On the time required to establish chemical and isotopic equilibrium in the carbon dioxide system in seawater

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Abstract

Dissolved inorganic carbon in sea water plays a key role in understanding the properties of the oceanic carbon reservoir within the global carbon cycle. For instance, fluxes between the atmosphere and the ocean are estimated using the stable carbon isotopes $^{12}$C and $^{13}$C of atmospheric CO$_2$ and its dissolved forms within the ocean. Likewise, the investigation of carbon uptake by marine phytoplankton or the reconstruction of past oceans via stable isotope analysis demand a sound understanding of the sea water chemistry and associated carbon isotope fractionation. Chemical and isotopic disequilibrium is of particular interest when small length and time scales are considered. For example, within the microenvironment of marine plankton or within the surface boundary layer of the ocean (gas exchange atmosphere-ocean) the seawater carbonate chemistry deviates appreciably from equilibrium. It can be shown that a time-dependent description of the carbonate system is indispensable when time scales smaller than 90 s are involved (length scale of the diffusive boundary layer $\sim 10^{-4}$ m). Properties of the equilibrium state of the carbonate system in sea water are well known. However, hitherto there is little detailed work on the disequilibrium state of the chemical and in particular on the isotopic properties of the system. Here we present analytical and numerical techniques to determine the relaxation time of the chemical system including $\nu CO_2$, $HCO_3^-$, $CO_3^{2-}$, $H^+$, $OH^-$, $B(OH)_3^-$, and $B(OH)_4^-$, where $\nu =$ 12, 13, and 14. The calculated relaxation time for chemical equilibrium at a temperature of 25°C and a salinity of 35 at pH 8.2 is 15.9 s (only $^{12}$C species), while the time calculated for isotopic equilibrium is 17.5 s (all carbon isotopes considered). © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

A detailed understanding of the carbon dioxide system in seawater is a prerequisite for the investigation of a variety of phenomena in the marine environment. For example, the storage capacity of the ocean for anthropogenic CO$_2$ is limited by the buffer properties of the seawater chemistry (so called ‘Revelle’ factor (for review see, e.g., Siegenthaler, 1993; Stumm and Morgan, 1996)). Another example of the role of sea water...
chemistry in the global carbon cycle is the CO\textsubscript{2} exchange between ocean and atmosphere. The chemical state of the ocean and particularly the fluctuations of the ocean chemistry between glacial and interglacial periods are crucial for the atmospheric CO\textsubscript{2} content on this time scale (e.g., Broecker and Peng, 1993; Archer and Maier-Reimer, 1994).

While a description by equilibrium properties is reasonable for most of the mentioned phenomena an analogous treatment of processes on small time and length scales is inadequate. On small length scales (diffusive boundary layer \(\lesssim 10^{-2}\) m) where the transport or the supply of chemical substances is not governed by advection or turbulent mixing (Lazier and Mann, 1989), chemical conversion and diffusion are the dominant mechanisms. The characteristic time scale of diffusion can be estimated by \(\tau = l^2/D\), where \(l\) is the length scale (m) of the boundary layer and \(D \approx 10^{-9}\) m\(^2\) s\(^{-1}\) is the diffusion coefficient of the dissolved chemical species. With the typical length scale of the diffusive boundary layer of gas exchange at the ocean-atmosphere interface (0.3–1.5 \(\times 10^{-4}\) m (Emerson, 1995)) or of larger marine plankton such as aggregates or foraminifera (3 \(\times 10^{-4}\) m (Wolf-Gladrow et al., 1999)) one obtains a characteristic time scale of 1–90 s. Since the establishment of chemical equilibrium is of the same order of magnitude (as will be shown in this paper) processes faster than this cannot be adequately described by a time-independent consideration.

An example of the use of time-dependent descriptions of the carbonate system is the identification of sources of inorganic carbon for photosynthesis by marine phytoplankton via isotopic disequilibrium technique (Lehman, 1978; Korb et al., 1997). This technique compares the theoretically calculated relaxation time with the measured photosynthetic uptake of radiocarbon as a function of time to distinguish between CO\textsubscript{2} and HCO\textsubscript{3}\(^-\) uptake in marine diatoms. Thus, the relaxation time derived in this paper can be used to address a long-debated question concerning the inorganic carbon acquisition in marine phytoplankton. Where stable oxygen isotopes are concerned, disequilibrium properties may also help in comprehending nonequilibrium fractionations in synthetic carbonates (cf. Kim and O’Neil, 1997).

Moreover, disequilibrium of the carbonate system might subtly affect the interpretation of paleoceanographic records found in marine sediments. Spero et al. (1997) recently found that the sea water chemistry affects the stable carbon and oxygen isotope fractionation in the calcite shells of foraminifera, which provide an important tool in paleoceanography. Zeebe et al. (1999) applied a diffusion–reaction model to the microenvironment of foraminifera to show that this effect can be understood to a large degree in terms of an interaction between the sea water chemistry and the life processes of the organisms. However, some discrepancies between the model and observations remain and it is suggested that during the calcification process a mechanism is active which depends on the rate of calcite precipitation (first proposed by McCrea, 1950). Thus, a refined description of the incorporation of stable carbon and oxygen isotopes into the calcite lattice demands a time dependent model of the chemical environment which involves a disequilibrium of the fluxes and of the carbonate system. An important step towards this approach is a model of the response of a disturbed chemical system as a function of time (disequilibrium with respect to time, spatially homogeneous).

A specific question that can be addressed with this model concerns the experimental determination of the primary production in seawater by the uptake of radioactive \(^{14}\)C (e.g., Strickland and Parsons, 1968). In this method, radiocarbon (in the form of NaH\(^{14}\)CO\(_3\) or Na\(_2^{14}\)CO\(_3\)) is added at a known ratio to the total dissolved inorganic carbon content of the seawater sample. The uptake of radiocarbon by phytoplankton is converted to total carbon uptake using this radiocarbon:total carbon ratio. An underlying assumption is that the chemical and isotopic equilibrium (e.g., conversion from \(^{14}\)CO\(_3\)\(^-\) to H\(^{14}\)CO\(_3\)\(^-\), and from H\(^{14}\)CO\(_3\)\(^-\) to \(^{14}\)CO\(_2\), respectively) is already established. If this is not true, measurements of the primary production by the uptake of \(^{14}\)C would yield incorrect results.

Generally, the calculations to be presented here can be used to decide whether it is reasonable to use equilibrium or disequilibrium properties of the system. Particularly, the mathematical analysis of the chemical reactions (by use of the mathematical theory of dynamical systems) should lead to a detailed understanding of the mechanisms involved. Whereas a great number of articles have been published on the equilibrium behavior of the carbonate system (e.g., Maier-Reimer and Hasselmann, 1987; DOE, 1994; Millero, 1995) the chemical
and isotopic properties of the carbonate system in disequilibrium have hitherto received little attention. Lehman (1978) and Usdowski (1982) calculated the time required for the establishment of the chemical equilibrium of the carbon dioxide system. However, their results are restricted to a simplified model that assumes instantaneous equilibrium for the protonation of CO$_3^{2-}$ and the equilibrium of H$_2$O. Using this approximation, time scales smaller than seconds cannot be described adequately. In addition, boron compounds were not included in both analyses and the work by Usdowski (1982) considers a fresh water system.

