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

MINISTERSTVO ŠKOLSTVÍ, MLÁDEŽE A TĚLOVÝCHOVY

Chemical methods in geology

2a.

Hydrogeochemical Diagrams

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

Topics

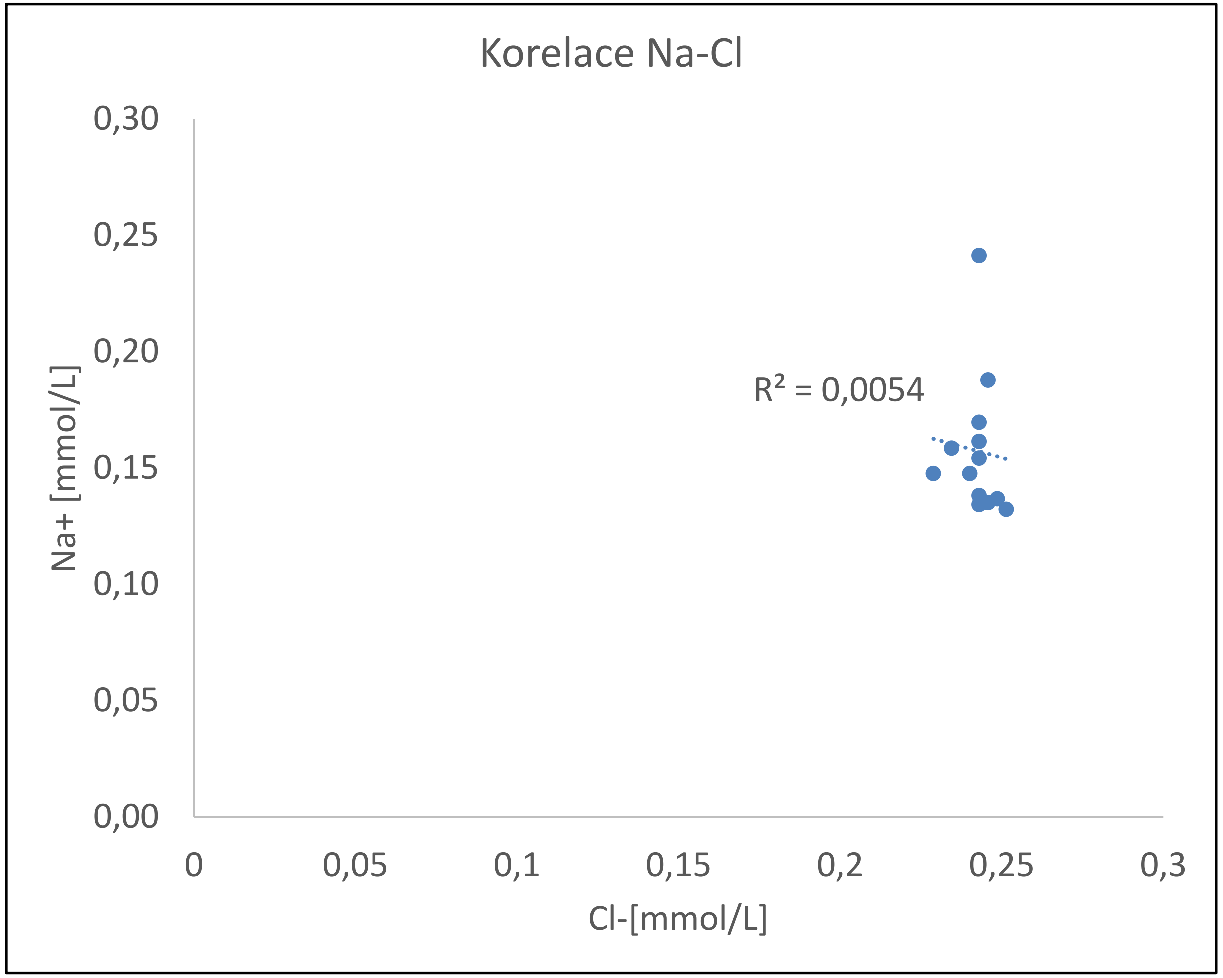
- Diagrams in hydrogeochemistry
  - Stiff diagram
  - Piper diagram
  - Durov diagram
  - pH- Eh

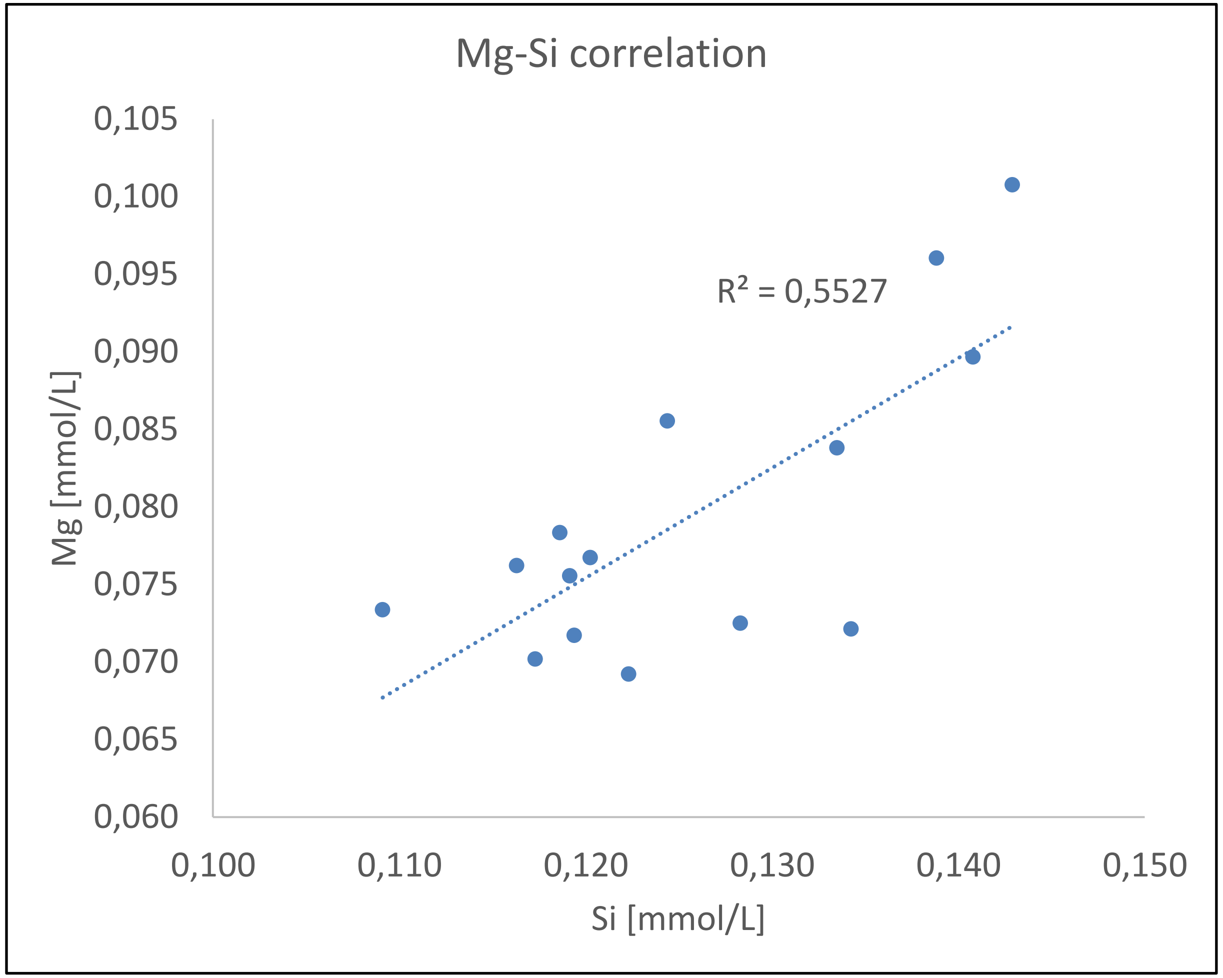
DIAGRAMS

Diagrams

- Clearer presentation of a larger number of samples
- Usually plot of basic ions (Mg^{2+}, Ca^{2+}, K^+, Na^+ and Cl^-, HCO_3^-, SO_4^{2-}, NO_3^-)
- Visual comparison – quick recognition of the same **types of water**
- Maps
- Point graphs expressing correlations are also handy (e.g. Na^+ and Cl^-)

XY dot charts – Scatterplot





Basic diagrams

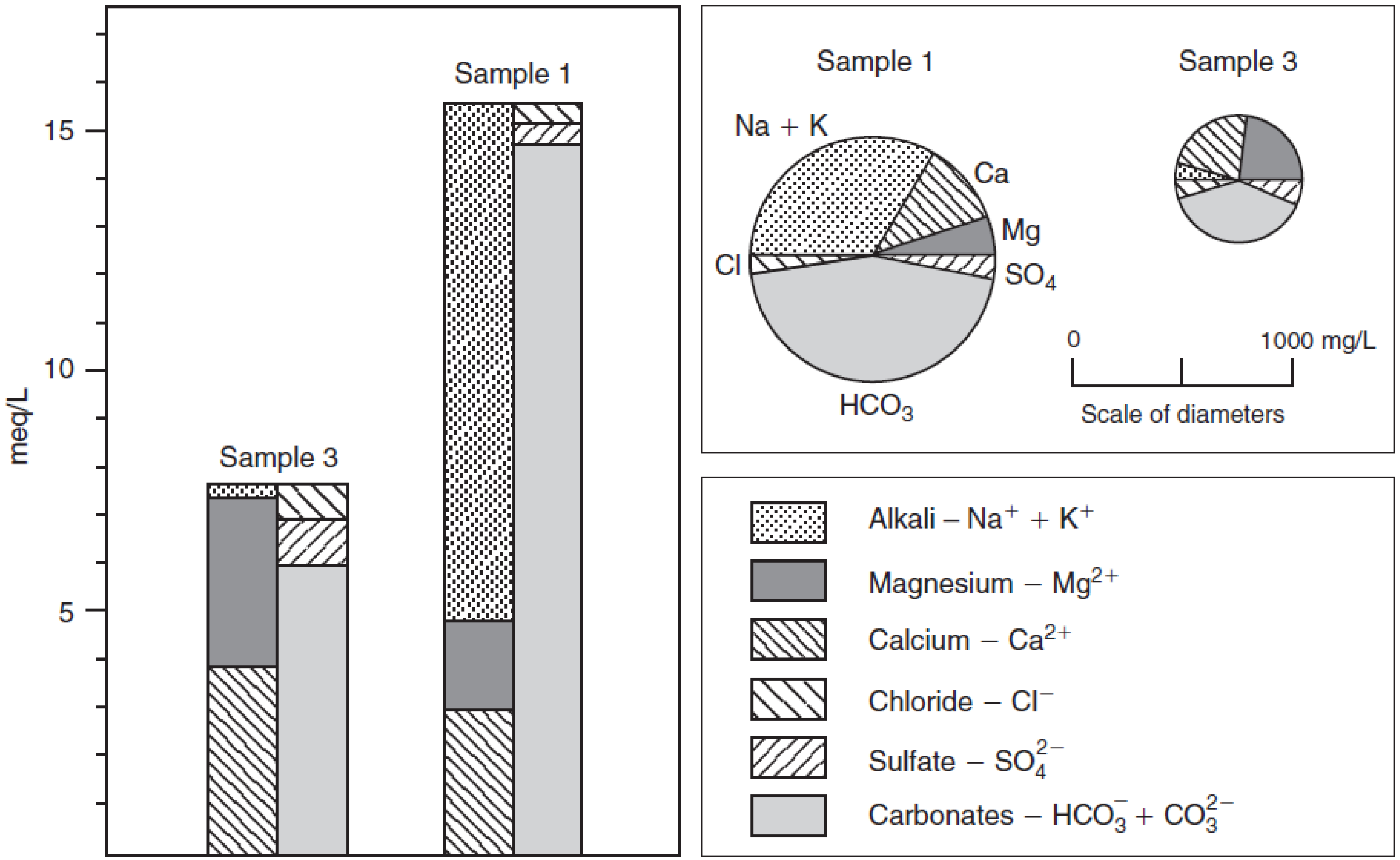
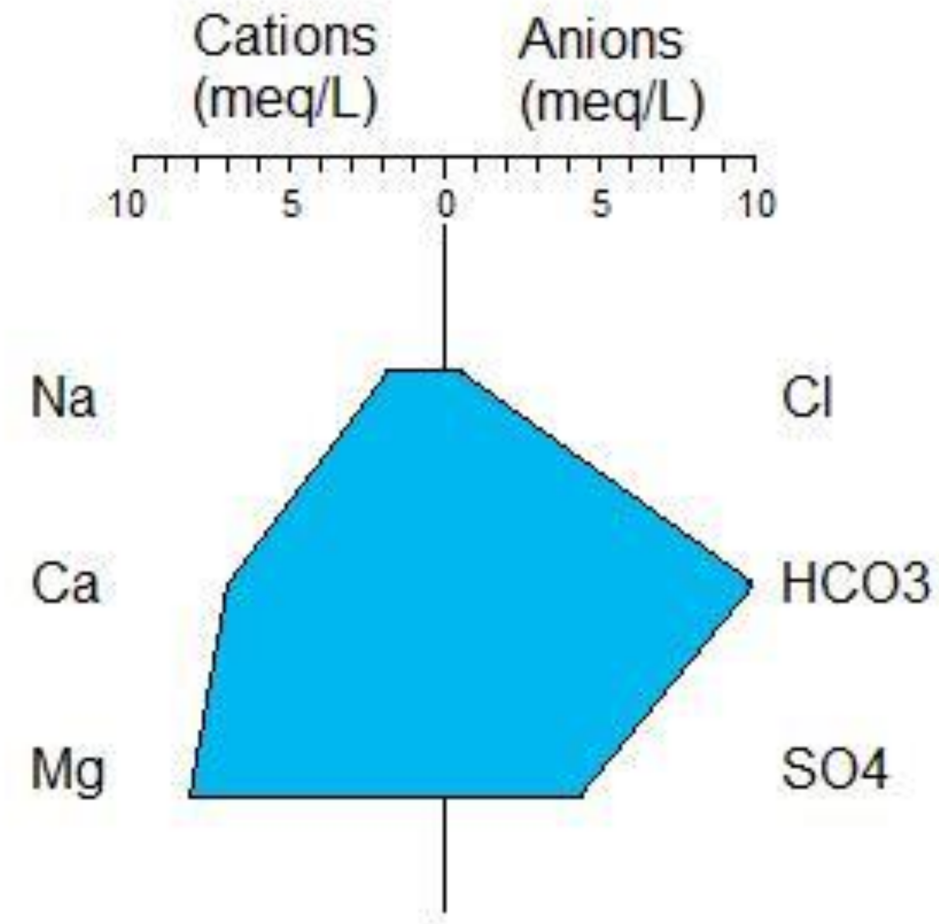


Figure 1.3. Bar and circle diagrams, two graphical methods to display the bulk chemical composition of groundwater (Domenico and Schwartz, 1997).

