

Early Diagenesis in Sediments

—

A one-dimensional model formulation

Guy MUNHOVEN
Université de Liège, Belgium
<http://www.astro.ulg.ac.be/~munhoven/>

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Chapter 1

General theory

The theoretical summary presented below is kept as concise as possible. Emphasis is put on coherency and comprehensiveness of the developments, based on the adopted definitions; some concepts are used in a simplified way, not taking possible subtleties into consideration.

1.1 General conservation equation

Let V be an arbitrary volume of sediment, fixed with respect to the coordinate system, and delimited by the (simple) surface S , as depicted in Figure 1.1. In each point of the delimiting surface S , the normal unit vector, pointing out of the volume, is denoted \mathbf{n} . Supposing that the continuity hypothesis holds on all concentrations, sinks and source terms, the conservation equation for constituent i in an arbitrary fixed volume V writes:

$$\frac{\partial}{\partial t} \iiint_V \hat{C}_i dV = - \iint_S \hat{\mathbf{J}}_i \cdot \mathbf{n} dS + \iiint_V \hat{R}_i^V dV. \quad (1.1)$$

In this equation,

- \hat{C}_i is the concentration of constituent i in units of mass per unit volume of total sediment (solid fraction + porewaters);
- $\hat{\mathbf{J}}_i$ the total flux of constituent i in units of mass per unit surface area of total sediment per unit time;
- $\hat{R}_i^V = \hat{P}_i^V - \hat{D}_i^V$ is the net rate at which constituent i gets produced, obtained as the difference between sources (i.e., *production rate*, $\hat{P}_i^V \geq 0$, which is understood to account for input by non-local transport processes) and sinks (i.e., *consumption or destruction rate*, $\hat{D}_i^V \geq 0$,

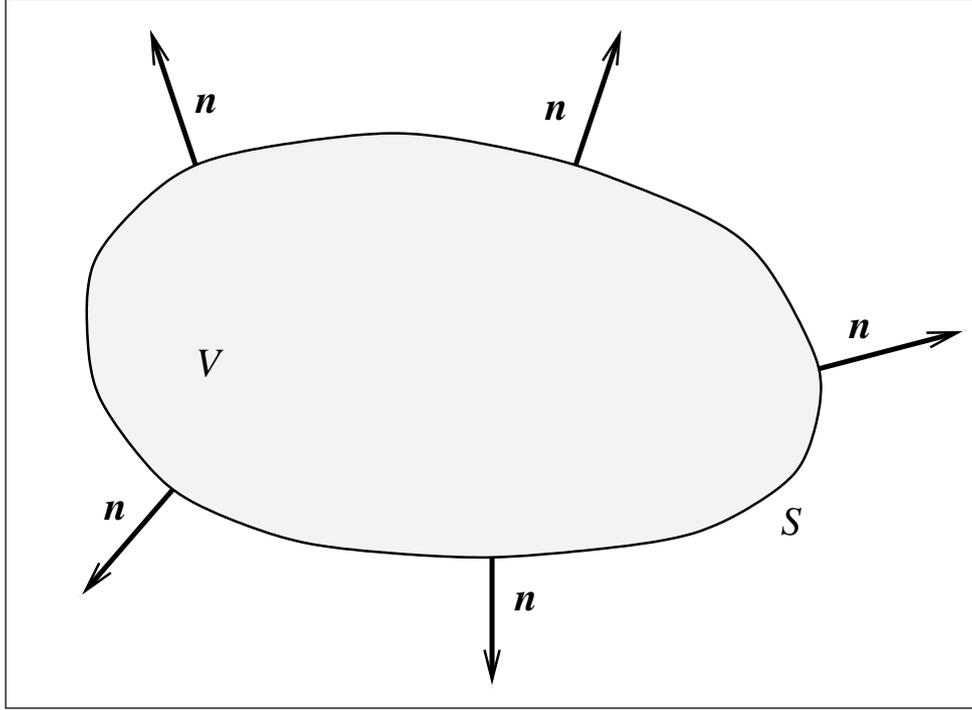


Figure 1.1: General setting: basic definitions and conventional vector orientations.

which is understood to account for output by non-local transport processes) inside V , in units of mass per unit volume of total sediment per unit time.

The derivative and the integral sign at the lefthand side of equation (1.1) commute because the volume V is fixed. The surface integral term of (1.1) can be transformed to

$$\iint_S \hat{\mathbf{J}}_i \cdot \mathbf{n} dS = \iiint_V \nabla \hat{\mathbf{J}}_i dV \quad (1.2)$$

by applying the divergence theorem. Equation (1.1) thus becomes

$$\iiint_V \left\{ \frac{\partial \hat{C}_i}{\partial t} + \nabla \hat{\mathbf{J}}_i - \hat{R}_i^V \right\} dV = 0 \quad (1.3)$$

As the volume V is arbitrary, identity (1.3) holds if and only if the integrand is equal to zero everywhere itself. The general conservation equa-

tion for a constituent i in a sediment may thus be written:

$$\frac{\partial \hat{C}_i}{\partial t} + \nabla \hat{J}_i - \hat{R}_i^V = 0 \quad (1.4)$$

Equation (1.4) is first order if \hat{J}_i does not depend on gradients, else it is of second or higher order.

1.2 Age of sediment constituents

In many instances, it is necessary to be able to trace the evolution of the age of particles as they transit the sediment. This is necessary for dating purposes, but might also be required if, e.g., reaction rates constants age-dependent. Age can be indirectly traced, e.g., by isotopic signatures of constituents, or directly by adequate age-related variables.

1.2.1 Concentration distribution function

The concentration distribution function $\hat{c}_i(\mathbf{x}, t, \tau)$ is defined such that, at any position \mathbf{x} and at any time t , $\hat{c}_i(\mathbf{x}, t, \tau) d\tau$ represents the amount of constituent i that has an age in the class $[\tau, \tau + d\tau]$.

The total concentration $\hat{C}_i(\mathbf{x}, t)$ of a constituent i is obviously obtained by integrating its concentration distribution function over the whole range of ages it may present:

$$\hat{C}_i(\mathbf{x}, t) = \int_0^{+\infty} \hat{c}_i(\mathbf{x}, t, \tau) d\tau.$$

The general conservation equation for $\hat{c}_i(\mathbf{x}, t, \tau)$ can be derived almost the same way than the one for $\hat{C}_i(\mathbf{x}, t)$ (equation (1.4)), except that an additional dimension is to be taken into account. Accordingly, it appears that a flux ("advection") term in the age direction must be considered [Delhez et al., 1999, Deleersnijder et al., 2001]. At any given time t , in any given place \mathbf{x} , constituent i is ageing, i. e., $\hat{c}_i(\mathbf{x}, t, \tau)$ is being carried away along the τ axis at a rate of 1 (yr/yr):

$$\frac{\partial \hat{c}_i}{\partial t} + \frac{\partial \hat{c}_i}{\partial \tau} + \nabla \hat{J}_i - \hat{r}_i^V = 0, \quad (1.5)$$

with $\hat{J}_i = \hat{J}_i(\mathbf{x}, t, \tau)$ and $\hat{r}_i = \hat{r}_i(\mathbf{x}, t, \tau)$ denoting the flux and the reaction rate (the latter including sources and sinks by non-local transport) of con-

stituent i , respectively, recalling that, in terms of production and destruction of i , $\hat{r}_i(\mathbf{x}, t, \tau) = \hat{p}_i(\mathbf{x}, t, \tau) - \hat{d}_i(\mathbf{x}, t, \tau)$. We may clearly assume that

$$\hat{\mathbf{J}}_i(\mathbf{x}, t) = \int_0^{+\infty} \hat{\mathbf{j}}_i(\mathbf{x}, t, \tau) d\tau$$

and

$$\hat{R}_i^V(\mathbf{x}, t) = \int_0^{+\infty} \hat{r}_i^V(\mathbf{x}, t, \tau) d\tau$$

The conservation equation (1.4) for $\hat{C}_i(\mathbf{x}, t)$ can now be derived from equation (1.5) by integration:

$$\frac{\partial \hat{C}_i}{\partial t} = \frac{\partial}{\partial t} \int_0^{+\infty} \hat{c}_i d\tau = \int_0^{+\infty} \frac{\partial \hat{c}_i}{\partial t} d\tau.$$

The integral over τ and the partial derivative with respect to t commute (the same holds of course for the partial derivatives with respect to the space directions). Hence

$$\begin{aligned} \frac{\partial \hat{C}_i}{\partial t} &= - \int_0^{+\infty} \left(\frac{\partial \hat{c}_i}{\partial \tau} + \nabla \hat{\mathbf{j}}_i - \hat{r}_i^V \right) d\tau \\ &= - \int_0^{+\infty} \frac{\partial \hat{c}_i}{\partial \tau} d\tau - \nabla \int_0^{+\infty} \hat{\mathbf{j}}_i d\tau + \int_0^{+\infty} \hat{r}_i^V d\tau. \end{aligned}$$

We may assume that $\lim_{\tau \rightarrow +\infty} \hat{c}_i = 0$, translating the fact that all matter has a finite age. Thus, the previous equation becomes

$$\frac{\partial \hat{C}_i}{\partial t} - \hat{c}_i(\mathbf{x}, t, \tau = 0) + \nabla \hat{\mathbf{J}}_i - \hat{R}_i^V = 0$$

which is identical to equation (1.4), except for the $\hat{c}_i(\mathbf{x}, t, \tau = 0)$ term. That term is generally equal to 0, except if there is a permanent production, or input of i with age 0 at position \mathbf{x} and at time t . This situation is conveniently handled by including this term in the reaction term as a Dirac impulse ($\delta(\tau) \times \hat{c}_i(\mathbf{x}, t, \tau = 0)$), and thus actually considering it to be a non-local source, or by specifying adequate boundary conditions [Delhez et al., 1999, Beckers et al., 2001, Deleersnijder et al., 2001]. As a consequence, the previous equation reduces identically to equation (1.4).

1.2.2 Mean age and age concentration

The mean age $\bar{A}_i(\mathbf{x}, t)$ of a constituent i , at a given position \mathbf{x} and at time t , is

$$\bar{A}_i(\mathbf{x}, t) = \frac{\int_0^{+\infty} \tau \hat{c}_i(\mathbf{x}, t, \tau) d\tau}{\int_0^{+\infty} \hat{c}_i(\mathbf{x}, t, \tau) d\tau} = \frac{\int_0^{+\infty} \tau \hat{c}_i(\mathbf{x}, t, \tau) d\tau}{\hat{C}_i(\mathbf{x}, t)}.$$

The numerator in the definition of $\bar{A}_i(\mathbf{x}, t)$ is called the *age concentration*, denoted $\hat{A}_i(\mathbf{x}, t)$:

$$\hat{A}_i(\mathbf{x}, t) = \int_0^{+\infty} \tau \hat{c}_i(\mathbf{x}, t, \tau) d\tau = \bar{A}_i(\mathbf{x}, t) \times \hat{C}_i(\mathbf{x}, t)$$

The time evolution of the mean age of a constituent i , \bar{A}_i can thus be calculated from the evolutions of \hat{C}_i and \hat{A}_i . It is straightforward to derive an evolution, or conservation equation, for $\hat{A}_i(z, t)$ on the basis of equation (1.5). That equation is first multiplied by τ , and then integrated for τ in $]0, +\infty[$:

$$\int_0^{+\infty} \tau \frac{\partial \hat{c}_i}{\partial t} d\tau + \int_0^{+\infty} \tau \frac{\partial \hat{c}_i}{\partial \tau} d\tau + \int_0^{+\infty} \tau \nabla \hat{j}_i d\tau - \int_0^{+\infty} \tau \hat{r}_i^V d\tau = 0. \quad (1.6)$$

The partial derivative operators with respect to space directions and t commute with τ , as τ is an independent variable. They also commute with integrals over τ . Hence,

$$\int_0^{+\infty} \tau \frac{\partial \hat{c}_i}{\partial t} d\tau = \frac{\partial}{\partial t} \int_0^{+\infty} \tau \hat{c}_i d\tau = \frac{\partial \hat{A}_i}{\partial t}$$

and

$$\int_0^{+\infty} \tau \nabla \hat{j}_i d\tau = \nabla \int_0^{+\infty} \tau \hat{j}_i d\tau.$$

Furthermore,

$$\int_0^{+\infty} \tau \frac{\partial \hat{c}_i}{\partial \tau} d\tau = [\tau \hat{c}_i]_{\tau=0}^{\tau \rightarrow +\infty} - \int_0^{+\infty} \hat{c}_i d\tau = -\hat{C}_i$$

as we may obviously assume that $\lim_{\tau \rightarrow 0} \tau \hat{c}_i = 0$ and $\lim_{\tau \rightarrow +\infty} \tau \hat{c}_i = 0$.

Defining

$$\hat{J}_{\tau i}(\mathbf{x}, t) = \int_0^{+\infty} \tau \hat{j}_i(\mathbf{x}, t, \tau) d\tau$$

and

$$\hat{R}_{\tau i}^V(\mathbf{x}, t) = \int_0^{+\infty} \tau \hat{r}_i^V(\mathbf{x}, t, \tau) d\tau,$$

equation (1.6) becomes

$$\frac{\partial \hat{A}_i}{\partial t} - \hat{C}_i + \nabla \hat{J}_{\tau i} - \hat{R}_{\tau i}^V = 0,$$

which is to be compared with equation (1.4)

$$\frac{\partial \hat{C}_i}{\partial t} + \nabla \hat{J}_i - \hat{R}_i^V = 0.$$

1.2.3 Alternative: mean production time and production time concentration

The age of a constituent i is not the most practical approach to consider. The model under development could possibly have material that leaves the explicit model zone, but which might return to this explicitly modelled zone later on. It would then be necessary to have the age of the constituent continue to evolve while the matter is not under complete model control any more. This can be avoided if the production or deposition time, π , is used instead of age.

Equations can now be obtained from the above, by first applying the variable change $(t, \tau) \rightarrow (t', \pi)$, with $t' = t$ and $\pi = t - \tau$. This variable change transforms (1.5) into

$$\frac{\partial \hat{c}_i}{\partial t'} + \nabla \hat{j}_i - \hat{r}_i^V = 0. \quad (1.7)$$

For the variable change, it is indispensable to keep t and t' separate, else the derivative change will not work out correctly. Once the fundamental equation (1.7) is established, this is nevertheless not required any more and we drop the prime from here on. Similarly to above, we have

$$\hat{C}_i(\mathbf{x}, t) = \int_{-\infty}^t \hat{c}_i(\mathbf{x}, t, \pi) d\pi.$$

Accordingly,

$$\begin{aligned} \frac{\partial \hat{C}_i}{\partial t} &= \frac{\partial}{\partial t} \int_{-\infty}^t \hat{c}_i(\mathbf{x}, t, \pi) d\pi \\ &= \hat{c}_i(\mathbf{x}, t, \pi = t) + \int_{-\infty}^t \frac{\partial}{\partial t} \hat{c}_i(\mathbf{x}, t, \pi) d\pi \\ &= \hat{c}_i(\mathbf{x}, t, \pi = t) - \nabla \int_{-\infty}^t \hat{j}_i d\pi + \int_{-\infty}^t \hat{r}_i^V d\pi \\ &= \hat{c}_i(\mathbf{x}, t, \pi = t) - \nabla \hat{J}_i + \hat{R}_i^V \end{aligned}$$

which is again identical to equation (1.4), except for the $\hat{c}_i(\mathbf{x}, t, \pi = t)$ term. As before, that term is generally equal to 0, except if there is a permanent production or input of i with production time t at position \mathbf{x} (i.e., age 0) and at time t . This situation is conveniently handled by including this term in the reaction term as a Dirac impulse ($\delta(\pi - t) \times \hat{c}_i(\mathbf{x}, t, \pi = t)$).

