Geochemical and Reactive Transport modelling

1. Introduction

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Groundwater geochemistry and reactive transport explore the processes controlling <u>groundwater quality</u>

- ✓ Quality of groundwater depends on the interaction between water, soil, nature and human activities

- ✓ Our **first concern** must be to insure that **water is drinkable**

EU provides directives for drinkable water parameters

Parameter	Max. value [mg/l]	Sources of contamination
As	0.01	Herbicide used on land and water
Benzene	0.001	Plastic production, dry cleaning, solvents and paints
Cd	0.005	Mines and industrial effluents
Cr	0.05	Industrial effluents
F^-	1.5	Steel and glass fiber industries
Pb	0.01	Industrial effluents
Hg	0.001	Hg minerals, combustion of coal and petroleum
NO_3^-	50	Organic fertilizers
NO_2^-	0.5	Organic fertilizers
Al	0.2	Fertilizers in tea plantation, soundproofing of tunnels
NH_4^+	0.5	Landfill
Na^+	200	NaCl brines
Cl^-	250	NaCl brines
pH	6.5 – 9.5	Acid rain, mines and industrial effluents
Fe	0.2	Mine drainage
Mn	0.05	Minerals of Mn
SO_4^{2-}	250	Oxidation of sulphides, brine lakes

[Council Directive 98/83/E; Appelo and Postma, 2005; Faure 1998]

Hydrogeochemical calculations are important to understand environmental processes

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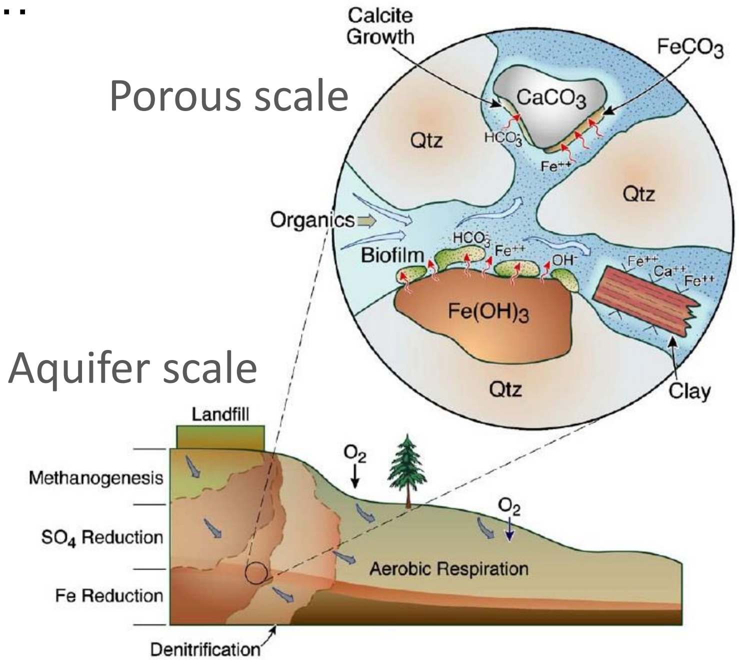
Danakil depression, 120 m b.m.s.l. in NE Ethiopia

- Water-rock interactions
- Ground/surface water contamination
- Mixing problems

…

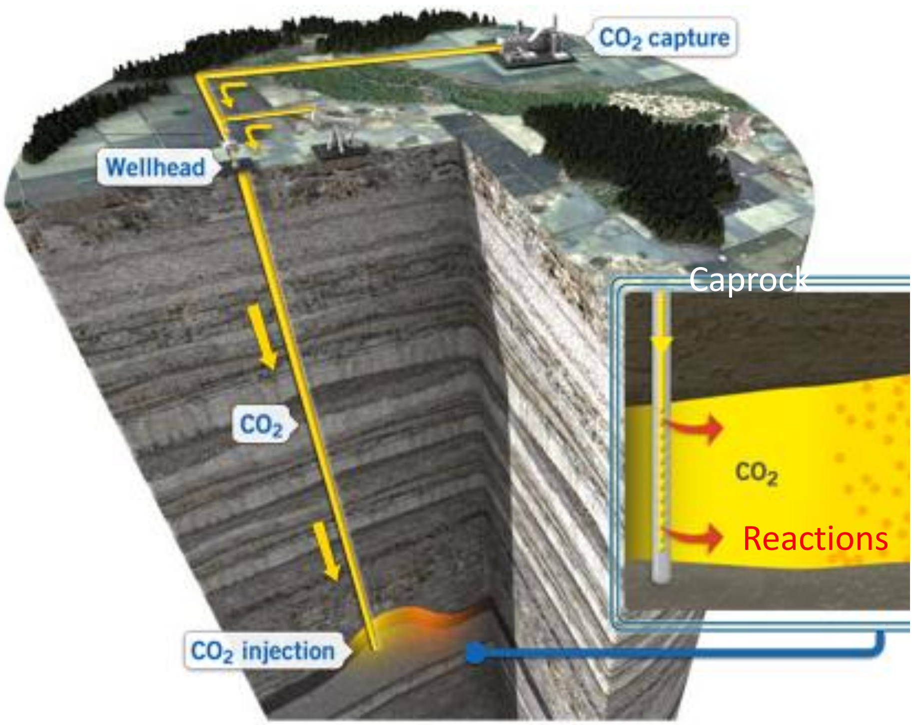


Porous scale

Aquifer scale

[Steefel et al., 2005]

Hydrogeochemical calculations are important to understand geo-energy related applications

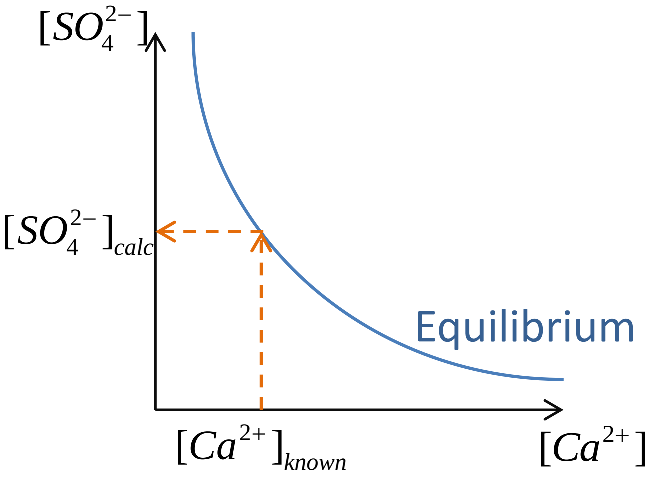


[http://www.globalccsinstitute.com]

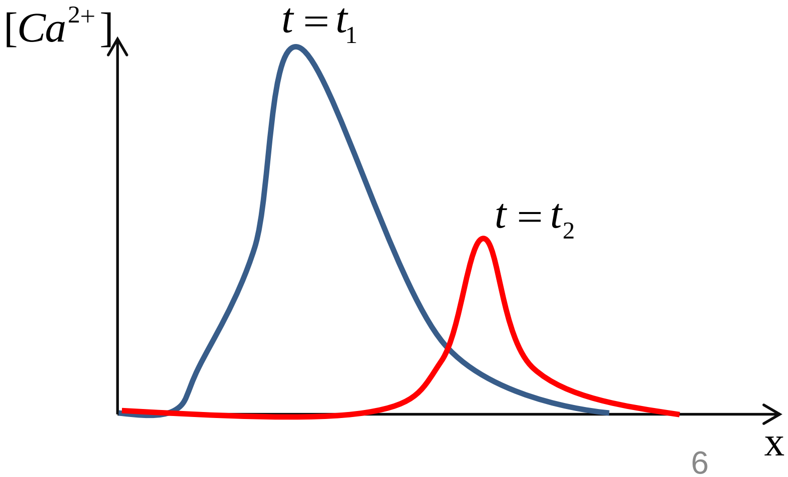
- Petroleum engineering
- CO$_2$ sequestration
- Conventional/unconventional gas extraction
- …

Many types of geochemical calculations are possible, but today we focus on

- Speciation



- Reactive transport



Models are important to confirm (or discard) our interpretation of reality and to make predictions

- ✓ Highly **non-linear** and **coupled** processes
  - ✓ Calculations can be complex (numerical methods necessary, but codes are available!)
- ✓ The **results depend on** many factors:
  - ✓ **Conceptual model** (Equations? Initial conditions? Boundary conditions?)
  - ✓ Parameters **heterogeneity**

Geochemical and Reactive Transport modelling

2. Equilibrium of solutions: Mass Action Laws (MALs)

Conservative transport processes: review

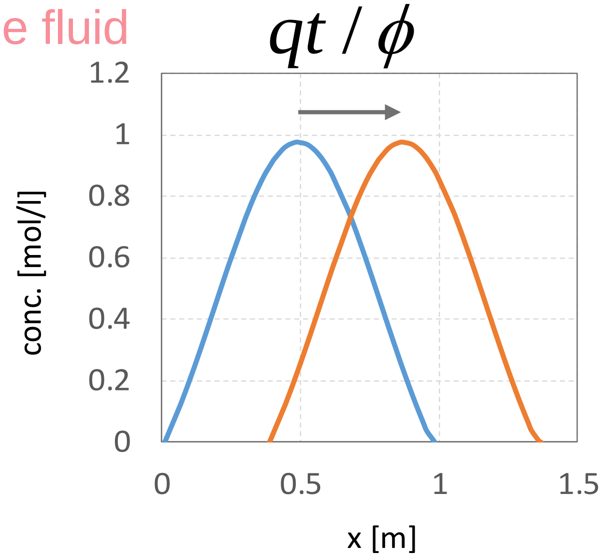
Solute mass balance equation for one species in porous media

$$\frac{\partial \phi c}{\partial t} = -\nabla \cdot \mathbf{J}_{Ad} - \nabla \cdot \mathbf{J}_{D} \qquad [\mathrm{M\ L^{-3}\ T^{-1}}]$$

- ✓ c : solute concentration $[\mathrm{M\ L^{-3}}]$
- ✓ ϕ : porosity [-]
- ✓ $\mathbf{J}_{Ad}$: advective flux $[\mathrm{M\ L^{-2}\ T^{-1}}]$
  due to displacement (dragging) of the fluid

$$\mathbf{J}_{Ad} = \mathbf{q}c$$

↘ flow (e.g., Darcy) $[\mathrm{L^3\ L^{-2}\ T^{-1}}]$



Conservative transport processes: review

Solute mass balance equation for one species in porous media

$$\frac{\partial \phi c}{\partial t} = -\nabla \cdot \mathbf{J}_{Ad} - \nabla \cdot \mathbf{J}_D \qquad [\mathrm{M\ L^{-3}\ T^{-1}}]$$

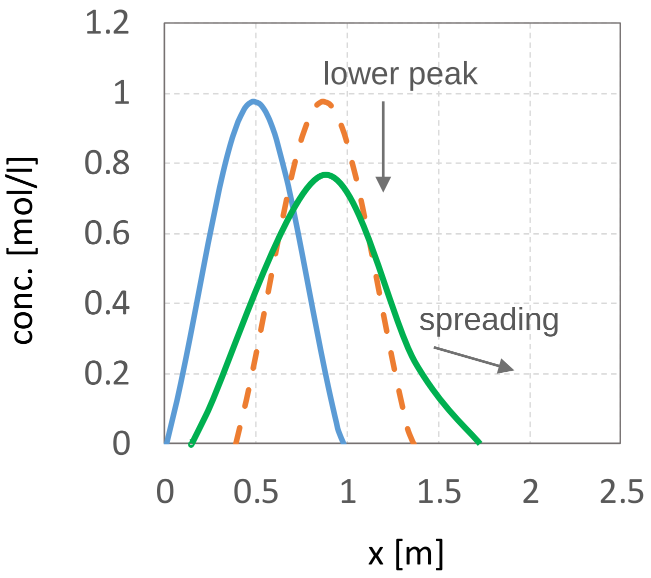
- ✓ $\mathbf{J}_D$: diffusive + dispersive flux [M L^{-2} T^{-1}]

  due to - concentration differences (diffusion)

  - heterogeneity of velocity field (dispersion)

$$\mathbf{J}_D = \mathbf{J}_{Dif} + \mathbf{J}_{Disp} = -\mathbf{D}\nabla c$$

$$\nabla c = grad(c) = \begin{pmatrix} \partial c/\partial x \\ \partial c/\partial y \\ \partial c/\partial z \end{pmatrix}$$



Conservative transport processes: review

Solute mass balance equation for one species in porous media

$$\frac{\partial \phi c}{\partial t} = -\nabla \cdot \mathbf{J}_{Ad} - \nabla \cdot \mathbf{J}_{D}$$

With definition of $\mathbf{J}_{Ad}$ and $\mathbf{J}_{D}$

$$\mathbf{J}_{Ad} = \mathbf{q}c$$

$$\mathbf{J}_{D} = \mathbf{J}_{Dif} + \mathbf{J}_{Disp} = -\mathbf{D}\nabla c$$

The **conservative transport equation** reads

$$\boxed{\frac{\partial \phi c}{\partial t} = -\nabla \cdot \left(\mathbf{q}c\right) + \nabla \cdot \left(\mathbf{D}\nabla c\right)}$$

Reactive transport equation

Solute mass balance equation for one species in porous media

$$\frac{\partial \phi c}{\partial t} = -\nabla \cdot (\mathbf{q} c) + \nabla \cdot (\mathbf{D} \nabla c) \boxed{+ r_e + r_k}$$

Production/consumption in unit time due to **chemical reactions**
[M L^{-3} T^{-1}]

- ✓ $r_e \neq r_k$ -> difference between **equilibrium** and **kinetic reactions**
- ✓ $r_k = f(c)$ -> explicit expression of concentrations

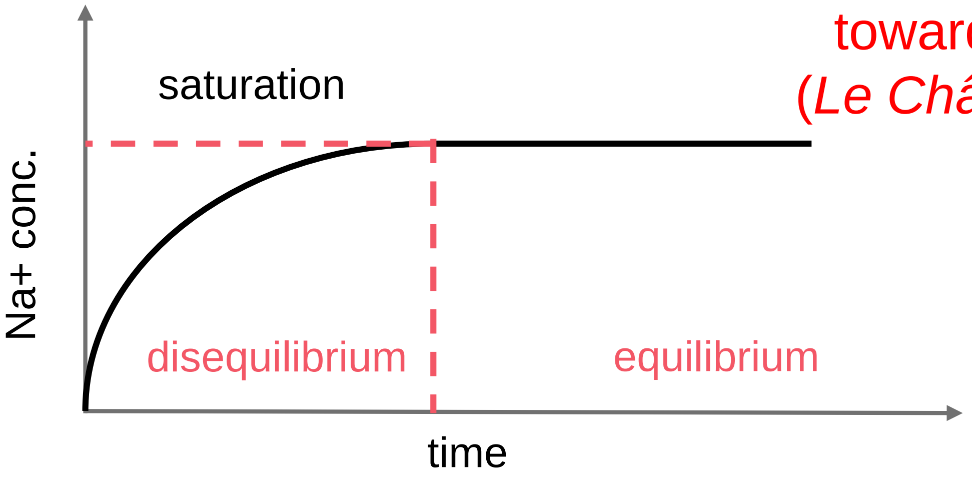
- ✓ **Chemical reactions in nature** commonly take place **in** presence of **water**
- ✓ Chemical reactions are represented by means of algebraic equations **-> balance of masses and charges of reactants and products**

Chemical reactions and equilibria

Sodium chloride NaCl(s) dissolution in water at room temperature (25ºC) and atmospheric pressure (1 atm)

$$\mathrm{NaCl}_{(s)} = \mathrm{Na}^{+} + \mathrm{Cl}^{-}$$

Chemical reactions have a natural tendency to move towards equilibrium (*Le Châtelier principle*)



Mass action laws (MALs)

- When a reaction reaches **equilibrium** the **amounts of reactants and products per unit weight (or volume) of water** become **constant**
- At equilibrium the rate of forward reactions is equal to the rate of backward reaction

$$\mathrm{A + B = C + D}$$

Rates: $r_\mathrm{f} = k_\mathrm{f}\,(\mathrm{A})(\mathrm{B})$

$r_\mathrm{b} = k_\mathrm{b}\,(\mathrm{C})(\mathrm{D})$

$(\cdot) = \text{conc.}$

At equilibrium: $k_\mathrm{f}\,(\mathrm{A})(\mathrm{B}) = k_\mathrm{b}\,(\mathrm{C})(\mathrm{D})$

$$\frac{k_\mathrm{f}}{k_\mathrm{b}} = \frac{(\mathrm{C})(\mathrm{D})}{(\mathrm{A})(\mathrm{B})} = K_{eq}$$

Equilibrium constant

In general $a\mathrm{A} + b\mathrm{B} = c\mathrm{C} + d\mathrm{D}$

$$\boxed{\frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b} = K_{eq}}$$

Mass action law

$[\cdot] = \text{activities}$

Mass action laws (MALs)

- ✓ Concept of **activity very important for non ideal solutions**

- ✓ Activity: $a = \gamma c$

  Activity coefficient

  For ideal solutions (infinite dilution): $\gamma = 1$
  For non ideal solutions: $0 < \gamma < 1$
  For H_2O and pure solids: $\gamma = 1$

- ✓ For a reaction $a\mathrm{A} + b\mathrm{B} = c\mathrm{C} + d\mathrm{D}$

  two equivalent ways of writing MALs

$$\frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b} = K_{eq} \qquad \frac{a_C^c\ a_D^d}{a_A^a\ a_B^b} = K_{eq}$$

Ion Activity Product (IAP)

At equilibrium:
IAP = K_{eq}

Mass action laws (MALs)

- ✓ For reaction

$$aA + bB = cC + dD$$

- ✓ Mass action law:

$$\frac{a_C^c \; a_D^d}{a_A^a \; a_B^b} = K_{eq}$$

- ✓ MAL in logarithmic form?