In this paper, we present analytical and numerical calculations that determine the time required to establish the chemical and isotopic equilibrium of the carbon compounds of the carbon dioxide system in sea water. We take advantage of the full set of kinetic rate constants for the carbonate system (including boron) given by Wolf-Gladrow and Riebesell (1997) which enables us to analyze the system on time scales ranging from microseconds to minutes. The obtained results can be utilized for, e.g., identification of inorganic carbon sources in marine diatoms (isotope disequilibrium technique) or determination of isotope equilibration times in measurements of primary production. Particularly, a further development of the presented model (including chemical and isotopic disequilibrium processes within the vicinity of a growing crystal) should help to understand nonequilibrium fractionation in synthetic and biogenic carbonates.

2. Analytical and numerical calculations

The results of the following calculations might indeed be of practical interest for biologists or geochemists — the way to obtain these results is, however, rather theoretical. The description of the time development of the chemical species of the carbonate system leads to a set of ordinary differential equations of first order, and can therefore be analyzed by the mathematical theory of dynamical systems.

2.1. Decoupled reactions of CO$_2$ and H$_2$O

To demonstrate the technique of the determination of relaxation constants of a chemical system, a highly simplified system is considered first: the hydration of CO$_2$ and the reaction of H$_2$O, OH$^-$, and H$^+$. In this section these reactions will be analyzed separately and decoupled from any other reaction of the carbonate system. The coupling of both reactions is examined in Section 2.2, whereas the complete system (including boron) will be solved numerically in Section 2.3.

2.1.1. Hydration of CO$_2$

The hydration of CO$_2$ is described by the following reaction:

\[
\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HCO}_3^-
\]

where \(k_{+1}\) and \(k_{-1}\) are the rate constants for the forward and backward reactions, respectively; see Wolf-Gladrow and Riebesell (1997) for numerical values. (If not otherwise indicated, all calculated results in this paper refer to \(T = 25^\circ\text{C}, \text{pH} = 8.2, \text{and} \ S = 35\). The rate laws for the chemical species are

\[
\frac{d[\text{CO}_2]}{dt} = +k_{-1}[\text{H}^+][\text{HCO}_3^-] - k_{+1}[\text{CO}_2]
\]

\[
\frac{d[\text{HCO}_3^-]}{dt} = -k_{-1}[\text{H}^+][\text{HCO}_3^-] + k_{+1}[\text{CO}_2]
\]

\[
\frac{d[\text{H}^+]}{dt} = -k_{-1}[\text{H}^+][\text{HCO}_3^-] + k_{+1}[\text{CO}_2]
\]

.
from which one can see that
\[
\frac{d[CO_2]}{dt} = -\frac{d[\text{HCO}_3^-]}{dt} = -\frac{d[\text{H}^+]}{dt}. \tag{3}
\]

Thus, the system of differential equations can be reduced to one equation for CO₂ because it follows from Eq. (3) that
\[
[\text{HCO}_3^-] = C_0 - [\text{CO}_2]
\]
and
\[
[\text{H}^+] = C_1 - [\text{CO}_2]
\]
where \(C_0\) and \(C_1\) are constants. Here, the total dissolved inorganic carbon (ΣCO₂) is the sum of HCO₃⁻ and CO₂ and thus \(C_0 = ΣCO₂\). Introducing the alkalinity (\(\text{Alk} = [\text{HCO}_3^-] - [\text{H}^+]\)), it is obvious that \(C_1 = ΣCO₂ - \text{Alk}\). The equation for CO₂ therefore reads
\[
\frac{d[\text{CO}_2]}{dt} = +k_{-1}(ΣCO₂ - \text{Alk} - [\text{CO}_2])(ΣCO₂ - [\text{CO}_2]) - k_{+1}[\text{CO}_2]. \tag{4}
\]
This is a nonlinear first order equation for CO₂. To calculate the relaxation time for a small perturbation in CO₂, Eq. (4) is expanded in the vicinity of the equilibrium \([\text{CO}_2]^*_r\), where the equilibrium is given by (see reaction (1)):
\[
\frac{[\text{HCO}_3^-]^*[\text{H}^+]^*}{[\text{CO}_2]^*_r} = \frac{k_{+1}}{k_{-1}}
\]
Inserting \([\text{CO}_2] = [\text{CO}_2]^*_r + δ\text{CO}_2\) into Eq. (4), where \(δ\text{CO}_2\) is the deviation of CO₂ from equilibrium, using \(d[\text{CO}_2]^*_r/dt = 0\) and neglecting quadratic terms of \(δ\text{CO}_2\) one obtains
\[
δ\text{CO}_2 = -\left[k_{+1} + k_{-1}(\text{H}^+)^* + [\text{HCO}_3^-]^*_r\right]δ\text{CO}_2
\]
The solution is
\[
δ\text{CO}_2 = δ\text{CO}_2^0 \exp(-t/τ_1)
\]
where \(δ\text{CO}_2^0\) is the perturbation in CO₂ at \(t = 0\), and \(τ_1\) is given by:
\[
τ_1 = \frac{1}{k_{+1} + k_{-1}(\text{H}^+)^* + [\text{HCO}_3^-]^*_r}. \tag{6}
\]
A small perturbation in CO₂ therefore decreases exponentially with time constant \(τ_1\). Given \(k_{+1} = 0.036\ \text{s}^{-1}\), \(k_{-1} = 3.3 \times 10^4\ \text{kg mol}^{-1}\ \text{s}^{-1}\), \(\text{H}^+)^* = 6.3 \times 10^{-3}\ \text{mol kg}^{-1}\), and \([\text{HCO}_3^-]^*_r = 1.8 \times 10^{-3}\ \text{mol kg}^{-1}\), \(τ_1\) is 0.017 s. In summary, if the hydration of CO₂ is the only reaction considered, chemical equilibrium is achieved in about two hundredth of a second.

2.1.2. Water

For the reaction between \(\text{H}^+, \text{OH}^-,\) and \(\text{H}_2\text{O}\), namely
\[
\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \tag{7}
\]
a similar calculation yields a time constant \(τ_2\) for the relaxation of small deviations of \(\text{H}^+\) and \(\text{OH}^-\) from equilibrium (the notation of the rate constants for the chemical reactions follows Wolf-Gladrow and Riebesell,

---

Relaxation times in this paper are calculated as the time required to achieve 37% of the initial perturbation (≈ \(1/e\times100\)). Provided that the decrease is exponential one can calculate the time to achieve 99% of the equilibrium value, which is about 4.6 (≈ \(-\ln(0.01)\)) times larger than the relaxation time.
1997). The change in the concentration of H$_2$O is negligible because the concentration of water (55.56 mol kg$^{-1}$) is more than 10$^5$ times larger than the concentrations of H$^+$ and OH$^-$ (4 < pH < 10). The relaxation constant $\tau_2$ is:

$$
\tau_2 = \frac{1}{k_{-6}([H^+]^+ + [OH^-]^-)}. 
$$

(8)

Given $k_{-6} = 2.8 \times 10^{10}$ kg mol$^{-1}$ s$^{-1}$, $[H^+]^+ = 6.3 \times 10^{-9}$ mol kg$^{-1}$, and $[OH^-]^+ = 7.4 \times 10^{-6}$ mol kg$^{-1}$, $\tau_2$ is $4.8 \times 10^{-6}$ s. Here, this calculation is used to determine $\tau_2$ from $k_{-6}$. However, to determine the value of $k_{-6}$ from experiment the reversed approach is commonly used: $\tau_2$ is determined from temperature jump methods and the reaction rate is calculated from the relaxation time (this is actually the way to obtain $k_{-6}$ (Atkins, 1990)). The time required to establish an equilibrium between H$^+$, OH$^-$, and H$_2$O is therefore in the order of several microseconds.