Similarly to the mean age of constituent i , we may define its mean production time

$$\bar{\Pi}_i(\mathbf{x}, t) = \frac{\int_{-\infty}^t \pi \hat{c}_i(\mathbf{x}, t, \pi) d\pi}{\int_{-\infty}^t \hat{c}_i(\mathbf{x}, t, \pi) d\pi} = \frac{\int_{-\infty}^t \pi \hat{c}_i(\mathbf{x}, t, \pi) d\pi}{\hat{C}_i(\mathbf{x}, t)}.$$

The numerator in the definition of $\bar{\Pi}_i(\mathbf{x}, t)$ is now called the *production time concentration*, denoted $\hat{\Pi}_i(\mathbf{x}, t)$:

$$\hat{\Pi}_i(\mathbf{x}, t) = \int_{-\infty}^t \pi \hat{c}_i(\mathbf{x}, t, \pi) d\pi = \bar{\Pi}_i(\mathbf{x}, t) \times \hat{C}_i(\mathbf{x}, t)$$

The time derivative of $\hat{\Pi}_i$ then becomes

$$\begin{aligned} \frac{\partial \hat{\Pi}_i}{\partial t} &= \frac{\partial}{\partial t} \int_{-\infty}^t \pi \hat{c}_i(\mathbf{x}, t, \pi) d\pi \\ &= t \hat{c}_i(\mathbf{x}, t, \pi = t) + \int_{-\infty}^t \pi \frac{\partial}{\partial t} \hat{c}_i(\mathbf{x}, t, \pi) d\pi \\ &= t \hat{c}_i(\mathbf{x}, t, \pi = t) - \nabla \int_{-\infty}^t \pi \hat{j}_i d\pi + \int_{-\infty}^t \pi \hat{r}_i^V d\pi. \end{aligned}$$

The term $t \hat{c}_i(\mathbf{x}, t, \pi = t)$ is treated as in the general equation. Defining

$$\hat{J}_{\pi i}(\mathbf{x}, t) = \int_{-\infty}^t \pi \hat{j}_i(\mathbf{x}, t, \pi) d\pi$$

and

$$\hat{R}_{\pi i}^V(\mathbf{x}, t) = \int_{-\infty}^t \pi \hat{r}_i^V(\mathbf{x}, t, \pi) d\pi,$$

the conservation equation for Π_i can be written as

$$\boxed{\frac{\partial \hat{\Pi}_i}{\partial t} + \nabla \hat{J}_{\pi i} - \hat{R}_{\pi i}^V = 0.} \quad (1.8)$$

1.2.4 Age-independent transport and reaction

The most general case is comparatively complicated to manage. For most applications, though, age is not an active but only a passive parameter. One may, e.g., consider that reaction rates do not depend on the age of the reactants. In this case, the equations strongly simplify.

Transport

In a continuum, the general formulation for the advective-diffusive transport of a constituent i is

$$\hat{\mathbf{j}}_i = -\mathbf{K} \cdot \nabla \hat{c}_i(\mathbf{x}, t, \pi) + \mathbf{u} \hat{c}_i(\mathbf{x}, t, \pi)$$

where \mathbf{K} is the diffusivity tensor and \mathbf{u} the transport velocity. Accordingly, the total transport of constituent i is

$$\hat{\mathbf{j}}_i(\mathbf{x}, t) = \int_{-\infty}^t \hat{\mathbf{j}}_i(\mathbf{x}, t, \pi) d\pi = \int_{-\infty}^t (-\mathbf{K} \cdot \nabla \hat{c}_i(\mathbf{x}, t, \pi) + \mathbf{u} \hat{c}_i(\mathbf{x}, t, \pi)) d\pi.$$

We may in general assume that \mathbf{K} and \mathbf{u} only depend on \mathbf{x} and t , but not on π . Hence

$$\hat{\mathbf{j}}_i(\mathbf{x}, t) = -\mathbf{K} \cdot \nabla \left(\int_{-\infty}^t \hat{c}_i(\mathbf{x}, t, \pi) d\pi \right) + \mathbf{u} \int_{-\infty}^t \hat{c}_i(\mathbf{x}, t, \pi) d\pi,$$

i. e.,

$$\hat{\mathbf{j}}_i(\mathbf{x}, t) = -\mathbf{K} \cdot \nabla \hat{C}_i + \mathbf{u} \hat{C}_i.$$

Similarly

$$\begin{aligned} \hat{\mathbf{j}}_{\pi i}(\mathbf{x}, t) &= \int_{-\infty}^t \pi \hat{\mathbf{j}}_i(\mathbf{x}, t, \pi) d\pi \\ &= \int_{-\infty}^t \pi (-\mathbf{K} \cdot \nabla \hat{c}_i(\mathbf{x}, t, \pi) + \mathbf{u} \hat{c}_i(\mathbf{x}, t, \pi)) d\pi \\ &= -\mathbf{K} \cdot \nabla \left(\int_{-\infty}^t \pi \hat{c}_i(\mathbf{x}, t, \pi) d\pi \right) + \mathbf{u} \int_{-\infty}^t \pi \hat{c}_i(\mathbf{x}, t, \pi) d\pi. \end{aligned}$$

Hence,

$$\hat{\mathbf{j}}_{\pi i}(\mathbf{x}, t) = -\mathbf{K} \cdot \nabla \hat{\Pi}_i + \mathbf{u} \hat{\Pi}_i.$$

Reaction rates

If the reaction rate \hat{R}_i^V is independent of age or production time, then each fraction $\hat{c}_i(\mathbf{x}, t, \pi) d\pi$ has the same probability $p(\mathbf{x}, t)$ to react, so that we may formally write $\hat{r}_i(\mathbf{x}, t, \pi) = p(\mathbf{x}, t) \hat{c}_i(\mathbf{x}, t, \pi)$. Accordingly,

$$\begin{aligned} \hat{R}_i^V(\mathbf{x}, t) &= \int_{-\infty}^t \hat{r}_i^V(\mathbf{x}, t, \pi) d\pi = \int_{-\infty}^t p(\mathbf{x}, t) \hat{c}_i(\mathbf{x}, t, \pi) d\pi \\ &= p(\mathbf{x}, t) \int_{-\infty}^t \hat{c}_i(\mathbf{x}, t, \pi) d\pi \\ &= p(\mathbf{x}, t) \hat{C}_i(\mathbf{x}, t), \end{aligned}$$

from which we may deduce that

$$p(\mathbf{x}, t) = \frac{\hat{R}_i^V(\mathbf{x}, t)}{\hat{C}_i(\mathbf{x}, t)}.$$

Similarly,

$$\begin{aligned} \hat{R}_{\pi i}^V(\mathbf{x}, t) &= \int_{-\infty}^t \pi \hat{r}_i^V(\mathbf{x}, t, \pi) d\pi = \int_{-\infty}^t \pi p(\mathbf{x}, t) \hat{c}_i(\mathbf{x}, t, \pi) d\pi \\ &= p(\mathbf{x}, t) \int_{-\infty}^t \pi \hat{c}_i(\mathbf{x}, t, \pi) d\pi \\ &= p(\mathbf{x}, t) \hat{\Pi}_i(\mathbf{x}, t) \\ &= \hat{\Pi}_i(\mathbf{x}, t) \frac{\hat{R}_i^V(\mathbf{x}, t)}{\hat{C}_i(\mathbf{x}, t)}. \end{aligned}$$

If the rate law for \hat{R}_i^V is linear in \hat{C}_i , the same law can be used for $\hat{R}_{\pi i}^V$, with \hat{C}_i replaced by $\hat{\Pi}_i$.

Simplified general conservation equation

Under these relatively general conditions, the conservation equation for $\hat{\Pi}_i$ takes the following form, similar to that for \hat{C}_i under the same conditions:

$$\boxed{\frac{\partial \hat{\Pi}_i}{\partial t} + \nabla \cdot (-\mathbf{K} \cdot \nabla \hat{\Pi}_i + \mathbf{u} \hat{\Pi}_i) - \hat{R}_{\pi i}^V = 0.} \quad (1.9)$$

1.3 Conservation equations at discontinuities

In the presence of discontinuities (e.g., interfaces between two different sediments) equation (1.4) holds as long as it is written for a point outside the discontinuity. The respective equations for either sides of the sediment space must be linked “*in order to obtain continuity of the solutions across the interface*” [Boudreau, 1997, p. 172]. Similarly, the top or bottom boundaries must be correctly dealt with.

Let V again represent an arbitrary volume of sediment delimited by as simple, non-material surface S , situated astride an internal boundary (interface) Σ ; Σ' denotes that part of Σ that is enclosed in V . Σ partitions V into two parts V_1 and V_2 , respectively delimited by S_1 and Σ' , and by V_2 and Σ' (see Figure 1.2). Hence: $V = V_1 + V_2$ and $S = S_1 + S_2$. Conservation equations similar to equation 1.1 can be written for a constituent i in V , V_1

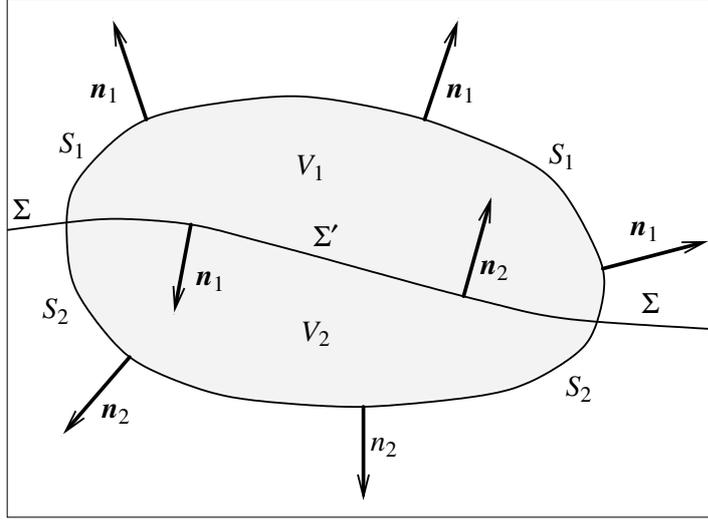


Figure 1.2: Interface continuity: basic definitions and conventional vector orientations.

and V_2 . Inside V , possible chemical reactions taking place on the interface Σ must be taken into account:

$$\frac{\partial}{\partial t} \iiint_V \hat{C}_i dV = - \iint_S \hat{\mathbf{J}}_i \cdot \mathbf{n} dS + \iint_{\Sigma'} \hat{R}_i^\Sigma dS + \iiint_V \hat{R}_i^V dV, \quad (1.10)$$

where $\mathbf{n} = \mathbf{n}_1$ on S_1 , and $\mathbf{n} = \mathbf{n}_2$ on S_2 . Similarly to \hat{R}_i^V , $\hat{R}_i^\Sigma = \hat{P}_i^\Sigma - \hat{D}_i^\Sigma$ represents the rate at which constituent i gets produced or consumed on the interface Σ , in units of mass per unit surface of total sediment per unit time. $\hat{P}_i^\Sigma \geq 0$ and $\hat{D}_i^\Sigma \geq 0$ are again the corresponding production and consumption rates. For V_1 and V_2 these equations become respectively:

$$\frac{\partial}{\partial t} \iiint_{V_1} \hat{C}_i dV = - \iint_{S_1} \hat{\mathbf{J}}_i \cdot \mathbf{n}_1 dS - \iint_{\Sigma'} \hat{\mathbf{J}}_i \cdot \mathbf{n}_1 dS + \iiint_{V_1} \hat{R}_i^V dV \quad (1.11)$$

and

$$\frac{\partial}{\partial t} \iiint_{V_2} \hat{C}_i dV = - \iint_{S_2} \hat{\mathbf{J}}_i \cdot \mathbf{n}_2 dS - \iint_{\Sigma'} \hat{\mathbf{J}}_i \cdot \mathbf{n}_2 dS + \iiint_{V_2} \hat{R}_i^V dV. \quad (1.12)$$

As

$$\begin{aligned}\iiint_V \hat{C}_i dV &= \iiint_{V_1} \hat{C}_i dV + \iiint_{V_2} \hat{C}_i dV, \\ \iiint_V \hat{R}_i^V dV &= \iiint_{V_1} \hat{R}_i^V dV + \iiint_{V_2} \hat{R}_i^V dV,\end{aligned}$$

and

$$\iint_S \hat{\mathbf{J}}_i \cdot \mathbf{n} dS = \iint_{S_1} \hat{\mathbf{J}}_i \cdot \mathbf{n}_1 dS + \iint_{S_2} \hat{\mathbf{J}}_i \cdot \mathbf{n}_2 dS,$$

and further noticing that $\mathbf{n}_2 = -\mathbf{n}_1$ on Σ' , subtracting equations (1.11) and (1.12) from equation (1.10) leads to

$$\iint_{\Sigma'} \left\{ \hat{R}_i^\Sigma + [\hat{\mathbf{J}}_i]_2^1 \cdot \mathbf{n}_1 \right\} dS = 0, \quad (1.13)$$

where we denote $[\hat{\mathbf{J}}_i]_2^1 = \hat{\mathbf{J}}_i|_1 - \hat{\mathbf{J}}_i|_2$. This equation holds for any portion Σ' of Σ and thus, the integrand must be identically equal to 0, leading to the following general continuity equation at interfaces:

$$\hat{R}_i^\Sigma + [\hat{\mathbf{J}}_i]_2^1 \cdot \mathbf{n}_1 = 0. \quad (1.14)$$

1.4 Derived conservation equations

We denote

- a given phase by the superscript 's' (solids) and 'f' (porewater, fluid), any phase by the superscript ' α ';
- $\varphi = \varphi(z, t)$ the porosity of the sediment, as a function of depth and time, which is equal to the ratio between the volume of the interconnected porewater to the bulk sediment volume;
- φ^f the fluid volume fraction and φ^s the solid volume fraction;
- I^f the inventory of porewater solutes and I^s that of solid constituents;
- ρ_i the density of constituent i ;
- ϑ_i the specific volume of constituent i , which we take as a constant for a given solid constituent, in which case we have $\vartheta_i = 1/\rho_i$;
- \hat{C}_i the (volumetric) concentration of a sediment constituent i with respect to the bulk sediment, and C_i^α its concentration with respect to the phase it belongs to ($\alpha = f, s$).

Neglecting not connected void spaces, and considering that there are only two phases in the porous medium under consideration, we have:

$$\varphi^f = \varphi(z, t) \quad (1.15)$$

$$\varphi^f + \varphi^s = 1 \quad (1.16)$$

$$\varphi^s = 1 - \varphi(z, t) \quad (1.17)$$

Furthermore

$$\hat{C}_i = \varphi^\alpha C_i^\alpha \quad (1.18)$$

where $\alpha = s, f$ denotes the phase i belongs to.

The total solids' volume conservation requires that

$$\sum_{i \in I^s} \vartheta_i \hat{C}_i = \varphi^s \quad \text{and} \quad \sum_{i \in I^s} \vartheta_i C_i^s = 1 \quad (1.19)$$

If the various ρ_i are independent of time and space, we further have

$$\sum_{i \in I^s} \left(\vartheta_i \frac{\partial \hat{C}_i}{\partial z} \right) = \frac{\partial \varphi^s}{\partial z} \quad \text{and} \quad \sum_{i \in I^s} \left(\vartheta_i \frac{\partial C_i^s}{\partial z} \right) = 0. \quad (1.20)$$

Chapter 2

One-dimensional sediment model

2.1 Basic hypotheses

In a first time, the model equations for the particular one-dimensional case are detailed, without any particular hypotheses on, e. g., compressibility of phases, time-dependency of porosity, etc. The only assumptions made are the following, serving only to clarify the adopted setting :

- the model covers a limited section of sediment, supposed to be horizontally homogeneous, with a bioturbated layer extending from the top of the sediment column, down to some depth above or at the bottom of the modelled section (see Figure 2.1);
- concentration profiles $C_i^\alpha = C_i^\alpha(z, t)$ are continuous in both time and space – their derivatives may, however, present discontinuities across given interfaces (e.g., the bottom of the bioturbated layer, or the bottom of the modelled section).