Concentration units

- ✓ Concentration units **for different phases**:
  - ✓ **Solutes** (dissolved species):
    - Solute mass / volume of water (g/l, mg/l, µg/l…)
    - Solute moles / volume of water (mol/l, mmol/l)
      (molar weight [g/mol] can be used to convert one to the other)
    - Solute equivalents / volume of water
      (1 eq = ion charge * mol/l:
      $5.02 \cdot 10^{-3}$ Ca^{2+} mol/l = $2 \times 5.02 \cdot 10^{-3} = 1.04 \cdot 10^{-2}$ eq/l Ca^{2+})
    - Molality (mol/kgw) = mol/l only if density = 1kg/l

Concentration units

✓ Concentration units for different phases:

✓ **Solid phase** (minerals and sorbed species):

- Mass of mineral (or sorbed) / Total solid mass
- Mass of mineral (or sorbed) / Total volume
- Mass of mineral (or sorbed) / Liquid volume
- Moles and equivalents can also be used

✓ **Ideal gas phase**:

- Activity of gas = Partial pressure of the gas: $a_i = P_i$

Example: $O_{2(g)} = O_{2(l)}$

$$a_{O_2(l)} = P_{O_2(g)} K_H$$

Henry's constant

Activity coefficients models

- ✓ Several models exist for activity coefficients depending on ionic strength:

$$I = 0.5\sum_{i=1}^{Ns} m_i z_i^2$$

Ns = number of aqueous species
z_i = charge of species i
m_i = molality of species i

1. Debye-Hückel limiting law: for very diluted concentrations

$$\log\gamma_i = -Az_i^2\sqrt{I}$$

A=A(T)
A = 0.5085 @25ºC

2. Debye-Hückel exended (*I* < 0.1)

$$\log\gamma_i = -\frac{Az_i^2\sqrt{I}}{1+B\dot{a}_i\sqrt{I}}$$

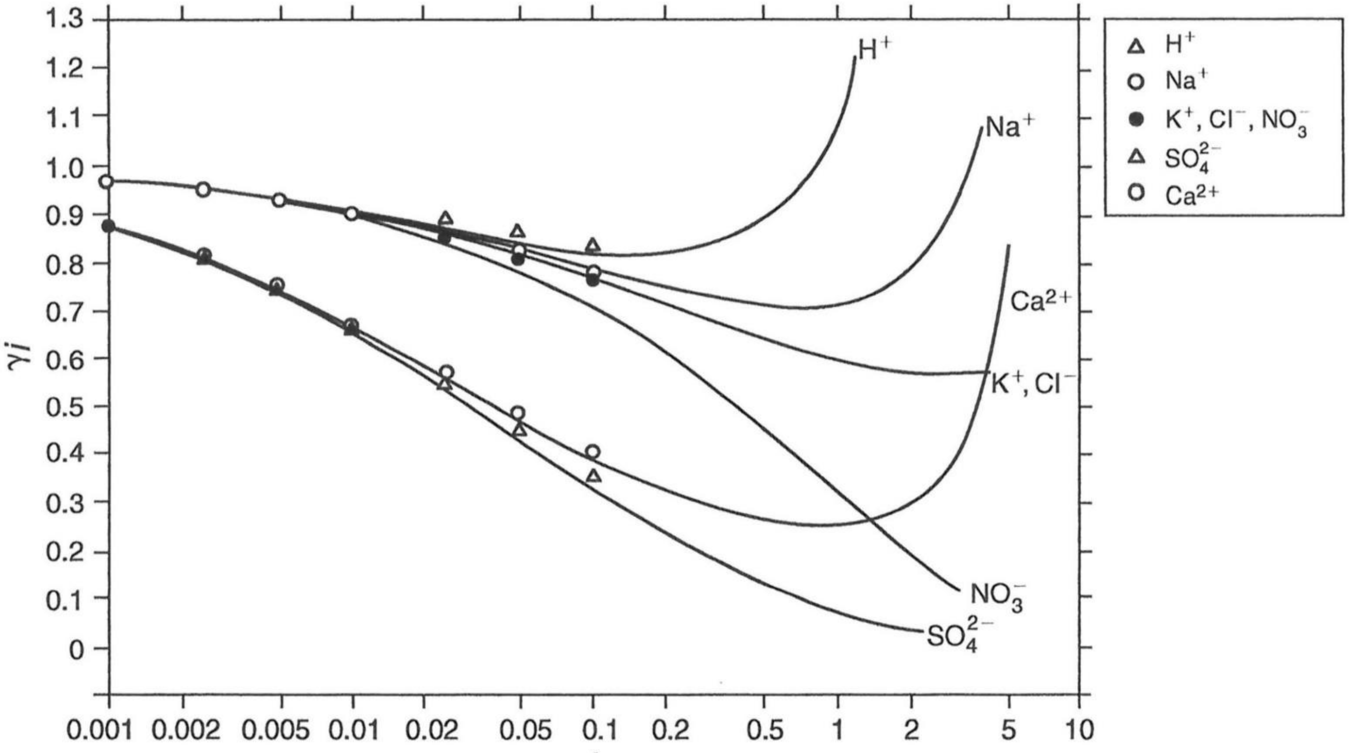
B=B(T)
a_i *= effective diameter of the hydrated ion*
B = 0.3285e+10 @25ºC

3. Trusdell Jones (*I* > 0.1)

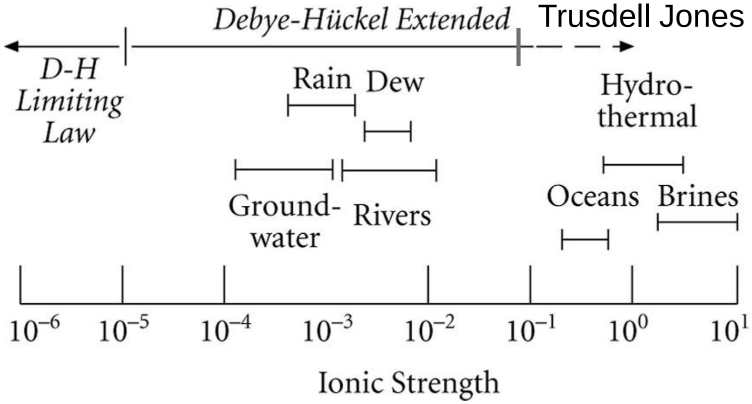
$$\log\gamma_i = -\frac{Az_i^2\sqrt{I}}{1+Ba_i\sqrt{I}} + b_i I$$

a_i *,* b_i *= ion specific fit parameters*

Activity coefficients



[Symbols: Debye-Hückel extended equation, lines: Trusdell Jones equation. Appelo and Postma, 2005]



Geochemistry, First Edition. William M. White.

For pure solid phases (e.g. minerals) a=1

- ✓ Example: anhydrite

$$\mathrm{CaSO}_{4(s)} = \mathrm{Ca}^{2+} + \mathrm{SO}_4^{2-} \qquad \log K_{eq} = -4.3064$$

$$\frac{a_{Ca^{2+}}\ a_{SO_4^{2-}}}{a_{CaSO_{4(s)}}} = a_{Ca^{2+}}\ a_{SO_4^{2-}} = K_{eq} = 10^{-4.3064}$$

Geochemical and Reactive Transport modelling

3. Reactions and concentrations calculation (speciation)

Important chemical reactions occur at the surface of the Earth

where solid phases are exposed to water, carbon dioxide, oxygen

Salar de Aracama, Chile, 2300 m.a.s.l.

Types of reactions

Reactions can be defined as:

- ✓ **Homogeneous**: all the species in the same phase
  - Acid-bases reaction (acid: proton donor, base: acceptor)
  - Ion complexation (association of ions carrying opposite charges)

- ✓ **Heterogeneous**: species in different phases
  - Mineral dissolution/precipitation
  - Sorption (absorption, adsorption, cation exchange)
  - Biogeochemical reactions
  - Gas dissolution

- ✓ **Redox reactions**: very important because they determine
  - the fate of contaminants in natural environments
  - natural concentrations of O_2, Fe^{2+}, SO_4^{2-}, H_2S, CH_4, NO_3^- in groundwater

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Homogeneous reactions

✓ **Acid-base reactions**:

- They involve an **exchange of protons**: **H^+**
- Important because they **affect the acidity of a solution**, i.e. solubility of minerals (i.e., how much minerals dissolve/precipitate)
- Useful parameter: **$pH = -\log[H^+]$**
  pH can be measured by electrical methods
- Example: dissolution of acetic acid (weak acid) in water

$$CH_3COOH = CH_3COO^- + H^+ \qquad \log K_{eq} = -4.755$$

- Neutrality of pure water:

$$H_2O = OH^- + H^+ \qquad \log K_{eq} = -14.0$$

$a_{OH-} = a_{H+} = 10^{-7}$ -> pH = 7

Homogeneous reactions

✓ **Ion complexation**:

- In aqueous solutions ions may become attached one another to form ion complexes

- Major cation complexes: $CaSO_4^0$, CaF^+, $CaOH^+$
- Heavy metal complexes: $CdCl^+$, $HgCl_3^-$, $PbOH^+$

- Mass action laws apply

$$\mathrm{Ca}^{2+} + \mathrm{SO}_4^{2-} = \mathrm{CaSO}_4^0 \qquad \log K_{eq} = 2.5$$

$$\log[\mathrm{CaSO}_4^0] - \log[\mathrm{Ca}^{2+}] - \log[\mathrm{SO}_4^{2-}] = 2.5$$

Heterogeneous reactions

✓ **Mineral dissolution/precipitation**:

- Minerals present in aquifers are often not pure phases but mixtures of different minerals
- However, today we will consider only pure phase minerals (i.e., *a* = 1)

- **Some minerals react fast upon contact with water** (more *soluble* minerals), e.g. $CaSO_4 \cdot 2H_2O$ (gypsum), NaCl (halite), CaF_2 (fluorite), carbonates such $CaCO_3$ (calcite)
- **Some others are slow**, e.g. silicates such as Mg_2SiO_4 (forsterite), Al_2SiO_5 (andalusite)

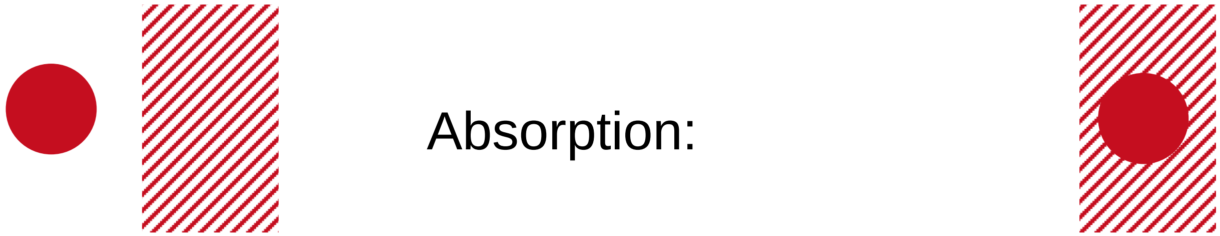
- If they are in **equilibrium** -> **MAL** for equilibrium
- If they are **slow** -> **kinetic expressions** for kinetic rate

- **Saturation index: $SI = \log(IAP/K_{eq})$**
  indicates if a mineral is under or over-saturated

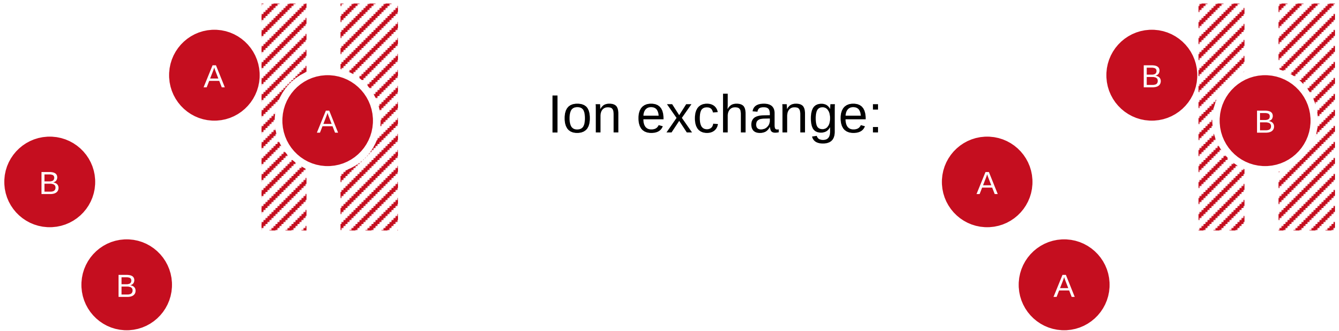
Heterogeneous reactions

- ✓ **Sorption**: clay minerals, organic matter and metal oxy-hydroxides can sorb chemicals
- ✓ **Very important for transport of pollutants in aquifers and soils**

Adsorption:



Absorption:

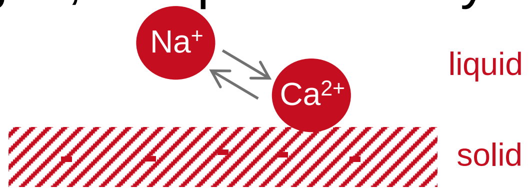


Ion exchange:

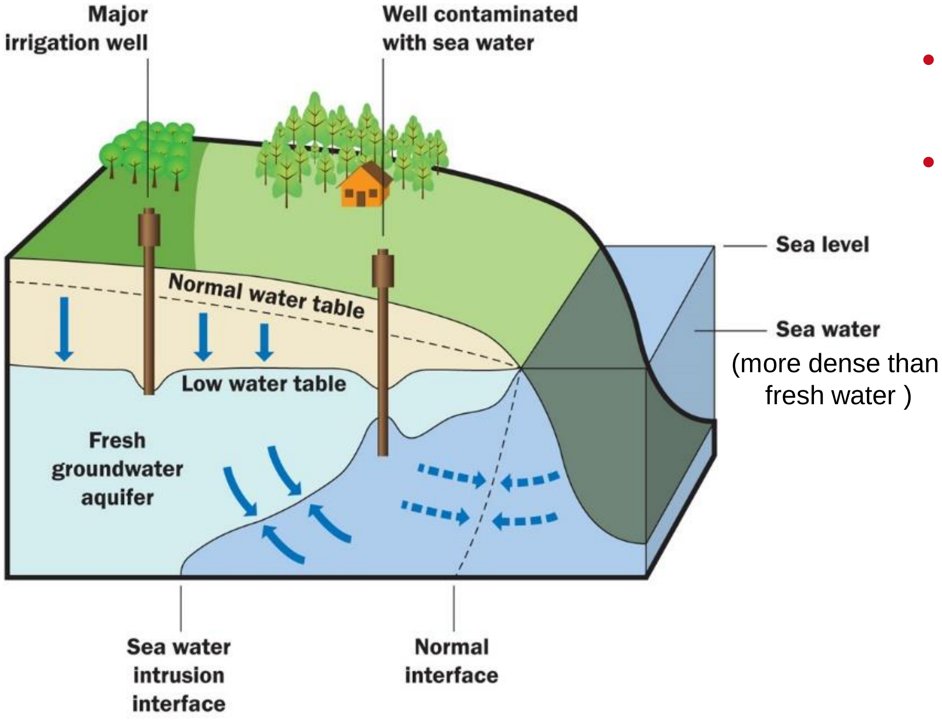
modified after Appelo and Postma, 2005

Heterogeneous reactions

- ✓ **Ion exchange**:
  - Solid is negatively charged, compensated by the positive charge in the liquid



