Modeling of geochemical processes

Reactive-Transport Models

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Modeling of geochemical processes

Dynamic models

Convection

concentration gradient

$C_{x=1}, C_{x=2}, C_{x=3}, C_{x=4}$ .... C_x

dC/dx

$$\frac{\partial C}{\partial t} = -\nu \frac{\partial C}{\partial x}$$

Discretization:

Taylor expansion

$$f(t+\Delta t) = f(t) + \frac{\Delta t}{1!} f'(t) + \frac{(\Delta t)^2}{2!} f''(t) + \ldots + \frac{(\Delta t)^n}{n!} f^{(n)}(t) + \ldots + R_n$$

$$\Longrightarrow \quad \frac{f(t+\Delta t) - f(t)}{\Delta t} = f'(t) \quad \Longrightarrow \quad \left(\frac{\partial C}{\partial t}\right)_x = \frac{C_x^{t_2} - C_x^{t_1}}{\Delta t}$$

$$f(x+\Delta x) = f(x) + \frac{\Delta x}{1!} f'(x) + \frac{(\Delta x)^2}{2!} f''(x) + \ldots + \frac{(\Delta x)^n}{n!} f^{(n)}(x) + \ldots + R_n$$

$$\Longrightarrow \quad \frac{f(x+\Delta x) - f(x)}{\Delta x} = f'(x) \quad \Longrightarrow \quad \left(\frac{\partial C}{\partial x}\right)_{t_1} = \frac{C_{x+1}^{t_1} - C_x^{t_1}}{\Delta x}$$

totally:

$$C_x^{t_2} = \frac{\Delta t}{\Delta x}\left(C_{x+1}^{t_1} - C_x^{t_1}\right) + C_x^{t_1}$$

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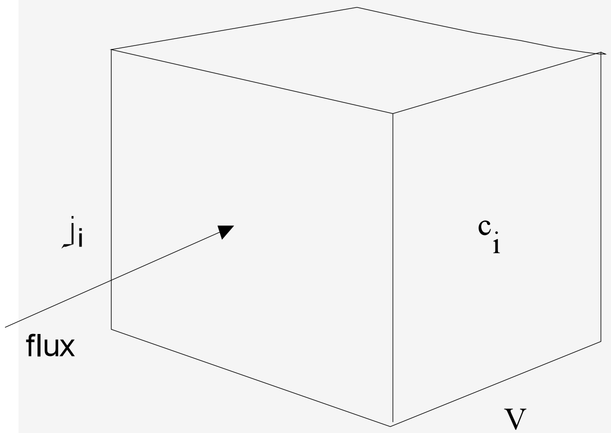
Dynamic models

Diffusion

Mass flux

The flux $\mathbf{j_i}$ into the volume element **V**. The flux $\mathbf{j_i}$ relates to an increment of content $\mathbf{m_i}$ in the volume element **V**:



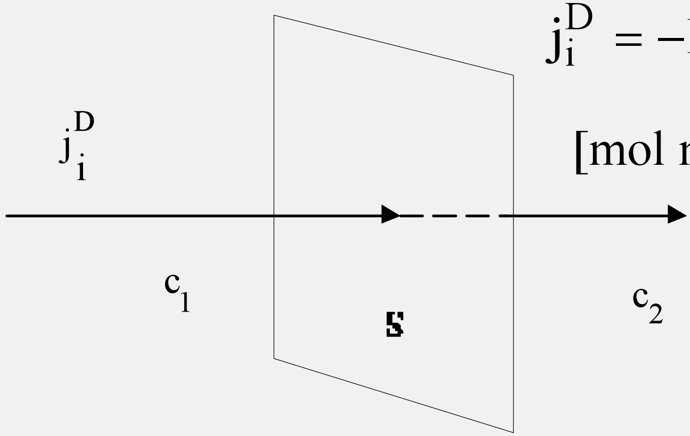
$$j_i = +\frac{\delta m_i}{\delta t}$$

$$j_i = +V\frac{\delta c_i}{\delta t}$$

[mol s^{-1}]

Diffusion flux

The flux $\mathbf{j_i^D}$ [mol m^{-2} s^{-1}] through area **S** [m^2] relates to a concentration gradient ($c_1 > c_2$) along a diffusional path **x** (one-dimensional diffusion along axis **x**).