2.2 General equations

2.2.1 Regular equation

The special equations for the one-dimensional case can be derived in a straight manner from the general equations (1.4) and (1.14). The coordinate base is depicted in Figure 2.1. z denotes the vertical coordinate, increasing with depth from $z = z_T$ at the sediment-water interface, e_z the base vector. A general transport flux \hat{J}_i can then be written as $\hat{J}_i = \hat{J}_i e_z$, just

like any other vector (e.g., $\mathbf{u} = ue_z$ or $\mathbf{w} = we_z$). As a consequence, the general equation (1.4) becomes

$$\frac{\partial \hat{C}_i}{\partial t} + \frac{\partial \hat{J}_i}{\partial z} - \hat{R}_i^V = 0. \quad (2.1)$$

Let us recall that $\hat{R}_i^V = \hat{P}_i^V - \hat{D}_i^V$, where $\hat{P}_i^V \geq 0$ and $\hat{D}_i^V \geq 0$ are respectively the total production and destruction (or disappearance) rates for constituent i .

2.2.2 Interface equation

General interface The normal vectors \mathbf{n} at the top and bottom interfaces, oriented as shown in Figure 2.1 are both equal to \mathbf{e}_z . Adopting that same orientation of the normal vector at an arbitrary interface located at $z = z_\Sigma$, the flux continuity equation (1.14) simplifies to

$$\hat{R}_i^\Sigma + (\hat{J}_i^- - \hat{J}_i^+) = 0. \quad (2.2)$$

Here, \hat{J}_i^- is the value for the flux of constituent i above the interface (at z_Σ^- , i.e., the limit value of \hat{J}_i in z_Σ obtained when z increases to z_Σ) and \hat{J}_i^+ is similarly the value of \hat{J}_i below the interface (at z_Σ^+ , i.e., the limit value of \hat{J}_i in z_Σ obtained when z decreases to z_Σ).

Sediment top and bottom interfaces In the special situations at the top and at the bottom it is convenient to write the external fluxes (i.e., \hat{J}_i^- at the top and \hat{J}_i^+ at the bottom) as the difference between algebraically positive source (\hat{I}_i : input) and sink (\hat{O}_i : output) terms, relative to the sediment body. If \hat{J}_i represents a net input flux ($\hat{I}_i \geq \hat{O}_i$), the adopted sign conventions imply that it is positive at the top (oriented along increasing z) and negative at the bottom, where an input flux is oriented along decreasing z . The opposite holds if \hat{J}_i represents a net output flux ($\hat{O}_i \geq \hat{I}_i$).

Hence, at the top, $\hat{J}_i^- = \hat{I}_i^{\text{top}} - \hat{O}_i^{\text{top}}$ while at the bottom, $\hat{J}_i^+ = \hat{O}_i^{\text{bot}} - \hat{I}_i^{\text{bot}}$. $\hat{I}_i^{\text{top}} \geq 0$ and $\hat{I}_i^{\text{bot}} \geq 0$ represent any inputs of constituent i by means of transport (and neither by reaction nor non-local exchange) at the top and at the bottom respectively. Similarly, $\hat{O}_i^{\text{top}} \geq 0$ and $\hat{O}_i^{\text{bot}} \geq 0$ represent any outputs. The special equations at the top and at the bottom of the represented sediment layer thus write

$$\hat{P}_i^{\Sigma \text{top}} - \hat{D}_i^{\Sigma \text{top}} + \hat{I}_i^{\text{top}} - \hat{O}_i^{\text{top}} - \hat{J}_i^{z_T^+} = 0 \quad (2.3)$$

and

$$\hat{P}_i^{\Sigma\text{bot}} - \hat{D}_i^{\Sigma\text{bot}} + \hat{I}_i^{\text{bot}} - \hat{O}_i^{\text{bot}} + \hat{J}_i^{\bar{z}_B} = 0, \quad (2.4)$$

where the net reaction rates $\hat{R}_i^{\Sigma\text{top}}$ and $\hat{R}_i^{\Sigma\text{bot}}$ have been detailed in terms of their respective production and transformation rates.

2.3 Integral conservation equation

Equation (2.1) can be integrated between any two given depths $z = z_1$ and $z = z_2$ ($z_1 \geq z_2$) to produce an integral mass balance equation:

$$\frac{\partial \hat{M}_i}{\partial t} = - \hat{J}_i|_{z=z_2} + \hat{J}_i|_{z=z_1} + \int_{z_1}^{z_2} \hat{R}_i^V dz, \quad (2.5)$$

where

$$\hat{M}_i = \int_{z_1}^{z_2} \hat{C}_i dz$$

is the total mass of constituent i (in units of mass per unit area of total sediment) contained in the sediment layer delimited by $z = z_1$ and $z = z_2$.

2.4 Types of fluxes in 1D

Various types of fluxes can be considered:

- advective fluxes;
- diffusive fluxes;
- non-local transport fluxes, which are more conveniently included as non-local source and sink terms in the reactions.

In the general local diagenesis equation, fluxes must be expressed in units of mass per unit surface area of *total* sediment per unit time.

2.4.1 Advection

Solutes.

For a solute i , of concentration C_i^f in porewater:

$$\hat{J}_{\text{adv}i} = u \hat{C}_i = \phi^f u C_i^f, \quad (2.6)$$

where $u = u(z, t)$ is the velocity of the porewater flow with respect to the sediment-water interface.

Solids.

For a solid constituent i , of concentration C_i^s in the solid phase:

$$\hat{J}_{adv i} = w\hat{C}_i = \varphi^s w C_i^s, \quad (2.7)$$

where $w = w(z, t)$ is the velocity of the solids with respect to the sediment-water interface.

2.4.2 Diffusion

Solutes: Molecular and Ionic Diffusion

Diffusion acts to eliminate gradients (of concentration or chemical potential). In porewater only, the diffusive transport of a solute i , in units of mass per unit surface area of “porewater surface” per unit time is given by

$$J_{diff i}^f = -D_i^{sed} \frac{\partial C_i^f}{\partial z}, \quad (2.8)$$

where

- D_i^{sed} is the effective (total) sediment diffusion coefficient of the solute in the pores;
- $\partial C_i^f / \partial z$ is the concentration gradient of solute i in the porewater along the vertical.

It must be noticed that

- $J_{diff i}^f$ needs to be related to $\hat{J}_{diff i}$, the mass flux per unit surface area of total sediment;
- diffusion actually follows a tortuous path, of length l , and not the direct vertical one, and thus sees other, smaller gradients.

D_i^{sed} is related to D_i^{sw} , the diffusion coefficient in free *seawater* solution (i. e., $\varphi = 1$) by

$$D_i^{sed} = \frac{D_i^{sw}}{\theta^2}, \quad (2.9)$$

where $\theta = dl/dz$ is the tortuosity. D_i^{sw} in turn can be related to D_i^0 , the diffusion coefficient in infinite solution at atmospheric pressure, by [Li and Gregory, 1974]

$$\frac{D_i^{sw}}{D_i^0} = \frac{\mu^0}{\mu^{sw}}, \quad (2.10)$$

Table 2.1: Parameterisations for tortuosity (θ^2) as a function of porosity (φ).

Name	Expression	Parameter values	Statistical r^2
Archie's law	$\theta^2 = \varphi^{1-m}$	$m = 2.14 \pm 0.03$	0.53
Burger-Frieke eqn.	$\theta^2 = \varphi + a(1 - \varphi)$	$a = 3.79 \pm 0.11$	0.64
Weissberg relat.	$\theta^2 = 1 - b \ln \varphi$	$b = 2.02 \pm 0.08$	0.65

where μ^0 and μ^{sw} are the dynamic viscosities of pure water at one atmosphere pressure and of seawater (at the required pressure), respectively.

Empirical measurement have shown that θ^2 is related to the porosity φ via a formation factor F (see, e.g., Ullman and Aller [1982]):

$$\theta^2 = \varphi F. \quad (2.11)$$

The formation factor is derived from electrical resistivity measurements:

$$F = \frac{\text{resistivity of total (bulk) sediment}}{\text{resistivity of porewater only}} \quad (2.12)$$

Various empirical parametrisations for $\theta = \theta(\varphi)$ have been proposed. The parametrisations from Table 2.1 are taken from the compilation of Boudreau [1997, pp. 129–132].

The relationship between $J_{\text{diff } i}^{\text{f}}$ and $\hat{J}_{\text{diff } i}$ can be derived as follows. The transfer of a mass ΔM_i of constituent i through a bulk sediment section, of surface area ΔA_{bsed} , where $\Delta A_{\text{bsed}} = \Delta A_{\text{pwat}} + \Delta A_{\text{soli}}$, with the subscript 'pwat' referring to the porewater and 'soli' referring to the solid phase of the sediment:

$$\begin{aligned} \hat{J}_{\text{diff } i} &= \frac{\Delta M_i}{\Delta A_{\text{bsed}} \Delta t} = \frac{\Delta M_i}{\Delta A_{\text{pwat}} \Delta t} \times \frac{\Delta A_{\text{pwat}} \Delta z}{\Delta A_{\text{bsed}} \Delta z} \\ &= J_{\text{diff } i}^{\text{f}} \times \frac{\Delta V_{\text{pwat}}}{\Delta V_{\text{bsed}}} \\ &= J_{\text{diff } i}^{\text{f}} \times \varphi^{\text{f}}, \end{aligned}$$

where Δz is an arbitrary small depth interval around the section under consideration. Hence,

$$\hat{J}_{\text{diff } i} = -\varphi^{\text{f}} D_i^{\text{sed}} \frac{\partial C_i^{\text{f}}}{\partial z} = -\varphi^{\text{f}} \frac{D_i^{\text{sw}}}{\theta^2} \frac{\partial C_i^{\text{f}}}{\partial z} \quad (2.13)$$

Table 2.2 reports a few parametrisations for D_i^0 for common dissolved constituents.

Table 2.2: Selected infinite dilution diffusion coefficient parametrisations

i	D_i^0	Reference
CO_3^{2-}	$(4.33 + 0.199^\circ t) \times 10^{-6}$	B97 Tab. 4.8
HCO_3^-	$(5.06 + 0.275^\circ t) \times 10^{-6}$	B97 Tab. 4.8
CO_2	$^\dagger 4.72 \times 10^{-9} T / (37.3^{0.6} \mu)$	B97 Eq. (4.57) & Tab. 4.3
	$0.05019 \times \exp(-19.51/RT)$	B97 Eq. (4.60) & Tab. 4.4
	$^\ddagger (0.1954 + 0.005089 T / \mu) \times 10^{-5}$	B97 Eq. (4.59) & Fig. 4.6
B(OH)_3	349	BC93
B(OH)_4^-	$= D_{\text{B(OH)}_3}^0 \times (D_{\text{HCO}_3^-}^0 / D_{\text{CO}_2}^0)$	BC93
O_2	$^\dagger 4.72 \times 10^{-9} T / (27.9^{0.6} \mu)$	B97 Eq. (4.57) & Tab. 4.3
	$^\ddagger (0.2604 + 0.006383 T / \mu) \times 10^{-5}$	B97 Eq. (4.58) & Fig. 4.5
H^+	$(54.4 + 1.555^\circ t) \times 10^{-6}$	B97 Tab. 4.7
OH^-	$(25.9 + 1.094^\circ t) \times 10^{-6}$	B97 Tab. 4.8

D_i^0 values obtained are in $\text{cm}^2 \text{s}^{-1}$. $^\circ t$ denotes temperature in $^\circ\text{C}$ and T temperature in K. μ is the dynamic viscosity of water in poise (formulae marked by †) or centipoise (formulae marked by ‡). μ can be parametrised as a function of pressure, temperature and salinity. Diffusion coefficients for seawater can be derived from those calculated here by applying equation (2.10). References: B97 – Boudreau [1997], BC93 – Boudreau and Canfield [1993].

Solids: Bioturbation

One possible mathematical representation of the biologically mediated mixing in sediments is to consider it as a diffusive process. There are two extreme possibilities that can be taken into account [Boudreau, 1997, p. 46]:

- to mix solids and fluid together to remove porosity gradients (*inter-phase mixing*), leading to

$$\hat{J}_{\text{inter } i} = -D^{\text{inter}} \frac{\partial \varphi^s C_i^s}{\partial z} \quad (2.14)$$

for a solid constituent of concentration C_i^s in the solid phase;

- not to mix solids with fluid, but both separately although simultaneously (*intrapphase mixing*), leading to

$$\hat{J}_{\text{intra } i} = -\varphi^s D_i^{\text{intra}} \frac{\partial C_i^s}{\partial z} \quad (2.15)$$

for a solid constituent of concentration C_i^s in the solid phase.

Table 2.3: Infinite dilution and effective diffusion coefficient values (in cm^2/yr).

i	20 °C	5 °C	2 °C	0.5 °C
	D_i^0			
CO_3^{2-}	262	168	149	140
HCO_3^-	333	203	177	164
CO_2	529	356	326	311
O_2	668	451	413	395
NO_3^-	545	361	324	306
NH_3	634	400	358	339
NH_4^+	560	365	326	306
	D_i^{sw} at DBSL = 0 m			
CO_3^{2-}	244	159	142	133
HCO_3^-	310	192	168	156
CO_2	492	336	309	297
O_2	621	426	392	377
NO_3^-	507	341	308	291
NH_3	590	377	340	323
NH_4^+	521	344	309	292
	D_i^{sw} in situ			
DBSL	8 m	1119 m	3069 m	5033 m
CO_3^{2-}	244	160	145	137
HCO_3^-	310	193	172	161
CO_2	492	339	316	305
O_2	621	429	401	388
NO_3^-	507	343	314	300
NH_3	590	380	347	333
NH_4^+	521	347	316	301

D^{inter} is the *interphase* biodiffusion coefficient, species-independent as whole packets of sediment are exchanged during this process; D_i^{intra} is the *intrapphase* biodiffusion coefficient, which might possibly depend on species [Meysman et al., 2005]. Bioturbational mixing also affects solutes:

- with *interphase mixing*, the corresponding flux is

$$\hat{J}_{\text{inter } i} = -D^{\text{inter}} \frac{\partial \varphi^f C_i^f}{\partial z} \quad (2.16)$$

for a dissolved constituent i , of concentration C_i^f in the porewaters;

- with *intrapphase mixing*, it writes

$$\hat{J}_{\text{intra } i} = -\varphi^f D_i^{\text{intra}} \frac{\partial C_i^f}{\partial z} \quad (2.17)$$

for a dissolved constituent i , of concentration C_i^f in the porewaters.

A complete discussion regarding the differences between inter- and intraphase mixing can be found in Boudreau [1986] and Boudreau [1997, pp. 42–47]. A recent revision of the diagenetic theory is presented by Meysman et al. [2005]. Typical expressions for the biodiffusion coefficient are reported in Table 2.4; Table 2.5 lists resulting values.

2.4.3 Non-local transport

Non-local fluxes represent processes that lead to a transport of material between distant points, and not locally.

Bioirrigation

Bioirrigation is a transport process that is more conveniently represented as a non-local process instead of a diffusional one.

