EVROPSKÁ UNIE
Evropské strukturální a investiční fondy
Operační program Výzkum, vývoj a vzdělávání

MINISTERSTVO ŠKOLSTVÍ, MLÁDEŽE A TĚLOVÝCHOVY

Chemical methods in geology

1 .

Introduction to geochemical modelling

Tento učební materiál vznikl v rámci projektu Rozvoj doktorského studia chemie
č. CZ.02.2.69/0.0/0.0/16_018/0002593

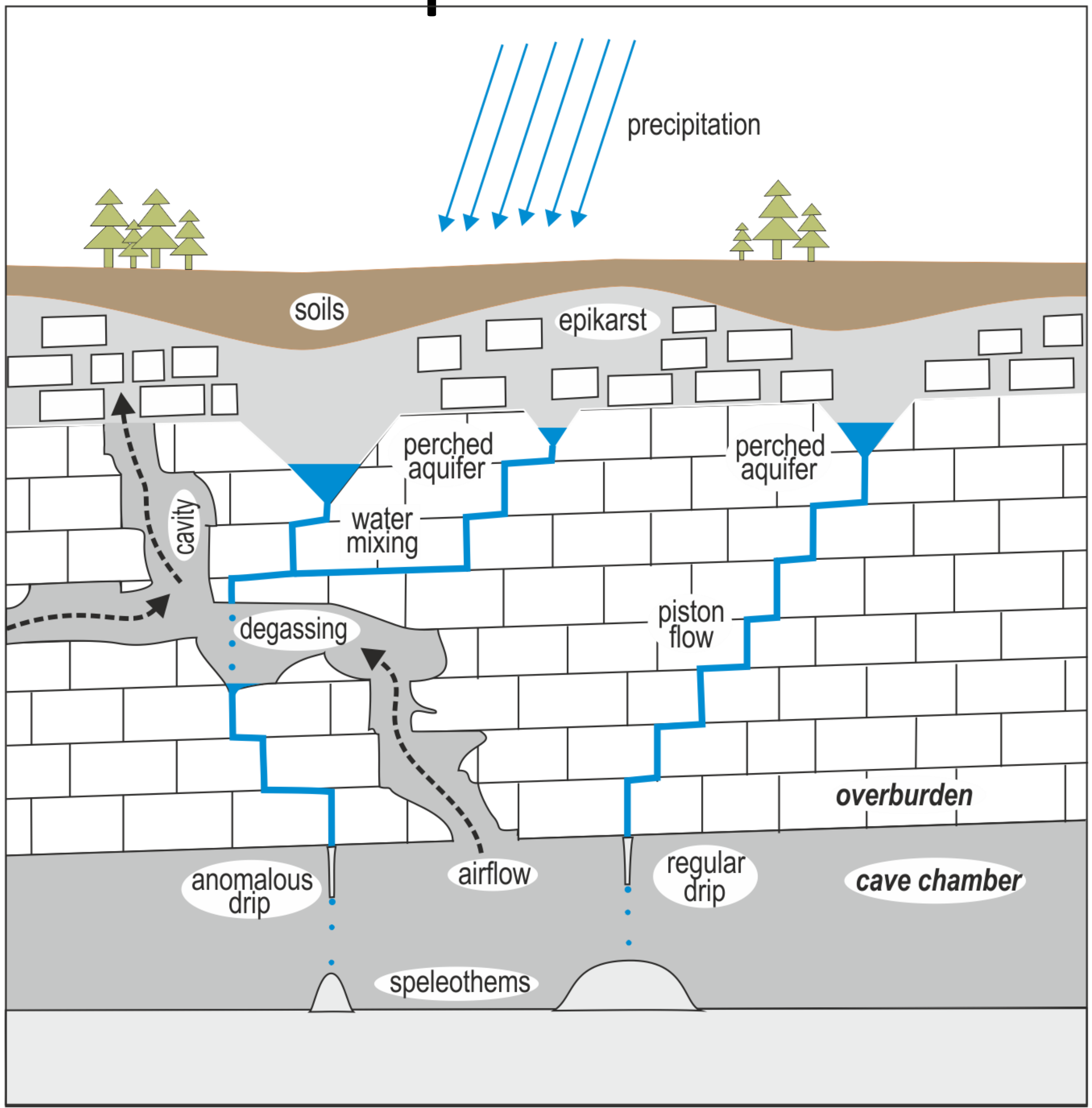
Modeling

- Regardless of the software used, it is necessary to have an idea of what I am doing and what do the results mean ☺
- The goal is to learn how to model **sensibly** – so that we get valid and useful results
- There are a variety of options and tools – learn basic rules and principles that are useful regardless of the tool used