$$j_i^D = -D\frac{\delta c_i}{\delta x}$$

[mol m^{-2} s^{-1}]

Diffusion coefficient **D** [m^2 s^{-1}]

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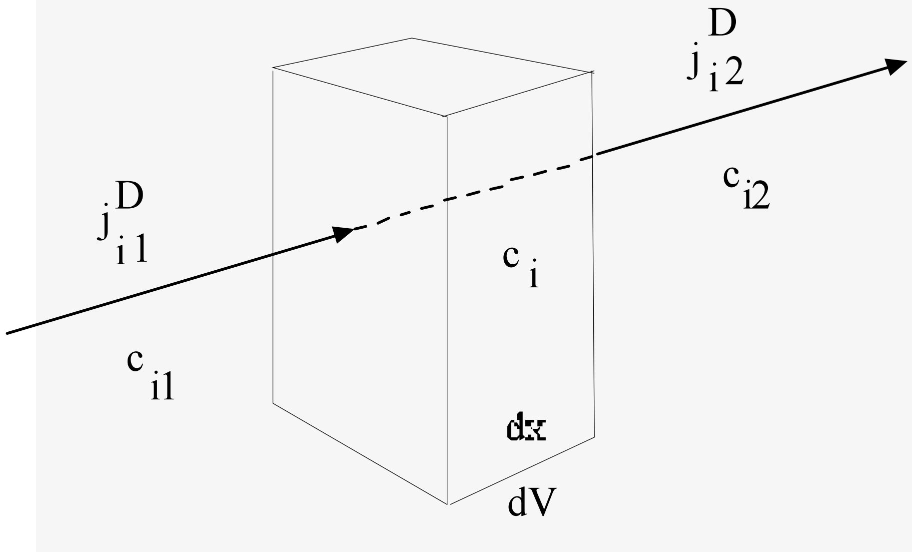
Dynamic models

The increment of concentration **dc_i** in the volume element **dV** in time **dt** equals to gradient of flux **j_i^D** in direction **x**:

$$\frac{\partial c_i}{\partial t} = -\frac{\partial j_i^D}{\partial x}$$



If the input and output fluxes /**j_{i1}^D** a **j_{i2}^D**/ were equal, the concentration in the volume element would not increase

The substitution for the flux gives

$$\frac{\partial c_i}{\partial t} = +D\frac{\partial^2 c_i}{\partial x^2}$$

Units control: $\frac{mol}{m^3}\frac{1}{s} = \frac{m^2}{s}\frac{mol}{m^3}\frac{1}{m^2}$

Modeling of geochemical processes

Dynamic models

Discretization Taylor expansion

first order equation:

$$f(t+\Delta t) = f(t) + \frac{\Delta t}{1!} f'(t) + \frac{(\Delta t)^2}{2!} f''(t) + \ldots + \frac{(\Delta t)^n}{n!} f^{(n)}(t) + \ldots + R_n$$

$$\Longrightarrow \quad \frac{f(t+\Delta t) - f(t)}{\Delta t} = f'(t) \quad \Longrightarrow \quad \left(\frac{\partial C}{\partial t}\right)_x = \frac{C_x^{t_2} - C_x^{t_1}}{\Delta t}$$

second order equation:

$$f(x+\Delta x) = f(x) + \frac{\Delta x}{1!} f'(x) + \frac{(\Delta x)^2}{2!} f''(x) + \ldots + \frac{(\Delta x)^n}{n!} f^{(n)}(x) + \ldots + R_n$$

$$f(x-\Delta x) = f(x) - \frac{\Delta x}{1!} f'(x) + \frac{(\Delta x)^2}{2!} f''(x) - \ldots + \frac{(\Delta x)^n}{n!} f^{(n)}(x) - \ldots + R_n$$

adding both equations gives

$$f(x+\Delta x) + f(x-\Delta x) = 2\, f(x) + 2\, \frac{\Delta x^2}{2!} f''(x) \quad \Longrightarrow \quad f''(x) = \frac{f(x+\Delta x) - 2\, f(x) + f(x-\Delta x)}{(\Delta x)^2}$$

$$\Longrightarrow \quad \left(\frac{\partial^2 C}{\partial x^2}\right)_{t_1} = \frac{C_{x+1}^{t_1} - 2\, C_x^{t_1} + C_{x-1}^{t_1}}{(\Delta x)^2}$$

