Geochemical and Reactive Transport modelling

1. Introduction

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Groundwater geochemistry and reactive transport explore the processes controlling groundwater quality

- 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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Max. value [mg/l]</th>
<th>Sources of contamination</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>0.01</td>
<td>Herbicide used on land and water</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.001</td>
<td>Plastic production, dry cleaning, solvents and paints</td>
</tr>
<tr>
<td>Cd</td>
<td>0.005</td>
<td>Mines and industrial effluents</td>
</tr>
<tr>
<td>Cr</td>
<td>0.05</td>
<td>Industrial effluents</td>
</tr>
<tr>
<td>F⁻</td>
<td>1.5</td>
<td>Steel and glass fiber industries</td>
</tr>
<tr>
<td>Pb</td>
<td>0.01</td>
<td>Industrial effluents</td>
</tr>
<tr>
<td>Hg</td>
<td>0.001</td>
<td>Hg minerals, combustion of coal and petroleum</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>50</td>
<td>Organic fertilizers</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>0.5</td>
<td>Organic fertilizers</td>
</tr>
<tr>
<td>Al</td>
<td>0.2</td>
<td>Fertilizers in tea plantation, soundproofing of tunnels</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>0.5</td>
<td>Landfill</td>
</tr>
<tr>
<td>Na⁺</td>
<td>200</td>
<td>NaCl brines</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>250</td>
<td>NaCl brines</td>
</tr>
<tr>
<td>pH</td>
<td>6.5 – 9.5</td>
<td>Acid rain, mines and industrial effluents</td>
</tr>
<tr>
<td>Fe</td>
<td>0.2</td>
<td>Mine drainage</td>
</tr>
<tr>
<td>Mn</td>
<td>0.05</td>
<td>Minerals of Mn</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>250</td>
<td>Oxidation of sulphides, brine lakes</td>
</tr>
</tbody>
</table>

Hydrogeochemical calculations are important to understand environmental processes

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

... 

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

[Steefel et al., 2005]
Hydrogeochemical calculations are important to understand geo-energy related applications

- Petroleum engineering
- CO₂ sequestration
- Conventional/unconventional gas extraction
- …

[http://www.globalccsinstitute.com]
Many types of geochemical calculations are possible, but today we focus on:

• Speciation

\[ \text{Equilibrium} \]

\[ [SO_4^{2-}] \]

\[ [Ca^{2+}]_{\text{known}} \]

\[ [Ca^{2+}] \]

\[ [SO_4^{2-}]_{\text{calc}} \]

• Reactive transport

\[ [Ca^{2+}] \]

\[ x \]

\[ t = t_1 \]

\[ t = t_2 \]
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)
Solute mass balance equation for one species in porous media

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

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

\( \mathbf{J}_{Ad} = qc \)

flow (e.g., Darcy) [L\(^3\) L\(^{-2}\) T\(^{-1}\)]
Solute mass balance equation for one species in porous media

\[
\frac{\partial \phi c}{\partial t} = -\nabla \cdot J_{Ad} - \nabla \cdot J_D \quad [M \, L^{-3} \, T^{-1}]
\]

✓ \( J_D \): diffusive + dispersive flux [M L^{-2} T^{-1}]

due to - concentration differences (diffusion)
- heterogeneity of velocity field (dispersion)

\[
J_D = J_{Dif} + J_{Disp} = -D \nabla c
\]

\[
\nabla c = \text{grad}(c) = \begin{pmatrix}
\frac{\partial c}{\partial x} \\
\frac{\partial c}{\partial y} \\
\frac{\partial c}{\partial z}
\end{pmatrix}
\]

![Diagram showing concentration profiles with lower peak and spreading](image)
Solute mass balance equation for one species in porous media

\[ \frac{\partial \phi c}{\partial t} = -\nabla \cdot J_{Ad} - \nabla \cdot J_D \]

With definition of \( J_{Ad} \) and \( J_D \)

\[ J_{Ad} = qc \]

\[ J_D = J_{Dif} + J_{Disp} = -D \nabla c \]

The conservative transport equation reads

\[ \frac{\partial \phi c}{\partial t} = -\nabla \cdot (qc) + \nabla \cdot (D \nabla c) \]
Reactive transport equation

Solute mass balance equation for one species in porous media

\[
\frac{\partial \phi c}{\partial t} = -\nabla \cdot (qc) + \nabla \cdot (Dc) + r_e + r_k
\]

✓ \( r_e \neq r_k \) \( \rightarrow \) difference between equilibrium and kinetic reactions

✓ \( r_k = f(c) \) \( \rightarrow \) explicit expression of concentrations

✓ Chemical reactions in nature commonly take place in presence of water

✓ Chemical reactions are represented by means of algebraic equations \( \rightarrow \) balance of masses and charges of reactants and products
Sodium chloride NaCl(s) dissolution in water at room temperature (25°C) and atmospheric pressure (1 atm)

\[ \text{NaCl}(s) = \text{Na}^+ + \text{Cl}^- \]

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

![Graph showing Na+ concentration over time with phases of disequilibrium and equilibrium marked.](image)
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

\[
A + B = C + D
\]

Rates: \( r_f = k_f (A)(B) \)  
\( r_b = k_b (C)(D) \)
\( (\cdot) = \text{conc.} \)

In general \( aA + bB = cC + dD \)

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

Mass action law

\( K_{eq} \) \text{ Equilibrium constant}

\[\text{=} \]