Table 2.4: Typical bioturbation coefficient expressions from the literature

Reference and notes	D^{bt} expression
Archer and Maier-Reimer [1994, caption to Fig. 1, p. 261], for organic matter only; calcite supposed to be well-mixed	$150 \text{ cm}^2 \text{ kyr}^{-1}$
Archer [1996, Table 1, p. 519]: slow and fast values for sensitivity tests	$0.15 \text{ cm}^2 \text{ kyr}^{-1}$ (standard), $0.45 \text{ cm}^2 \text{ kyr}^{-1}$ (fast) or $0.05 \text{ cm}^2 \text{ kyr}^{-1}$ (slow)
Archer et al. [2002], with reference to Martin and Sayles [1990] for the depth attenuation (which should probably be Martin and Sayles [1994], referring themselves to Christensen [1982]), Boudreau [1994] for the D^{bt} - w relationship (there are actually two of them), and Tromp et al. [1995] for the $\text{Rain}_{\text{OrgC}}$ - w relationship; the reported relationship cannot be reproduced the way it is presented: either the factor is 0.0614 and the exponent 0.71 (with Boudreau's power 0.6 law), or the factor is 0.0267 and the exponent 0.81 (with Boudreau's power 0.69 law).	$\frac{D^{bt}}{D_0^{bt}} = \exp\left(-\left(\frac{z}{z_{\text{mix}}}\right)^2\right) \times \frac{[\text{O}_2]_{\text{bw}}}{[\text{O}_2]_{\text{bw}} + 20 \mu\text{mol}'}$ $\text{with } \frac{D_0^{bt}}{[\text{cm}^2 \text{ yr}^{-1}]} = 0.0232 \times \left(\frac{\text{Rain}_{\text{OrgC}}}{[\text{mol cm}^2 \text{ yr}^{-1}]}\right)^{0.85} \text{ and } z_{\text{mix}} = 8 \text{ cm}$

Table 2.4 (cont'd): Typical bioturbation coefficient expressions from the literature

Reference	D^{bt} expression
Meile and Van Cappellen [2005], with reference to Boudreau [1994], Tromp et al. [1995], Middelburg et al. [1997] and Nie et al. [2001]	$\frac{D^{bt}}{D_0^{bt}} = \frac{1}{2} \operatorname{erfc}\left(\frac{z - z_{\text{mix}}}{s}\right), \quad \text{with } \frac{D_0^{bt}}{[\text{cm}^2 \text{ yr}^{-1}]} = 5.2 \times 10^{(0.76 - 0.40 \times \text{DBSL}/[\text{km}])}, \quad z_{\text{mix}} = 10 \text{ cm and } s = 1 \text{ cm}$
Boudreau [1994]	$\frac{D^{bt}}{[\text{cm}^2 \text{ yr}^{-1}]} = 15.7 \times \left(\frac{w}{[\text{cm yr}^{-1}]}\right)^{0.6}, \quad w \text{ being the sedimentation rate}$ $\frac{D^{bt}}{[\text{cm}^2 \text{ yr}^{-1}]} = 15.7 \times \left(\frac{w}{[\text{cm yr}^{-1}]}\right)^{0.69} \quad \text{from } ^{210}\text{Pb} \text{ analyses only}$
Soetaert et al. [1996a, p. 1028], with reference to Boudreau [1994] (who calls w the burial velocity)	$D^{bt} = D_0^{bt} \text{ for } z \leq z_b, \text{ and } \frac{D^{bt}}{D_0^{bt}} = \exp\left(-\frac{z - z_b}{d_b}\right) \text{ for } z > z_b,$ $\text{with } \frac{D_0^{bt}}{[\text{cm}^2 \text{ d}^{-1}]} = \frac{15}{365} \times \left(\frac{w}{[\text{cm yr}^{-1}]}\right)^{0.6} \text{ and } z_b = 5 \text{ cm}, d_b = 1 \text{ cm},$ $w \text{ being the sedimentation rate}$
Middelburg et al. [1996, Table 1, p. 663]	$\frac{D^{bt}}{[\text{cm}^2 \text{ yr}^{-1}]} = 4.4 \times 10^{(0.7624 - 0.000397 \times (DBSL/[\text{m}]))}$
Martin and Sayles [1996]	$\frac{D^{bt}}{D_0^{bt}} = \exp\left(-\left(\frac{z}{z_{\text{mix}}}\right)^2\right), \text{ with } D_0^{bt} = 0.3 \text{ cm}^2 \text{ yr}^{-1} \text{ and } z_{\text{mix}} = 5 \text{ cm}$

Table 2.4 (cont'd): Typical biodiffusion coefficient expressions from the literature

Reference	D^{bt} expression
Tromp et al. [1995, eq. 4, p. 1261]	$\log\left(\frac{D_0^{bt}}{[\text{cm}^2 \text{ yr}^{-1}]}\right) = 1.63 + 0.85 \times \log\left(\frac{w}{[\text{cm yr}^{-1}]}\right)$, where w is the sedimentation rate
Heinze et al. [1999, p. 228], citing Soetaert et al. [1996b]; low value to account for implicit numerically induced diffusion	$15 \text{ cm}^2 / (1000 \text{ yr}) = 0.015 \text{ cm}^2 \text{ yr}^{-1}$
Rabouille et al. [1997], by inversion of Southern Ocean silica recycling data	$D^{bt} = 0.126 - 0.315 \text{ cm}^2 \text{ yr}^{-1}$
Rabouille et al. [2001], for the BENGAL site in the North Atlantic Ocean, where DBSL = 4850 m	$D^{bt} = 0.32 \text{ cm}^2 \text{ yr}^{-1}$
Berner [1980, Table 3-5, p. 50]: ^{210}Pb - and Pu -based values only, for deep-sea, pelagic sediments	$D^{bt} = 1 - 14 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$
Munhoven [2007]: following Archer and Maier-Reimer [1994]	$D^{bt} = 0.15 \text{ cm}^2 \text{ yr}^{-1}$

Table 2.5: Biodiffusion coefficient values (in cm^2/yr)

Reference	$D_{0\text{cm}}^{\text{bt}}$	$D_{5\text{cm}}^{\text{bt}}$	$D_{10\text{cm}}^{\text{bt}}$	Notes
B80	0.0315–0.442			
B94 (pow. 0.6)		15.7		$w = 1 \text{ cm yr}^{-1}$
		1.92		$w = 0.03 \text{ cm yr}^{-1}$
		0.729		$w = 0.006 \text{ cm yr}^{-1}$
		0.201		$w = 0.0007 \text{ cm yr}^{-1}$
B94 (pow. 0.69)		15.7		$w = 1 \text{ cm yr}^{-1}$
		1.40		$w = 0.03 \text{ cm yr}^{-1}$
		0.460		$w = 0.006 \text{ cm yr}^{-1}$
		0.104		$w = 0.0007 \text{ cm yr}^{-1}$
MS96	0.3	0.110	0.00549	
Tea95		42.7		$w = 1 \text{ cm yr}^{-1}$
		2.17		$w = 0.03 \text{ cm yr}^{-1}$
		0.551		$w = 0.006 \text{ cm yr}^{-1}$
		0.0888		$w = 0.0007 \text{ cm yr}^{-1}$
Sea96	15.0	15.0	0.101	$w = 1 \text{ cm yr}^{-1}$
	1.83	1.83	0.0123	$w = 0.03 \text{ cm yr}^{-1}$
	0.697	0.697	0.00469	$w = 0.006 \text{ cm yr}^{-1}$
	0.192	0.192	0.00129	$w = 0.0007 \text{ cm yr}^{-1}$
Mea96		25.3		DBSL = 8 m
		9.15		DBSL = 1119 m
		1.54		DBSL = 3069 m
		0.256		DBSL = 5033 m
Rea97		0.315		DBSL = 4500–4900 m
Rea01		0.32		DBSL = 4850 m
MVC05	29.7	29.7	14.9	DBSL = 8 m
	10.7	10.7	5.34	DBSL = 1119 m
	1.77	1.77	0.886	DBSL = 3069 m
	0.290	0.290	0.145	DBSL = 5033 m

Continued next page.

Table 2.5 (cont'd): Biodiffusion coefficient values (cm²/yr)

Reference	$D_{0\text{cm}}^{\text{bt}}$	$D_{5\text{cm}}^{\text{bt}}$	$D_{10\text{cm}}^{\text{bt}}$	Notes
AMR94		0.150		
A96		0.00015		standard
		0.00045		fast
		0.00005		slow
Hea99		0.015		
Aea02	16.2	11.0	3.40	$F_{\text{OrgC}} = 2570 \mu\text{mol cm}^{-2} \text{yr}^{-1}$
	1.21	0.819	0.254	$F_{\text{OrgC}} = 130 \mu\text{mol cm}^{-2} \text{yr}^{-1}$
	0.380	0.257	0.0796	$F_{\text{OrgC}} = 33.2 \mu\text{mol cm}^{-2} \text{yr}^{-1}$
	0.0804	0.0544	0.0169	$F_{\text{OrgC}} = 5.35 \mu\text{mol cm}^{-2} \text{yr}^{-1}$

Values for different levels obtained by adopting $w = 1, 0.03, 0.006$ and $0.0007 \text{ cm yr}^{-1}$, converted to DBSL and F_{OrgC} by using Tromp et al.'s [1995] SWI- w and F^o - w relationships (their equations 17 and 20, respectively).

2.5 Sources and sinks: reactions

2.5.1 Carbonate mineral dissolution

The general rate expression for carbonate dissolution may be written, if constituent i is a carbonate mineral (aragonite, magnesian calcite, or calcite):

$$\bar{T}_{\text{diss } i}^V = \begin{cases} \bar{k}_i \times (K_{\text{sat } i} - K_{\text{act } i})^{n_i} & \text{if } K_{\text{sat } i} > K_{\text{act } i} \\ 0 & \text{if } K_{\text{sat } i} \leq K_{\text{act } i} \end{cases} \quad (2.18)$$

where $\bar{T}_{\text{diss } i}^V$ is the dissolution rate in units of mass of the carbonate mineral (aragonite, magnesian calcite, or calcite) in the dissolving particles, that gets dissolved per unit surface area of particles, $K_{\text{sat } i}$ is the saturation product of the dissolving mineral, and $K_{\text{act } i}$ is the actual, *in situ* concentration product, \bar{k}_i is the dissolution rate constant and n_i is the reaction rate order.

In order to link $\bar{T}_{\text{diss } i}^V$ to $\hat{T}_{\text{diss } i}^V$ (units of mass per unit volume of total sediment) required in equation 2.1, we may write

$$\hat{T}_{\text{diss } i}^V = \varphi^s \times C_i^s \times \bar{\mathcal{A}}_i \times \bar{T}_{\text{diss } i}^V \quad (2.19)$$

where C_i^s is the concentration of the dissolving carbonate particles in the solid phase of the sediment (units of mass per unit volume of solid sediment), and $\bar{\mathcal{A}}_i$ represents the specific surface area of the dissolving carbonate particles, in units of surface area per unit mass of carbonate particles.

$\bar{\mathcal{A}}_i$ is integrated into a new dissolution rate constant

$$k_i = \begin{cases} \bar{k}_i \times \bar{\mathcal{A}}_i \times (K_{\text{sat } i} - K_{\text{act } i})^{n_i} & \text{if } K_{\text{sat } i} > K_{\text{act } i} \\ 0 & \text{if } K_{\text{sat } i} \leq K_{\text{act } i} \end{cases} \quad (2.20)$$

With this definition, $\hat{T}_{\text{diss } i}^V$ becomes

$$\hat{T}_{\text{diss } i}^V = k_i \times \varphi^S \times C_i^S \quad (2.21)$$

Calcite

For calcite, $K_{\text{sat } i} = K_{\text{Calc}}$, which can be parametrised as a function of temperature (T), salinity (S) and applied pressure (P) or water depth below sea-level, and $K_{\text{act } i} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$. The calcium concentration $[\text{Ca}^{2+}]$ is directly related to salinity (S). Defining

$$k_{\text{Calc}} = \begin{cases} k_c \times \left(K_{\text{Calc}} - ([\text{Ca}^{2+}][\text{CO}_3^{2-}]) \right)^{n_c} & \text{if } K_{\text{Calc}} > [\text{Ca}^{2+}][\text{CO}_3^{2-}] \\ 0 & \text{if } K_{\text{Calc}} \leq [\text{Ca}^{2+}][\text{CO}_3^{2-}] \end{cases} \quad (2.22)$$

we may write the dissolution rate law as

$$\hat{T}_{\text{Calc diss}}^V = \varphi^S \times [\text{Calcite}] \times k_{\text{Calc}} \quad (2.23)$$

Aragonite

The rate law for aragonite is similar to that for calcite, except for the rate constant k_{Arag} , the solubility product (K_{Arag}) and possibly the rate order n_a . Accordingly,

$$k_{\text{Arag}} = \begin{cases} k_a \times \left(K_{\text{Arag}} - ([\text{Ca}^{2+}][\text{CO}_3^{2-}]) \right)^{n_a} & \text{if } K_{\text{Arag}} > [\text{Ca}^{2+}][\text{CO}_3^{2-}] \\ 0 & \text{if } K_{\text{Arag}} \leq [\text{Ca}^{2+}][\text{CO}_3^{2-}] \end{cases} \quad (2.24)$$

and

$$\hat{T}_{\text{Arag diss}}^V = k_{\text{Arag}} \times \varphi^S \times [\text{Aragonite}] \quad (2.25)$$

2.5.2 Organic matter degradation

For oxic organic matter degradation a Monod rate law expression is commonly adopted:

$$\hat{T}_{\text{OM degr}}^V = k_{\text{OM}} \times \varphi^S \times [\text{OrgMatter}] \times \frac{[\text{O}_2]}{M_{\text{O}_2} + [\text{O}_2]}. \quad (2.26)$$

Here, M_{O_2} is the half-saturation constant.

2.5.3 Dissolved carbon species interconversion reactions

If CO_3^{2-} is included as the only dissolved inorganic carbon species, there are actually no reactions to take into account.

If CO_2 and HCO_3^- are included together with CO_3^{2-} the following reaction needs to be considered,



where $r_{1/2}$ denotes the net (algebraic) rate at which the reaction proceeds from the left to the right.

If reaction (2.27) can be considered to be at equilibrium, then

$$K_2([\text{HCO}_3^-])^2 - K_1[\text{CO}_2][\text{CO}_3^{2-}] = 0, \quad (2.28)$$

where K_1 and K_2 are thermodynamic constants, that can be parameterised as a function of temperature (T), salinity (S) and pressure (P).

2.5.4 Borate species interconversion reactions

If borates are included in the model solutes as contributors to alkalinity, the following reaction also needs to be considered:



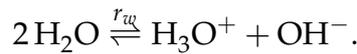
At equilibrium,

$$K_2[\text{B(OH)}_4^-][\text{HCO}_3^-] - K_b[\text{B(OH)}_3][\text{CO}_3^{2-}] = 0 \quad (2.30)$$

K_b is another thermodynamic constant, that is parametrised as a function of temperature (T), salinity (S) and pressure (P).

2.5.5 H_3O^+ and OH^-

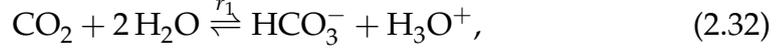
If either of OH^- or H_3O^+ is considered in conjunction with CO_3^{2-} , HCO_3^- and CO_2 , then the following reaction needs to be taken into account:



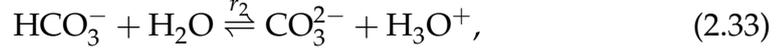
At equilibrium,

$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_w \quad (2.31)$$

In this case, it is more natural to split up reaction (2.27) in two parts



and



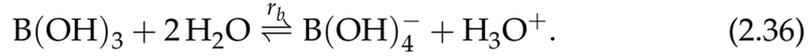
proceeding at respective rates r_1 and r_2 . The corresponding equilibrium relationships are

$$[\text{HCO}_3^-][\text{H}_3\text{O}^+] = K_1[\text{CO}_2]. \quad (2.34)$$

and

$$[\text{CO}_3^{2-}][\text{H}_3\text{O}^+] = K_2[\text{HCO}_3^-]. \quad (2.35)$$

If $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ are also considered, reaction (2.29) is replaced by



At equilibrium,

$$[\text{B}(\text{OH})_4^-][\text{H}_3\text{O}^+] = K_b[\text{B}(\text{OH})_3] \quad (2.37)$$

2.6 Detailed equations

The general 1D continuity equation (2.1) can now be detailed, simplified and further transformed in order to solve it.