### 2.2. Coupling of CO$_2$ and H$_2$O

From the results obtained in the previous sections one would expect that the relaxation time for the coupled chemical system (i.e., reactions (1) and (7) together) would be in the order of the slower reaction, i.e., about 0.02 s. However, we will show that the time constant of the coupled system is ca. 10 s which is about 500 times larger than the estimated relaxation time of the hydration of CO$_2$ in Section 2.1.1. The chemical reactions considered are:

$$
\text{CO}_2 + \text{H}_2\text{O} \xrightleftharpoons{\kappa_{+1}}^{\kappa_{-1}} \text{H}^+ + \text{HCO}_3^- 
$$

(9)

$$
\text{H}_2\text{O} \xrightarrow{\kappa_{+4}} \text{H}^+ + \text{OH}^- .
$$

(10)

The set of differential equations therefore reads:

$$
\frac{d[\text{CO}_2]}{dt} = +k_{-1}[\text{H}^+][\text{HCO}_3^-] - k_{+1}[\text{CO}_2]
$$

$$
\frac{d[\text{HCO}_3^-]}{dt} = -k_{-1}[\text{H}^+][\text{HCO}_3^-] + k_{+1}[\text{CO}_2]
$$

(11)

$$
\frac{d[\text{H}^+]}{dt} = -k_{-1}[\text{H}^+][\text{HCO}_3^-] + k_{+1}[\text{CO}_2] + k_{+6} - k_{-6}[\text{H}^+][\text{OH}^-]
$$

$$
\frac{d[\text{OH}^-]}{dt} = +k_{+6} - k_{-6}[\text{H}^+][\text{OH}^-]
$$

HCO$_3^-$ and H$^+$ can be eliminated because

$$
\frac{d[\text{HCO}_3^-]}{dt} = - \frac{d[\text{CO}_2]}{dt}
$$

and

$$
\frac{d[\text{H}^+]}{dt} = - \frac{d[\text{CO}_2]}{dt} + \frac{d[\text{OH}^-]}{dt}
$$

and therefore

$$
[\text{HCO}_3^-] = \Sigma\text{CO}_2 - [\text{CO}_2]
$$

$$
[\text{H}^+] = \text{C}_2 - [\text{CO}_2] + [\text{OH}^-]
$$
with $C_2 = \Sigma CO_2 - Alk$ (note that $Alk = [HCO_3^-] + [OH^-] - [H^+]$ in this case). The equations for $CO_2$ and $OH^-$ then read:

$$
R_{CO_2} := \frac{d[CO_2]}{dt} = +k_{-1}(\Sigma CO_2 - [CO_2])(\Sigma CO_2 - Alk - [CO_2] + [OH^-]) - k_{+1}[CO_2] \tag{12}
$$

$$
R_{OH^-} := \frac{d[OH^-]}{dt} = +k_{+6} - k_{-6}(\Sigma CO_2 - Alk - [CO_2] + [OH^-])[OH^-] \tag{13}
$$

The behavior of this dynamical system in the vicinity of the equilibrium is described by:

$$
\begin{pmatrix}
\frac{d(\delta CO_2)}{dt} \\
\frac{d(\delta OH^-)}{dt}
\end{pmatrix} = \mathcal{D} \cdot \begin{pmatrix}
\delta CO_2 \\
\delta OH^-
\end{pmatrix} \tag{14}
$$

where $\delta CO_2$ and $\delta OH^-$ are small deviations from equilibrium, and $\mathcal{D}$ is the Jacobian of Eqs. (12) and (13) at equilibrium:

$$
\mathcal{D} = \begin{pmatrix}
\frac{\partial R_{CO_2}}{\partial [CO_2]} & \frac{\partial R_{CO_2}}{\partial [OH^-]} \\
\frac{\partial R_{OH^-}}{\partial [CO_2]} & \frac{\partial R_{OH^-}}{\partial [OH^-]} \end{pmatrix} = \begin{pmatrix}
-k_{+1} + k_{-1}([H^+]^* + [HCO_3^-]^*) + k_{-1}[HCO_3^-]^* & -k_{+1}[HCO_3^-]^* \\
-k_{-6}[OH^-]^* & -k_{-6}[OH^-]^*
\end{pmatrix}
$$

or introducing the relaxation times of the decoupled reactions:

$$
\mathcal{D} = \begin{pmatrix}
-1/\tau_1 & k_{-1}[HCO_3^-]^* \\
k_{-6}[OH^-]^* & -1/\tau_2
\end{pmatrix} \tag{16}
$$

The eigenvalues $\lambda^{a,b}$ of $\mathcal{D}$ determine the behavior of the coupled system:

$$
\lambda^{a,b} = -\frac{1/\tau_1 + 1/\tau_2}{2} \pm \sqrt{\left(\frac{1/\tau_1 + 1/\tau_2}{2}\right)^2 - \frac{1}{\tau_1\tau_2} + k_{-1}k_{-6}[HCO_3^-]^*[OH^-]^*}. \tag{17}
$$

The time constants are given by the inverse of the eigenvalues. Using the numerical values stated above, one obtains:

$$
\tau_3^a = -1/\lambda^a \quad = \quad 11.5 \text{ s} \\
\tau_3^b = -1/\lambda^b \quad = \quad 4.8 \times 10^{-6} \text{ s}
$$

Thus, the coupled system exhibits two extremely different relaxation times. Such equations are called ‘stiff’. This property is expressed by the ratio of the largest and the smallest eigenvalue which gives $2.4 \times 10^6$. It should be emphasized that the relaxation time of the entire chemical system is given by the slowest process and is therefore of the order of 10 s. Remark: the behavior of the linearized system (14) can be deduced from the eigenvalues alone, therefore the exact solution (see Appendix B) was not discussed here.
2.2.1. Chemical background

A priori it is not clear why the coupled chemical system takes such a long time to achieve equilibrium, particularly, because each of the single reactions relaxes faster ($\approx 10^{-6}$ and 0.02 s). This phenomenon can be explained by examining the time evolution of a small perturbation in $\delta CO_2$. For the decoupled reaction the relaxation of $\delta CO_2$ is given by:

$$\delta CO_2 = -(1/\tau_1) \delta CO_2$$

where $\tau_1$ is positive, which means that a perturbation in $CO_2$ is exclusively damped exponentially. For the coupled system the time evolution of $\delta CO_2$ can be written as:

$$\delta CO_2 = -(1/\tau_1) \delta CO_2 + k_{-1}[HCO_3^-] \delta OH^-.$$  \hspace{1cm} (18)

In this case, a perturbation in $CO_2$ is damped by the first term $-(1/\tau_1) \delta CO_2$ in Eq. (18) but amplified by the second term $k_{-1}[HCO_3^-] \delta OH^-$. Since the influence of the dampening term is slightly higher than the influence of the amplifying term the overall time development results in a slow relaxation of the system. The coupled system therefore exhibits a much larger relaxation time than the decoupled reactions. The chemical mechanism can be described as follows: A conversion of $CO_2$ to $HCO_3^-$ results in a release of $H^+$. The production of hydrogen ions, however, is not arbitrary since the alkalinity must be conserved during this process. The coupling therefore slows down the conversion from carbon dioxide to bicarbonate.

