Reactive transport modeling of carbonate diagenesis on unstructured grids

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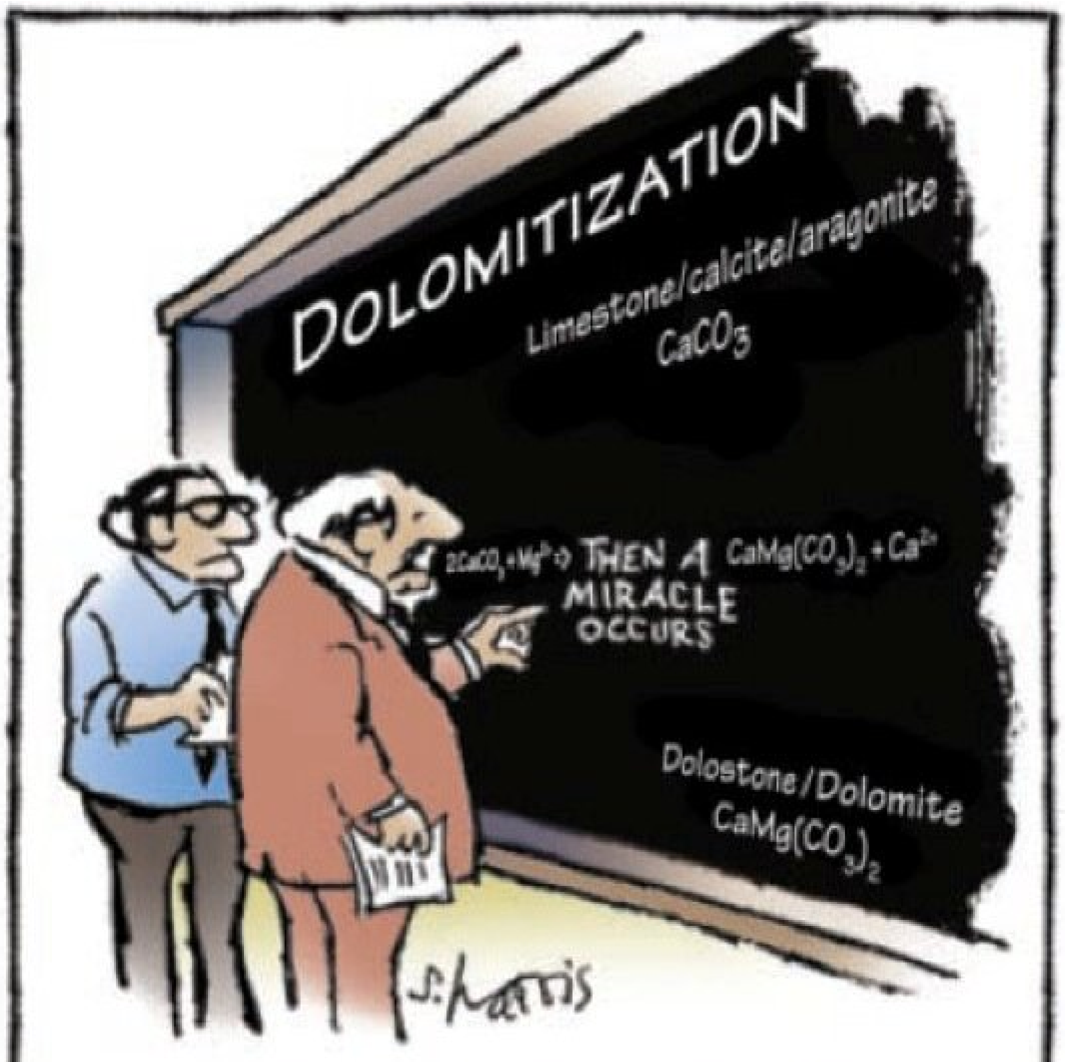
Dolomitization and geochemical modeling



"I think you should be more explicit here in step two."

"Hollywood may never make a movie about geochemical modeling, but the field has its roots in top-secret efforts to formulate rocket fuels in the 1940s and 1950s. Anyone who reads cheap novels knows that these efforts involved brilliant scientists endangered by spies, counterspies,hidden microfilm, and beautiful but treacherous women."

(Bethke, C. Geochemical and Biogeochemical Reaction Modeling, Cambridge University Press 2008)

Agenda

- **Method description. Software design**
- Benchmark 1d: calcite dissolution – dolomite precipitation
- Calcite dolomitization on a 2d cross-section with realistic geology

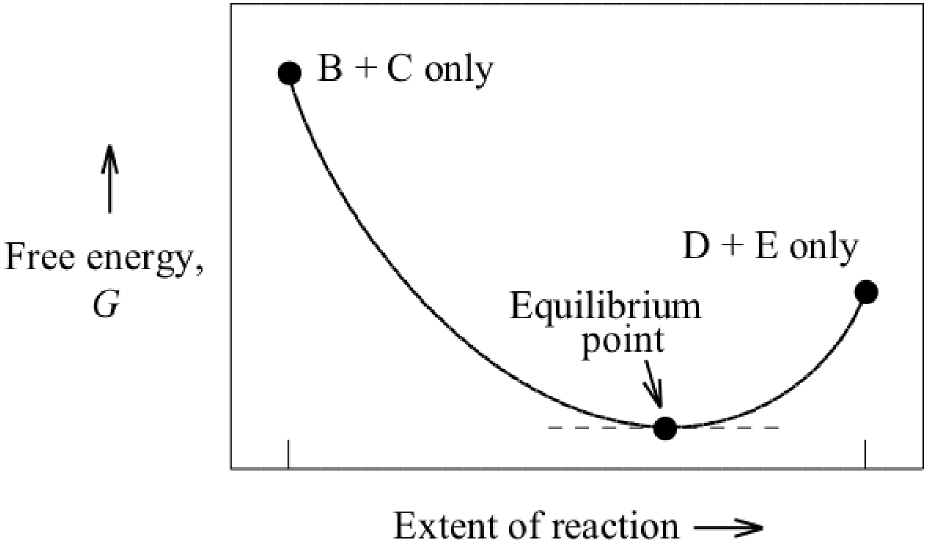
Chemical modeling

Equilibrium constant method

Minimization of Gibbs free energy

TOUGH, PHREEQC

GEMS



Variation in free energy G with reaction progress for the reaction

$bB+cC \leftrightarrow dD+eE$.

