Geochemical Modeling With PHREEQC
Outline and Objectives

• Introduction to geochemical modeling concepts and PHREEQC
• Overview of the *PHREEQC for Windows* interface
• Learn how to create PHREEQC input files
What geochemical processes determine the chemistry of natural waters?

- Aqueous speciation
- Mineral dissolution and precipitation
- Ion exchange and sorption
- (Bio-)geochemical redox reactions
- (Mixing)
Groundwater Chemical Evolution

from: Custodio, 1987
Geochemical Processes
# What Information Can Be Extracted From a Water Analysis?

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How to make a sensible interpretation of water quality?
Geochemical Models - Quantitative Tools to Improve Understanding

Quantitative models force the investigator to validate or invalidate ideas by putting real numbers into an often vague hypothesis, ...

_from_ Lichtner et al., 1996
What Is a Geochemical Model?

Input Solution Composition

- SO$_4$
- Ca
- Mg
- Na
- Cl
- Fe
- HCO$_3$

Speciation calculation

Saturation Indices

Distribution of Species

Inverse modeling (mass balance)

Reaction modeling (mass transfer)

Reactive transport modeling
Concentration Units in PHREEQC

- Internally, PHREEQC uses moles and moles/kg_{water}
- Can define concentrations in mole/kg, mole/L, ppm, mg/L in input file; program converts to moles/kg_{w}
- mg/L can lead to confusion (NO_{3} vs NO_{3}-N)
- all reactions are defined in moles
- PHT3D requires use of moles exclusively
Law of Mass Action

\[ aA + bB \leftrightarrow cC + dD \]

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

\[ CaSO_4 \cdot 2H_2O \leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O \]

(gypsum)

\[ K = \frac{[Ca^{2+}][SO_4^{2-}][H_2O]^2}{[CaSO_4 \cdot 2H_2O]} = 10^{-4.60} \]
Concentration and Activity

• Activity $\neq$ concentration
• Why?
  – Ions interact
  – Ion-solvent (water) interactions - electrostatic shielding
  – Ion-ion interactions - aqueous complexes and ion pairs
Electrostatic shielding

\[ [Ca^{2+}] = \gamma_{Ca^{2+}} \cdot m_{Ca^{2+}} \]

Debye – Huckel:

\[
\log \gamma_i = -0.5085z_i^2 \left( \frac{\sqrt{l}}{1 + \sqrt{l}} - 0.3l \right)
\]

\[ l = \frac{1}{2} \sum m_i \cdot z_i^2 \]

Pretty straightforward, can be done by hand...
Activity Coefficients

- Effect of a single ion in solution cannot be measured directly (charge balance)
- Mean Ion Activity Coefficient – determined for a salt (e.g. KCl, MgSO₄):
  \[ \gamma_{\pm \text{KCl}} = \sqrt{\gamma_{\text{K}^+} \gamma_{\text{Cl}^-}} \]
  \[ K_{sp} = \gamma_{\pm \text{KCl}}^2 m_{\text{K}^+} m_{\text{Cl}^-} \]
- MacInnes Convention: \[ \gamma_{\pm \text{KCl}} = \gamma_{\text{K}^+} = \gamma_{\text{Cl}^-} \]
- Measure other salts in KCl electrolyte and substitute \[ \gamma_{\pm \text{KCl}} \] in for one ion to measure the other ion w.r.t. \[ \gamma_{\pm \text{KCl}} \] and \[ \gamma_{\pm \text{salt}} \]
Debye-Hückel

\[ \log \gamma_i = \frac{-Az_i^2 \sqrt{l}}{1 + Ba_i \sqrt{l}} \]

- \( z_i \) is charge of ion
- \( a_i \) is effective diameter of ion (in angstroms)
- A and B are “constants”: A=0.5085, B=0.3281 for water at 25° C.

