

Geochemical and Reactive Transport modelling

Exercises

Dr. - Ing. Francesca De Gaspari

TU Berlin | Angewandte Geowissenschaften | Fachgebiet Hydrogeologie Summerschool | 8th October 2018



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] [HCO₃⁻] 2 [CO₃²⁻] [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 (CaSO₄·2H₂O) dissolves in clean water until equilibrium is reached

$$CaSO_4 - 2H_2O \rightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$$
 $logK = -4.6$

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

 $[Ca^{2+}] = x$ x = moles of dissolved gypsum / volume $<math>[SO_4^{2-}] = x$

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:

 $CaSO_4 \cdot 2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O$ logK = -4.6

Datum: $Ca_{tot} = Ca^{2+} = 10^{-2} \text{ mol/l}$

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

✓ What if $\gamma \neq 1$?

Speciation calculation for gypsum



✓ Mass Action Law:

$$CaSO_4 \cdot 2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O$$
 logK = -4.6

✓ Datum:

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

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

	K = 2	.51189E-05		
iteration	m(Ca+2)	m(SO4-2)	Ι	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_s	04-2)	2.55E-05		

Programs to solve speciation



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: $[H^+] + 2 [Ca^{+2}] [HCO_3^{-1}] 2 [CO_3^{2-1}] [OH^{-1}]$
 - Total concentrations of dissolved species: C,_{tot}, Ca,_{tot}
 - Alkalinity: [OH⁻] + [HCO₃⁻] + 2 [CO₃²⁻]
 - 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, γ, 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, ...



- 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



PHREEQC Interactive - [laboratorio.p	qi]	
👙 File Edit View Options Wind	dow Help	_ 8 ×
🗅 🚅 🖬 🗿 👗 🖻 🛍 🚑 🛛	🚴 🔟 🛛 Bun	
Initial conditions 🍶 🌆 🔰 🗙 🏥	≠ i	
Forward and inverse modeling 谢 🚳		
	× TITLE Problema - Mineral Dissolution	
Input files Input fil	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 02 (g) -0.68 CO2 (g) -0.68 CO2(g) -3.5 gypymum 0.0 0.0 calcite 0.0 0.0 al(OH)3(a) 0.0 0.0 selectteD_OUTPUT -file laboratorio.sel -ph -molalities Fe(OH)3 Al(OH)3 CaSO4 -si gypsum calcite -304	E
👙 Input 🕂 Errors/Warnings	L END	
eady		NUM



Image: Solution pile Solution 1	_ 8 ×
Initial conditions ↓ X Forward and inverse modeling ↓ C ↓ C ↓ K I ↓ K I ↓ TITLE Problema - Mineral Dissolution ↓ SoluTION 1	- <u> </u>
Forward and inverse modeling 🊰 🐼 🌡 🗠 🏦 🎋 K I 👬 🛗 TITLE Problema - Mineral Dissolution Solution 1 Solution 1	
× TITLE Problema - Mineral Dissolution Image: Solution pqi Solution	
SOLUTION 1	
i solution 1	*
Image: Sendation 2 units ppm pt 3.1 pt 16.0 G 469.3 Mg 69.6 Na 58.0 Fe 198.0 All 92.2 Cl 100.0 C 100.0 S(6) 222.0.0 as SO4 REACTION 1 # Calcita dissolution: 1.5 kg of (Calcite 0.015 moles in 100 steps Equilibrium (PHARSES) 02 (0) -0.68 CO2 (0) -3.5 0.0 0.0 ggpsum 0.0 0.0 fc(0H)3(a) 0.0 0.0 selectibe 0.0 0.0 1.0 selectibe 7 (0H)3 Al (0H) 3 CaSO4 -file laboratorio.sel -ph -molalities Fe(0H)3 Al (0H) 3 CaSO4	
END	
Solution Provide American State Contract State S	
Ready	