The reaction's equilibrium point is the minimum along the free energy curve

Two methods are computationally and conceptually equivalent (Zeleznik and Gordon (1960, 1968) and Brinkley (1960))

Chemical reactions and Math

$A+B \leftrightarrow C$

“Fast” reaction
(aqueous complexation)

takes place at a significantly greater rate than the transport processes that redistribute mass

$$K_{eq}=\frac{[A][B]}{[C]}$$

$$[C]=\frac{1}{K_{eq}}[A][B]$$

Algebraic system
of nonlinear equations

“Slow” reaction
(dissolution-precipitation)

takes place at a significantly smaller rate than the transport processes that redistribute mass, requires a kinetic description because the flow system can remove products and reactants before reactions can proceed to equilibrium

$$\frac{d[C]}{dt}=-r([A],[B],T,SA,SI\,...)$$

System of ordinary
differential equations (ODE)

Simple carbonate system

One reaction for each mineral and each secondary species

$$
\begin{aligned}
CaCO_3 &\leftrightarrows Ca^{2+} + CO_3^{2-} \\
CaMg(CO_3)_2 &\leftrightarrows Ca^{2+} + Mg^{2+} + 2CO_3^{2-} \\
OH^- &\leftrightarrows H_2O - H^+ \\
HCO_3^- &\leftrightarrows H^+ + CO_3^{2-} \\
CO_2 &\leftrightarrows -H_2O + 2H^+ + CO_3^{2-}
\end{aligned}
$$

$$
\begin{aligned}
K_1 &= [Ca^{2+}][CO_3^{2-}] \\
K_2 &= [Ca^{2+}][Mg^{2+}][CO_3^{2-}]^2
\end{aligned}
$$

$$OH^- = \frac{1}{K_3}\frac{1}{[H^+]} \qquad HCO_3^- = \frac{1}{K_4}[H^+][CO_3^{2-}]$$

$$CO_2 = \frac{2}{K_5}[H^+]^2[CO_3^{2-}]$$

Secondary species concentrations are expressed using concentrations of primary species and equilibrium constants

Mass conservation

For each primary species total concentration in mobile and immobile components remains constant

$$
\begin{aligned}
T_{Ca^{2+}} &= [Ca^{2+}] + n_{CaCO3} + n_{CaMg(CO_3)_2} \\
T_{Mg^{2+}} &= [Mg^{2+}] + n_{CaMg(CO_3)_2} \\
T_{H^+} &= [H^+] - \frac{1}{K_3}\frac{1}{[H^+]} + \frac{1}{K_4}[H^+][CO_3^{2-}] + \frac{2}{K_5}[H^+]^2[CO_3^{2-}] \\
T_{CO_3^{2-}} &= [CO_3^{2-}] + \frac{1}{K_4}[H^+][CO_3^{2-}] + \frac{1}{K_5}[H^+]^2[CO_3^{2-}] \\
&\quad + n_{CaCO3} + 2\, n_{CaMg(CO_3)_2}
\end{aligned}
$$

n_{CaCO3}, $n_{CaMg(CO_3)_2}$ – mineral concentrations for calcite and dolomite

Chemical system of equations. Change of variables

$$\begin{aligned}
e^{x_1} + x_5 + x_6 - T_1 - n_1 - n_2 &= 0 \\
e^{x_2} + x_6 - T_2 - n_2 &= 0 \\
e^{x_3} - e^{-k_3 - x_3} + e^{-k_4 + x_3 + x_4} + 2e^{-k_5 + 2x_3 + x_4} - T_3 &= 0 \\
e^{x_4} + e^{-k_4 + x_3 + x_4} + e^{-k_5 + 2x_3 + x_4} + x_5 + 2x_6 - T_4 - n_1 - 2n_2 &= 0 \\
-k_1 + x_1 + x_4 &= 0 \\
-k_2 + x_1 + x_2 + 2x_4 &= 0
\end{aligned}$$

$$\begin{aligned}
&x_1 = ln([Ca^{2+}]), x_2 = ln([Mg^{2+}]), \\
&x_3 = ln([H^+]),\ x_4 = ln([CO_3^{2-}]), \\
&x_5 = n_{CaCO3},\ x_6 = n_{CaMg(CO_3)_2} \\
&k_i = ln(K_i),\ i = \overline{1,5}
\end{aligned}$$

$T_1,\ T_2,\ T_3,\ T_4$

- initial total aqueous concentrations of primary species

n_1, n_2

- initial mineral amounts

Reactive transport modeling

$$\frac{d}{dt}T + L(C) = q$$

- transport equations written for each primary species,

$$\Phi(X, T) = 0$$

- mass conservation equations

$$C - C(X) = 0$$

T – total concentration of chemical species (mobile and immobile),
C – mobile concentration of chemical species,
L – transport operator (advection-diffusion-dispersion),
q – source term

Sequential non-iterative approach (SNIA)