- Assumes ions interact coulombically, ion size does not vary with ionic strength, and ions of same sign do not interact
- Accurate up to \( I = 0.1 \) M (most fresh waters)
Higher Ionic Strengths

• Activity coefficients decrease to minimal values around 1 - 10 M, then increase again
  – the fraction of water molecules surrounding ions in hydration spheres becomes significant
  – Activity of water decreases $\rightarrow$ in a 5 M NaCl solution, $\sim1/2$ of the H$_2$O is complexed, decreasing the activity to 0.8
  – Ion pairing also increases, further increasing the activity effects (e.g. NaCl$^0$)
Davies Equation

\[
\log \gamma_i = -Az_i^2 \left( \frac{\sqrt{l}}{1 + \sqrt{l}} - 0.3l \right)
\]

- No ion size parameter – only really accurate for monovalent ions \((z_i=\pm 1)\)
- Often used for seawater (working range up to 0.7 M)
Extended Debye-Hückel (WATEQ)

\[ \log \gamma_i = -Az^2 \left( \frac{-Az_i^2 \sqrt{I}}{1 + Ba_i \sqrt{I}} - b_i I \right) \]

- Adds a correction term to account for increase of \( \gamma_i \) at higher ionic strength.
Pitzer Activity Coefficients

- Accurate for high ionic strength (>1 M)

\[
\ln \gamma_M = z_M^2 F + \sum_{a} m_a (2B_{Ma} + ZC_{Ma}) + \sum_{c} m_c (\Phi_{Mc} + \sum_{a} M_a \psi_{Mca}) + \\
\sum_{a < a'} m_a m_{a'} \psi_{aa'} + |z_m| \sum_{c} \sum_{a} m_c m_a C_{ca}
\]

- \(m_a\) is concentration of anion
- \(m_c\) is concentration of cation
- \(C, B, \Phi, \Psi\) are ion-specific parameters
- \(f^\gamma\) is a function of \(l\), molalities of cations and anions
Specific Ion Interaction Theory (SIT) Activity Coefficients

- Ion and electrolyte-specific approach for activity coefficients
- Limited data, assumes no interaction with neutral species

\[
\ln \gamma_i = Az_i^2 \frac{\sqrt{l}}{1 + B\sqrt{l}} + \sum_k \varepsilon_{ik} m_k
\]

- \( \varepsilon_{ik} \): interaction parameter
- \( m_k \): concentration of ion \( k \)
- \( A = 0.51, B = 1.5 \) at 25°C
Setchenow Equation

\[ \log \gamma_i = K_i I \]

- For neutral (uncharged) species such as dissolved gases, weak acids, and organic species
- \( K_i \) is generally <0.2
- \( \gamma_i > 1 \), meaning that if a reaction is at equilibrium, \( m_i \) must decrease with increasing \( I \) (“salting out” effect)
Aqueous Complexes and Ion Pairs

\[ m_{Ca} = m_{Ca^{2+}} + m_{CaOH^+} + m_{CaCO_3^0} + m_{CaSO_4^0} \]
\[ + m_{CaPO_4^-} + m_{CaF^+} + \ldots \]

Cannot be calculated by hand...
Enter aqueous geochemical models!
How Do Yo Do It?

- Solve simultaneous equations for:
  - mass action
  - mass balance
  - charge balance
- Numerically solved by iteration (until convergence is reached)
Aqueous Models

Ion association (D-H, Davies)

- **Pros**
  - Data available for most elements (Al, Si)
  - Redox species
  - Relatively easy to add new elements

- **Cons**
  - Ionic strength < 1
  - Best suited for Na-Cl medium
  - Inconsistent thermodynamic data
  - Temperature dependence
Aqueous Models

Pitzer

• Pros
  – Accurate to high ionic strength
  – Thermodynamic consistency for mixtures of electrolytes

• Cons
  – Limited number of elements
  – Very limited redox
  – Difficult to add new elements
  – Limited data on temperature dependence
Aqueous Models