[\cdot] = activities
Mass action laws (MALs)

✓ Concept of activity very important for non ideal solutions

✓ Activity: \( a = \gamma c \)

For ideal solutions (infinite dilution): \( \gamma = 1 \)
For non ideal solutions: \( 0 < \gamma < 1 \)
For H\(_2\)O and pure solids: \( \gamma = 1 \)

✓ For a reaction \( aA + bB = cC + dD \)

two equivalent ways of writing MALs

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

\[
\frac{a^c}{a^a} \frac{a^d}{a^b} = K_{eq}
\]

Ion Activity Product (IAP)

At equilibrium: \( \text{IAP} = K_{eq} \)
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:

✓ **Solute** (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:
     \[5.02 \times 10^{-3} \text{ Ca}^{2+} \text{ mol/l} = 2 \times 5.02 \times 10^{-3} = 1.04 \times 10^{-2} \text{ eq/l Ca}^{2+}\])
  - 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
Several models exist for activity coefficients depending on ionic strength:

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

\[
\log \gamma_i = -A z_i^2 \sqrt{I}
\]

\[A = A(T)\]

\[A = 0.5085 @25^\circ C\]

2. Debye-Hückel extended \((I < 0.1)\)

\[
\log \gamma_i = -\frac{A z_i^2 \sqrt{I}}{1 + B a_i \sqrt{I}}
\]

\[B = B(T)\]

\[a_i = \text{effective diameter of the hydrated ion}\]

\[B = 0.3285e+10 @25^\circ C\]

3. Trusdell Jones \((I > 0.1)\)

\[
\log \gamma_i = -\frac{A z_i^2 \sqrt{I}}{1 + B a_i \sqrt{I}} + b_i I
\]

\[a_i, b_i = \text{ion specific fit parameters}\]
Activity coefficients

[Symbols: Debye-Hückel extended equation, lines: Trusdell Jones equation. Appelo and Postma, 2005]
For pure solid phases (e.g. minerals) $a=1$

✓ Example: anhydrite

$$\text{CaSO}_4(s) = \text{Ca}^{2+} + \text{SO}_4^{2-} \quad \log K_{eq} = -4.3064$$

$$\frac{a_{\text{Ca}^{2+}} \cdot a_{\text{SO}_4^{2-}}}{a_{\text{CaSO}_4(s)}} = a_{\text{Ca}^{2+}} \cdot a_{\text{SO}_4^{2-}} = K_{eq} = 10^{-4.3064}$$
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.
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
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

  \[
  \text{CH}_3\text{COOH} = \text{CH}_3\text{COO}^- + H^+ \quad \log K_{eq} = -4.755
  \]

- Neutrality of pure water:

  \[
  \text{H}_2\text{O} = \text{OH}^- + H^+ \quad \log K_{eq} = -14.0
  \]

  $a_{\text{OH}^-} = a_{H^+} = 10^{-7} \rightarrow pH = 7$
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

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

$$\log[\text{CaSO}_4^0] - \log[\text{Ca}^{2+}] - \log[\text{SO}_4^{2-}] = 2.5$$
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. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum), $\text{NaCl}$ (halite), $\text{CaF}_2$ (fluorite), carbonates such as $\text{CaCO}_3$ (calcite)
- **Some others are slow**, e.g. silicates such as $\text{Mg}_2\text{SiO}_4$ (forsterite), $\text{Al}_2\text{SiO}_5$ (andalusite)

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

- **Saturation index**: $\text{SI} = \log(\text{IAP}/K_{eq})$ 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

![Diagram showing ion exchange](image)

- 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:** \[2\text{Na}^+ + (\text{Ca-X}_2) = (\text{Na-X}) + \text{Ca}^{2+}\]

**Freshening:** \[\text{Ca}^{2+} + 2(\text{Na-X}) = (\text{Ca-X}_2) + 2\text{Na}^+\]

X: soil exchanger
Heterogeneous reactions

✓ **Adsorption:**

- Solid phases with a large specific area will adsorb the most $\rightarrow$ **adsorption capacity depends on grain size**
- Clay fractions ($< 2\mu m$) have **large specific area**

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

<table>
<thead>
<tr>
<th>Material</th>
<th>CEC, meq/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>30–150</td>
</tr>
<tr>
<td>Halloysite</td>
<td>50–100</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>800–1200</td>
</tr>
<tr>
<td>Vermiculite</td>
<td>1000–2000</td>
</tr>
<tr>
<td>Glaucnite</td>
<td>50–400</td>
</tr>
<tr>
<td>Illite</td>
<td>200–500</td>
</tr>
<tr>
<td>Chlorite</td>
<td>100–400</td>
</tr>
<tr>
<td>Allophane</td>
<td>up to 1000</td>
</tr>
<tr>
<td>Goethite and hematite:</td>
<td>up to 1000 (pH &gt; 8.3, discussed in Chapter 7)</td>
</tr>
<tr>
<td>Organic matter (C) or, accounting for pH-dependence:</td>
<td>1500–4000 (at pH = 8, discussed in Chapter 7)</td>
</tr>
<tr>
<td></td>
<td>$510 \times \text{pH} - 590 = \text{CEC}$ per kg organic carbon (Scheffer and Schachtschabel, 2002).</td>
</tr>
</tbody>
</table>