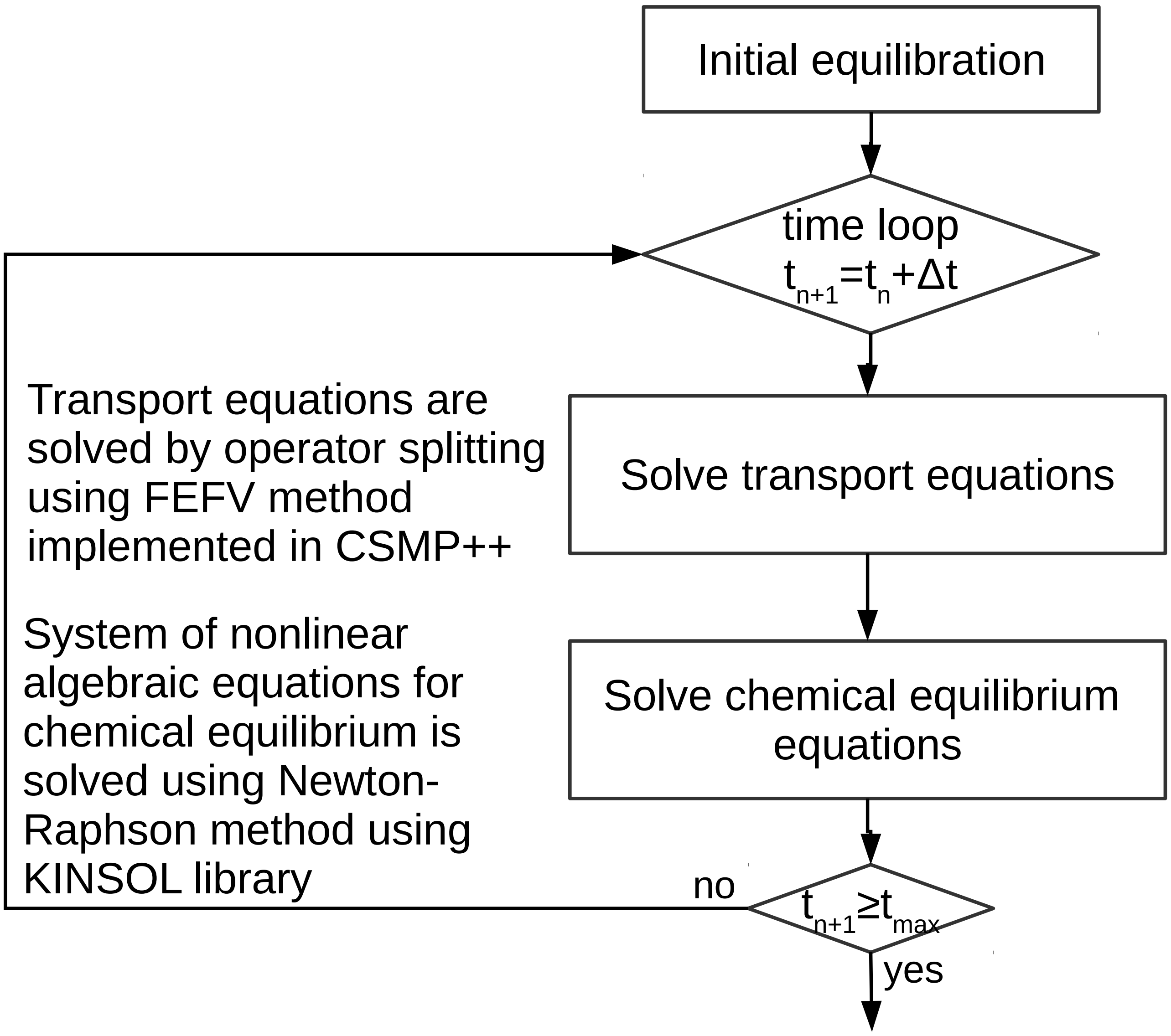
$$T^{n+1} + \Delta t\, L(C^n) - T^n = \Delta t\, q^n$$
$$\Phi(X, T^{n+1}) = 0$$
$$C^{n+1} - C(X) = 0$$

Sequential iterative approach (SIA)

$$T^{n+1} + \Delta t\, L(C^{n+1}) - T^n = \Delta t\, q^n$$
$$\Phi(X, T^{n+1}) = 0$$
$$C^{n+1} - C(X) = 0$$

(after C. de Dieuleveult, J. Erhel, M. Kern A global strategy for solving reactive transport equations, Journal of Computational Physics, 2009)

Solution procedure



Initial equilibration

time loop
$t_{n+1}=t_n+\Delta t$

Solve transport equations

Solve chemical equilibrium equations

$t_{n+1} \geq t_{max}$

no

yes

Transport equations are solved by operator splitting using FEFV method implemented in CSMP++

- for all finite volumes
- for each basic species separately

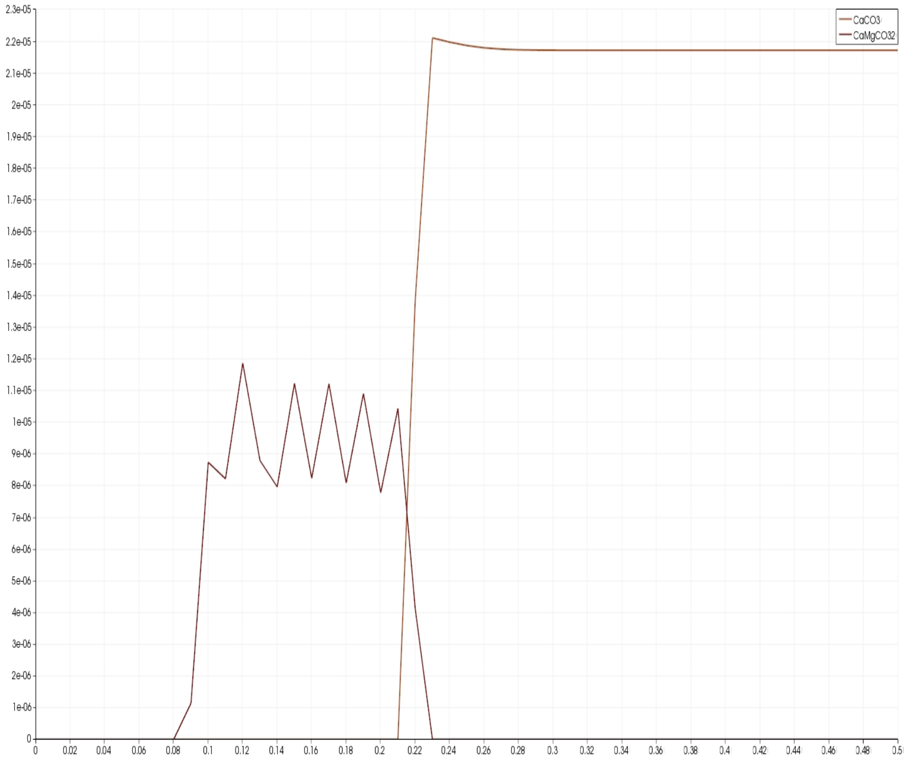
System of nonlinear algebraic equations for chemical equilibrium is solved using Newton-Raphson method using KINSOL library