Appelo & Postma (2005)

- Bar
  - In miliequivalents
  - Cation (left) and anion (right) part
  - They should be equal = electroneutrality
- Pie
  - In milliequivalents
  - Circle size represents total mineralization
  - Cation (top) and anion (bottom) part – electroneutrality
- Quick recognition of the same water types

Stiff diagram



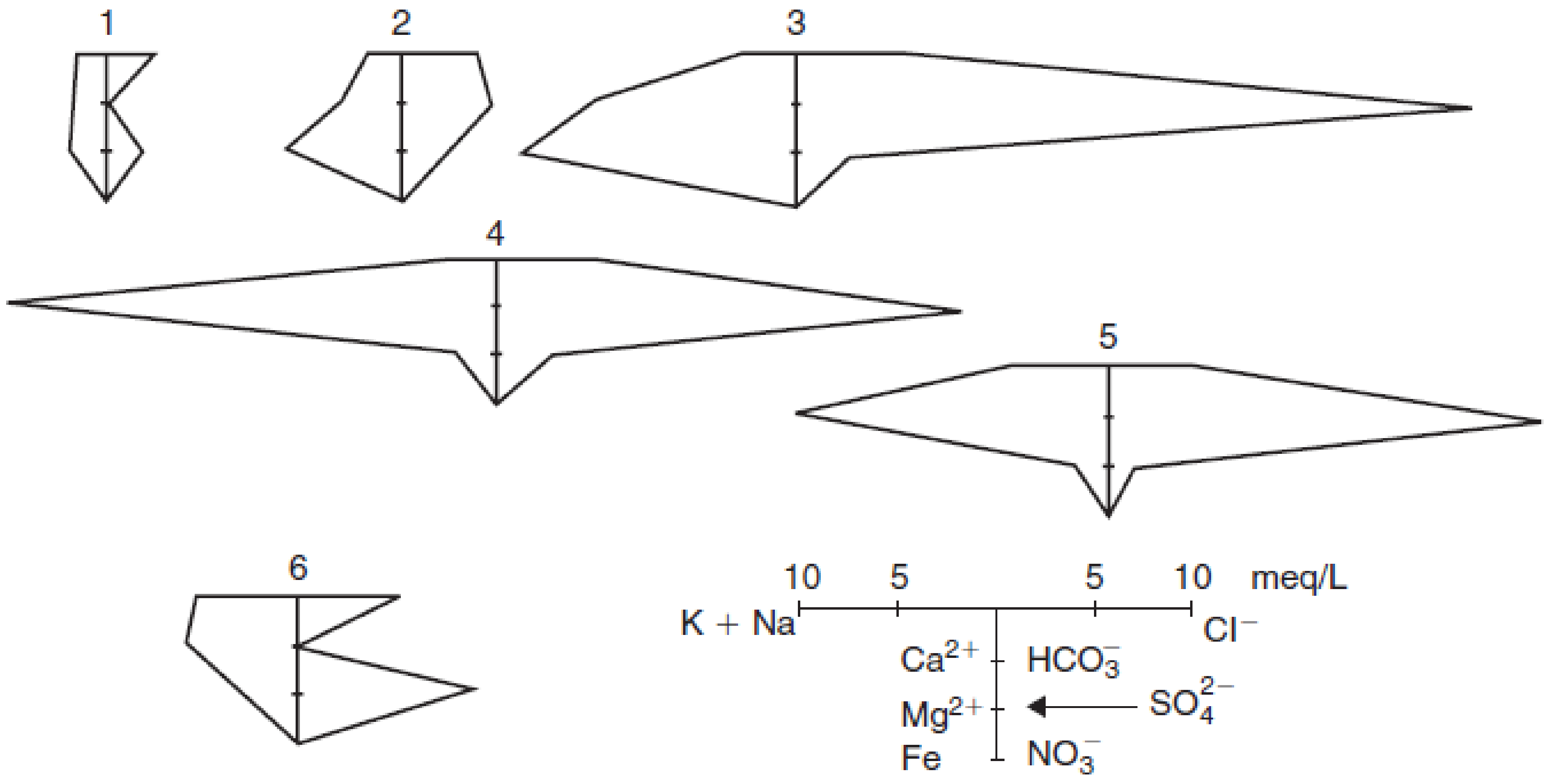
Seawater

Dissolving carbonates

The other two main components of water

+ sometimes 4 axes (according to the needs of the given study)

- Qualitative and quantitative composition
- Three to four axes
- On each axis a cation on left and an anion on the right in meq /L
- A characteristic shape is formed



What are the properties of the waters shown?

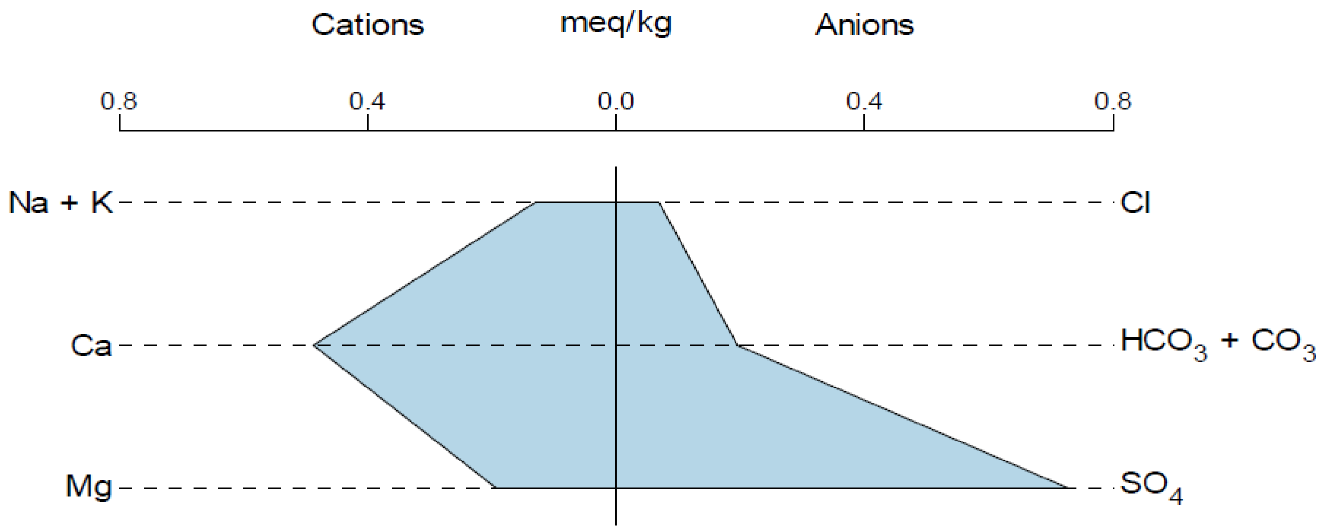
What environment will they match?

Which one will correspond to rainwater?

Calcite karst?

Dolomite karst?

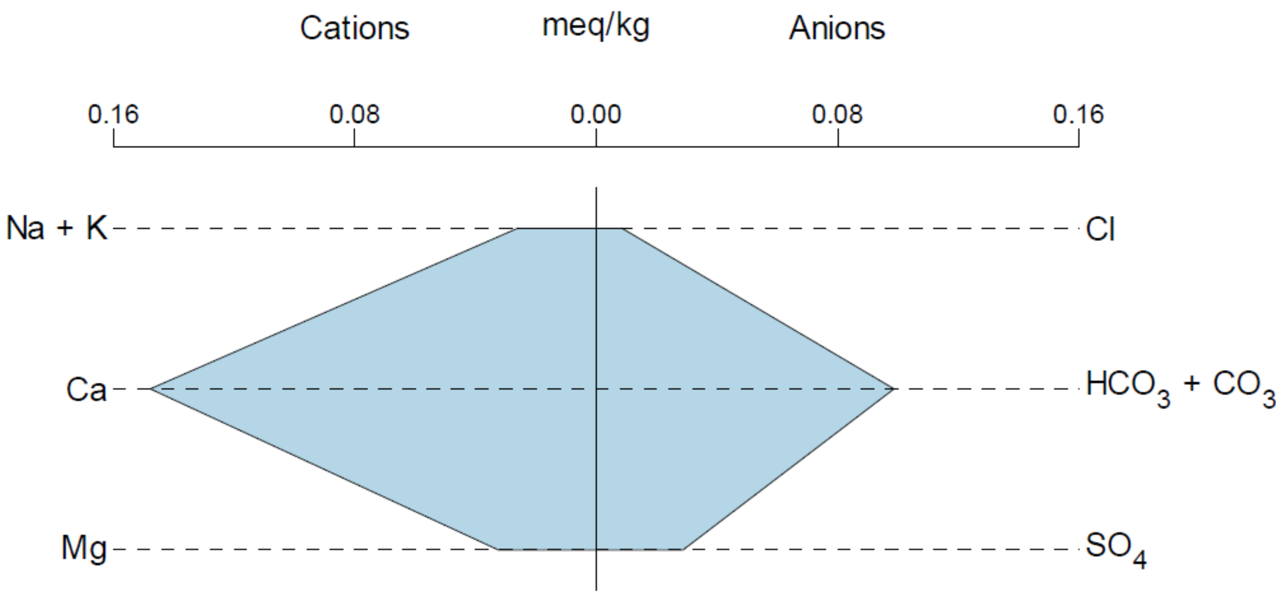
Appelo & Postma (2005)



Obr. 7 Stiffův diagram složení podzemní vody – Staré Ransko, typ ho

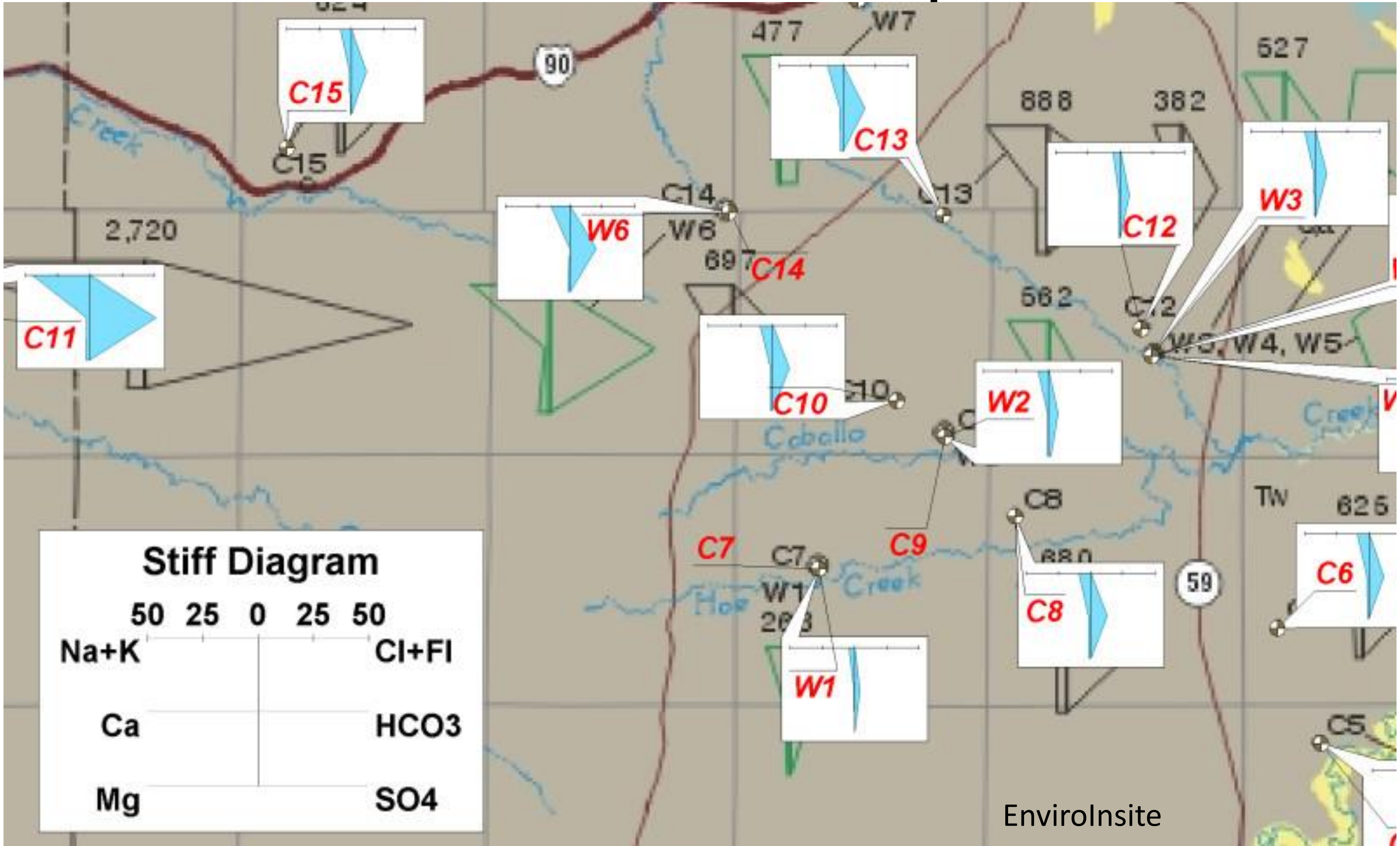
Goal 2013

How are the waters different?