Appelo and Postma, 2005
Mass action laws apply, but activities of exchangeable ions have to be defined:

\[
2\text{Na}^+ + (\text{Ca-X}_2) = 2(\text{Na-X}) + \text{Ca}^{2+} \quad K_{Na/Ca} = \frac{[\text{Na-X}]^2[\text{Ca}^{2+}]}{[\text{Na}^+]^2[\text{Ca-X}_2]}
\]

\[
\beta_{Ca} = \frac{meq(\text{Ca-X}_2)}{CEC} = \frac{meq_{1-X_i}}{\sum_{1, j, k \ldots} meq_{1-X_i}} \quad [\text{Gaines-Thomas}]
\]

\[
\sum_m \beta_m = 1 \quad m = \text{number of exchangeable ions}
\]
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

- 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

  \[ Fe^{2+} = Fe^{3+} + e^- \]

- 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 $\text{H}_2\text{O}(l)$ in natural environments

$2\text{H}_2\text{O}(l) = 2\text{H}_2(g) + \text{O}(g) \quad \log K_{eq} = -83.1$

$\text{O}_2(g) + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$

$\text{H}_2(g) = 2\text{H}^+ + 2\text{e}^-$

Area in which all natural chemical reactions take place in presence of water at $25^\circ\text{C}$, 1atm

$2\log[\text{H}_2\text{O}] - \log[\text{O}_2(g)] - 4\log[\text{H}^+] - 4\log[\text{e}^-] = 83.1$

$pe = 20.78 - pH$

$ppe = pH$
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

![Elemental Composition of the Earth’s Crust](chart)

![Atmosphere composition](chart)
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

<table>
<thead>
<tr>
<th>Reaction</th>
<th>logK</th>
<th>$E_n^0$ [V]</th>
<th>$\Delta G_r^0$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2$ reduction</td>
<td>20.8</td>
<td>1.23</td>
<td>-118</td>
</tr>
<tr>
<td>Denitrification</td>
<td>21.0</td>
<td>1.24</td>
<td>-120</td>
</tr>
<tr>
<td>Mn(IV) reduction</td>
<td>20.9</td>
<td>1.24</td>
<td>-119</td>
</tr>
<tr>
<td>Fe(III) reduction</td>
<td>16.2</td>
<td>0.96</td>
<td>-92</td>
</tr>
<tr>
<td>Sulphate reduction</td>
<td>4.1</td>
<td>0.24</td>
<td>-24</td>
</tr>
<tr>
<td>$N_2$ reduction</td>
<td>4.7</td>
<td>0.28</td>
<td>-27</td>
</tr>
<tr>
<td>CO$_2$ reduction</td>
<td>3.80</td>
<td>0.23</td>
<td>-22</td>
</tr>
<tr>
<td>OM oxidation</td>
<td></td>
<td>-0.8</td>
<td>4</td>
</tr>
<tr>
<td>Sulphur oxidation</td>
<td></td>
<td>-4.1</td>
<td>24</td>
</tr>
<tr>
<td>Fe(II) oxidation</td>
<td></td>
<td>-16.2</td>
<td>92</td>
</tr>
<tr>
<td>Nitrification</td>
<td></td>
<td>-14.9</td>
<td>85</td>
</tr>
<tr>
<td>Mn(II) oxidation</td>
<td></td>
<td>-20.9</td>
<td>119</td>
</tr>
</tbody>
</table>

- $NO_3^-$ $\rightarrow$ $N_2(g)$
- Mn(IV) $\rightarrow$ Mn(II)
- Fe(III) $\rightarrow$ Fe(II)
Redox sequence in natural waters