Model

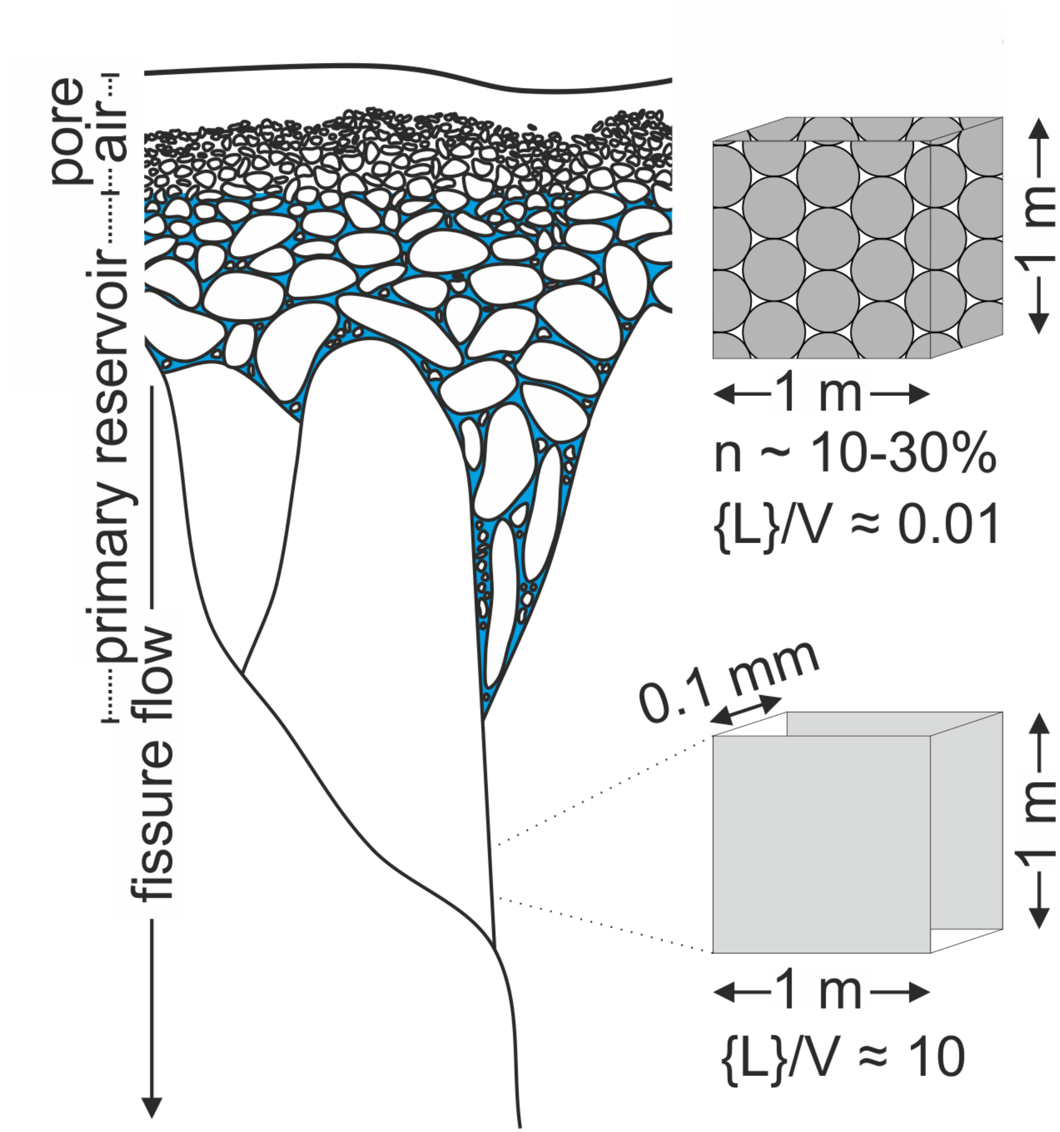
- Model – a construct describing real conditions
  - **Conceptual model** – a qualitative approximation of the system (used to understand the overall nature – how we think the system works)
  - **Mathematical model** – a mathematical construct based on governing equations and boundary/initial conditions that we assume describe the environment
    - **Numerical model** – approximate solution of the mathematical model (usually using a computer)

Conceptual model



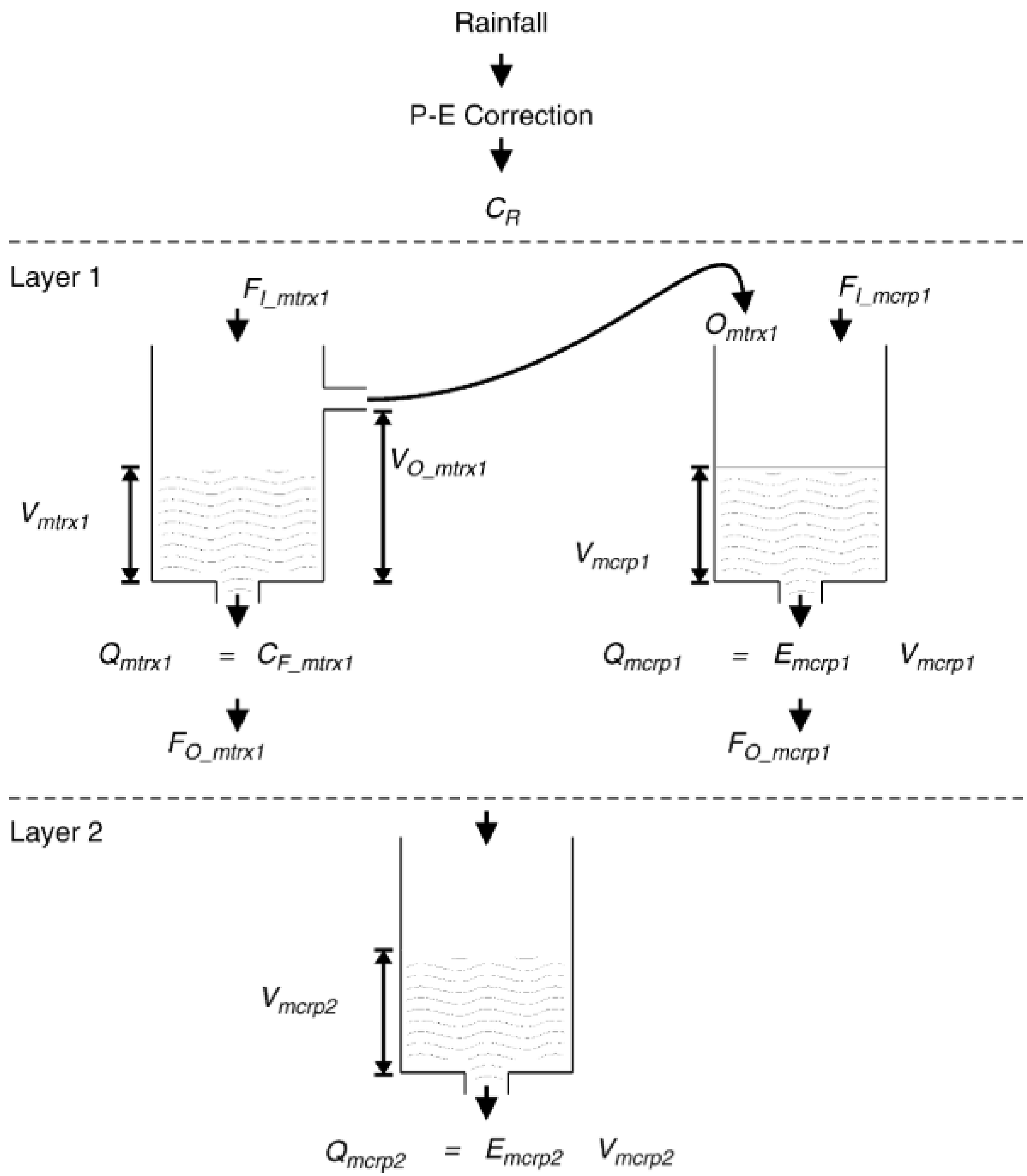
Pracný, P., Faimon , J., Sracek, O., Kabelka, L., Hebelka, J., 2016. Anomalous drip in the Punkva caves (Moravian Karst): relevant implications for paleoclimatic proxies . Hydrol . Process . 30, 1506–1520. https://doi.org/10.1002/hyp.10731