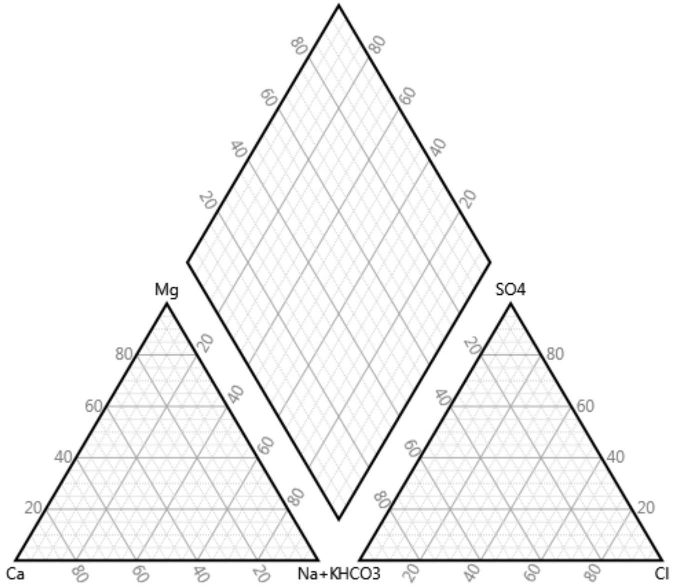
Obr. 8 Stiffův diagram složení podzemní vody - Český masiv, typ horniny - žula.

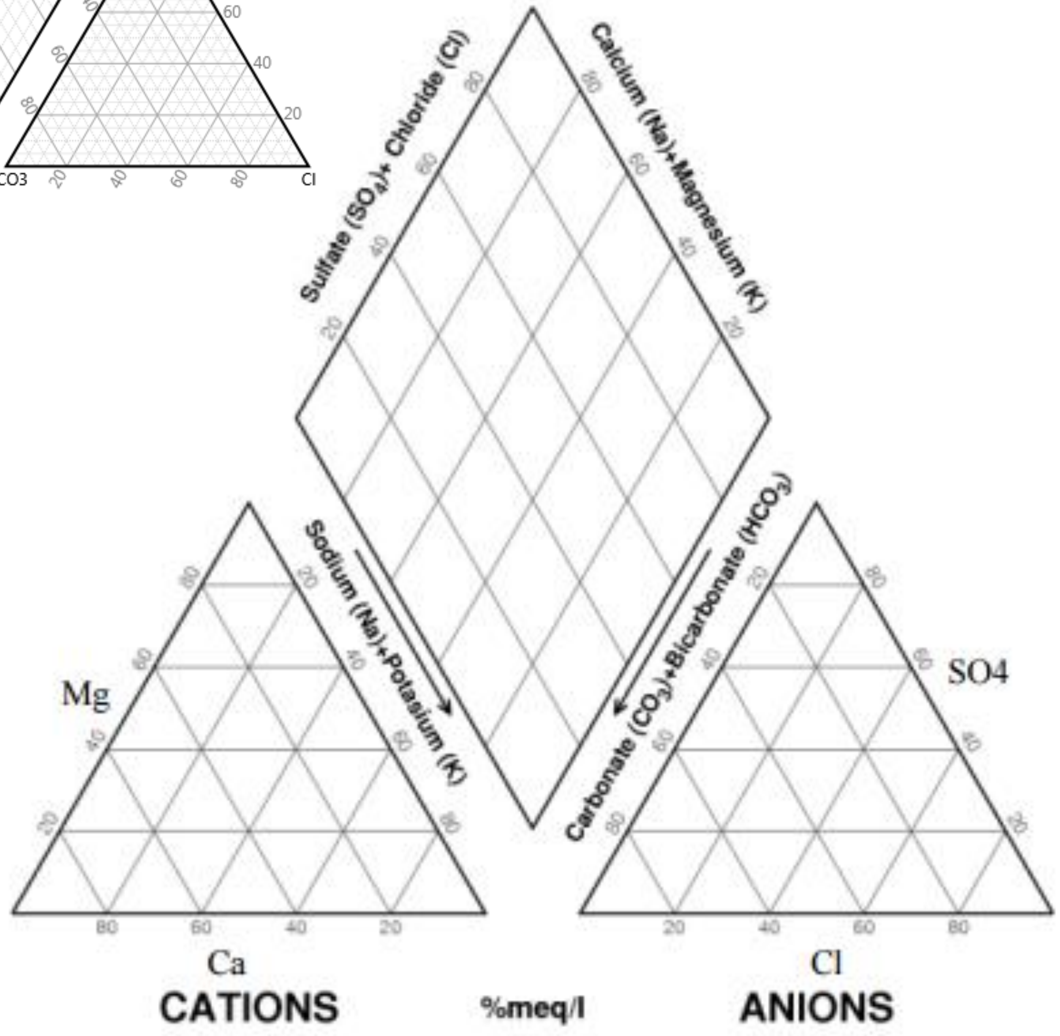
Stiff on the map



EnviroInsite

Piper diagram





- Especially suitable for large amounts of samples
- We present **the percentages of total meq/l** of cations and anions separately
  - Main cations in the left triangle
  - Main anion in the right triangle
  - Projection into the central rhombus as a single point
- Qualitative diagram
  - Assessment of water types
- Quantity added through the shape or size of symbols
  - – Typically total mineralization via size

Appelo & Postma (2005)

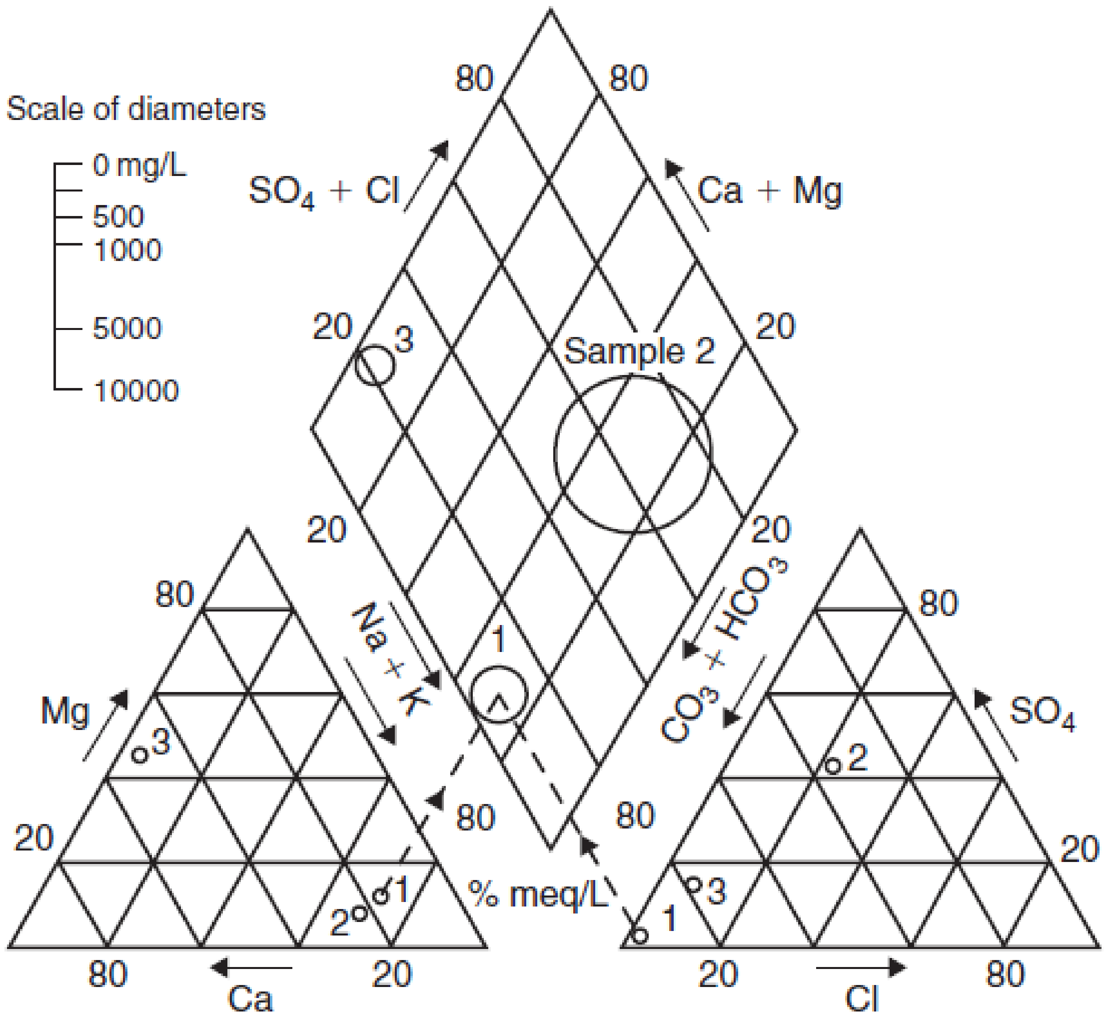
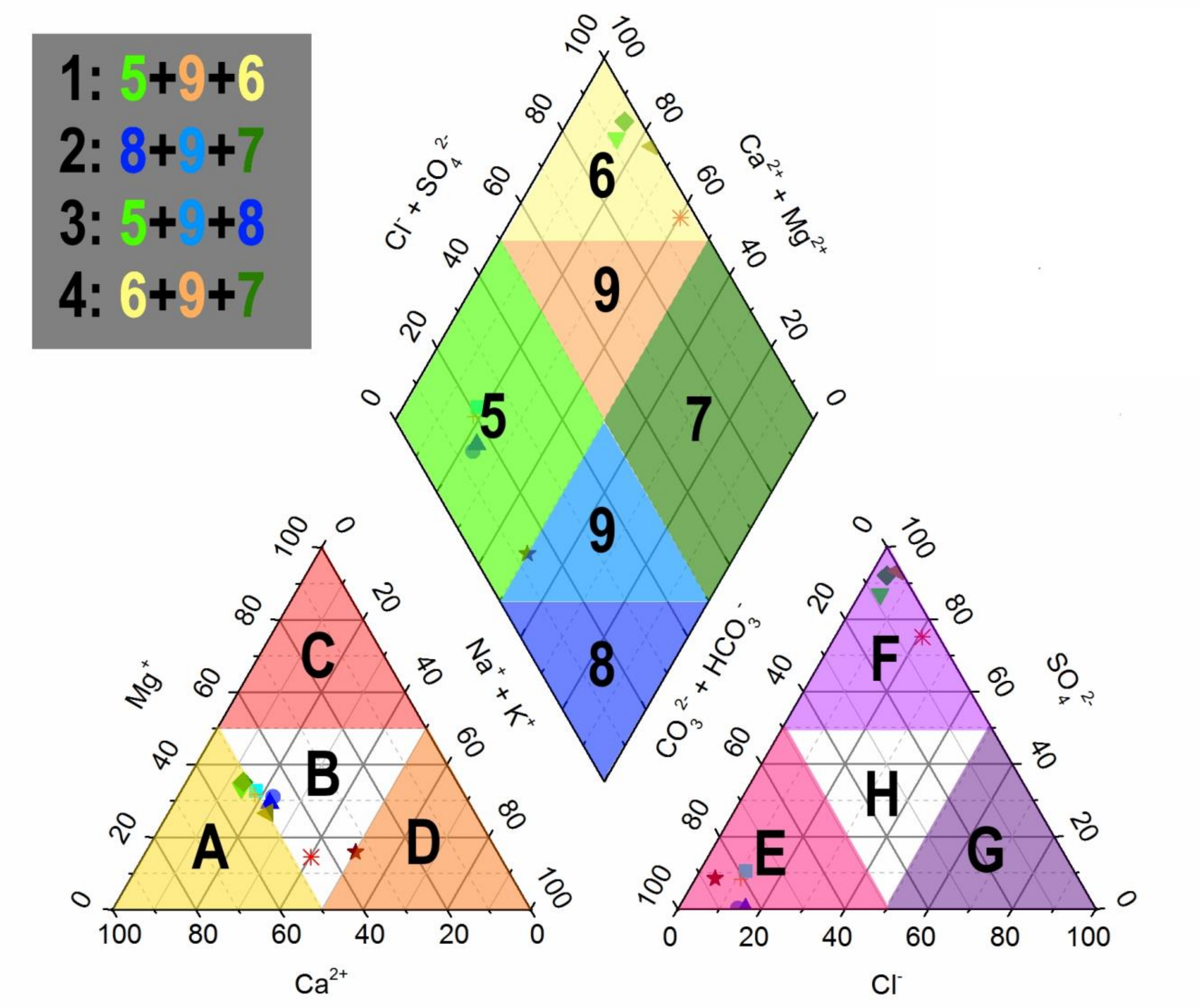


Figure 1.5. The Piper diagram, used for graphically displaying the bulk chemical composition of groundwaters. The two triangular plots give the relative composition of cations and anions, expressed in percentage of total cation or anion meq/L. From the triangular diagrams the points are conducted to the diamond shaped diagram parallel to the outer side of the diagram until they intersect (dotted lines for sample 1). The size of the circle in the diamond indicates the total dissolved solid concentration (Domenico and Schwartz, 1997). Free software for constructing Piper diagrams can be downloaded from http://water.usgs.gov/nrp/gwsoftware/GW_Chart/GW_Chart.html

Water classification

Legend

A: Calcium type
B: No dominant type
C: Magnesium type
D: Sodium and potassium type
E: Bicarbonate type
F: Sulphate type
G: Chloride type
1: Alkaline earths exceed alkalies
2: Alkalies exceed alkaline earths
3: Weak acids exceed strong acids
4: Strong acids exceed weak acids
5: Magnesium bicarbonate type
6: Calcium chloride type
7: Sodium chloride type
8: Sodium bicarbonate type
9: Mixed type