PHREEQC Interactive - [laboratorio.pq		
👙 File Edit View Options Windo	ow Help	_ 8)
🗋 🗁 🖬 🎒 🕺 🖻 🛍 🎒 🗋	L Run	
Initial conditions 🍶 🌆 🄰 🗙 🏙 :		
Forward and inverse modeling 😵	🜡 ら 🏦 🏂 K I 🎬 🋗	
i x	TITLE Problema - Mineral Dissolution	
Input files input files inpu	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 504 REACTION : 0.015 moles of calcite are added to the solution 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		
eady		NUM

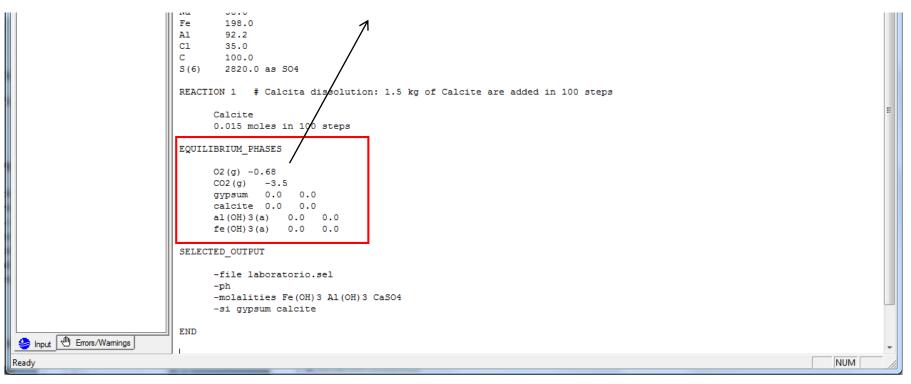


PRECCO Interactive * [aboration option] Initial conditions Initial conditions <th></th> <th></th> <th></th>			
Image: Second and inverse modeling if the second and i	PHREEQC Interactive - [laboratorio.pq	0	
helad conditions 2 1 3 × 1 ~ 6 ~ 6 Forward and inverse modeling 2 • 7 & £ / K I 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1			_ <i>B</i> ×
Forward and inverse modeling			
<pre>TillE Problema - Mineral Dissolution SolUTION 1 Units pen pH 3.1 pE 16.0 Ca 499.3 Mg 69.8 Na 58.0 Fe 198.0 Al 92.2 Cl 33.0 C 100.0 as S04 REACTION: Calcite 0.0 0.0 S(6) 2820.0 as S04 REACTION: Calcite 1.00 steps EQUILIBRIUM_PHARES O2(9) -0.68 O2(9) -0.6</pre>			
Solution 1 Units ppm PH 5.1 ppm pt 5.0 Sinuation 1 pt 6.0 Sinuation 1 pt 7.0 File Edit View Options Window Help pt 7.0 File Edit View Options Window Help statistic conditions 2 Sinuation 1 statistic conditions 2 Sinuation 1 pt 7.0 File Edit View Options Window Help statistic conditions 2 Sinuation 1 statistic	Forward and inverse modeling 불 🚳		
Sourrion 1 Sourrion 2 Sourrion 1 Sourrion 2 Sourrion 2 Souri	×	TITLE Problema - Mineral Dissolution	
Image: Simulation 2 units ppm pH 3.1 pZ 16.0 Cc 17.0 Cc <	iaboratorio.pgi	SOLUTION 1	
pH 3.1 pE 16.0 Ca 499.3 Mg 69.8 Ng 69.8 Ng 69.8 Ng 69.2 Ca 192.0 Al 92.2 Cl 35.0 Ca 100.0 S(6) 2820.0 as \$04 REACTION : Calcite 0.015 moles in 100 steps TILL Problema - Mineral Dissolutio Calcite 0.015 moles in 100 steps EQUILIBRIUM_PHASES Ca 0.2(g) -0.68 Ca(g) -3.5 CO2(g) -3.5 Gypsum 0.0 Global CO2(g) -3.5 Simple Color Global CO2(g) -3.5 Simple Color Global CO2(g) -3.5 Simple Color Calcite 0.0 0.0 Calcite 1.0 2e-3 END END * inductive Fe (OR) 3 ALI (OR) 3 CaSO4 Simple Calcite addded * inductive Fe (OR) 3 ALI (OR) 3 CaSO4 Simple Calcite addded	Simulation 1	מרות sits מרות	
PE 16.0 Ca 489.3 Mg 69.8 Na S8.0 Fe 199.0 A Na 58.0 Fe 199.0 A Imited conditions @ a > x = i < e + e + e + e + e + e + e + e + e + e	Simulation 2	pH 3.1	PHREEQC Interactive - [ejemplo.pqi]
Wg cose Sole Run. Na 560 Fe 198.0 Al 92.2 Initial conditions @ @ % A @ @ % A @ @ % A C1 35.0 C 100.0 C (2 220.0 as 504 Forward and inverse modeling @ % A @ @ % A @ @ % A REACTION : Initial conditions @ @ % A @ @ % A @ @ % A @ @ % A @ @ % A @ @ % A @ @ % A @ @ % A @ @ % A @ A & A & A & A & A & A & A & A & A &		II -	
Na 58.0 Fe 198.0 Al 92.2 Cl 35.0 C 100.0 S(6) 2820.0 as S04 REACTION : Calcite 0.015 moles in 100 steps EQUILIBRIUM_PHASES 02(g) -0.68 CO2(g) -3.5 gypsum 0.0 0.015 moles in 100 steps EQUILIBRIUM_PHASES 02(g) -0.68 CO2(g) -3.5 gypsum 0.0 calcite 0.0 al(0H)3(a) 0.0 0.0 selectric -file laboratorio.sel -ph -molalities Fe(OH)3 Al(OH)3 CaSO4 -si gypsum calcite 2e-3 mol of Prod Wennog Calcite added		Mg 69.8	