2.6.1 Solids: general form of the equations

The total flux of a solid i , of concentration $\hat{C}_i = \varphi^s C_i^s$ is

$$\hat{J}_i = \hat{J}_i^{\text{inter}} + \hat{J}_i^{\text{intra}} + \hat{J}_i^{\text{adv}} \quad (2.38)$$

which, when taking into account the flux expressions from the previous sections, becomes

$$\hat{J}_i = -D^{\text{inter}} \frac{\partial \varphi^s C_i^s}{\partial z} - D_i^{\text{intra}} \varphi^s \frac{\partial C_i^s}{\partial z} + \varphi^s w C_i^s. \quad (2.39)$$

Both *interphase* and *intrapphase* mixing are considered here. In general, the biodiffusion coefficients may be depth-dependent, or even dependent on concentrations of other constituents.

In this version of the model, we suppose nevertheless that

1. $D_i^{\text{intra}} = D^{\text{intra}}$, i.e., the intraphase biodiffusion coefficient does not depend on species;
2. D^{intra} and D^{inter} may be depth-dependent functions;
3. the porosity profile is at steady-state ($\frac{\partial \varphi}{\partial t} = 0$).

The first of these hypotheses may represent an oversimplification [Bard, 2001, Meysman et al., 2005]. The last one may possibly lead to inconsistencies, as shown by Meysman et al. [2005]. In the present model, this is, however, not the case. First of all, the effect from heterogeneous reactions cannot be neglected here and they have a large influence on the compaction of the sediment here. On the other hand, the contradictions mentioned by Meysman et al. [2005] are avoided here, as the velocity is not prescribed here but calculated on the basis of volume conservation arguments.

If we develop equation (2.39), we can transform it into

$$\hat{J}_i = -\varphi^s (D^{\text{inter}} + D_i^{\text{intra}}) \frac{\partial C_i^s}{\partial z} + \left(\varphi^s w - D^{\text{inter}} \frac{\partial \varphi^s}{\partial z} \right) C_i^s \quad (2.40)$$

Notice that according to Meysman et al. [2005, eqn. (62)], the mass averaged velocity $w_{(m)}$, and the compaction velocity w_{comp} are related

$$w_{(m)} = w_{\text{comp}} - \frac{D^{\text{inter}}}{\varphi^s} \frac{\partial \varphi^s}{\partial z}.$$

Considering the grouping found for the linear term in C_i^s in equation (2.40), and further taking into account the hypothesis of incompressible phases in Meysman et al. [2005], the velocity w turns out to be the compaction velocity.

The complete equation describing the evolution of a solid i thus writes

$$\frac{\partial \varphi^s C_i^s}{\partial t} + \frac{\partial}{\partial z} \left(-\varphi^s (D^{\text{inter}} + D_i^{\text{intra}}) \frac{\partial C_i^s}{\partial z} + \left(\varphi^s w - D^{\text{inter}} \frac{\partial \varphi^s}{\partial z} \right) C_i^s \right) - \hat{R}_i^V = 0. \quad (2.41)$$

Taking our basic hypotheses into account, and defining

$$D^{\text{bt}} = D^{\text{inter}} + D_i^{\text{intra}} = D^{\text{inter}} + D^{\text{intra}} \quad (2.42)$$

and defining $\beta = \beta(z)$ such that

$$D^{\text{inter}} = \beta * D^{\text{bt}}, \quad (2.43)$$

we finally get the model equation considered here:

$$\boxed{\varphi^s \frac{\partial C_i^s}{\partial t} + \frac{\partial}{\partial z} \left(-\varphi^s D^{\text{bt}} \frac{\partial C_i^s}{\partial z} + \left(\varphi^s w - \beta D^{\text{bt}} \frac{\partial \varphi^s}{\partial z} \right) C_i^s \right) - \hat{R}_i^V = 0.} \quad (2.44)$$

2.6.2 Solids: derived relationships

There are a few relationships that can now be derived from the preceding. From equation (2.40),

$$\begin{aligned} \sum_{i \in I^s} \vartheta_i \hat{J}_i &= -\varphi^s D^{\text{inter}} \sum_{i \in I^s} \left(\vartheta_i \frac{\partial C_i^s}{\partial z} \right) - \varphi^s \sum_{i \in I^s} \left(D_i^{\text{intra}} \vartheta_i \frac{\partial C_i^s}{\partial z} \right) \\ &\quad + \left(\varphi^s w - D^{\text{inter}} \frac{\partial \varphi^s}{\partial z} \right) \sum_{i \in I^s} \vartheta_i C_i^s \end{aligned}$$

leading to

$$\sum_{i \in I^s} \vartheta_i \hat{J}_i = -\varphi^s \sum_{i \in I^s} \left(\vartheta_i D_i^{\text{intra}} \frac{\partial C_i^s}{\partial z} \right) + \varphi^s w - D^{\text{inter}} \frac{\partial \varphi^s}{\partial z} \quad (2.45)$$

after taking equations (1.19) and (1.20) into account.

Considering the basic hypotheses, equation (2.45) simplifies to

$$\boxed{\sum_{i \in I^s} \vartheta_i \hat{J}_i = \varphi^s w - \beta D^{\text{bt}} \frac{\partial \varphi^s}{\partial z}} \quad (2.46)$$

If equation (2.41) is written for all the solids i , each one multiplied by its respective ϑ_i , and all of them then summed up, we find that

$$\frac{\partial}{\partial t} \left(\sum_{i \in I^s} \vartheta_i \hat{C}_i \right) + \frac{\partial}{\partial z} \left(\sum_{i \in I^s} \vartheta_i \hat{J}_i \right) - \sum_{i \in I^s} \vartheta_i \hat{R}_i^V = 0,$$

which simplifies to

$$\frac{\partial \varphi^s}{\partial t} + \frac{\partial}{\partial z} \left(\sum_{i \in I^s} \vartheta_i \hat{J}_i \right) - \sum_{i \in I^s} \vartheta_i \hat{R}_i^V = 0. \quad (2.47)$$

Considering now equations (1.19) and (2.45), the previous equation can be developed to yield

$$\frac{\partial \varphi^s}{\partial t} + \frac{\partial}{\partial z} \left(-\varphi^s \sum_{i \in I^s} \left(\vartheta_i D_i^{\text{intra}} \frac{\partial C_i^s}{\partial z} \right) + \left(\varphi^s w - D^{\text{inter}} \frac{\partial \varphi^s}{\partial z} \right) \right) = \sum_{i \in I^s} \vartheta_i \hat{R}_i. \quad (2.48)$$

Equations (2.47) and (2.48) are valid in general, as long as different solids do not get advected at different rates, i. e., as long as w depends on z and t alone, but not on i .

Further taking our basic hypotheses into account, we get

$$\boxed{\frac{\partial}{\partial z} \left(\varphi^s w - \beta D^{bt} \frac{\partial \varphi^s}{\partial z} \right) = \sum_{i \in I^s} \vartheta_i \hat{R}_i.} \quad (2.49)$$

2.6.3 Solids: particular equations

All constituents will be identified by a one to three letter code indicated in each header.

Clay (cly)

Clay is supposed to be inert in the sediment column and thus $\hat{R}_{\text{cly}}^V \equiv 0$. Hence, setting $C_{\text{cly}}^s = [\text{Clay}]$

$$\varphi^s \frac{\partial C_{\text{cly}}^s}{\partial t} + \frac{\partial}{\partial z} \left(-\varphi^s D^{bt} \frac{\partial C_{\text{cly}}^s}{\partial z} + (\varphi^s w - \beta D^{bt} \frac{\partial \varphi^s}{\partial z}) C_{\text{cly}}^s \right) = 0. \quad (2.50)$$

Aragonite (arg)

Aragonite dissolves in the sediment column, depending on the degree of undersaturation. This is (currently) the only reaction considered for aragonite. Thus,

$$\hat{R}_{\text{arg}}^V = -\hat{T}_{\text{Arag diss}}^V.$$

Denoting $C_{\text{arg}}^s = [\text{Aragonite}]$, we thus have

$$\varphi^s \frac{\partial C_{\text{arg}}^s}{\partial t} + \frac{\partial}{\partial z} \left(-\varphi^s D^{bt} \frac{\partial C_{\text{arg}}^s}{\partial z} + (\varphi^s w - \beta D^{bt} \frac{\partial \varphi^s}{\partial z}) C_{\text{arg}}^s \right) + \hat{T}_{\text{Arag diss}}^V = 0. \quad (2.51)$$

with

$$\hat{T}_{\text{Arag diss}}^V = k_{\text{Arag}} \times \varphi^s \times C_{\text{arg}}^s$$

according to equation (2.25). The dissolution rate constant k_{Arag} is defined by equation (2.24), with $[\text{CO}_3^{2-}] = C_{\text{dc2}}^f$ – see below.

Calcite (clt)

Calcite dissolves in the sediment column, depending on the degree of undersaturation. This is (currently) the only reaction considered for calcite. Thus,

$$\hat{R}_{\text{clt}}^V = -\hat{T}_{\text{Calc diss}}^V$$

Denoting $C_{\text{clt}}^s = [\text{Calcite}]$, we thus have

$$\varphi^s \frac{\partial C_{\text{clt}}^s}{\partial t} + \frac{\partial}{\partial z} \left(-\varphi^s D^{\text{bt}} \frac{\partial C_{\text{clt}}^s}{\partial z} + (\varphi^s w - \beta D^{\text{bt}} \frac{\partial \varphi^s}{\partial z}) C_{\text{clt}}^s \right) + \hat{T}_{\text{Calc diss}}^V = 0. \quad (2.52)$$

with

$$\hat{T}_{\text{Calc diss}}^V = k_{\text{Calc}} \times \varphi^s \times C_{\text{clt}}^s$$

according to equation (2.23). The dissolution rate constant k_{Calc} being defined by equation (2.22), with $[\text{CO}_3^{2-}] = C_{\text{dc2}}^f$ – see below.

Organic Matter (om)

Organic matter degrades in the sediment column, releasing all of its constituents into solution. Relevant for the present model is only the release of dissolved $[\text{CO}_2]$. Thus,

$$\hat{R}_{\text{om}}^V = -\hat{T}_{\text{OM degr}}^V$$

Denoting $C_{\text{om}}^s = [\text{OrgMatter}]$, we thus have

$$\varphi^s \frac{\partial C_{\text{om}}^s}{\partial t} + \frac{\partial}{\partial z} \left(-\varphi^s D^{\text{bt}} \frac{\partial C_{\text{om}}^s}{\partial z} + (\varphi^s w - \beta D^{\text{bt}} \frac{\partial \varphi^s}{\partial z}) C_{\text{om}}^s \right) + \hat{T}_{\text{OM degr}}^V = 0. \quad (2.53)$$

with

$$\hat{T}_{\text{OM degr}}^V = k_{\text{OM}} \times \varphi^s \times C_{\text{om}}^s$$

(equation (2.26)).

2.6.4 Solutes: general form of the equations

The total flux of a solute i of concentration $\hat{C}_i^f = \varphi C_i^f$ is

$$\hat{j}_i = \hat{j}_i^{\text{diff}} + \hat{j}_i^{\text{inter}} + \hat{j}_i^{\text{intra}} + \hat{j}_i^{\text{adv}}, \quad (2.54)$$

Table 2.6: Rapid interconversion rate expressions

	with OH^- and H_3O^+	without OH^- and H_3O^+
$r_{\text{dc}2}$	r_2	$-r_{1/2} - r_{2/b}$
$r_{\text{dc}1}$	$r_1 - r_2$	$2r_{1/2} + r_{2/b}$
$r_{\text{dc}0}$	$-r_1$	$-r_{1/2}$
$r_{\text{db}1}$	r_b	$r_{2/b}$
$r_{\text{db}0}$	$-r_b$	$-r_{2/b}$
r_{oh}	r_w	—
$r_{\text{h}3\text{o}}$	$r_1 + r_2 + r_b + r_w$	—

When developed with the flux expressions derived in the previous section, equation (2.54) becomes

$$\hat{J}_i = -\varphi^f \frac{D_i^{\text{sw}}}{\theta^2} \frac{\partial C_i^f}{\partial z} - D^{\text{inter}} \frac{\partial \varphi^f C_i^f}{\partial z} - \varphi^f D_i^{\text{intra}} \frac{\partial C_i^f}{\partial z} + \varphi^f u C_i^f$$

Bioturbation is in general orders of magnitude slower than molecular and ionic diffusion in mixing porewater solutes (D^{inter} and D_i^{intra} are orders of magnitude smaller than D_i^{sw}). The effect of bioturbation on solutes will therefore be neglected here. Hence, the previous equation simplifies to

$$\hat{J}_i = -\varphi^f \frac{D_i^{\text{sw}}}{\theta^2} \frac{\partial C_i^f}{\partial z} + \varphi^f u C_i^f \quad (2.55)$$

The complete equation describing the evolution of a solute i then writes:

$$\boxed{\varphi^f \frac{\partial C_i^f}{\partial t} + \frac{\partial}{\partial z} \left(-\varphi^f \frac{D_i^{\text{sw}}}{\theta^2} \frac{\partial C_i^f}{\partial z} + \varphi^f u C_i^f \right) - \hat{R}_i^V = 0.} \quad (2.56)$$

2.6.5 Solutes: particular equations

In the following listing of equations, irrelevant terms in the reaction terms (i.e., contributions of not represented terms) should simply be neglected.

Dissolved inorganic carbon species

CO_3^{2-} (dc2)

Possible contributions to the reaction term in the evolution equation for CO_3^{2-} , $\hat{R}_{\text{dc}2}^V$ come from the dissolution of aragonite, calcite, and the chem-

ical reactions with other solutes:

$$\hat{R}_{dc2}^V = \hat{T}_{Arag\ diss}^V / \chi_{arg} + \hat{T}_{Calc\ diss}^V / \chi_{clt} + r_{dc2}.$$

The form of the rapid interconversion rate r_{dc2} depends on whether OH^- and H_3O^+ are included in the set of solute species in the model or not (see Table 2.6). χ_{arg} and χ_{clt} are conversion factors to respectively convert the mass of aragonite and calcite minerals dissolved into equivalent CO_3^{2-} yields. Denoting $C_{dc2}^f = [\text{CO}_3^{2-}]$, we thus have

$$\begin{aligned} \varphi^f \frac{\partial C_{dc2}^f}{\partial t} + \frac{\partial}{\partial z} \left(-\varphi^f \frac{D_{dc2}^{sw}}{\theta^2} \frac{\partial C_{dc2}^f}{\partial z} + \varphi^f u C_{dc2}^f \right) \\ - \hat{T}_{Arag\ diss}^V / \chi_{arg} - \hat{T}_{Calc\ diss}^V / \chi_{clt} - r_{dc2} = 0. \end{aligned} \quad (2.57)$$

HCO_3^- (dc1)

Chemical reactions with other dissolved constituents are currently the only reactions to be considered for HCO_3^- :

$$\hat{R}_{dc1}^V = r_{dc1}$$

Denoting $C_{dc1}^f = [\text{HCO}_3^-]$, we thus have

$$\varphi^f \frac{\partial C_{dc1}^f}{\partial t} + \frac{\partial}{\partial z} \left(-\varphi^f \frac{D_{dc1}^{sw}}{\theta^2} \frac{\partial C_{dc1}^f}{\partial z} + \varphi^f u C_{dc1}^f \right) - r_{dc1} = 0. \quad (2.58)$$

CO_2 (dc0)

Organic matter degradation and reactions with other chemical constituents provide the potential terms to be included in the reaction term \hat{R}_{dc0}^V :

$$\hat{R}_{dc0}^V = \hat{T}_{OM\ degr}^V / \chi_{om} + r_{dc0}$$

χ_{om} is another conversion factor to convert the mass of organic matter remineralised into the equivalent yield of CO_2^{2-} . Denoting $C_{dc0}^f = [\text{CO}_2]$, we thus have

$$\varphi^f \frac{\partial C_{dc0}^f}{\partial t} + \frac{\partial}{\partial z} \left(-\varphi^f \frac{D_{dc0}^{sw}}{\theta^2} \frac{\partial C_{dc0}^f}{\partial z} + \varphi^f u C_{dc0}^f \right) - \hat{T}_{OM\ degr}^V / \chi_{om} - r_{dc0} = 0. \quad (2.59)$$

2.6.6 Total alkalinity contributors

Besides HCO_3^- and CO_3^{2-} , we consider B(OH)_4^- , and OH^- and H_3O^+ as potential contributors to total alkalinity.