Modeling of geochemical processes

Dynamic models

The complete diffusion equation is:

Explicit solution:

If θ = 0, then *explicit scheme*

$$\frac{C_x^{t_2} - C_x^{t_1}}{\Delta t} = D\,\frac{C_{x-1}^{t_1} - 2C_x^{t_1} + C_{x+1}^{t_1}}{(\Delta x)^2}$$

Defining a parameter **r** (mixing factor)

$$r = \frac{D\,\Delta t}{(\Delta x)^2}$$

yields

$$C_x^{t_2} = r\,C_{x-1}^{t_1} + (1-2r)\,C_x^{t_1} + C_{x+1}^{t_1}$$

The Explicit Solution is stable for **r** < 0,5 or **r** < 1/3

Modeling of geochemical processes
Dynamic models

Example - diffusion

$\Delta t =$ 0.05

$D =$ 0.15 $[cm^2\, hod^{-1}]$

$(\Delta x)^2 =$ 0.04

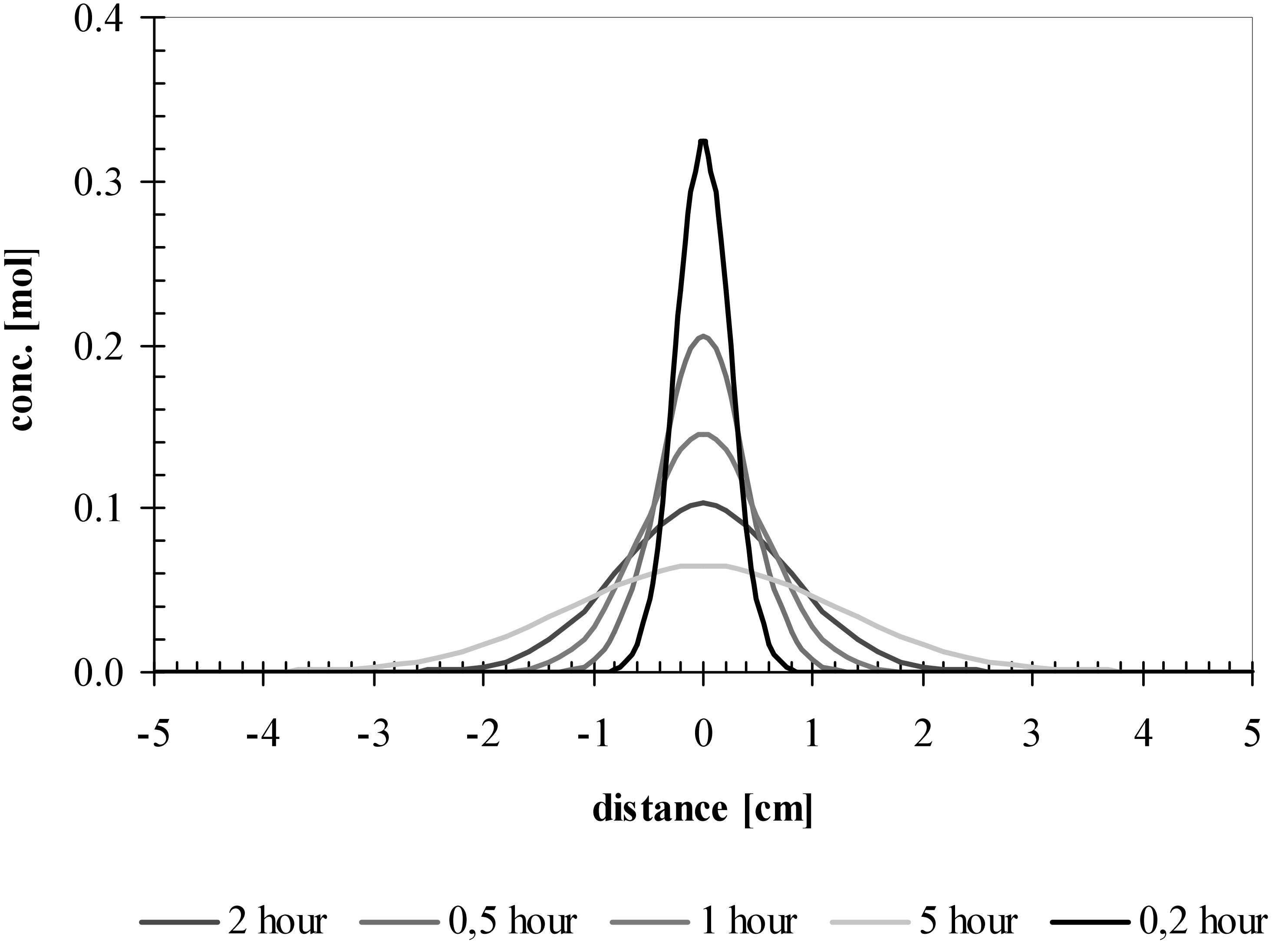
$r =$ 0.19

$$C_x^{t_2} = r\,C_{x-1}^{t_1} + (1-2r)C_x^{t_1} + r\,C_{x+1}^{t_1}$$