Further information can be deduced by examining the eigenvectors of the Jacobian at equilibrium. The time evolution of a small deviation from equilibrium is given by (see Eq. (14)):

$$\begin{pmatrix} \delta CO_2 \\ \delta OH^- \end{pmatrix} = \mathcal{D}^* \begin{pmatrix} \delta CO_2 \\ \delta OH^- \end{pmatrix}$$

which means that the perturbations ($\delta CO_2$ and $\delta OH^-$) are mapped by the matrix $\mathcal{D}^*$ to yield the changes in time of these components ($\delta CO_2$ and $\delta OH^-$). The eigenvectors $\vec{u}$ and $\vec{v}$ of $\mathcal{D}^*$ are defined such that their direction is invariant when mapped by $\mathcal{D}^*$ (only the length changes), for instance:

$$\mathcal{D}^* \cdot \vec{u} = \lambda^u \vec{u}$$

where $\lambda^u$ is the corresponding eigenvalue to eigenvector $\vec{u}$. The numerical values of the eigenvalues and normalized eigenvectors at pH 8.2 are:

$$\lambda^u = -0.087; \quad \vec{u} = \begin{pmatrix} 0.7074 \\ 0.7068 \end{pmatrix}$$

$$\lambda^b = -2.1 \times 10^5; \quad \vec{v} = \begin{pmatrix} -2.88 \times 10^{-4} \\ 1 - 4.155 \times 10^{-8} \end{pmatrix} \approx \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$  

The eigenvectors and the vector field ($\delta CO_2$, $\delta OH^-$) in the vicinity of the equilibrium are shown in Fig. 1. The equilibrium is at the origin of the coordinate system ($\delta CO_2 = \delta OH^- = 0$). The first eigenvector $\vec{u}$ is nearly parallel to the diagonal; the angle between the $\delta CO_2$ axis and the first eigenvector is $\approx 45^\circ$. The second eigenvector $\vec{v}$ is nearly parallel to the $\delta OH^-$ axis. Thus, the system has two eigenvectors which are not orthogonal to one another.

The time development of the components can be seen by following the arrows. Initializing the deviation from equilibrium ($\delta CO_2$, $\delta OH^-$) $= (0.6, 0.1) \mu mol kg^{-1}$ as indicated by the dashed line, the system jumps to a higher OH$^-$ concentration within $10^{-6}$ s along the direction $\vec{v}$. This is approximately the time required to establish a ‘near-equilibrium state’ between H$^+$ and OH$^-$ (the product of [OH$^-$] and [H$^+$]) is nearly constant.
The vector field \((\delta \text{CO}_2, \delta \text{OH}^-)\) in the vicinity of the equilibrium of the coupled system. The origin of the coordinate system represents the equilibrium concentrations. The vectors define the velocity field corresponding to the time development of the chemical reactions. The eigenvectors \(\vec{u}\) and \(\vec{v}\) are not orthogonal to one another (left lower corner). The streamlines of the vector field are indicated by the thin lines, whereas the dashed arrow shows the development of a perturbation in \(\text{OH}^-\) and \(\text{CO}_2\) with initial values \((\delta \text{CO}_2, \delta \text{OH}^-) = (0.6, 0.1) \mu\text{mol kg}^{-1}\).

After this time, \([\text{CO}_2]\) and \([\text{OH}^-]\) decrease slowly along the direction of \(\vec{u}\) ([\text{CO}_2] / [\text{OH}^-] \approx 1:1) until equilibrium is achieved.

The temporal course of \(\delta \text{OH}^-\) and \(\delta \text{CO}_2\) is explicitly displayed in Fig. 2. The horizontal axis is chosen logarithmic to show the characteristic time scales involved (note that there is no functional dependence such as \(\delta \text{OH}^- \propto \log(t)\), even though the curve appears to be linear within different intervals). Starting at a value of 0.1 \(\mu\text{mol kg}^{-1}\), \(\delta \text{OH}^-\) increases to about 0.6 \(\mu\text{mol kg}^{-1}\) within several microseconds (vertical dot-dashed line No. 1, compare \(\tau^{\circ}_{\delta}\)). After this time the perturbation in \(\text{OH}^-\) and \(\text{CO}_2\) decrease slowly with the relaxation constant...
In the pH range from 7 to 9 the graphs can excellently be approximated by (see Appendix B):
\[
\delta \text{OH}^- (t) = \delta \text{CO}_3^2 \exp(-t/\tau^+_{\text{b}}) + \left( \delta \text{OH}^- - \delta \text{CO}_3^2 \right) \exp(-t/\tau^+_{\text{s}})
\]
\[
\delta \text{CO}_3^2 (t) = \delta \text{CO}_3^2 \exp(-t/\tau^+_{\text{b}})
\]
where \(\delta \text{OH}^-\) and \(\delta \text{CO}_3^2\) are the initial perturbations in \(\text{OH}^-\) and \(\text{CO}_3^2\) at \(t = 0\). A remarkable result of this analysis is that the perturbation of \(\text{OH}^-\) first increases abruptly to six times the initial value (depending on the perturbation in \(\text{CO}_3^2\), see Fig. 1). This feature is known as the problem of ‘nonnormal’ eigenfunctions which arises in other scientific fields such as fluid mechanics or numerical analysis. In cases where a system shows chaotic behavior (most chemical systems are dampened or at most oscillatory) the sudden increase of a perturbation can push the system from a region of regular behavior into a region of chaotic behavior. An example of such a breakdown of order is the transition from a regular flow of a fluid to a turbulent flow at Reynolds numbers far below the critical threshold value (e.g., Trefethen et al., 1993).

The reason for the relaxation of \(\text{CO}_3^2\) and \(\text{OH}^-\) occurring in a ratio of approximately 1:1 after achieving the ‘near-equilibrium’ with \(\text{H}_2\text{O}\) is the conservation of charge (alkalinity). The definitions of alkalinity and \(\Sigma \text{CO}_3^2\) in this particular case are:

\[
\text{Alk} = [\text{HCO}_3^-] + [\text{OH}^-] - [\text{H}^+]
\]
\[
\Sigma \text{CO}_3^2 = [\text{CO}_3^2] + [\text{HCO}_3^-].
\]

If we assume that \(\text{OH}^-\) and \(\text{H}^+\) are almost in equilibrium it follows that:

\[
[\text{CO}_3^2] = \Sigma \text{CO}_3^2 - \text{Alk} + [\text{OH}^-] - K_w/[\text{OH}^-]
\]

with

\[
K_w = \frac{k_{+6}}{k_{-6}} = [\text{H}^+][\text{OH}^-]
\]

and therefore

\[
\frac{d[\text{CO}_3^2]}{d[\text{OH}^-]} = 1 + K_w/[\text{OH}^-]^2.
\]

Since \(K_w/[\text{OH}^-]^2\) is in the order of \(10^{-4}\) the ratio of \(\text{CO}_3^2:\text{OH}^-\) decrease is approximately 1:1.

