# Geochemical and Reactive Transport modelling

## Exercises

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Technische Universität Berlin

# Geochemical and Reactive Transport modelling

## 1. Speciation calculations

# Speciation

- ✓ **Speciation is the calculation of the concentrations of all the species in a chemical system**

- ✓ Speciation **requires** solution of a **system of equations**:
  - **Mass action laws**
    - $H_2O = H^+ + OH^-$
    - $HCO_3^- = H^+ + CO_3^{2-}$
    - $CaCO_{3(s)} = Ca^{+2} + CO_3^{2-}$

  - **Data equations** – based on our knowledge of the system
    - $pH = -\log[H^+]$
    - Charge balance: $[H^+] + 2\,[Ca^{+2}] - [HCO_3^-] - 2\,[CO_3^{2-}] - [OH^-]$
    - Total concentrations of dissolved species: $C_{,tot}$, $Ca_{,tot}$
    - Alkalinity: $[OH^-] + [HCO_3^-] + 2\,[CO_3^{2-}]$
    - Electrical conductivity
    - Equilibrium with mineral
    - Equilibrium with gas
    - …

# Gypsum solubility calculation

Calculate how much gypsum ($CaSO_4 \cdot 2H_2O$) dissolves in clean water until equilibrium is reached

$$CaSO_4 \cdot 2H_2O \rightarrow Ca^{2+} + SO_4^{2-} + 2H_2O \qquad \log K = -4.6$$

- Mass action law: $\log[Ca^{2+}] + \log[SO_4^{2-}] = -4.6$
- Mass balance:

  $[Ca^{2+}] = x$ x = moles of dissolved gypsum / volume

  $[SO_4^{2-}] = x$

- Solution

$[Ca^{2+}] = [SO_4^{2-}] = x = 10^{-2.3}$

$\rightarrow$ Moles of dissolved gypsum = $10^{-2.3} = 5.0 \cdot 10^{-3}$ mol/l

# Speciation calculation for gypsum

- ✓ Mass Action Law:

$$CaSO_4 \cdot 2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O \qquad \log K = -4.6$$

- ✓ Datum:

  $Ca_{tot} = Ca^{2+} = 10^{-2}$ mol/l

- ✓ Solution is trivial if a = c -> $SO_4^{2-} = 10^{-4.6} * 10^{-2} = 10^{-2.6} = 0.00251$ mol/l

- ✓ **What if $\gamma \neq 1$?**

# Speciation calculation for gypsum

- ✓ Mass Action Law:

$$CaSO_4 \cdot 2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O \qquad \log K = -4.6$$

- ✓ Datum:

  $Ca_{tot} = Ca^{2+} = 10^{-2}$ mol/l

- ✓ **If $\gamma \neq 1$: iterative process**

| | K = | 2.51189E-05 | | |
|---|---|---|---|---|
| iteration | m(Ca+2) | m(SO4-2) | I | γ |
| 0 | | | | 1 |
| 1 | 0.01 | 0.002511886 | 0.025024 | 0.546336 |
| 2 | 0.01 | 0.008415521 | 0.036831 | 0.495419 |
| 3 | 0.01 | 0.0102342 | 0.040468 | 0.48311 |
| 4 | 0.01 | 0.010762362 | 0.041525 | 0.479757 |
| 5 | 0.01 | 0.010913333 | 0.041827 | 0.478815 |
| 6 | 0.01 | 0.010956295 | 0.041913 | 0.478549 |
| 7 | 0.01 | 0.010968506 | 0.041937 | 0.478473 |
| 8 | 0.01 | 0.010971975 | 0.041944 | 0.478452 |
| 9 | 0.01 | 0.01097296 | 0.041946 | 0.478446 |
| 10 | 0.01 | 0.01097324 | 0.041946 | 0.478444 |
| Relative error (m_so4-2) | | 2.55E-05 | | |

# Programs to solve speciation

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- ✓ Speciation requires solution of a system of equations:
  - Mass action laws
    - $H_2O = H^+ + OH^-$
    - $HCO_3^- = H^+ + CO_3^{2-}$
    - $CaCO_{3(s)} = Ca^{+2} + CO_3^{2-}$
  - Data equations – based on our knowledge of the system
    - $pH = -\log[H^+]$
    - Charge balance: $[H^+] + 2\,[Ca^{+2}] - [HCO_3^-] - 2\,[CO_3^{2-}] - [OH^-]$
    - Total concentrations of dissolved species: $C_{,tot}$, $Ca_{,tot}$
    - Alkalinity: $[OH^-] + [HCO_3^-] + 2\,[CO_3^{2-}]$
    - Electrical conductivity
    - Equilibrium with mineral
    - Equilibrium with gas
    - …
- ✓ Problem: it is a **non-linear system**
- ✓ **Iterative method** is **needed**
- ✓ **A few codes exist to solve speciation**

# Programs to solve speciation

- ✓ Some of the **most common codes**:
  - Minteq (Pacific Northwest Laboratory)
  - EQ3NR (Lawrence Livermore National Laboratory)
  - **Phreeqc** (USGS)
  - …
- ✓ They use thermodynamic databases (logK and species properties)
- ✓ They calculate activity coefficients, $\gamma$, by means of the different models (Debye-Hückel, Trusdell Jones, Davis…)
- ✓ They have numerical methods to solve speciation (Picard, Newton-Raphson…)
- ✓ As **output**: they calculate **concentrations of all species, saturation indices for minerals, pressure for gases, …**