t/cm	-5	-4.8	…	-0.4	-0.2	0	0.2	0.4	…	4.8	5
0	0.00E+00	0.00E+00	…	0.00E+00	0.00E+00	1.00E+00	0.00E+00	0.00E+00	…	0.00E+00	0.00E+00
0.05	0.00E+00	0.00E+00	…	0.00E+00	1.88E-01	6.25E-01	1.88E-01	0.00E+00	…	0.00E+00	0.00E+00
0.1	0.00E+00	0.00E+00	…	3.52E-02	2.34E-01	4.61E-01	2.34E-01	3.52E-02	…	0.00E+00	0.00E+00
…	…	…	…	…	…	…	…	…	…	…	…
4.8	8.41E-06	2.06E-05	…	6.29E-02	6.55E-02	6.65E-02	6.55E-02	6.29E-02	…	2.06E-05	8.41E-06
4.85	9.12E-06	2.22E-05	…	6.26E-02	6.52E-02	6.61E-02	6.52E-02	6.26E-02	…	2.22E-05	9.12E-06
4.9	9.87E-06	2.40E-05	…	6.23E-02	6.49E-02	6.58E-02	6.49E-02	6.23E-02	…	2.40E-05	9.87E-06
4.95	1.07E-05	2.58E-05	…	6.20E-02	6.46E-02	6.54E-02	6.46E-02	6.20E-02	…	2.58E-05	1.07E-05
5	1.15E-05	2.77E-05	…	6.17E-02	6.43E-02	6.51E-02	6.43E-02	6.17E-02	…	2.77E-05	1.15E-05