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

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G_r^0$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$ reduction</td>
<td>$e^- + 0.25O_2(g) + H^+ = 0.5H_2O$</td>
</tr>
<tr>
<td>Denitrification</td>
<td>$e^- + 0.2NO_3^- + 1.2H^+ = 0.1 N_2(g) + 0.6H_2O$</td>
</tr>
<tr>
<td>Mn(IV) reduction</td>
<td>$e^- + MnO_2(s) + 1.5H^+ + 0.5HCO_3^- = MnCO_3(s) + H_2O$</td>
</tr>
<tr>
<td>Fe(III) reduction</td>
<td>$e^- + FeOOH(s) + 2H^+ + HCO_3^- = FeCO_3(s) + 2H_2O$</td>
</tr>
<tr>
<td>Sulphate reduction</td>
<td>$e^- + 0.125SO_4^{2-} + 1.125H^+ = 0.125 HS^- + 0.5H_2O$</td>
</tr>
<tr>
<td>N$_2$ reduction</td>
<td>$e^- + 0.167N_2(g) + 1.333H^+ = 0.333NH_4^+$</td>
</tr>
<tr>
<td>CO$_2$ reduction</td>
<td>$e^- + 0.125HCO_3^- + 1.125H^+ = 0.125 CH_4(g) + 0.25H_2O$</td>
</tr>
<tr>
<td>OM oxidation</td>
<td>$0.25 CH_2O + 0.25H_2O = e^- + 0.25HCO_3^- + 1.25H^+$</td>
</tr>
<tr>
<td>Sulphur oxidation</td>
<td>$0.125 HS^- + 0.5H_2O = e^- + 0.125SO_4^{2-} + 1.125H^+$</td>
</tr>
<tr>
<td>Fe(II) oxidation</td>
<td>$FeCO_3(s) + 2H_2O = e^- + FeOOH(s) + 2H^+ + HCO_3^-$</td>
</tr>
<tr>
<td>Nitrification</td>
<td>$0.125NH_4^+ + 0.375H_2O = e^- + 0.2NO_3^- + 1.2H^+$</td>
</tr>
<tr>
<td>Mn(II) oxidation</td>
<td>$MnCO_3(s) + H_2O = e^- + MnO_2(s) + 1.5H^+ + 0.5HCO_3^-$</td>
</tr>
</tbody>
</table>
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$_2$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>logK</th>
<th>$\Delta G_r^0$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Aerobic respiration</strong></td>
<td>20.0</td>
<td>-114</td>
</tr>
<tr>
<td>$0.25$CH$_2$O + 0.25O$_2$(g) =</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$0.25$HCO$_3^-$ + 0.25H$^+$</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Denitrification</strong></td>
<td>20.3</td>
<td>-116</td>
</tr>
<tr>
<td>$0.25$CH$_2$O + 0.2NO$_3^-$ =</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$0.25$HCO$_3^-$ + 1.25H$^+$ + 0.1 N$_2$(g) + 0.6H$_2$O</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Mn(IV) reduction</strong></td>
<td>20.1</td>
<td>-115</td>
</tr>
<tr>
<td>$0.25$CH$_2$O + 0.5MnO$_2$(s) +</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$0.25$H$^+$ + 0.25HCO$_3^-$ =</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$0.5$MnCO$_3$(s) + 0.5H$_2$O</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Fe(III) reduction</strong></td>
<td>15.4</td>
<td>-88</td>
</tr>
<tr>
<td>$0.25$CH$<em>2$O + FeOOH$</em>{(s)}$ +</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$0.75$H$^+$ + 0.75HCO$_3^-$ =</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeCO$_3$(s) + 1.5H$_2$O</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Sulphate reduction</strong></td>
<td>3.4</td>
<td>-19</td>
</tr>
<tr>
<td>$0.25$CH$_2$O + 0.125SO$_4^{2-}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$0.25$HCO$_3^-$ + 0.125 H$^+$</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Methanogenesis</strong></td>
<td>3.1</td>
<td>-18</td>
</tr>
<tr>
<td>$0.25$CH$_2$O + 0.125H$_2$O =</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$0.125$HCO$_3^-$ + 0.125 CH$_4$(g) + 0.125H$^+$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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 \((\text{NO}_3^-\text{valence} = +5)\) and proceeds through a complicated pathway with several metastable intermediates

\[
\text{NO}_3^- \rightarrow \text{NO}_2 \rightarrow \text{NO} \rightarrow \text{N}_2\text{O}_2(\text{g}) \rightarrow \text{N}_2(\text{g})
\]

- **Denitrification** is a non-reversible reaction
Mass Action Laws (MALs): Matrix notation

✓ Normal notation:

- \( \text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-} \)  \( \log(a_{\text{H}^+}) + \log(a_{\text{CO}_3^{2-}}) - \log(a_{\text{HCO}_3^-}) = \log k_1 \)
- \( \text{H}_2\text{CO}_3 = 2\text{H}^+ + \text{CO}_3^{2-} \)  \( 2\log(a_{\text{H}^+}) + \log(a_{\text{CO}_3^{2-}}) - \log(a_{\text{H}_2\text{CO}_3}) = \log k_2 \)

✓ Matrix notation:  \( S_e \log a - \log k = 0 \)

\[
\begin{pmatrix}
1 & 1 & -1 & 0 \\
2 & 1 & 0 & -1
\end{pmatrix}
\begin{pmatrix}
\log a_{\text{H}^+} \\
\log a_{\text{CO}_3^{2-}} \\
\log a_{\text{HCO}_3^-} \\
\log a_{\text{H}_2\text{CO}_3}
\end{pmatrix} =
\begin{pmatrix}
\log k_1 \\
\log k_2
\end{pmatrix}
\]

\( S_e (N_{re} \times N_s) = \) Eq. stoichiometric matrix
\( a(N_s) = \) Activities vector \( (a_i = \gamma_i c_i) \)
\( k(N_{re}) = \) 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 equations: \[ g(c) - x = 0 \] \( (N_1) \)

✔ MALs: \[ S_e \log a - \log k = 0 \] \( (N_2) \)

✔ \( N^0 \) of unknowns = \( N_s = N_1 + N_2 \)

✔ \( N^0 \) of equations = \( N_s = N_1 + N_2 \)

\[ \text{nº of data} = \text{nº of independent variables} \ (N_1 = N_s - N_{re}) \]

✔ 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 $A(x)x = b(x)$
  - Iterative system is solved for $x^{i+1}$ in which $A$ and $B$ depend on $x^i$

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

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

  $$J^i(x^{i+1} - x^i) = -f^i$$

where $J^i$ is the Jacobian matrix and $f$ is the residual vector.
Both methods can diverge: discretization has to be changed, or new “starting point” $x^0$ has to be chosen.
Convergence criteria

- Maximum absolute error of the unknown

\[
\left| X^{i+1} - X^i \right|_{\text{max}} < \varepsilon_{x,\text{abs}}
\]

- Maximum relative error of the unknown

\[
\left| \frac{X^{i+1} - X^i}{X^{i+1}} \right|_{\text{max}} < \varepsilon_{x,\text{rel}}
\]