B(OH)_4^- (db1) and B(OH)_3 (db0)

Chemical reactions with other dissolved constituents are currently the only reactions to be considered for B(OH)_4^- and B(OH)_3 :

$$\hat{R}_{\text{db1}}^V = r_{\text{db1}}$$

Denoting $C_{\text{db1}}^f = [\text{B(OH)}_4^-]$, we thus have

$$\varphi^f \frac{\partial C_{\text{db1}}^f}{\partial t} + \frac{\partial}{\partial z} \left(-\varphi^f \frac{D_{\text{db1}}^{\text{sw}}}{\theta^2} \frac{\partial C_{\text{db1}}^f}{\partial z} + \varphi^f u C_{\text{db1}}^f \right) - r_{\text{db1}} = 0. \quad (2.60)$$

Similarly,

$$\hat{R}_{\text{db0}}^V = r_{\text{db0}}.$$

Denoting $C_{\text{db0}}^f = [\text{B(OH)}_3]$, we thus have

$$\varphi^f \frac{\partial C_{\text{db0}}^f}{\partial t} + \frac{\partial}{\partial z} \left(-\varphi^f \frac{D_{\text{db0}}^{\text{sw}}}{\theta^2} \frac{\partial C_{\text{db0}}^f}{\partial z} + \varphi^f u C_{\text{db0}}^f \right) - r_{\text{db0}} = 0. \quad (2.61)$$

H_3O^+ (h3o) and OH^- (oh)

Chemical reactions with other dissolved constituents are currently the only reactions to be considered for H_3O^+ (h3o) and OH^- (oh): **!!! Organic degradation to be included !!!**

$$\hat{R}_{\text{oh}}^V = r_{\text{oh}}.$$

Denoting $C_{\text{oh}}^f = [\text{OH}^-]$, we thus have

$$\varphi^f \frac{\partial C_{\text{oh}}^f}{\partial t} + \frac{\partial}{\partial z} \left(-\varphi^f \frac{D_{\text{oh}}^{\text{sw}}}{\theta^2} \frac{\partial C_{\text{oh}}^f}{\partial z} + \varphi^f u C_{\text{oh}}^f \right) - r_{\text{oh}} = 0. \quad (2.62)$$

Similarly,

$$\hat{R}_{\text{h3o}}^V = r_{\text{h3o}}.$$

Denoting $C_{\text{h3o}}^f = [\text{H}_3\text{O}^+]$, we thus have

$$\varphi^f \frac{\partial C_{\text{h3o}}^f}{\partial t} + \frac{\partial}{\partial z} \left(-\varphi^f \frac{D_{\text{h3o}}^{\text{sw}}}{\theta^2} \frac{\partial C_{\text{h3o}}^f}{\partial z} + \varphi^f u C_{\text{h3o}}^f \right) - r_{\text{h3o}} = 0. \quad (2.63)$$

Equilibrium interconversion reactions

In general the chemical interconversion reactions proceed at rates that are orders of magnitudes faster than all other reactions. The reactions can thus be supposed to evolve in quasi-equilibrium. The reaction terms can then be eliminated from the equations by considering appropriate linear combinations of concentrations, and by including the thermodynamic equilibrium equations in the system of equations.

Dissolved inorganic carbon (dic)

A first such combination is dissolved inorganic carbon defined by $C_{\text{dic}}^f = C_{\text{dc2}}^f + C_{\text{dc1}}^f + C_{\text{dc0}}^f$. The corresponding linear combination of equations (2.57), (2.58) and (2.59) yields

$$\begin{aligned} & \varphi^f \frac{\partial}{\partial t} (C_{\text{dc2}}^f + C_{\text{dc1}}^f + C_{\text{dc0}}^f) \\ & + \frac{\partial}{\partial z} \left(-\frac{\varphi^f}{\theta^2} (D_{\text{dc2}}^{\text{sw}} \frac{\partial C_{\text{dc2}}^f}{\partial z} + D_{\text{dc1}}^{\text{sw}} \frac{\partial C_{\text{dc1}}^f}{\partial z} + D_{\text{dc0}}^{\text{sw}} \frac{\partial C_{\text{dc0}}^f}{\partial z}) \right. \\ & \quad \left. + \varphi^f u (C_{\text{dc2}}^f + C_{\text{dc1}}^f + C_{\text{dc0}}^f) \right) \\ & - (\hat{T}_{\text{Arag diss}}^V / \chi_{\text{arg}} + \hat{T}_{\text{Calc diss}}^V / \chi_{\text{clt}} + \hat{T}_{\text{OM degr}}^V / \chi_{\text{om}}) = 0. \end{aligned} \quad (2.64)$$

Total alkalinity (alk)

A second combination is obtained by considering total alkalinity, defined by $C_{\text{alk}}^f = C_{\text{dc1}}^f + 2C_{\text{dc2}}^f + C_{\text{db1}}^f + C_{\text{oh}}^f - C_{\text{h3o}}^f$. The corresponding linear combination of equations (2.58) + 2 × (2.57) + (2.60) + (2.62) – (2.63) gives

$$\begin{aligned} & \varphi^f \frac{\partial}{\partial t} (C_{\text{dc1}}^f + 2C_{\text{dc2}}^f + C_{\text{db1}}^f + C_{\text{oh}}^f - C_{\text{h3o}}^f) \\ & + \frac{\partial}{\partial z} \left(-\frac{\varphi^f}{\theta^2} (D_{\text{dc1}}^{\text{sw}} \frac{\partial C_{\text{dc1}}^f}{\partial z} + 2D_{\text{dc2}}^{\text{sw}} \frac{\partial C_{\text{dc2}}^f}{\partial z} \right. \\ & \quad \left. + D_{\text{db1}}^{\text{sw}} \frac{\partial C_{\text{db1}}^f}{\partial z} + D_{\text{oh}}^{\text{sw}} \frac{\partial C_{\text{oh}}^f}{\partial z} + D_{\text{h3o}}^{\text{sw}} \frac{\partial C_{\text{h3o}}^f}{\partial z}) \right. \\ & \quad \left. + \varphi^f u (C_{\text{dc1}}^f + 2C_{\text{dc2}}^f + C_{\text{db1}}^f + C_{\text{oh}}^f - C_{\text{h3o}}^f) \right) \\ & - (2\hat{T}_{\text{Arag diss}}^V / \chi_{\text{arg}} + 2\hat{T}_{\text{Calc diss}}^V / \chi_{\text{clt}}) = 0. \end{aligned} \quad (2.65)$$

Total dissolved boron (dbt)

Another combination is the total dissolved boron, defined by $C_{\text{dbt}}^f = C_{\text{db1}}^f + C_{\text{db0}}^f$. The corresponding linear combination of equations (2.60) + (2.61) yields

$$\begin{aligned} & \varphi^f \frac{\partial}{\partial t} (C_{\text{db1}}^f + C_{\text{db0}}^f) \\ & + \frac{\partial}{\partial z} \left(-\frac{\varphi^f}{\theta^2} (D_{\text{db1}}^{\text{sw}} \frac{\partial C_{\text{db1}}^f}{\partial z} + D_{\text{db0}}^{\text{sw}} \frac{\partial C_{\text{db0}}^f}{\partial z}) + \varphi^f u (C_{\text{db1}}^f + C_{\text{db0}}^f) \right) = 0. \end{aligned} \quad (2.66)$$

2.6.7 Constrained systems

System $\text{CO}_2\text{-HCO}_3^- \text{-CO}_3^{2-}$

The system of equations (2.57)-(2.58)-(2.59) that describes the evolution of the solute concentrations C_{dc2}^f , C_{dc1}^f and C_{dc0}^f is replaced by the system (2.64)-(2.65)-(2.28), where terms relevant to not considered elements are simply dropped. The replacement system also describes the evolution of the three single species, but now in terms of dissolved inorganic carbon, C_{dic}^f , and total alkalinity (actually carbonate alkalinity in this case), C_{alk}^f , with the speciation between the three being set by the equilibrium condition (2.28).

System $\text{CO}_2\text{-HCO}_3^- \text{-CO}_3^{2-} \text{-B(OH)}_4^- \text{-B(OH)}_3$

The system of equations (2.57)-(2.58)-(2.59)-(2.60)-(2.61) that describes the evolution of the solute concentrations C_{dc2}^f , C_{dc1}^f , C_{dc0}^f , C_{db1}^f and C_{db0}^f is replaced by the system (2.64)-(2.65)-(2.28)-(2.66)-(2.30). The two last equations in the replacement system describe the evolution of total dissolved boron, C_{dbt}^f , and the speciation between the two boron species.

System $\text{CO}_2\text{-HCO}_3^- \text{-CO}_3^{2-} \text{-B(OH)}_4^- \text{-B(OH)}_3 \text{-H}_3\text{O}^+ \text{-OH}^-$

The equation system (2.57)-(2.58)-(2.59)-(2.60)-(2.61)-(2.62)-(2.63) that describes the evolution of the solute concentrations C_{dc2}^f , C_{dc1}^f , C_{dc0}^f , C_{db1}^f , C_{db0}^f , C_{oh}^f and C_{h3o}^f is replaced by the system (2.64)-(2.65)-(2.34)-(2.35)-(2.66)-(2.37)-(2.31).

2.7 Sediment accumulation rate profile

The profile of sediment burial velocities can be easily obtained by integrating equation (2.47)

$$\frac{\partial \varphi^s}{\partial t} + \frac{\partial}{\partial z} \left(\sum_{i \in I^s} \vartheta_i \hat{J}_i \right) - \sum_{i \in I^s} \vartheta_i \hat{R}_i^V = 0$$

from the sediment-water interface at z_T and any depth z below :

$$\int_{z_T}^z \frac{\partial \varphi^s}{\partial t} dz' + \left[\sum_{i \in I^s} \vartheta_i \hat{J}_i \right]_{z_T}^z - \int_{z_T}^z \sum_{i \in I^s} \vartheta_i \hat{R}_i^V(z') dz' = 0. \quad (2.67)$$

Let $\Phi^s(z)$ denote the total integrated volume of solids between the sediment-water interface, down to the depth z , i.e.,

$$\Phi^s(z) = \int_{z_T}^z \varphi^s dz'.$$

The first term in equation (2.67) then represents the time derivative of $\Phi^s(z)$. The second term, which can be developed with equations (2.45) for z and equation (2.3) for z_T , will bring in the required w . Introducing these two expressions into equation (2.67) and rearranging it, we find that

$$\begin{aligned} & \varphi^s w - \varphi^s \sum_{i \in I^s} \left(\vartheta_i D_i^{\text{intra}} \frac{\partial \hat{C}_i}{\partial z} \right) - D^{\text{inter}} \frac{\partial \varphi^s}{\partial z} \\ &= \sum_{i \in I^s} \vartheta_i \left(\hat{P}_i^{\Sigma \text{top}} - \hat{T}_i^{\Sigma \text{top}} + \hat{I}_i^{\text{top}} - \hat{O}_i^{\text{top}} \right) + \int_{z_T}^z \sum_{i \in I^s} \vartheta_i \hat{R}_i^V(z') dz' - \frac{\partial \Phi^s}{\partial t} \end{aligned}$$

Taking all the basic hypotheses inherent to our model into account and supposing furthermore that there are no interface reactions at the surface ($\hat{P}_i^{\Sigma \text{top}} = \hat{T}_i^{\Sigma \text{top}} = 0$), and no output of solids back to the water column ($\hat{O}_i^{\text{top}} = 0$), the previous equation simplifies to

$$\boxed{\varphi^s w - \beta D^{\text{bt}} \frac{\partial \varphi^s}{\partial z} = \sum_i \vartheta_i \hat{I}_i^{\text{top}} + \int_{z_T}^z \sum_i \vartheta_i \hat{R}_i^V(z') dz'.} \quad (2.68)$$

2.8 Interface equations

2.8.1 General interface equation for solids

Using the general solid flux expression (2.40), the general continuity equation (2.2) valid at a given interface Σ located at $z = z_\Sigma$,

$$\hat{J}_i^+ = \hat{J}_i^- + \hat{R}_i^\Sigma,$$

can be developed to give

$$\begin{aligned} & \left(-\varphi_s D^{\text{bt}} \frac{\partial B_i}{\partial z} + \left(\varphi_s w - \beta D^{\text{bt}} \frac{\partial \varphi_s}{\partial z} \right) B_i \right) \Big|_{z_\Sigma^+} \\ &= \left(-\varphi_s D^{\text{bt}} \frac{\partial B_i}{\partial z} + \left(\varphi_s w - \beta D^{\text{bt}} \frac{\partial \varphi_s}{\partial z} \right) B_i \right) \Big|_{z_\Sigma^-} + \hat{R}_i^\Sigma \end{aligned} \quad (2.69)$$

The combination of equation (2.46) with continuity equation (2.2) yields the following constraint for w at the interface:

$$\left(\varphi_s w - \beta D^{\text{bt}} \frac{\partial \varphi_s}{\partial z} \right) \Big|_{z_\Sigma^+} = \left(\varphi_s w - \beta D^{\text{bt}} \frac{\partial \varphi_s}{\partial z} \right) \Big|_{z_\Sigma^-} + \sum_i \vartheta_i \hat{R}_i^\Sigma \quad (2.70)$$

2.8.2 Top of sediment

Solids

Boundary conditions for solids at the surface of the sediment are third kind conditions, resulting from the application of the top flux continuity equation (2.3) with detailed production and destruction terms for $\hat{P}_i^{\Sigma \text{top}}$:

$$\hat{F}_i^{z_T^+} = \hat{P}_i^{\Sigma \text{top}} - \hat{T}_i^{\Sigma \text{top}} + \hat{I}_i^{\text{top}} - \hat{O}_i^{\text{top}}$$

When developing $\hat{F}_i^{z_T^+}$ in the previous equation with the expression (2.40), the equation becomes

$$\left(-\varphi_s D^{\text{bt}} \frac{\partial B_i}{\partial z} + \left(\varphi_s w - \beta D^{\text{bt}} \frac{\partial \varphi_s}{\partial z} \right) B_i \right) \Big|_{z_T^+} = \hat{P}_i^{\Sigma \text{top}} - \hat{T}_i^{\Sigma \text{top}} + \hat{I}_i^{\text{top}} - \hat{O}_i^{\text{top}}.$$

$w(z_T^+)$ may be derived, e.g., from equation (2.68), yielding:

$$\left(\varphi_s w - \beta D^{\text{bt}} \frac{\partial \varphi_s}{\partial z} \right) \Big|_{z_T^+} = \sum_i \vartheta_i \left(\hat{P}_i^{\Sigma \text{top}} - \hat{T}_i^{\Sigma \text{top}} + \hat{I}_i^{\text{top}} - \hat{O}_i^{\text{top}} \right). \quad (2.71)$$

If there are no interface reactions ($\hat{P}_i^{\Sigma\text{top}} = \hat{T}_i^{\Sigma\text{top}} = 0$) and there is no output of solids back to the water column ($\hat{O}_i^{\text{top}} = 0$), the previous condition simplifies to

$$\left(\varphi_s w - \beta D^{\text{bt}} \frac{\partial \varphi_s}{\partial z} \right) \Big|_{z_T^+} = \sum_i \vartheta_i \hat{I}_i^{\text{top}}. \quad (2.72)$$

Solutes

Boundary conditions for solutes at the surface sediment interface are of the first kind (Dirichlet conditions). The solutes' concentrations are directly prescribed:

$$C_i(z_T^+, t) = C_i^T(t) \quad (2.73)$$

If there is no diffusive boundary layer to be considered, $C_i^T(t)$ is equal to the concentration of the solute i in the overlying seawater; else, $C_i^T(t)$ is the concentration of i at the contact interface between the boundary layer and the sediment column.