### 2.3. The complete chemical system

The complete chemical system (including boron) considered is:

\[
\text{CO}_3^2 + \text{H}_2\text{O} \overset{k_{+1}}{\rightleftharpoons} \text{H}^+ + \text{HCO}_3^-
\]

\[
\text{CO}_3^2 + \text{OH}^- \overset{k_{-3}}{\rightleftharpoons} \text{HCO}_3^-
\]

\[
\text{CO}_3^2^- + \text{H}^+ \overset{k_{-5}}{\rightleftharpoons} \text{HCO}_3^-
\]

\[
\text{H}_2\text{O} \overset{k_{-6}}{\rightleftharpoons} \text{H}^+ + \text{OH}^-
\]

\[
\text{B(OH)}_3 + \text{H}_2\text{O} \overset{k_{+7}}{\rightleftharpoons} \text{B(OH)}_4^- + \text{H}^+.
\]


The total dissolved carbon and the alkalinity are defined by:

\[
\begin{align*}
\Sigma CO_2 &= [CO_3^2^-] + [HCO_3^-] + [CO_2^+] \\
Alk &= [HCO_3^-] + 2[CO_3^2^-] + [OH^-] + [B(OH)_4^-] - [H^+].
\end{align*}
\]

The corresponding set of coupled differential equations (see Appendix A) was integrated numerically by a Runge–Kutta routine of order four with fixed step size (Press et al., 1988). An algorithm with variable step size often gains an advantage. However, it was not useful in this case since even very small deviations from equilibrium in \( H^+ \) and \( OH^- \) required a time step \( < 5 \times 10^{-5} \) s throughout the integration in order to ensure the stability of the algorithm.

The results of the integration are presented in Fig. 3. Starting from equilibrium at \( pH 8.2 \) and \( [CO_2] = 10.4 \mu mol kg^{-1} \), \( CO_2 \) is increased by a factor of 50% at \( t = 0 \) to \( 15.6 \mu mol kg^{-1} \). In addition \( HCO_3^- \) and \( OH^- \) are decreased and increased, respectively, at \( t = 0 \) by \( \delta CO_2 \), in order to keep \( \Sigma CO_2 \) and the alkalinity constant. As a response, the \( pH \) increases by ca. 0.017 units within several microseconds. Subsequently, \( CO_2 \) is converted to \( HCO_3^- \) while \( H^+ \) is released. The \( pH \) decreases and eventually reaches the equilibrium value of 8.2. The time constant for the e-folding time of the calculated decrease in \( CO_2 \) is 15.9 s which agrees roughly with the theoretical value of 11.5 s calculated for the simplified system (excluding \( CO_3^2^- \) and boron compounds).

The same results as in Fig. 3 are displayed in Fig. 4 with logarithmic time axis. The decrease of \( CO_2 \) is the slowest process and occurs on a time scale of 10 s (Fig. 4a). The concentration of \( HCO_3^- \) \((CO_3^2^-)\) is first decreasing (increasing) after ca. \( 10^{-2} \) s and then relaxes to the equilibrium value (Fig. 4b,c). This temporal

![Fig. 3](image-url)

**Fig. 3.** Numerical results of the relaxation of the carbon species for a perturbation in \( CO_2 \) \((HCO_3^-) \) at \( t = 0 \) was reduced by \( \delta CO_2 \) to keep \( \Sigma CO_2 \) constant, whereas \( OH^- \) was increased by \( \delta CO_2 \) to keep the alkalinity constant). All chemical species including boron are considered. The dashed lines indicate the equilibrium values of each species which were calculated from \( \Sigma CO_2 \) and alkalinity.
evolution of the carbon compounds can be explained by examining the pH (Fig. 4d). After ca. 10^{-6} s (see vertical dot-dashed line No. 1 in Fig. 4d) the pH increases due to the recombination of OH^- + H^+ = H_2O (OH^- was initially raised and thus H^+ is consumed). Since the pH is higher after that time interval, the carbonate ion concentration shifts to a higher value within 10^{-2} s (vertical dot-dashed line No. 2) while HCO_3^- is consumed and H^+ is produced (HCO_3^- = CO_3^{2-} + H^+). Finally, CO_2 is converted to HCO_3^- (on a time scale of 10 s) and all components relax to their respective equilibrium values (vertical dot-dashed line No. 3). The outlined analysis of the complete chemical system allows the identification of the involved processes and their characteristic time scales (see Table 1).

Table 1
Reactions and time scale of the carbonate system

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction</th>
<th>Time scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recombination of H^+ and OH^-</td>
<td>H_2O ⇌ H^+ + OH^-</td>
<td>10^{-6} s</td>
</tr>
<tr>
<td>Proton transfer HCO_3^- / CO_3^-</td>
<td>CO_3^{2-} + H^+ ⇌ HCO_3^-</td>
<td>10^{-2} s</td>
</tr>
<tr>
<td>Boron compounds</td>
<td>B(OH)_3 + H_2O ⇌ B(OH)_3^- + H^+</td>
<td>10^{-2} s</td>
</tr>
<tr>
<td>Conversion CO_2 / HCO_3^-</td>
<td>CO_2 + H_2O ⇌ H^+ + HCO_3^-</td>
<td>10 s</td>
</tr>
<tr>
<td>Conversion CO_2 / HCO_3^-</td>
<td>CO_2 + OH^- ⇌ HCO_3^-</td>
<td>10 s</td>
</tr>
</tbody>
</table>

aThe indicated time scales are characteristic for the respective reactions (note that the times were obtained by the analysis of the complete system, see text).
3. Stable carbon isotopes $^{12}\text{C}$ and $^{13}\text{C}$

In the previous sections a carbon dioxide system was considered that contained only one species of carbon isotopes. Consequently, the calculated relaxation time reflects the chemical equilibrium of the system. When different isotopes of variable concentrations are present in the solution, the slower reaction rates of the heavier isotopes lead to fractionation effects between the carbon species. For example, the hydration step of CO$_2$ to HCO$_3^-$ (reaction (20) forward) results in isotopically ‘lighter’ HCO$_3^-$ of about $13\%e$. On the other hand, the dehydration step (reaction (20) backward) results in ‘lighter’ CO$_2$ of about $22\%e$ (O’Leary et al., 1992). The difference between the forward and backward reaction equals the equilibrium fractionation between CO$_2$ and HCO$_3^-$ of about $9\%e$ (the equilibrium value given by Mook (1986) is $8.97\%e$ at $25^\circ$C). These effects will be included in the formulas given in this section.