- Residual value of the equation

\[
\left| A X^{i+1} - b^{i+1} \right|_{\text{max}} < \varepsilon_{eq}
\]
How to solve a speciation problem

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

\[
c = \begin{pmatrix} c_1 \\ c_2(c_1) \end{pmatrix}
\]

Primary conc.

\[
c = \begin{pmatrix} c_1 \\ c_2(c_1) \end{pmatrix}
\]

Secondary conc. (function of \(c_1\) through MALs)

✓ Secondary species concentrations can be expressed as function of \(c_1\) through mass action laws

✓ MALs can then be rewritten as

\[
S_{e1} \log a_1 + S_{e2} \log a_2 - \log k = 0
\]

\[
a = \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}
\]

✓ \(a_2\) then reads

\[
\log a_2 = -(S_{e2})^{-1} S_{e1} \log a_1 + (S_{e2})^{-1} \log k
\]

\[
= S^* \log a_1 + \log k^*
\]

✓ Careful: \(S_{e2}\) must be invertible!
✓ For a simple chemical system:

- \( \text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-} \)
  \[ \log(a_{\text{H}^+}) + \log(a_{\text{CO}_3^{2-}}) - \log(a_{\text{HCO}_3^-}) = \log K_1 \]

- \( \text{H}_2\text{CO}_3 = 2\text{H}^+ + \text{CO}_3^{2-} \)
  \[ 2\log(a_{\text{H}^+}) + \log(a_{\text{CO}_3^{2-}}) - \log(a_{\text{H}_2\text{CO}_3}) = \log K_2 \]

\[ \begin{pmatrix} \log a_{\text{H}^+} \\ \log a_{\text{CO}_3^{2-}} \\ \log a_{\text{HCO}_3^-} \\ \log a_{\text{H}_2\text{CO}_3} \end{pmatrix} = \begin{pmatrix} 1 & 1 & -1 & 0 \\ 2 & 1 & 0 & -1 \end{pmatrix} \begin{pmatrix} \log K_1 \\ \log K_2 \end{pmatrix} \]

\[ \log a_2 = -\left( \begin{pmatrix} 1 \\ 1 \\ -1 \\ 0 \end{pmatrix} \right)^{-1} \begin{pmatrix} 1 & 0 \\ 1 & 1 \\ -1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \log K_1 \\ \log K_2 \end{pmatrix} \]

\[ \log(a_{\text{HCO}_3^-}) = \log(a_{\text{H}^+}) + \log(a_{\text{CO}_3^{2-}}) - \log K_1 \]
\[ \log(a_{\text{H}_2\text{CO}_3}) = 2\log(a_{\text{H}^+}) + \log(a_{\text{CO}_3^{2-}}) - \log K_2 \]
Newton-Raphson algorithm for speciation

- If there is explicit expression for chemistry: \( \log c_2 = S^* \log c_1 + \log k^* \)

  a: \( f = g(c) - x = c_1 + (S^*)^T \cdot c_2(c_1) - x = 0 \)  
  - Aqueous total concentrations

  b: \( f = c_1 - c_1^{measured} = 0 \) or \( f = c_2(c_1) - c_2^{measured} = 0 \)  
  - Measured concentrations

- Newton-Raphson: \( J^i \left( c_1^{i+1} - c_1^i \right) = -f^i \) (*)

  where \( J^i = \frac{\partial f}{\partial c_1^i} = I + S^{*T} \frac{\partial c_2}{\partial c_1^i} \)
Newton-Raphson algorithm for speciation

- If there is explicit expression for chemistry: \( \log c_2 = S^* \log c_1 + \log k^* \)

a: \( f = g(c) - x = c_1 + (S^*)^T \cdot c_2(c_1) - x = 0 \)

b: \( f = c_1 - c_1^{\text{measured}} = 0 \) or \( f = c_2(c_1) - c_2^{\text{measured}} = 0 \)

- Newton-Raphson: \( J^i \left( c_1^{i+1} - c_1^i \right) = -f^i \) (*)

0: Set \( c_1^0 \)

1: \( J^i = \frac{\partial f}{\partial c_1^i} = I + (S^*)^T \frac{\partial c_2}{\partial c_1^i} \)

where \( \frac{\partial c_2}{\partial c_1} = \frac{c_2}{c_1} \frac{\partial \ln c_2}{\partial \ln c_1} \)

2: Solve system (*) to calculate \( c_1^1 \)

3: Check convergence (see previous slide)

4: If convergence not reached: set \( c_1^i = c_1^1 \), go back to 1, solve again
If there is NO explicit expression for chemistry: another non-linear system has to be solved to calculate $c_2 = f(c_1)$

$$\log c_2 + \log \gamma_2 = S^* \log (c_1 + \gamma_1) + \log k^*$$

$$\log \gamma_i = -\frac{Az_i^2 \sqrt{I}}{1 + Ba_i \sqrt{I}} + bI \quad I = \frac{1}{2} \sum_i c_i z_i^2$$

Two systems to calculate $c_2$ and $\partial c_2/\partial c_1$

$$\frac{\partial f_{MAL}}{\partial c_2} (c_{2}^{j+1} - c_{2}^{j}) = -f_{MAL}$$

$$\frac{\partial f_{MAL}}{\partial c_2} \frac{\partial c_2}{\partial c_1} = - \frac{\partial f_{MAL}}{\partial c_1} \quad \frac{df_{MAL}}{dc_1} = 0 = \frac{\partial f_{MAL}}{\partial c_2} \frac{\partial c_2}{\partial c_1} + \frac{\partial f_{MAL}}{\partial c_1}$$