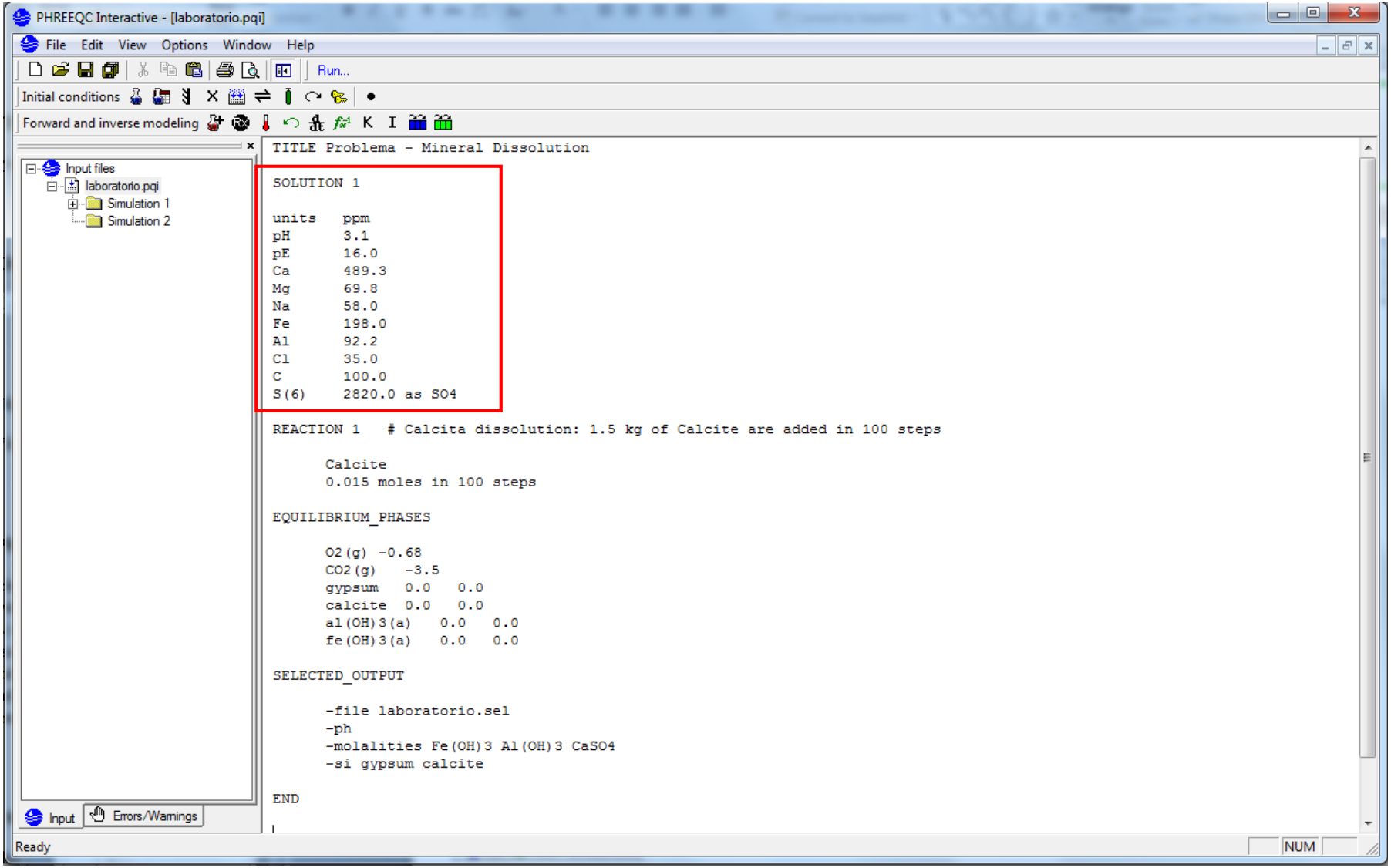
# Phreeqcl

- ✓ Phreeqc input file is organized in KEYWORDS and associated data blocks

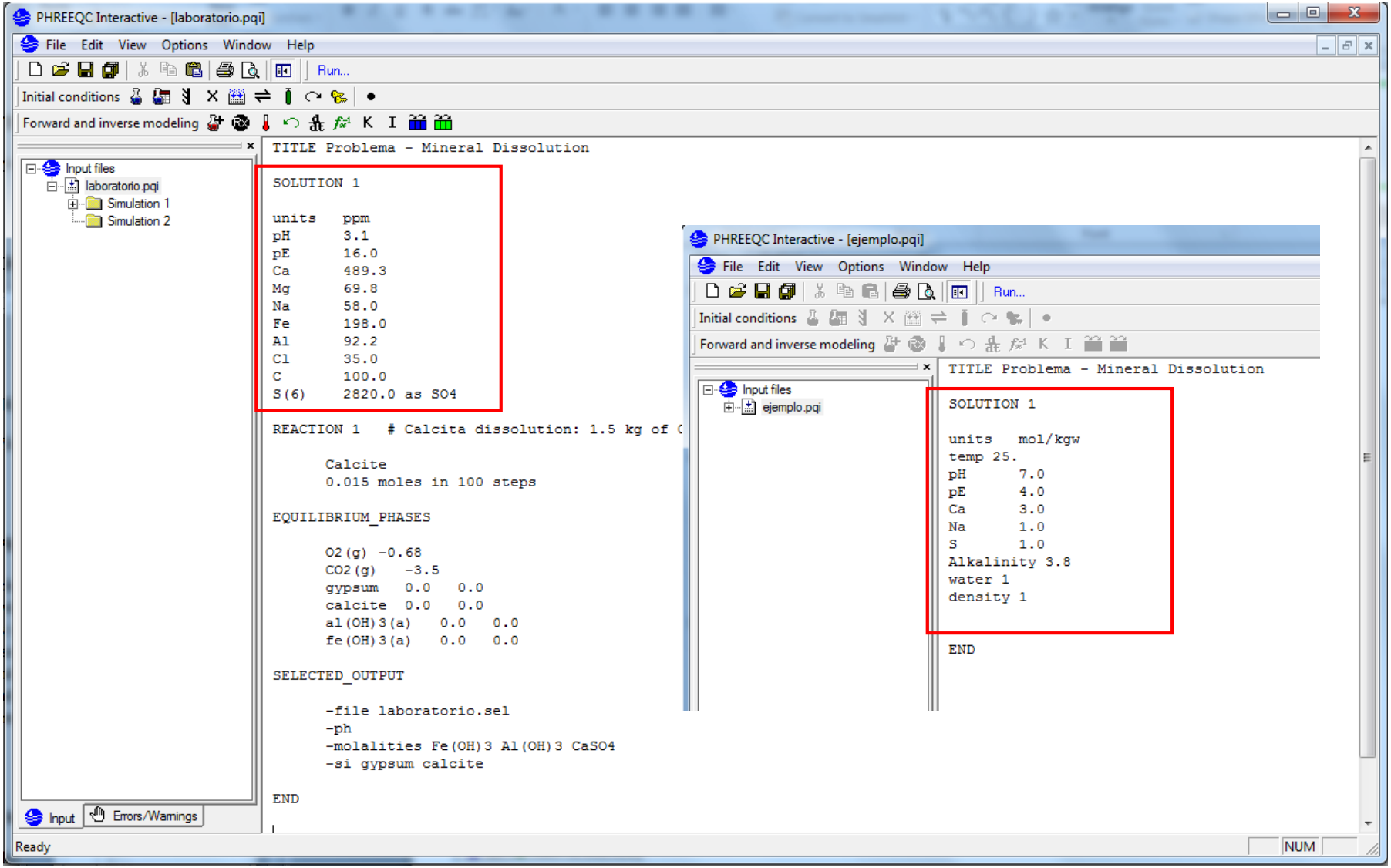
  - SOLUTION
  - EQUILIBRIUM_PHASES
  - REACTION
  - KINETICS
  - EXCHANGE
  - SURFACE
  - GAS_PHASE
  - SOLID_SOLUTION
  - SELECTED_OUTPUT
  - END

- ✓ To solve a speciation, the keyword SOLUTION is needed, followed by the water composition

