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A theoretical study of the kinetics of the boric acid–borate equilibrium in seawater

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Abstract

Dissolved boron in seawater occurs mainly in the form of boric acid ($B(OH)_3$) and borate ($B(OH)_4^-$). While the equilibrium properties of the dissociation of boric acid have been studied in detail, very little work has focused on the kinetics of the boric acid–borate equilibrium in seawater. Here, we present a theoretical study of the relaxation of the seawater borate–carbonate system towards equilibrium using the experimental data of Mallo et al. [Nouv. J. Chim. 8 (1984) 373] and Waton et al. [J. Phys. Chem. 88 (1984) 3301]. The reaction rate constants are two to four orders of magnitude smaller than typical rate constants of diffusion-controlled reactions of other acid–base equilibria. This is presumably due to the substantial structural change that is involved in the conversion from planar $B(OH)_3$ to tetrahedral $B(OH)_4$. The time required to establish the boric acid–borate equilibrium in seawater is calculated to be $\sim 95 \mu s$ at temperature $T = 25°C$ and salinity $S = 35$. Considering stable boron isotopes ^{11}B and ^{10}B, the isotopic equilibration time is $\sim 125\ \mu s$. As a result, kinetic isotope effects during coprecipitation of boron in calcium carbonate are unlikely and therefore do not affect the use of stable boron isotopes as a paleo-pH recorder. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Boric acid; Borate; Kinetics; Paleo-pH

1. Introduction

Dissolved boron in the ocean contributes to the alkalinity balance and to the buffering properties of seawater. Although borate ($B(OH)_4^-$) represents only about 5% of the total alkalinity at typical seawater pH of 8.2, boron compounds have to be taken into account in quantitative calculations of carbonate system parameters (cf. e.g., DOE, 1994). The boric acid–borate equilibrium also affects physical properties of seawater. For example, sound absorption in the ocean in the 1 kHz frequency range involves chemical equilibria with relaxation rates which have been identified as the boric acid–borate relaxation rates (e.g., Yeager et al., 1973; Mellen et al., 1980; Mallo et al., 1984). Recently, the stable isotopes of boron have received attention as they provide a means of reconstructing the pH of the paleocean (e.g., Spivack et al., 1993; Sanyal et al., 1995; Palmer et al., 1998).

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The majority of the studies mentioned above assumes that chemical and isotopic equilibrium between boric acid and borate has been established. As will be discussed below, this assumption is valid only on long time scales and large spatial scales. On time scales in the order of 10^{-4} s and shorter and on spatial scales in the order of 10^{-6} m and smaller, this assumption is not valid (considering disequilibria on tiny spatial scales, diffusion becomes the dominant process). The main objective of the present paper is to provide a detailed study of the nonequilibrium properties of the boric acid–borate reactions in seawater. This goal is achieved by using data from physico-chemical studies (Mallo et al., 1984; Waton et al., 1984).

The results presented here should be useful for researchers in marine chemistry and chemical oceanography dealing with the kinetics of boron compounds in seawater. We will answer questions such as: what is the turnover time of the reaction between $B(OH)_3$ and $B(OH)_4^-$ and how quickly is the chemical and isotopic equilibrium established? The latter question is of great importance for example, in experimental studies when isotopically spiked substances are added to, say, a seawater solution (the isotope abundances of spiked materials is very different from the natural abundances). It is often desired that the distribution of the isotopically enriched/depleted material among the different compounds of the system is completed before the experiment is started. This study shows that for practical purposes (usually involving time scales of seconds to hours), it can indeed be assumed that chemical and isotopic equilibrium between the dissolved boron species is established. Another objective of our study is to provide basic input parameters for modeling efforts of the kinetics of the carbonate system on small spatial scales (e.g., Wolf-Gladrow and Riebesell, 1997; Wolf-Gladrow et al., 1999).

An important issue in the context of boron isotope equilibration is the isotopic fractionation of boron during incorporation in calcium carbonate. Based on the boron isotope composition of biogenic $CaCO_3$ (e.g., of foraminifera and corals) and of inorganic calcite, it has been suggested that the dissolved boron species $B(OH)_4^-$ is preferentially adsorbed (in preference to the neutral species $B(OH)_3$) before incorporation of boron into the carbonate (e.g., Hemming and Hanson, 1992; Sanyal et al., 1996; Sanyal et al., 2000). One of the questions often discussed in connection with boron coprecipitation in $CaCO_3$ is: are kinetic isotope effects to be expected during the incorporation of boron isotopes into the carbonates? It has been speculated whether or not the growth rate of the carbonate crystal would affect the amount of coprecipitation and the isotopic fractionation of boron in $CaCO_3$ (Hobbs and Reardon, 1999; Sanyal et al., 2000). One way to address this question is to compare the characteristic time scale for crystal growth and the characteristic time scale for isotopic equilibration between the dissolved boron species in solution. If the time scale for crystal growth and thus coprecipitation of boron is much larger than the time scale for isotope equilibration between the dissolved boron species, kinetic isotope effects are unlikely to occur. This is because the rate limiting step in this case is the crystal growth and not the equilibration between $B(OH)_4^-$ and $B(OH)_3$. The equilibration times to be derived in the present paper enable us to address this question which is important for evaluating the potential of stable boron isotopes as a paleo-pH proxy.