Conceptual model



Pracný, P., Faimon , J., Všianský, D., Kabelka, L., 2017. Evolution of Mg/Ca Ratios During Limestone Dissolution Under Epikarstic Conditions . Aquat . Geochemistry 23, 119–139. https://doi.org/10.1007/s10498-017-9313-y

Conceptual model



Fairchild , IJ, Tuckwell , GW, Baker , A., Tooth , AF, 2006. Modeling of dripwater hydrology and hydrogeochemistry in a weakly karstified aquifer (Bath , UK): Implications for climate change studies . J. Hydrol . 321, 213–231. https://doi.org/10.1016/j.jhydrol.2005.08.002

Mathematical models

- Include the quantitative expression of processes
- In order to evaluate the model, we need to solve the system of equations
- Solution is possible in two ways
  - Analytical solution – exact solution of the mathematical model, applicable to simple problems (e.g. pH calculations in a carbonate system)
  - Numerical solution – an approximate solution, typically using a computer, applicable even to very complex models

Mathematical model

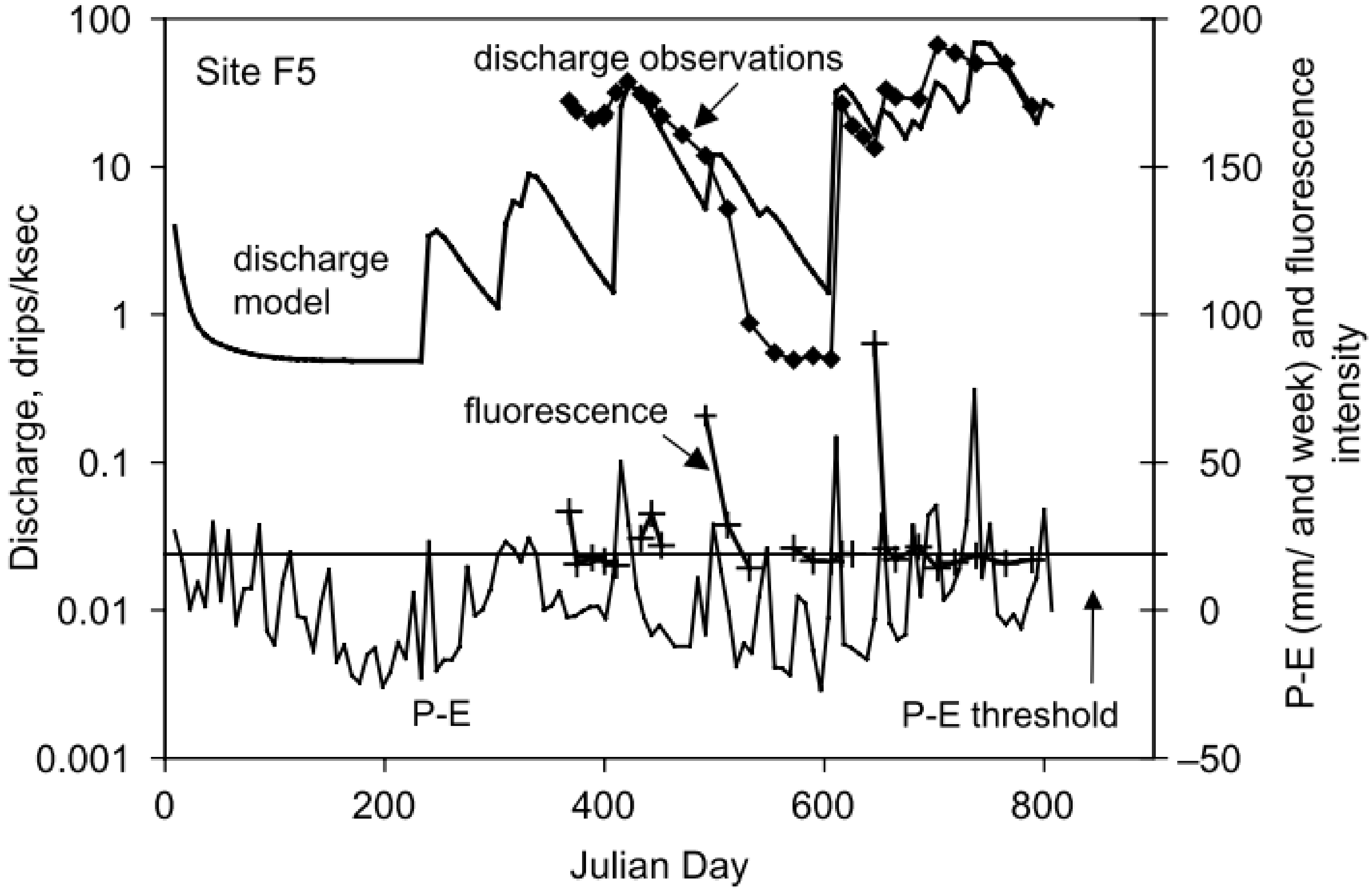
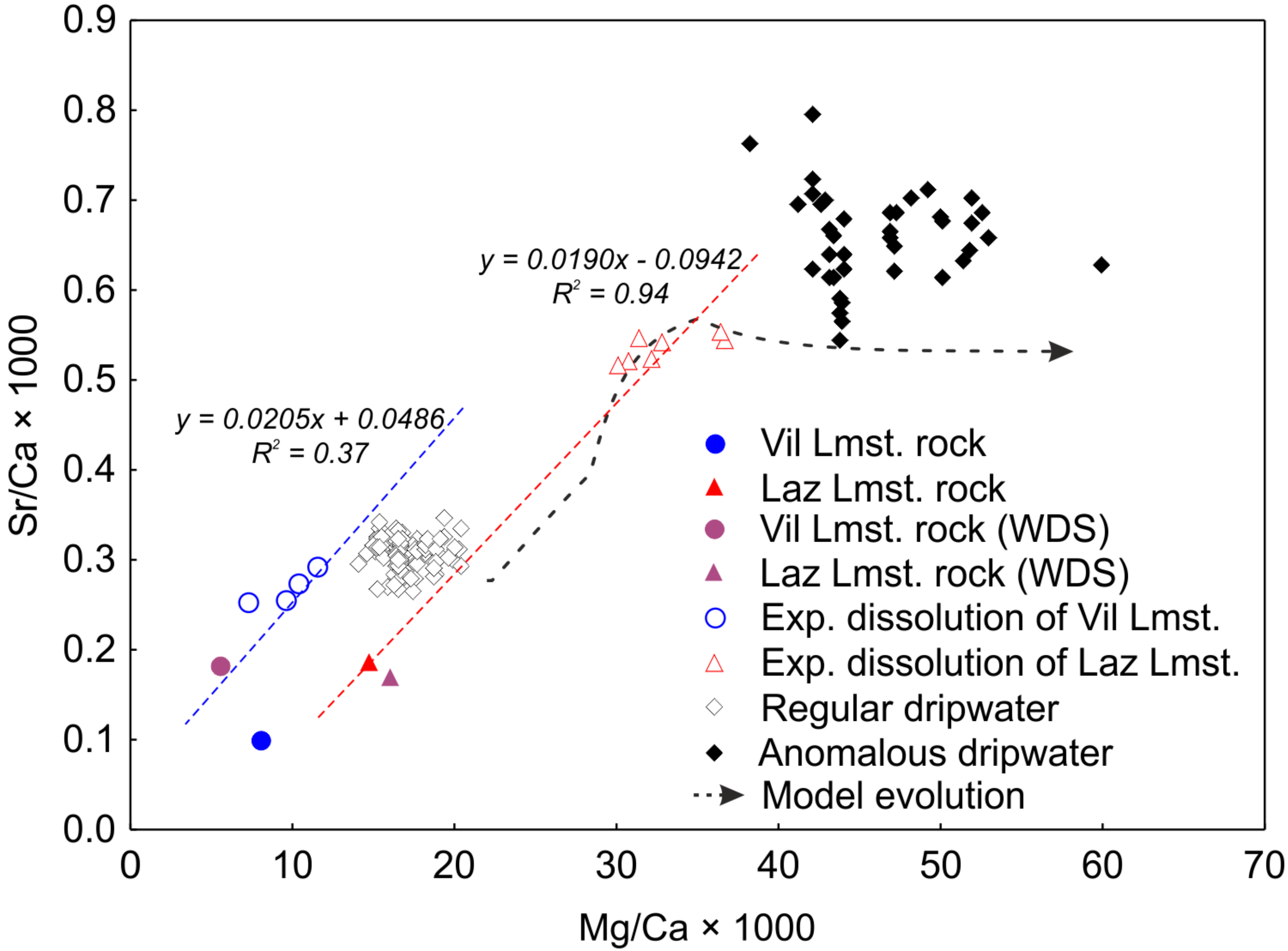