3.1. Concept

Including $^{12}\text{C}$ and $^{13}\text{C}$ components, six carbon species have to be considered which can be grouped into two compartments:

![Carbon Compartment Diagram]

Obviously, there are no direct reactions between the two compartments since each isotope is conserved during reaction. Thus, there are two independent systems, except for the coupling via $\text{H}^+$ and $\text{OH}^-$. Consequently, isotopic equilibrium is achieved when chemical equilibrium is achieved in each compartment.

3.2. The simplified system

Analogously to Section 2.2 we estimate the time to establish equilibrium in a simplified system including the hydration of $^{12}\text{CO}_2$, $^{13}\text{CO}_2$ and the equilibrium of H$_2$O (the complete system is again integrated numerically, see Section 3.3). The chemical reactions are:

\begin{align}
^{12}\text{CO}_2 + \text{H}_2\text{O} &\rightleftharpoons ^{12}\text{HCO}_3^- + \text{H}^+ & (25) \\
^{13}\text{CO}_2 + \text{H}_2\text{O} &\rightleftharpoons ^{13}\text{HCO}_3^- + \text{H}^+ & (26) \\
\text{H}_2\text{O} &\rightleftharpoons \text{H}^+ + \text{OH}^- & (27)
\end{align}

where the $k’$ are reaction rates of $^{13}\text{C}$ compounds (for values, see Section 3.3). The time constants can again be derived via the eigenvalues of the Jacobian at equilibrium (see Section 2.2). Utilizing the conservation of alkalinity and $\Sigma\text{CO}_2$, we have:

\[
\Phi = 
\begin{pmatrix}
-1/\tau_1 & -k_1[^{12}\text{HCO}_3^-]^+ & +k_{-1}[^{12}\text{HCO}_3^-]^* \\
-k_{-1'}[^{13}\text{HCO}_3^-]^* & -1/\tau_1 & +k_{-1'}[^{13}\text{HCO}_3^-]^* \\
+k_{-6}[\text{OH}^-]^* & +k_{-6}[\text{OH}^-]^* & -1/\tau_2
\end{pmatrix}
\]
with
\[ 1/^{12}\tau_1 = k_{+1} + k_{-1} \left( [H^+]^+ + [H^{12}CO_3^-]^- \right) \]
\[ 1/^{13}\tau_1 = k_{+1} + k_{-1} \left( [H^+]^+ + [H^{13}CO_3^-]^- \right) \]
\[ 1/\tau_2 = k_{-6} \left( [H^+]^+ + [OH^-]^- \right). \]

Since \( \mathcal{D}^+ \) is a \( 3 \times 3 \) matrix the eigenvalues are the solution of a cubic polynomial. The relaxation times of the system are given by:
\[ \tau_a = 28.0 \text{ s} \]
\[ \tau_b = 11.5 \text{ s} \]
\[ \tau_c = 4.8 \times 10^{-6} \text{ s}. \]

The characteristic relaxation times of the system correspond to the different mechanisms involved. The shortest time (\( 4.8 \times 10^{-6} \) s) can be attributed to the recombination of \( H^+ \) and \( OH^- \). The second time (11.5 s) is required to establish chemical equilibrium within the \( ^{12}C \) compartment (compare the time calculated in Section 2.2 which was 11.5 s). The third time corresponds to the establishment of chemical equilibrium within the \( ^{13}C \) compartment and is consequently the time required for isotopic equilibrium. It is emphasized that the slower relaxation of the \( ^{13}C \) compounds is a result of the lower concentration in this compartment, rather than a result of different isotopic fractionations of \( ^{13}C \) and \( ^{12}C \).

### 3.3. The complete system including \(^{13}C\) compounds

To calculate the time for isotopic equilibrium in the complete system (including \( CO_3^{2-} \) and boron compounds) reactions for the \(^{13}C\) species are added to the set of reactions for the carbon dioxide system (20)–(24). The chemical reactions for the \(^{13}C\) species are:

\[ ^{13}CO_2 + H_2O \rightleftharpoons H^+ + H^{13}CO_3^- \]  
(29)

\[ ^{13}CO_2 + OH^- \rightleftharpoons H^{13}CO_3^- \]  
(30)

\[ ^{13}CO_3^{2-} + H^+ \rightleftharpoons H^{13}CO_3^- \]  
(31)

Values for the ratios of reaction rates for the hydration and hydroxylation of \( CO_2 \) (20) and (21) forward used in the calculations are

\[ k_{+1}' / k_{+1} = 0.987 \] at 24°C, O’Leary et al., 1992  
(32)

\[ k_{+4}' / k_{+4} = 0.989 \] O’Leary (pers. comm.).  
(33)

Values for the backward reactions (Eqs. (20) and (21)) were calculated from equilibrium fractionation:

\[ k_{-1}' / k_{-1} = 0.987 \times \alpha_{(CO_2-HCO_3^-)} \]  
(34)

\[ k_{-4}' / k_{-4} = 0.989 \times \alpha_{(CO_2-HCO_3^-)} \]  
(35)

where \( \alpha_{(CO_2-HCO_3^-)} \) is the equilibrium fractionation between \( CO_2 \) and \( HCO_3^- \) (Mook, 1986). The fact that there are no data available for \( k_{+5}' \), and \( k_{-5}' \) is of minor importance because the equilibrium fractionation between \( HCO_3^- \) and \( CO_2^{2-} \) is very small (~0.5%). It is much smaller than the fractionation between \( CO_2 \) and \( HCO_3^- \).
because the proton transfer reaction is several orders of magnitude faster than the carbon–oxygen bond change reaction. The value of $k_{+5}'$ was set to the value of $k_{+5}$ whereas $k'_{-5}$ was calculated from equilibrium fractionation given by Mook (1986).

The set of differential Eqs. (A1), (A2), (A3), (A4), (A5) and (A6) has to be expanded for the equations of the $^{13}$C species:

$$\frac{d[^{13}\text{CO}_2]}{dt} = +\left(k_{-4}[\text{H}^+] + k_{-4}[\text{OH}^-]\right)[^{13}\text{CO}_2] - \left(k_{+4} + k_{+4}[\text{OH}^-]\right)[^{13}\text{CO}_2]$$

$$\frac{d[^{13}\text{HCO}_2]}{dt} = +k_{-4}[^{13}\text{CO}_2] - k_{-4}[\text{H}^+] + k_{-4}[^{13}\text{CO}_2] + k_{+4}[^{13}\text{CO}_2][\text{OH}^-] - k_{-4}[^{13}\text{CO}_2] + k_{+4}[^{13}\text{CO}_2][^{15}\text{CO}_2]$$

$$\frac{d[^{13}\text{CO}_2^-]}{dt} = +k_{-4}[^{13}\text{CO}_2] - k_{-4}[\text{H}^+] [^{13}\text{CO}_2^-] \tag{36}$$

The results of the numerical integration are presented in Fig. 5. The model was initialized with a $\delta^{13}\Sigma_{\text{CO}_2}$ of 2.0‰ and a perturbation in $^{13}\text{CO}_2$ which produced an initial $\delta^{13}\text{C}$ of $^{13}\text{CO}_2$ of ca. 3‰. The concentration of $^{13}\text{HCO}_2^-$ was simultaneously decreased by the same amount to keep $\Sigma_{^{13}\text{CO}_2}$ and $\delta^{13}\Sigma_{^{13}\text{CO}_2}$ constant. Subsequently, all components relax to reach the equilibrium state. The calculated relaxation time for $\delta^{13}\Sigma_{^{13}\text{CO}_2}$ is 17 s. This is faster than the relaxation time of the simplified system (28 s) mostly due to the inclusion of the additional pathway of the conversion from $^{13}\text{CO}_2$ to $^{13}\text{HCO}_2^-$ ($^{13}\text{CO}_2 + \text{OH}^- \rightarrow ^{13}\text{HCO}_2^-$) in the complete system.