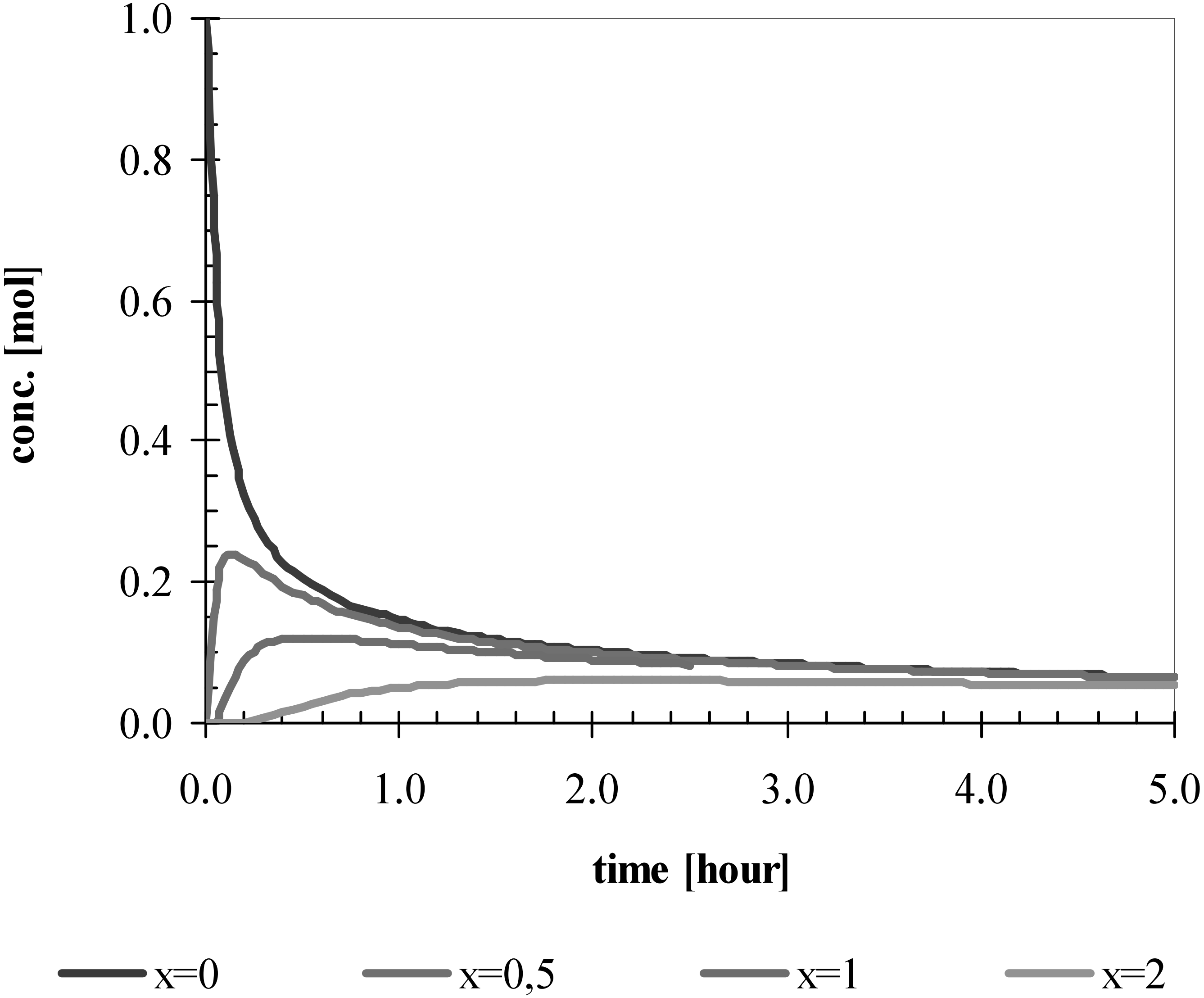
Modeling of geochemical processes

Dynamic models



Modeling of geochemical processes

Dynamic models



Modeling of geochemical processes

Dynamic models

Combining the processes

The change in concentration due to

(1) transport,

(2) dispersion (diffusion) and

(3) reaction

$$\left(\frac{\partial C}{\partial t}\right)_x = -\nu\left(\frac{\partial C}{\partial x}\right)_t + D_L\left(\frac{\partial^2 C}{\partial x^2}\right)_{t.} - \left(\frac{\partial C}{\partial t}\right)_x$$

transport **dispersion** **reaction**

Modeling of geochemical processes

Dynamic models

Diffusion and reaction

$$\left(\frac{\partial C}{\partial t}\right)_x^{celk} = D\left(\frac{\partial^2 C}{\partial x^2}\right)_t + F(C)^{reakce}$$

Discretization:

$$\frac{C_x^{t_2} - C_x^{t_1}}{\Delta t} = D\,\frac{C_{x-1}^{t_1} - 2\,C_x^{t_1} + C_{x+1}^{t_1}}{\Delta x^2} + F(C_x^{t_1})$$

$$C_x^{t_2} = C_x^{t_1} + \frac{\Delta t\, D}{\Delta x^2}\left(C_{x-1}^{t_1} - 2\,C_x^{t_1} + C_{x+1}^{t_1}\right) + \Delta t\, F(C_x^{t_1})$$

$$\frac{\Delta t\, D}{\Delta x^2} = r$$

$$C_x^{t_2} = (1 - 2r)\,C_x^{t_1} + r\,C_{x-1}^{t_1} + r\,C_{x+1}^{t_1} + \Delta t\, F(C_x^{t_1})$$