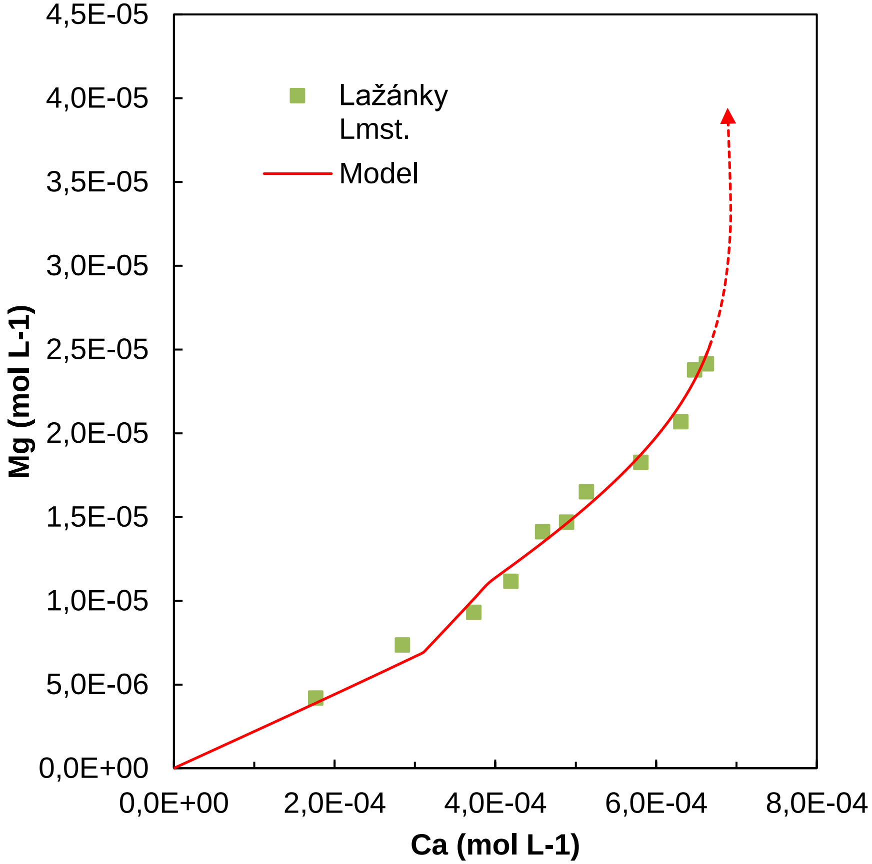
Fig. 8. Equivalent diagram to Fig. 6 for site F5.