  - Typical process occurring, for example, at the salt/fresh water interface due to seasonal variations of the water table



- In **sea water Na^+** and Cl^- are the **dominant** ions
- The **fresh groundwater** in coastal areas the **dominant** ions are **Ca^{2+}** and HCO_3^- due to calcite dissolution

Salinization: $2Na^+ + (Ca\text{-}X_2) = (Na\text{-}X) + Ca^{2+}$

Freshening: $Ca^{2+} + 2(Na\text{-}X) = (Ca\text{-}X_2) + 2Na^+$

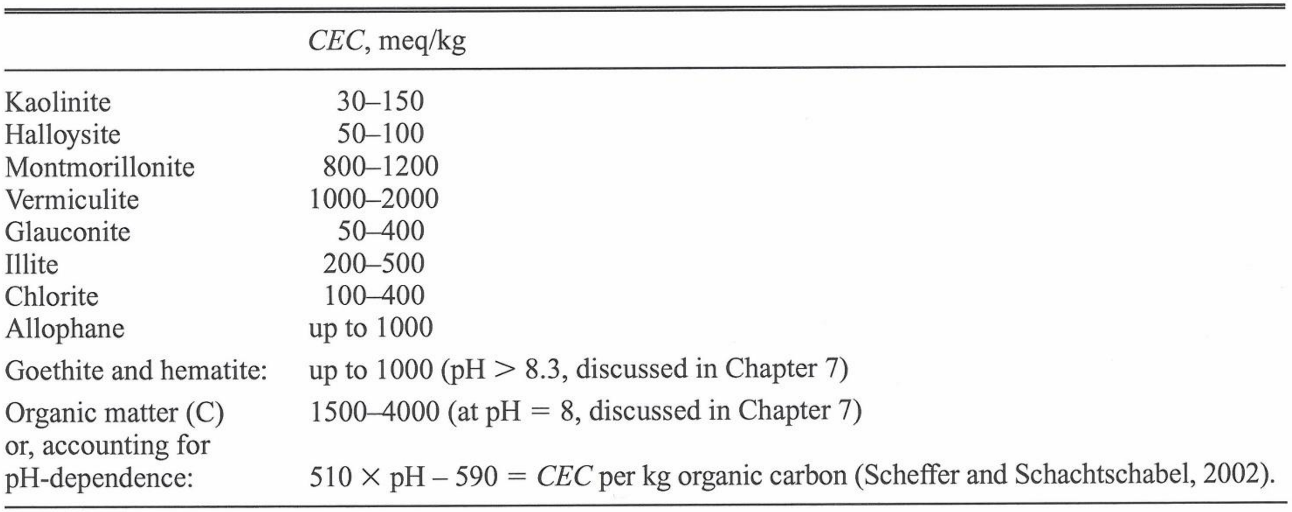
X : soil exchanger

Heterogeneous reactions

✓ **Adsorption**:

- Solid phases with a large specific area will adsorb the most -> **adsorption capacity depends on grain size**
- **Clay** fractions (< 2µm) have **large specific area**

- **CEC** = **cation exchange capacity** (meq/kg), depends on the type of soil



	CEC, meq/kg
Kaolinite	30–150
Halloysite	50–100
Montmorillonite	800–1200
Vermiculite	1000–2000
Glauconite	50–400
Illite	200–500
Chlorite	100–400
Allophane	up to 1000
Goethite and hematite:	up to 1000 (pH > 8.3, discussed in Chapter 7)
Organic matter (C)	1500–4000 (at pH = 8, discussed in Chapter 7)
or, accounting for pH-dependence:	510 × pH – 590 = *CEC* per kg organic carbon (Scheffer and Schachtschabel, 2002).
Sand	10

Appelo and Postma, 2005

Exchange equations

- Mass action laws apply, but activities of exchangeable ions have to be defined:

$$2\mathrm{Na}^{+} + (\mathrm{Ca\text{-}X}_2) = 2(\mathrm{Na\text{-}X}) + \mathrm{Ca}^{2+} \qquad \mathrm{K}_{Na/Ca} = \frac{[\mathrm{Na\text{-}X}]^2[\mathrm{Ca}^{2+}]}{[\mathrm{Na}^{+}]^2[\mathrm{Ca\text{-}X}_2]}$$

$$\left\{ \begin{array}{l} \beta_{Ca} = \dfrac{meq(\mathrm{Ca\text{-}X}_2)\ \text{per kg sediment}}{CEC} = \dfrac{meq_{\mathrm{I\text{-}X}_i}}{\sum\limits_{I,J,K\ldots} meq_{\mathrm{I\text{-}X}_i}} \\[2em] \sum\limits_{m} \beta_m = 1 \end{array} \right.$$

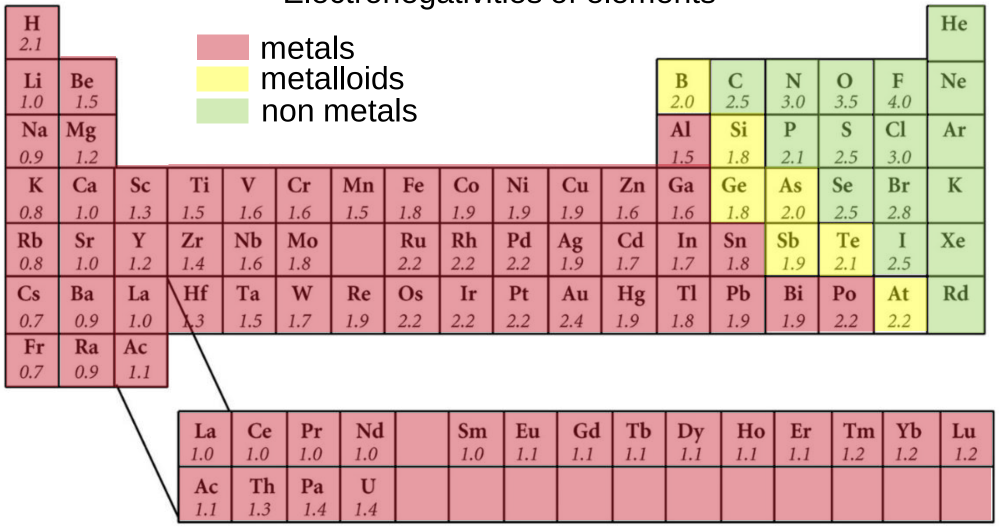
[Gaines-Thomas]

m = number of exchangeable ions

Redox reactions

- ✓ **Redox reactions involve an exchange of electrons (e^-)**
- ✓ Elements in periodic table can be divided in ***electron donors*** (**metals**) and ***electron acceptors*** (**non metals**), depending on their electronegativity

Electronegativities of elements



🟥 metals
🟨 metalloids
🟩 non metals

H 2.1																	He
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.5	Br 2.8	K
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8		Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe
Cs 0.7	Ba 0.9	La 1.0	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.2	At 2.2	Rd
Fr 0.7	Ra 0.9	Ac 1.1															

La 1.0	Ce 1.0	Pr 1.0	Nd 1.0		Sm 1.0	Eu 1.1	Gd 1.1	Tb 1.1	Dy 1.1	Ho 1.1	Er 1.1	Tm 1.2	Yb 1.2	Lu 1.2
Ac 1.1	Th 1.3	Pa 1.4	U 1.4											

Geochemistry, First Edition. William M. White.

- ✓ Orbitals of metals quite empty -> they are more likely to donate electrons
- ✓ **Number of electrons** that an element will **exchange** is its ***valence***

Redox reactions

- ✓ Red = Ox + e^-
  Reductant (Red) = electron donor
  Oxidant (Ox) = electron acceptor

$$\mathrm{Fe}^{2+} = \mathrm{Fe}^{3+} + e^-$$

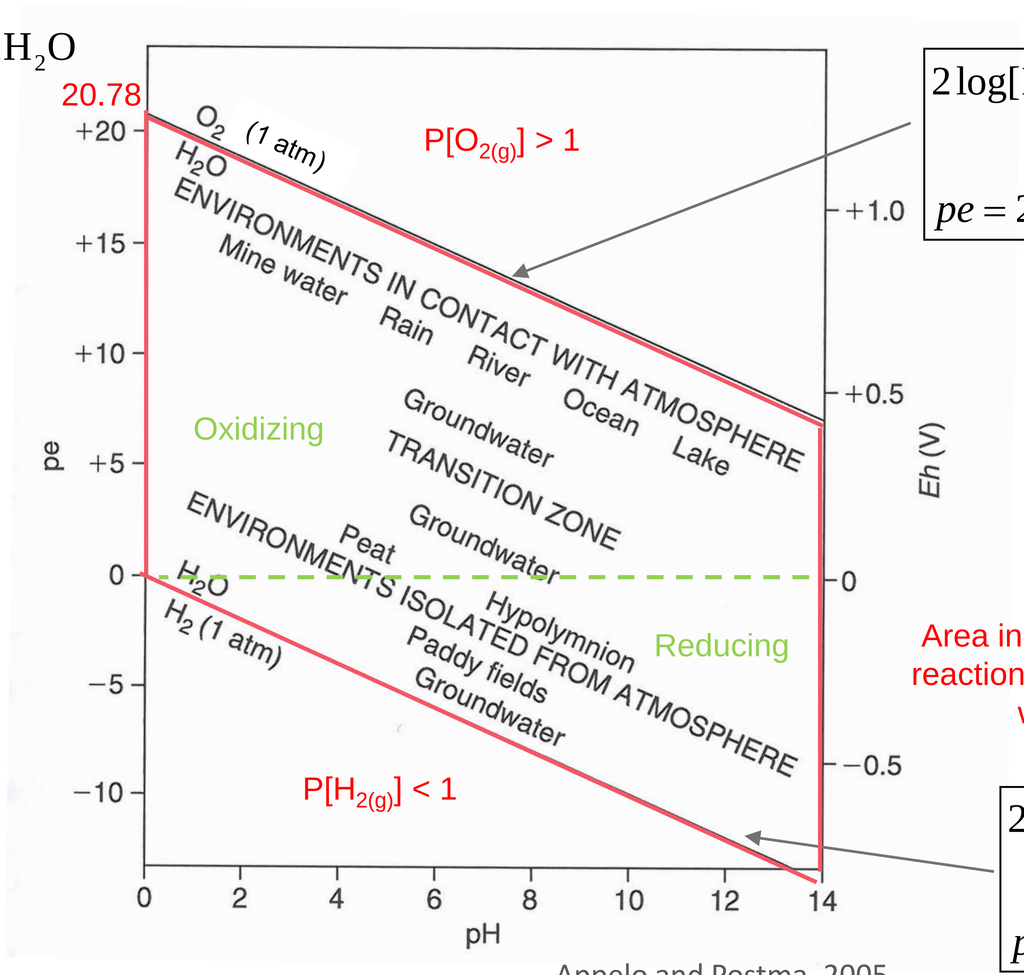
- ✓ **Electrons only exchange between atoms, they do not exist in free state** -> normally they don't appear in balanced redox reactions

- ✓ **pe = $-\log[e^-] = E_h/0.059$ (at 25°C)**
  E_h = electrical potential in Volts

Stability limits of $H_2O_{(l)}$ in natural environments

$$2H_2O(l) = 2H_2(g) + O(g) \qquad \log K_{eq} = -83.1$$

$$O_2(g) + 4H^+ + 4e^- = 2H_2O$$



Appelo and Postma, 2005

$$2\log[H_2O] - \log[O_2(g)] - 4\log[H^+] - 4\log[e^-] = 83.1$$

$$pe = 20.78 - pH$$

Area in which all natural chemical reactions take place in presence of water at 25ºC, 1atm

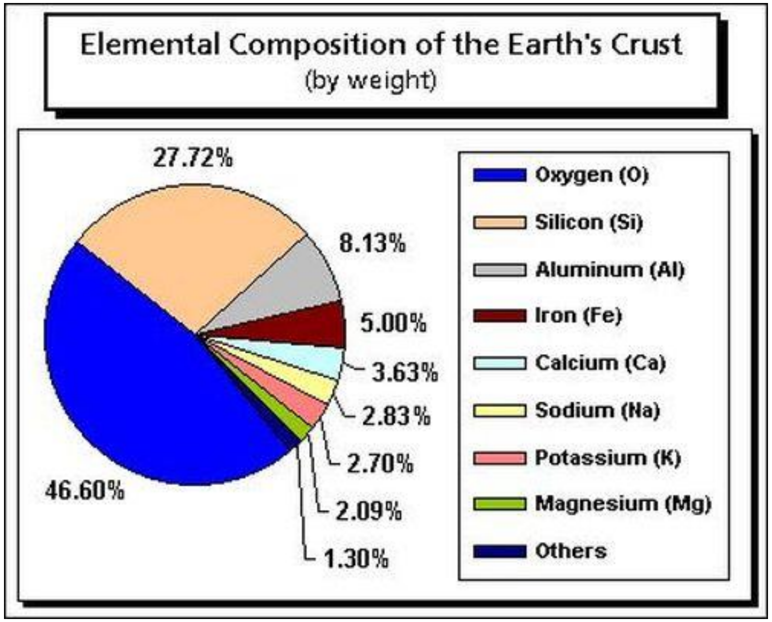
$$H_2(g) = 2H^+ + 2e^-$$

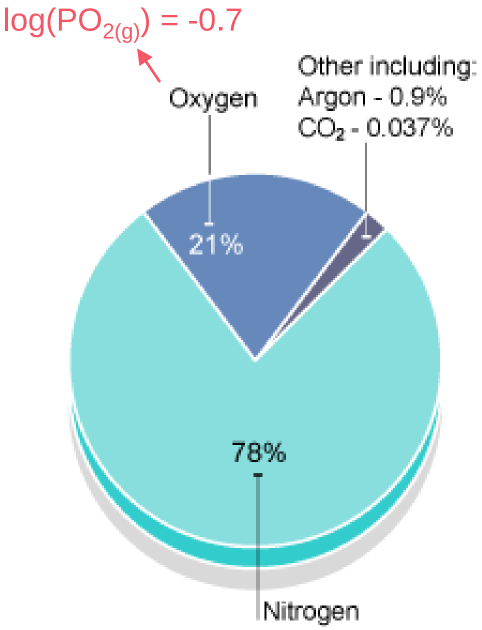
$$2\log(H^+) + 2\log(e^-) - \log(H_2(g)) = 0$$

$$pe = -pH$$

Microorganisms play a key role in redox reactions

- ✓ They have a remarkable **impact on the physical and chemical makeup of our planet**
- ✓ They are **responsible for cycling the chemical elements essential for life**, e.g., C, N, S, H, O
- ✓ More than 90% of the cells in our bodies are microbes





$\log(PO_{2(g)}) = -0.7$

Atmosphere composition

Life requisites

- ✓ **Energy**
  - It always involves redox reactions
  - Two main sources of energy: light , redox

- ✓ **Nutrients**
  - C
  - Macronutrients: O, H, N, P, S
  - Micronutrients (required in small quantities: Fe, Mn, I…)

- ✓ **Conditions**
  - Temperature, salinity, pH…

Redox sequence in natural waters

✓ They provide energy and are accelerated by means of enzymes

spontaneous reactions

	Reaction	logK	E_h^0 [V]	ΔG_r^0 [kJ/mol]
O_2 reduction	$e^- + 0.25O_{2(g)} + H^+ = 0.5H_2O$	20.8	1.23	-118
Denitrification	$e^- + 0.2NO_3^- + 1.2H^+ = 0.1\ N_{2(g)} + 0.6H_2O$	21.0	1.24	-120
Mn(IV) reduction	$e^- + MnO_{2(s)} + 1.5H^+ + 0.5HCO_3^- = MnCO_{3(s)} + H_2O$	20.9	1.24	-119
Fe(III) reduction	$e^- + FeOOH_{(s)} + 2H^+ + HCO_3^- = FeCO_{3(s)} + 2H_2O$	16.2	0.96	-92
Sulphate reduction	$e^- + 0.125SO_4^{2-} + 1.125H^+ = 0.125\ HS^- + 0.5H_2O$	4.1	0.24	-24
N_2 reduction	$e^- + 0.167N_{2(g)} + 1.333H^+ = 0.333NH_4^+$	4.7	0.28	-27
CO_2 reduction	$e^- + 0.125HCO_3^- + 1.125H^+ = 0.125\ CH_{4(g)} + 0.25H_2O$	3.80	0.23	-22
OM oxidation	$0.25\ CH_2O + 0.25H_2O = e^- + 0.25HCO_3^- + 1.25H^+$	-0.8	0.04	4
Sulphur oxidation	$0.125\ HS^- + 0.5H_2O = e^- + 0.125SO_4^{2-} + 1.125H^+$	-4.1	0.24	24
Fe(II) oxidation	$FeCO_{3(s)} + 2H_2O = e^- + FeOOH_{(s)} + 2H^+ + HCO_3^-$	-16.2	0.96	92
Nitrification	$0.125NH_4^+ + 0.375H_2O = e^- + 0.2NO_3^- + 1.2H^+$	-14.9	0.88	85
Mn(II) oxidation	$MnCO_{3(s)} + H_2O = e^- + MnO_{2(s)} + 1.5H^+ + 0.5HCO_3^-$	-20.9	1.24	119