Appelo & Postma (2005)

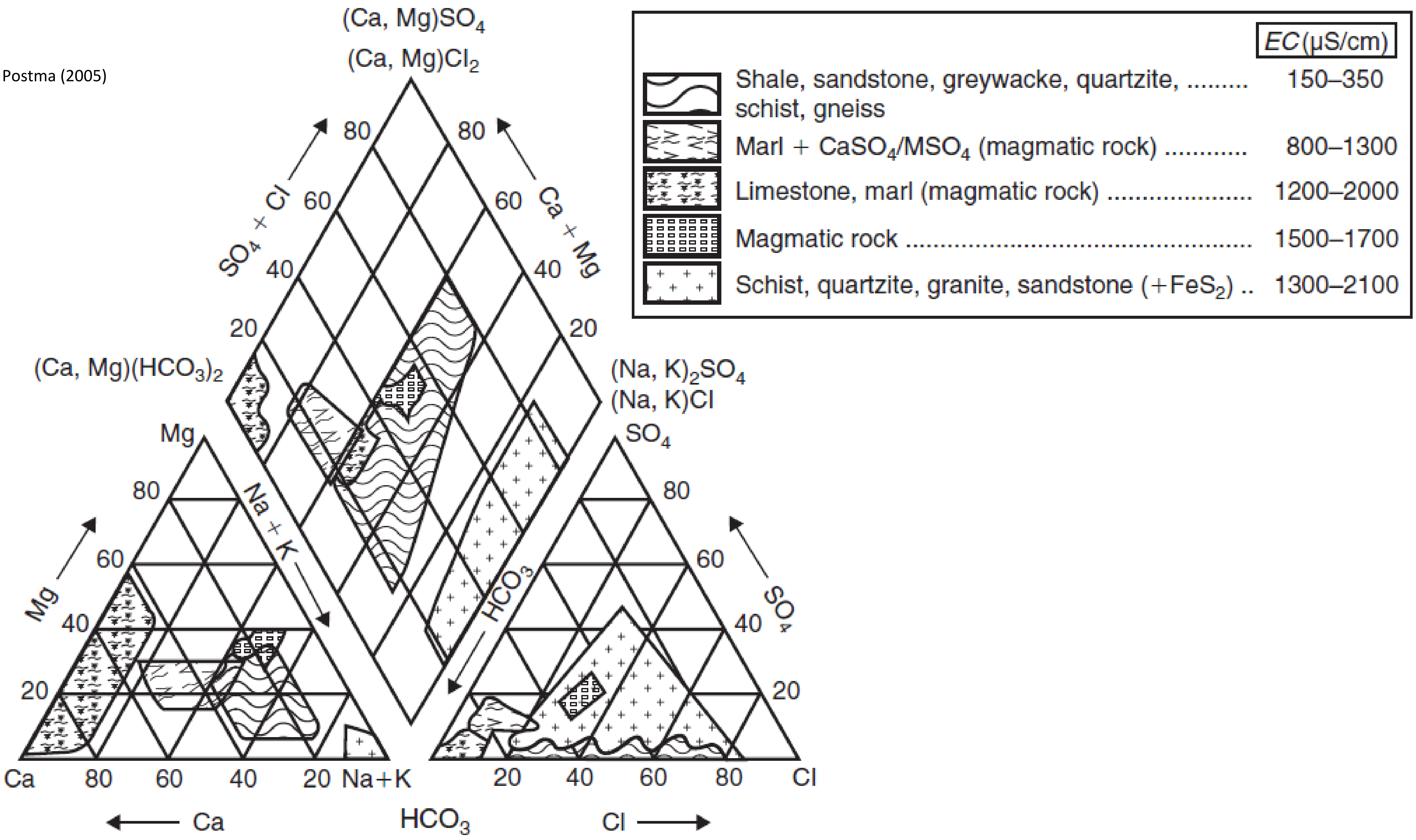
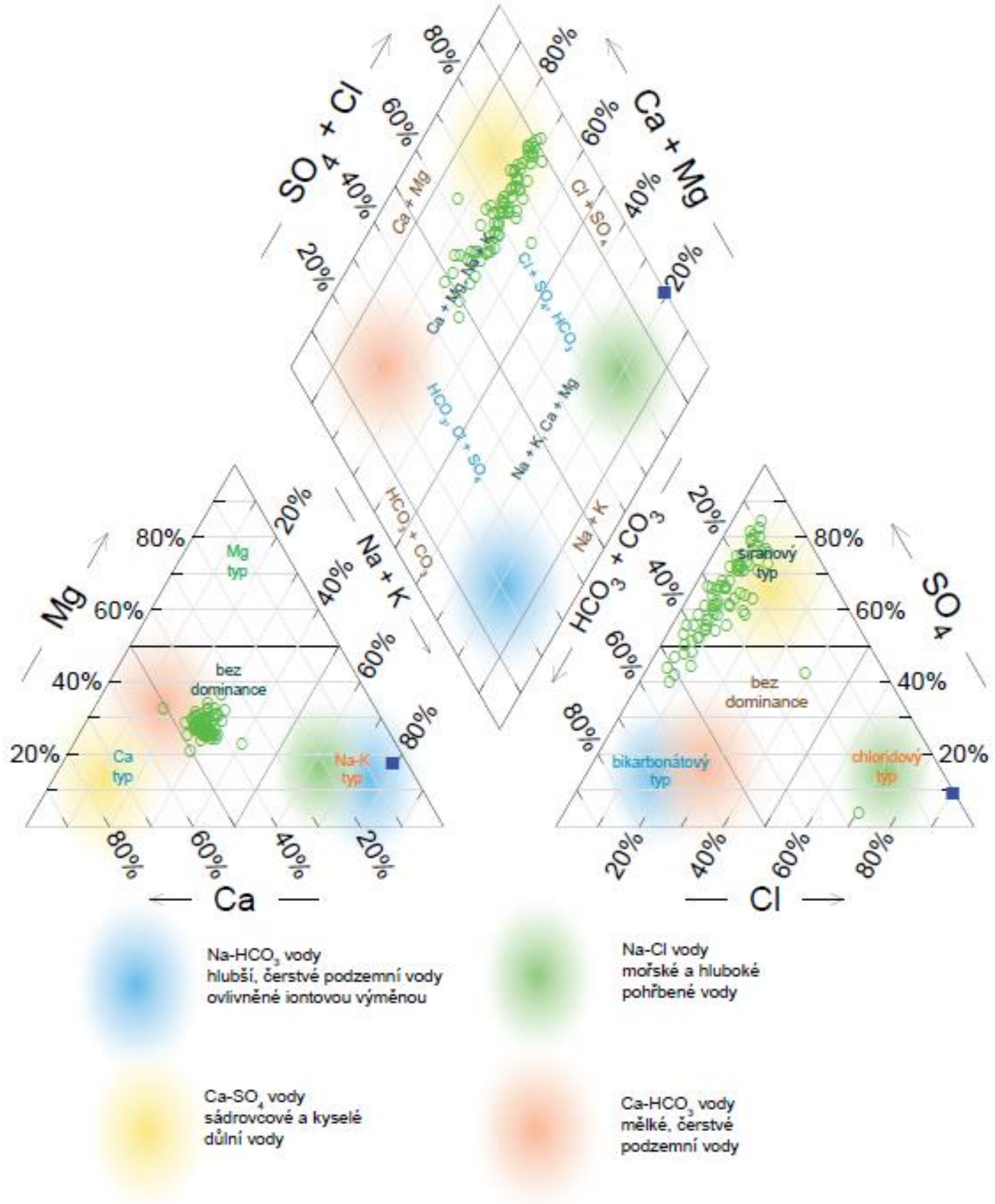
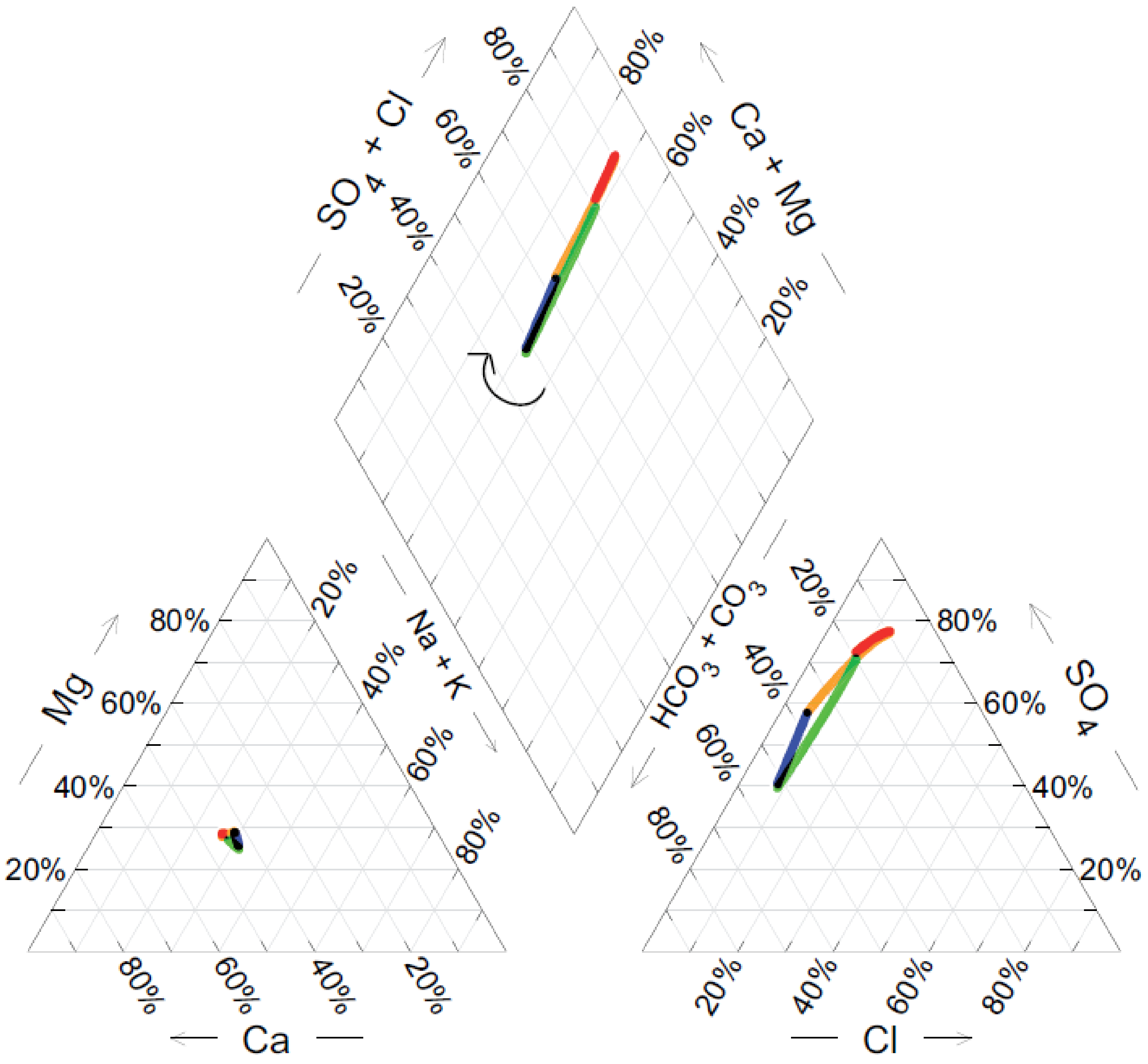


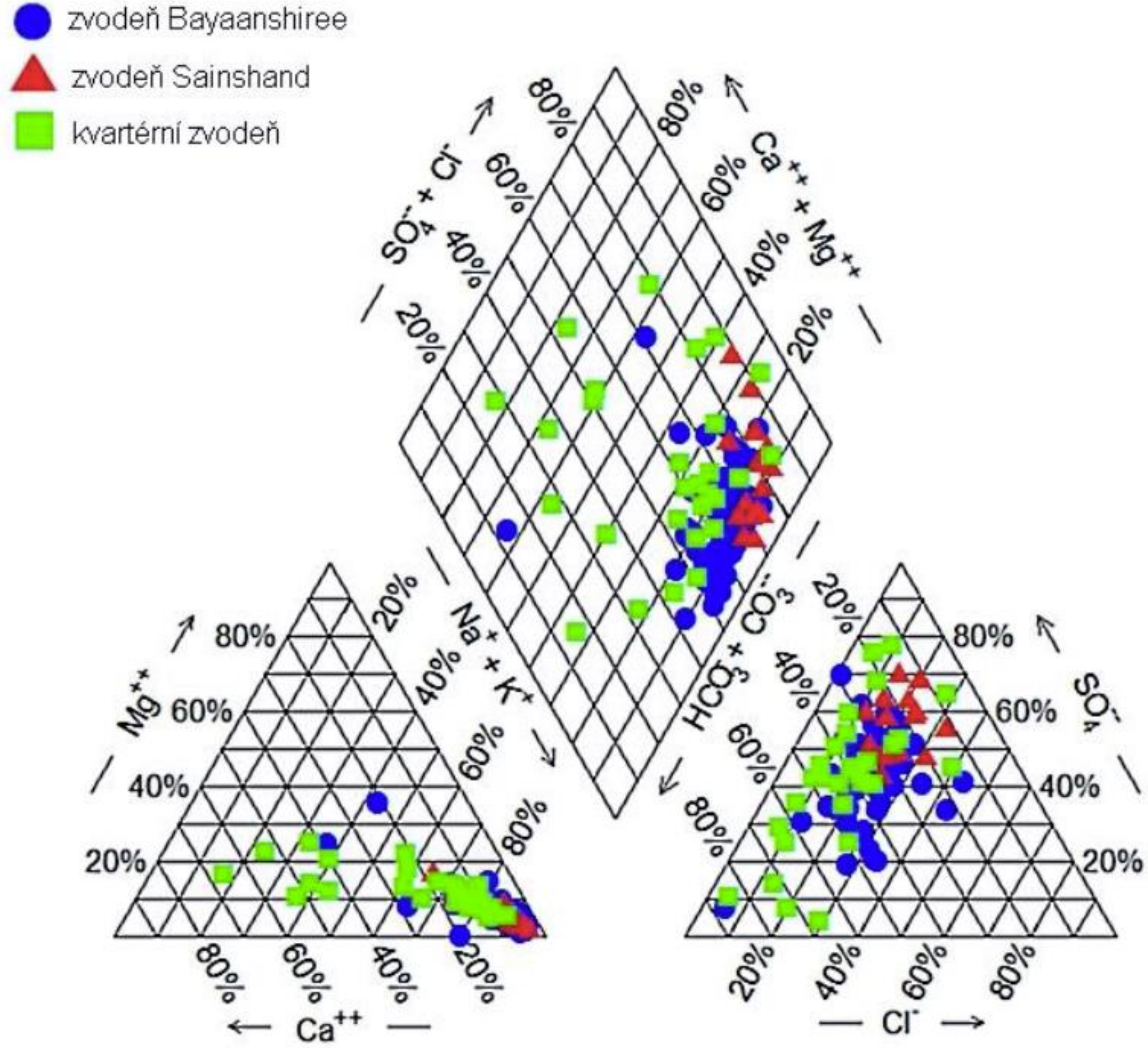
Figure 1.6. A Piper plot of European bottled mineral waters and their relation to the rock type from which the water was extracted (modified from Zuurdeeg and Van der Weiden, 1985).