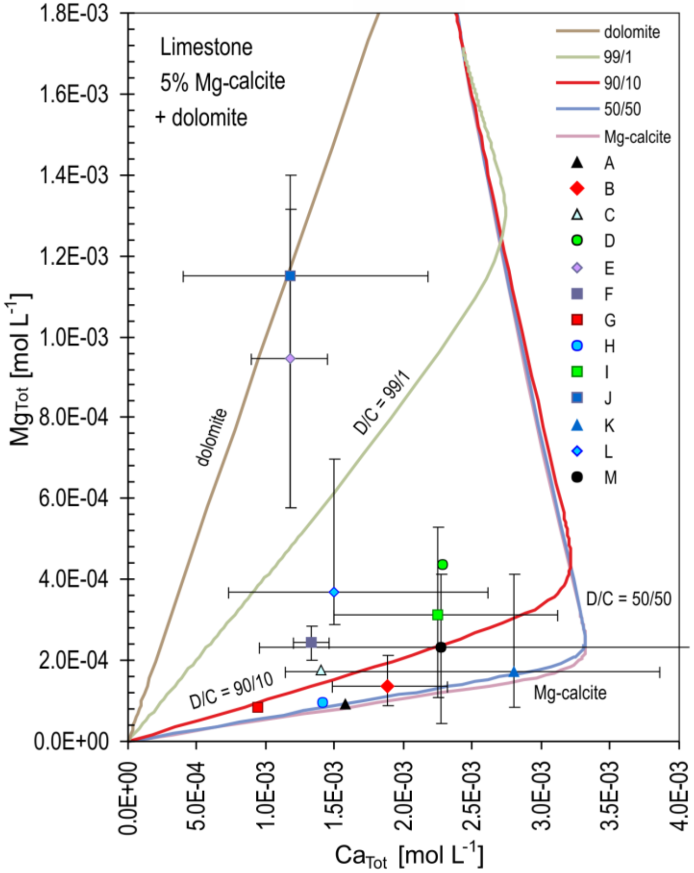
Fairchild , IJ, Tuckwell , GW, Baker , A., Tooth , AF, 2006. Modeling of dripwater hydrology and hydrogeochemistry in a weakly karstified aquifer (Bath , UK): Implications for climate change studies . J. Hydrol . 321, 213–231. https://doi.org/10.1016/j.jhydrol.2005.08.002

Mathematical model



Mathematical model





Geochemist's Workbench

- Paid software (subscription)
- Graphical interface – more user-friendly
- Speciation, diagrams, reactions, kinetics, spreadsheet...
- Community edition with limited functionality (useful especially for speciation and diagrams)
  - Annual license

SpecE8 module

- Speciation calculations for solutions (similar to the SOLUTION command in PHREEQC)
- Input solution composition (directly species) - software calculates the distribution of other species, saturation, etc.
- Interchange of species = "swapping" (e.g. H^+ for pH)
- Function „explain“
- Connectivity with Gplot – direct data plotting in diagrams (e.g. Piper)

Model 1: Speciation in seawater

Table 9. Seawater composition.
[Concentration is in parts per million (ppm) unless specified otherwise]

Analysis	PHREEQC notation	Concentration
Calcium	Ca	412.3
Magnesium	Mg	1291.8
Sodium	Na	10768.0
Potassium	K	399.1
Iron	Fe	0.002
Manganese	Mn	0.0002
Silica, as SiO_2	Si	4.28
Chloride	Cl	19353.0
Alkalinity, as HCO_3^-	Alkalinity	141.682
Sulfate, as SO_4^{2-}	S(6)	2712.0
Nitrate. as NO_3^-	N(5)	0.29
Ammonium, as NH_4^+	N(-3)	0.03
Uranium	U	0.0033
pH, standard units	pH	8.22
pe, unitless	pe	8.451
Temperature, °C	temperature	25.0
Density, kilograms per liter	density	1.023

Parkhurst & Appelo (2013)

- Use the SpecE8 module to find saturation index values for minerals dissolved in seawater
- Which mineral is it most supersaturated with?
- In what form will carbonates be dominant?
- For raw data see the file Data_pro_modely.xlsx

Speciation in seawater

In the publication

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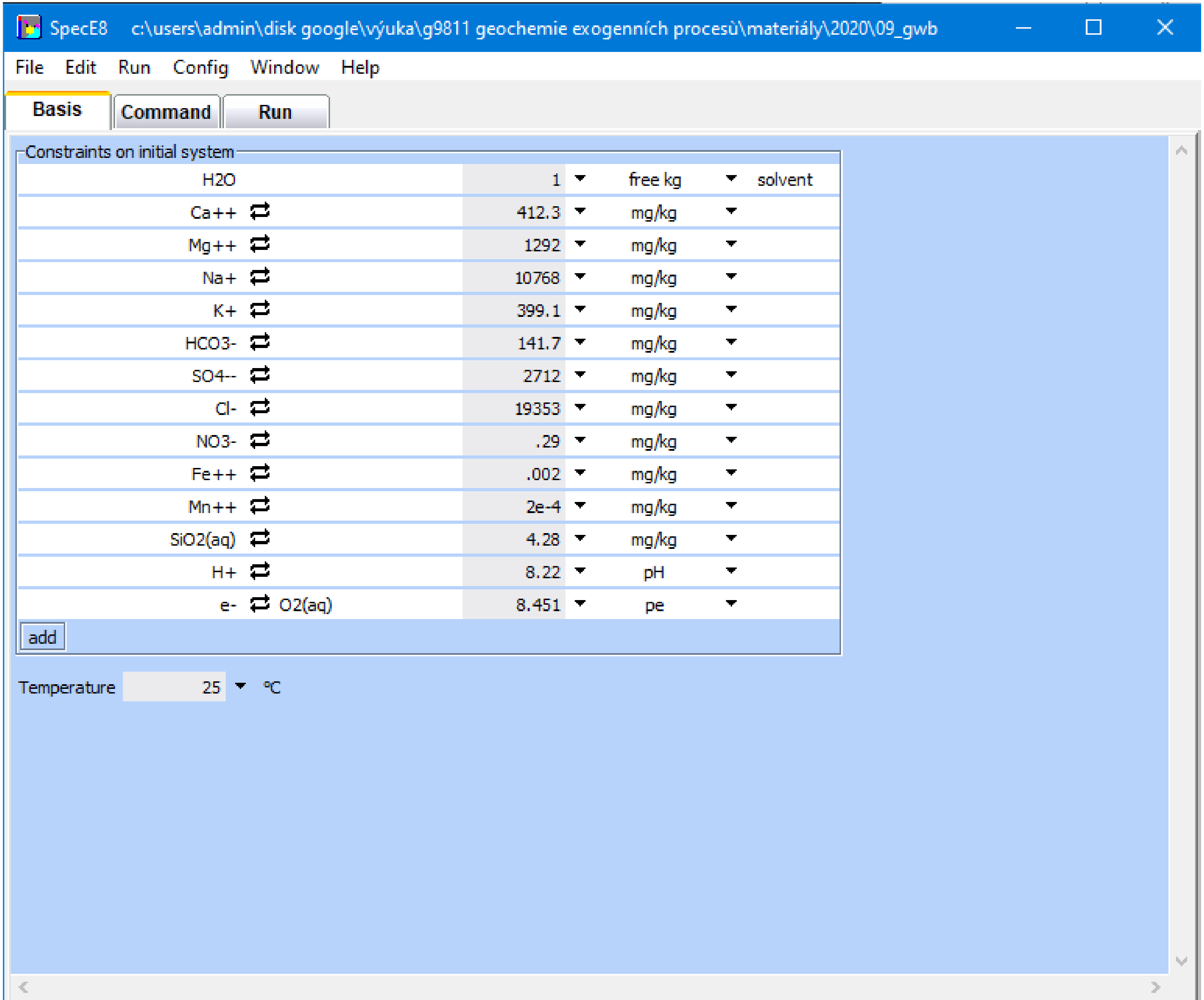
pe, unitless	pe	8.451
Temperature, °C	temperature	25.0
Density, kilograms per liter	density	1.023

