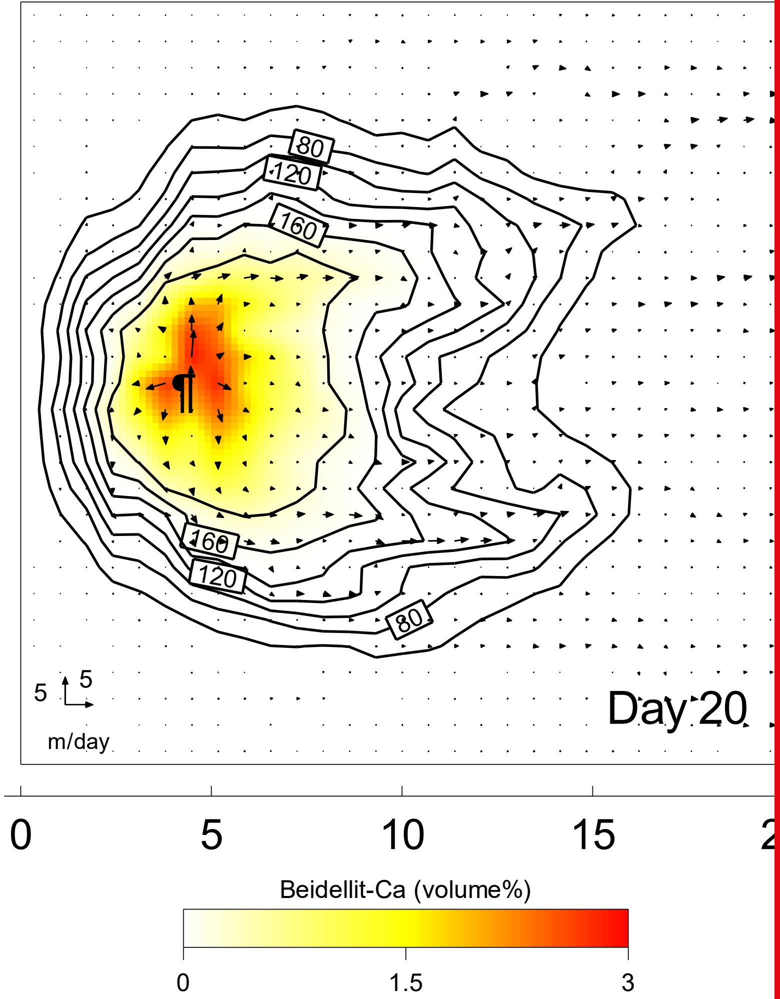

Geochemical modeling II

ENV-200

Meret Aeppli

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Last lecture-recap

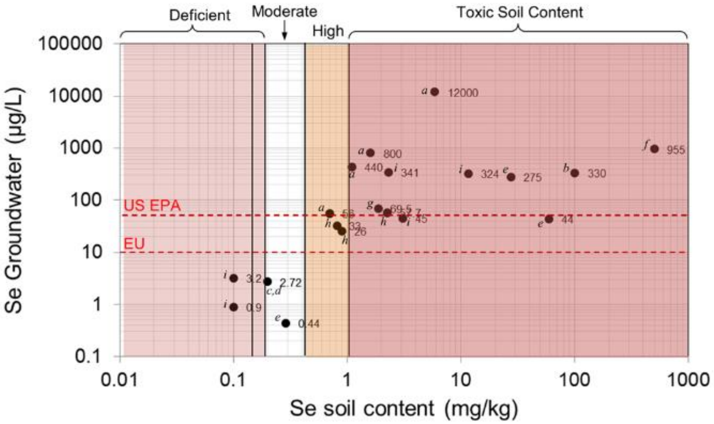
We discussed what geochemical modeling is useful for.