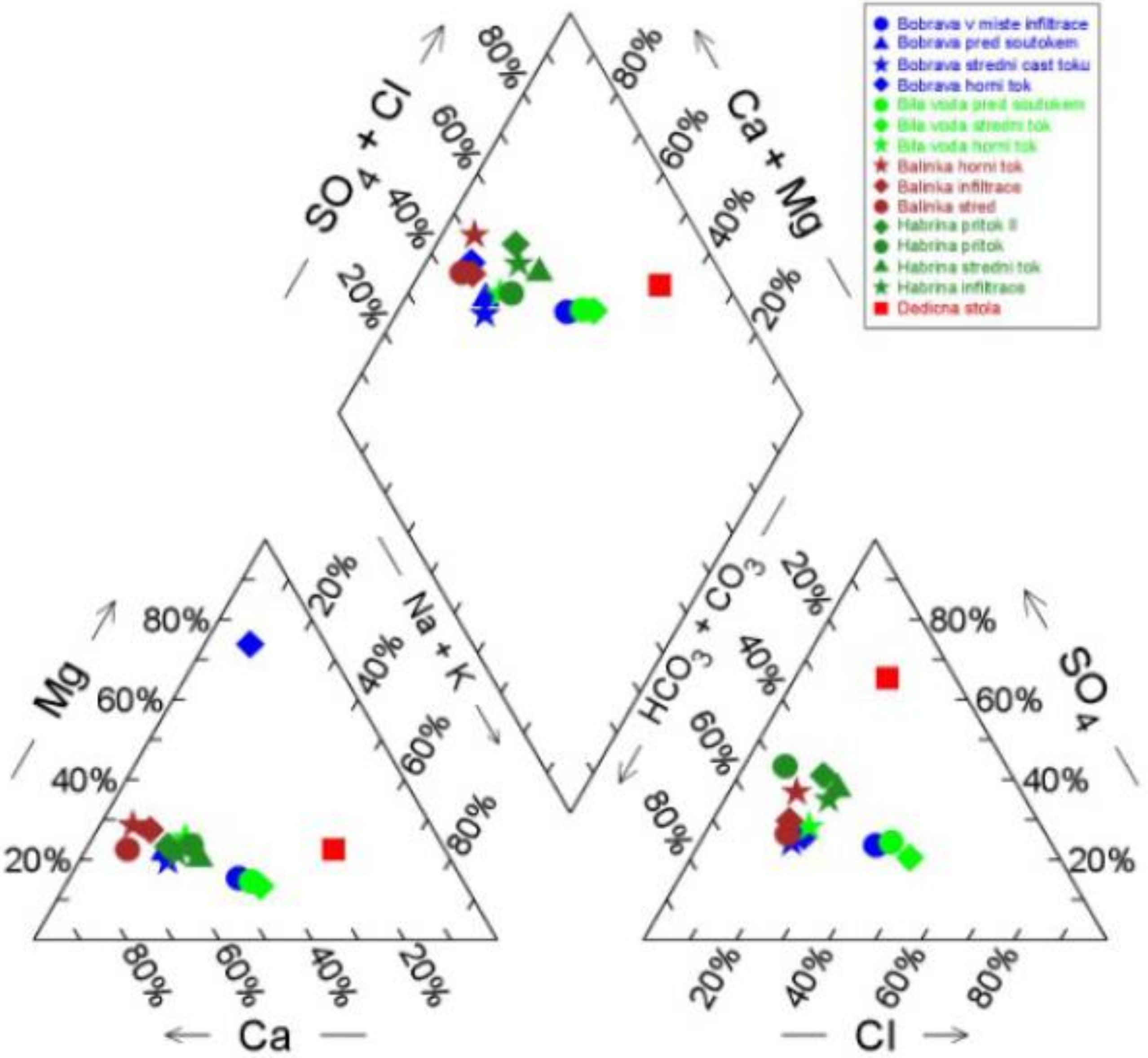
Forejtová 2008



Forejtová 2008

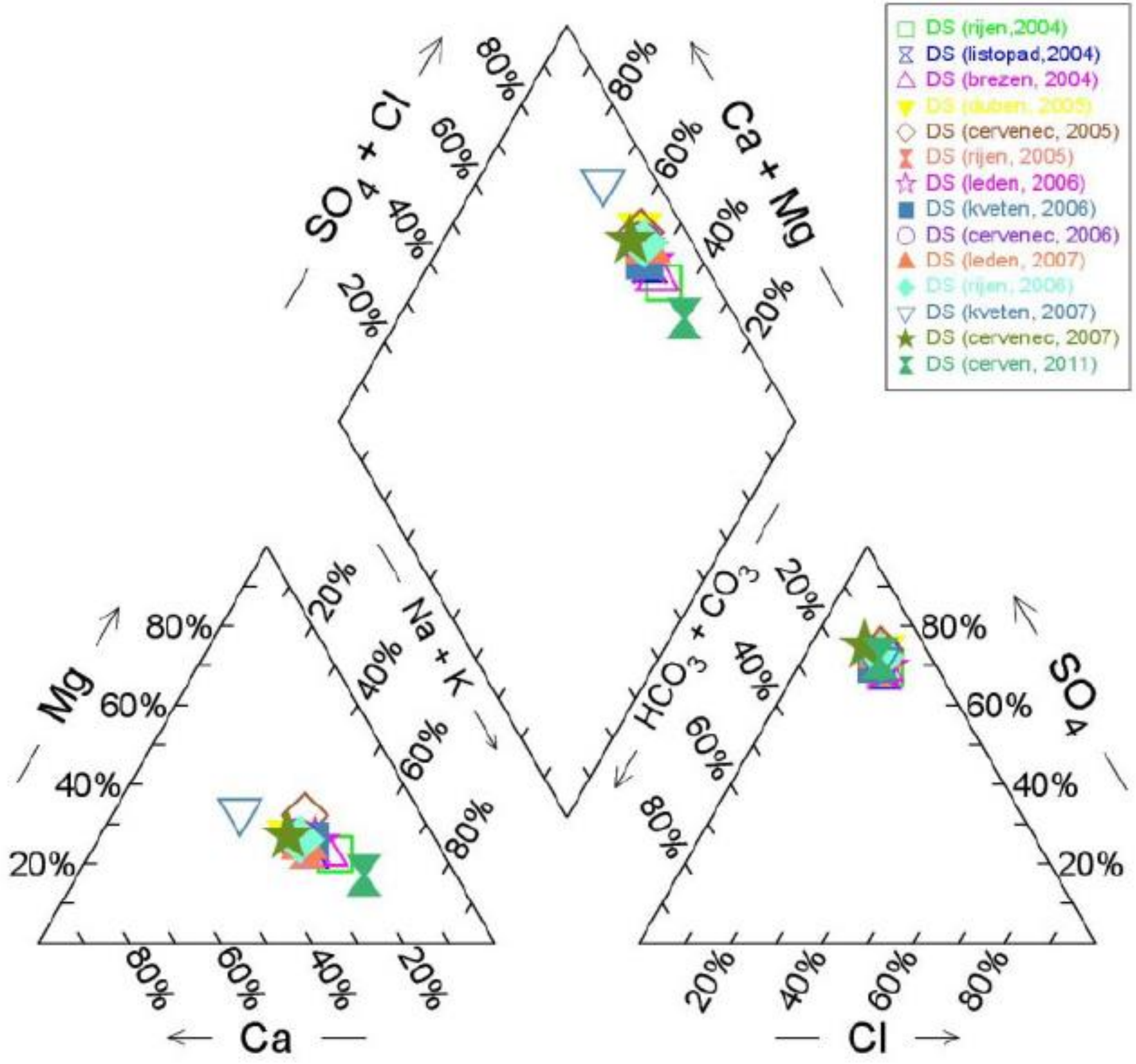


Láznička 2016



Seifertová 2014

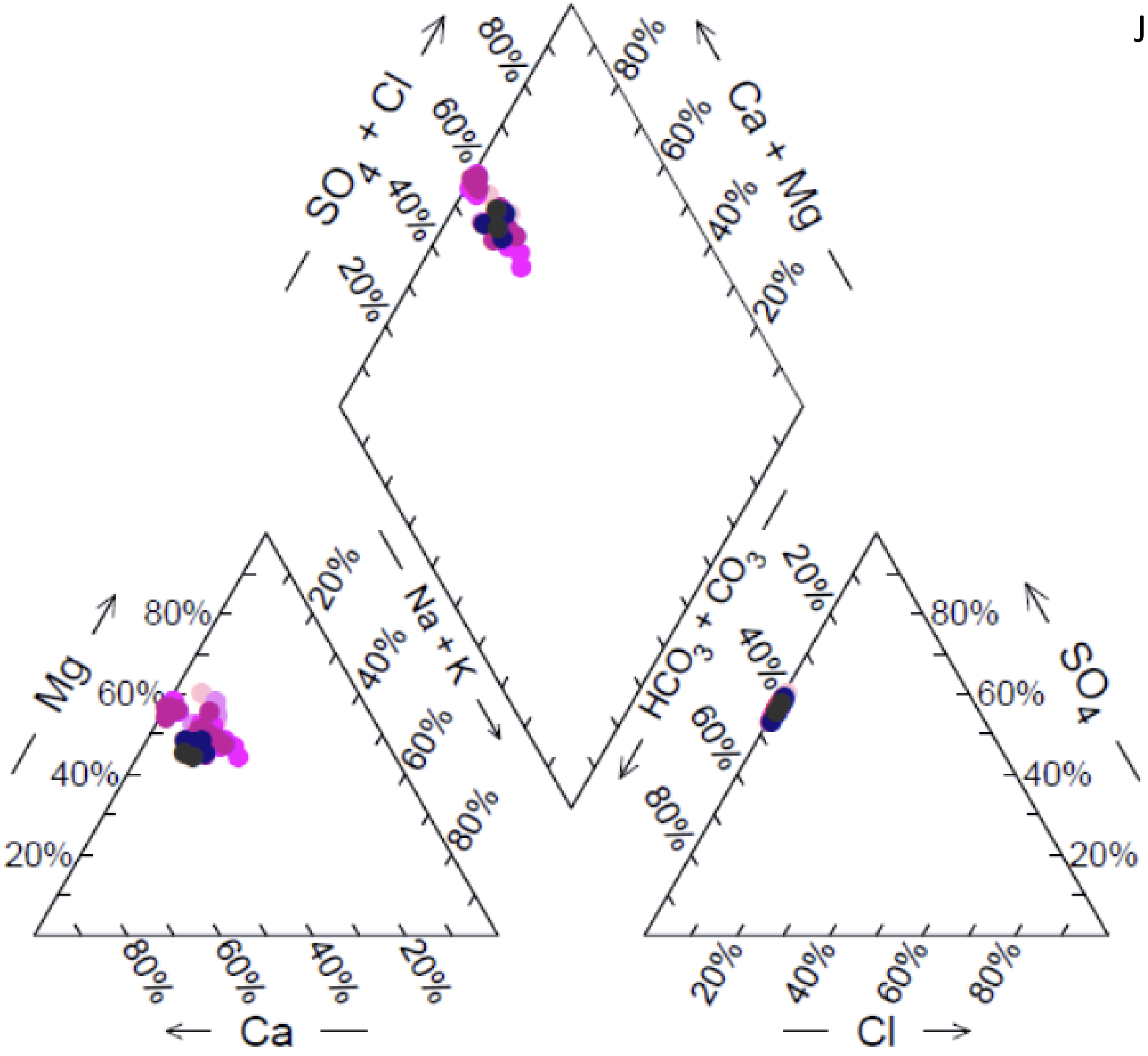
Obr. 1 Piperův diagram pro složení povrchových vod