- for each finite volume separately
- for all species

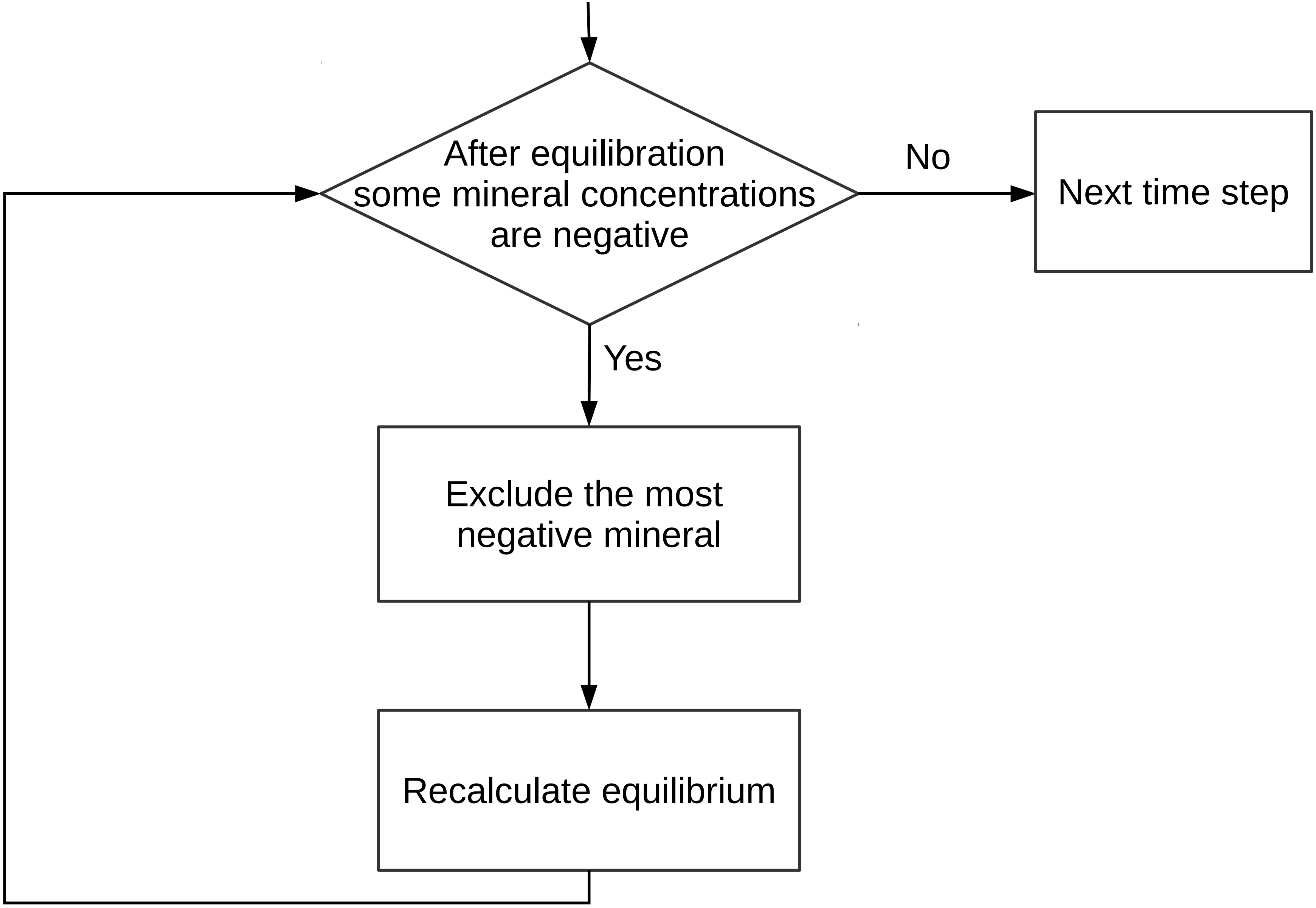
Numerical issues. Oscillations

Initial guess for
Newton-Raphson:

- Always choose the most abundant species as primary species
- 95% of total species aqueous concentration is a good initial approximation for [Ca^{2+}] and [Mg^{2+}]
- For [CO_3^{2-}] initial guess from the previous time step



Mineral swap procedure



After equilibration some mineral concentrations are negative

No

Next time step

Yes

Exclude the most negative mineral

Recalculate equilibrium

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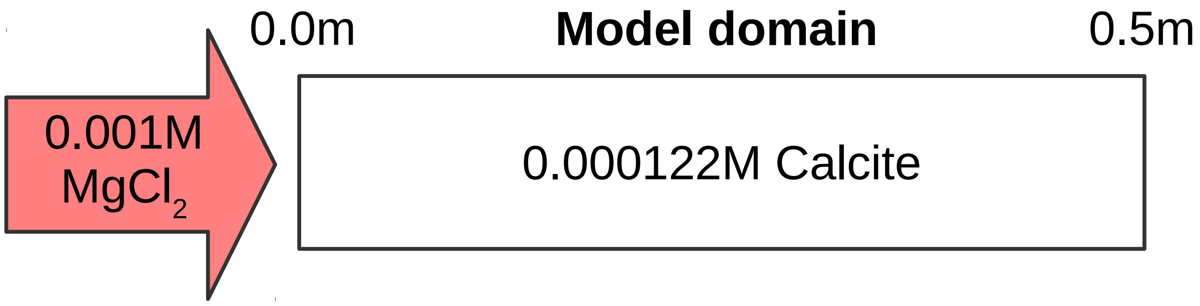
Benchmark: calcite dissolution, dolomite precipitation



0.0m **Model domain** 0.5m

0.001M $MgCl_2$

0.000122M Calcite

temperature	25°C
pressure	1atm
mesh size	0.01m
time step	200s

Material properties

Parameter	**Value**	**Unit**
Column length	0.5	*m*
Porosity	0.32	-
Bulk density	1800	kg/m^3
Pore velocity	9.375×10^{-6}	*m/s*
Flow rate	3×10^{-6}	*m/s*

- Pore fluid in 1D column is initially equilibrated with calcite
- Column is flushed with $MgCl_2$ solution
- Calcite dissolves, dolomite is formed temporarily as a moving zone

P. Engesgaard, K., Kipp, *A geochemical transport model for redox-controlled movement of mineral fronts in groundwater flow systems: A case of nitrate removal by oxidation of pyrite*, Water Resources Research, 28, pp. 2829-2843, 1992.