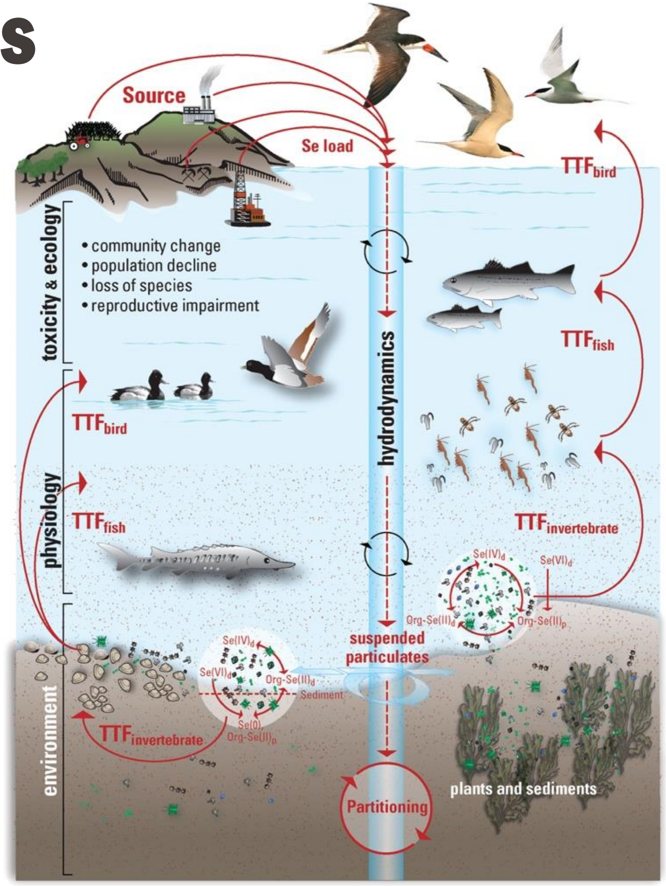
We started exploring the Geochemist’s Workbench.

Today, we will continue working with the Geochemist’s Workbench. We will also estimate how fast the Dreimühlen waterfall is growing.

Act2: Create stability diagrams

- Why is it important to understand Se speciation?
- Selenium is a trace element. It is an essential element as it forms part of enzymes but is toxic in high concentrations.
- The environmental contamination of selenium is a growing global concern due to rapidly increasing quantities being introduced by modern agricultural, mining, and energy generation practices.
- The bioavailability and therefore toxicity are highly contingent on the selenium species in question.





Bailey, RT, Hydrogeol J, ***2017****, 25:1191-1217.*

Luoma, NL and Presser, TS, Environ Sci Technol, ***2009****, 43(22), 8483-8487.*

Create an E_H-pH diagram with Act2

Start the program and move to the Basis pane:

1. Under “diagram species”, click on “???” and select “SeO3−−”. Set activity to 10^-6.
2. Under “on axes”, for “on x axis” click on “???” and select “H+”. Change the unit from “log activity” to “pH”. The axis automatically spans from 0 to 14, but you can adjust the range.
3. For “on y axis” click on “???” and select “O2(aq)”. Click on the swap button next to the basis entry for “O2(aq)” and select Aqueous…→ e−. Change the unit from “log activity” to “Eh”.