NO_3^- -> $N_{2(g)}$

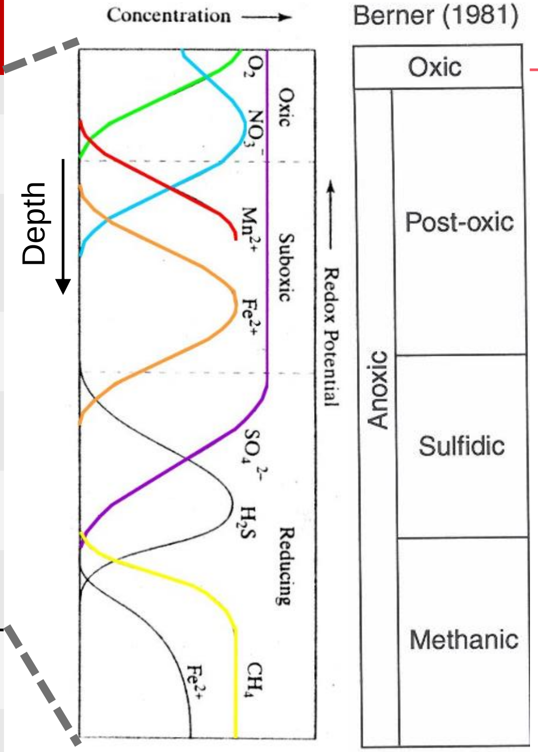
Mn(IV) -> Mn(II)

Fe(III) -> Fe(II)

Redox sequence in natural waters

- ✓ **Sequence** can be **identified** observing change **in water chemistry in depth**

	Reaction	ΔG_r^0 [kJ/mol]
O_2 reduction	$e^- + 0.25O_{2(g)} + H^+ = 0.5H_2O$	-118
Denitrification	$e^- + 0.2NO_3^- + 1.2H^+ = 0.1\ N_{2(g)} + 0.6H_2O$	-120
Mn(IV) reduction	$e^- + MnO_{2(s)} + 1.5H^+ + 0.5HCO_3^- = MnCO_{3(s)} + H_2O$	-119
Fe(III) reduction	$e^- + FeOOH_{(s)} + 2H^+ + HCO_3^- = FeCO_{3(s)} + 2H_2O$	-92
Sulphate reduction	$e^- + 0.125SO_4^{2-} + 1.125H^+ = 0.125\ HS^- + 0.5H_2O$	-24
N_2 reduction	$e^- + 0.167N_{2(g)} + 1.333H^+ = 0.333NH_4^+$	-27
CO_2 reduction	$e^- + 0.125HCO_3^- + 1.125H^+ = 0.125\ CH_{4(g)} + 0.25H_2O$	-22
OM oxidation	$0.25\ CH_2O + 0.25H_2O = e^- + 0.25HCO_3^- + 1.25H^+$	4
Sulphur oxidation	$0.125\ HS^- + 0.5H_2O = e^- + 0.125SO_4^{2-} + 1.125H^+$	24
Fe(II) oxidation	$FeCO_{3(s)} + 2H_2O = e^- + FeOOH_{(s)} + 2H^+ + HCO_3^-$	92
Nitrification	$0.125NH_4^+ + 0.375H_2O = e^- + 0.2NO_3^- + 1.2H^+$	85
Mn(II) oxidation	$MnCO_{3(s)} + H_2O = e^- + MnO_{2(s)} + 1.5H^+ + 0.5HCO_3^-$	119



→ O_2(dissolved) > 10^{-6} M

Appelo and Postma, 2005

Organic matter is common electron donor in natural environment

✓ Organic matter degradation:

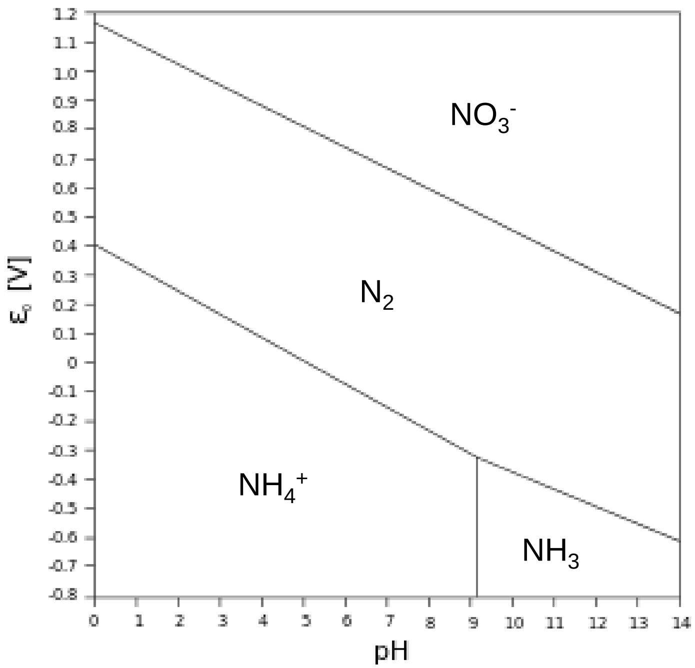
1) In aerobic conditions: by means of O_2
2) In anaerobic conditions: by means of NO_3^-, MnO_2, Fe(III), SO_4^{2-}, CO_2

	Reaction	logK	ΔG_r^0 [kJ/mol]
Aerobic respiration	$0.25CH_2O + 0.25O_2(g) = 0.25HCO_3^- + 0.25H^+$	20.0	-114
Denitrification	$0.25CH_2O + 0.2NO_3^- = 0.25HCO_3^- + 1.25H^+ + 0.1\ N_{2(g)} + 0.6H_2O$	20.3	-116
Mn(IV) reduction	$0.25CH_2O + 0.5MnO_{2(s)} + 0.25H^+ + 0.25HCO_3^- = 0.5MnCO_{3(s)} + 0.5H_2O$	20.1	-115
Fe(III) reduction	$0.25CH_2O + FeOOH_{(s)} + 0.75H^+ + 0.75HCO_3^- = FeCO_{3(s)} + 1.5H_2O$	15.4	-88
Sulphate reduction	$0.25CH_2O + 0.125SO_4^{2-} = 0.25HCO_3^- + 0.125\ HS^- + 0.125H^+$	3.4	-19
Methanogenesis	$0.25CH_2O + 0.125H_2O = 0.125HCO_3^- + 0.125\ CH_{4(g)} + 0.125H^+$	3.1	-18

Denitrification

- ✓ Denitrification: **microbial reduction of NO_3^- to N_2 by organic carbon**

- ✓ **Nitrate pollution** is **caused by** extensive **use of fertilizers** in agriculture (remember: NO_3^- max = 50 mg/l)



→ Nitrate is stable only under highly oxidizing conditions

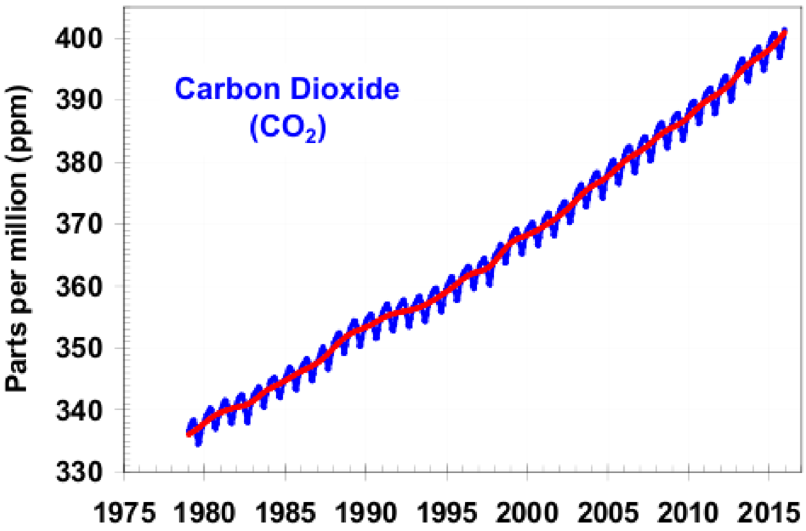
→ Ammonia is stable only under highly reducing conditions

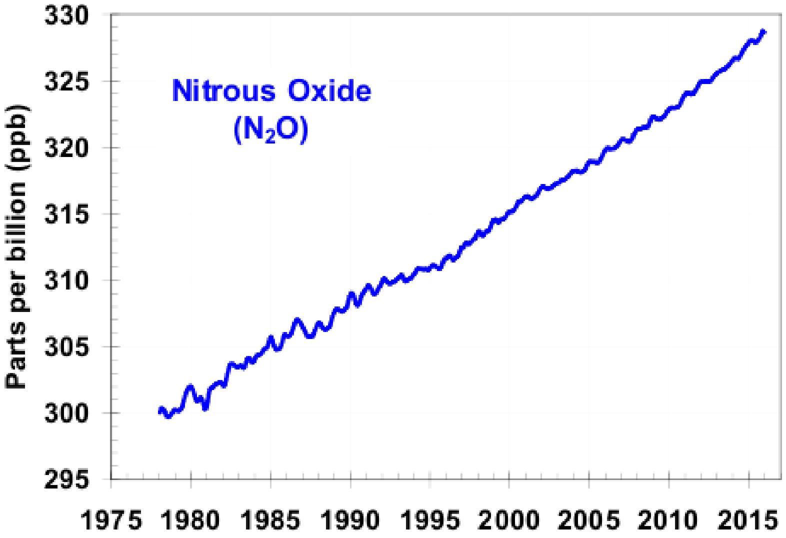
Denitrification

- ✓ The **overall reaction** involves a transfer of five electrons (NO_3^- valence = +5) and proceeds through a complicated pathway with several metastable intermediates

$$NO_3^- \rightarrow NO_2 \rightarrow NO \rightarrow N_2O_{(g)} \rightarrow N_{2(g)}$$

- ✓ **Denitrification** is a **non-reversible** reaction





Mass Action Laws (MALs): Matrix notation

✓ **Normal notation**:

- $HCO_3^- = H^+ + CO_3^{2-}$ $\qquad \log(\mathrm{a}_{H^+}) + \log(\mathrm{a}_{CO_3^{2-}}) - \log(\mathrm{a}_{HCO_3^-}) = \log k_1$
- $H_2CO_3 = 2H^+ + CO_3^{2-}$ $\qquad 2\log(\mathrm{a}_{H^+}) + \log(\mathrm{a}_{CO_3^{2-}}) - \log(\mathrm{a}_{H_2CO_3^-}) = \log k_2$

✓ **Matrix notation**: $\mathbf{S}_e \log \mathbf{a} - \log \mathbf{k} = \mathbf{0}$

$$\begin{pmatrix} 1 & 1 & -1 & 0 \\ 2 & 1 & 0 & -1 \end{pmatrix} \begin{pmatrix} \log \mathrm{a}_{H^+} \\ \log \mathrm{a}_{CO_3^{2-}} \\ \log \mathrm{a}_{HCO_3^-} \\ \log \mathrm{a}_{H_2CO_3^-} \end{pmatrix} = \begin{pmatrix} \log k_1 \\ \log k_2 \end{pmatrix}$$

$\mathbf{S}_e(N_{re} \times N_s) = \text{Eq. stoichiometric matrix}$

$\mathbf{a}(N_s)$=Activities vector $(\mathrm{a}_i = \gamma_i c_i)$

$\mathbf{k}(N_{re})$=Eq. constants vector

What is “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** (one for every equilibrium reaction)
    - $H_2O = H^+ + OH^-$
    - $HCO_3^- = H^+ + CO_3^{2-}$
    - $CaCO_{3(s)} = Ca^{+2} + CO_3^{2-}$

  - **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
    - …

Speciation: system of equations

- **System to be solved**:

Data measured

  - **Data equations**: $\mathbf{g(c)} - \mathbf{x} = \mathbf{0}$ (N_1)
  - **MALs**: $\mathbf{S}_e \log \mathbf{a} - \log \mathbf{k} = \mathbf{0}$ (N_2)

- Nº of unknowns = $N_s = N_1 + N_2$
- Nº of equations = $N_s = N_1 + N_2$

nº of data = nº of independent variables ($N_1 = N_s - N_{re}$)

- It’s a **non linear system of equations**: **iterative methods** are **necessary** to find a solution

Iterative methods for non linear systems

- ✓ Picard method:
  - ✓ System is written as $\mathbf{A}(\mathbf{x})\mathbf{x} = \mathbf{b}(\mathbf{x})$
  - ✓ Iterative system is solved for **x**$^{i+1}$ in which **A** and **B** depend on **x**^{i}

$$\mathbf{A}(\mathbf{x}^{i})\mathbf{x}^{i+1} = \mathbf{b}(\mathbf{x}^{i})$$

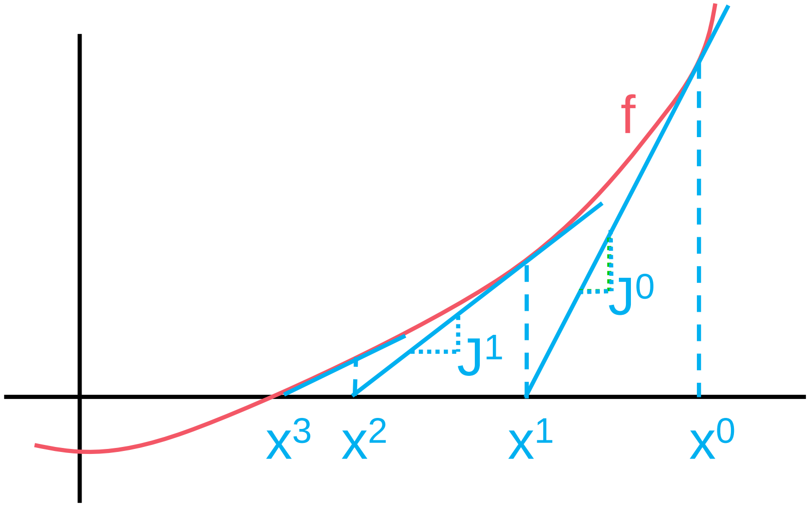
- ✓ Newton-Raphson:
  - ✓ System is written as $\mathbf{f}(\mathbf{x}) = \mathbf{0}$
  - ✓ Iterative system is solved for **x**$^{i+1}$ by means of a linear system until convergence

$$\mathbf{J}^{i}\left(\mathbf{x}^{i+1} - \mathbf{x}^{i}\right) = -\mathbf{f}^{i}$$

Jacobian matrix

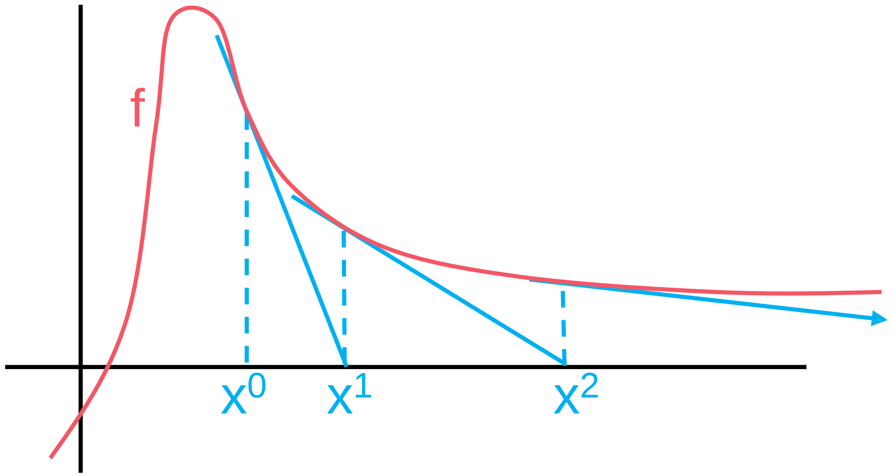
Residual vector

$$\mathbf{J}^{i} = \frac{\partial \mathbf{f}}{\partial \mathbf{x}^{i}} = \begin{pmatrix} \frac{\partial f_1}{\partial x_1^i} & \frac{\partial f_1}{\partial x_2^i} & \cdots & \frac{\partial f_1}{\partial x_n^i} \\ \frac{\partial f_2}{\partial x_1^i} & \frac{\partial f_2}{\partial x_2^i} & \cdots & \frac{\partial f_2}{\partial x_n^i} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial f_n}{\partial x_1^i} & \frac{\partial f_n}{\partial x_2^i} & \cdots & \frac{\partial f_n}{\partial x_n^i} \end{pmatrix}$$



Iterative methods for non linear systems

- ✓ **Both methods can diverge**: discretization has to be changed, or new "starting point" x^0 has to be chosen



Convervence criteria

- ✓ Maximum absolute error of the unknown

$$\left|\mathbf{x}^{i+1}-\mathbf{x}^{i}\right|_{\max} < \varepsilon_{x,abs}$$

- ✓ Maximum relative error of the unknown

$$\left|\frac{\mathbf{x}^{i+1}-\mathbf{x}^{i}}{\mathbf{x}^{i+1}}\right|_{\max} < \varepsilon_{x,rel}$$

- ✓ Residual value of the equation

$$\left|\mathbf{A}\mathbf{x}^{i+1}-\mathbf{b}^{i+1}\right|_{\max} < \varepsilon_{eq}$$

How to solve a speciation problem

- ✓ **Species** are **divided in** ‘**primary**’ and ‘**secondary**’ :

$$\mathbf{c} = \begin{pmatrix} \mathbf{c}_1 \\ \mathbf{c}_2(\mathbf{c}_1) \end{pmatrix}$$

Primary conc.