Benchmark: calcite dissolution, dolomite precipitation

$CaCO_3(s) = Ca^{2+} + CO_3^{2-}$ (-8.47)

$CaMg(CO_3)_2 = Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$ (-17.17)

$Ca^{2+} + CO_3^{2-} = CaCO_3(aq)$ (3.23)

$Mg^{2+} + CO_3^{2-} = MgCO_3(aq)$ (2.98)

$H^+ + OH^- = H_2O$ (-14.01)

$H^+ + CO_3^{2-} = HCO_3$ (10.31)

$2H^+ + CO_3^{2-} = H_2O + CO_2(aq)$ (16.71)

$Cl^- = Cl^-$

Component and solid concentrations

	Boundary	Initial
pH	7.06	9.91
Ca^{2+}	0.0	1.239e-4
CO_3^{2-}	0.0	1.239e-4
Mg^{2+}	1.e-3	0.0
Cl^-	2.e-3	0.0
$CaCO_3(s)$	0.0	2.17e-5
$CaMg(CO_3)_2$	0.0	0.0

P. Engesgaard, K., Kipp, *A geochemical transport model for redox-controlled movement of mineral fronts in groundwater flow systems: A case of nitrate removal by oxidation of pyrite*, Water Resources Research, 28, pp. 2829-2843, 1992.

Benchmark: calcite dissolution, dolomite precipitation

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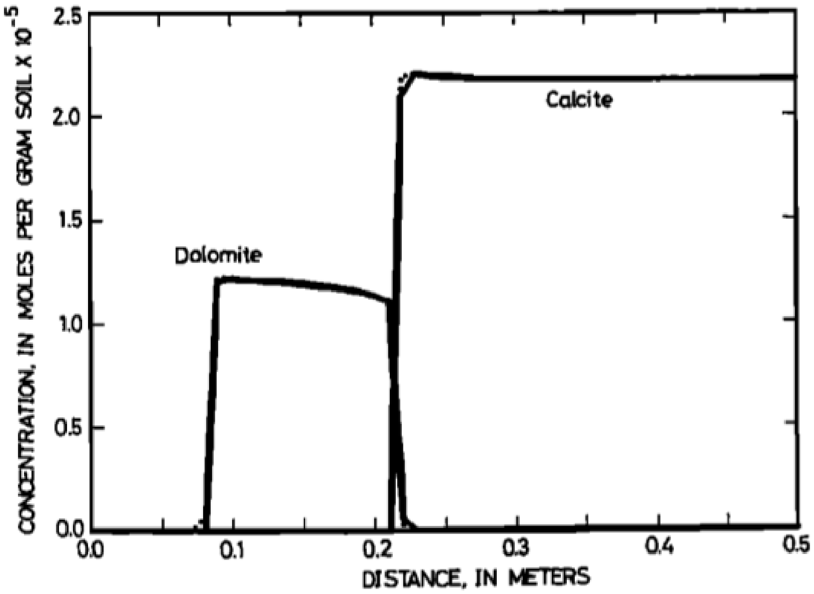
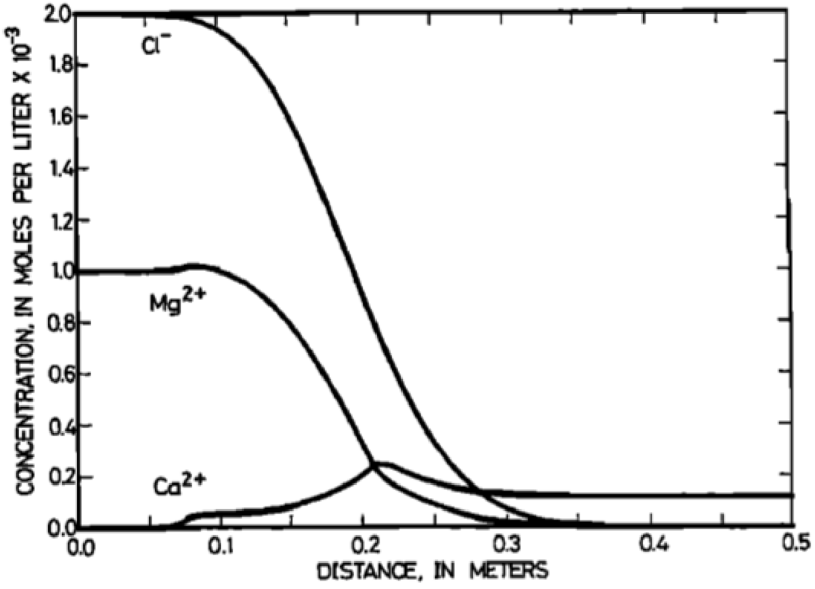
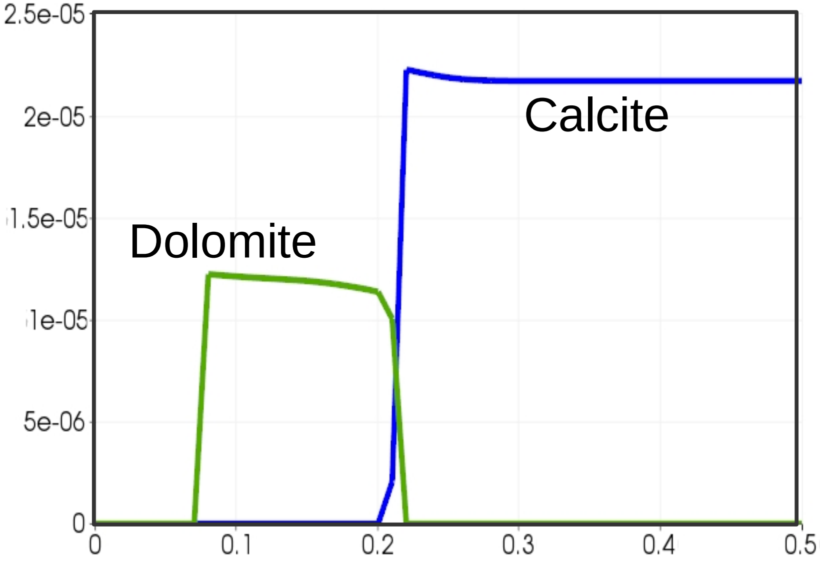
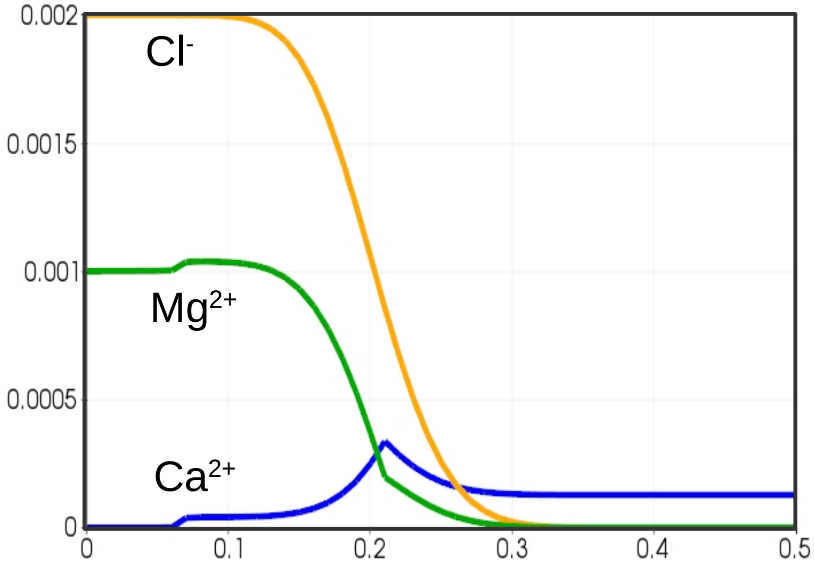