Configure your diagram on the **Basis** pane

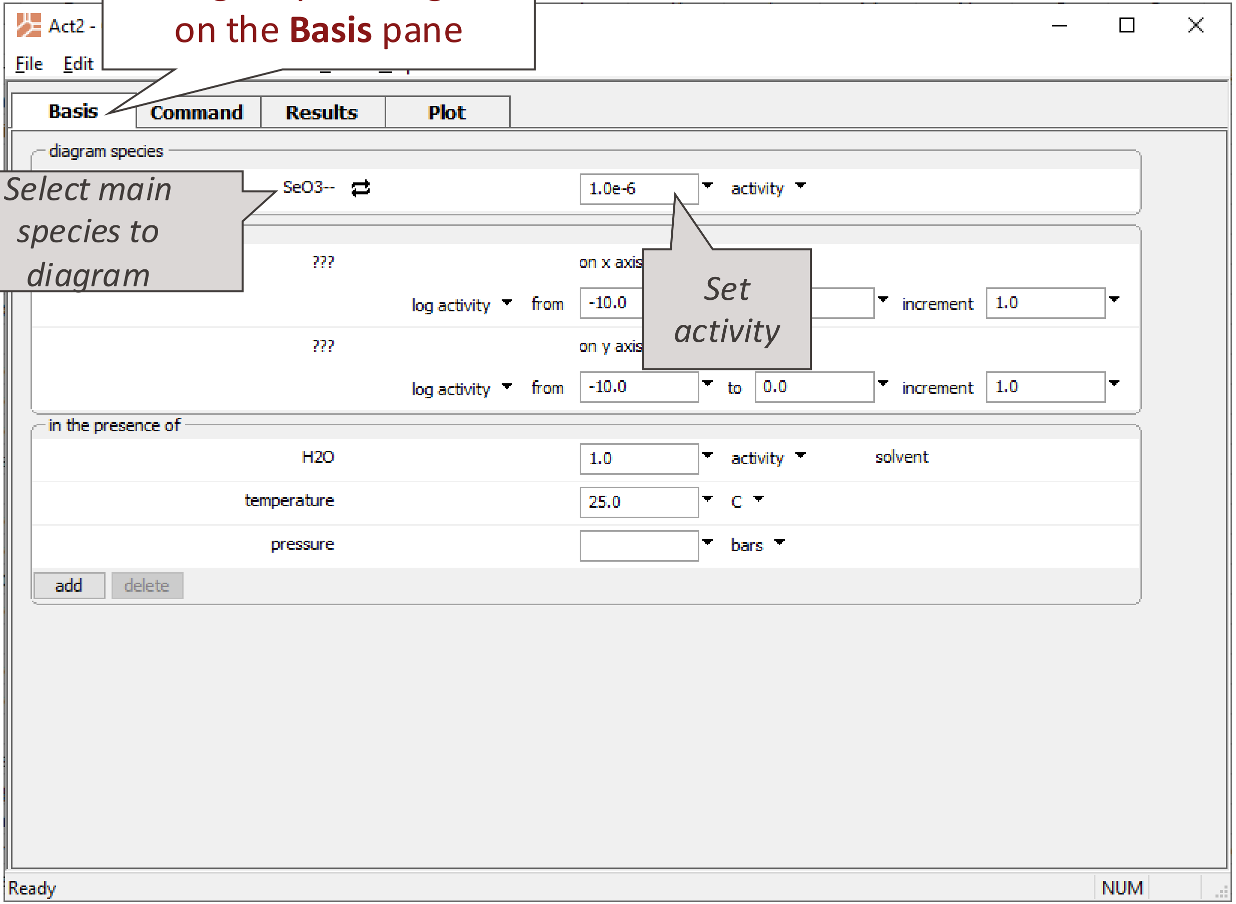


diagram species

SeO3-- 1.0e-6 activity

??? on x axis

log activity from -10.0 increment 1.0

??? on y axis

log activity from -10.0 to 0.0 increment 1.0

in the presence of