All 92.2 C 100.0 S(6) 2820.0 as 504 REACTION : Calcite 0.015 moles in 100 steps EQUILIBRIUM_PHASES 02(g) -0.68 CO2(g) -3.5 gyppum 0.0 0.015 moles in 0.0 calcite 0.0 0.015 moles in 100 steps EQUILIBRIUM_PHASES 0.010, 3(a) 0.0 0.010, al(0H)3(a) 0.0 calcite 0.0 0.00 SELECTED_OUTPUT -file laboratorio.sel -ph -molalities Fe(0H)3 Al(0H)3 CaS04 -molalities Fe(0H)3 Al(0H)3 CaS04 -ph -molalities GrowWarmings			
C 100.0 S(6) 2820.0 as 304 REACTION : Calcite 0.015 moles in 100 steps EQUILIBRIUM_PHASES 02(g) -0.68 CO2(g) -3.5 Gypsum 0.0 0.0 calcite 0.0 0.0 calcite 0.0 0.0 fe(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 PD From Wernings 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 denaity 1 REACTION 1 Calcite 1.0 2e-3 END END END END Calcite added		Al 92.2	Forward and inverse modeling 🖉 🕲 🌡 🗠 🏦 🎋 K 🗉 🎬 🎬
<pre>\$ (6) 2920.0 as S04 REACTION : Calcite 0.015 moles in 100 steps EQUILIBRIUM_PRASES 02 (g) -0.68 CO2 (g) -3.5 gypsum 0.0 0.0 calcite 0.0 0.0 al (0H)3(a) 0.0 0.0 fe(0H)3(a) 0.0 0.0 SELECTED_OUTPUT -file laboratorio.sel -ph -molalities Fe(0H)3 Al (0H)3 CaS04 -si gypsum calcite END END Selection addeed END END Calcite addeed Selection addeed END</pre> SolUTION 1 Units mol/kgw temp 25. pH 7.0			× TITLE Problema - Mineral Dissolution
<pre>REACTION : Calcite 0.015 moles in 100 steps EQUILIBRIUM_PHASES C2 (g) -0.68 C02 (g) -0.68 C02 (g) -3.5 Gyppum 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</pre>		S(6) 2820.0 as SO4	E-S Input files
Calcite 0.015 moles in 100 steps EQUILIBRIUM_EHASES 02 (g) -0.68 CO2 (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 END Market 1 density 1 REACTION 1 Calcite 1.0 2e-3 END END Calcite added 		REACTION :	
0.015 moles in 100 steps EQUILIBRIUM_PHASES 02 (g) -0.68 CO2 (g) -0.68 CO2 (g) -3.5 gypsum 0.0 0.0 calcite 0.0 0.0 calcite 0.0 0.0 calcite 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 END PH 7.0 Ca 3.0 Na 1.0 Alkalinity 3.8 water 1 density 1 REACTION 1 Calcite 1.0 2e-3 END 2e-3 mol of ✓ calcite added			
Equilibrium_PHASES O2 (g) -0.68 C02 (g) -0.68 Stillating 3.8 water 1 density 1 REACTION 1 Calcite 1.0 2e-3 END END END END END END END END			
O2 (g) -0.68 CO2 (g) -3.5 CO2 (g) -3.5 Gypsum 0.0 0.0 calcite 0.0 0.0 calcite 0.0 0.0 calcite 0.0 0.0 fe (OH) 3 (a) 0.0 0.0 fe (OH) 3 (a) 0.0 0.0 fe (OH) 3 (a) 0.0 0.0 selectreD_oUTPUT -file laboratorio.sel -ph -molalities Fe (OH) 3 Al (OH) 3 CaSO4 -si gypsum calcite 2e-3 mol of END Calcite added			
<pre>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</pre>		LEQUILIBRIOM_PHASES	
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 END END END Calcite added			
<pre>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 END END END Calcite added .</pre>			
fe (OB) 3 (a) 0.0 0.0 SELECTED_OUTPUT -file laboratorio.sel -ph -molalities Fe (OH) 3 Al (OH) 3 CaSO4 -si gypsum calcite END END END END END Calcite 1.0 2e-3 END Calcite added			density i
SELECTED_OUTPUT -file laboratorio.sel -ph -molalities Fe (OH) 3 Al (OH) 3 CaSO4 -si gypsum calcite END END END END Calcite added			
<pre></pre>		SET FOTED OUTDUT	
-ph -molalities Fe (OH) 3 Al (OH) 3 CaSO4 -si gypsum calcite END END END Enors/Warnings			
→molalities Fe (OH) 3 Al (OH) 3 CaSO4 →si gypsum calcite 2e-3 mol of ✓ END calcite added			END
Send Calcite added		-molalities Fe(OH)3 Al(OH)3 CaSO4	
Send Calcite added		-si gypsum calcite	2e-3 mol of 🖌
		END	
NUM	Sinput Corres/Warnings],	
	eady		NUM