(Engesgaard, Kipp, 1992)





time = 21000*s*

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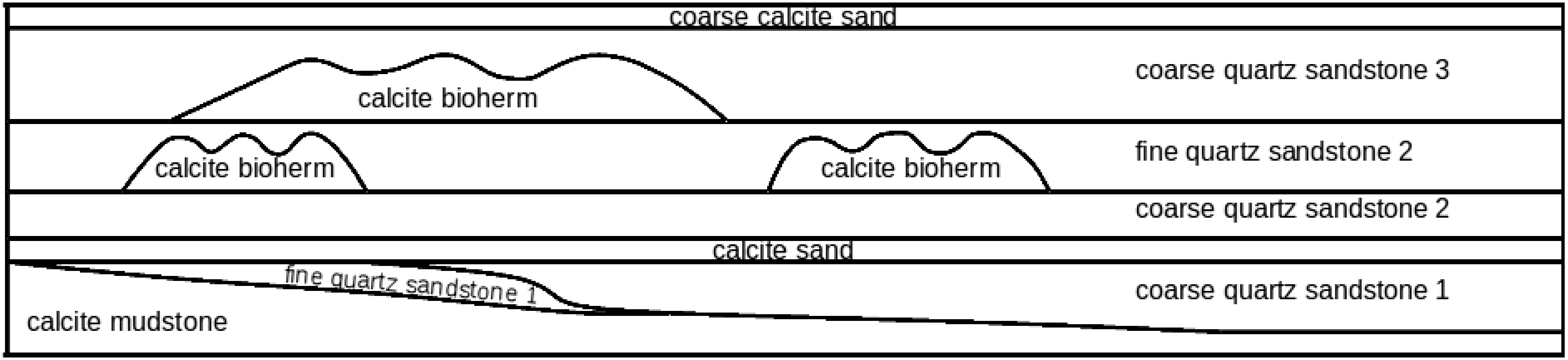