Modeling of geochemical processes
Dynamic models

Diffusion of aqueous Fe through alkaline solution in pore environment

Precipitation of Fe-hydroxide far from equilibrium at constant concentration of OH^- ions

pH =	7.9
r_{Fe} =	0.32
[OH] =	8.00E-07
k_1 =	1.00E+18
k_2 =	1.00E-20
K =	1.00E+38

$$Fe^{3+} + 3\,OH^- \xrightarrow{k_1} Fe(OH)_3$$

$D_{Fe} = 1{,}5.10^{-6}$ cm^2 s^{-1} = $1{,}3.10^{-1}$ cm^2 den^{-1}

$$\frac{\Delta t\, D_{Fe}}{\Delta x^2} = r_{Fe}$$

$[Fe^{3+}]_{t=0} = 1.10^{-2}$ mol l^{-1}

$$[Fe]_x^{t_2} = (1 - 2\,r_{Fe})[Fe]_x^{t_1} + r_{Fe}\,[Fe]_{x-1}^{t_1} + r_{Fe}\,[Fe]_{x+1}^{t_1} - \Delta t\; k_1 [Fe]_x^{t_1}\left([OH]_x^{t_1}\right)^3$$

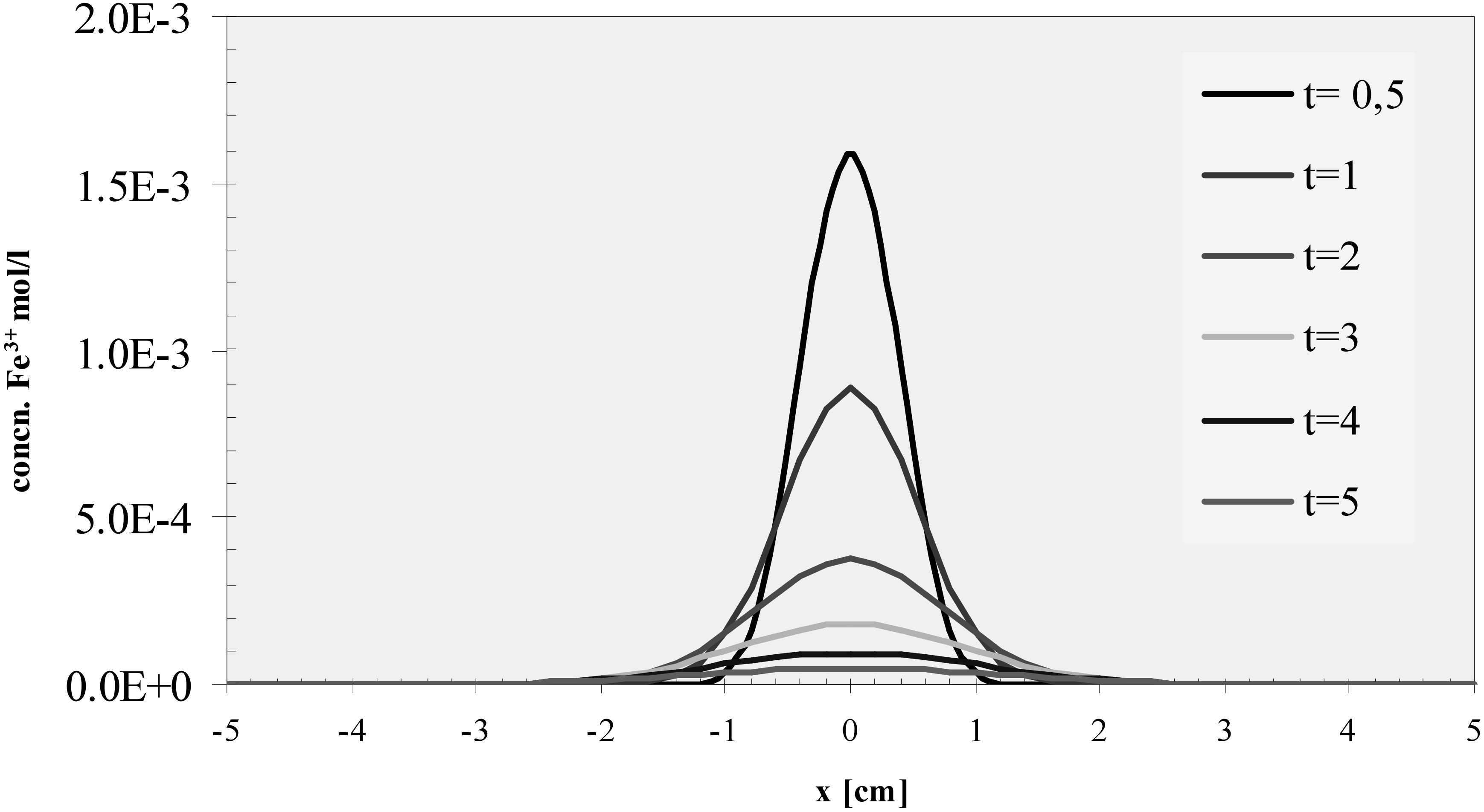
Modeling of geochemical processes

Dynamic models

t/x	-5.0	-4.8	…	-0.4	-0.2	0.0	0.2	0.4	…	4.8	5.0
0.0	0.00E+00	0.00E+00	…	0.00E+00	0.00E+00	1.00E-02	0.00E+00	0.00E+00	…	0.00E+00	0.00E+00
0.1	0.00E+00	0.00E+00	…	0.00E+00	3.24E-03	3.01E-03	3.24E-03	0.00E+00	…	0.00E+00	0.00E+00
0.2	0.00E+00	0.00E+00	…	1.05E-03	1.95E-03	3.00E-03	1.95E-03	1.05E-03	…	0.00E+00	0.00E+00
0.3	0.00E+00	0.00E+00	…	9.47E-04	1.90E-03	2.17E-03	1.90E-03	9.47E-04	…	0.00E+00	0.00E+00
…	…	…	…	…	…	…	…	…	…	…	…
…	…	…	…	…	…	…	…	…	…	…	…
4.8	2.30E-09	6.11E-09	…	5.24E-05	5.49E-05	5.57E-05	5.49E-05	5.24E-05	…	6.11E-09	2.30E-09
4.9	2.67E-09	7.01E-09	…	4.93E-05	5.15E-05	5.23E-05	5.15E-05	4.93E-05	…	7.01E-09	2.67E-09
5.0	3.07E-09	7.95E-09	…	4.64E-05	4.84E-05	4.91E-05	4.84E-05	4.64E-05	…	7.95E-09	3.07E-09

Modeling of geochemical processes

Dynamic models



Modeling of geochemical processes

Dynamic models

The analytical solution

The Gaussian function

$$G(x) = A\,e^{-\frac{x^2}{2\sigma^2}}$$