Seifertová 2014

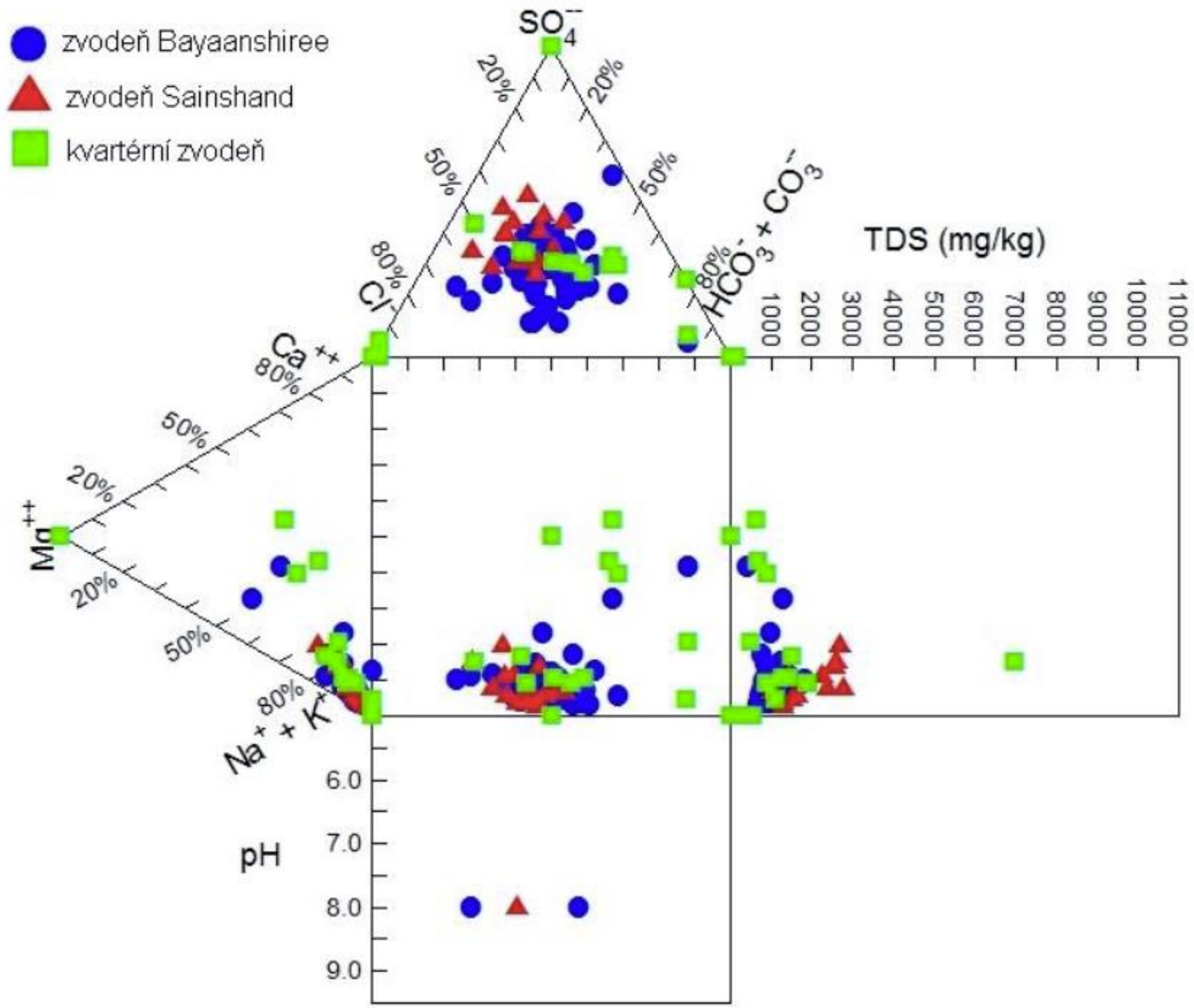
Obr. 2 Piperův diagram pro složení důlních vod

Jeřábková 2013



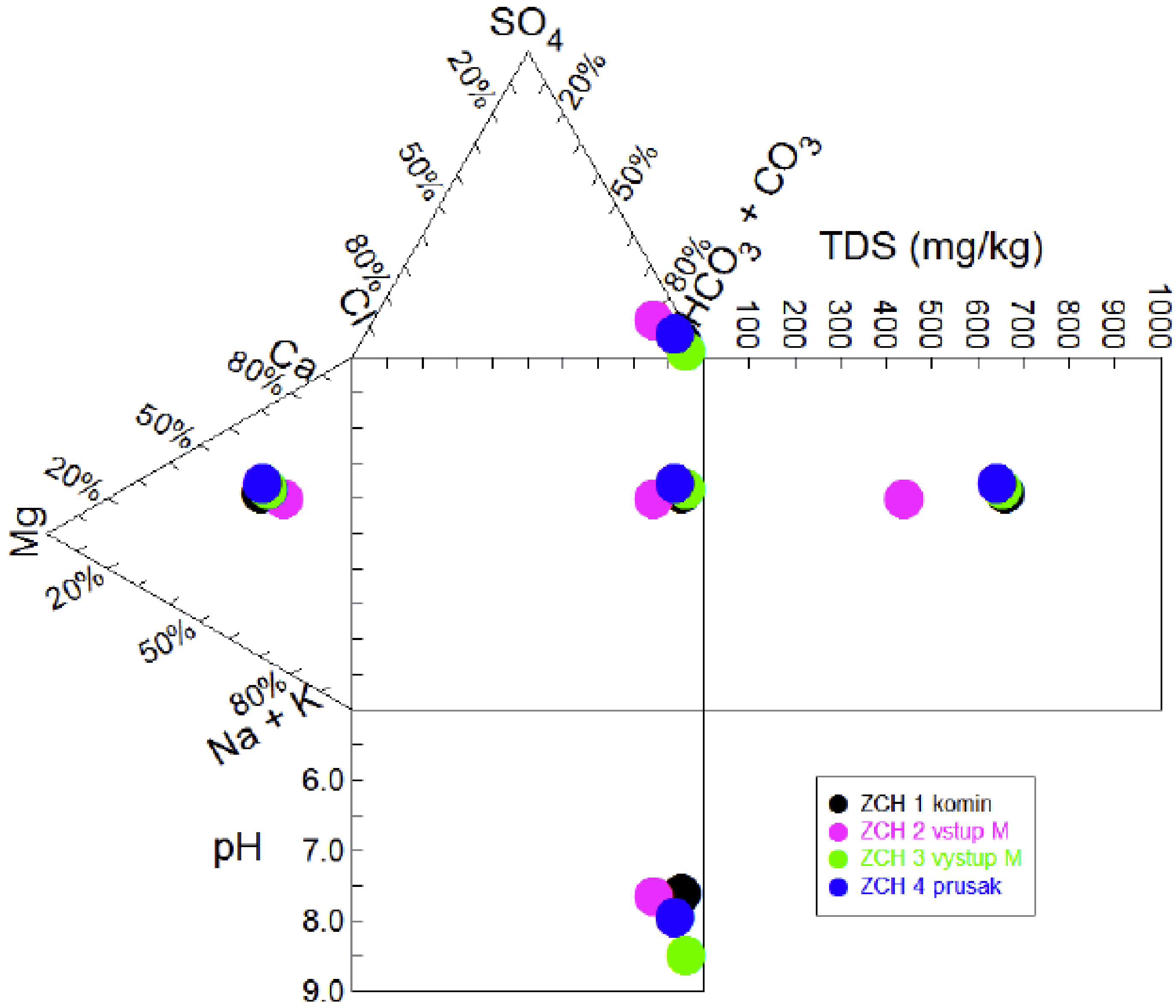
Obr. 11 Piperův diagram s hodnotami charakterizujícími důlní vody na Kaňku. Jednotlivé body charakterizují vývoj hodnot v čase od nejstarších (nejsvětlejší) po nejnovější analýzy (nejtmavší).

Durov diagram



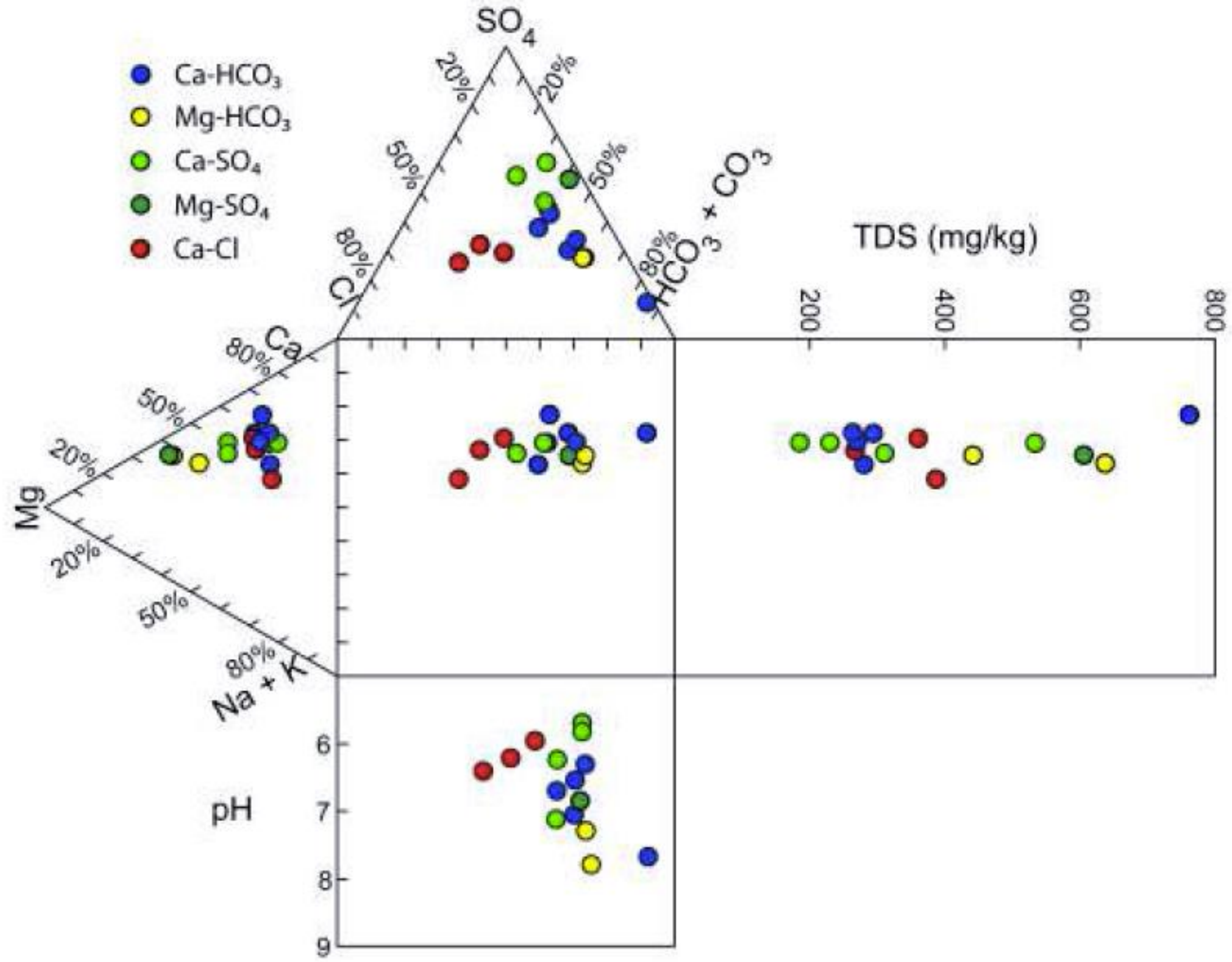
- Application similar to a Piper diagram
- Especially suitable for large amounts of data
- **The percentages of total meq/l** of cations and anions plotted separately
  - Projection into the center square
  - Projection into pH and TDS rectangles
- Semi-quantitative diagram

Láznička 2016



Obr.5 Durovův diagram pro body ZCh 1 – ZCh 4.

Ušelová 2014



Obr. 45 Durovův diagram s rozdělením vod vzorkovaných přítoků do 5 hydrogeochemických typů.

Říčka 2010

Schoeller diagram

Clark (2015)

- Quantitative comparison of the hydrochemical nature of waters
- A smaller number of samples

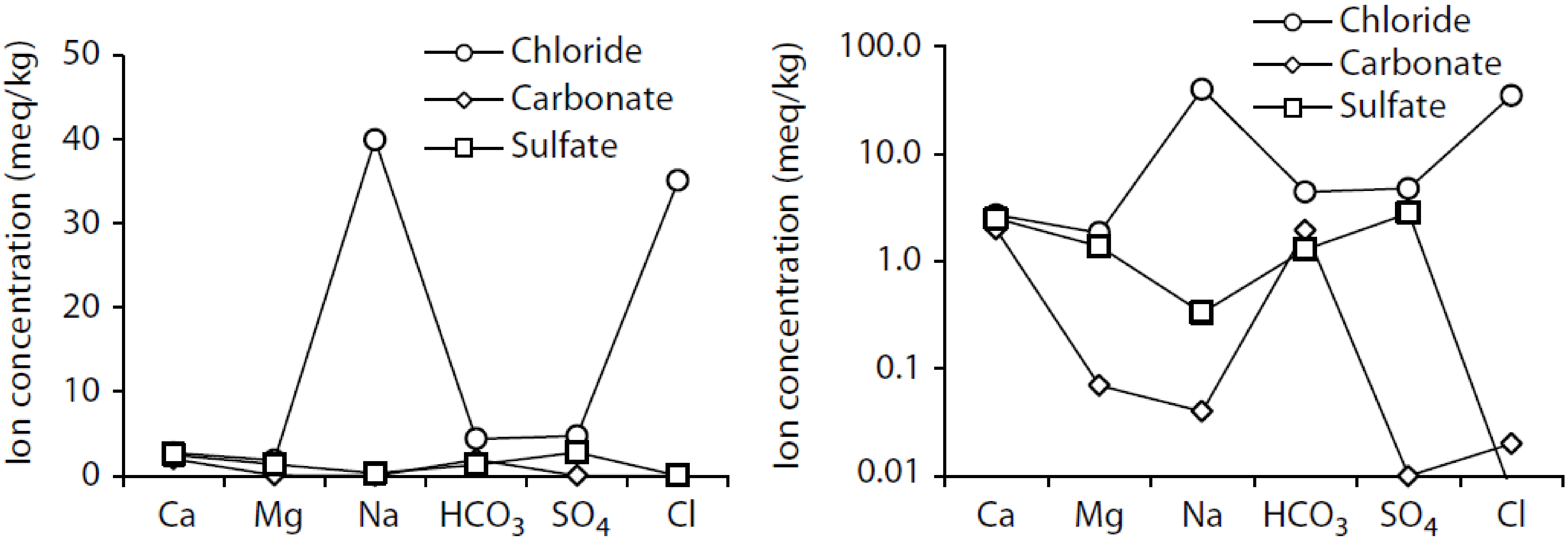


FIGURE 7.22 Normal and semilogarithmic Schoeller diagrams for spring waters in Table 7.2.