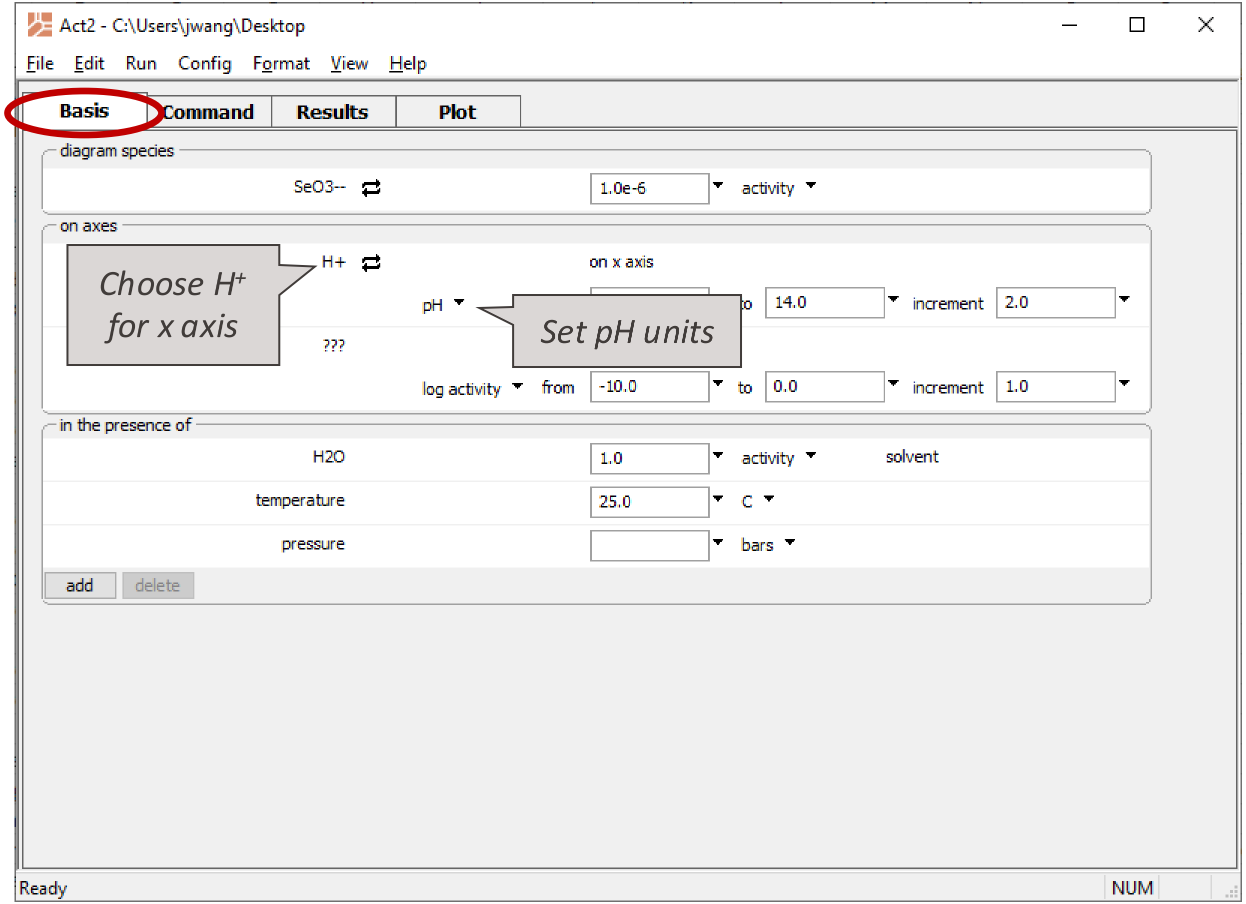
H2O 1.0 activity solvent

temperature 25.0 C

pressure bars

Select main species to diagram

Set activity



Act2 - C:\Users\jwang\Desktop

diagram species

SeO3-- 1.0e-6 activity

on axes

H+ on x axis

pH to 14.0 increment 2.0

???