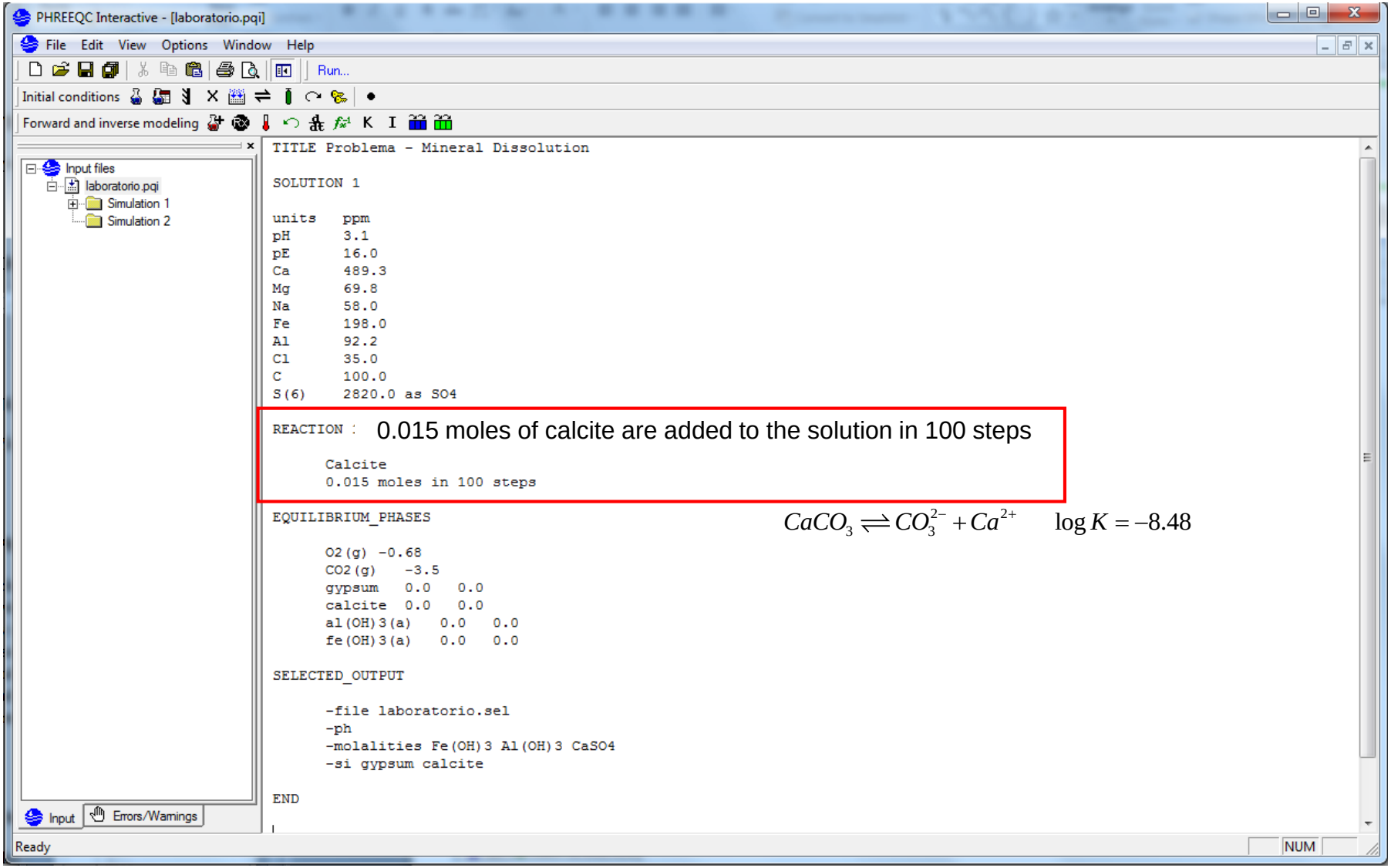
# Phreeqcl


PHREEQC Interactive - [laboratorio.pqi]
File Edit View Options Window Help
Run...
Initial conditions
Forward and inverse modeling
Input files
laboratorio.pqi
Simulation 1
Simulation 2
TITLE Problema - Mineral Dissolution
SOLUTION 1
units ppm
pH 3.1
pE 16.0
Ca 489.3
Mg 69.8
Na 58.0
Fe 198.0
Al 92.2
Cl 35.0
C 100.0
S(6) 2820.0 as SO4
REACTION 1 # Calcita dissolution: 1.5 kg of Calcite are added in 100 steps
Calcite
0.015 moles in 100 steps
EQUILIBRIUM_PHASES
O2(g) -0.68
CO2(g) -3.5
gypsum 0.0 0.0
calcite 0.0 0.0
al(OH)3(a) 0.0 0.0
fe(OH)3(a) 0.0 0.0
SELECTED_OUTPUT
-file laboratorio.sel
-ph
-molalities Fe(OH)3 Al(OH)3 CaSO4
-si gypsum calcite
END
Input
Errors/Warnings
Ready
NUM