Piper diagram construction

Pleiades of paid software

- GWB

Free tools (Diagrammes, GW_Plot) – older, not recommended

On paper

In Excel - extremely impractical, but doable

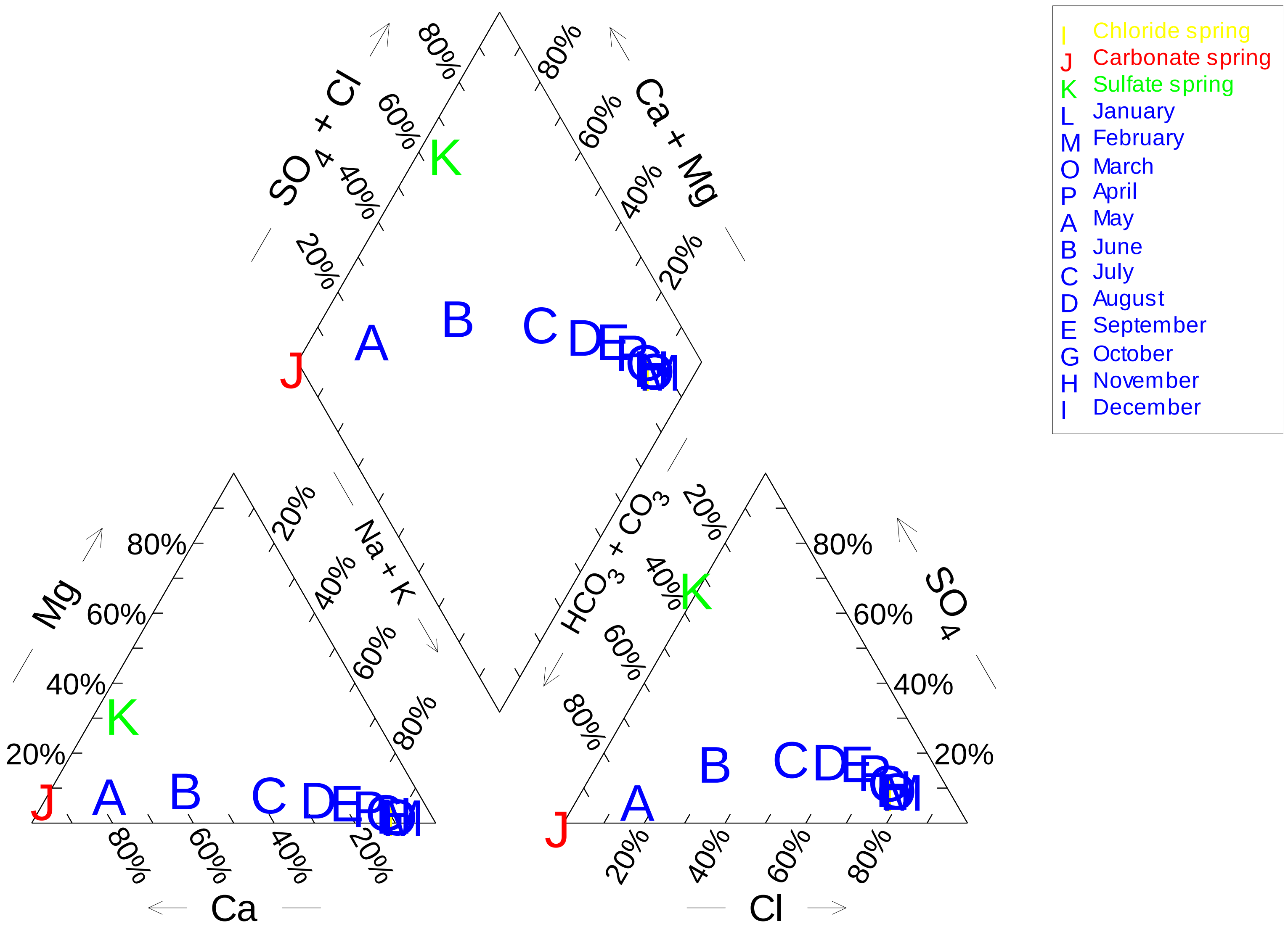
Macros for Python, R and other solutions

Construction of diagrams in GWB

- Data in GSS
- Plot – Piper diagram, Stiff etc.

Data from Clark 2015 (Table 7.2) – file Data_diagram.gss

Sample	Discharge (m3/s)	TDS	Ca2+	Mg2+	Na+K	HCO3-	SO42-	Cl-
			meq/L					
Chloride spring		2869	2.7	1.84	45.6	4.41	4.76	35.1
Carbonate spring		170	2.3	0.21	0.04	1.95	0.01	0.02
Sulfate spring		287	2.5	1.37	0.33	1.28	2.8	0.007
River water								
January	1.8	2607	2.7	1.8	41.1	4.1	4.5	31.6
February	1.6	2791	2.7	1.8	44.2	4.3	4.7	34
March	2	2341	2.6	1.6	36.5	3.9	4.1	28.1
April	4	1308	2.6	1.4	18.4	2.6	3.3	14
May	151.7	203	2.3	0.3	0.5	1.9	0.2	0.4
June	52.5	274	2.4	0.5	1.5	1.9	0.7	1.1
July	19.9	421	2.4	0.7	3.8	1.9	1.2	2.8
August	10.6	622	2.4	0.9	7	2.1	1.8	5.3
September	6.4	903	2.5	1.2	11.6	2.2	2.6	8.8
October	2.9	1689	2.6	1.5	25.2	3.1	3.5	19.3
November	2.1	2218	2.6	1.7	34.3	3.7	4.1	26.3
December	1.9	2476	2.7	1.8	41.1	4.1	4.5	31.6

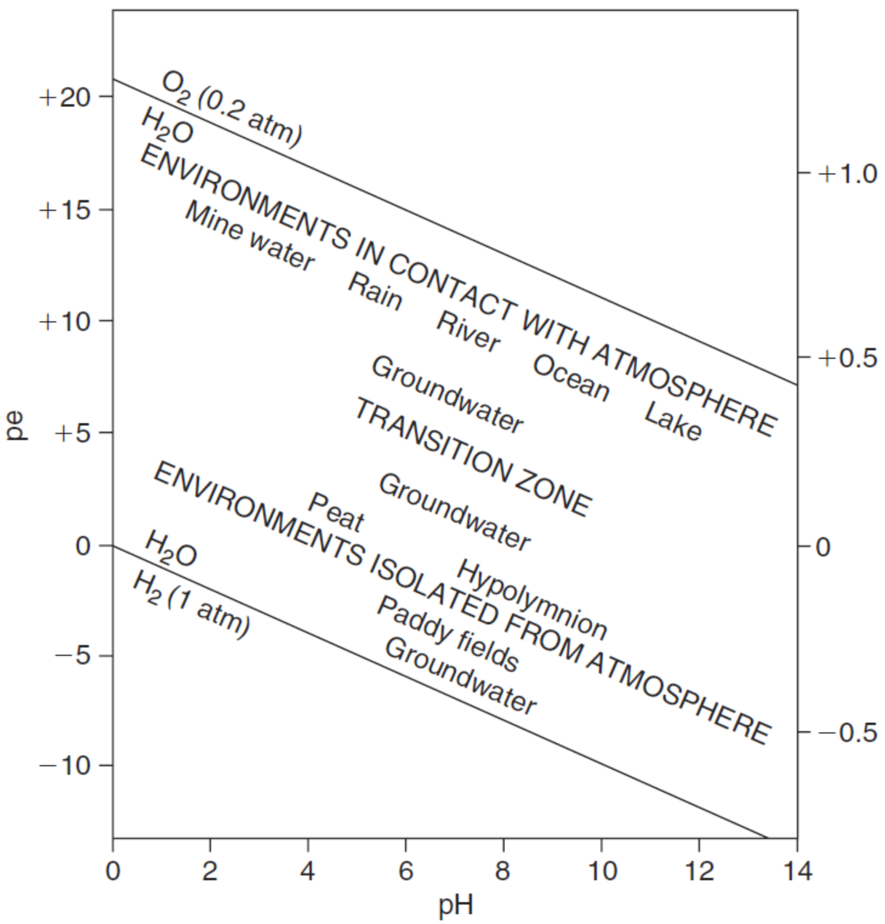


SO4 + Cl
Ca + Mg
Na + K
HCO3 + CO3
Mg
Ca
Cl
SO4
20%
40%
60%
80%
I Chloride spring
J Carbonate spring
K Sulfate spring
L January
M February
O March
P April
A May
B June
C July
D August
E September
G October
H November
I December

Eh -pH diagrams

- Visualization of acid-base and redox conditions in the environment
- Assessment of speciation
  - Mobility, toxicity, environmental connections, geochemical evolution
- Data plot

Natural conditions



Appelo & Postma (2005)

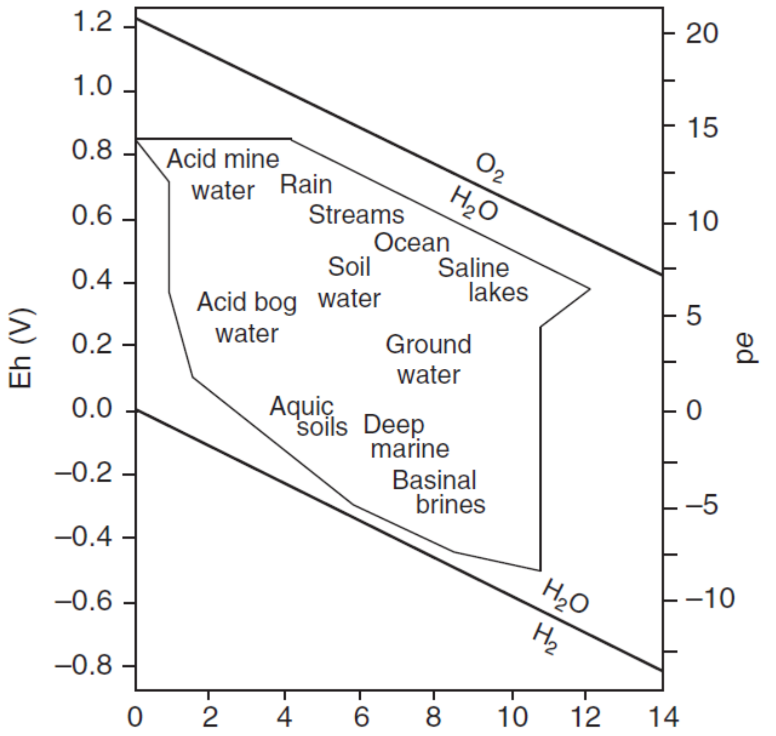
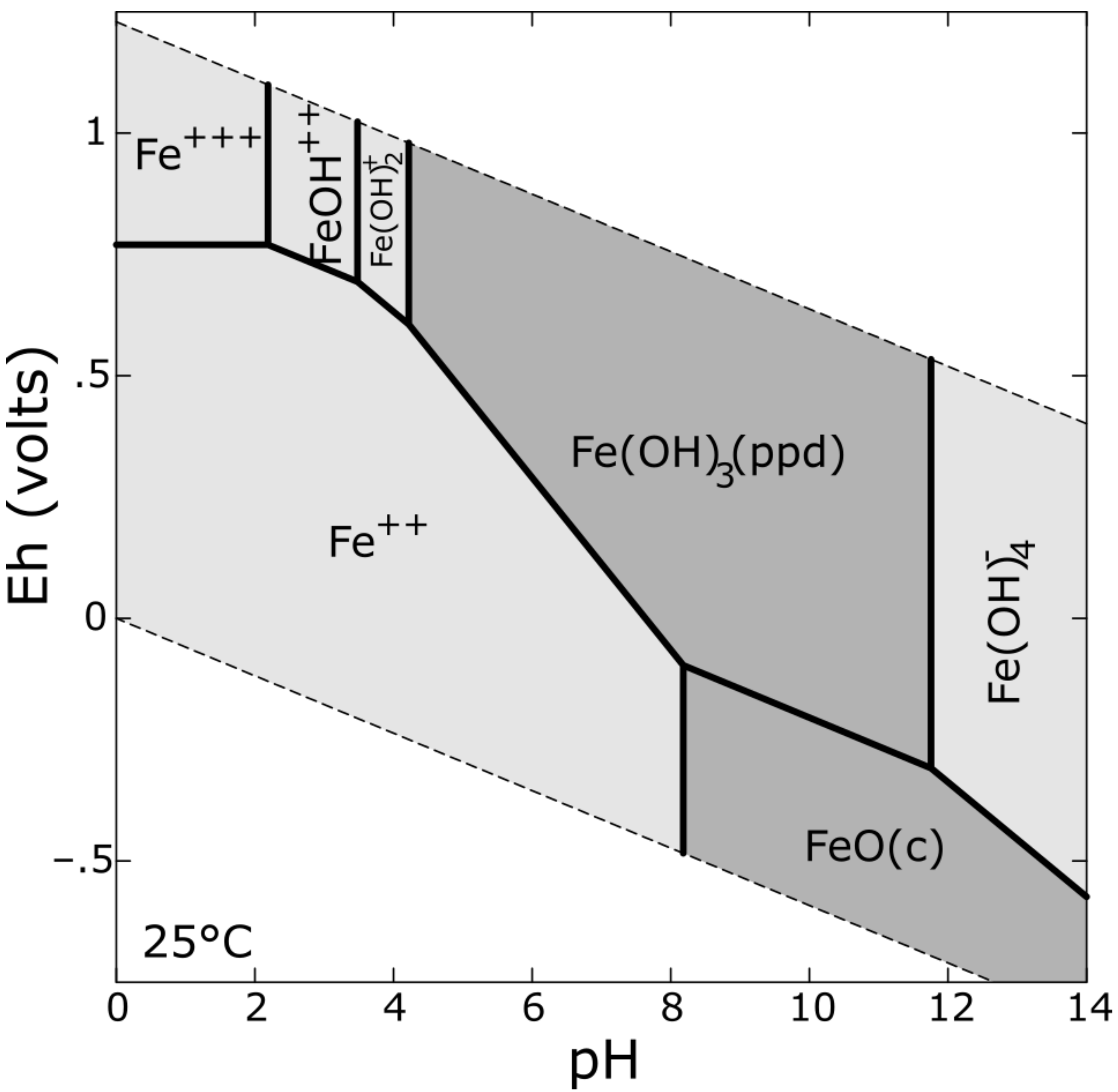
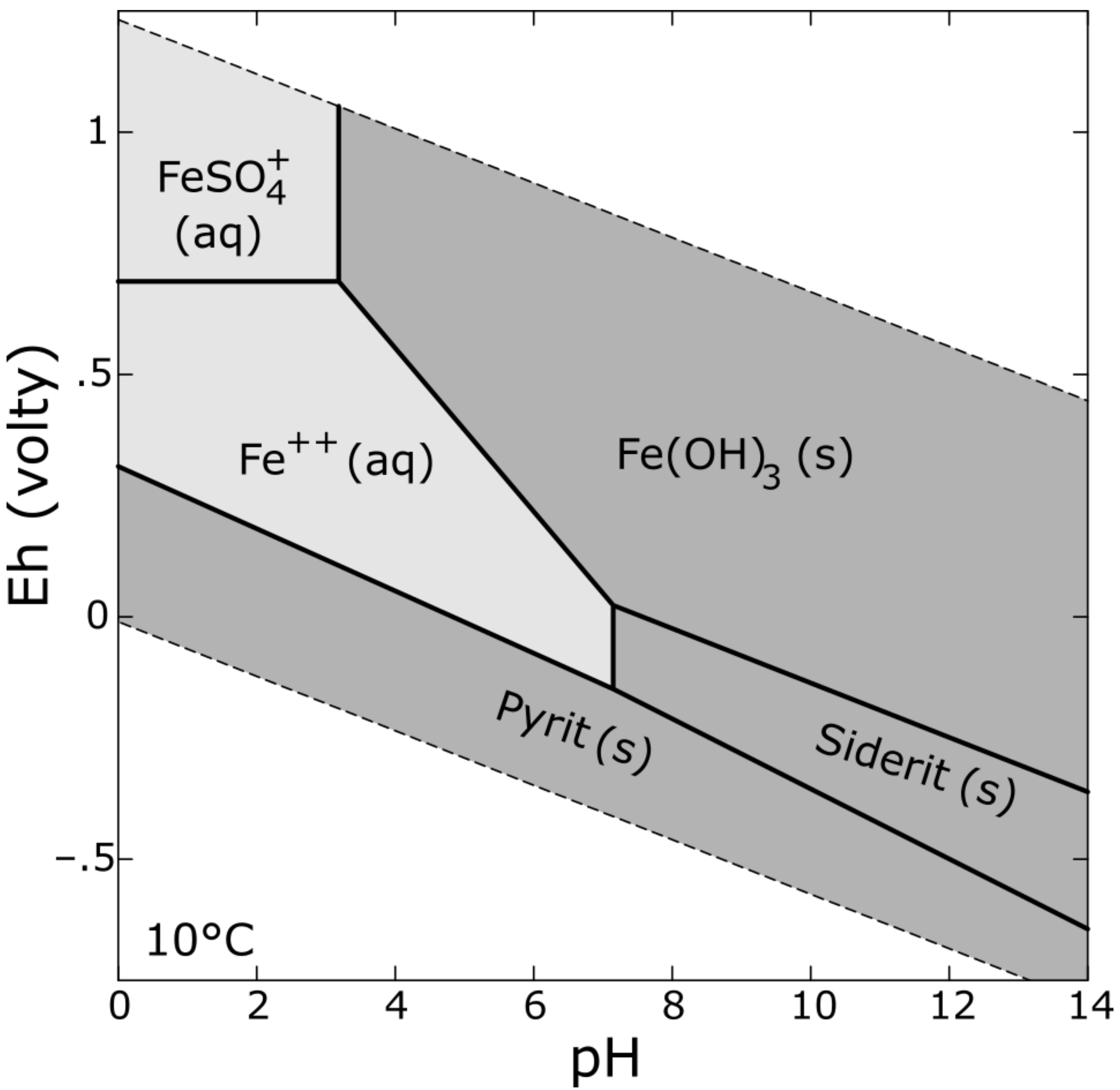