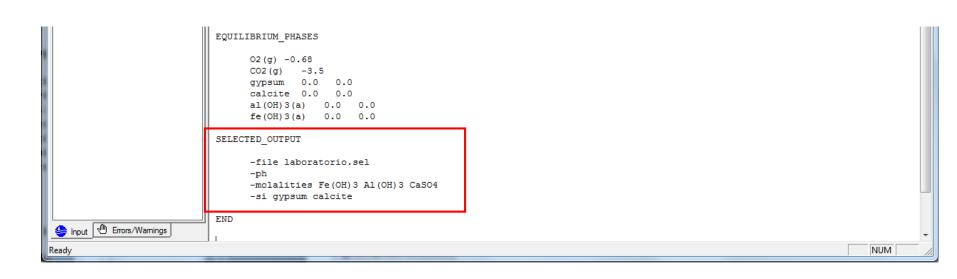
 EQUILIBRIUM_PHASES: to equilibrate the solution with a mineral or with a gas

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





 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



Geochemical and Reactive Transport modelling

2. Reactive transport calculations



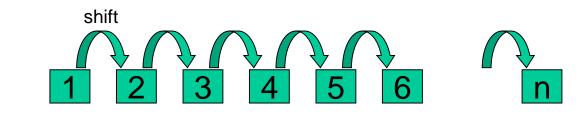
- Phreeqc allows to solve 1D transport of solutes, water, colloids and heat
- All the chemical processes modeled by Phreeqc, including kinetically controlled reactions, can be included in an advective-dispersive transport simulation