where σ is referred to as the spread or standard deviation and *A* is a constant

The function can be normalized

yielding the normalized Gaussian:

$$G(x) = \frac{1}{\sqrt{2\pi}\,\sigma}\,e^{-\frac{x^2}{2\sigma^2}}$$

The Error function $\operatorname{erf} x = \frac{2}{\sqrt{\pi}} \int_0^x e^{-u^2}\,du$

The relation between the normalized Gaussian distribution and the error function equals:

$$\int_{-x}^{x} G(x)\,dx = Erf\left(\frac{x}{\sigma\sqrt{2}}\right)$$

A series approximation for small value of *x* is given by:

$$\operatorname{erf} x = \frac{2}{\sqrt{\pi}}\left(x - \frac{x^3}{3\cdot 1!} + \frac{x^5}{5\cdot 2!} + \frac{x^7}{7\cdot 3!} + \ \dots\ \right)$$

Modeling of geochemical processes
Dynamic models

An approximate expression for large values of x can be obtained from:

$$\operatorname{erf} x \cong 1 - \frac{e^{-x^2}}{\sqrt{\pi}\, x}\left(1 - \frac{1}{2x^2} + \frac{1\cdot 3}{(2x^2)^2} + \frac{1\cdot 3\cdot 5}{(2x^2)^3} + \ \ldots\right)$$

The Complementary Error function

The complementary error function equals one minus the error function yielding:

$$\operatorname{erfc} x = 1 - \operatorname{erf} x = \frac{2}{\sqrt{\pi}} \int_x^{\infty} e^{-u^2}\, du$$

which, combined with the series expansion of the error function listed above, provides approximate expressions for small and large values of x:

$$\operatorname{erfc} x = 1 - \frac{2}{\sqrt{\pi}}\left(x - \frac{x^3}{3\cdot 1!} + \frac{x^5}{5\cdot 2!} + \frac{x^7}{7\cdot 3!} + \ \ldots\right)$$

$$\operatorname{erfc} x \cong \frac{e^{-x^2}}{\sqrt{\pi}\, x}\left(1 - \frac{1}{2x^2} + \frac{1\cdot 3}{(2x^2)^2} + \frac{1\cdot 3\cdot 5}{(2x^2)^3} + \ \ldots\right)$$