Fig. 4.12 Approximate locations of selected natural systems as a function of reduction–oxidation potential and pH. Note that redox units are given in terms of Eh (left) and p*e*. The thin line bounding the natural environments indicates the limits of nearly all natural waters (after Bass Becking et al. 1960).

Adapted from Ryan (2014)



Fe+++
FeOH++
Fe(OH)2+
Fe(OH)3(ppd)
Fe++
Fe(OH)4-
FeO(c)
25°C
Eh (volts)
1
.5
0
-.5
0
2
4
6
8
10
12
14
pH


FeSO$_4^+$
(aq)
Fe^{++} (aq)
Fe(OH)$_3$ (s)
Pyrit (s)
Siderit (s)
10°C
Eh (volty)
pH
1
.5
0
-.5
0
2
4
6
8
10
12
14

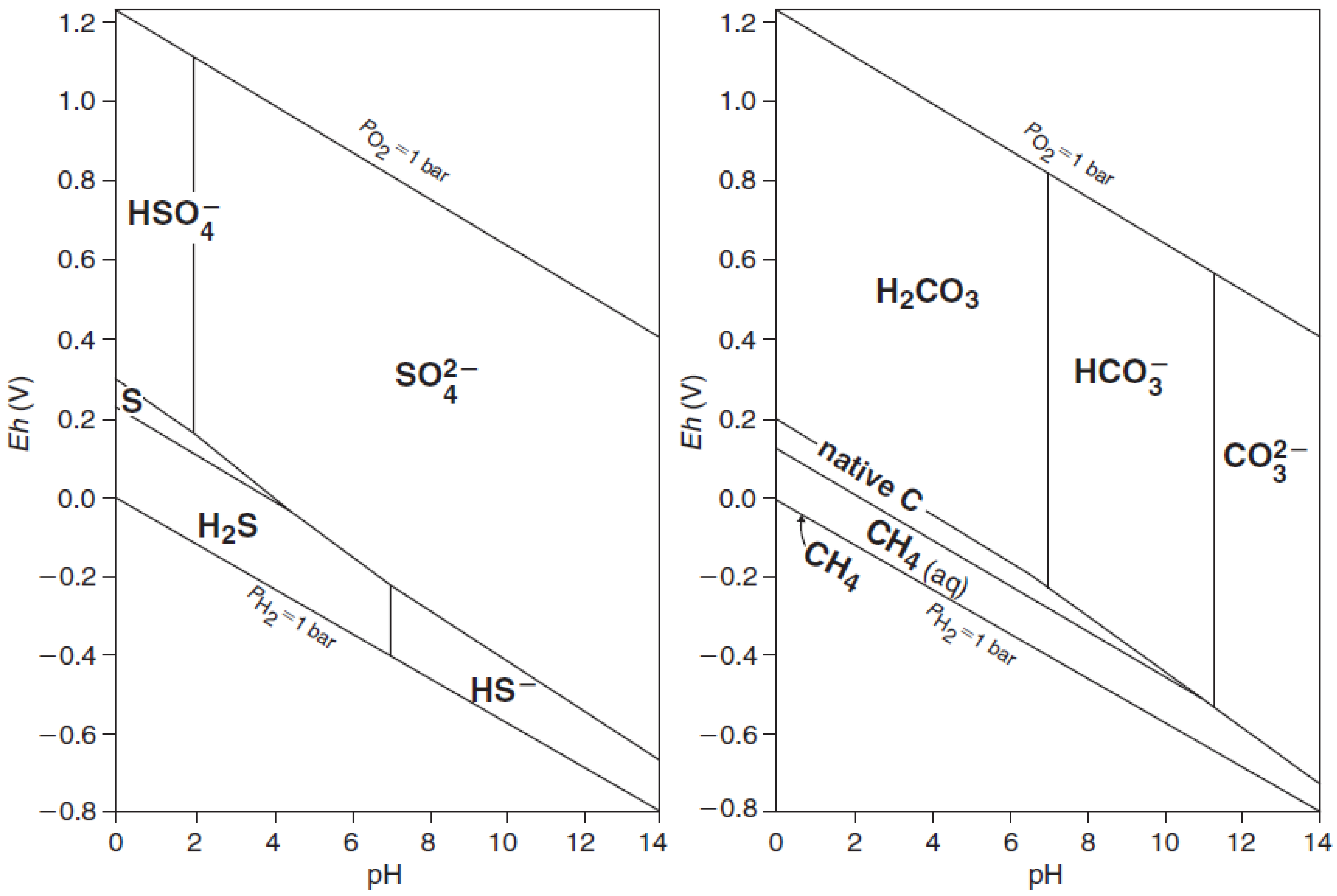


Figure 9.7. Redox diagrams for sulfur and carbon at 25°C. Total activity of dissolved species is 10^{-3}. Native C indicates dissolved CH_2O. S indicates elemental sulfur (Brookins, 1988).

Appelo & Postma (2005)

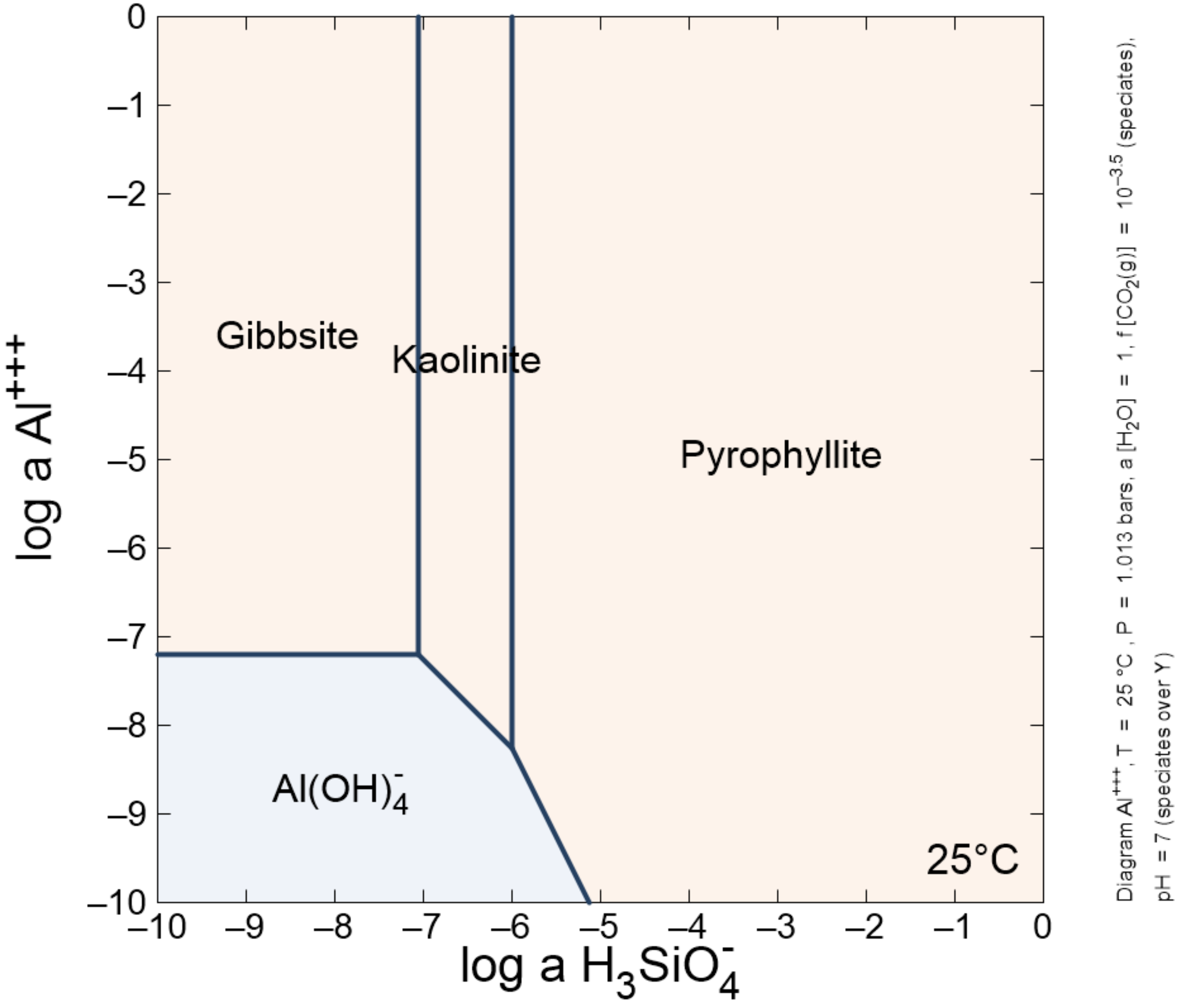
Speciation of Al

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

Speciation of Fe

- Construct an Eh-pH diagram for iron
- Fe^{2+} activity = 10^{-5}
- The presence of sulfur (10^{-3}) and carbonates (10^{-3})

Speciation diagrams



Visualization of the dependence of speciation on the composition of the system

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Tento učební materiál vznikl v rámci projektu Rozvoj doktorského studia chemie

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References

- Presented diagrams are created for this material or used from theses available online at: https://is.muni.cz/thesis/
- Other sources:

- APPELO, CAJ and Dieke POSTMA. *Geochemistry , groundwater and pollution :.* _ 2nd ed . Leiden: AA Balkema publishers , c2005. ISBN 0-415-36421-3.
- CLARK, I. (2015): Groundwater Geochemistry and Isotopes.BocaRaton , Florida: CRC Press.
- Ryan, P. (2014). Environmental and low temperature geochemistry. John Wiley and Sons. 402p. ISBN 978-1-4051-8612-4 (pbk .)