Edited for input into GSS

Sample ID	Unit	Seawater
pH	pH	8.22
Fr	Fr	8.451
Ca++	mg/kg	412.3
Mg++	mg/kg	1292
On+	mg/kg	10768.0
K+	mg/kg	399.1
HCO3-	mg/kg	141.7
SO4--	mg/kg	2712
Cl-	mg/kg	19353.0
NO3-	mg/kg	0.29
Fe++	mg/kg	0.002
Mn++	mg/kg	200E-6
SiO2(aq)	mg/kg	4.28


SpecE8 c:\users\admin\disk google\výuka\g9811 geochemie exogenních procesù\materiály\2020\09_gwb
File Edit Run Config Window Help
Basis
Command
Run
Constraints on initial system
H2O 1 free kg solvent
Ca++ 412.3 mg/kg
Mg++ 1292 mg/kg
Na+ 10768 mg/kg
K+ 399.1 mg/kg
HCO3- 141.7 mg/kg
SO4-- 2712 mg/kg
Cl- 19353 mg/kg
NO3- .29 mg/kg
Fe++ .002 mg/kg
Mn++ 2e-4 mg/kg
SiO2(aq) 4.28 mg/kg
H+ 8.22 pH
e- O2(aq) 8.451 pe
add
Temperature 25 °C

Model 2: Groundwater speciation

- By interacting with the rocks, groundwater acquired a specific composition.

a) What complexes and species will be in the water?

b) What will be the saturation states of the various minerals?

- Same input as Model 0 for PHREEQC

Phreeqc input:

```
TITLE Speciation of water
SOLUTION 1
Temp            15
pH              6.05
units mol/L
Al              1E-6
Si              1E-5
Na              1.3E-5
Cl              5E-5
Ca              5.5E-4
S               3.5E-4
C               1E-3
END
```

GSS module

- Spreadsheet Manager (i.e. from the same rank as Excel)
- Enables convenient work with geochemical data, their conversions, calculations and export to graphic outputs

Model 3: Karst water

	mol/L	
	TC	CP
Mg	6.17E-05	5.76E-05
Ca	1.31E-03	3.50E-03
SO4--	4.07E-04	5.53E-04
Cl	2.26E-04	1.97E-04
Alkalinity as HCO3-	1.92E-03	6.02E-03
Sr	9.99E-07	1.18E-06
Na	8.70E-05	9.13E-05
K	1.82E-05	1.92E-05
NO3-	1.05E-04	5.97E-05
Si	8.76E-05	9.62E-05
pH	8.08	8.09
Temp	7	8

- Enter the following data into the GSS and calculate the saturation indices for calcite and dolomite, the total content of dissolved substances (total dissolved solids TDS) and charge imbalance in %.
- Data – Calculate

			1	2
Sample ID			TC	CP
Mg^{++}	molar		61.7E-6	57.6E-6
Ca^{++}	molar		0.00131	0.0035
SO_4^{--}	molar		407E-6	553E-6
Cl^-	molar		226E-6	197E-6
HCO_3^-	molar		0.00192	0.00602
Sr^{++}	molar		999E-9	1.18E-6
Na^+	molar		87E-6	91.3E-6
K^+	molar		18.2E-6	19.2E-6
NO_3^-	molar		105E-6	59.7E-6
$SiO_2(aq)$	molar		87.6E-6	96.2E-6
pH			8.08	8.09
Temperature	C		7	8

Model 4: Water from sanitation

- The following slide shows water analyzes from the area of Stráž pod Ralskem, where remediation is taking place after uranium mining by leaching
- Input water solution to GSS, calculate charge balance and TDS
- Plot the data in diagrams
  - Piper
  - Column
- Graphs – Piper

Příloha 6. Parametry vybraných vod upravené pro použití v modelu a parametry po nábojovém vyrovnání