log activity from -10.0 to 0.0 increment 1.0

in the presence of

H2O 1.0 activity solvent

temperature 25.0 C

pressure bars

Choose H^+ for x axis

Set pH units

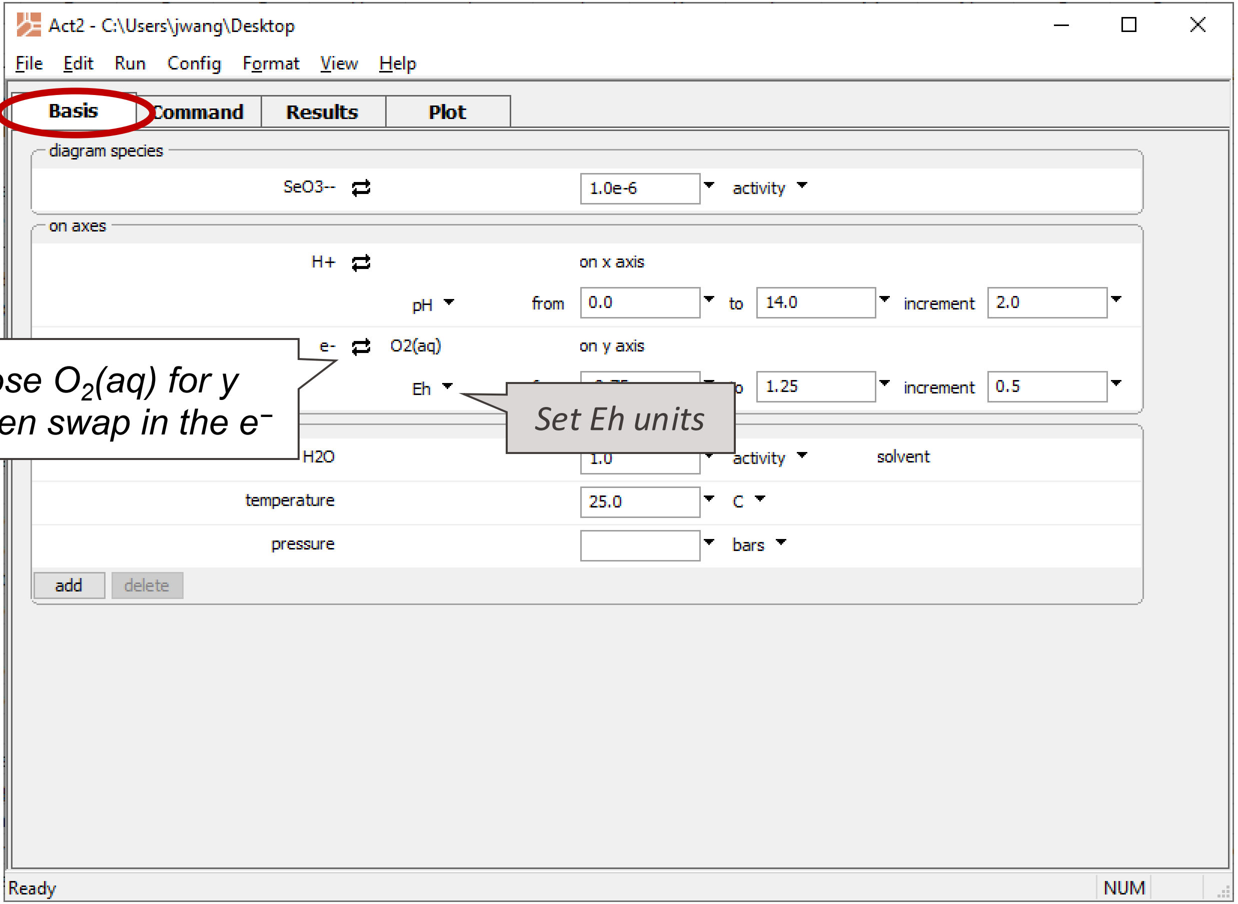


diagram species

SeO3-- 1.0e-6 activity

on axes

H+ on x axis

pH from 0.0 to 14.0 increment 2.0

e- O2(aq) on y axis

Eh to 1.25 increment 0.5

