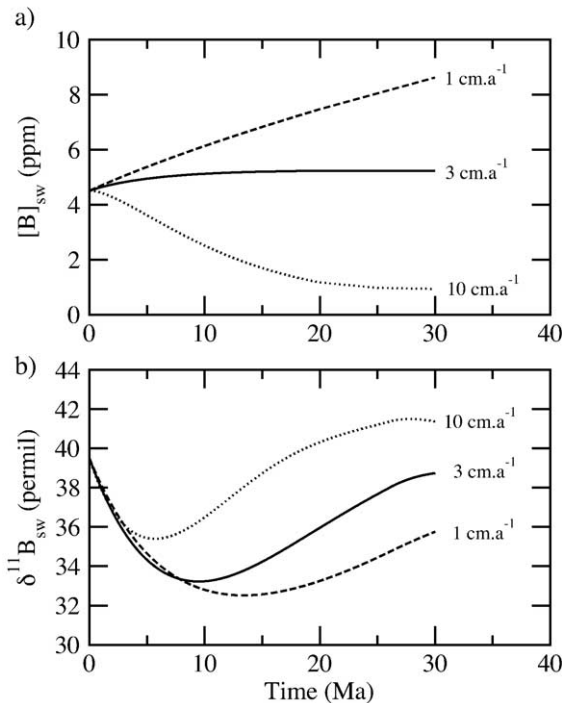


Fig. 8. Boron concentration (a) and isotopic composition (b) of seawater with expansion rate of oceanic crust of 1 (dashed line), 3 (plain line) and 10 cm year<sup>-1</sup> (dotted line). Initial water–rock ratio is set to 1 and the closure time is 20 My.

the brackish waters (90% of seawater;  $\delta^{11}\text{B}=40$ ;  $\text{pH}=7.85$ ) of La Martinique Island has a  $\delta^{11}\text{B}$  of 17.4‰, a value comparable to several Mesozoic brachiopods (Table 2). In fact, variations in the pH of littoral present-day marine waters could be equal or even larger than those expected to result from the solely effect of modelled changes in the atmospheric  $p\text{CO}_2$  over the past 150 My (Berner and Kothavala, 2001). Finally, boron isotope compositions of biogenic carbonates are suspected to be species-dependent and affected by temperature variations (Deyhle et al., 2003; Hoenisch et al., 2003).

### 5.3. Hydrothermally altered oceanic rocks: a proxy of seawater $\delta^{11}\text{B}$ ?

Boron isotope compositions of hydrothermally altered oceanic rocks could be considered as valuable proxies of seawater pH and composition. Boron incorporated into the crystal lattice of neoformed phyllosilicates (serpentine, chlorite) is more resistant to fluid–mineral interactions than B present in biogenic sediments (Grew, 1996; Leeman and Sisson, 1996). The oceanic rocks that are altered under high  $W/R$  ratios have their  $\delta^{11}\text{B}$  controlled by both seawater pH

and boron isotope composition. Ophiolites and deep rocks from oceanic ridges, such as peridotites, may then record boron isotope composition changes of the world ocean. However, the main problem of this approach is that the isotopic fractionation between phyllosilicates and water is not well known. It should also be important to choose samples that are altered under high  $W/R$  ratios, such as fully serpentinised peridotites or hydrothermal veins. We need to keep in mind that B isotope compositions of peridotites could be affected by a strong Rayleigh effect.

Nevertheless, it is interesting to compare the  $\delta^{11}\text{B}$  values of oceanic peridotites from Cretaceous to present-day oceanic ridges. The Oman ophiolite represents a fragment of Cretaceous (100 My; Gnos et al., 1997) fast-spreading oceanic crust (Boudier and Nicolas, 1985) that interacted with seawater under a context of greenhouse climate. Similarly to the  $\delta^{11}\text{B}$  of well-preserved Cretaceous brachiopods, the boron isotope compositions of peridotites fully serpentinised by seawater are indistinguishable ( $\delta^{11}\text{B}=7.8 \pm 2.5\text{‰}$ ) from those sampled from various modern oceanic environments ( $\delta^{11}\text{B}=8.9 \pm 1.2\text{‰}$ ; Table 3). These data suggest that the boron isotope composition of the