2. Equilibrium: the dissociation of boric acid

Dissolved boron is found mainly in the form of $B(OH)_3$ and $B(OH)_4^-$ in seawater. Since polynuclear boron species such as $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{2-}$, and $B_5O_6(OH)_4^-$ are negligible at concentrations smaller than 25 mmol kg^{-1} (Su and Suarez, 1995), they can be safely ignored at total seawater boron concentrations of ~ 0.42 mmol kg^{-1}. The dissociation of boric acid in seawater can be described by the equilibrium:

$$B(OH)_3 + H_2O \overset{K_B}{\rightleftharpoons} B(OH)_4^- + H^+ \tag{1}$$

where K_B is the dissociation constant of boric acid. The pK value ($= -\log(K_B)$) of boric acid has been determined to be p$K_B = 8.60$ in artificial seawater at $T = 25°C$, $S = 35$, total pH scale (Dickson, 1990). Since several authors have investigated the dissociation of boric acid, a good working knowledge on this subject has been obtained in both fresh water and seawater (e.g., Buch, 1933; Owen and King, 1943;

Hansson, 1973; Hershey et al., 1986; Dickson, 1990; Roy et al., 1993). Unfortunately, the equilibrium properties (reaction (1)) do not tell us much about the kinetic pathways by which the equilibrium is established. In order to elucidate the kinetics of the boric acid–borate equilibrium we will make use of results published in a series of papers by Waton et al. (1984), Mallo et al. (1984,1985), and Waton and Mallo (1987).

3. The kinetics of the boric acid–borate equilibrium

Waton et al. (1984) employed a temperature-jump method to investigate the kinetics of the boric acid–borate equilibrium (for review, see Eigen and De Maeyer, 1963). They studied the following reaction mechanism (cf. Mellen et al., 1981):

$$B(OH)_3 + OH^- \xrightarrow{k_{+3}} B(OH)_4^- \qquad (2)$$

and examined the dependence of the rate constant k_{+3} on temperature and ionic strength (note that the subscript 3 and not 1 is used for the rate constant here in order to avoid confusion with the rate constants k_{+1} and k_{+2} which are often used in connection with the dissociation constants K_1 and K_2 of carbonic acid). The temperature dependence of k_{+3} as determined by Waton et al. (1984) at ionic strength $I = 0.1$ is shown in Fig. 1. For their experiments, they used simple NaCl, $BaCl_2$, and $NaClO_4$ solutions and observed only a marginal effect of ionic strength on k_{+3} when I varied between 0.1 and 0.7. Mallo et al. (1984) showed that using artificial seawater (instead of simple solutions studied by Waton et al. (1984)) had a negligible influence on the relaxation time. In addition to, e.g., Cl^- and Na^+ ions of simple solutions, seawater also contains Mg^{2+}, SO_4^{2-}, Ca^{2+}, K^+, HCO_3^- ions and more. Thus, the values of k_{+3} and the temperature dependence at $I = 0.1$ as reported by Waton et al. (1984) should also be applicable to seawater ($I \approx 0.7$). With regard to the boric acid–borate equilibration time, it is also of minor importance whether natural or artificial seawater is considered. Yeager et al. (1973) obtained very similar results for the relaxation time in natural and in artificial seawater.

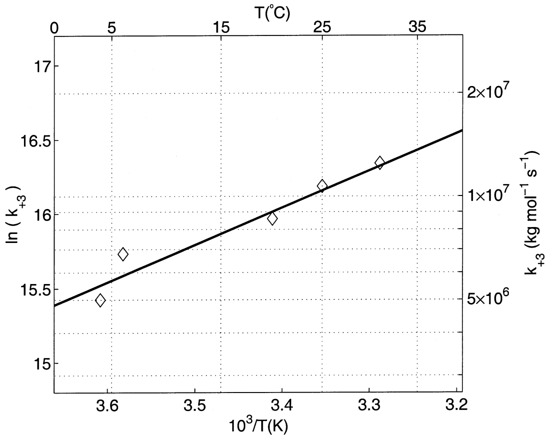

Fig. 1. Arrhenius plot of the rate constant k_{+3}. Diamonds show the experimental results of Waton et al. (1984). The solid line represents the best linear fit to the data when $\ln(k_{+3})$ is plotted vs. $10^3/T$(K). Note that the rate constant is two to four orders of magnitude smaller than typical rate constants of diffusion-controlled reactions of other acid–base equilibria.

The temperature dependence of kinetic rate constants can often be fit by an Arrhenius equation:

$$k = A\exp(-E_a/RT)$$

where A is the pre-exponential factor or Arrhenius factor, $R = 8.3145$ J mol^{-1} K^{-1} is the gas constant, T is the absolute temperature in Kelvin, and E_a is the activation energy. A fit of an Arrhenius equation to the data of k_{+3} (i.e., a linear regression of $\ln(k_{+3})$ vs. $1/T$) yields $A = 4.58 \times 10^{10}$ kg mol^{-1} s^{-1} and $E_a = 20.8 \pm 5.1$ kJ mol^{-1}. Thus, the rate constant k_{+3} can be expressed as:

$$k_{+3} = 4.58 \times 10^{10} \exp(-20.8 \times 10^3/RT)$$

which yields $k_{+3} = 1.0 \times 10^7$ kg mol^{-1} s^{-1} at 25°C (Fig. 1 and Table 1). It is emphasized that, in contrast to many other acid–base equilibria, reaction (2) is not diffusion-controlled. This is probably due to the substantial structural change that is involved in the conversion from planar $B(OH)_3$ to tetrahedral $B(OH)_4^-$ (Mellen et al., 1983). The rate constant is two to four orders of magnitude smaller than typical rate constants of diffusion-controlled reactions which are on the order of 10^9–10^{11} kg mol^{-1} s^{-1} (Eigen and Hammes, 1963).