2.8.3 Bottom of the bioturbated zone

Only solids have to meet a boundary condition at the bottom of the bioturbation layer. The kind of boundary condition depends on the local behaviour of the biodiffusion coefficient D^{bt} in the vicinity of the boundary: all that can be taken for granted is that $D^{\text{bt}}|_{z_Z^+} = 0$; $D^{\text{bt}}|_{z_Z^-}$ is not necessarily equal to zero.

First of all, equation (2.70), when written for the bioturbation bottom boundary, tells us that

$$\left(\varphi_s w - \beta D^{\text{bt}} \frac{\partial \varphi_s}{\partial z} \right) \Big|_{z_Z^-} = (\varphi_s w) \Big|_{z_Z^+} - \sum_i \vartheta_i \hat{R}_i^{\Sigma Z}. \quad (2.74)$$

From this equation, we can already conclude that, even if there are no interface reactions at the current boundary, w will not be continuous across the boundary, unless $\beta(z_Z) = 0$, i.e., unless bioturbation operates only by intraphase mixing, or D^{bt} is continuous in the vicinity of $z = z_Z$ and is equal to 0 in $z = z_Z$. Equation (2.69) written for the bioturbation bottom boundary, with the previous identity taken into account then reads

$$\begin{aligned} & (\varphi_s w) \Big|_{z_Z^+} B_i \Big|_{z_Z^+} \\ &= - \left(\varphi_s D^{\text{bt}} \frac{\partial B_i}{\partial z} \right) \Big|_{z_Z^-} + \left((\varphi_s w) \Big|_{z_Z^+} - \sum_i \vartheta_i \hat{R}_i^{\Sigma Z} \right) B_i(z_Z^-) + \hat{R}_i^{\Sigma Z}, \end{aligned}$$

which can be reformulated as

$$(\varphi_s w)|_{z_Z^+} (B_i|_{z_Z^+} - B_i|_{z_Z^-}) = - \left(\varphi_s D^{\text{bt}} \frac{\partial B_i}{\partial z} \right) \Big|_{z_Z^-} - \left(\sum_i \vartheta_i \hat{R}_i^{\Sigma Z} \right) B_i|_{z_Z^-} + \hat{R}_i^{\Sigma Z}. \quad (2.75)$$

Equations (2.74) and (2.75) are valid in all generality. In the model presented here, one of the basic hypotheses is that the concentration profiles $B_i(z)$ are continuous throughout the whole column. Hence, equation (2.75) actually reduces to

$$\left(\varphi_s D^{\text{bt}} \frac{\partial B_i}{\partial z} \right) \Big|_{z_Z^-} + \left(\sum_i \vartheta_i \hat{R}_i^{\Sigma Z} \right) B_i|_{z_Z^-} = \hat{R}_i^{\Sigma Z}. \quad (2.76)$$

If there are no interface reactions at the bioturbation bottom boundary, as it will be generally the case, equations (2.74) and (2.76) considerably simplify:

$$\left(\varphi_s w - \beta D^{\text{bt}} \frac{\partial \varphi_s}{\partial z} \right) \Big|_{z_Z^-} = (\varphi_s w)|_{z_Z^+} \quad (2.77)$$

and

$$\left(\varphi_s D^{\text{bt}} \frac{\partial B_i}{\partial z} \right) \Big|_{z_Z^-} = 0 \quad (2.78)$$

If further $D^{\text{bt}}|_{z_Z^-} = D^{\text{bt}}|_{z_Z^+} = 0$ or $\beta(z_Z) = 0$, then equation (2.74) only states that w is continuous across $z = z_Z$.

It now becomes clear why the actual boundary condition for B_i depends on the behaviour of D^{bt} in the vicinity of $z = z_Z$:

- if $D^{\text{bt}}|_{z_Z^-} \neq 0$, equation (2.78) provides a boundary condition of the second kind (Neumann condition) at $z = z_Z$:

$$\frac{\partial B_i}{\partial z} \Big|_{z_Z^-} = 0. \quad (2.79)$$

- If $D^{\text{bt}}|_{z_Z^-} = 0$, equation (2.78) does not provide any constraint at all, and we must resort to the evolution equation (2.44). If we develop the derivative of the flux in that equation, we obtain

$$\begin{aligned} \varphi_s \frac{\partial B_i}{\partial t} &- \frac{\partial B_i}{\partial z} \frac{\partial}{\partial z} \left(\varphi_s D^{\text{bt}} \right) - \varphi_s D^{\text{bt}} \frac{\partial^2 B_i}{\partial z^2} \\ &+ B_i \frac{\partial}{\partial z} \left(\varphi_s w - \beta D^{\text{bt}} \frac{\partial \varphi_s}{\partial z} \right) \\ &+ \left(\varphi_s w - \beta D^{\text{bt}} \frac{\partial \varphi_s}{\partial z} \right) \frac{\partial B_i}{\partial z} - \hat{R}_i^V = 0. \end{aligned}$$

If we evaluate this equation in the limit as $z \rightarrow z_Z^-$, we obtain the following equation to fulfill:

$$\begin{aligned} \left(\varphi_s \frac{\partial B_i}{\partial t} \right) \Big|_{z_Z^-} + \frac{\partial B_i}{\partial z} \Big|_{z_Z^-} \left(\varphi_s w - \frac{\partial}{\partial z} \left(\varphi_s D^{\text{bt}} \right) \right) \Big|_{z_Z^-} \\ + B_i \Big|_{z_Z^-} \frac{\partial}{\partial z} \left(\varphi_s w - \beta D^{\text{bt}} \frac{\partial \varphi_s}{\partial z} \right) \Big|_{z_Z^-} - \hat{R}_i^V \Big|_{z_Z^-} = 0. \end{aligned}$$

Identity (2.49) can be used to resolve the unknown derivative of $\varphi_s w$. If the bottom of the bioturbated zone and the bottom of the modelled sediment column are not the same, then, regarding solids, the section between them is characterised by advection and reaction only. $B_i|_{z_Z^+}$ is then set equal to $B_i|_{z_Z^-}$ (hypothesis of continuity of B_i profiles); $w|_{z_Z^+}$ is calculated from $w|_{z_Z^-}$ via equation (2.77), whatever the behaviour of D^{bt} in the vicinity of $z = z_Z$. Whatever the evolution of D^{bt} across $z = z_Z$, for $z_Z < z \leq z_B$ (provided $z_Z < z_B$, with z_B the depth of the location of the bottom of the modelled sediment section), the evolution equation for solids reduces to a plain advection equation:

$$\varphi_s \frac{\partial B_i}{\partial t} + \frac{\partial}{\partial z} (\varphi_s w B_i) - \hat{R}_i^V \Big|_{z_Z^-} = 0.$$

2.8.4 Bottom of sediment column

The bottom of the model sediment column is located at $z = z_B$. Boundary conditions, if necessary are similar to the conditions at the top, or at the bottom of the bioturbation zone.

Solids

Unless $w|_{z_B^-} < 0$ (chemical erosion is taking place), there is no boundary condition required for solids. Else, the boundary condition for solids is similar to the top boundary condition, where the input fluxes now results from the input (unburial) of sediment layers below the model section.

Solutes

There are several ways to prescribe bottom boundary conditions for solutes, depending on the supplemental assumptions made.

- The closure of the bottom boundary is made via a no-flux condition $\hat{F}_i|_{z_B^+} = 0$. Under this hypothesis, the full condition from equation (2.2) reads

$$\hat{R}_i^{\Sigma B} + \hat{F}_i|_{z_B^-} = 0,$$

which, when developed, becomes

$$\hat{R}_i^{\Sigma B} - \left(\varphi \frac{D_i^{\text{sw}}}{\theta^2} \right) \Big|_{z_B^-} \left(\frac{\partial C_i}{\partial z} \right) \Big|_{z_B^-} + (\varphi u)|_{z_B^-} C_i|_{z_B^-} = 0$$

$u|_{z_B^-}$ can be derived from the profile of w . In case there are no interface reactions taking place at the bottom boundary layer

$$- \left(\varphi \frac{D_i^{\text{sw}}}{\theta^2} \right) \Big|_{z_B^-} \left(\frac{\partial C_i}{\partial z} \right) \Big|_{z_B^-} + (\varphi u)|_{z_B^-} C_i|_{z_B^-} = 0 \quad (2.80)$$

- A slightly different approach is to suppose that the diffusional transport alone ceases at the bottom, and that porewater advection is the only way of transporting solutes into and out of the sediment section. The corresponding condition is

$$\left(\frac{\partial C_i}{\partial z} \right) \Big|_{z_B^-} \left(\varphi \frac{D_i^{\text{sw}}}{\theta^2} \right) \Big|_{z_B^-} = 0$$

which, as D_i^{sw} hardly ever reduces to zero, is equivalent to a classical boundary condition of the second kind (Neumann condition)

$$\left(\frac{\partial C_i}{\partial z} \right) \Big|_{z_B^-} = 0. \quad (2.81)$$

This condition would also have been recovered with the previous approach, supposing that surface reactions and porewater advection can be neglected.

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Table 7: Full Clay-Aragonite-Calcite-OrgMatter- $[\text{CO}_3^{2-}]$ - $[\text{HCO}_3^-]$ - $[\text{CO}_2]$ - $[\text{B}(\text{OH})_3]$ - $[\text{B}(\text{OH})_4^-]$ - $[\text{H}_3\text{O}^+]$ - $[\text{OH}^-]$ model

i	$\frac{\partial \hat{B}_i}{\partial t}$	$+\frac{\partial \hat{F}_i}{\partial z}$	$-\hat{R}_i = 0$
Clay	$\varphi_s \frac{\partial B_{\text{cly}}}{\partial t}$	$+\frac{\partial}{\partial z} \left(-\varphi_s D^{\text{bt}} \frac{\partial B_{\text{cly}}}{\partial z} + (\varphi_s w - \beta D^{\text{bt}} \frac{\partial \varphi_s}{\partial z}) B_{\text{cly}} \right)$	$= 0$
Aragonite	$\varphi_s \frac{\partial B_{\text{arg}}}{\partial t}$	$+\frac{\partial}{\partial z} \left(-\varphi_s D^{\text{bt}} \frac{\partial B_{\text{arg}}}{\partial z} + (\varphi_s w - \beta D^{\text{bt}} \frac{\partial \varphi_s}{\partial z}) B_{\text{arg}} \right)$	$+\hat{T}_{\text{Arag diss}}^V = 0$
Calcite	$\varphi_s \frac{\partial B_{\text{clt}}}{\partial t}$	$+\frac{\partial}{\partial z} \left(-\varphi_s D^{\text{bt}} \frac{\partial B_{\text{clt}}}{\partial z} + (\varphi_s w - \beta D^{\text{bt}} \frac{\partial \varphi_s}{\partial z}) B_{\text{clt}} \right)$	$+\hat{T}_{\text{Calc diss}}^V = 0$
CO_3^{2-}	$\varphi \frac{\partial C_{\text{dc}2}}{\partial t}$	$+\frac{\partial}{\partial z} \left(-\varphi \frac{D_{\text{dc}2}^{\text{sw}}}{\theta^2} \frac{\partial C_{\text{dc}2}}{\partial z} + \varphi u C_{\text{dc}2} \right)$	$-\left\{ \begin{array}{l} r_2 \\ -r_{1/2} - r_{2/b} \end{array} \right\} - \frac{\hat{T}_{\text{Arag diss}}^V}{M_{\text{arg}}} - \frac{\hat{T}_{\text{Calc diss}}^V}{M_{\text{clt}}} = 0$
HCO_3^-	$\varphi \frac{\partial C_{\text{dc}1}}{\partial t}$	$+\frac{\partial}{\partial z} \left(-\varphi \frac{D_{\text{dc}1}^{\text{sw}}}{\theta^2} \frac{\partial C_{\text{dc}1}}{\partial z} + \varphi u C_{\text{dc}1} \right)$	$-\left\{ \begin{array}{l} r_1 - r_2 \\ 2r_{1/2} + r_{2/b} \end{array} \right\} = 0$
CO_2^-	$\varphi \frac{\partial C_{\text{dc}0}}{\partial t}$	$+\frac{\partial}{\partial z} \left(-\varphi \frac{D_{\text{dc}0}^{\text{sw}}}{\theta^2} \frac{\partial C_{\text{dc}0}}{\partial z} + \varphi u C_{\text{dc}0} \right)$	$-\left\{ \begin{array}{l} -r_1 \\ -r_{1/2} \end{array} \right\} - \frac{\hat{T}_{\text{OM degr}}^V}{M_{\text{om}}} = 0$
$\text{B}(\text{OH})_4^-$	$\varphi \frac{\partial C_{\text{db}1}}{\partial t}$	$+\frac{\partial}{\partial z} \left(-\varphi \frac{D_{\text{db}1}^{\text{sw}}}{\theta^2} \frac{\partial C_{\text{db}1}}{\partial z} + \varphi u C_{\text{db}1} \right)$	$-\left\{ \begin{array}{l} r_b \\ r_{2/b} \end{array} \right\} = 0$
$\text{B}(\text{OH})_3$	$\varphi \frac{\partial C_{\text{db}0}}{\partial t}$	$+\frac{\partial}{\partial z} \left(-\varphi \frac{D_{\text{db}0}^{\text{sw}}}{\theta^2} \frac{\partial C_{\text{db}0}}{\partial z} + \varphi u C_{\text{db}0} \right)$	$-\left\{ \begin{array}{l} -r_b \\ -r_{2/b} \end{array} \right\} = 0$
H_3O^+	$\varphi \frac{\partial C_{\text{h}30}}{\partial t}$	$+\frac{\partial}{\partial z} \left(-\varphi \frac{D_{\text{h}30}^{\text{sw}}}{\theta^2} \frac{\partial C_{\text{h}30}}{\partial z} + \varphi u C_{\text{h}30} \right)$	$-\left\{ \begin{array}{l} r_1 + r_2 + r_b + r_w \\ - \end{array} \right\} = 0$
OH^-	$\varphi \frac{\partial C_{\text{oh}}}{\partial t}$	$+\frac{\partial}{\partial z} \left(-\varphi \frac{D_{\text{oh}}^{\text{sw}}}{\theta^2} \frac{\partial C_{\text{oh}}}{\partial z} + \varphi u C_{\text{oh}} \right)$	$-\left\{ \begin{array}{l} r_w \\ - \end{array} \right\} = 0$
OrgMatter	$\varphi_s \frac{\partial B_{\text{om}}}{\partial t}$	$+\frac{\partial}{\partial z} \left(-\varphi_s D^{\text{bt}} \frac{\partial B_{\text{om}}}{\partial z} + (\varphi_s w - \beta D^{\text{bt}} \frac{\partial \varphi_s}{\partial z}) B_{\text{om}} \right)$	$+\hat{T}_{\text{OM degr}}^V = 0$