# Phreeqcl

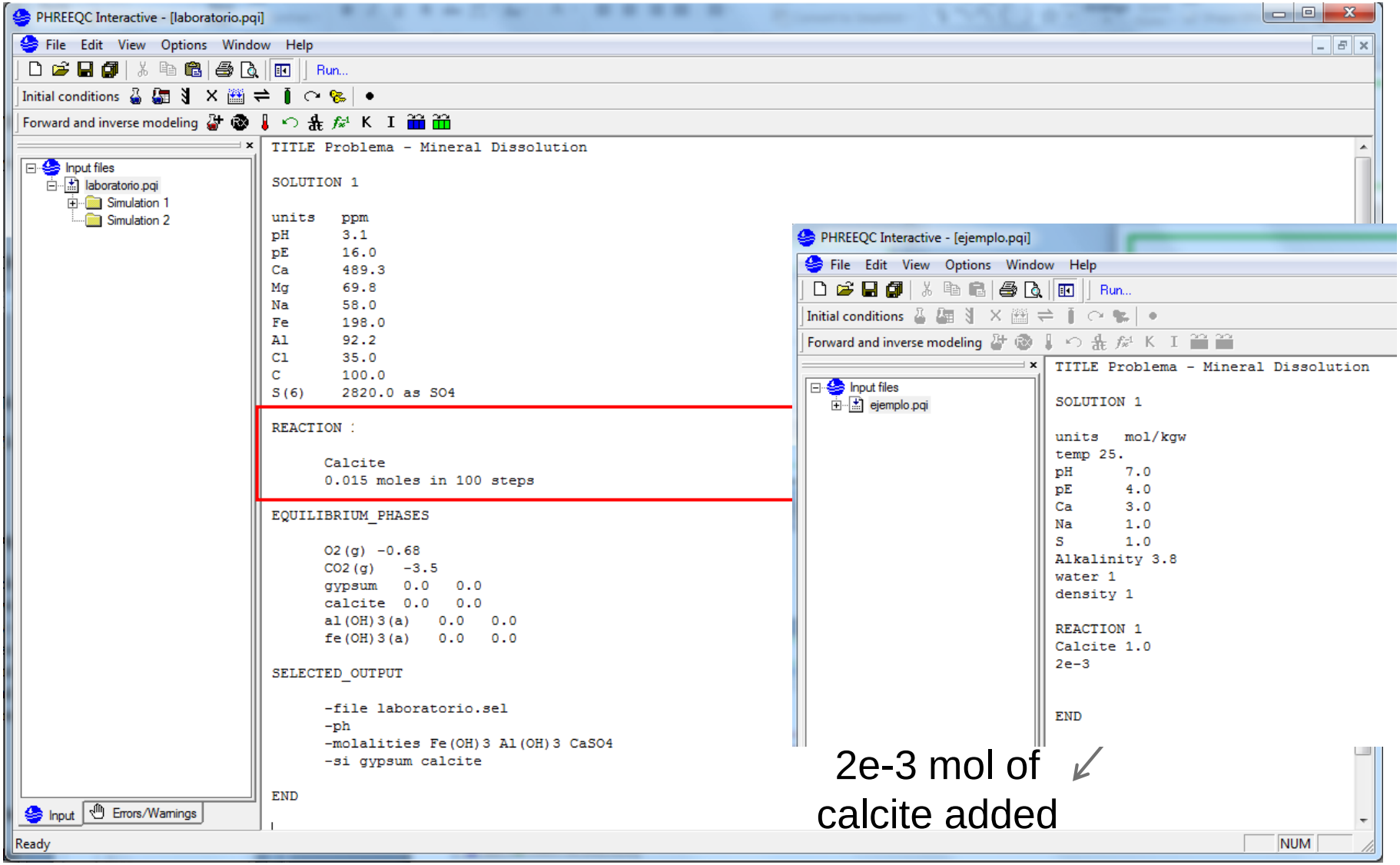

PHREEQC Interactive - [laboratorio.pqi]
File Edit View Options Window Help
Run...
Initial conditions
Forward and inverse modeling
Input files
laboratorio.pqi
Simulation 1
Simulation 2
TITLE Problema - Mineral Dissolution
SOLUTION 1
units ppm
pH 3.1
pE 16.0
Ca 489.3
Mg 69.8
Na 58.0
Fe 198.0
Al 92.2
Cl 35.0
C 100.0
S(6) 2820.0 as SO4
REACTION 1 # Calcita dissolution: 1.5 kg of
Calcite
0.015 moles in 100 steps
EQUILIBRIUM_PHASES
O2(g) -0.68
CO2(g) -3.5
gypsum 0.0 0.0
calcite 0.0 0.0
al(OH)3(a) 0.0 0.0
fe(OH)3(a) 0.0 0.0
SELECTED_OUTPUT
-file laboratorio.sel
-ph
-molalities Fe(OH)3 Al(OH)3 CaSO4
-si gypsum calcite
END
Input
Errors/Warnings
Ready
NUM
PHREEQC Interactive - [ejemplo.pqi]
File Edit View Options Window Help
Run...
Initial conditions
Forward and inverse modeling
Input files
ejemplo.pqi
TITLE Problema - Mineral Dissolution
SOLUTION 1
units mol/kgw
temp 25.
pH 7.0
pE 4.0
Ca 3.0
Na 1.0
S 1.0
Alkalinity 3.8
water 1
density 1
END