To solve:

1. Newton-Raphson with components and chemistry (Ns unknowns)
2. Picard: $\gamma^{i+1} = \gamma(c^i)$
Geochemical and Reactive Transport modelling

4. Reactive transport
Reactive transport equation

Solute mass balance equation for one species in porous media

\[
\frac{\partial \phi c}{\partial t} = -\nabla \cdot (qc) + \nabla \cdot (D \nabla c) + r_e + r_k
\]

- \( r_e \neq r_k \) -> 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”
Solute mass balance equation for several species in porous media, with equilibrium and kinetic reactions ($\phi = \text{const}$)

$$\frac{\partial c}{\partial t} = -\nabla \cdot (qc) + \nabla \cdot (D \nabla c) + S^t_e r_e + S^t_k r_k$$

**Reactive transport equation**

- For aqueous species:
  $$L(.) = -\frac{q}{\phi} \nabla (.). + \frac{1}{\phi} \nabla D \nabla (.).$$
  $$c(N_s) = \text{Conc. vector}$$
  $$S_e (N_{re} \times N_s) = \text{Eq. stoichiometric matrix}$$
  $$r_e (N_{re}) = \text{Eq. rates vector}$$

- For solid species:
  $$L(.) = 0$$
  $$S_k (N_{rk} \times N_s) = \text{Kin. stoichiometric matrix}$$
  $$r_k (N_{rk}) = \text{Kin. rates vector}$$
Solute mass balance equation for several species in porous media, with equilibrium and kinetic reactions ($\phi = \text{const}$)

\[
\frac{\partial c}{\partial t} = -\nabla \cdot (qc) + \nabla \cdot (D\nabla c) + S'_e r_e + S'_k r_k
\]

$\nabla \cdot$ Linear operator

$\nabla \cdot$ Equilibrium reactions

$\nabla \cdot$ Kinetic reactions

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

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

$S_k (N_{rk} \times N_s) = \text{Kin. stoichiometric matrix}$

$r_e (N_{re}) = \text{Eq. rates vector}$

$r_k (N_{rk}) = \text{Kin. rates vector}$
Solute mass balance equation for several species in porous media, with equilibrium and kinetic reactions ($\phi = \text{const}$)

$$\frac{\partial c}{\partial t} = -\nabla \cdot (qc) + \nabla \cdot (D\nabla c) + S_e^t r_e + S_k^t r_k$$

**Linear operator**

$$L(c)$$

**Equilibrium reactions**

$S_e^t r_e$

**Kinetic reactions**

$S_k^t r_k$

$c(N_s)$ = Conc. vector

$S_e (N_{re} \times N_s)$ = Eq. stoichiometric matrix

$S_k (N_{rk} \times N_s)$ = Kin. stoichiometric matrix

$r_e (N_{re})$ = Eq. rates vector

$r_k (N_{rk})$ = Kin. rates vector

What are the unknowns in this system?
Equations:

1. $N_s$ transport equations

\[ \frac{\partial c}{\partial t} = L(c) + S_e^t r_e + S_k^t r_k \]

2. $N_{re}$ mass action laws

\[ S_e \log c = \log k \]

Unknowns:

1. $c (N_s)$
2. $r_e (N_{re})$  

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!

To simplify we suppose $a = c$
How to eliminate $r_e$

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

$$CaSO_{4(s)} = Ca^{2+} + SO_4^{2-} \quad \log K = -4.48$$

(1): \[ \frac{d[Ca^{2+}]}{dt} = L([Ca^{2+}]) + r_e \]
(2): \[ \frac{d[SO_4^{2-}]}{dt} = L([SO_4^{2-}]) + r_e \]
(3): \[ \frac{d[CaSO_{4(s)}]}{dt} = -r_e \]

(4): \[ \log[Ca^{2+}] + \log[SO_4^{2-}] = \log K \]

1st Linear combination of mass balance

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

(2) + (3): \[ \frac{d[SO_4^{2-}]}{dt} + \frac{d[CaSO_{4(s)}]}{dt} = L([SO_4^{2-}]) \]

(4): \[ \log[Ca^{2+}] + \log[SO_4^{2-}] = \log K \]

2nd Linear combination of mass balance

\[ \frac{d[Ca^{2+}]}{dt} - \frac{d[SO_4^{2-}]}{dt} = L([Ca^{2+}]) - L([SO_4^{2-}]) \]
How to eliminate $r_e$

1<sup>st</sup> Linear combination of mass balance

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

\[
(2) + (3) : \frac{d[SO_{4}^{2-}]}{dt} + \frac{d[CaSO_{4(s)}]}{dt} = L([SO_{4}^{2-}])
\]

2<sup>nd</sup> Linear combination of mass balance

\[
\frac{d[Ca^{2+}]}{dt} - \frac{d[SO_{4}^{2-}]}{dt} = L([Ca^{2+}]) - L([SO_{4}^{2-}])
\]

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

✓ 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: $u_1 = [Ca^{2+}] + [CaSO_{4(s)}]$
   $u_2 = [SO_{4}^{2-}] + [CaSO_{4(s)}]$

1. We have 1 equation in 1 variable: $u_1 = [Ca^{2+}] - [SO_{4}^{2-}]$
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: $u = (u_1 \ u_2)^T$

✓ Definition: $u = U \ast c$

✓ U is called “component matrix”

✓ U is defined in such a way that: $US_e^T = 0$

✓ U dimension: $(N_s-N_re) \times N_s = N_c \times N_s$

✓ $N_c = \text{number of components (u dimension)}$
Elimination of equilibrium reaction rates ($r_e$)

- From the definition of the component matrix: $US_e^t = 0$
- Multiplying transport equation times $U$:

$$U \frac{\partial c}{\partial t} = UL(c) + US_e^t r_e + US_k^t r_k$$

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

Unknowns:
1. $c$ ($N_s$)

The component matrix eliminates equilibrium reaction rates ($r_e$), reducing the number of unknowns
How do we calculate $U$?