![Graphs showing relaxation of carbon species](image)

Fig. 5. Numerical results of the relaxation of the complete system ($^{13}$C and $^{12}$C components) and the resulting $\delta^{13}$C of the carbon species for a perturbation in $^{13}\text{CO}_2$ and $^{13}\text{HCO}_2^-$. All chemical species including boron are considered. The numerically calculated relaxation time is 17 s.
When this reaction is included in the calculations via the Jacobian at equilibrium, a very similar relaxation time of 17.5 s is obtained (see Section 4).

4. Radiocarbon ($^{14}$C)

Radiocarbon plays an important role as a tracer for ocean mixing (e.g., Broecker, 1974), in hydrogeological studies (e.g., Mook, 1980; Fontes, 1992) or as a tool for the determination of marine primary production (Strickland and Parsons, 1968). Due to the multiple applications of radiocarbon the radioactivity/concentration of $^{14}$C that occurs in the respective investigations may range from $10^1$ to $10^{15}$ dpm g$^{-1}$ C (disintegrations per minute per gram of carbon). This range includes the natural activity of, e.g., atmospheric CO$_2$ and the measurements of photosynthetic rates. In order to obtain insight into the behavior of the carbonate system under different circumstances the relaxation time for radiocarbon components in seawater will be investigated for various concentrations and pH in this section. The calculations are comparable to the treatment of the stable isotope $^{13}$C. However, the relative influence of the fractionation, whether equilibrium or kinetic, is twice as large for $^{14}$C as it is for $^{13}$C (see Mook (1980) and references therein).

For the purpose of numerical calculations, the amount of radiocarbon in solution which is often expressed in terms of radioactivity has to be converted to a concentration. The following calculation is straightforward; however, it is worth mentioning it since the authors did not find such a calculation in the literature. Radioactivities are usually given in units of Curie (Ci) or Becquerel (Bq). One Becquerel is the amount of radioactive material in which the average number of disintegrations in 1 s is one.

$$1\text{ Ci} = 3.7 \times 10^{10} \text{ Bq (disint. s}^{-1})$$

From a given activity of a solution (commonly expressed in $\mu$Ci l$^{-1}$) and the definition of Ci and Bq the concentration can be calculated. Using the law of radioactive decay the following formula is derived:

$$[c] = \frac{A}{N_A} \frac{3.7 \times 10^{10}}{\ln 2} t_{1/2} = \frac{A}{62.43}$$

where $[c]$ is the concentration ($\mu$mol 1$^{-1}$) of the radiocarbon, $A$ is the activity ($\mu$Ci l$^{-1}$), $t_{1/2} = 5730$ years ($1.807 \times 10^{11}$ s) is the half-life of $^{14}$C (Mook, 1980), and $N_A = 6.022136 \times 10^{23}$ mol$^{-1}$ is Avogadros constant. Hence, from activities typical for measurements of primary production ($120$–$1200$ $\mu$Ci) follow total concentrations of $^{14}$C ($\Sigma^{14}$CO$_2$) ranging from 2 to 20 $\mu$mol 1$^{-1}$.

To determine the time for the relaxation of $^{12}$C, $^{13}$C, and $^{14}$C compounds the following reactions are considered:

$^{8}$CO$_2$ + H$_2$O $\xrightleftharpoons[k_{+1}]{k_{-1}}$ H$^+$ + H$^+$CO$_3^-$

$^{6}$CO$_2$ + OH$^-$ $\xrightleftharpoons[k_{+4}]{k_{-4}}$ H$^+$CO$_3^-$

$^{4}$CO$_2^+$ + H$^+$ $\xrightleftharpoons[k_{+5}]{k_{-5}}$ H$^+$CO$_3^-$

H$_2$O $\xrightleftharpoons[k_{+6}]{k_{-6}}$ H$^+$ + OH$^-$

where $\nu$ is 12, 13, and 14. Even though the calculation of the Jacobian (see Section 3.2) is somewhat lengthy (using the conservation of alkalinity and the conservation of the sum of 12-, 13-, and 14-C the Jacobian is a $7 \times 7$ matrix), this approach saves time since the subsequent analysis of the system (e.g., parameter studies) by
evaluation of the eigenvalues is fast. Analysis by numerical integration of the differential equations requires appreciably more time since the stiffness of the equations demands a very small time step.

The relaxation time of the system at $pH = 8.2$, $\Sigma^{14}CO_2 = 2$ and $20 \mu\text{mol kg}^{-1}$ was 17.467 and 17.463 s, respectively. Thus, the relaxation time is virtually independent of the concentration over this range. The relaxation time $\tau$ as a function of $pH$ is presented in Fig. 6. The maximum relaxation time was calculated at $pH 7.18$ to be 25.4 s. The dependence on $pH$ results from the different paths of conversion of $CO_2$ to $HCO_3^-$. At low $pH$ the concentrations of $CO_2$ and $H^+$ are high, thus equilibrium with $HCO_3^-$ and $OH^-$ (reaction (37)) is achieved quickly. At high $pH$ the concentrations of $HCO_3^-$ and $OH^-$ are high, thus equilibrium with $CO_2$ and $H^+$ (reaction (38)) is achieved quickly. In the $pH$ range where all chemical species exhibit similar concentrations equilibrium is achieved more slowly around $pH 7$. This property can also be deduced from the relaxation constants: For instance, $\tau_2$ is of the form $\tau_2 \propto f = 1/([H^+]^+ + [OH^-]^+)$ (compare Eq. (8)). For $pH 7$, $f = 0.5 \times 10^7 \text{ kg } \mu\text{mol}^{-1}$, whereas for $pH 4$ and $pH 10$, $f = 10^4 \text{ kg } \mu\text{mol}^{-1}$.

In summary, the time required to establish chemical and isotopic equilibrium in the considered carbon dioxide system is in the order of minutes. The relaxation time is virtually independent of the amount of the radiocarbon present in the solution, when the concentrations range from 2 to 20 $\mu\text{mol kg}^{-1}$ (activity ca. 120–1200 $\mu\text{Ci}$).