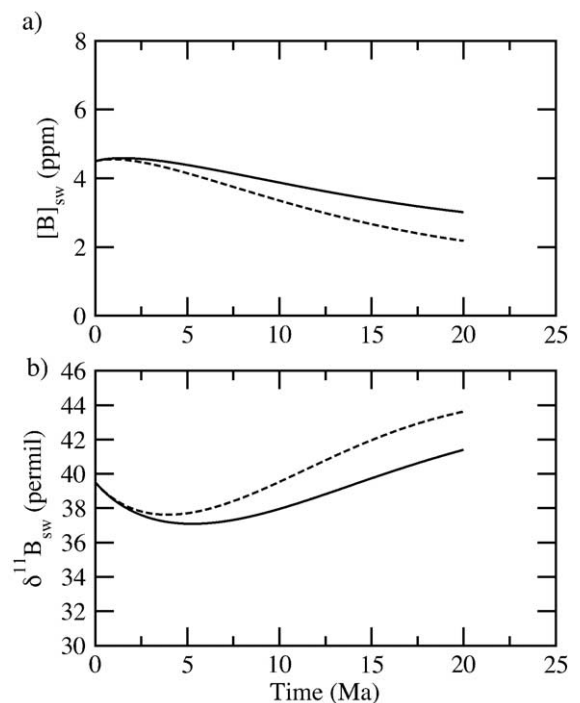


Fig. 9. Boron concentration (a) and isotopic composition (b) of seawater considering a vein-free crust (plain line) and 5 wt.% of hydrothermal chlorite veins (dashed line). The closure time is set to 20 My, and the initial water–rock ratio is set to 3.

Table 3  
Boron isotope compositions of serpentinized seafloor and ophiolitic peridotites

Sample	Site	Rock type	$\delta^{11}\text{B}$
<i>Seafloor peridotites</i>			
V-11D-2	Vema Fracture Zone	Serpentinized peridotite	8.5
V-16D-6	Vema Fracture Zone	Serpentinized peridotite	7.0
107-16	Thyrrhenian Sea, ODP Leg 107	Serpentinized peridotite	9.6
147-111	Hess Deep, ODP Leg 147	Serpentinized peridotite	9.9
149-45	Galicia Margin, ODP Leg 149	Serpentinized peridotite	9.4
<i>Ophiolitic peridotites (Oman)</i>			
96 OA 101	Wadi Al Ghail	Serpentinized harzburgite	8.8
96 OA 101	Wadi Al Ghail	Serpentinized harzburgite	8.2
95 OD 54	Maqsad	Serpentinized werhlite	10.0
91 OA 111	Maqsad	Serpentinized werhlite	4.3

Cretaceous ocean was not very different from the present-day value of 40‰.

## 6. Conclusion

A time-dependent box model of the boron cycle which includes exchange between the oceanic crust and seawater suggests that present-day boron content and isotope composition of seawater are close to steady-state. The steady-state is obtained for an oceanic crust production of 3 cm year<sup>-1</sup> and seawater–crust ratios between 1 and 3 with a residence time of boron in seawater close to 10 My. However, strong variations in the boron isotope composition of seawater between +30‰ and +50‰ are computed as a function of crust permeability, expansion rate and closure time of the hydrothermal system. This range of  $\delta^{11}\text{B}$  was obtained without any variation in the inputs and outputs fluxes of the other reservoirs implied in the boron geochemical cycle such as the riverine flux. Such predicted variations in the boron isotope composition of seawater preclude the use of the  $\delta^{11}\text{B}$  of biogenic carbonates for estimating the pH of past seawater as long as further data are required to constrain the secular evolution of the boron isotope composition of seawater. Moreover,  $\delta^{11}\text{B}$  values of some Jurassic and Cretaceous marine biogenic carbonates that are lower than 16‰ may be also partly attributed to a diagenetic alteration. However, it is noteworthy that well-preserved Cretaceous brachiopods have  $\delta^{11}\text{B}$  values comparable to modern brachiopods. In a similar way, the boron isotope compositions of serpentinites from the Oman ophiolite are indistinguishable from those sampled in various modern oceanic environments. These results obtained from both metamorphic rocks and biogenic minerals suggest that the boron isotope composition of the Cretaceous ocean was not very different from present-days.

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