Secondary conc. (function of c1 through MALs)

- ✓ Secondary species concentrations can be expressed as function of $\mathbf{c}_1$ through mass action laws
- ✓ MALs can then be rewritten as

$$\mathbf{S}_{e1} \log \mathbf{a}_1 + \mathbf{S}_{e2} \log \mathbf{a}_2 - \log \mathbf{k} = \mathbf{0}$$

$$\mathbf{a} = \begin{pmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \end{pmatrix}$$

- ✓ $\mathbf{a}_2$ then reads

$$\begin{aligned} \log \mathbf{a}_2 &= -(\mathbf{S}_{e2})^{-1} \mathbf{S}_{e1} \log \mathbf{a}_1 + (\mathbf{S}_{e2})^{-1} \log \mathbf{k} \\ &= \mathbf{S}^* \log \mathbf{a}_1 + \log \mathbf{k}^* \end{aligned}$$

$$\mathbf{S}_e = (\mathbf{S}_{e1} \quad \mathbf{S}_{e2})$$

- ✓ Careful: $\mathbf{S}_{e2}$ must be invertible!

Primary/secondary species example

- ✓ For a simple chemical system:
  - $HCO_3^- = H^+ + CO_3^{2-}$ $\log(a_{H^+}) + \log(a_{CO_3^{2-}}) - \log(a_{HCO_3^-}) = \log K_1$
  - $H_2CO_3 = 2H^+ + CO_3^{2-}$ $2\log(a_{H^+}) + \log(a_{CO_3^{2-}}) - \log(a_{H_2CO_3^-}) = \log K_2$

$$\begin{array}{cc} S_{e1} = S^* & S_{e2} \\ \left(\boxed{\begin{matrix}1 & 1\\ 2 & 1\end{matrix}}\;\boxed{\begin{matrix}-1 & 0\\ 0 & -1\end{matrix}}\right) & \end{array}\begin{pmatrix}\log a_{H^+}\\ \log a_{CO_3^{2-}}\\ \log a_{HCO_3^-}\\ \log a_{H_2CO_3}\end{pmatrix} = \begin{pmatrix}\log K_1\\ \log K_2\end{pmatrix}$$

I (identity matrix)

$$\log \mathbf{a}_2 = \boxed{-(\mathbf{S}_{e2})^{-1}}\,\mathbf{S}_{e1}\log \mathbf{a}_1 + (\mathbf{S}_{e2})^{-1}\log \mathbf{k}$$

$$\log(a_{HCO_3^-}) = \log(a_{H^+}) + \log(a_{CO_3^{2-}}) - \log K_1$$

$$\log(a_{H_2CO_3^-}) = 2\log(a_{H^+}) + \log(a_{CO_3^{2-}}) - \log K_2$$

Newton-Raphson algorithm for speciation

- **If there is explicit expression for chemistry:** $\log \mathbf{c}_2 = \mathbf{S}^* \log \mathbf{c}_1 + \log \mathbf{k}^*$

a: $\mathbf{f} = \mathbf{g}(\mathbf{c}) - \mathbf{x} = \mathbf{c}_1 + (\mathbf{S}^*)^T \cdot \mathbf{c}_2(\mathbf{c}_1) - \mathbf{x} = \mathbf{0}$ ← Aqueous total concentrations

b: $\mathbf{f} = \mathbf{c}_1 - \mathbf{c}_1^{measured} = \mathbf{0}$ or $\mathbf{f} = \mathbf{c}_2(\mathbf{c}_1) - \mathbf{c}_2^{measured} = \mathbf{0}$ ← Measured concentrations

- Newton-Raphson : $\mathbf{J}^i \left(\mathbf{c}_1^{i+1} - \mathbf{c}_1^i \right) = -\mathbf{f}^i$ (*)

where $\mathbf{J}^i = \dfrac{\partial \mathbf{f}}{\partial \mathbf{c}_1^i} = \mathbf{I} + \mathbf{S}^{*T} \dfrac{\partial \mathbf{c}_2}{\partial \mathbf{c}_1^i}$

Newton-Raphson algorithm for speciation

- **If there is explicit expression for chemistry**: $\log \mathbf{c}_2 = \mathbf{S}^* \log \mathbf{c}_1 + \log \mathbf{k}^*$

  a: $\mathbf{f} = \mathbf{g}(\mathbf{c}) - \mathbf{x} = \mathbf{c}_1 + (\mathbf{S}^*)^T \cdot \mathbf{c}_2(\mathbf{c}_1) - \mathbf{x} = \mathbf{0}$ ← Aqueous total concentrations

  b: $\mathbf{f} = \mathbf{c}_1 - \mathbf{c}_1^{measured} = \mathbf{0}$ or $\mathbf{f} = \mathbf{c}_2(\mathbf{c}_1) - \mathbf{c}_2^{measured} = \mathbf{0}$ ← Measured concentrations

- Newton-Raphson : $\mathbf{J}^i\left(\mathbf{c}_1^{i+1} - \mathbf{c}_1^i\right) = -\mathbf{f}^i$ (*)

  0: Set $\mathbf{c}_1^0$

  1: $\mathbf{J}^i = \dfrac{\partial \mathbf{f}}{\partial \mathbf{c}_1^i} = \mathbf{I} + (\mathbf{S}^*)^T \dfrac{\partial \mathbf{c}_2}{\partial \mathbf{c}_1^i}$

  where $\dfrac{\partial c_{2,j}}{\partial c_{1,k}} = \dfrac{c_{2,j} \partial \ln c_{2,j}}{c_{1,i} \partial \ln c_{1,k}}$ $\quad \dfrac{\partial \ln \mathbf{c}_2}{\partial \ln \mathbf{c}_1^i} = \mathbf{S}^*$

  2: Solve system (*) to calculate $\mathbf{c}_1^1$
  3: Check convergence (see previous slide)
  4: If convergence not reached: set $\mathbf{c}_1^i = \mathbf{c}_1^1$, go back to 1, solve again

Newton-Raphson algorithm for speciation

- **If there is NO explicit expression for chemistry**: another non-linear system has to be solved to calculate $\mathbf{c}_2 = f(\mathbf{c}_1)$

$$\log \mathbf{c}_2 + \log \boldsymbol{\gamma}_2 = \mathbf{S}^* \log(\mathbf{c}_1 + \boldsymbol{\gamma}_1) + \log \mathbf{k}^*$$

$$\log \gamma_i = -\frac{A z_i^2 \sqrt{I}}{1 + B a_i \sqrt{I}} + bI \qquad I = \tfrac{1}{2} \sum_i c_i z_i^2$$

- Two systems to calculate $\mathbf{c}_2$ and $\partial \mathbf{c}_2 / \partial \mathbf{c}_1$

$$\frac{\partial \mathbf{f}_{MAL}}{\partial \mathbf{c}_2} \left(\mathbf{c}_2^{j+1} - \mathbf{c}_2^{j} \right) = -\mathbf{f}_{MAL}$$

$$\frac{\partial \mathbf{f}_{MAL}}{\partial \mathbf{c}_2} \frac{\partial \mathbf{c}_2}{\partial \mathbf{c}_1} = -\frac{\partial \mathbf{f}_{MAL}}{\partial \mathbf{c}_1} \longleftarrow \frac{d\mathbf{f}_{MAL}}{d\mathbf{c}_1} = 0 = \frac{\partial \mathbf{f}_{MAL}}{\partial \mathbf{c}_2} \frac{\partial \mathbf{c}_2}{\partial \mathbf{c}_1} + \frac{\partial \mathbf{f}_{MAL}}{\partial \mathbf{c}_1}$$

- To solve:
    1. Newton-Raphson with components and chemistry (Ns unknowns)
    2. Picard: $\gamma^{i+1} = \gamma(\mathbf{c}^{i})$

Geochemical and Reactive Transport modelling

4. Reactive transport

Reactive transport equation

Solute mass balance equation for one species in porous media

$$\frac{\partial \phi c}{\partial t} = -\nabla \cdot (\mathbf{q} c) + \nabla \cdot (\mathbf{D} \nabla c) + r_e + r_k$$

- ✓ $r_e \neq r_k$ –> equilibrium and kinetic reactions
- ✓ $r_k = f(c)$ –> explicit expression of concentrations
- ✓ **r_e doesn't have explicit expression** –> it's normally eliminated by means of linear combinations of equations
- ✓ In order to get rid of r_e we have to write the **mass balance equations in terms of "components"**

Reactive transport equation

Solute mass balance equation for several species in porous media, with equilibrium and kinetic reactions (ϕ = const)

$$\frac{\partial \mathbf{c}}{\partial t} = \underbrace{-\nabla\cdot\left(\mathbf{qc}\right)+\nabla\cdot\left(\mathbf{D}\nabla\mathbf{c}\right)}_{\substack{L(\mathbf{c})\\ \text{Linear operator}}} + \underset{\searrow\ \text{Equilibrium reactions}}{\mathbf{S}_e^t\mathbf{r}_e} + \underset{\searrow\ \text{Kinetic reactions}}{\mathbf{S}_k^t\mathbf{r}_k}$$

- For aqueous species:

$$L(.) = -\frac{q}{\phi}\nabla(.) + \frac{1}{\phi}\nabla D\nabla(.)$$

- For solid species:

$$L(.) = 0$$

$\mathbf{c}(N_s)$= Conc. vector

$\mathbf{S}_e(N_{re}\times N_s) =$ Eq. stoichiometric matrix

$\mathbf{S}_k(N_{rk}\times N_s)$= Kin. stoichiometric matrix

$\mathbf{r}_e\,(N_{re}) =$ Eq. rates vector

$\mathbf{r}_k\,(N_{rk}) =$ Kin. rates vector

Reactive transport equation

Solute mass balance equation for several species in porous media, with equilibrium and kinetic reactions (ϕ = const)

$$\frac{\partial \mathbf{c}}{\partial t} = \underbrace{-\nabla\cdot\left(\mathbf{q}\mathbf{c}\right)+\nabla\cdot\left(\mathbf{D}\nabla\mathbf{c}\right)}_{L(\mathbf{c})} + \mathbf{S}_e^t\mathbf{r}_e + \mathbf{S}_k^t\mathbf{r}_k$$

Linear operator

Equilibrium reactions

Kinetic reactions

$$\boxed{\frac{\partial \mathbf{c}}{\partial t} = L\left(\mathbf{c}\right) + \mathbf{S}_e^t\mathbf{r}_e + \mathbf{S}_k^t\mathbf{r}_k}$$

$\mathbf{c}(N_s)$= Conc. vector

$\mathbf{S}_e(N_{re}\times N_s)=$ Eq. stoichiometric matrix

$\mathbf{S}_k(N_{rk}\times N_s)$= Kin. stoichiometric matrix

$\mathbf{r}_e\,(N_{re})=$ Eq. rates vector

$\mathbf{r}_k\,(N_{rk})=$ Kin. rates vector

Reactive transport equation

Solute mass balance equation for several species in porous media, with equilibrium and kinetic reactions (ϕ = const)

$$\frac{\partial \mathbf{c}}{\partial t} = \underbrace{-\nabla\cdot(\mathbf{qc}) + \nabla\cdot(\mathbf{D}\nabla\mathbf{c})}_{L(\mathbf{c})} + \mathbf{S}_e^t\mathbf{r}_e + \mathbf{S}_k^t\mathbf{r}_k$$

Linear operator

Equilibrium reactions

Kinetic reactions

$$\boxed{\frac{\partial \mathbf{c}}{\partial t} = L(\mathbf{c}) + \mathbf{S}_e^t\mathbf{r}_e + \mathbf{S}_k^t\mathbf{r}_k}$$

What are the unknowns in this system?

$\mathbf{c}(N_s)$= Conc. vector

$\mathbf{S}_e(N_{re} \times N_s) =$ Eq. stoichiometric matrix

$\mathbf{S}_k(N_{rk} \times N_s)$= Kin. stoichiometric matrix

$\mathbf{r}_e(N_{re}) =$ Eq. rates vector

$\mathbf{r}_k(N_{rk}) =$ Kin. rates vector

Reactive transport equations

Equations:

1. N_s transport equations

To simplify we suppose **a** = **c**

$$\frac{\partial \mathbf{c}}{\partial t} = L(\mathbf{c}) + \mathbf{S}_e^t \mathbf{r}_e + \mathbf{S}_k^t \mathbf{r}_k$$

2. N_{re} mass action laws $\mathbf{S}_e \log \mathbf{c} = \log \mathbf{k}$

Unknowns:

1. **c** (N_s)
2. $\mathbf{r}_e$ (N_{re}) ⟶ Problem: no explicit expression!

Imagine to solve this equation for ‘n’ nodes and ‘k’ time_steps, how many unknowns do we have? (hint: many!)