SIT

• Pros
  – Better option than ion association for higher ionic strength
  – Fewer parameters than Pitzer
  – Redox
  – Actinides

• Cons
  – Temperature dependence
  – Consistency?
Saturation states

Solubility Product:  \( K_{\text{gypsum}} = [Ca^{2+}][SO_4^{2-}] \)

Ion Activity Product:  \( IAP_{\text{gypsum}} = [Ca^{2+}][SO_4^{2-}] \)

At equilibrium:  \( K_{\text{gypsum}} = IAP_{\text{gypsum}} \)

\[
SI_{\text{gypsum}} = \log \left( \frac{IAP_{\text{gypsum}}}{K_{\text{gypsum}}} \right) = 0
\]

Supersaturated:  \( SI_{\text{gypsum}} > 0 \)

Undersaturated:  \( SI_{\text{gypsum}} < 0 \)
Seawater Speciation


A CHEMICAL MODEL FOR SEA WATER AT 25°C AND ONE ATMOSPHERE TOTAL PRESSURE*

R. M. GARRELS and M. E. THOMPSON

Department of Geological Sciences, Harvard University, Cambridge, Massachusetts

ABSTRACT. Dissociation constants involving Ca++, Mg++, Na+, K+, SO₄⁻, HCO₃⁻, and CO₃⁻ ions, and individual ion activity coefficients have been used to calculate the distribution of dissolved species in sea water at 25°C and one atmosphere total pressure. The distribution obtained for sea water of chlorinity 19‰ and pH 8.1 are:

<table>
<thead>
<tr>
<th>Ion</th>
<th>Molality (Total)</th>
<th>% Free Ion</th>
<th>% Me-SO₄⁻ pair</th>
<th>% Me-HCO₃⁻ pair</th>
<th>% Me-CO₃⁻ pair</th>
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<td>Ca++</td>
<td>0.0104</td>
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<td>8</td>
<td>1</td>
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<td>Mg++</td>
<td>0.0340</td>
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<td>Na⁺</td>
<td>0.4752</td>
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<td>0.01</td>
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<tr>
<td>K⁺</td>
<td>0.0100</td>
<td>99</td>
<td>1</td>
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</table>

<table>
<thead>
<tr>
<th>Ion</th>
<th>Molality (Total)</th>
<th>% Free Ion</th>
<th>% Ca-anion pair</th>
<th>% Mg-anion pair</th>
<th>% Na-anion pair</th>
<th>% K-anion pair</th>
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<td>CO₃⁻</td>
<td>0.000269</td>
<td>9</td>
<td>7</td>
<td>67</td>
<td>17</td>
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</table>

The activities calculated for free ions are $a_{\text{Ca}^{++}} = 0.00264$, $a_{\text{Mg}^{++}} = 0.0169$, $a_{\text{Na}^+} = 0.356$, $a_{\text{K}^+} = 0.0063$, $a_{\text{CO}_3^{--}} = 4.7(10^{-4})$, $a_{\text{HCO}_3} = 9.75 (10^{+4})$, $a_{\text{SO}_4^{--}} = 1.79(10^{+2})$. 
Seawater Speciation

Result  $SI_{\text{calcite}} = 0.4$
PHREEQC: What Can It Do?

- Developed by David Parkhurst and Tony Apello
- Calculate the equilibrium composition of a system (speciation)
- Calculate the change in composition in response to reactions
  - Mineral/gas equilibria
  - Ion exchange
  - Surface complexation
  - Kinetic reactions (time-dependent)
- Calculate the change in composition in response to 1-D transport (and reactions)
Thermodynamic Databases in PHREEQC

- phreeqc.dat
- wateq4f.dat
- llnl.dat
- minteq.dat
- pitzer.dat
- sit.dat
- iso.dat
PHREEQC Thermodynamic Databases