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



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

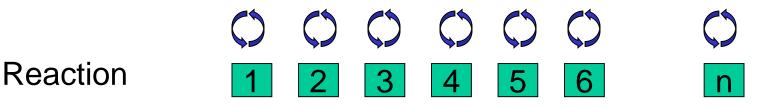
1. The mobile cell content is moved to the next cell



Advection



- ✓ One time step ("shift") contains 4 sub-steps in Phreeqc:
 - 2. Reactions between the solution and immobile phases (e.g., minerals, exchangers...) are calculated

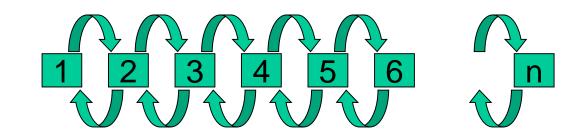




✓ One time step ("shift") contains 4 sub-steps in Phreeqc:

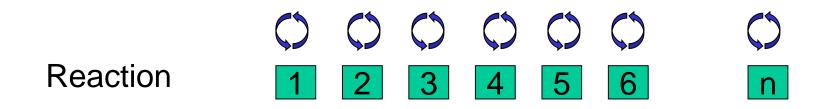
3. Dispersion is calculated by mixing the contents of adjacent cells

Dispersion





- 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"



Line 0: TRANSE	PORT	
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



Example of "TRANSPORT" block for Phreeqc input file:

Line 0. TRANCDORT

Line 0: TRAN	ISPORT	
Line 1:	-cells	5 — Number of cells in the column
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	t 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



Line 0: TRANSPORT				
Line 1: -cells		5		
Line 2: -shifts		25	Number of	time steps in simulation
Line 3: -time_step	,	1 yr 2.0		
Line 4: -flow_dire	ection	forward		
Line 5: -boundary_	conditions	flux consta	ant	
Line 6: -lengths		4*1.0 2.0		
Line 7: -dispersiv	vities	4*0.1 0.2		
Line 8: -correct_d	lisp	true		
Line 9: -diffusion	n_coefficient	1.0e-9		
Line 10: -stagnant		1 6.8e-6	0.3	0.1
Line 11: -thermal_c	liffusion	3.0 0.5e	- 6	
Line 12: -initial_t	time	1000		
Line 13: -print_cel	lls	1-3 5		
Line 14: -print_fre	equency	5		
Line 15: -punch_cel	lls	2-5		
Line 16: -punch_fre	equency	5		



Line 0: TRANS	PORT	shifts / cells = number of pore volumes injected
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



Example of "TRANSPORT" block for Phreeqc input file:

Line 0. TRANCDORT

Line 0: TRAN	ISPORT		
Line 1:	-cells	5	
Line 2:	-shifts	25 [* = 0	OPTIONAL ARGUMENT]
Line 3:	-time_step	1 yr* 2.0*	of each shift [unit*, substeps*]
Line 4:	-flow_direction	forward	
Line 5:	-boundary_conditions	flux constant	time_step = L / velocity
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	t 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	



Example of "TRANSPORT" block for Phreeqc input file:

Line 0. TRANCDOPT

Line 0: TRAN	ISPORT	
Line 1:	-cells	5
Line 2:	-shifts	25
Line 3:	-time_step	1 yr 2.0
Line 4:	-flow_direction	forward Direction of flow into higher numbered cells
Line 5:	-boundary_conditions	flux constant [alternative: backward]
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



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_condition	\mathbf{s} flux constant \longrightarrow	
Line 6: -lengths	4*1.0 2.0	 constant: c = c₀ (Dirichlet) closed: no flux at boundary, v = 0
Line 7: -dispersivities	4*0.1 0.2	(Neumann)
Line 8: -correct_disp	true	1) flux (default): a given mass enters
Line 9: -diffusion_coeffici	ent 1.0e-9	per unit time
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	