Table 8: Clay-Aragonite-Calcite-OrgMatter- $[\text{CO}_3^{2-}]$ - $[\text{HCO}_3^-]$ - $[\text{CO}_2]$ - $[\text{B}(\text{OH})_3]$ - $[\text{B}(\text{OH})_4^-]$ - $[\text{H}_3\text{O}^+]$ - $[\text{OH}^-]$ model with chemical equilibria

i	$\frac{\partial \hat{B}_i}{\partial t} + \frac{\partial \hat{F}_i}{\partial z}$	$-\hat{R}_i^V = 0$
Clay	$\frac{\partial B_{\text{cly}}}{\partial t} + \frac{\partial}{\partial z} \left(-\varphi_s D^{\text{bt}} \frac{\partial B_{\text{cly}}}{\partial z} + (\varphi_s w - \beta D^{\text{bt}} \frac{\partial \varphi_s}{\partial z}) B_{\text{cly}} \right)$	$= 0$
Aragonite	$\frac{\partial B_{\text{arg}}}{\partial t} + \frac{\partial}{\partial z} \left(-\varphi_s D^{\text{bt}} \frac{\partial B_{\text{arg}}}{\partial z} + (\varphi_s w - \beta D^{\text{bt}} \frac{\partial \varphi_s}{\partial z}) B_{\text{arg}} \right)$	$+ \hat{T}_{\text{Arag diss}}^V = 0$
Calcite	$\frac{\partial B_{\text{clt}}}{\partial t} + \frac{\partial}{\partial z} \left(-\varphi_s D^{\text{bt}} \frac{\partial B_{\text{clt}}}{\partial z} + (\varphi_s w - \beta D^{\text{bt}} \frac{\partial \varphi_s}{\partial z}) B_{\text{clt}} \right)$	$+ \hat{T}_{\text{Calc diss}}^V = 0$
DIC	$\frac{\partial C_{\text{dic}}}{\partial t} + \frac{\partial}{\partial z} \left(-\frac{\varphi}{\theta^2} (D_{\text{dc}2}^{\text{sw}} \frac{\partial C_{\text{dc}2}}{\partial z} + D_{\text{dc}1}^{\text{sw}} \frac{\partial C_{\text{dc}1}}{\partial z} + D_{\text{dc}0}^{\text{sw}} \frac{\partial C_{\text{dc}0}}{\partial z}) + \varphi u(C_{\text{dic}}) \right)$	$-\frac{\hat{T}_{\text{Arag diss}}^V}{M_{\text{arg}}} - \frac{\hat{T}_{\text{Calc diss}}^V}{M_{\text{clt}}} - \frac{\hat{T}_{\text{OM degr}}^V}{M_{\text{om}}} = 0$
TALK	$\frac{\partial C_{\text{alk}}}{\partial t} + \frac{\partial}{\partial z} \left(-\frac{\varphi}{\theta^2} (2D_{\text{dc}2}^{\text{sw}} \frac{\partial C_{\text{dc}2}}{\partial z} + D_{\text{dc}1}^{\text{sw}} \frac{\partial C_{\text{dc}1}}{\partial z} + D_{\text{db}1}^{\text{sw}} \frac{\partial C_{\text{db}1}}{\partial z} + D_{\text{h}30}^{\text{sw}} \frac{\partial C_{\text{h}30}}{\partial z}) + \varphi u(C_{\text{alk}}) \right)$	$-\frac{\hat{T}_{\text{Arag diss}}^V}{M_{\text{arg}}} - 2\frac{\hat{T}_{\text{Calc diss}}^V}{M_{\text{clt}}} = 0$
Equil. 1	$C_{\text{dc}1} C_{\text{h}30} - K_1 C_{\text{dc}0} = 0$	
Equil. 2	$C_{\text{dc}2} C_{\text{h}30} - K_2 C_{\text{dc}1} = 0$	
DIB	$\frac{\partial C_{\text{dib}}}{\partial t} + \frac{\partial}{\partial z} \left(-\frac{\varphi}{\theta^2} (D_{\text{db}1}^{\text{sw}} \frac{\partial C_{\text{db}1}}{\partial z} + D_{\text{db}0}^{\text{sw}} \frac{\partial C_{\text{db}0}}{\partial z}) + \varphi u(C_{\text{dib}}) \right) = 0$	
Equil b	$C_{\text{db}1} C_{\text{h}30} - K_b C_{\text{db}0} = 0$	
Equil w	$C_{\text{h}30} C_{\text{oh}} - K_w = 0$	
OrgMatter	$\frac{\partial B_{\text{om}}}{\partial t} + \frac{\partial}{\partial z} \left(-\varphi_s D^{\text{bt}} \frac{\partial B_{\text{om}}}{\partial z} + (\varphi_s w - \beta D^{\text{bt}} \frac{\partial \varphi_s}{\partial z}) B_{\text{om}} \right)$	$+ \hat{T}_{\text{OM degr}}^V = 0$

Dissolved Inorganic Carbon, DIC = $[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{CO}_2]$; $C_{\text{dic}} = C_{\text{dc}2} + C_{\text{dc}1} + C_{\text{dc}0}$

TALK = $2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] - [\text{H}_3\text{O}^+]$; $C_{\text{alk}} = 2C_{\text{dc}2} + C_{\text{dc}1} + C_{\text{db}1} + C_{\text{oh}} - C_{\text{h}30}$

Dissolved Inorganic Boron, DIB = $[\text{B}(\text{OH})_4^-] + [\text{B}(\text{OH})_3]$; $C_{\text{dib}} = C_{\text{db}1} + C_{\text{db}0}$

Table 9: Clay-Aragonite-Calcite-OrgMatter- $[\text{CO}_3^{2-}]$ - $[\text{HCO}_3^-]$ - $[\text{CO}_2]$ - $[\text{B}(\text{OH})_3]$ - $[\text{B}(\text{OH})_4^-]$ model with chemical equilibria

i	$\frac{\partial \hat{B}_i}{\partial t} + \frac{\partial \hat{F}_i}{\partial z}$	$-\hat{R}_i^V = 0$
Clay	$\varphi_s \frac{\partial B_{\text{cly}}}{\partial t} + \frac{\partial}{\partial z} \left(-\varphi_s D^{\text{bt}} \frac{\partial B_{\text{cly}}}{\partial z} + (\varphi_s w - \beta D^{\text{bt}} \frac{\partial \varphi_s}{\partial z}) B_{\text{cly}} \right)$	$= 0$
Aragonite	$\varphi_s \frac{\partial B_{\text{arg}}}{\partial t} + \frac{\partial}{\partial z} \left(-\varphi_s D^{\text{bt}} \frac{\partial B_{\text{arg}}}{\partial z} + (\varphi_s w - \beta D^{\text{bt}} \frac{\partial \varphi_s}{\partial z}) B_{\text{arg}} \right)$	$+ \hat{T}_{\text{Arag diss}}^V = 0$
Calcite	$\varphi_s \frac{\partial B_{\text{cIt}}}{\partial t} + \frac{\partial}{\partial z} \left(-\varphi_s D^{\text{bt}} \frac{\partial B_{\text{cIt}}}{\partial z} + (\varphi_s w - \beta D^{\text{bt}} \frac{\partial \varphi_s}{\partial z}) B_{\text{cIt}} \right)$	$+ \hat{T}_{\text{Calc diss}}^V = 0$
DIC	$\varphi \frac{\partial C_{\text{dic}}}{\partial t} + \frac{\partial}{\partial z} \left(-\frac{\varphi}{\theta^2} (D_{\text{dc2}}^{\text{sw}} \frac{\partial C_{\text{dc2}}}{\partial z} + D_{\text{dc1}}^{\text{sw}} \frac{\partial C_{\text{dc1}}}{\partial z} + D_{\text{dc0}}^{\text{sw}} \frac{\partial C_{\text{dc0}}}{\partial z}) + \varphi u(C_{\text{dic}}) \right)$	$-\frac{\hat{T}_{\text{Arag diss}}^V}{M_{\text{arg}}} - \frac{\hat{T}_{\text{Calc diss}}^V}{M_{\text{cIt}}} - \frac{\hat{T}_{\text{OM degr}}^V}{M_{\text{om}}} = 0$
TALK	$\varphi \frac{\partial C_{\text{alk}}}{\partial t} + \frac{\partial}{\partial z} \left(-\frac{\varphi}{\theta^2} (2D_{\text{dc2}}^{\text{sw}} \frac{\partial C_{\text{dc2}}}{\partial z} + D_{\text{dc1}}^{\text{sw}} \frac{\partial C_{\text{dc1}}}{\partial z} + D_{\text{db1}}^{\text{sw}} \frac{\partial C_{\text{db1}}}{\partial z}) + \varphi u(C_{\text{alk}}) \right)$	$-\frac{\hat{T}_{\text{Arag diss}}^V}{M_{\text{arg}}} - 2 \frac{\hat{T}_{\text{Calc diss}}^V}{M_{\text{cIt}}} = 0$
Equil. 1/2	$K_2(C_{\text{dc1}})^2 - K_1 C_{\text{dc0}} C_{\text{dc2}} = 0$	
DIB	$\varphi \frac{\partial C_{\text{dib}}}{\partial t} + \frac{\partial}{\partial z} \left(-\frac{\varphi}{\theta^2} (D_{\text{db1}}^{\text{sw}} \frac{\partial C_{\text{db1}}}{\partial z} + D_{\text{db0}}^{\text{sw}} \frac{\partial C_{\text{db0}}}{\partial z}) + \varphi u(C_{\text{dib}}) \right) = 0$	
Equil 2/b	$K_2 C_{\text{db1}} C_{\text{dc1}} - K_b C_{\text{db0}} C_{\text{dc2}} = 0$	
OrgMatter	$\varphi_s \frac{\partial B_{\text{om}}}{\partial t} + \frac{\partial}{\partial z} \left(-\varphi_s D^{\text{bt}} \frac{\partial B_{\text{om}}}{\partial z} + (\varphi_s w - \beta D^{\text{bt}} \frac{\partial \varphi_s}{\partial z}) B_{\text{om}} \right)$	$+ \hat{T}_{\text{OM degr}}^V = 0$

Dissolved Inorganic Carbon, DIC = $[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{CO}_2]$; $C_{\text{dic}} = C_{\text{dc2}} + C_{\text{dc1}} + C_{\text{dc0}}$

Total Alkalinity, TALK = $2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{B}(\text{OH})_4^-]$; $C_{\text{alk}} = 2C_{\text{dc2}} + C_{\text{dc1}} + C_{\text{db1}}$

Dissolved Inorganic Boron, DIB = $[\text{B}(\text{OH})_4^-] + [\text{B}(\text{OH})_3]$; $C_{\text{dib}} = C_{\text{db1}} + C_{\text{db0}}$

Table 10: Clay-Calcite-OrgMatter- $[\text{CO}_3^{2-}]$ - $[\text{HCO}_3^-]$ - $[\text{CO}_2]$ model with chemical equilibrium

i	$\frac{\partial \hat{B}_i}{\partial t} + \frac{\partial \hat{f}_i}{\partial z}$	$-\hat{R}_i^V = 0$
Clay	$\frac{\partial B_{\text{cly}}}{\partial t} + \frac{\partial}{\partial z} \left(-\varphi_s D^{\text{bt}} \frac{\partial B_{\text{cly}}}{\partial z} + (\varphi_s w - \beta D^{\text{bt}} \frac{\partial \varphi_s}{\partial z}) B_{\text{cly}} \right)$	$= 0$
Calcite	$\frac{\partial B_{\text{clt}}}{\partial t} + \frac{\partial}{\partial z} \left(-\varphi_s D^{\text{bt}} \frac{\partial B_{\text{clt}}}{\partial z} + (\varphi_s w - \beta D^{\text{bt}} \frac{\partial \varphi_s}{\partial z}) B_{\text{clt}} \right)$	$+\hat{T}_{\text{Calc diss}}^V = 0$
DIC	$\frac{\partial C_{\text{dic}}}{\partial t} + \frac{\partial}{\partial z} \left(-\frac{\varphi}{\theta^2} (D_{\text{dc2}}^{\text{sw}} \frac{\partial C_{\text{dc2}}}{\partial z} + D_{\text{dc1}}^{\text{sw}} \frac{\partial C_{\text{dc1}}}{\partial z} + D_{\text{dc0}}^{\text{sw}} \frac{\partial C_{\text{dc0}}}{\partial z}) + \varphi u(C_{\text{dic}}) \right)$	$-\frac{\hat{T}_{\text{Calc diss}}^V}{M_{\text{clt}}} - \frac{\hat{T}_{\text{OM degr}}^V}{M_{\text{om}}} = 0$
TALK	$\frac{\partial C_{\text{alk}}}{\partial t} + \frac{\partial}{\partial z} \left(-\frac{\varphi}{\theta^2} (2D_{\text{dc2}}^{\text{sw}} \frac{\partial C_{\text{dc2}}}{\partial z} + D_{\text{dc1}}^{\text{sw}} \frac{\partial C_{\text{dc1}}}{\partial z}) + \varphi u(C_{\text{alk}}) \right)$	$-\frac{\hat{T}_{\text{Calc diss}}^V}{M_{\text{clt}}} = 0$
Equil. 1/2	$K_2(C_{\text{dc1}})^2 - K_1 C_{\text{dc0}} C_{\text{dc2}} = 0$	
OrgMatter	$\frac{\partial B_{\text{om}}}{\partial t} + \frac{\partial}{\partial z} \left(-\varphi_s D^{\text{bt}} \frac{\partial B_{\text{om}}}{\partial z} + (\varphi_s w - \beta D^{\text{bt}} \frac{\partial \varphi_s}{\partial z}) B_{\text{om}} \right)$	$+\hat{T}_{\text{OM degr}}^V = 0$

Dissolved Inorganic Carbon, DIC = $[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{CO}_2]$; $C_{\text{dic}} = C_{\text{dc2}} + C_{\text{dc1}} + C_{\text{dc0}}$
 Total Alkalinity, TALK = $2[\text{CO}_3^{2-}] + [\text{HCO}_3^-]$; $C_{\text{alk}} = 2C_{\text{dc2}} + C_{\text{dc1}} + C_{\text{db1}}$

Symbol	Dimensions	Signification
\hat{A}	$T M^{-1} L^3$	age concentration
φ	$L^3 L^{-3}$	porosity
φ^α		volume fraction of phase α
ρ_i	$M L^{-3}$	specific mass of constituent i
θ_i	$L M^{-1}$	specific volume of constituent i
τ	T	age
c_i	$M L^{-3} T^{-1}$	concentration distribution of i as a function of age
C_i	$M L^{-3}$	concentration of constituent i per unit volume of the phase it belongs to
\hat{C}_i	$M L^{-3}$	concentration of constituent i per unit volume of total sediment
f	–	as superscript: fluid-phase
I^x	–	inventory of constituents in phase α
\hat{r}_i^V	$M L^{-3} T^{-2}$	reaction rate of constituent i per unit volume of total sediment per unit τ ($\hat{r}_i^V > 0$ if i gets produced, $\hat{r}_i^V < 0$ if i gets consumed)
\hat{R}_i^V	$M L^{-3} T^{-1}$	reaction rate of constituent i per unit volume of total sediment ($\hat{R}_i^V > 0$ if i gets produced, $\hat{R}_i^V < 0$ if i gets consumed)
s	–	as superscript: solid-phase
t	T	time
z	L	vertical coordinate (positive downwards)
α	–	as superscript: α -phase
$\hat{\rho}_i^V$	$M L^{-3} T^{-1}$	reaction rate of constituent i per unit volume of total sediment ($\hat{R}_i^V > 0$ if i gets produced, $\hat{R}_i^V < 0$ if i gets consumed)

Meaning of dimensions: N – number of particles; M – mass; T – time; L – length