# Phreeqcl




$$CaCO_3 \rightleftharpoons CO_3^{2-} + Ca^{2+} \qquad \log K = -8.48$$

# Phreeqcl

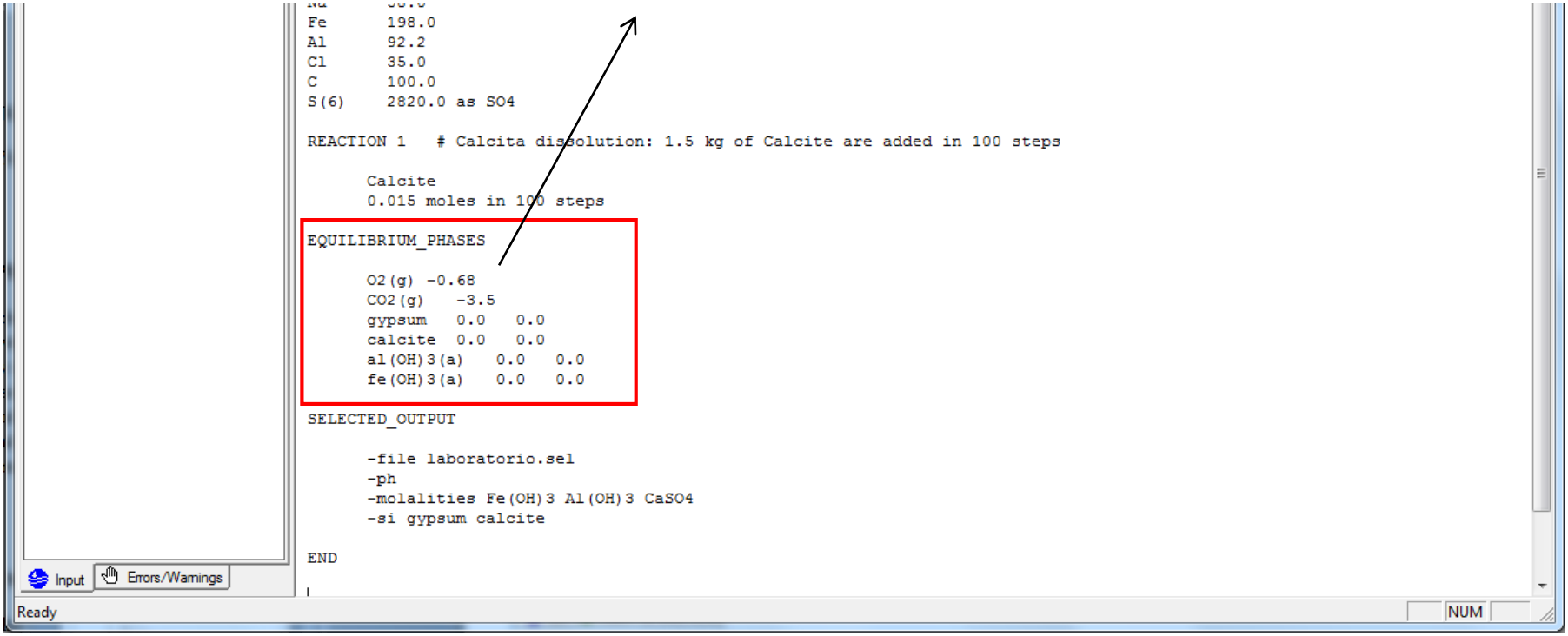



2e-3 mol of calcite added

# Phreeqcl

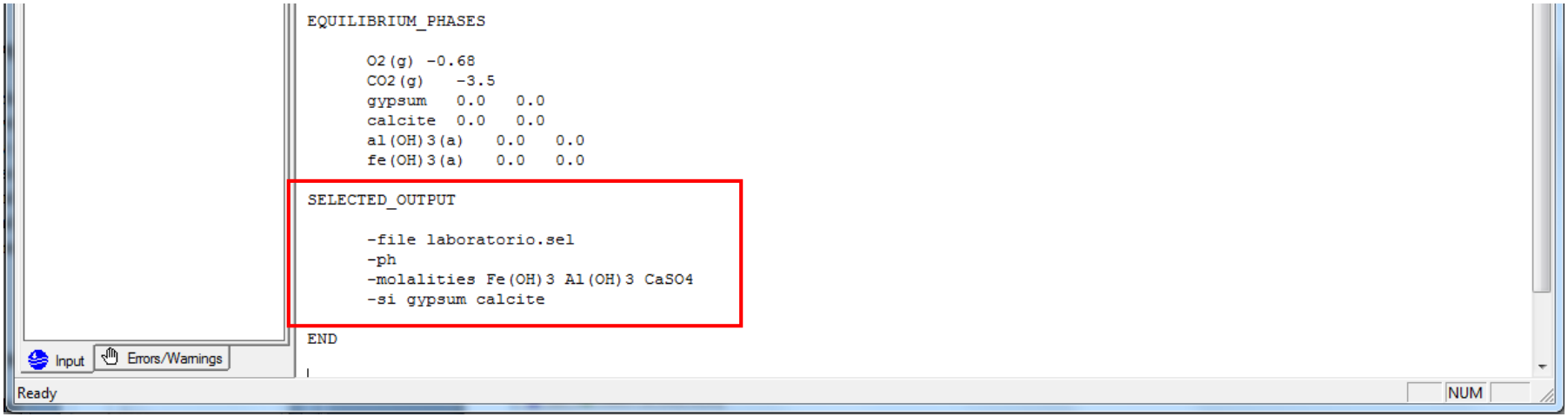
- ✓ EQUILIBRIUM_PHASES: to equilibrate the solution with a mineral or with a gas

Column 1: SI=logΩ (for gases = log[$P_i$])
Column 2: initial quantity (default = 10mol)



# Phreeqcl

- ✓ SELECTED_OUTPUT: to print on file a series of output, chosen by the user




Open Phreeqcl on your computer and let's see how it works

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# Geochemical and Reactive Transport modelling

## 2. Reactive transport calculations

# Reactive transport modelling with Phreeqc

- ✓ **Phreeqc allows to solve 1D transport** of solutes, water, colloids and heat

- ✓ All the chemical processes modeled by Phreeqc, including kinetically controlled reactions, can be included in an advective-dispersive transport simulation

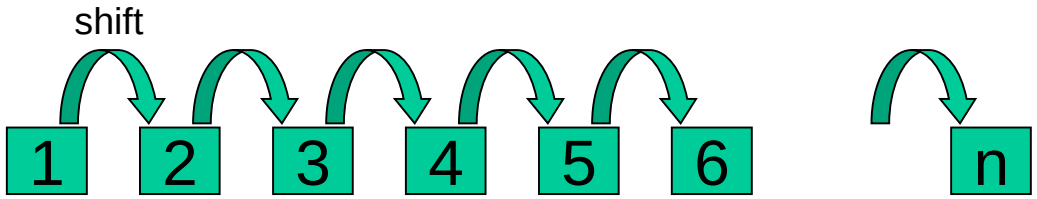
$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} + v\frac{\partial c}{\partial x} + R$$

# Reactive transport modelling with Phreeqc

- ✓ One time step (“shift”) contains 4 sub-steps in Phreeqc:

  1. The mobile cell content is moved to the next cell

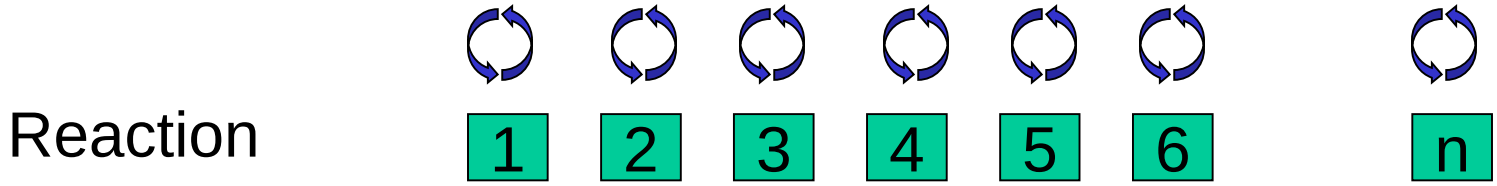
Advection



# Reactive transport modelling with Phreeqc

- ✓ One time step (“shift”) contains 4 sub-steps in Phreeqc:

  2. Reactions between the solution and immobile phases (e.g., minerals, exchangers…) are calculated

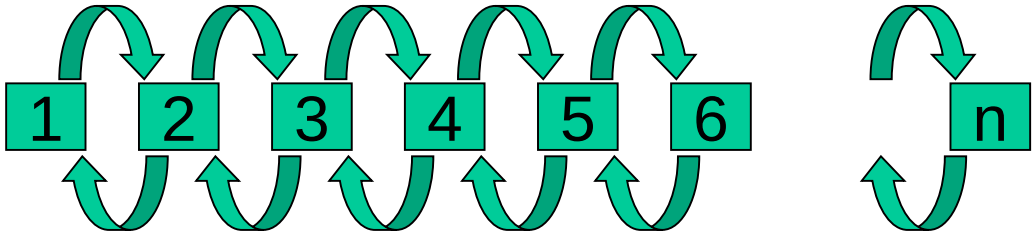


# Reactive transport modelling with Phreeqc

- ✓ One time step (“shift”) contains 4 sub-steps in Phreeqc:

  3. Dispersion is calculated by mixing the contents of adjacent cells

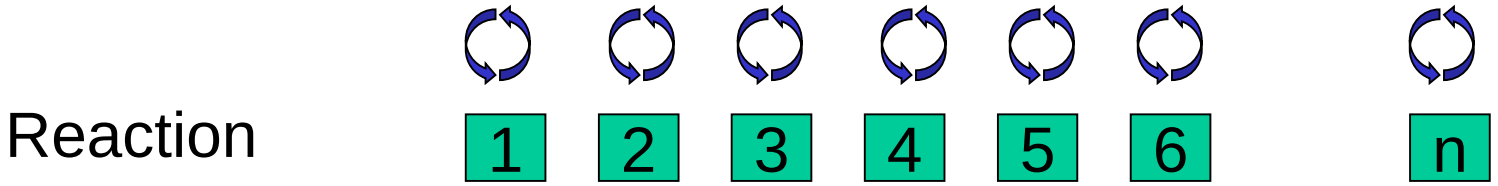
Dispersion



# Reactive transport modelling with Phreeqc

- ✓ One time step (“shift”) contains 4 sub-steps in Phreeqc:

  4. Again, reactions between the solution and immobile phases (e.g., minerals, exchangers…) are calculated




- ✓ The **keyword to solve reactive transport** is “**TRANSPORT**”