Table 1
Reaction rate constants of the boric acid–borate equilibrium in seawater (see text for details)

T (°C)	$k_{+3} \times 10^{-7}$ (kg mol^{-1} s^{-1})	k_{-3} (s^{-1})	$k_{+4} \times 10^{-6}$ (kg mol^{-1} s^{-1})	$k_{-4} \times 10^{-6}$ (kg mol^{-1} s^{-1})
0	0.5	20	3.2	1.1
5	0.6	34	3.8	1.4
15	0.8	96	5.2	2.1
20	0.9	157	6.0	2.7
25	1.0	250	7.0	3.3
35	1.4	592	9.1	4.8

The rate constant of the backward reaction can be calculated as follows. The equilibrium constant of reaction (2) is:

$$K = \frac{k_{+3}}{k_{-3}} = \frac{[\mathrm{B(OH)_4^-}]}{[\mathrm{B(OH)_3}][\mathrm{OH^-}]}.$$

With the dissociation constant of boric acid:

$$K_\mathrm{B} = \frac{[\mathrm{B(OH)_4^-}][\mathrm{H^+}]}{[\mathrm{B(OH)_3}]}$$

and the ion product of water:

$$K_\mathrm{w} = [\mathrm{H^+}][\mathrm{OH^-}]$$

the rate constant of the backward reaction, k_{-3}, can be determined from:

$$k_{-3} = \frac{k_{+3}}{K} = k_{+3} \times \frac{K_\mathrm{w}}{K_\mathrm{B}}. \tag{3}$$

Using values for K_w and K_B in seawater as summarized in, e.g., DOE (1994) (total pH scale), values for k_{-3} can then be calculated ranging from 20 to 592 s^{-1} over the temperature range 0–35°C (Fig. 2 and Table 1).

It was mentioned above that the rate constant of reaction (2) is not very sensitive to changes of ionic strength. Thus, the value of the forward rate constant k_{+3} should hold in both fresh water and seawater. Since the backward rate constant, k_{-3}, is calculated using the equilibrium constants K_w and K_B (Eq. (3)) which depend on salinity, k_{-3} also depends on salinity. The salinity dependence is, however, rather small: k_{-3} varies only by about 10% if salinity varies between $S = 20$ and $S = 40$. This is because k_{-3} is a function of the ratio $K_\mathrm{w}/K_\mathrm{B}$. Whereas the value of each equilibrium constant changes strongly with salinity, their ratio does not.

3.1. Acid–base exchange between $B(OH)_3$ / $B(OH)_4^-$ and HCO_3^- / CO_3^{2-}

From what has been said so far, it is concluded that the overall ionic strength of the medium does not have a large effect on the boron relaxation times. However, it was observed that the concentration of specific ions (particularly dissolved bicarbonate) has a marked effect on the boron relaxation times, indicating interactions of the boron compounds with $\mathrm{HCO_3^-}$ and $\mathrm{CO_3^{2-}}$ ions (Mellen et al., 1981, 1983; Mallo et al., 1984; Waton and Mallo, 1987). Since seawater contains a considerable amount of bicarbonate and carbonate ions, this effect has to be taken into account.

Mellen et al. (1981) suggested the following reaction mechanism for the coupling between boric acid–borate and bicarbonate–carbonate:

$$\mathrm{CO_3^{2-}} + \mathrm{B(OH)_3} + \mathrm{H_2O} \underset{k_{-4}}{\overset{k_{+4}}{\rightleftharpoons}} \mathrm{B(OH)_4^-} + \mathrm{HCO_3^-}. \tag{4}$$

It is important to note that this mechanism may approximate a more complex process that involves

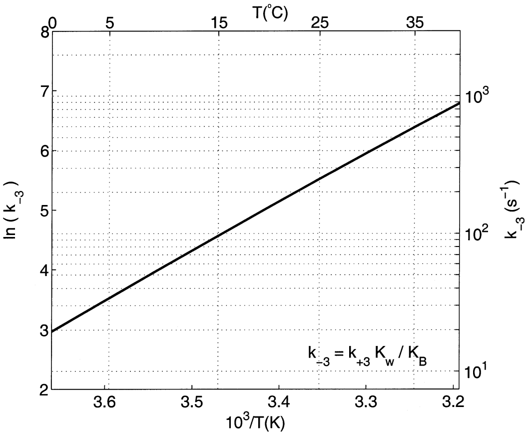

Fig. 2. The rate constant k_{-3} as calculated from $k_{-3} = k_{+3} \times K_\mathrm{w}/K_\mathrm{B}$, where K_w and K_B are the dissociation constants of water and boric acid, respectively. Note that K_w and K_B in seawater are complicated functions of temperature and salinity. Thus, k_{-3} is not a linear function of temperature (see text for details).

intermediate steps and a sequence of coupled reactions (compare Mellen et al. (1983) and discussion at the end of this section).

Mallo et al. (1984) determined the forward rate constant of reaction (4) to be $k_{+4} = 1.5 \times 10^7$ kg mol^{-1} s^{-1} at 20°C (note that the concentration of H_2O is large compared to all other concentrations and can therefore be assumed constant. Hence, it does not show up in the kinetic rate law—see Eq. (18) in Appendix A—and k_{+4} and k_{-4} have the same unit: kg mol^{-1} s^{-1}). Mallo et al. (1984) determined the value of k_{+4} by a fit to their experimental data using equilibrium constants for the dissociation of carbonic and boric acid in dilute NaCl solutions. As those constants are not appropriate for seawater, we have recalculated the value for k_{+4} at 20°C by a fit of Eq. (7) (see below) to their results for artificial seawater at ionic strength $I = 0.7$, using seawater constants. The result is $k_{+4} = 6 \times 10^6$ kg mol^{-1} s^{-1} at 20°C (see Table 1).

The temperature dependence of k_{+4} has (to the best of our knowledge) not been studied so far. It is very likely that the activation energy of this reaction is similar to that of reaction (2) since the rate limiting step is most probably the change of the coordination of the boron compounds in both cases. This assumption is in line with the observation that the rate constants of both reactions are similar at 20°C. It follows that the temperature dependence of k_{+4} is equal to that of k_{+3}. In summary, the rate constant k_{+4} may be expressed as:

$$k_{+4} = 3.05 \times 10^{10} \exp\left(-20.8 \times 10^3 / RT\right).$$

Values for k_{+4} as a function of temperature are given in Table 1.