5. Summary and conclusions

The presented analysis of the disequilibrium properties of the carbon dioxide system in sea water led to a detailed understanding of the mechanisms which determine the chemical behavior of the system on time scales ranging from microseconds to minutes. The analytical calculations for the simplified system (Section 2.2) showed the essential features of the complete system. Therefore, an expression for the relaxation of a perturbation in $^{12}CO_2$ can be given which is a very good approximation to the exact solution at $pH 8.2$ (see Appendix B):

$$\delta^{12}CO_2(\tau) = \delta^{12}CO_2^0 \exp(-\tau/\tau_a)$$

where $\tau_a = 15.9$ s. The numerical results indicate that the isotopic relaxation time is 17.5 s at $pH 8.2$ when the carbon isotopes $^{12}C$, $^{13}C$ and $^{14}C$ are considered. This time is virtually independent of the concentration of the

Fig. 6. Relaxation time for chemical and isotopic equilibrium in the carbon dioxide system with respect to the carbon isotopes $^{12}C$, $^{13}C$, and $^{14}C$ as a function of $pH$. The equilibrium is achieved more slowly when the concentrations of the chemical species exhibit similar concentrations around $pH 7$. 
radiocarbon. However, the relaxation time depends on the pH. It decreases by one order of magnitude when the pH decreases from 7 to 4 or increases from 7 to 10 (Fig. 6).

The measurement of total primary production via addition of radiocarbon yields correct results with regard to isotopic equilibrium provided that an equilibration time of ca. 2 min is taken into account (Figs. 5 and 6). Otherwise, the carbon uptake by phytoplankton could be underestimated because the added $^{14}$CO$_3^-$ has not been converted to $^{14}$CO$_2$. This property can, on the other hand, be utilized to identify carbon sources for photosynthesis of marine phytoplankton (Korb et al., 1997). The relaxation times derived in this paper can therefore be used to address an important question concerning the inorganic carbon acquisition in marine phytoplankton.

We hope that our results will serve to decide whether equilibrium or disequilibrium properties of the carbonate system should be used. Particularly, it is desired that our approach will help in the development of a time dependent model of carbon and oxygen fractionation in inorganic and biogenic calcite. As proposed by McCrea (1950) and Spero et al. (1997) kinetic isotope effects appear to play a key role in determining the extent of isotopic fractionation during calcite precipitation. It is suggested that disequilibrium of the carbonate chemistry (and isotopes) in the vicinity of the growing crystal is responsible for kinetic isotope effects.

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Appendix A. Differential equations of the carbon dioxide system (including boron)

\[
\frac{d[C\text{O}_3^-]}{dt} = + (k_{-1}[H^+] + k_{-4})[H\text{CO}_3^-] - (k_{+1} + k_{+4}[OH^-])[C\text{O}_2] \tag{A1}
\]

\[
\frac{d[H\text{CO}_3^-]}{dt} = + k_{+1}[C\text{O}_2] - k_{-4}[H^+] [H\text{CO}_3^-] - k_{-4}[H\text{CO}_3^-] + k_{+4}[C\text{O}_2][OH^-]
\]

\[
- k_{-5}[H\text{CO}_3^-] + k_{+5}[H^+] [CO_2^-] \tag{A2}
\]

\[
\frac{d[C\text{O}_2^-]}{dt} = + k_{-5}[H\text{CO}_3^-] - k_{+5}[H^+] [CO_2^-] \tag{A3}
\]

\[
\frac{d[H^+]}{dt} = + (k_{-5} - k_{-4}[H^+])[H\text{CO}_3^-] + k_{+1}[C\text{O}_2] - k_{+5}[H^+] [CO_2^-]
\]

\[
+ k_{+6} - k_{-6}[H^+][OH^-] + k_{+7}[B\text{(OH)}_3] - k_{-7}[H^+] [B\text{(OH)}_3] \tag{A4}
\]

\[
\frac{d[OH^-]}{dt} = + k_{-4}[H\text{CO}_3^-] - k_{+4}[C\text{O}_2][OH^-] + k_{+6} - k_{-6}[H^+][OH^-] \tag{A5}
\]

\[
\frac{d[B\text{(OH)}_3]}{dt} = - k_{+7}[B\text{(OH)}_3] + k_{-7}[H^+] [B\text{(OH)}_3] \tag{A6}
\]

\[
\frac{d[B\text{(OH)}_4]}{dt} = k_{+7}[B\text{(OH)}_3] - k_{-7}[H^+] [B\text{(OH)}_4] \tag{A7}
\]
Appendix B. Exact solution of the simplified, linearized system

The system (14) is linear and can be solved exactly. It is of the form:

\[
\tilde{\delta} = \mathcal{D} \lambda \tilde{\delta}
\]

(B8)

Let \( \tilde{u} = (u_1, u_2) \) and \( \tilde{v} = (v_1, v_2) \) denote eigenvectors of \( \mathcal{D}^* \) corresponding to eigenvalues \( \lambda^a \) and \( \lambda^b \). The time development of \( \tilde{u} \) and \( \tilde{v} \) is given by:

\[
\tilde{u}(t) = \tilde{u}(0) \exp(\lambda^a t)
\]

\[
\tilde{v}(t) = \tilde{v}(0) \exp(\lambda^b t)
\]

Since the set of eigenvectors is a basis, every \( \tilde{\delta} \) can be expressed by:

\[
\tilde{\delta} = a \tilde{u} + b \tilde{v}
\]

which is also a solution of Eq. (B8). Thus, one has to find the coefficients \( a \) and \( b \). They are calculated from the initial condition \( \lambda^a = 0 \). Basically, this procedure represents a transformation of the coordinates of the eigenspace to be the actual coordinates. The result is (replacing \( \tilde{\delta} \) by \( (\delta^{12}\text{CO}_2, \delta\text{OH}^-) \)):

\[
\begin{align*}
\delta\text{OH}^- (t) &= \left( \delta^{12}\text{CO}_2 - \alpha^0 \right) \frac{u_2}{u_1} \exp(-t/\tau^a) + \alpha^b \frac{v_2}{v_1} \exp(-t/\tau^b) \\
\delta^{12}\text{CO}_2 (t) &= \left( \delta^{12}\text{CO}_2 - \alpha^0 \right) \exp(-t/\tau^a) + \alpha^0 \exp(-t/\tau^b)
\end{align*}
\]

(B9)

with

\[
\alpha^0 = \frac{\delta\text{OH}^- \delta^{12}\text{CO}_2}{u_2 \delta^{12}\text{CO}_2 - u_1}
\]

and

\[
\tau^a = -1/\lambda^a \\
\tau^b = -1/\lambda^b.
\]

Using numerical values of the components of the eigenvectors at pH 8.2, \( \tilde{u} = (0.7074, 0.7068) \) and \( \tilde{v} = (0.7074, 0.7068) \). One sees that \( u_2/u_1 \approx 1, |v_2/v_1| \gg u_2/u_1 \), and thus \( |\delta^{12}\text{CO}_2| \gtrsim \alpha^0 \) (these relations are valid in the pH range from 7 to 9). Therefore Eq. (B9) can be approximated by:

\[
\begin{align*}
\delta\text{OH}^- (t) &= \delta^{12}\text{CO}_2 \exp(-t/\tau^a) + \left( \delta\text{OH}^- - \delta^{12}\text{CO}_2 \right) \exp(-t/\tau^b) \\
\delta^{12}\text{CO}_2 (t) &= \delta^{12}\text{CO}_2 \exp(-t/\tau^a)
\end{align*}
\]

(B10)

which was given in Section 2.2.1 (compare Eq. (19)).

References