# Reactive transport modelling with Phreeqc

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- ✓ **Example** of “TRANSPORT” block for Phreeqc input file:

```
Line 0: TRANSPORT
Line 1:      -cells                  5
Line 2:      -shifts                 25
Line 3:      -time_step              1 yr 2.0
Line 4:      -flow_direction         forward
Line 5:      -boundary_conditions    flux constant
Line 6:      -lengths                4*1.0 2.0
Line 7:      -dispersivities         4*0.1 0.2
Line 8:      -correct_disp           true
Line 9:      -diffusion_coefficient 1.0e-9
Line 10:     -stagnant               1  6.8e-6   0.3   0.1
Line 11:     -thermal_diffusion      3.0   0.5e-6
Line 12:     -initial_time           1000
Line 13:     -print_cells            1-3 5
Line 14:     -print_frequency        5
Line 15:     -punch_cells            2-5
Line 16:     -punch_frequency        5
```

# Reactive transport modelling with Phreeqc

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- ✓ Example of “TRANSPORT” block for Phreeqc input file:

```
Line 0: TRANSPORT
Line 1:      -cells                5
Line 2:      -shifts               25
Line 3:      -time_step            1 yr 2.0
Line 4:      -flow_direction       forward
Line 5:      -boundary_conditions  flux constant
Line 6:      -lengths              4*1.0 2.0
Line 7:      -dispersivities       4*0.1 0.2
Line 8:      -correct_disp         true
Line 9:      -diffusion_coefficient 1.0e-9
Line 10:     -stagnant             1  6.8e-6   0.3   0.1
Line 11:     -thermal_diffusion    3.0   0.5e-6
Line 12:     -initial_time         1000
Line 13:     -print_cells          1-3 5
Line 14:     -print_frequency      5
Line 15:     -punch_cells          2-5
Line 16:     -punch_frequency      5
```

→ Number of cells in the column

# Reactive transport modelling with Phreeqc

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- ✓ Example of “TRANSPORT” block for Phreeqc input file:

```
Line 0: TRANSPORT
Line 1:      -cells                 5
Line 2:      -shifts                25
Line 3:      -time_step             1 yr 2.0
Line 4:      -flow_direction        forward
Line 5:      -boundary_conditions   flux constant
Line 6:      -lengths               4*1.0 2.0
Line 7:      -dispersivities        4*0.1 0.2
Line 8:      -correct_disp          true
Line 9:      -diffusion_coefficient 1.0e-9
Line 10:     -stagnant              1  6.8e-6   0.3   0.1
Line 11:     -thermal_diffusion     3.0   0.5e-6
Line 12:     -initial_time          1000
Line 13:     -print_cells           1-3 5
Line 14:     -print_frequency       5
Line 15:     -punch_cells           2-5
Line 16:     -punch_frequency       5
```

→ Number of time steps in simulation

# Reactive transport modelling with Phreeqc

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- ✓ Example of “TRANSPORT” block for Phreeqc input file:

```
Line 0: TRANSPORT
Line 1:      -cells                5
Line 2:      -shifts               25
Line 3:      -time_step            1 yr 2.0
Line 4:      -flow_direction       forward
Line 5:      -boundary_conditions  flux constant
Line 6:      -lengths              4*1.0 2.0
Line 7:      -dispersivities       4*0.1 0.2
Line 8:      -correct_disp         true
Line 9:      -diffusion_coefficient 1.0e-9
Line 10:     -stagnant             1  6.8e-6   0.3   0.1
Line 11:     -thermal_diffusion    3.0   0.5e-6
Line 12:     -initial_time         1000
Line 13:     -print_cells          1-3 5
Line 14:     -print_frequency      5
Line 15:     -punch_cells          2-5
Line 16:     -punch_frequency      5
```

shifts / cells = number of pore volumes injected

# Reactive transport modelling with Phreeqc

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- ✓ Example of “TRANSPORT” block for Phreeqc input file:

```
Line 0: TRANSPORT
Line 1:      -cells                 5
Line 2:      -shifts                25
Line 3:      -time_step             1 yr* 2.0*
Line 4:      -flow_direction        forward
Line 5:      -boundary_conditions   flux constant
Line 6:      -lengths               4*1.0 2.0
Line 7:      -dispersivities        4*0.1 0.2
Line 8:      -correct_disp          true
Line 9:      -diffusion_coefficient 1.0e-9
Line 10:     -stagnant              1  6.8e-6   0.3   0.1
Line 11:     -thermal_diffusion     3.0   0.5e-6
Line 12:     -initial_time          1000
Line 13:     -print_cells           1-3 5
Line 14:     -print_frequency       5
Line 15:     -punch_cells           2-5
Line 16:     -punch_frequency       5
```

[* = OPTIONAL ARGUMENT ]

-time_step → length of each shift [unit*, substeps*]

time_step = L / velocity

# Reactive transport modelling with Phreeqc

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- ✓ Example of “TRANSPORT” block for Phreeqc input file:

```
Line 0: TRANSPORT
Line 1:      -cells                5
Line 2:      -shifts               25
Line 3:      -time_step            1 yr 2.0
Line 4:      -flow_direction       forward
Line 5:      -boundary_conditions  flux constant
Line 6:      -lengths              4*1.0 2.0
Line 7:      -dispersivities       4*0.1 0.2
Line 8:      -correct_disp         true
Line 9:      -diffusion_coefficient 1.0e-9
Line 10:     -stagnant             1  6.8e-6   0.3   0.1
Line 11:     -thermal_diffusion    3.0   0.5e-6
Line 12:     -initial_time         1000
Line 13:     -print_cells          1-3 5
Line 14:     -print_frequency      5
Line 15:     -punch_cells          2-5
Line 16:     -punch_frequency      5
```

Direction of flow into higher numbered cells [alternative: backward]

# Reactive transport modelling with Phreeqc

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- ✓ Example of “TRANSPORT” block for Phreeqc input file:

```
Line 0: TRANSPORT
Line 1:      -cells                5
Line 2:      -shifts               25
Line 3:      -time_step            1 yr 2.0
Line 4:      -flow_direction       forward
Line 5:      -boundary_conditions  flux constant
Line 6:      -lengths              4*1.0 2.0
Line 7:      -dispersivities       4*0.1 0.2
Line 8:      -correct_disp         true
Line 9:      -diffusion_coefficient 1.0e-9
Line 10:     -stagnant             1  6.8e-6   0.3   0.1
Line 11:     -thermal_diffusion    3.0   0.5e-6
Line 12:     -initial_time         1000
Line 13:     -print_cells          1-3 5
Line 14:     -print_frequency      5
Line 15:     -punch_cells          2-5
Line 16:     -punch_frequency      5
```

B.C. for first and last cell:

1) **constant**: $c = c_0$ (Dirichlet)
2) **closed**: no flux at boundary, v = 0 (Neumann)
1) **flux (default)**: a given mass enters per unit time

# Reactive transport modelling with Phreeqc

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- ✓ Example of “TRANSPORT” block for Phreeqc input file:

```
Line 0: TRANSPORT
Line 1:      -cells                 5
Line 2:      -shifts                25
Line 3:      -time_step             1 yr 2.0
Line 4:      -flow_direction        forward
Line 5:      -boundary_conditions   flux constant
Line 6:      -lengths               4*1.0 2.0
Line 7:      -dispersivities        4*0.1 0.2
Line 8:      -correct_disp          true
Line 9:      -diffusion_coefficient 1.0e-9
Line 10:     -stagnant              1  6.8e-6   0.3   0.1
Line 11:     -thermal_diffusion     3.0   0.5e-6
Line 12:     -initial_time          1000
Line 13:     -print_cells           1-3 5
Line 14:     -print_frequency       5
Line 15:     -punch_cells           2-5
Line 16:     -punch_frequency       5
```