• SOLUTION_MASTER_SPECIES—Redox states and gram formula mass
• SOLUTIONSPECIES—Reaction and log K
• PHASES—Reaction and log K
Optional:
• EXCHANGE_MASTER_SPECIES—Names
• EXCHANGESPECIES—Reaction and log K
• SURFACE_MASTER_SPECIES—Names
• SRFACE_SPECIES—Reaction and log K
Thermodynamic Databases

\[ \Sigma(\text{As}) = 10^{-7} \]

**wateq.dat**

- \( \text{H}_3\text{AsO}_4^- \)
- \( \text{H}_2\text{AsO}_4^- \)
- \( \text{H}_3\text{AsO}_3^- \)
- \( \text{AsO}_4^{3-} \)

**llnl.dat**

- \( \text{H}_3\text{AsO}_4(\text{aq}) \)
- \( \text{H}_2\text{AsO}_4^- \)
- \( \text{HAsO}_4^{2-} \)
- \( \text{AsO}_4^{3-} \)

Eh (volts) vs pH at 25°C
Thermodynamic Databases

\[ \Sigma(\text{As}) = 10^{-7} \]
\[ \Sigma(\text{S}) = 10^{-3} \]
Where Does the Thermodynamic Data Come From?

**As$_2$S$_3$ Solubility**

![Graph showing comparison of predicted and measured arsenic concentrations in equilibrium with As$_2$S$_3$.](image)

**Figure 1.** Comparison of predicted and measured arsenic concentrations in equilibrium with As$_2$S$_3$.


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**Table 1.** Optimized equilibrium model for As$_2$S$_3$ solubility in aqueous sulfide solutions at 25°C.

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<th>Reaction</th>
<th>log K (s.e.)</th>
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<tr>
<td>As$_2$S(s) + 6 H$_2$O = 2 H$_2$AsO$_5^-$ + 3 HS$^-$ + 5 H$^+$</td>
<td>-64.66 (0.12)</td>
</tr>
<tr>
<td>Webster (synthetic orpiment)</td>
<td>-64.66 (0.12)</td>
</tr>
<tr>
<td>Mironova (natural orpiment)</td>
<td>-64.72 (0.25)</td>
</tr>
<tr>
<td>Neuberger (natural orpiment)</td>
<td>-64.70 (0.44)</td>
</tr>
<tr>
<td>Eary (amorphous As$_2$S$_3$)</td>
<td>-62.51 (0.40)</td>
</tr>
<tr>
<td>H$_2$AsO$_4^-$ = H$_2$AsO$_5^-$ + H$^+$</td>
<td>-9.17$^*$</td>
</tr>
<tr>
<td>H$_2$AsO$_4^-$ = HAAsO$_3^{2-}$ + H$^+$</td>
<td>-14.06$^*$</td>
</tr>
<tr>
<td>H$_2$AsO$_4^-$ = AsO$_3^{3-}$ + 2 H$^+$</td>
<td>-29.05$^*$</td>
</tr>
<tr>
<td>H$_2$AsS$_4^-$ + 3 H$_2$S = H$_2$AsS$_3^-$ + 3 H$_2$O</td>
<td>7.75 (0.44)</td>
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<tr>
<td>H$_2$AsS$_4^-$ = H$_2$AsS$_3^-$ + H$^+$</td>
<td>-2.14 (0.46)</td>
</tr>
<tr>
<td>H$_2$AsS$_4^-$ = HAAsS$_3^{2-}$ + H$^+$</td>
<td>-7.19 (0.39)</td>
</tr>
<tr>
<td>H$_2$AsO$_4$ + H$_2$S = H$_2$AsSO$_3$ + H$_2$O</td>
<td>4.68 (0.18)</td>
</tr>
<tr>
<td>H$_2$AsSO$_4$ = H$_2$AsSO$_3^-$ + H$^+$</td>
<td>-5.26 (0.26)</td>
</tr>
</tbody>
</table>