- Dividing $S_e$ in $S_{e1}$ and $S_{e2}$:

$$S_e = \begin{pmatrix} S_{e1} & S_{e2} \end{pmatrix}$$

- And building the component matrix as follows:

$$U = \begin{pmatrix} I \mid -S_{e1}^T \left( S_{e2}^T \right)^{-1} \end{pmatrix}$$

$$(S^*)^T$$

- $r_e$ can therefore be eliminated:

$$U (S_e)^T = 0 \Rightarrow \begin{pmatrix} I \mid -S_{e1}^T \left( S_{e2}^T \right)^{-1} \end{pmatrix} \begin{pmatrix} S_{e1}^T \\ S_{e2}^T \end{pmatrix} = S_{e1}^T - S_{e1}^T \left( S_{e2}^T \right)^{-1} S_{e2}^T = 0$$

**Note**: Remember

$$\log a_2 = -\left( S_{e2} \right)^{-1} S_{e1} \log a_1 + \left( S_{e2} \right)^{-1} \log k$$

$$= S^* \log a_1 + \log k^*$$
How do we calculate $U$?

$$U(S_e)^T = 0 \Rightarrow \left( I - S_{e1}^T S_{e2}^{-T} \right) \begin{pmatrix} S_{e1}^T \\ S_{e2}^T \end{pmatrix} = 0$$

Example:

1. $\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$
2. $\text{H}_2\text{CO}_3 = 2\text{H}^+ + \text{CO}_3^{2-}$

$$S_{e1} = S^* \quad S_{e2}$$

$$U = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - \begin{pmatrix} 1 & 2 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}^{-1} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 2 \\ 1 & 1 \end{pmatrix} (S^*)^T$$
Meaning of total concentrations of components (u)

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

\[ u = Uc \]

\[ u = \begin{pmatrix} H^+ & CO_3^{2-} & HCO_3^- & H_2CO_3 \\ 1 & 0 & 1 & 2 \end{pmatrix} \begin{pmatrix} c_{H^+} \\ c_{CO_3^{2-}} \\ c_{HCO_3^-} \\ c_{H_2CO_3} \end{pmatrix} = \begin{pmatrix} c_{H^+} + c_{HCO_3^-} + 2c_{H_2CO_3} \\ c_{CO_3^{2-}} + c_{HCO_3^-} + c_{H_2CO_3} \end{pmatrix} \]

- Total H conc.
- TIC

If there are no kinetic reactions and all species are aqueous \( \rightarrow \) RT equation becomes analogous to conservative transport equation in u

\[ \frac{\partial u}{\partial t} = L(u) \]
Example of RT problem:

✓ Simplifying: \( a = c \)

1. \( \text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-} \)
2. \( \text{H}_2\text{CO}_3 = 2\text{H}^+ + \text{CO}_3^{2-} \)

✓ Equations to be solved (6):

\[
\frac{\partial}{\partial t} \begin{pmatrix} c_{\text{H}^+} \\ c_{\text{CO}_3^{2-}} \\ c_{\text{HCO}_3^-} \\ c_{\text{H}_2\text{CO}_3} \end{pmatrix} = L \begin{pmatrix} c_{\text{H}^+} \\ c_{\text{CO}_3^{2-}} \\ c_{\text{HCO}_3^-} \\ c_{\text{H}_2\text{CO}_3} \end{pmatrix} + \begin{pmatrix} r_1 + 2r_2 \\ r_1 + r_2 \\ -r_1 \\ -r_2 \end{pmatrix}
\]

\[
\frac{c_{\text{H}^+} c_{\text{CO}_3^{2-}}}{c_{\text{HCO}_3^-}} = K_1
\]

\[
\frac{c^2_{\text{H}^+} c_{\text{CO}_3^{2-}}}{c_{\text{H}_2\text{CO}_3}} = K_2
\]

✓ Unknowns (6):  \( c_{\text{H}^+}, c_{\text{CO}_3^{2-}}, c_{\text{HCO}_3^-}, c_{\text{H}_2\text{CO}_3}, r_1, r_2 \)
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:

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

$$\frac{c_{H^+}^2 \cdot c_{CO_3^{2-}}}{c_{H_2CO_3^-}} = K_2 \Rightarrow c_{H_2CO_3^-} = \frac{c_{H^+}^2 \cdot c_{CO_3^{2-}}}{K_2}$$
We can substitute MALs into components definition:

\[
\frac{\partial}{\partial t} \left( \begin{array}{c}
    c_{H^+} + \frac{c_{H^+} c_{CO_3^{2-}}}{K_1} + 2 \frac{c_{H^+}^2 c_{CO_3^{2-}}}{K_2} \\
    c_{CO_3^{2-}} + \frac{c_{H^+} c_{CO_3^{2-}}}{K_1} + \frac{c_{H^+}^2 c_{CO_3^{2-}}}{K_2}
\end{array} \right) = L \left( \begin{array}{c}
    c_{H^+} + \frac{c_{H^+} c_{CO_3^{2-}}}{K_1} + 2 \frac{c_{H^+}^2 c_{CO_3^{2-}}}{K_2} \\
    c_{CO_3^{2-}} + \frac{c_{H^+} c_{CO_3^{2-}}}{K_1} + \frac{c_{H^+}^2 c_{CO_3^{2-}}}{K_2}
\end{array} \right)
\]

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: $\text{HCO}_3^-$ = $\text{H}^+$ + $\text{CO}_3^{2-}$
  - R2: $\text{H}_2\text{O}$ = $\text{H}^+$ + $\text{OH}^-$
  - R3: $\text{CaCO}_3(s)$ = $\text{Ca}^{2+}$ + $\text{CO}_3^{2-}$
  - R4: $X_2\text{Ca}$ + $2\text{Na}^+$ = $2X\text{Na}$ + $\text{Ca}^{2+}$

- **Stoichiometric matrix**

<table>
<thead>
<tr>
<th></th>
<th>$\text{Ca}^{2+}$</th>
<th>$\text{HCO}_3^-$</th>
<th>$\text{Na}^+$</th>
<th>$X\text{Na}$</th>
<th>$\text{O}^-$</th>
<th>$\text{CaCO}_3(s)$</th>
<th>$X_2\text{Ca}$</th>
<th>$\text{H}^+$</th>
<th>$\text{OH}^-$</th>
<th>$\text{CO}_3^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>R2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>R3</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>R4</td>
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<td>0</td>
<td>-2</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

- **Component matrix**

<table>
<thead>
<tr>
<th></th>
<th>$\text{Ca}^{2+}$</th>
<th>$\text{HCO}_3^-$</th>
<th>$\text{Na}^+$</th>
<th>$X\text{Na}$</th>
<th>$\text{O}^-$</th>
<th>$\text{CaCO}_3(s)$</th>
<th>$X_2\text{Ca}$</th>
<th>$\text{H}^+$</th>
<th>$\text{OH}^-$</th>
<th>$\text{CO}_3^{2-}$</th>
</tr>
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<tbody>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>R2</td>
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<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>-1</td>
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</tr>
<tr>
<td>R3</td>
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<td>0</td>
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<td>0</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>0</td>
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</tr>
<tr>
<td>R4</td>
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<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

- Aqueous
- Solid
With more complex chemical system

✓ Total concentrations of components: \( u = u_a + u_s \)

\[
\frac{\partial u_a}{\partial t} + \frac{\partial u_s}{\partial t} = L\left(u_a\right)
\]

\[
u = u_a + u_s = \begin{pmatrix}
c_{Ca^{2+}} + c_{H^+} - c_{OH^-} - c_{CO_3^{2-}} \\
c_{HCO_3^-} + c_{H^+} - c_{OH^-} \\
c_{Na^+} \\
c_{H_2O} + c_{OH^-} \\
-c_{H^+} + c_{OH^-} + c_{CO_3^{2-}}
\end{pmatrix}
\]

\[
+ \begin{pmatrix}
c_{X_{2Ca}} \\
0 \\
-2c_{X_{2Ca}} \\
c_{X_{Na}} + 2c_{X_{2Ca}} \\
0 \\
c_{CaCO_3}
\end{pmatrix}
\]

✓ 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.
✓ 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
Uranium isotopes exist.

- with half-lives varying between 159,200 years and 4.5 billion years

- Uranium is redox sensitive

- Unfortunately, uranium mining and processing were done with little consideration for the environment
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]
what processes and reactions we need to take into account for a RT model?

[Saaltink and Carrera, notes from RT courses]
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 (NO₃⁻) in groundwater
  -> very heterogeneous distribution of NO₃⁻
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?
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 mine drainage - processes

- O$_2$ transport in unsaturated zone for diffusion: $J_{\text{dif}} = -\theta D_0 \nabla c$
  $(D_{0,\text{gas}} \approx 10^5 D_{0,\text{water}})$

- Low pH triggers:
  - Carbonates dissolution (relatively fast)
    $\text{CaCO}_3(s) + H^+ = \text{Ca}^{2+} + \text{HCO}_3^-$
  - Silicates dissolution (very slow)
    $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 + 8H^+ + 2\text{H}_2\text{O} = \text{K}^+ + 3\text{Al(OH)}_2^+ + 3\text{H}_4\text{SiO}_4$
  - Secondary 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
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:

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

Activity: \( a = \gamma \cdot c \)

(\( \gamma \) = activity coefficient)

Activity = 1 for pure solid phases (e.g., minerals) and water
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

\[
\begin{align*}
\text{g(c) - x} &= 0 \\
S_e \log a - \log k &= 0
\end{align*}
\]

**Iterative methods to solve speciation**: Picard, Newton-Raphson
Summary #3

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

\[
\frac{\partial c}{\partial t} = - \nabla \cdot (qc) + \nabla \cdot (D \nabla c) + S'_{e} r_{e} + S'_{k} r_{k}
\]

✓ in terms of components

\[
U \frac{\partial c}{\partial t} = UL(c) + US'_{k} r_{k}
\]

✓ 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)