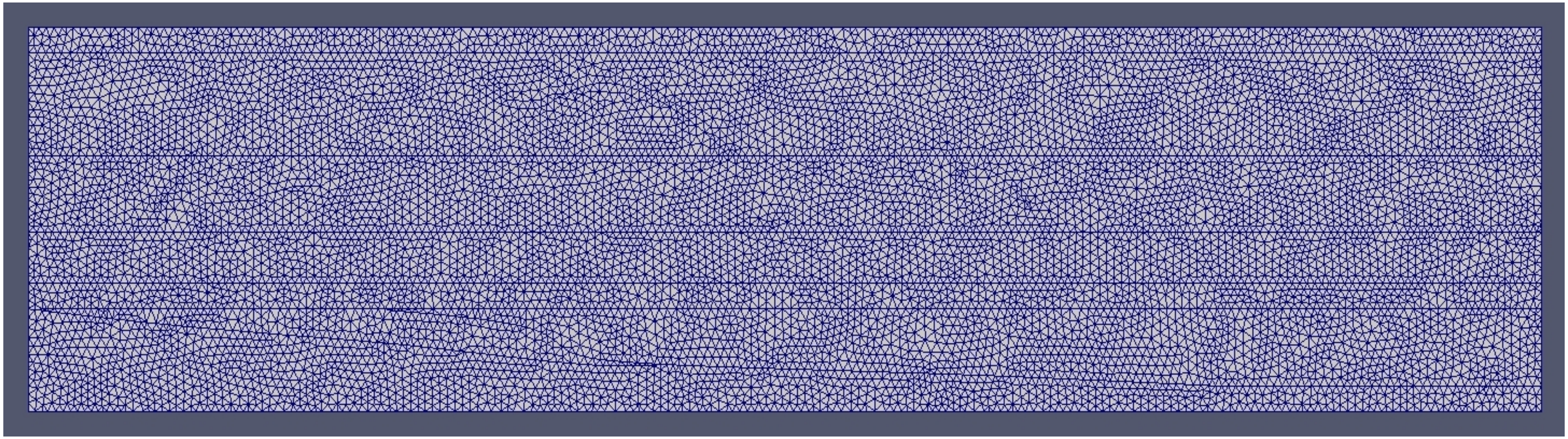
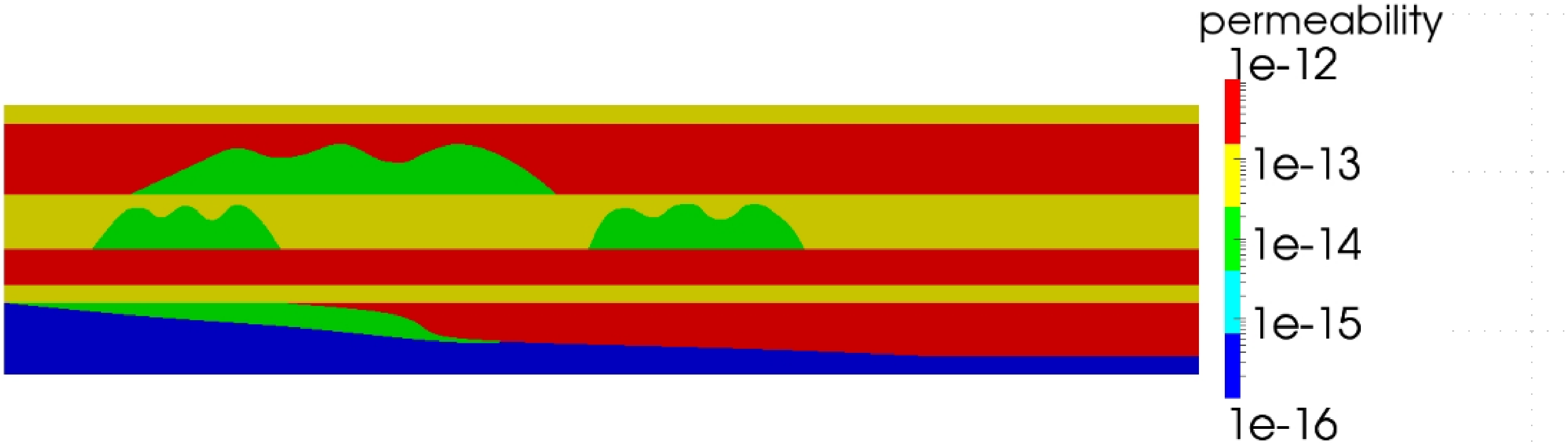
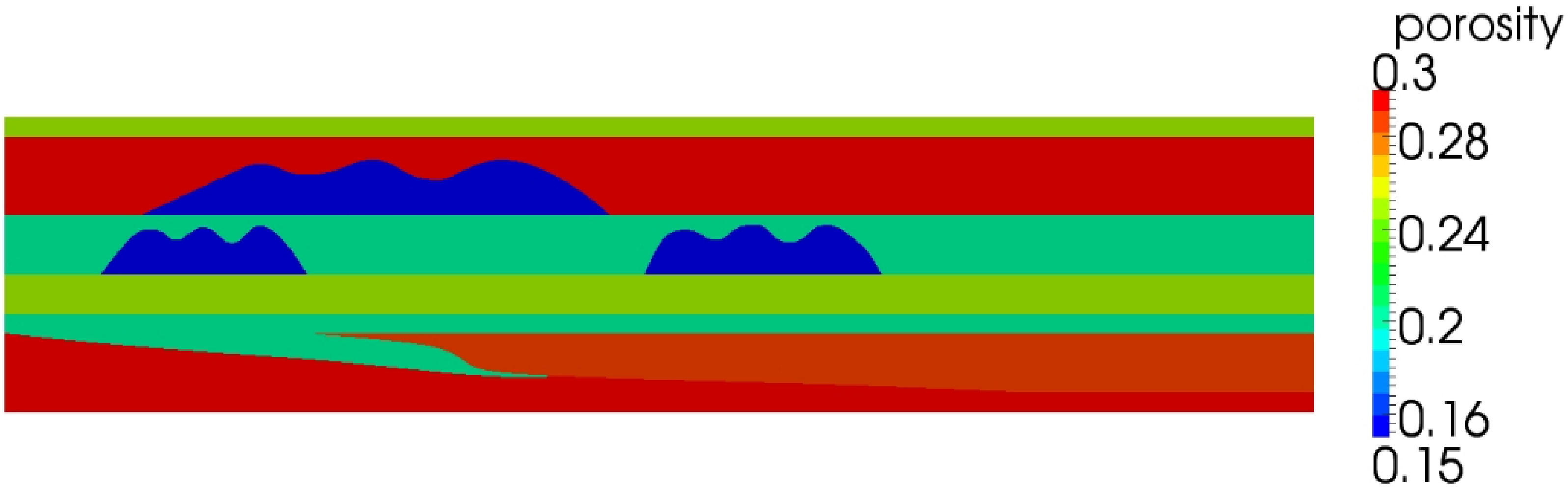
2D simulation:geological cross-section