		Původní složení upravené pro GWB				Složení po nábojovém vyrovnání			
		1	6	8	Cenoman	1	6	8	Cenoman
pH		1,1	1,9	3,68	7,63	1,10	1,90	3,68	7,63
Eh	mV		407			273	407	112	744
Electrical conductivity	uS/cm	4560	1087	79,7	327		7556	712	308
TDS	mg/l	90380	19310	764	286	71138	15040	564	292
Al+++	mg/l	8100	1740	26,83	0,025	8230	1747	26,84	0,025
Ca++	mg/l	231	198	72,13	48,1	235	199	72,14	48,1
Cl-	mg/l	16	7,5	7,2	1,9	16	7,5	7,2	1,9
F-	mg/l	460	79	4,88	0,3	467	79	4,88	0,3
Fe++	mg/l	1230	261	7,90	5,E-05*	1250	262	7,90	5,E-05
HCO3--	mg/l	1,E-30	1,E-30	1,E-30	210	1,E-30	1,E-30	1,E-30	226,683
HPO4--	mg/l	152	40	0,078	1,E-30	162	41	0,079	1,E-30
K+	mg/l	151	16	4,42	4,6	153	16	4,42	4,6
Mg++	mg/l	67	36,5	10,82	10,2	68	36,6	10,82	10,2
Mn++	mg/l	14	2,1	3,39	0,074	14	2,1	3,39	0,074
Na+	mg/l	18	5,2	7,69	6,1	18	5,2	7,69	6,1
NH4+**	mg/l	1163	257	8,86	0,19*	1182	258	8,86	0,19
O2(aq)	mg/l	1,E-30	1,E-30	0,62	0,2	3,E-13	1,E-03	-4,E-17	0,2
SO4--	mg/l	52000	12160	473	0,3	62318	12588	415	0,3
Zn++	mg/l	59	63	0,747	0,01	60	63	0,747	0,01
H+	mg/l					278	34	0	0,153

Pozn.: *hodnota nastavena na detekční limit, **použité hodnoty NH_4^+ zahrnují původní koncentraci NH_4^+ a koncentraci NO_3^- přepočtenou na NH_4^+.

Schrimple (2018)

		1	2	3	4
Sample ID		Voda 1	Voda 6	Voda 8	Cenoman
Al^{+++}	mg/l	8230	1747	26.84	0.025
Ca^{++}	mg/l	235	199	72.14	48.1
Cl^{-}	mg/l	16	7.5	7.2	1.9
F^{-}	mg/l	467	79	4.88	0.3
Fe^{++}	mg/l (as Fe)	1250	262	7.9	50E-6
HCO_3^{-}	mg/l	1E-30	1E-30	1E-30	226.7
HPO_4^{--}	mg/l	162	41	0.079	0.001
K^{+}	mg/l	153	16	4.42	4.6
Mg^{++}	mg/l	68	36.6	10.82	10.2
Mn^{++}	mg/l	14	2.1	3.39	0.074
Na^{+}	mg/l	18	5.2	7.69	6.1
NH_4^{+}	mg/l	1182	258	8.86	0.19
SO_4^{--}	mg/l	62318.0	12588.0	415	0.3
Zn^{++}	mg/l	60	63	0.747	0.01
pH		1.1	1.9	3.68	7.63
Eh	mV	273	407	112	744
H^{+}	molal	0.2842	0.0337	-0.01252	150E-6
H^{+}	molal	0.2842	0.0337	-0.01252	150E-6

Act2 module

- Used to construct diagrams – speciation , activity, Eh-pH...
- We can input data from GSS and plot it as points in diagrams
- Using the "suppress" command, we can suppress phases and species that will not occur or for some other reason we do not want in the diagram

Model 5a: Carbonate speciation

- Construct the Eh-pH diagram for HCO_3^- speciation
- Activity of HCO_3^- = 3×10^{-3} mol/L
- Plot data from Stráž (Model 4)
- File – Open – Scatter Data

Model 5b: Al speciation

- Construct an Eh-pH diagram for aluminum
- Al activity = $10^{-7.8}$ mol/L

Model 5c: Speciation of As

- Construct an Eh-pH diagram for arsenic
- As activity = 10^{-6} mol/L
- In the presence of sulfur with an activity of 10^{-2} mol/L

Model 5d: Speciation of Fe

- Fe^{2+} activity = 10^{-6}
- Suppression of unwanted species with "suppress"
- Config – Suppress

Other modules

- Rxn – balance of reactions
- React – reaction models
- Modules for the construction of other types of diagrams (P-T, phase)
- Reaction transport modeling

PHREEQC

- Freely available in versions for Windows, Mac and Linux
- Coding
- Speciation, interaction, mixing, kinetics, reaction-transport calculations…
- Possibility of programming in Basic , connection with R, Matlab, etc.
- There is a GUI version for Windows (Phreeqci)

Possible problems

- All numbers must be entered with a decimal point – commas will not work!
- Output path issues (diacritics in folder names) – issue especially with PHREEQCi

Modeling

- Regardless of the software used, it is necessary to have an idea of what I am doing and what I am finding out ☺
- A geochemical model is a mathematical model
  - In order to evaluate the model, we need to solve the system of governing equations
  - The solution is possible in two ways

1. Analytical solution - exact solution to the mathematical model, applicable to simple problems (last week's pH calculation)
2. Numerical solution – an approximate solution, typically using a computer, applicable even to very complex models

Types of geochemical models

1. Speciation modeling
2. Water mixing
3. Modeling of direct interactions
   a) Equilibrium
   b) Irreversible processes
4. Inverse modeling
5. Reaction-transport modeling
6. Kinetic modeling
7. **And more ...**

Speciation models

- Evaluation of the composition of the water sample
  - Distribution of total concentrations on the activities of individual species in solution
  - E.g. distribution of total carbonates
  - It only counts components and species defined in the database (it may be necessary to define new ones)
  - It does not consider kinetics – only a thermodynamic assessment of stabilities
  - Pure mineral phases only (no solid solutions, impurities or non-ideal stoichiometry)
  - Generally a problem with organics (not enough thermodynamic data)

Model 0

- By interacting with the rock, groundwater acquired a specific composition.

a) What complexes and species will be in the water?

b) What will be the saturation states of the various minerals?