- **Eliminate r_e to reduce number of unknowns!**

How to eliminate r_e

- ✓ Components allow to reduce number of unknowns
- ✓ Example: gypsum dissolution

$$\mathrm{CaSO}_{4(s)} = \mathrm{Ca}^{2+} + \mathrm{SO}_4^{2-} \quad \log K = -4.48$$

$$(1): \frac{d[\mathrm{Ca}^{2+}]}{dt} = L([\mathrm{Ca}^{2+}]) + r_e$$

$$(2): \frac{d[\mathrm{SO}_4^{2-}]}{dt} = L([\mathrm{SO}_4^{2-}]) + r_e$$

$$(3): \frac{d[\mathrm{CaSO}_{4(s)}]}{dt} = -r_e$$

$$(4): \log[\mathrm{Ca}^{2+}] + \log[\mathrm{SO}_4^{2-}] = \log K$$

1st Linear combination of mass balance

$$(1)+(3): \frac{d[\mathrm{Ca}^{2+}]}{dt} + \frac{d[\mathrm{CaSO}_{4(s)}]}{dt} = L([\mathrm{Ca}^{2+}])$$

$$(2)+(3): \frac{d[\mathrm{SO}_4^{2-}]}{dt} + \frac{d[\mathrm{CaSO}_{4(s)}]}{dt} = L([\mathrm{SO}_4^{2-}])$$

(-)

2nd Linear combination of mass balance

$$\frac{d[\mathrm{Ca}^{2+}]}{dt} - \frac{d[\mathrm{SO}_4^{2-}]}{dt} = L([\mathrm{Ca}^{2+}]) - L([\mathrm{SO}_4^{2-}])$$

How to eliminate r_e

1st Linear combination of mass balance

$$(1)+(3): \frac{d[\mathrm{Ca}^{2+}]}{dt} + \frac{d[\mathrm{CaSO}_{4(s)}]}{dt} = L([\mathrm{Ca}^{2+}])$$

$$(2)+(3): \frac{d[\mathrm{SO}_4^{2-}]}{dt} + \frac{d[\mathrm{CaSO}_{4(s)}]}{dt} = L([\mathrm{SO}_4^{2-}])$$

(-)

2nd Linear combination of mass balance

$$\frac{d[\mathrm{Ca}^{2+}]}{dt} - \frac{d[\mathrm{SO}_4^{2-}]}{dt} = L([\mathrm{Ca}^{2+}]) - L([\mathrm{SO}_4^{2-}])$$

$$(4): \log[\mathrm{Ca}^{2+}] + \log[\mathrm{SO}_4^{2-}] = \log\mathrm{K}$$

- ✓ **Both combinations** 1 and 2 are **valid to solve RT system**
- ✓ The **difference** lies in the **definition and number of unknowns**:

1. We have 2 equations in 2 variables: $u_1 = [\mathrm{Ca}^{2+}] + [\mathrm{CaSO}_{4(s)}]$
   $u_2 = [\mathrm{SO}_4^{2-}] + [\mathrm{CaSO}_{4(s)}]$

1. We have 1 equation in 1 variable: $u_1 = [\mathrm{Ca}^{2+}] - [\mathrm{SO}_4^{2-}]$

Components definition

- ✓ **u** is called “**total concentration of component**”
- ✓ **u** is a **linear combination of concentrations**
- ✓ When we have more than one component (e.g., 1st linear combination of previous slide) u_1 and u_2 can be stored in a vector: $\mathbf{u} = (u_1 \;\; u_2)^T$
- ✓ Definition: $\mathbf{u} = \mathbf{U} * \mathbf{c}$
  - ✓ **U** is called “component matrix”
  - ✓ **U** is defined in such a way that : $\mathbf{U}\mathbf{S}_e^t = \mathbf{0}$
  - ✓ **U** dimension: $((N_s - N_{re}) \times N_s = N_c \times N_s)$
  - ✓ N_c = number of components (**u** dimension)

Elimination of equilibrium reaction rates (r_e)

- ✓ From the definition of the component matrix: $\mathbf{U}\mathbf{S}_e^t = \mathbf{0}$
- ✓ Multiplying transport equation times **U**:

$$\mathbf{U}\frac{\partial \mathbf{c}}{\partial t} = \mathbf{U}L(\mathbf{c}) + \cancel{\mathbf{U}\mathbf{S}_e^t\mathbf{r}_e} + \mathbf{U}\mathbf{S}_k^t\mathbf{r}_k$$

<u>Equations</u>:

1. N_s-N_{re} transport equations
2. N_{re} mass action laws

<u>Unknowns</u>:

1. **c** (N_s)

The component matrix eliminates equilibrium reaction rates ($\mathbf{r}_e$), reducing the number of unknowns

How do we calculate U?

- Dividing $\mathbf{S}_e$ in $\mathbf{S}_{e1}$ and $\mathbf{S}_{e2}$:

$$\mathbf{S}_e = \left(\mathbf{S}_{e1} \middle| \quad \mathbf{S}_{e2}\right)$$

- And building the component matrix as follows:

$$\mathbf{U} = \left(\mathbf{I} \middle| \underbrace{-\mathbf{S}_{\mathbf{e}1}{}^T \left(\mathbf{S}_{\mathbf{e}2}{}^T\right)^{-1}}_{\left(\mathbf{S}^*\right)^T}\right)$$

remember

$$\boxed{\begin{aligned}\log \mathbf{a}_2 &= -\left(\mathbf{S}_{e2}\right)^{-1} \mathbf{S}_{e1} \log \mathbf{a}_1 + \left(\mathbf{S}_{e2}\right)^{-1} \log \mathbf{k} \\ &= \mathbf{S}^* \log \mathbf{a}_1 + \log \mathbf{k}^*\end{aligned}}$$

- $\mathbf{r}_e$ can therefore be eliminated:

$$\mathbf{U}\left(\mathbf{S}_\mathbf{e}\right)^T = \mathbf{0} \Rightarrow \left(\mathbf{I} \middle| -\mathbf{S}_{\mathbf{e}1}{}^T \left(\mathbf{S}_{\mathbf{e}2}{}^T\right)^{-1}\right) \begin{pmatrix} \mathbf{S}_{\mathbf{e}1}{}^T \\ \mathbf{S}_{\mathbf{e}2}{}^T \end{pmatrix} = \mathbf{S}_{\mathbf{e}1}{}^T - \mathbf{S}_{\mathbf{e}1}{}^T \left(\mathbf{S}_{\mathbf{e}2}{}^T\right)^{-1} \mathbf{S}_{\mathbf{e}2}{}^T = \mathbf{0}$$

How do we calculate U?

$$\mathbf{U}(\mathbf{S}_{\mathbf{e}})^T = \mathbf{0} \Rightarrow \left(\mathbf{I} \middle| -\mathbf{S}_{\mathbf{e}1}{}^T\left(\mathbf{S}_{\mathbf{e}2}{}^T\right)^{-1}\right)\begin{pmatrix}\mathbf{S}_{\mathbf{e}1}{}^T\\ \mathbf{S}_{\mathbf{e}2}{}^T\end{pmatrix} = \mathbf{0}$$

Example:

1. $HCO_3^- = H^+ + CO_3^{2-}$
2. $H_2CO_3 = 2H^+ + CO_3^{2-}$

$$\left(\underbrace{\boxed{\begin{matrix}1 & 1\\ 2 & 1\end{matrix}}}_{\mathbf{S_{e1} = S^*}}\ \underbrace{\boxed{\begin{matrix}-1 & 0\\ 0 & -1\end{matrix}}}_{\mathbf{S_{e2}}}\right)\begin{pmatrix}\log a_{H^+}\\ \log a_{CO_3^{2-}}\\ \log a_{HCO_3^-}\\ \log a_{H_2CO_3}\end{pmatrix} = \begin{pmatrix}\log K_1\\ \log K_2\end{pmatrix}$$

Species

Components

$$\mathbf{U} = \left(\begin{matrix}1 & 0\\ 0 & 1\end{matrix}\middle| -\left(\boxed{\begin{matrix}1 & 2\\ 1 & 1\end{matrix}}\right)\left(\boxed{\begin{matrix}-1 & 0\\ 0 & -1\end{matrix}}\right)^{-1}\right) = \begin{array}{c|cccc|l} & H^+ & CO_3^{2-} & HCO_3^- & H_2CO_3 & \\ \hline & 1 & 0 & 1 & 2 & H^+\\ & 0 & 1 & 1 & 1 & CO_3^{2-}\end{array}$$

$$\underbrace{\begin{matrix}1 & 2\\ 1 & 1\end{matrix}}_{\mathbf{(S^*)^T}}$$

Meaning of total concentrations of components (u)

- ✓ Sometimes components have a physical meaning (often they represent total concentrations, TIC, CEC…)

$$\mathbf{u}=\mathbf{U}\mathbf{c}$$

$$\mathbf{u}=\left(\begin{array}{cccc} \mathrm{H^+} & \mathrm{CO_3^{\,2-}} & \mathrm{HCO_3^{\,-}} & \mathrm{H_2CO_3} \\ 1 & 0 & 1 & 2 \\ 0 & 1 & 1 & 1 \end{array}\right)\begin{pmatrix} c_{\mathrm{H^+}} \\ c_{\mathrm{CO_3^{2-}}} \\ c_{\mathrm{HCO_3^-}} \\ c_{\mathrm{H_2CO_3}} \end{pmatrix}=\begin{pmatrix} c_{\mathrm{H^+}}+c_{\mathrm{HCO_3^-}}+2c_{\mathrm{H_2CO_3}} \\ c_{\mathrm{CO_3^{2-}}}+c_{\mathrm{HCO_3^-}}+c_{\mathrm{H_2CO_3}} \end{pmatrix}\begin{array}{l} \longleftarrow \text{Total H conc.} \\ \longleftarrow \text{TIC} \end{array}$$

- ✓ **If** there are **no kinetic reactions and all species** are **aqueous** → **RT equation** becomes analogous **to conservative transport** equation in **u**

$$\frac{\partial\mathbf{u}}{\partial t}=L(\mathbf{u})$$

Example of RT problem:

✓ Simplifying: **a** = **c**

1. $HCO_3^- = H^+ + CO_3^{2-}$
2. $H_2CO_3 = 2H^+ + CO_3^{2-}$

✓ Equations to be solved (6):

$$\frac{\partial}{\partial t}\begin{pmatrix} c_{H^+} \\ c_{CO_3^{2-}} \\ c_{HCO_3^-} \\ c_{H_2CO_3} \end{pmatrix} = L\begin{pmatrix} c_{H^+} \\ c_{CO_3^{2-}} \\ c_{HCO_3^-} \\ c_{H_2CO_3} \end{pmatrix} + \begin{pmatrix} r_1 + 2r_2 \\ r_1 + r_2 \\ -r_1 \\ -r_2 \end{pmatrix}$$

$$\frac{c_{H^+}\ c_{CO_3^{2-}}}{c_{HCO_3^-}} = K_1$$

$$\frac{c^2_{H^+}\ c_{CO_3^{2-}}}{c_{H_2CO_3^-}} = K_2$$

✓ Unknowns (6): $c_{H^+}, c_{CO_3^{2-}}, c_{HCO_3^-}, c_{H_2CO_3}, r_1, r_2$

Example of RT problem:

- Writing mass balance in terms of components allows eliminating r_1 and r_2:

$$\frac{\partial}{\partial t}\begin{pmatrix} u_1 \\ u_2 \end{pmatrix} = L\begin{pmatrix} u_1 \\ u_2 \end{pmatrix}$$

- where $u_1 = c_{H^+} + c_{HCO_3^-} + 2c_{H_2CO_3}$

$$u_2 = c_{CO_3^{2-}} + c_{HCO_3^-} + c_{H_2CO_3}$$

- From MALs:

$$\frac{c_{H^+}\ c_{CO_3^{2-}}}{c_{HCO_3^-}} = K_1 \Rightarrow c_{HCO_3^-} = \frac{c_{H^+}\ c_{CO_3^{2-}}}{K_1}$$

$$\frac{c^2_{H^+}\ c_{CO_3^{2-}}}{c_{H_2CO_3^-}} = K_2 \Rightarrow c_{H_2CO_3^-} = \frac{c^2_{H^+}\ c_{CO_3^{2-}}}{K_2}$$

Example of RT problem:

- ✓ We can substitute MALs into components definition:

$$\frac{\partial}{\partial t}\begin{pmatrix} c_{H^+} + \dfrac{c_{H^+}\, c_{CO_3^{2-}}}{K_1} + 2\dfrac{c^2_{H^+}\, c_{CO_3^{2-}}}{K_2} \\ c_{CO_3^{2-}} + \dfrac{c_{H^+}\, c_{CO_3^{2-}}}{K_1} + \dfrac{c^2_{H^+}\, c_{CO_3^{2-}}}{K_2} \end{pmatrix} = L\begin{pmatrix} c_{H^+} + \dfrac{c_{H^+}\, c_{CO_3^{2-}}}{K_1} + 2\dfrac{c^2_{H^+}\, c_{CO_3^{2-}}}{K_2} \\ c_{CO_3^{2-}} + \dfrac{c_{H^+}\, c_{CO_3^{2-}}}{K_1} + \dfrac{c^2_{H^+}\, c_{CO_3^{2-}}}{K_2} \end{pmatrix}$$

  - ✓ where the unknowns are: $c_{H^+}, c_{CO_3^{2-}}$ (“primary species”)
  - ✓ Once $c_{H^+}, c_{CO_3^{2-}}$ have been calculated, we can also calculate the other (“secondary”) species (from MALs) and *r* (from mass balance in concentrations).

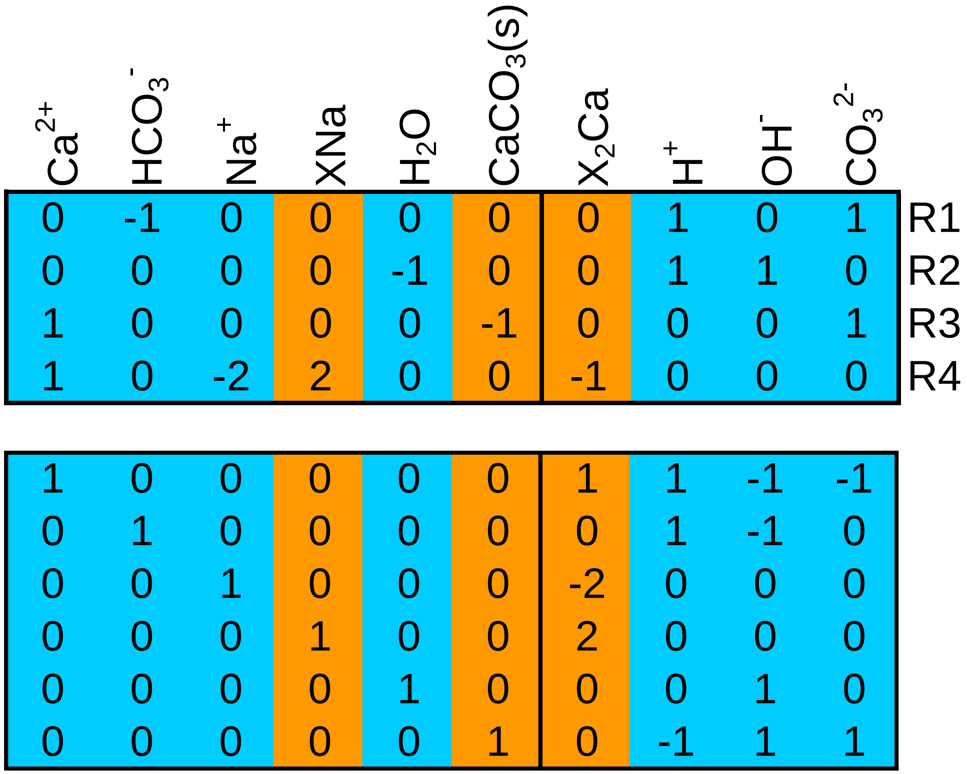
With more complex chemical system

- ✓ Reactions
  - ✓ R1: $HCO_3^- = H^+ + CO_3^{2-}$
  - ✓ R2: $H_2O = H^+ + OH^-$
  - ✓ R3: $CaCO_3(s) = Ca^{2+} + CO_3^{2-}$
  - ✓ R4: $X_2Ca + 2Na^+ = 2XNa + Ca^{2+}$

🟦 Aqueous

🟧 Solid

- ✓ Stoichiometric matrix
- ✓ Component matrix



$$\begin{array}{cccccc|cccc|l}
Ca^{2+} & HCO_3^- & Na^+ & XNa & H_2O & CaCO_3(s) & X_2Ca & H^+ & OH^- & CO_3^{2-} & \\
0 & -1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & R1 \\
0 & 0 & 0 & 0 & -1 & 0 & 0 & 1 & 1 & 0 & R2 \\
1 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 1 & R3 \\
1 & 0 & -2 & 2 & 0 & 0 & -1 & 0 & 0 & 0 & R4
\end{array}$$

$$\begin{array}{cccccc|cccc}
1 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & -1 & -1 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & -2 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 2 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & -1 & 1 & 1
\end{array}$$

With more complex chemical system

- ✓ Total concentrations of components: $\mathbf{u} = \mathbf{u}_a + \mathbf{u}_s$

$$\frac{\partial \mathbf{u}_a}{\partial t} + \frac{\partial \mathbf{u}_s}{\partial t} = L(\mathbf{u}_a)$$

$$\mathbf{u} = \mathbf{u}_a + \mathbf{u}_s = \begin{pmatrix} c_{\mathrm{Ca}^{2+}} + c_{\mathrm{H}^+} - c_{\mathrm{OH}^-} - c_{\mathrm{CO}_3^{-2}} \\ c_{\mathrm{HCO}_3^-} + c_{\mathrm{H}^+} - c_{\mathrm{OH}^-} \\ c_{\mathrm{Na}^+} \\ 0 \\ c_{\mathrm{H_2O}} + c_{\mathrm{OH}^-} \\ -c_{\mathrm{H}^+} + c_{\mathrm{OH}^-} + c_{\mathrm{CO}_3^{-2}} \end{pmatrix} + \begin{pmatrix} c_{\mathrm{X_2Ca}} \\ 0 \\ -2c_{\mathrm{X_2Ca}} \\ c_{\mathrm{XNa}} + 2c_{\mathrm{X_2Ca}} \\ 0 \\ c_{\mathrm{CaCO_3}} \end{pmatrix}$$

- ✓ If there is adsorption or kinetics we need specific numerical methods to solve the equations

Geochemical and Reactive Transport modelling

5. Aquifer contamination

When we model reactive transport processes we need to take into account:

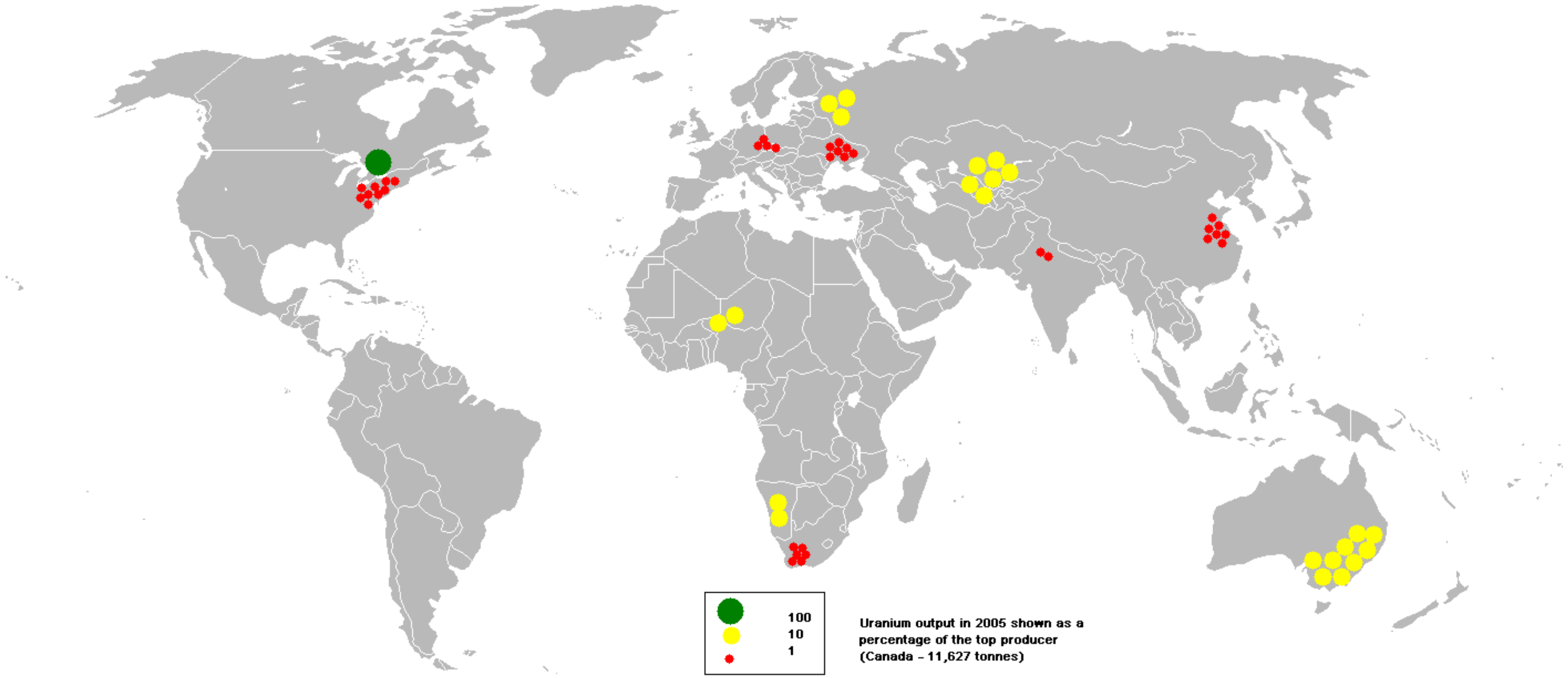
- ✓ Conservative transport processes (advection, diffusion, dispersion)
- ✓ Reactions (kinetic or equilibrium)

But what processes and reactions do we need to include in our models?

It depends on what problem we want to simulate

Uranium

- ✓ Miners first noticed **uranium minerals** in 1565 **in Saxony**
- ✓ The states of **Saxony and Thuringia** in southeastern Germany were the **third largest uranium producers in the world in the Cold War**



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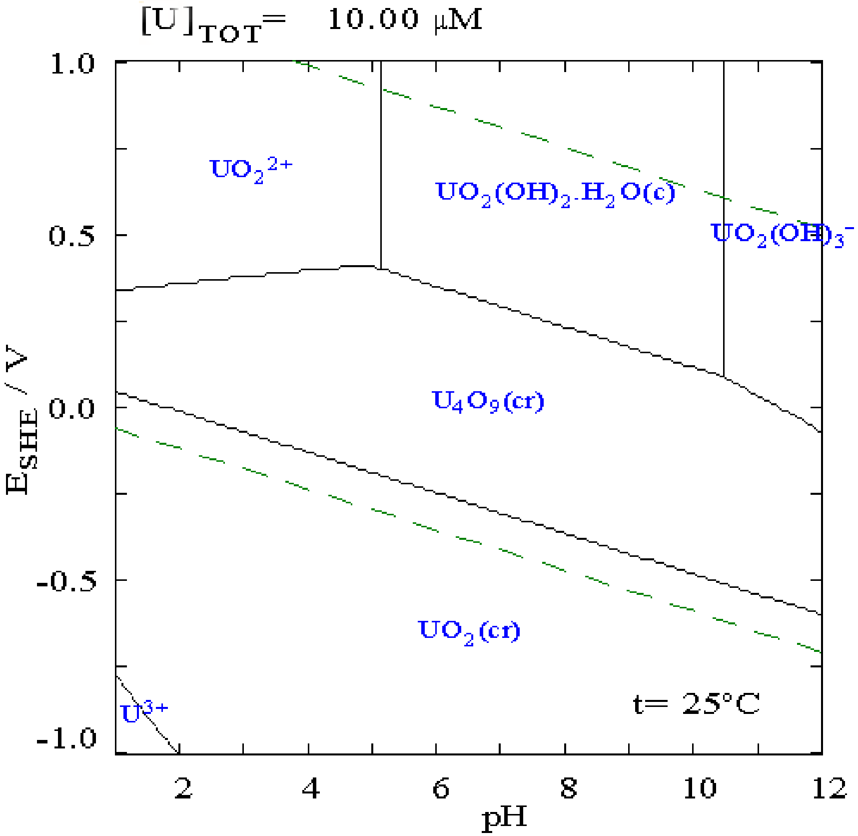
Uranium

- 6 uranium isotopes exist..
- ..with half-lives varying between 159,200 years and 4.5 billion years
- Uranium is redox sensitive



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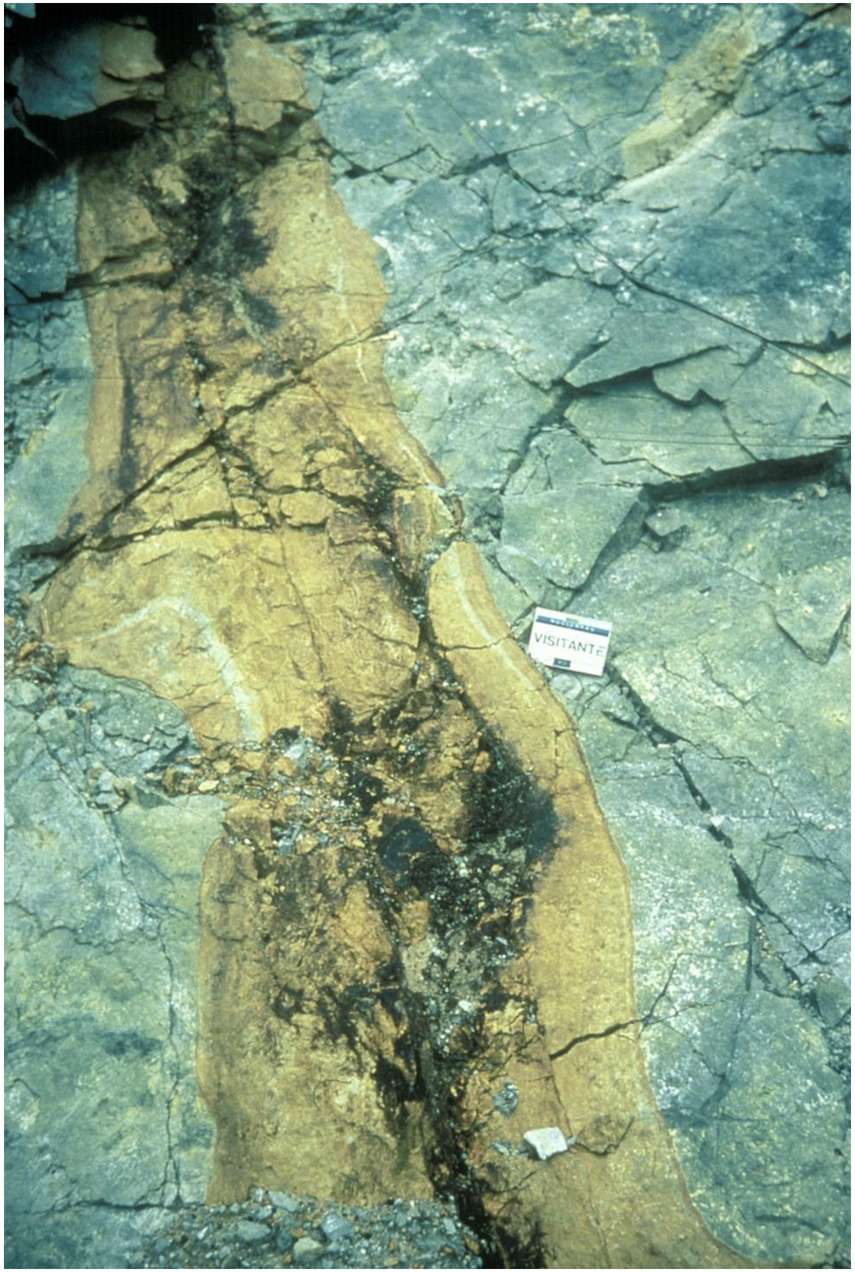
- Unfortunately, uranium mining and processing were done with little consideration for the environment

Uranium



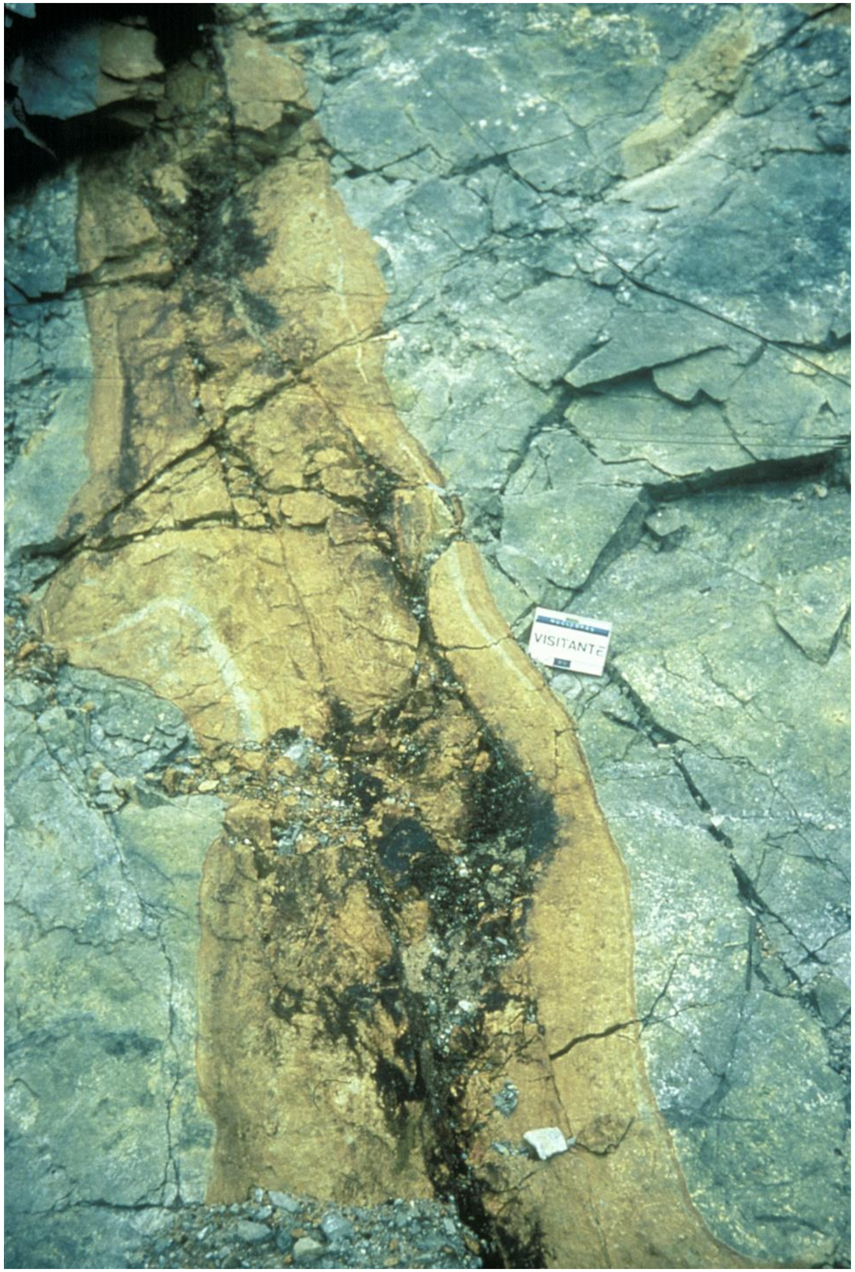
- The **contamination** impact **of uranium mines remains an issue** despite decades of remediation initiatives

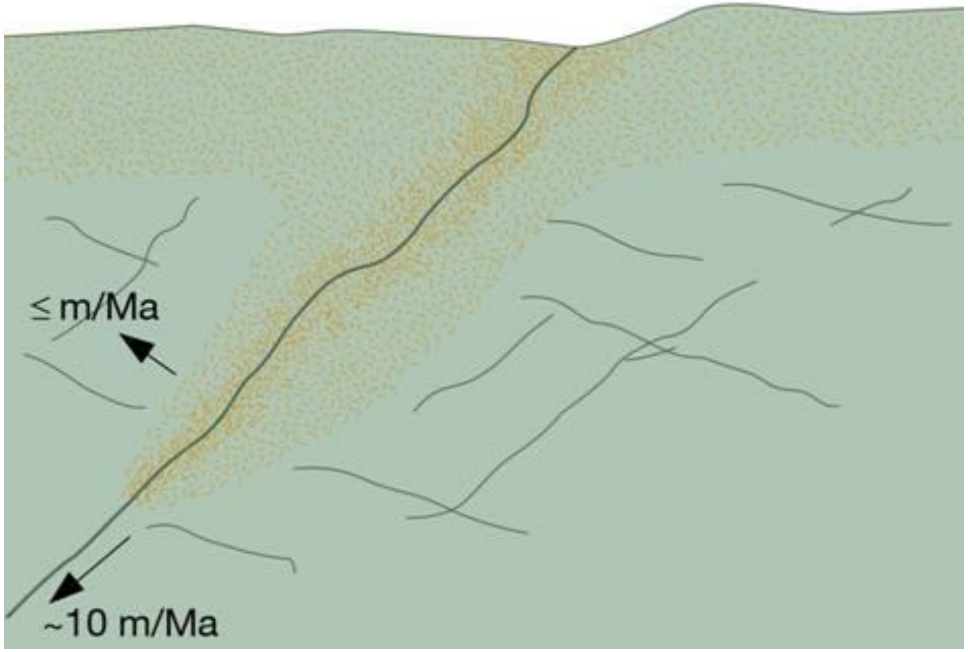
- During uranium mining and extraction, large amounts of ore were excavated because the minerals often contain only between 0.1% and 0.2% uranium

- Consequently, **abandoned uranium mine waste dumps and tailings** may be **sources of** not only radioactive pollutants but **also heavy metals** (e.g. iron, copper, zinc, cadmium, nickel, cobalt), arsenic and sulphates

[Mkandawire and Dudel, 2005]

Uranium



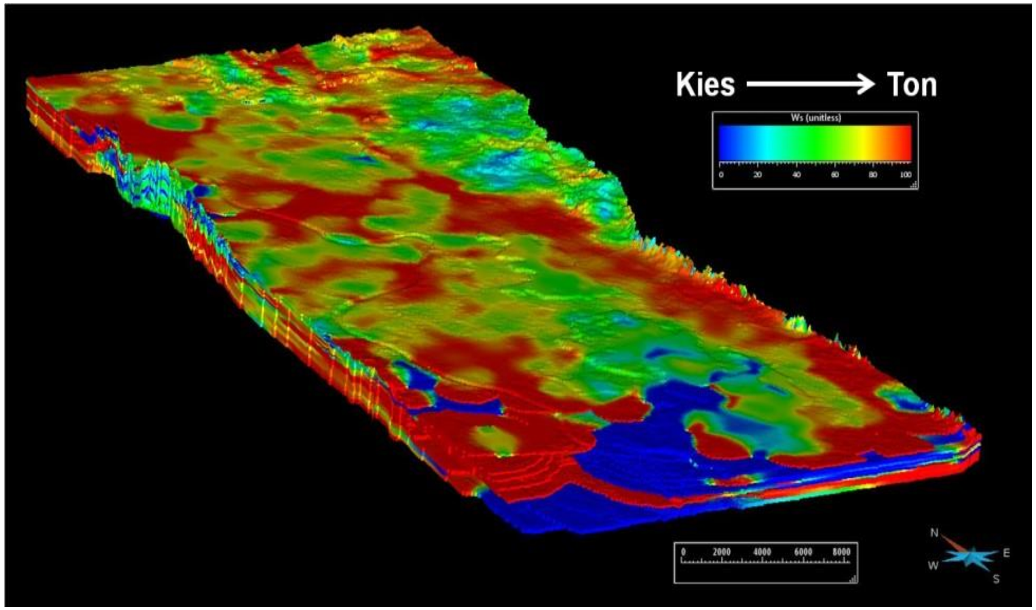


[Saaltink and Carrera, notes from RT courses]

what processes and reactions we need to take into account for a RT model?