2D simulation: rock properties





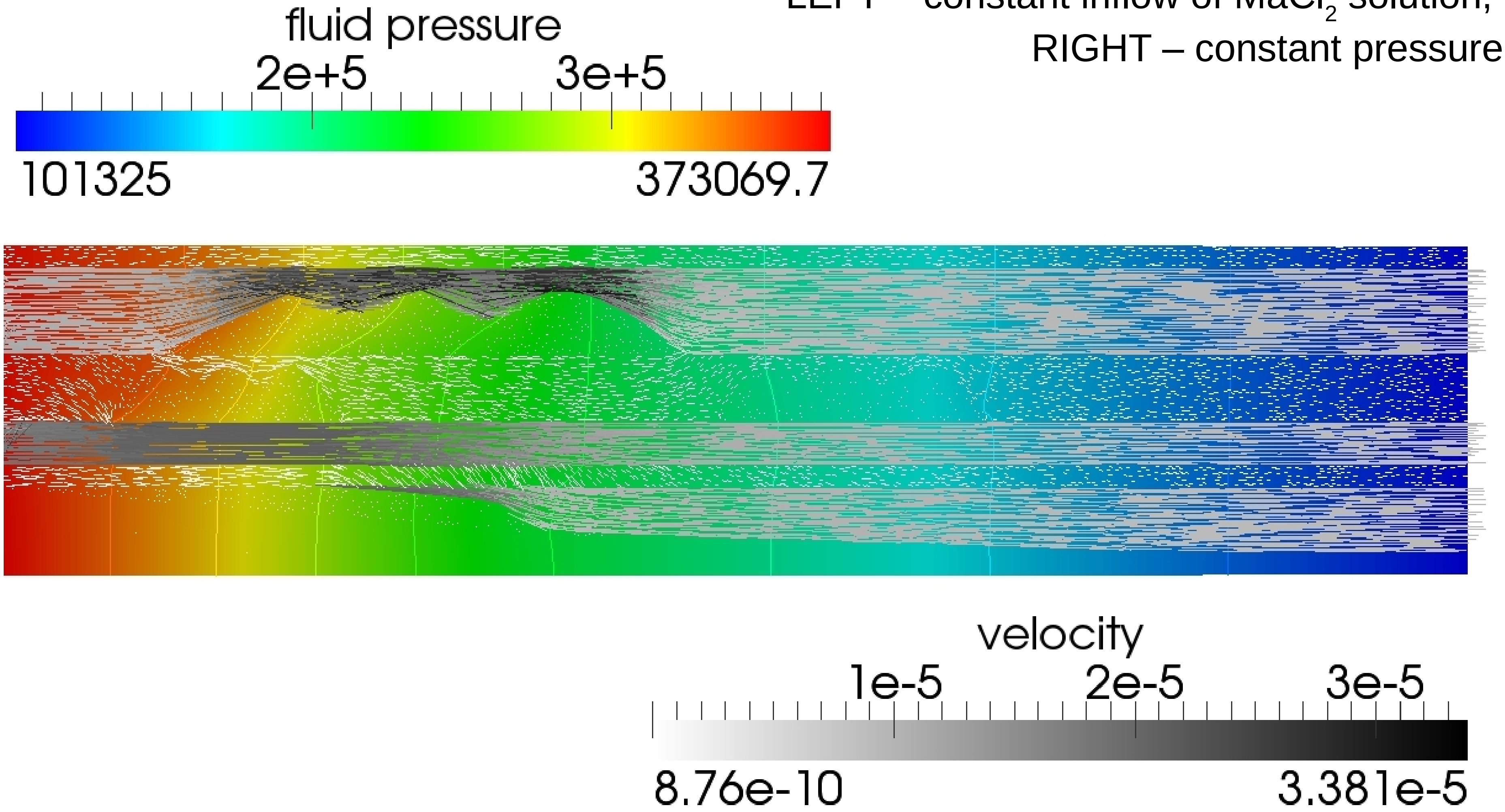
2D simulation: essential conditions

Initial conditions: water equilibrated with calcite

Boundary conditions:

LEFT – constant inflow of MaCl$_2$ solution,

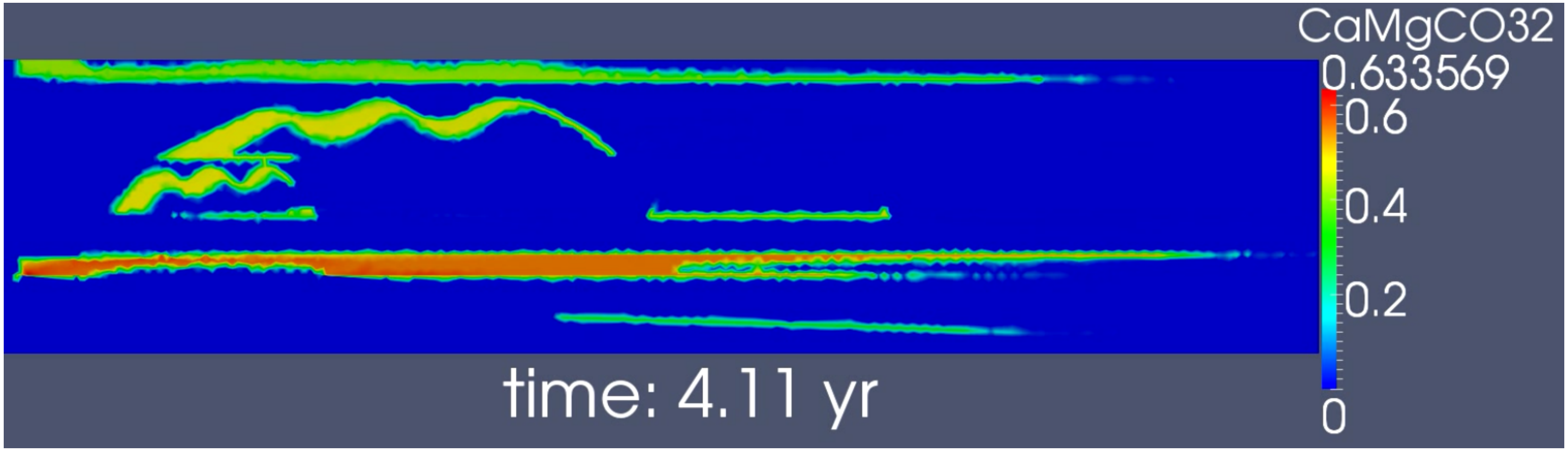
RIGHT – constant pressure



2D simulation: results

Conclusions: 2D simulation

- Bioherms get partially dolomitized in the direction of fluid flow
- Calcite sands get partially dolomitized due to Mg provided from permeable sandstone layers
- Calcite mudstone layer gets partially dolomitized after calcite sand layer gets completely dolomitized in the middle part



Conclusions: general

- RTM prototype module was implemented in CSMP
- 1D benchmark was conducted and results are in a good agreement
- 2D simulation was performed and the ability of combining chemistry with transport with realistic geometry was shown
- General framework for further software development was established

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Thank you
for your attention!

Future work

- Include more minerals and aqueous species
- Pitzer activity model
- Kinetic control reactions
- New porosity/permeability correlation
- 3d simulations