The rate constant of the backward reaction, k_{-4} is determined from equilibrium relations. One sees from reaction (4) that:

$$\frac{k_{+4}}{k_{-4}} = \frac{\left[\mathrm{B(OH)}_4^-\right]\left[\mathrm{HCO}_3^-\right]}{\left[\mathrm{B(OH)}_3\right]\left[\mathrm{CO}_3^{2-}\right]} = \frac{K_\mathrm{B}}{K_2}$$

where K_2 is the second dissociation constant of carbonic acid in seawater:

$$K_2 = \frac{\left[\mathrm{CO}_3^{2-}\right]\left[\mathrm{H}^+\right]}{\left[\mathrm{HCO}_3^-\right]}.$$

It follows:

$$k_{-4} = k_{+4}\frac{K_2}{K_\mathrm{B}}.$$

Values for k_{-4} as a function of temperature are also given in Table 1.

Whereas the kinetics associated with reaction (2) are widely accepted, uncertainties exist regarding the reaction kinetics of the coupling of the boric acid and carbonic acid systems as indicated by reaction (4). Based on the investigation of chemical sound absorption in seawater by the resonator method, Mellen et al. (1983) proposed a four-state model to couple the boric acid and carbonic acid systems which also includes ion pairing with Ca^{2+}. This was necessary to explain the observed sound absorption measured in seawater, which requires that a volume change is associated with the reaction in order to couple the reaction to the pressure wave.

On the other hand, Mallo et al. (1984) performed temperature-jump experiments from which values for the kinetic rate constants for the proposed reaction (4) were derived. They observed relaxation frequencies in the 1 kHz range and fitted their data to a reaction scheme according to Eq. (4). Good agreement was obtained between experimental data and their model when the results were plotted vs. boric acid concentration, bicarbonate concentration, and pH. They also investigated the influence of Ca^{2+} ions on the coupling of the boric acid and carbonic acid systems. Mallo et al. (1984) varied the Ca^{2+} concentration between 0 and 10 mmol kg^{-1} and measured the relaxation frequency. They concluded that within the experimental accuracy the relaxation time is independent of the Ca^{2+} concentration.

In summary, it appears that Ca^{2+} ions—which are needed to explain sound absorption in seawater (Mellen et al., 1983)—have little or no effect on the proton transfer reactions between the acid–base couples of the boric acid and carbonic acid systems as studied by Mallo et al. (1984). Sound absorption in seawater is a complex phenomenon and it is likely that the considered frequency range is of importance here. It is desired that further work will clarify the influence of Ca^{2+} ions on sound absorption in more detail. At present, we believe that the coupling of the boric acid and carbonic acid systems can be most adequately described by using the experimental results of Mallo et al. (1984).

4. Relaxation times

The rate constants as summarized in the previous section enable us to calculate the time required to establish chemical and isotopic equilibrium of the boric acid–borate system in seawater. The relaxation time τ used here refers to the time after which a perturbation of the system has decreased to $\sim 37\% \simeq 1/\mathrm{e}$ of its initial value. For an exponentially decreasing function $x(t)$:

$$x(t) = x_0 \exp(-kt),$$

where x_0 is the initial value at $t = 0$, the relaxation time τ is given by $\tau = 1/k$ because at $t = \tau = 1/k$, we have:

$$x(\tau) = x_0 \times 1/\mathrm{e} \simeq x_0 \times 0.3679.$$

As noted in the Introduction, the relaxation frequency, f, of the boric acid–borate equilibrium is on the order of 1 kHz and therefore causes sound absorption in this frequency range in the ocean. The corresponding relaxation time is given by $\tau = 1/(2\pi f)$ which is on the order of 100 μs. This is valuable information since chemical equilibria established much faster than this time scale ($\lesssim 10$ μs) can safely be assumed to be in equilibrium.

This is the case for the recombination of H^+ and OH^-:

$$H_2O \overset{K_w}{\rightleftharpoons} H^+ + OH^- \tag{5}$$

(ion product of water) and for the equilibrium between bicarbonate and carbonate:

$$HCO_3^- \overset{K_2}{\rightleftharpoons} CO_3^{2-} + H^+ \tag{6}$$

for which the rate constants are diffusion-controlled and the relaxation times are on the order of a few microseconds (see Eigen, 1964). Additionally, aqueous carbon dioxide does not have to be considered at all since the equilibration time for this species is much longer (~ 10 s, see e.g., Zeebe et al., 1999) than that of the boric acid–borate equilibrium (~ 100 μs). Consequently, the only reactions that need to be considered for the kinetic rate law are:

$$B(OH)_3 + OH^- \underset{k_{-3}}{\overset{k_{+3}}{\rightleftharpoons}} B(OH)_4^-$$

$$CO_3^{2-} + B(OH)_3 + H_2O \underset{k_{-4}}{\overset{k_{+4}}{\rightleftharpoons}} B(OH)_4^- + HCO_3^-.$$

It is shown in Appendix A that the relaxation time for these reactions can be calculated using the conservation of total dissolved inorganic carbon (ΣCO_2), total boron (B_T), total alkalinity (TA), and the equilibrium constants of reactions (5) and (6). The result for the relaxation time τ of the boric acid–borate equilibrium is:

$$\begin{aligned}\tau^{-1} = {} & +k_{+3}([OH^-] + \alpha[B(OH)_3]) + k_{-3} \\ & + k_{+4}\left([CO_3^{2-}] + \alpha\beta[B(OH)_3]\right) \\ & + k_{-4}\left([HCO_3^-] + \alpha\beta\left[B(OH)_4^-\right]\right)\end{aligned} \tag{7}$$

where

$$\alpha = \frac{1}{1 + \beta + [H^+]^2/K_w} \tag{8}$$

and

$$\beta = \frac{[CO_3^{2-}][H^+]/K_w}{1 + K_2/[H^+]}. \tag{9}$$

Approximate values of carbon system parameters at $pH = 8.2$, $\Sigma CO_2 = 2$ mmol kg^{-1}, $B_T = 0.42$ mmol