Modeling of geochemical processes

Dynamic models

Numeric solution of diffusion equation

The Method of Finite Differential

Creation of a uniform net by discretization of the variables **x** and **t**

- Let **Δx** and **Δt** are discrete steps on variables **x** and **t**, respectively. The variables **x** and **t** are defined as $x = i\,\Delta x$ and $t = j\,\Delta t$, respectively.
- The index **i** or **j** relates to a step number. **i** and **j** are 0,1,2...n!
- The concentration relates to a point in the two-dimensional net with coordinates $x = i\Delta x$ a $t = j\Delta t$.

Let ***δx*** is a ***central differential operator*** (in the point **j**) : $\delta_x C_i^j = C_{i+\frac{1}{2}}^j - C_{i-\frac{1}{2}}^j$

Second order differential is

$$\delta_x^2 C_i^j = \delta_x\left(\delta_x C_i^j\right) = \delta_x\left(C_{i+\frac{1}{2}}^j - C_{i-\frac{1}{2}}^j\right) = \left(C^j_{\left(i+\frac{1}{2}\right)+\frac{1}{2}} - C^j_{\left(i-\frac{1}{2}\right)+\frac{1}{2}}\right) - \left(C^j_{\left(i+\frac{1}{2}\right)-\frac{1}{2}} - C^j_{\left(i-\frac{1}{2}\right)-\frac{1}{2}}\right)$$

$$\delta_x^2 C_i^j = C_{i-1}^j - 2\,C_i^j + C_{i+1}^j$$

Modeling of geochemical processes

Dynamic models

Differentiation with respect **x** (in the point **j**) can be replaced by finite difference:

$$\frac{\partial C(x,t)}{\partial x} \cong \frac{C^{j}_{i+1/2} - C^{j}_{i-1/2}}{\Delta x}$$

and

$$\frac{\partial^2 C(x,t)}{\partial x^2} \cong \frac{C^{j}_{i-1} - 2C^{j}_{i} + C^{j}_{i+1}}{\Delta x^2}$$

Central differential operator δt (for time) : **t** is in the middle of the interval **t** + **Δt**:

$$\delta_t C_i^{j+1/2} = C_i^{(j+1/2)+1/2} - C_i^{(j+1/2)-1/2} = C_i^{j+1} - C_i^{j}$$

Time derivation in point **t = j + 1/2**:

$$\frac{\partial C(x,t)}{\partial t} \cong \frac{C_i^{j+1} - C_i^{j}}{\Delta x}$$

Druhá derivace podle **x** pak může být nahrazena lineární kombinací konečných diferencí druhého řádu v bodech **t** a **t + Dx** (čili v bodech **j** a **j + 1**!) :

$$\frac{\partial^2 C(x,t)}{\partial x^2} \cong \theta \frac{\delta_x^2 C_i^{j+1}}{\Delta x^2} + (1-\theta)\frac{\delta_x^2 C_i^{j}}{\Delta x^2}$$

Modeling of geochemical processes

Dynamic models

The complete diffusion equation is:

$$\frac{\delta_t C_i^{j+\frac{1}{2}}}{\Delta t} \cong D\left[\theta \frac{\delta_x^2 C_i^{j+1}}{\Delta x^2} + (1-\theta)\frac{\delta_x^2 C_i^{j}}{\Delta x^2}\right]$$

where θ is a parameter on the interval [0, 1].

Explicit solution:

If θ = 0, then *explicit scheme*

$$\frac{C_i^{j+1} - C_i^{j}}{\Delta t} = D\,\frac{C_{i-1}^{j} - 2C_i^{j} + C_{i+1}^{j}}{\Delta x^2}$$

Defining a parameter **r** (mixing factor, mixf)

$$r = \frac{D\,\Delta t}{\Delta x^2}$$

yields

$$C_i^{j+1} = r\,C_{i-1}^{j} + (1-2r)\,C_i^{j} + C_{i+1}^{j}$$

The Explicit Solution is stable for **r** < 0,5 or **r** < 1/3