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**PhreePlot:**

PHREEQC with fitting

(www.phreeplot.org)
Sorption Reaction Databases

- Measured sorption edges, isotherms for Cd and Pb for three different soils
- Used PEST to fit universal set of log K’s for ion exchange on clays, sorption of Fe-oxides
- Tested transferability on isotherm data for fourth soil

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Serrano et al (2009) GCA
PHREEQC for Windows (PfW)

• Graphic interface developed by Vincent Post
• Based on PHREEQC version 2.xx
• Includes:
  – input editor
  – output editor
  – database editor
  – basic spreadsheet
  – graphical output (USER_GRAPH)
TITLE Example 2.--Temperature dependence of solubility of gypsum and anhydrite
5 SOLUTION 1 Pure water
4 pH 7.0
5 temp 25.0
6 EQUILIBRIUM PHASES 1
7 Gypsum 0.0 1.0
8 Anhydrite 0.0 1.0
9 REACTION TEMPERATURE 1
10 25.0 75.0 in 51 steps
11 SELECTED_OUTPUT
12 -file ex2.sel
13 -si anhydrite gypsum
14 USER_GRAPH
15 -headings Temperature SI(Gypsum) SI(Anhydrite)
16 -chart_title "Example 2"
17 axis_scale x_axis 25 75
18 axis_scale y_axis -0.3 0.1
19 axis_titles "TEMPERATURE IN DEGREES CELSIUS" "SATURATION INDEX"
20 -initial_solutions false
21 -start
22 10 graph_x TC
23 20 graph_y SI("Gypsum") SI("Anhydrite")
24 -end
25 END
PHREEQC Keywords

- Start
  - COPY
  - DATABASE
  - END
  - SAVE
  - SOLUTION
  - SOLUTION_SPREAD
  - TITLE
  - USE

- Chemical reaction
  - EQUILIBRIUM_PHASES
  - EXCHANGE
  - GAS_PHASE
  - INCREMENTAL_REACTIONS
  - INVERSE_MODELING
  - REACTION
  - HEAT_TREAT
  - HTR
  - SURFACE

- Physical action
  - ADVECTION
  - MIX
  - TRANSPORT

- Output
  - PRINT
  - SELECTED_OUTPUT
  - USER_GRAPH
  - USER_PRINT
  - USER_PUNCH

- PHREEQC BASIC statements
  - GENERAL BASIC statements
SOLUTION 1  Seawater
  temp     25
  pH       7
  pe       4
  redox    pe
  units    ppm
  density  1
  Ca       412.3
  Mg       1291.8
  Na       10768
  K        399.1
  Fe       0.002
  Alkalinity 141.682 as HCO3
  Cl       19353
  S(6)     2712
  -water   1 # kg
<table>
<thead>
<tr>
<th>pH</th>
<th>Cl</th>
<th>S(6)</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>K</th>
<th>Alkalinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.23</td>
<td>5050</td>
<td>498</td>
<td>149</td>
<td>290</td>
<td>2440</td>
<td>98.2</td>
<td>301 mg/l as CaCO3</td>
</tr>
<tr>
<td>6.04</td>
<td>5600</td>
<td>516</td>
<td>154</td>
<td>296</td>
<td>2740</td>
<td>105</td>
<td>214</td>
</tr>
<tr>
<td>6.17</td>
<td>4880</td>
<td>397</td>
<td>154</td>
<td>278</td>
<td>2550</td>
<td>90.9</td>
<td>299</td>
</tr>
<tr>
<td>5.91</td>
<td>8880</td>
<td>578</td>
<td>157</td>
<td>299</td>
<td>2610</td>
<td>91.2</td>
<td>138</td>
</tr>
<tr>
<td>6.00</td>
<td>7660</td>
<td>800</td>
<td>159</td>
<td>328</td>
<td>2700</td>
<td>91.5</td>
<td>133</td>
</tr>
</tbody>
</table>
SOLUTION or SOLUTION_SPREAD