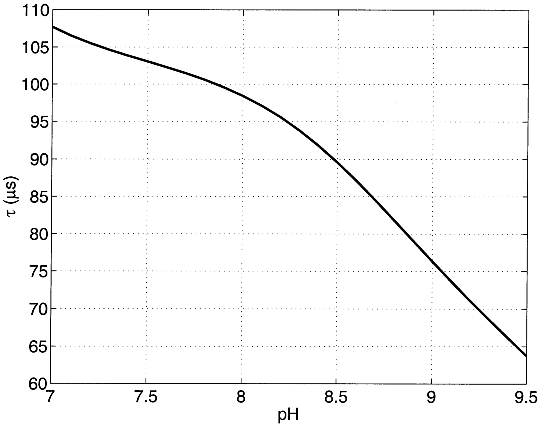

Fig. 3. Relaxation time of the boric acid–borate equilibrium as a function of pH at constant $\Sigma CO_2 = 2$ mmol kg^{-1} ($T = 25°C$, $S = 35$).

kg^{-1}, $T = 25°C$, and $S = 35$ are: $[HCO_3^-] = 1.7 \times 10^{-3}$ mol kg^{-1}, $[CO_3^{2-}] = 3.2 \times 10^{-4}$ mol kg^{-1}, $[H^+] = 6.3 \times 10^{-9}$ mol kg^{-1}, $[OH^-] = 9.6 \times 10^{-6}$ mol kg^{-1}, $[B(OH)_3] = 3.0 \times 10^{-4}$ mol kg^{-1}, and $[B(OH)_4^-] = 1.2 \times 10^{-4}$ mol kg^{-1}. Using these values and $pK_w = 13.22$ and $pK_2 = 8.92$, one obtains:

$$\tau \simeq 95\,\mu s.$$

The relaxation time of the boric acid–borate equilibrium as a function of pH is shown in Fig. 3. The variation of τ with pH is moderate when compared to, e.g., the variation of the $CO_2(aq.)$ equilibration time with pH, see Zeebe et al. (1999); τ is decreasing at higher pH due to the higher concentration of hydroxyl ions in solution.

The temperature dependence of τ at constant $pH = 8.2$ and $\Sigma CO_2 = 2$ mmol kg^{-1} is shown in Fig. 4a. As expected from the temperature dependence of the rate constants, the relaxation time decreases with increasing temperature (elevated temperature allows more molecules to surmount the energy barrier of the activation energy, therefore leading to higher reaction rates).

The dependence of τ on ΣCO_2 at constant $pH = 8.2$ and $T = 25°C$ is shown in Fig. 4b. The relaxation time decreases with increasing concentration of ΣCO_2. As is obvious from Eq. (7), the relaxation time is inversely proportional to the concentrations of HCO_3^- and CO_3^{2-}. Thus, an increase of ΣCO_2 (which leads to an increase of $[HCO_3^-]$ and $[CO_3^{2-}]$) produces a higher reaction rate and hence a smaller relaxation time.

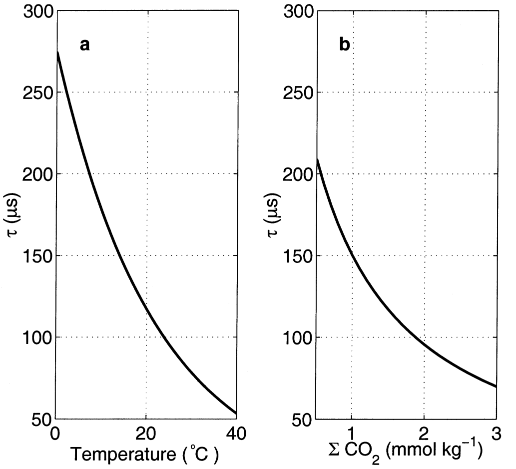

Fig. 4. Relaxation time of the boric acid–borate equilibrium as a function of (a) temperature and (b) ΣCO_2 at constant pH = 8.2.

Using the information given so far, we can also calculate the turnover time of, e.g., $B(OH)_4^-$ for the chemical reaction between $B(OH)_4^-$ and $B(OH)_3$ in seawater. The turnover time of $B(OH)_4^-$ is given by the concentration of $B(OH)_4^-$ divided by the forward reaction rate (cf. Eq. (18) of Appendix A):

$$t_{\text{tov}} = \frac{[B(OH)_4^-]}{k_{+3}[B(OH)_3][OH^-] + k_{+4}[B(OH)_3][CO_3^{2-}]}$$

$$\simeq 150\,\mu s.$$

In other words, an amount of $B(OH)_4^-$ which is equal to the total concentration of $B(OH)_4^-$ undergoes chemical reaction within 150 μs.

5. Stable boron isotopes ^{11}B and ^{10}B

Boron has two stable isotopes with natural abundances ^{11}B: 80.18% and ^{10}B: 19.82% (IUPAC, 1998). With regard to the dissolved boron species in seawater, it follows that about 80% of $B(OH)_3$ and $B(OH)_4^-$ contains the heavy isotope ^{11}B, whereas about 20% of these molecules contains the light isotope ^{10}B. The question to be addressed in this section is: what happens if the system is perturbed by, say adding boric acid to the system which has a different isotopic composition than the species in solution—i.e., how quickly is isotopic equilibrium established? It is emphasized that the times calculated here for isotope equilibration refer to a closed volume of seawater, i.e., no fluxes due to mass transport are considered. Such fluxes are of great importance when for example, carbon isotope exchange between seawater and a gas phase is considered, which affects the isotopic equilibration time significantly (e.g., Broecker and Peng, 1974).