Phreeqc input

```
TITLE Speciation of water
SOLUTION 1
Temp            15
pH              6.05
units mol/L
Al              1E-6
Si              1E-5
Na              1.3E-5
Cl              5E-5
Ca              5.5E-4
S               3.5E-4
C               1E-3
END
```

Direct interaction models

- Predicts final composition of water after interactions (with other phases or after the reaction of components in water).
- Again, it does not assess kinetics, it is based purely on the thermodynamics of processes.
- EQUILIBRIUM_PHASES command
  - Phase name, saturation index (SI) and amount in moles
  - SI = 0 … the system will calculate to balance
  - In the case of gases, it is the log of fugacity

Model 1

- **What is the pH** of pure water in equilibrium with atmospheric CO_2?
- $T = 25°C$
- $P_{CO2} = 4\times10^{-4}$
  - $\log P_{CO2} = -3.4$
  - *When calculating the equilibrium with gases, we enter the value of the logarithm of the partial pressure (or fugacity) and then we can also enter the molar content (how many moles are available; the default value is 10)*

Model 2

- **What is the pH** of pure water in equilibrium with atmospheric CO_2 and calcite (open systém conditions)?
- $T = 25°C$
- $P_{CO2} = 4 \times 10^{-4}$
  - $\log P_{CO2} = -3.4$
- $SI_{calcite} = 0$
  - *When balancing with minerals, we enter the value of the saturation index, and then we can also enter the molar content (how many moles are available; the default value is 10)*

Model 3

- **What is the pH** of pure water in equilibrium with atmospheric CO_2 and calcite (closed system conditions)?
- $T = 25°C$
- $P_{CO2} = 4 \times 10^{-4}$
  - Log $P_{CO2} = -3.4$
- $SI_{calcite} = 0$

Model 3b

- **What is the pH** of pure water in equilibrium with atmospheric CO_2 and calcite (closed systém conditions) if the temperature drops at the same time before contact with calcite?
- T = 8°C
- $P_{CO2} = 4\times10^{-4}$
  - Log $P_{CO2} = -3.4$
- $SI_{calcite} = 0$

Model 4a

- We have water of given initial composition:
- pH = 7.3
- T = 25°C
- Units mol/L
- Ca = 1.64×10^{-3} mol/L
- Alkalinity = 3.30×10^{-3} eq/L as HCO_3^-
- **What will be the saturation with respect to calcite?**
- **What will the "partial pressure of CO_2 in water" be?**
  - *(The partial pressure of CO_2 above the water with which the dissolved carbonates would be in equilibrium).*

Model 4b

- *We have water of given initial composition:*
- $T = 25°C$
- $Ca = 1.64×10^{-3}$ mol/L
- Alkalinity = $3.30×10^{-3}$ mol/L as HCO_3^-
- pH = 7.3
- The solution will establish equilibrium with atmospheric P_{CO2}
- $P_{CO2} = 4×10^{-4}$
  - $\text{Log } P_{CO2} = -3.4$
- **What will be the saturation index value with respect to calcite?**

Model 4c

- We have water of given initial composition:
- T = 25°C
- Ca = 1.64×10^{-3} mol/L
- Alkalinity = 3.30×10^{-3} mol/L as HCO_3^-
- pH = 7.3
- The solution establishes equilibrium with atmospheric P_{CO2}
- $P_{CO2} = 4\times10^{-4}$
  - Log $P_{CO2} = -3.4$
- The solution will also balance with calcite (ie, excess calcium and carbonates will precipitate).
  - $SI_{calcite} = 0$
- **What will be the concentrations of Ca $^{2+}$, total carbonates and the resulting pH?**

Other models according to the samples in the PHREEQC documentation

Solution to Model 1

```
Title Model 1
Solution 1
Temp 25

Equilibrium_phases
CO2(g) -3.4

end
```

Solution to Model 2

```
Title Model 2
Solution 1
Temp 25

Equilibrium_phases
CO2(g) -3.4
Calcite 0

end
```

Solution to Model 3

```
Title Model 3
Solution 1
Temp 25

Equilibrium_phases
CO2(g) -3.4

Save Solution 2

end

Use Solution 2
Equilibrium_phases
Calcite 0

end
```

Solution to Model 3

```
Title Model 3b
Solution 1
Temp 25

Equilibrium_phases
CO2(g) -3.4

Save Solution 2

end
# here we enter a lower temperature for further interaction
Reaction_Temperature
8

Use Solution 2
Equilibrium_phases
Calcite 0

end
```

Solution to Model 4a

```
Title Model 4a
Solution 1
Temp 25

Equilibrium_phases
CO2(g) -3.4

Save Solution 2

end

Use Solution 2
Equilibrium_phases
Calcite 0

end
```

Solution to Model 4b

```
Title Model 4b
#we are interested in saturation with respect to calcite and CO2
Solution 1
Temp 25
pH 7.3
Units mol/L

Ca              1.64e-3
Alkalinity      3.30e-3 as HCO3-

Save Solution 1
end

# water in next step attains balance with atmospheric CO2
Use Solution 1
Equilibrium_Phases
CO2(g) -3.4

end
```

Solution to Model 4c

```
Title Model 4c
# we are interested in saturation with respect to calcite and CO2
Solution 1
Temp 25
pH 7.3
Units mol/L

Ca                    1.64e-3
Alkalinity                       3.30e-3 as HCO3-

Save Solution 1
end

# water in next step attains balance with atmospheric CO2
Use Solution 1
Equilibrium_Phases
CO2(g) -3.4

Save Solution 2
end

# in the last step water precipitates calcite, with respect to which it is supersaturated
Use Solution 2
Equilibrium_Phases
Calcite 0
CO2(g) -3.4

end
```

EVROPSKÁ UNIE
Evropské strukturální a investiční fondy
Operační program Výzkum, vývoj a vzdělávání

MINISTERSTVO ŠKOLSTVÍ, MLÁDEŽE A TĚLOVÝCHOVY

Tento učební materiál vznikl v rámci projektu Rozvoj doktorského studia chemie

č. CZ.02.2.69/0.0/0.0/16_018/0002593

Resources

- Parkhurst, DL, and Appelo , CAJ, 2013, Description of input and examples for PHREEQC version 3 — A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: US Geological Survey Techniques and Methods, book 6, chap. A43, 497 p., available only at http://pubs.usgs.gov/tm/06/a43/.
- SCHRIMPELOVA, Kateřina. A Geochemical Model of the Groundwater of the Guardian Area Leach Fields [online]. Brno, 2018 [cit. 2020-12-01]. Available from: <https://theses.cz/id/ puiiey />. Thesis. Masaryk University, Faculty of Science. Supervisor doc. RNDr. Josef Zeman, CSc..