- Distribution of species
- Saturation indices
- Initial conditions for reaction path calculations
- Initial/final compositions for inverse modeling
- Initial and boundary conditions for reactive-transport modeling
MIX

MIX
1 0.75
2 0.25

EQUILIBRIUM_PHASES

EQUILIBRIUM_PHASES 1
Calcite 0 0
Dolomite 0 1.5
CO2(g) -2.0
EXCHANGE

EXCHANGE 1
    -equil with solution 1
X       1.0

SURFACE

SURFACE 1
    -equil solution 1
# assume 1/10 of iron is HFO
Hfo_w     0.07    600.    30.
REACTION

CH2O  1
10 mmol in 10 steps

KINETICS

KINETICS 1
K-feldspar
-m0  2.16  # 10% K-fsp, 0.1 mm cubes
-m  1.94
-parms 1.36e4  0.1
RATES

K-feldspar

-start

10 dif_temp = 1/TK - 1/298
20 pk_H = 12.5 + 3134 * dif_temp
30 pk_w = 15.3 + 1838 * dif_temp
40 pk_OH = 14.2 + 3134 * dif_temp
50 pk_CO2 = 14.6 + 1677 * dif_temp
60 rate = 10^-pk_H * ACT("H+")^0.5 + 10^-pk_w + 10^-pk_OH * ACT("OH-")^0.3
70 rate = rate + 10^-pk_CO2 * (10^SI("CO2(g)")^0.6
80 moles = parm(1) * parm(2) * rate * (1 - SR("K-feldspar")) * time
90 if SR("K-feldspar") > 1 then moles = moles * 0.1
100 save moles
-end
SAVE

SOLUTION 1
REACTION 1

NaCl 1
1.0 mol
SAVE solution 10
END

USE

USE solution 10
EQUILIBRIUM_PHASES 21
   CO2(g)  -3.5
SAVE solution 11
SAVE equilibrium_phases 11
END
SELECTED_OUTPUT

SELECTED_OUTPUT
-file r11.csv
-reset false
-reaction
-totals O(0) C(4) C(-4) Fe(3) Fe(2) S(6) S(-2)
-equilibrium_phases mackinawite

USER_PUNCH

USER_PUNCH
-head pH Ca_mg/L Mg_mg/L
-start
10 PUNCH -la("H+")
20 PUNCH TOT("Ca")*40.1*1e3
30 PUNCH TOT("Mg")*24.3*1e3
-end
USER_GRAPH

-heading time Si
-axis_titles YEARS CONCENTRATION
-headings Years
-axis_scale y_axis 0 1.e-4
-axis_scale x_axis 0 10
-start
10 graph_x total_time/3.1536e7  # time in years on x-axis
20 graph_y tot("Si") # parameter on y-axis
-end
Additional Keyword Data Blocks

SOLUTION_MASTER_SPECIES
SOLUTION_SPECIES

EXCHANGE_MASTER_SPECIES
EXCHANGE_SPECIES

SURFACE_MASTER_SPECIES
SURFACE_SPECIES

PHASES
INVERSE_MODELING

INVERSE_MODELING 1
-solutions 10 5
-uncertainty 0.1
-phases
  pyrite
  Fe(OH)$_3$(a)
  H$_2$O(g)
  Calcite
  OC
  CaX2
  KX
  NaX
-balances
  Alkalinity 0.05 0.05
  C 0.05 0.05
  Ca 0.05 0.05
  Cl 0.05 0.05
  Fe 0.05 0.05
  Mg 0.05 0.05
  Na 0.05 0.05
  S 0.05 0.05
PHREEQC Transport Calculations

Advection

1 2 3 4 5 6 ... n

Dispersion/
Diffusion

1 2 3 4 5 6 ... n

Reaction

1 2 3 4 5 6 ... n