Before getting into the calculation of the equilibration time for the stable boron isotopes ^{11}B and ^{10}B, some general remarks might be useful. Consider the following reactions for the dissolved boron species containing the heavy and the light isotope, respectively:

$$^{11}\mathrm{B(OH)_3} + \mathrm{OH^-} \underset{k_{-3}}{\overset{k_{+3}}{\rightleftharpoons}} {}^{11}\mathrm{B(OH)_4^-} \tag{10}$$

$$^{10}\mathrm{B(OH)_3} + \mathrm{OH^-} \underset{k'_{-3}}{\overset{k'_{+3}}{\rightleftharpoons}} {}^{10}\mathrm{B(OH)_4^-} \tag{11}$$

where k'_{+3} and k'_{-3} are the reaction rates of the boron species containing the light isotope ^{10}B. The reaction rates of the species containing the light isotope are usually a little larger than those of the species containing the heavy isotope (e.g., Melander and Saunders, 1980). The differences are, however, generally on the order of per mil and do not affect the relaxation time noticeably (see below). With respect to stable boron isotopes, the system consists of two independent compartments: one compartment containing the species $^{11}\mathrm{B(OH)_3}$ and $^{11}\mathrm{B(OH)_4^-}$, the other compartment containing $^{10}\mathrm{B(OH)_3}$ and $^{10}\mathrm{B(OH)_4^-}$.

COMPARTMENT 1

$$\boxed{^{11}\mathrm{B(OH)_4^-} \quad \longleftrightarrow \quad {}^{11}\mathrm{B(OH)_3}}$$

COMPARTMENT 2

$$\boxed{^{10}\mathrm{B(OH)_4^-} \quad \longleftrightarrow \quad {}^{10}\mathrm{B(OH)_3}}$$

There are no direct reactions between the two compartments since each isotope is conserved during reaction. The systems are chemically coupled by the reaction with $\mathrm{OH^-}$. It follows that isotopic equilibrium is achieved when chemical equilibrium is achieved in each compartment.

The equilibration time for the system can be calculated analogous to the procedure outlined in Appendix A for total boron. The new feature being that reactions (10), (11) and

$$\mathrm{CO_3^{2-}} + {}^{11}\mathrm{B(OH)_3} + \mathrm{H_2O} \underset{k_{-4}}{\overset{k_{+4}}{\rightleftharpoons}} {}^{11}\mathrm{B(OH)_4^-} + \mathrm{HCO_3^-} \tag{12}$$

$$\mathrm{CO_3^{2-}} + {}^{10}\mathrm{B(OH)_3} + \mathrm{H_2O} \underset{k'_{-4}}{\overset{k'_{+4}}{\rightleftharpoons}} {}^{10}\mathrm{B(OH)_4^-} + \mathrm{HCO_3^-} \tag{13}$$

have to be considered. It is noted that the rate constants for the ^{11}B-species (k_{+3}, k_{-3}, k_{+4}, and k_{-4}) are assumed to be equal to the rate constants for the total boron species (as used in Section 4) which contain a mixture of ^{11}B and ^{10}B according to their natural abundances. As already said, small differences in the reaction rates have virtually no effect on the relaxation times.

Since we are dealing with two compartments in this case (as opposed to one in the case discussed in Section 4), there are two more variables of which one variable can be eliminated by, e.g., the conservation of the total ^{10}B concentration. Since the calculation of the relaxation time of the system containing different isotopes ($^{11}\tau$) is similar to that given in Appendix A, the details shall not be elaborated here (see Zeebe et al. (1999) for particulars). Finally, $^{11}\tau$ is given by a quadratic equation which has the solution:

$$\left({}^{11}\tau_{\mathrm{a,b}}\right)^{-1} = \frac{1/\tau + 1/\tau'}{2} \pm \sqrt{\left(\frac{1/\tau + 1/\tau'}{2}\right)^2 - \frac{1}{\tau\tau'} + \frac{1}{\tau_{12}\tau_{21}}}\,. \tag{14}$$

Note that the index a and b refers to the solution involving the '+' and '−' sign, respectively. The quantities τ and τ' are given by Eq. (7) where $\mathrm{B} = {}^{11}\mathrm{B}$ (in case of τ) and $\mathrm{B} = {}^{10}\mathrm{B}$, $k_i = k'_i$ (in case of τ'), respectively. Furthermore,

$$\tau_{12}^{-1} = k_{+3}\alpha\left[{}^{11}\mathrm{B(OH)_3}\right] + k_{+4}\alpha\beta\left[{}^{11}\mathrm{B(OH)_3}\right] + k_{-4}\alpha\beta\left[{}^{11}\mathrm{B(OH)_4^-}\right]$$

$$\tau_{21}^{-1} = k'_{+3}\alpha\left[{}^{10}\mathrm{B(OH)_3}\right] + k'_{+4}\alpha\beta\left[{}^{10}\mathrm{B(OH)_3}\right] + k'_{-4}\alpha\beta\left[{}^{10}\mathrm{B(OH)_4^-}\right]$$

where α and β are given by Eqs. (8) and (9), see Section 4. Using typical values of the carbonate system parameters at pH 8.2, $T = 25°C$, and $S = 35$, the relaxation times are calculated as:

$$^{11}\tau_a \simeq 95\,\mu s$$

$$^{11}\tau_b \simeq 123\,\mu s.$$

The relaxation time $^{11}\tau_a \simeq 95$ μs and $^{11}\tau_b \simeq 123$ μs corresponds to the relaxation of the total boron compounds (see previous section) and ^{10}B compounds, respectively. The reason for the slightly longer relaxation time of the ^{10}B compounds is the smaller concentration of ^{10}B compared to ^{11}B.