Line 0: TRANS	SPORT	
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 — List of lengths for each cell [m]
Line 7:	-dispersivities	4*0.1 0.2 (alternative to specify total length: -length 100)
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



Example of "TRANSPORT" block for Phreeqc input file:

Line 0: TRAN	ISPORT	
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 → List of dispersivities for each cell [m]
Line 8:	-correct_disp	true
Line 9:	-diffusion_coefficien	t 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:	<pre>-print_frequency</pre>	5
Line 15:	-punch_cells	2-5
Line 16:	<pre>-punch_frequency</pre>	5



Line 0: TRAN	SPORT		
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 Dispersivity is multiplied by (1,1/colle) for	
Line 7:	-dispersivities	4*0.1 0.2 Dispersivity is multiplied by (1+1/cells) for column ends with flux B.C. to improve mod	lelling
Line 8:	-correct_disp	true	•
Line 9:	-diffusion_coefficient	L 1.0e-9 Default: false	
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	



Line 0: TRAN	ISPORT	
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 Effective diffusion coefficient [m ² /s]
Line 9:	-diffusion_coefficient	
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:	<pre>-punch_frequency</pre>	5



Line 0: TRA	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_coefficien	t 1.0e-9	
Line 10:	-stagnant	1 6.8e-6 0.3 0.1	
Line 11:	-thermal_diffusion	3.0 0.5e-6 List of maximum immobile cells that can	
Line 12:	-initial_time	1000 be associated to every mobile cell	
Line 13:	-print_cells	1-3 5	
Line 14:	<pre>-print_frequency</pre>	5	
Line 15:	-punch_cells	2-5	
Line 16:	-punch_frequency	5	



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_coefficien	t 1.0e-9
Line 10: -stagnant	1 6.8e-6 0.3 0.1
Line 11: -thermal_diffusion	3.0 0.5e-6 Factors to calculate diffusive part of heat
Line 12: -initial_time	1000 transport (T retardation factor, thermal
Line 13: -print_cells	1-3 5 diffusion coefficients)
Line 14: -print_frequency	5
Line 15: -punch_cells	2-5
Line 16: -punch_frequency	5



Line 0: TRA	NSPORT	
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_coefficien	t 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 — Time to begin transport calculation
Line 13:	-print_cells	1-3 5 (if omitted initial time is zero)
Line 14:	<pre>-print_frequency</pre>	5
Line 15:	-punch_cells	2-5
Line 16:	<pre>-punch_frequency</pre>	5



Example of "TRANSPORT" block for Phreeqc input file:

Line 0: TRAN	NSPORT	
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_coefficien	t 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 \longrightarrow Llist of cells for which results are written in the
Line 14:	-print_frequency	5 output file
Line 15:	-punch_cells	2-5
Line 16:	<pre>-punch_frequency</pre>	5



Line 0: TRA	NSPORT	
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:	<pre>-correct_disp</pre>	true
Line 9:	-diffusion_coefficien	t 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 List of shifts for which results are printed in the output
Line 15:	-punch_cells	2-5 file
Line 16:	<pre>-punch_frequency</pre>	5



Example of "TRANSPORT" block for Phreeqc input file:

Line 0: TRA	NSPORT	
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_coefficien	t 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 — List of cells for which results are printed in the
Line 16:	-punch_frequency	5 selected_output file



Example of "TRANSPORT" block for Phreeqc input file:

Line 0: TRA	ISPORT	
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_coefficien	t 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:	<pre>-print_frequency</pre>	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



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



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)



✓ 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 NO₃ and 10^{-4} mol of SO₄.

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
         13.6 equilibrium with P(O_2)
     units mol/kgw
    C(+4)
    N(5)
     3(6)
          equilibrium with Fe(OH)3 (a)
    Fe
          equilibrium with MnO2(s)
    Мn
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.
- \checkmark The domain is flushed with 0.6 mM CaCl₂ 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?
- Change diffusion_coefficient value to 1e-9 m²/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?