→ List of lengths for each cell [m]
(alternative to specify total length: **-length** 100)

# Reactive transport modelling with Phreeqc

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- ✓ Example of “TRANSPORT” block for Phreeqc input file:

```
Line 0: TRANSPORT
Line 1:      -cells                 5
Line 2:      -shifts                25
Line 3:      -time_step             1 yr 2.0
Line 4:      -flow_direction        forward
Line 5:      -boundary_conditions   flux constant
Line 6:      -lengths               4*1.0 2.0
Line 7:      -dispersivities        4*0.1 0.2
Line 8:      -correct_disp          true
Line 9:      -diffusion_coefficient 1.0e-9
Line 10:     -stagnant              1  6.8e-6   0.3   0.1
Line 11:     -thermal_diffusion     3.0   0.5e-6
Line 12:     -initial_time          1000
Line 13:     -print_cells           1-3 5
Line 14:     -print_frequency       5
Line 15:     -punch_cells           2-5
Line 16:     -punch_frequency       5
```

→ List of dispersivities for each cell [m]

# Reactive transport modelling with Phreeqc

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- ✓ Example of “TRANSPORT” block for Phreeqc input file:

```
Line 0: TRANSPORT
Line 1:      -cells                  5
Line 2:      -shifts                 25
Line 3:      -time_step              1 yr 2.0
Line 4:      -flow_direction         forward
Line 5:      -boundary_conditions    flux constant
Line 6:      -lengths                4*1.0 2.0
Line 7:      -dispersivities         4*0.1 0.2
Line 8:      -correct_disp           true
Line 9:      -diffusion_coefficient  1.0e-9
Line 10:     -stagnant               1  6.8e-6   0.3   0.1
Line 11:     -thermal_diffusion      3.0   0.5e-6
Line 12:     -initial_time           1000
Line 13:     -print_cells            1-3 5
Line 14:     -print_frequency        5
Line 15:     -punch_cells            2-5
Line 16:     -punch_frequency        5
```

Dispersivity is multiplied by (1+1/cells) for column ends with flux B.C. to improve modelling of effluent composition in case of few cells. Default: false

# Reactive transport modelling with Phreeqc

- ✓ Example of “TRANSPORT” block for Phreeqc input file:

```
Line 0: TRANSPORT
Line 1:      -cells                 5
Line 2:      -shifts                25
Line 3:      -time_step             1 yr 2.0
Line 4:      -flow_direction        forward
Line 5:      -boundary_conditions   flux constant
Line 6:      -lengths               4*1.0 2.0
Line 7:      -dispersivities        4*0.1 0.2
Line 8:      -correct_disp          true
Line 9:      -diffusion_coefficient 1.0e-9
Line 10:     -stagnant              1  6.8e-6   0.3   0.1
Line 11:     -thermal_diffusion     3.0   0.5e-6
Line 12:     -initial_time          1000
Line 13:     -print_cells           1-3 5
Line 14:     -print_frequency       5
Line 15:     -punch_cells           2-5
Line 16:     -punch_frequency       5
```

Effective diffusion coefficient [$m^2/s$]
Default: 0.3e-9 $m^2/s$

# Reactive transport modelling with Phreeqc

- ✓ Example of “TRANSPORT” block for Phreeqc input file:

```
Line 0: TRANSPORT
Line 1:      -cells                  5
Line 2:      -shifts                 25
Line 3:      -time_step              1 yr 2.0
Line 4:      -flow_direction         forward
Line 5:      -boundary_conditions    flux constant
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Line 13:     -print_cells            1-3 5
Line 14:     -print_frequency        5
Line 15:     -punch_cells            2-5
Line 16:     -punch_frequency        5
```

List of maximum immobile cells that can be associated to every mobile cell

# Reactive transport modelling with Phreeqc

Technische Universität Berlin

- ✓ Example of “TRANSPORT” block for Phreeqc input file:

```
Line 0: TRANSPORT
Line 1:      -cells                5
Line 2:      -shifts               25
Line 3:      -time_step            1 yr 2.0
Line 4:      -flow_direction       forward
Line 5:      -boundary_conditions  flux constant
Line 6:      -lengths              4*1.0 2.0
Line 7:      -dispersivities       4*0.1 0.2
Line 8:      -correct_disp         true
Line 9:      -diffusion_coefficient 1.0e-9
Line 10:     -stagnant             1  6.8e-6   0.3   0.1
Line 11:     -thermal_diffusion    3.0   0.5e-6
Line 12:     -initial_time         1000
Line 13:     -print_cells          1-3 5
Line 14:     -print_frequency      5
Line 15:     -punch_cells          2-5
Line 16:     -punch_frequency      5
```

→ Factors to calculate diffusive part of heat transport (T retardation factor, thermal diffusion coefficients)

# Reactive transport modelling with Phreeqc

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```
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Line 1:      -cells                 5
Line 2:      -shifts                25
Line 3:      -time_step             1 yr 2.0
Line 4:      -flow_direction        forward
Line 5:      -boundary_conditions   flux constant
Line 6:      -lengths               4*1.0 2.0
Line 7:      -dispersivities        4*0.1 0.2
Line 8:      -correct_disp          true
Line 9:      -diffusion_coefficient 1.0e-9
Line 10:     -stagnant              1  6.8e-6   0.3   0.1
Line 11:     -thermal_diffusion     3.0   0.5e-6
Line 12:     -initial_time          1000
Line 13:     -print_cells           1-3 5
Line 14:     -print_frequency       5
Line 15:     -punch_cells           2-5
Line 16:     -punch_frequency       5
```

→ Time to begin transport calculation (if omitted initial time is zero)

# Reactive transport modelling with Phreeqc

Technische Universität Berlin

- ✓ Example of “TRANSPORT” block for Phreeqc input file:

```
Line 0: TRANSPORT
Line 1:      -cells                  5
Line 2:      -shifts                 25
Line 3:      -time_step              1 yr 2.0
Line 4:      -flow_direction         forward
Line 5:      -boundary_conditions    flux constant
Line 6:      -lengths                4*1.0 2.0
Line 7:      -dispersivities         4*0.1 0.2
Line 8:      -correct_disp           true
Line 9:      -diffusion_coefficient 1.0e-9
Line 10:     -stagnant               1  6.8e-6   0.3   0.1
Line 11:     -thermal_diffusion      3.0   0.5e-6
Line 12:     -initial_time           1000
Line 13:     -print_cells            1-3 5
Line 14:     -print_frequency        5
Line 15:     -punch_cells            2-5
Line 16:     -punch_frequency        5
```

→ Llist of cells for which results are written in the output file

# Reactive transport modelling with Phreeqc

Technische Universität Berlin

- ✓ Example of “TRANSPORT” block for Phreeqc input file:

```
Line 0: TRANSPORT
Line 1:      -cells                 5
Line 2:      -shifts                25
Line 3:      -time_step             1 yr 2.0
Line 4:      -flow_direction        forward
Line 5:      -boundary_conditions   flux constant
Line 6:      -lengths               4*1.0 2.0
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Line 9:      -diffusion_coefficient 1.0e-9
Line 10:     -stagnant              1  6.8e-6   0.3   0.1
Line 11:     -thermal_diffusion     3.0   0.5e-6
Line 12:     -initial_time          1000
Line 13:     -print_cells           1-3 5
Line 14:     -print_frequency       5
Line 15:     -punch_cells           2-5
Line 16:     -punch_frequency       5
```

→ List of shifts for which results are printed in the output file

# Reactive transport modelling with Phreeqc

- ✓ Example of “TRANSPORT” block for Phreeqc input file:

```
Line 0: TRANSPORT
Line 1:      -cells                 5
Line 2:      -shifts                25
Line 3:      -time_step             1 yr 2.0
Line 4:      -flow_direction        forward
Line 5:      -boundary_conditions   flux constant
Line 6:      -lengths               4*1.0 2.0
Line 7:      -dispersivities        4*0.1 0.2
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Line 9:      -diffusion_coefficient 1.0e-9
Line 10:     -stagnant              1  6.8e-6   0.3   0.1
Line 11:     -thermal_diffusion     3.0   0.5e-6
Line 12:     -initial_time          1000
Line 13:     -print_cells           1-3 5
Line 14:     -print_frequency       5
Line 15:     -punch_cells           2-5
Line 16:     -punch_frequency       5
```

→ List of cells for which results are printed in the selected_output file

# Reactive transport modelling with Phreeqc

Technische Universität Berlin

- ✓ Example of “TRANSPORT” block for Phreeqc input file:

```
Line 0: TRANSPORT
Line 1:      -cells                 5
Line 2:      -shifts                25
Line 3:      -time_step             1 yr 2.0
Line 4:      -flow_direction        forward
Line 5:      -boundary_conditions   flux constant
Line 6:      -lengths               4*1.0 2.0
Line 7:      -dispersivities        4*0.1 0.2
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Line 9:      -diffusion_coefficient 1.0e-9
Line 10:     -stagnant              1  6.8e-6   0.3   0.1
Line 11:     -thermal_diffusion     3.0   0.5e-6
Line 12:     -initial_time          1000
Line 13:     -print_cells           1-3 5
Line 14:     -print_frequency       5
Line 15:     -punch_cells           2-5
Line 16:     -punch_frequency       5
```

→ List of shifts for which results are printed in the selected_output file

# Reactive transport modelling with Phreeqc

- ✓ The sequence of keywords for RT modelling is:

```
SOLUTION 1-5    # initial solution in the column
…(chemical composition)
END

SOLUTION 0      # solution injected in the column
…(chemical composition)

TRANSPORT       # transport parameters definition
…(transport parameters)

USER_GRAPH      # print (also SELECTED_OUTPUT is possible)
…

END
```

# Reactive transport modelling with Phreeqc

- ✓ Today these commands are relevant:

```
SOLUTION 1-5    # initial solution in the column
…
(optional)EXCHANGE
…
(optional)EQUILIBRIUM_PHASES
…
END

SOLUTION 0      # solution injected in the column
…(chemical composition)

TRANSPORT       # transport parameters definition
…(transport parameters)

USER_GRAPH      # print (also SELECTED_OUTPUT is possible)
…

END
```

# Reactive transport modelling with Phreeqc

- ✓ USER_GRAPH allows to plot results directly in Phreeqc:

```
USER_GRAPH    # print (also SELECTED_OUTPUT is possible, see Slide 14)
-headings Ca Mg...
-chart_title “title"
-axis_titles "Pore Volumes" "c [mol/L]"
-plot_concentration_vs time
-start
10 graph_x (step_no + 0.5) / cell_no # to print pore_volume on x-axis
20 graph_y tot(“Ca"), tot(“Mg"), -la("H+"), SI("Goethite"), ... # You have to choose the appropriate variables
-end
```

# Exercise 1 : Acid mine drainage

- ✓ Objective: to simulate a treatment of an acidic water by means of adding calcite to the system

- ✓ Using the SOLUTION 1 of the previous exercises:

  - ✓ Change the initial pH to 5.23
  - ✓ Delete equilibrium conditions with calcite and CO2(g)
  - ✓ Define a REACTION with calcite: add 1.0 moles in 20 steps
  - ✓ Write the results in an Excel file (SELECTED_OUTPUT)
  - ✓ Plot main results (pH, Saturation Index of calcite, Ca,tot, CO2) and comment: were you expecting this results? If so, why?

# Exercise 2: Organic matter degradation

Consider the bed of a lake (1L), in equilibrium at first with atmospheric oxygen (logP[$O_{2(g)}$]=-0.7 bar) and organic matter, $10^{-4}$ mol of $Fe(OH)_{3(a)}$ and $10^{-4}$ mol of pyrolusite ($MnO_{2(s)}$), and, as regards the water, with pH = 7, TIC= $10^{-3}$ mol/l and a concentration of $10^{-4}$ mol of $NO_3$ and $10^{-4}$ mol of $SO_4$.

Evaluate the evolution of the system (pH, pe, concentrations) in parallel with the organic matter degradation.

Use the following syntax for the input file

```
SOLUTION 1

     pH    7
     pe    13.6    equilibrium with P(O2)
     units   mol/kgw
     C(+4)
     N(5)
     S(6)
     Fe      equilibrium with Fe(OH)3 (a)
     Mn      equilibrium with MnO2(s)

EQUILIBRIUM_PHASES 1 # Equilibrium of the matter on the lake bed with Fe(OH)3
# and with pyrolusite

     Fe(OH)3(a)
     Pyrolusite

REACTION 1

    CH2O 1.0
    0.001 mol in 50 steps

SELECTED_OUTPUT
...
```

# Exercise 3: 1D RT model with Phreeqc

- ✓ Consider a 1D domain, 8 mm long, filled with coarse sand (CEC = 1.1 meq/L) and pore water. The initial solution is 1mM $NaNO_3$.
- ✓ The pore water flow velocity is 3.17 * $10^{-6}$ m/s and initial dispersivity and diffusion are null.
- ✓ The domain is flushed with 0.6 mM $CaCl_2$ solution.
- ✓ What chemical process do you think will be relevant in this model? How do you expect the fronts to be?

# Exercise 3: 1D RT model with Phreeqc

1. Run this example with Phreeqc and plot the results using USER_GRAPH keyword. Comment the results: which species are exchanged?

2. Change diffusion_coefficient value to 1e-9 $m^2/s$: how do the results change?

3. Change the dispersivity value to 2 mm: how do the results change?

4. Add also 0.2 mM $KNO_3$ to the composition of the initial solution and comment the results: which species are exchanged?