The values of the rate constants of the isotopic species used in the calculations shall be briefly discussed here. To the best of our knowledge, the ratio of the kinetic rate constants k' (^{10}B compounds) to k (^{11}B compounds) has hitherto not been measured. From the work of Kakihana et al. (1977), it follows, however, that k'/k has to be larger than 1.020 because the equilibrium fractionation between $B(OH)_3$ and $B(OH)_4^-$ is ~ 1.020. As a first guess it was assumed that the ratio of the kinetic rate constants k' to k is $k'/k = 1.030$, i.e., the kinetic fractionation is 30‰, which gave $^{11}\tau_a \simeq 95$ μs and $^{11}\tau_b \simeq 123$ μs (see above). Assuming a much larger (arbitrary) value of $k'/k = 1.080$ yields very similar results: $^{11}\tau_a \simeq 94$ μs and $^{11}\tau_b \simeq 119$ μs. This demonstrates that the differences between the rate constants of molecules containing the heavy and the light isotope of boron are too small to affect the relaxation time significantly.

5.1. *Kinetic isotope effects during coprecipitation of boron in $CaCO_3$*

Using the isotope equilibration times between the dissolved boron species as derived in the previous section, we can now discuss the possibility of kinetic isotope effects during the coprecipitation of boron in $CaCO_3$. As already said in the Introduction, it is believed that the charged species $B(OH)_4^-$ is preferentially adsorbed (in preference to the neutral species $B(OH)_3$) before incorporation of boron into the carbonate based on empirical evidence (e.g., Hemming and Hanson, 1992; Sanyal et al., 1996, 2000). This scenario, in which the isotopically lighter $B(OH)_4^-$ species is taken up in isotopic equilibrium with $B(OH)_3$, can be considered the equilibrium fractionation case.

Let us now consider kinetic fractionation. In this scenario, $B(OH)_4^-$ shall also be the sole species adsorbed on the carbonate. However, the light molecules $^{10}B(OH)_4^-$ are adsorbed more readily than the heavy molecules $^{11}B(OH)_4^-$. If this isotopically light boron (lighter than dissolved $B(OH)_4^-$) is buried immediately below subsequent layers of $CaCO_3$ (i.e., no further exchange with the dissolved boron species is allowed), kinetic isotope effects are to be expected. If on the other hand, exchange with the dissolved boron species is possible (and rapid), kinetic isotope effects are unlikely to occur. In order to evaluate the likelihood of the two scenarios, one has to estimate the relative velocities of the processes. Thus, the crucial quantities are the characteristic time scale for crystal growth and the characteristic time scale for isotopic equilibration between the dissolved boron species in solution.

The characteristic time scale of the crystal growth τ_c can roughly be estimated by:

$$\tau_c \simeq \frac{d}{\Delta H/\Delta t} \tag{15}$$

where $d \sim 5$ Å (1 Å $= 10^{-10}$ m) is the thickness of an atomic layer of $CaCO_3$ and $\Delta H/\Delta t$ is the linear extension rate of the crystal in the direction of growth. In foraminifera and corals, $\Delta H/\Delta t$ is on the order of μm day^{-1} and mm year^{-1}, respectively (Hemleben et al., 1989; McConnaughey, 1989). This yields characteristic time scales for the crystal growth of 43 and 16 s, respectively. In inorganic calcite, the growth rate may vary significantly, ranging from 10^{-6} to 10^{-1} mol m^{-2} h^{-1} (e.g., Zuddas and Mucci, 1994) which translates into $\Delta H/\Delta t \sim 4 \times 10^{-5}$–4 μm h^{-1}, where the molecular weight, 100 g mol^{-1}, and the density $\rho = 2.7 \times 10^6$ g m^{-3} of calcite have been used. The characteristic time scale of inorganic crystal growth may therefore range from 0.5 s to 13 h. Since the time scale for the equilibration between the dissolved boron species is $\tau \sim 1 \times 10^{-4}$ s, the time scale for crystal growth in biogenic and inorganic calcium carbonate is about three to eight orders of magnitude larger than τ. Thus, kinetic isotope effects during coprecipitation of boron in $CaCO_3$ are unlikely because the rate limiting step is clearly the crystal growth and not the equilibration between $B(OH)_4^-$ and $B(OH)_3$. This assumes that the isotopic exchange between surface bound boron species is of the same order of magnitude as the isotopic exchange between dissolved boron species in solution.

6. Summary and conclusions

In this paper, we have presented a detailed study of the kinetics of the boric acid–borate equilibrium in seawater. The reaction pathways and the rate constants of those reactions were hitherto widely unknown in marine chemistry and chemical oceanography. We have obtained information on this subject from physico-chemical studies which investigated sound absorption in seawater. The theoretically calculated relaxation time for chemical and isotopic equilibrium is ~ 95 and ~ 125 μs, respectively, for typical seawater conditions at temperature $T = 25°C$ and salinity $S = 35$. It follows that for practical purposes (i.e., when time scales of minutes and hours are considered), it can safely be assumed that the dissolved boron species and the stable boron isotope composition of those species is in equilibrium.

The equilibration times as derived in the present paper were used to shed light on kinetic isotope effects during the incorporation of boron into carbonates. Kinetic isotope effects are unlikely because the rate limiting step during coprecipitation of boron in calcium carbonate is the crystal growth and not the equilibration between $B(OH)_4^-$ and $B(OH)_3$. Thus, the $\delta^{11}B$ of the carbonates should be largely independent of growth rate effects. This result is of importance for evaluating the potential of stable boron isotopes as a paleo-pH proxy. Provided that the charged species $B(OH)_4^-$ is preferentially adsorbed (in preference to the neutral species $B(OH)_3$) before incorporation into the carbonate, the isotopic composition of boron in the carbonate should be close to the equilibrium composition of dissolved $B(OH)_4^-$ in solution. Since the $\delta^{11}B$ of dissolved $B(OH)_4^-$ in the ocean is primarily controlled by seawater pH (on time scales smaller than the residence time of boron in the ocean, ~ 15 million years, Vengosh et al., 1991), also the $\delta^{11}B$ of the carbonates should be primarily controlled by the seawater pH. The latter statement is one of the fundamental assumptions for the use of stable boron isotopes as a paleo-pH recorder. Our study corroborates this assumption.