Hessian Ried

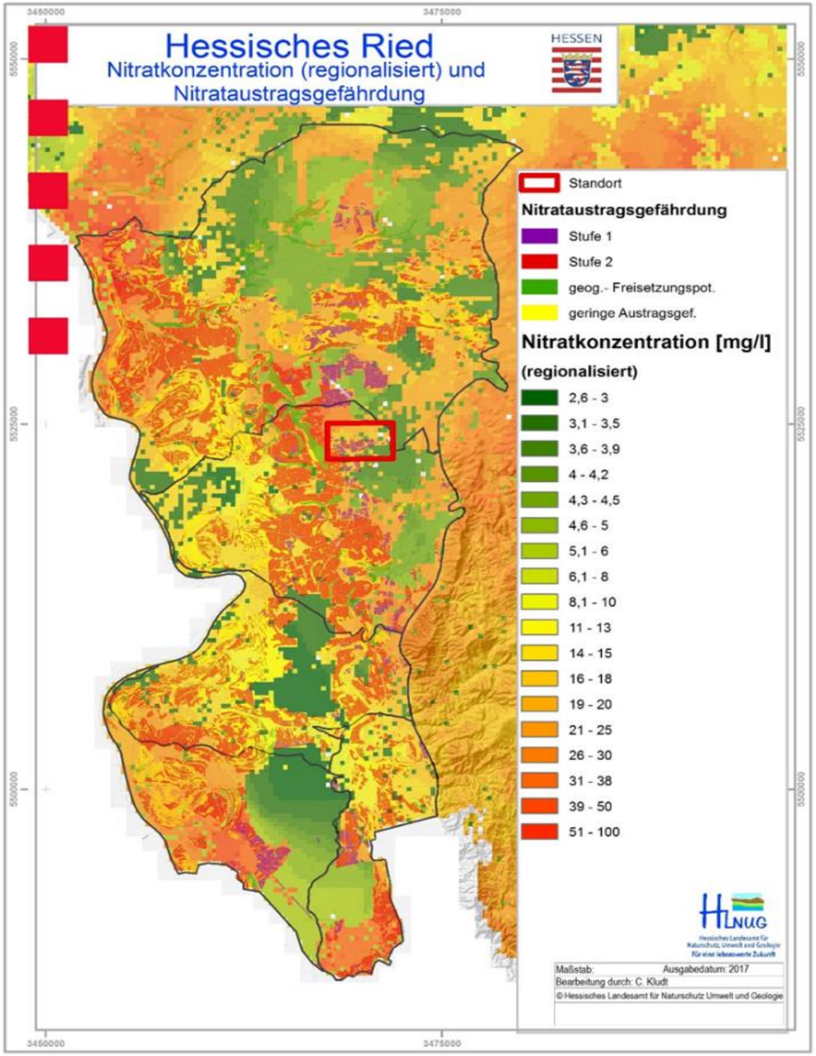
- Region of South Hesse, Germany, intensively exploited for agricultural purposes -> **large amounts of fertilizers used**
- Upper Rhine Graben consist of sedimentary layer of Pliocene and calcite-rich quaternary material, such as fluviatile and limnic **silt**, **sand**, and **gravel**
- **Very heterogeneous aquifer**

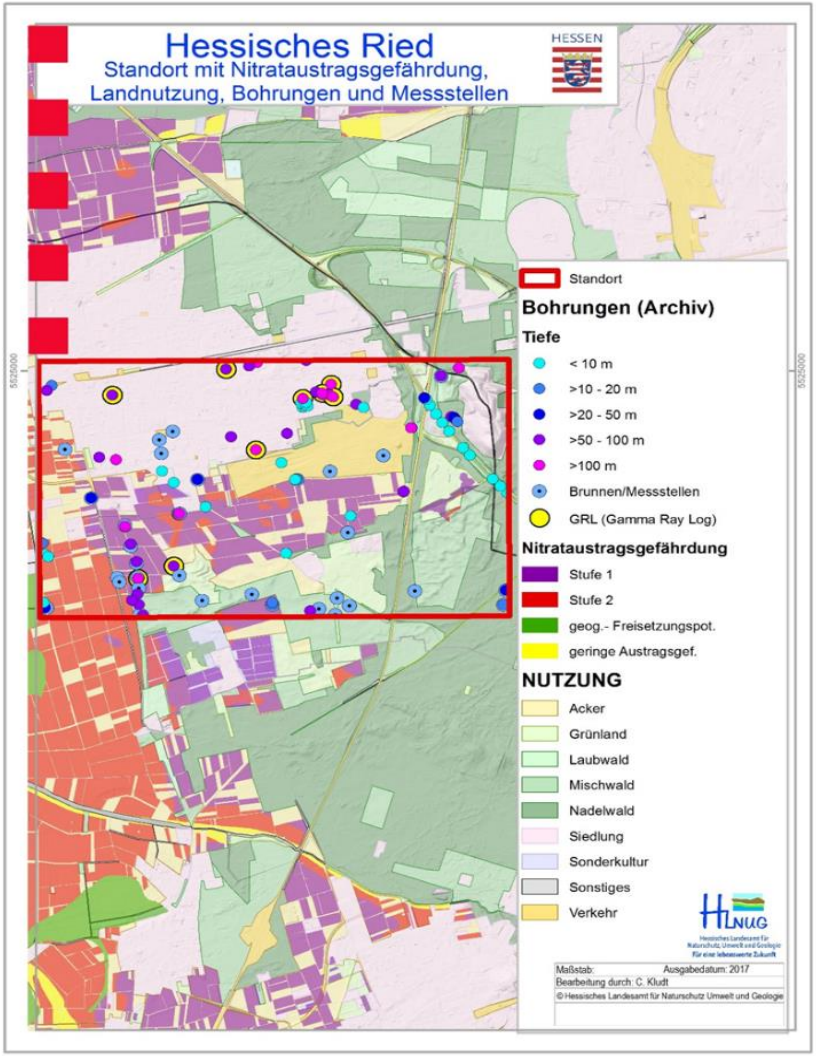


GOCAD Model of the Northern Upper Rhine Graben (HLUG 2012)

Hessian Ried

- ✓ High fertilizers contents have been used in the area for many years
  -> **high levels of nitrate** (NO_3^-) **in groundwater**
  -> very heterogeneous distribution of NO_3^-

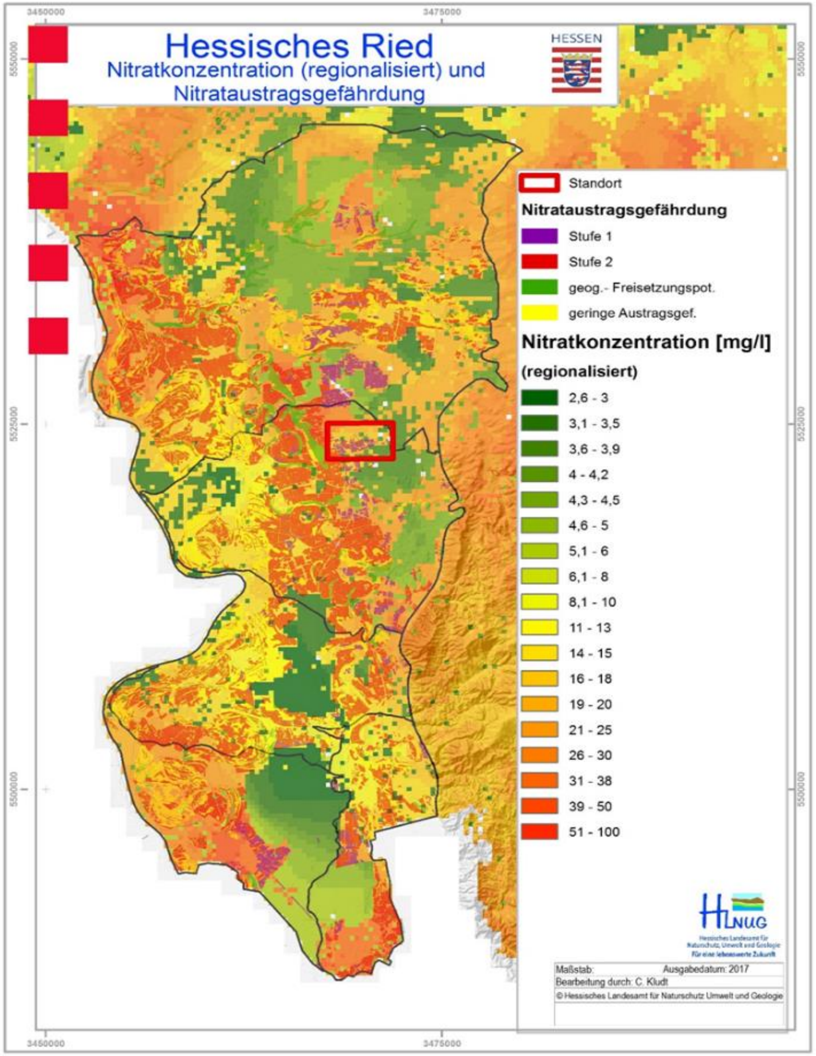


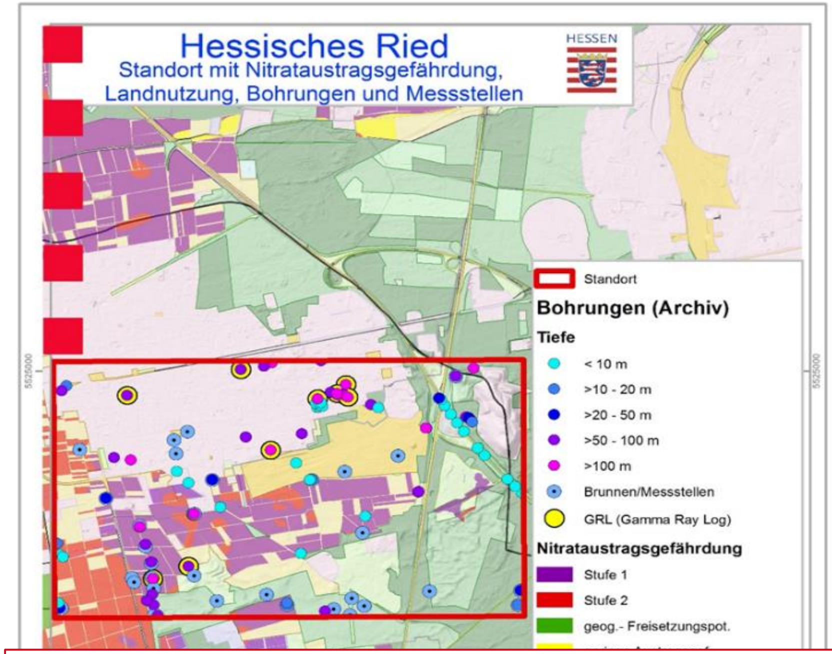


[HLNUG]

Hessian Ried

- ✓ High levels of organic matter and pyrite (FeS_2) in the sediments





what processes and reactions we need to take into account for a RT model?

[HLNUG]

Acid mine drainage

- ✓ In mines to extract metals:
  - ✓ Material is grinded and extracted by means of flotation techniques
  - ✓ Residues contain water and fine material composed by sulphures, e.g.
    - ✓ Pyrite (FeS_2), Galena (PbS, lead sulfide), Chalcopyrite ($CuFeS_2$), Zinc sulfide (ZnS)
    - ✓ Phases co-precipitated with heavy metals, e.g.
      - ✓ Instead of FeS_2: $Fe_{0.98}Cu_{0.02}S_2$
      - ✓ Instead of FeS_2: $FeS_{1.99}As_{0.01}$
  - ✓ Materials are stored in big ponds

Acid mine drainage

- ✓ Risk of spilling and negative environmental impact is strong

Acid drainage

Old mine

Acid mine drainage - processes

- O_2 transport **in unsaturated zone** for **diffusion**: $\mathbf{J}_{dif} = -\theta \mathbf{D}_0 \nabla c$
  ($D_{0,gas} \cong 10^5 D_{0,water}$)

  $\uparrow$ the dryer, the higher

- **Low pH triggers**:
  - **Carbonates dissolution** (relatively fast)
    $CaCO_{3(s)} + H^+ = Ca^{2+} + HCO_3^-$
  - **Silicates dissolution** (very slow)
    $KAl_3Si_3O_{10}(OH)_2 + 8H^+ + 2H_2O = K^+ + 3Al(OH)_2^+ + 3H_4SiO_4$
  - **Secundary minerals precipitation**
    Ferrihydrate ($Fe(OH)_3$): if pH not too low
    Gypsum ($CaSO_{4(s)}$): if there is Ca
    Jarosite ($KFe_3(SO_4)_2(OH)_6$)
    Melanterite ($FeSO_4$): very soluble mineral

Summary #1

- ✓ Groundwater geochemistry and reactive transport explore the processes controlling **groundwater quality**
- ✓ **Models** are **important to confirm** (**or discard**) **our interpretation** of reality **and** to **make predictions**
- ✓ Many types of geochemical calculations are possible, but today we have focused on **speciation** and **reactive transport**
- ✓ **Mass action laws** for equilibrium reactions: $$\frac{[\mathrm{C}]^{c}[\mathrm{D}]^{d}}{[\mathrm{A}]^{a}[\mathrm{B}]^{b}} = K_{eq}$$
- ✓ Activity: $a = \gamma \cdot c$
  (γ = activity coefficient)
- ✓ Activity = 1 for pure solid phases (e.g., minerals) and water

Summary #2

- Several **types of reactions**:
  - Acid-base reactions
  - Ion complexation
  - Mineral dissolution/precipitation
  - Sorption (ion-exchange, adsorption, absorption)
  - Redox reactions

- **Microorganisms** play a **key role in redox reactions**, especially in natural waters

- **Speciation: calculation of the concentrations of all the species** in a chemical system given
  - Data equations
  - Mass action laws

$$\begin{cases} \mathbf{g}(\mathbf{c}) - \mathbf{x} = \mathbf{0} \\ \mathbf{S}_e \log \mathbf{a} - \log \mathbf{k} = \mathbf{0} \end{cases}$$

- Iterative methods to solve speciation: Picard, Newton-Raphson

Summary #3

- ✓ **Solute mass balance equation for several species:**
  - ✓ in terms of concentrations

$$\frac{\partial \mathbf{c}}{\partial t} = -\nabla \cdot \left(\mathbf{q}\mathbf{c}\right) + \nabla \cdot \left(\mathbf{D}\nabla\mathbf{c}\right) + \mathbf{S}_e^t \mathbf{r}_e + \mathbf{S}_k^t \mathbf{r}_k$$

  - ✓ in terms of components $\mathbf{U}\frac{\partial \mathbf{c}}{\partial t} = \mathbf{U}L\left(\mathbf{c}\right) + \mathbf{U}\mathbf{S}_k^t \mathbf{r}_k$

  - ✓ **Solution algorithm for simple problem**
  - ✓ For more complex problem, iterative methods needed

- ✓ When we model **reactive transport** processes we need to **take into account:**
  - ✓ **Conservative transport processes** (advection, diffusion, dispersion)
  - ✓ **Reactions** (kinetic or equilibrium)

- ✓ The choice of the processes and reactions depends on the problem we want to simulate (e.g., uranium and nitrate contamination, acid mine drainage)