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Appendix A. Calculation of the relaxation time τ

On the time scale of the relaxation of the boric acid–borate equilibrium, the chemical reactions that need to be considered for the kinetic rate law are:

$$B(OH)_3 + OH^- \underset{k_{-3}}{\overset{k_{+3}}{\rightleftharpoons}} B(OH)_4^- \qquad (16)$$

$$CO_3^{2-} + B(OH)_3 + H_2O \underset{k_{-4}}{\overset{k_{+4}}{\rightleftharpoons}} B(OH)_4^- + HCO_3^-. \qquad (17)$$

The kinetic rate law for, e.g., $[B(OH)_4^-]$ reads:

$$\begin{aligned}\frac{d[B(OH)_4^-]}{dt} = &+k_{+3}[B(OH)_3][OH^-] \\ &- k_{-3}[B(OH)_4^-] \\ &+ k_{+4}[B(OH)_3][CO_3^{2-}] \\ &- k_{-4}[B(OH)_4^-][HCO_3^-]. \qquad (18)\end{aligned}$$

This is a first order, non-linear differential equation for $[B(OH)_4^-]$. In order to solve this equation analytically, we use the linear form of it and express all concentrations of the right hand side of Eq. (18) in terms of $[B(OH)_4^-]$. Then, Eq. (18) can finally be rewritten as:

$$\frac{dx}{dt} = -\frac{1}{\tau}x$$

where $x = [\mathrm{B(OH)_4^-}] - [\mathrm{B(OH)_4^-}]_{\mathrm{eq}}$ is a perturbation (small deviation from equilibrium) of $[\mathrm{B(OH)_4^-}]$ and τ is the relaxation time of the system after which the perturbation has decreased to $\sim 37\% \simeq 1/\mathrm{e}$ of its initial value. The solution is:

$$x(t) = x_0 \exp(-t/\tau).$$

In order to express all concentrations of the right hand side of Eq. (18) in terms of $[\mathrm{B(OH)_4^-}]$, we use quantities of the system which are conserved in the course of the reaction. Including $\mathrm{H^+}$ (which is required for the calculation of pH), there are six chemical species or variables: $\mathrm{HCO_3^-}$, $\mathrm{CO_3^{2-}}$, $\mathrm{OH^-}$, $\mathrm{H^+}$, $\mathrm{B(OH)_3}$, and $\mathrm{B(OH)_4^-}$. Using the conservation of total dissolved inorganic carbon ($\Sigma\mathrm{CO_2}$), total boron ($\mathrm{B_T}$), and total alkalinity (TA):

$$\Sigma\mathrm{CO_2} = [\mathrm{HCO_3^-}] + [\mathrm{CO_3^{2-}}]$$

$$\mathrm{B_T} = [\mathrm{B(OH)_3}] + [\mathrm{B(OH)_4^-}]$$

$$\mathrm{TA} = [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}] + [\mathrm{OH^-}] + [\mathrm{B(OH)_4^-}] - [\mathrm{H^+}] \qquad (19)$$

and the equilibrium relations:

$$K_2 = \frac{[\mathrm{CO_3^{2-}}][\mathrm{H^+}]}{[\mathrm{HCO_3^-}]}$$

$$K_{\mathrm{w}} = [\mathrm{H^+}][\mathrm{OH^-}] \qquad (20)$$

there are five equations and six variables, enabling us to express all concentrations in terms of $[\mathrm{B(OH)_4^-}]$ (see below).

The linear form of Eq. (18) for a small deviation from equilibrium of $[\mathrm{B(OH)_4^-}]$ reads:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \Big[+k_{+3}(\gamma[\mathrm{OH^-}] - \alpha[\mathrm{B(OH)_3}]) - k_{-3} + k_{+4}(\gamma[\mathrm{CO_3^{2-}}] + \epsilon[\mathrm{B(OH)_3}]) - k_{-4}([\mathrm{HCO_3^-}] + \delta[\mathrm{B(OH)_4^-}])\Big] x \qquad (21)$$

where all concentrations ('[]') refer to equilibrium concentrations. The Greek letters α, γ, δ, and ϵ represent the derivatives of $[\mathrm{OH^-}]$, $[\mathrm{B(OH)_3}]$, $[\mathrm{HCO_3^-}]$, and $[\mathrm{CO_3^{2-}}]$, with respect to $[\mathrm{B(OH)_4^-}]$ at equilibrium:

$$\alpha = \frac{1}{1 + \beta + [\mathrm{H^+}]^2/K_{\mathrm{w}}}$$

$$\gamma = -1$$

$$\delta = \alpha\beta$$

$$\epsilon = -\alpha\beta \qquad (22)$$

where β is given by:

$$\beta = \frac{[\mathrm{CO_3^{2-}}][\mathrm{H^+}]/K_{\mathrm{w}}}{1 + K_2/[\mathrm{H^+}]}.$$

Eq. (22) has been derived by differentiating the expressions of the conserved quantities (Eqs. (19) and (20)) with respect to $[\mathrm{B(OH)_4^-}]$ and solving the resulting set of equations for α, γ, δ, and ϵ. Using Eq. (21) and remembering that $\mathrm{d}x/\mathrm{d}t = -(1/\tau)\, x$, one finally obtains:

$$\frac{1}{\tau} = +k_{+3}([\mathrm{OH^-}] + \alpha[\mathrm{B(OH)_3}]) + k_{-3} + k_{+4}([\mathrm{CO_3^{2-}}] + \alpha\beta[\mathrm{B(OH)_3}]) + k_{-4}([\mathrm{HCO_3^-}] + \alpha\beta[\mathrm{B(OH)_4^-}]) \qquad (23)$$

which was given in Section 4.

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