H2O 1.0 activity solvent

temperature 25.0 C

pressure bars

Choose O_2(aq) for y axis, then swap in the e^-

Set Eh units

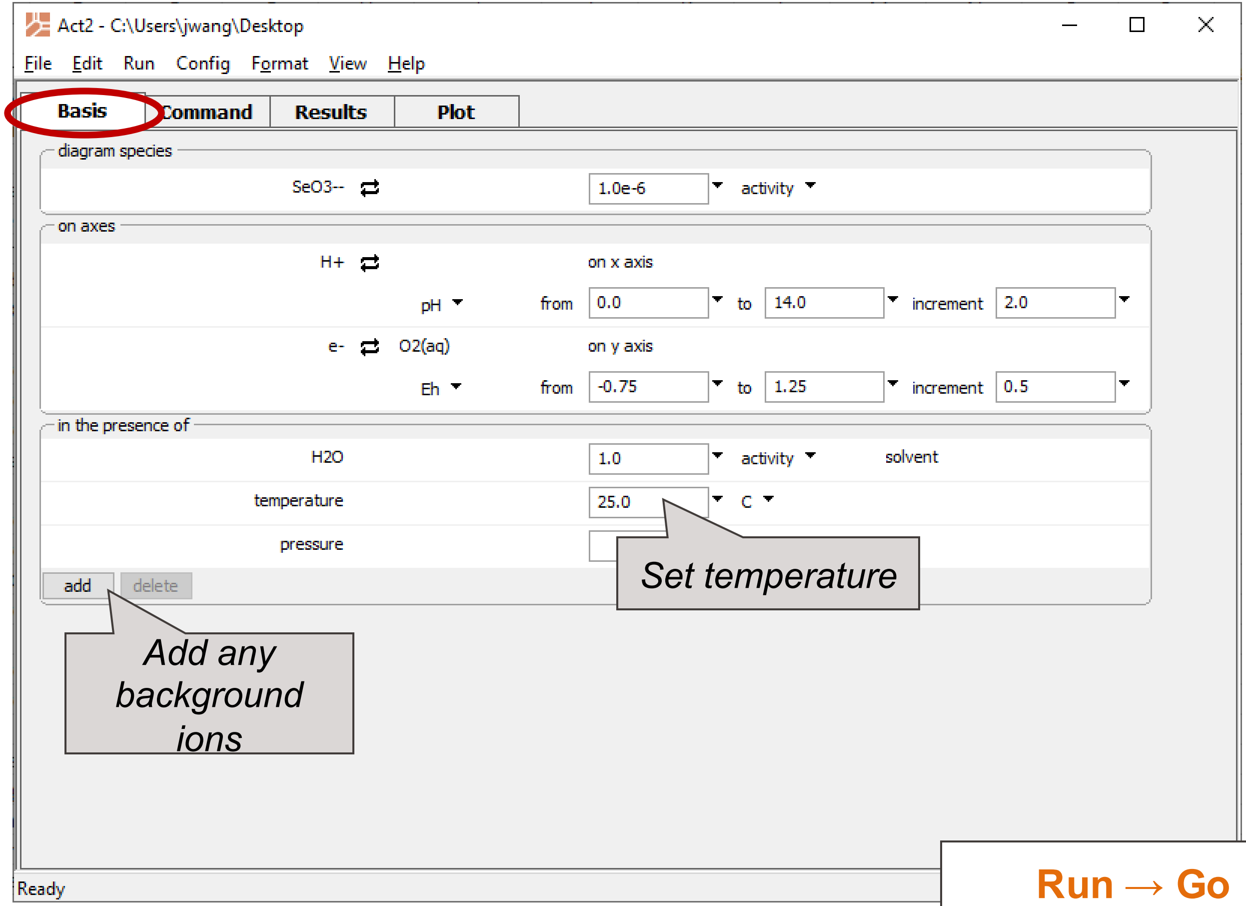


diagram species

SeO3-- 1.0e-6 activity

on axes

H+ on x axis

pH from 0.0 to 14.0 increment 2.0

e- O2(aq) on y axis

Eh from -0.75 to 1.25 increment 0.5

in the presence of

H2O 1.0 activity solvent

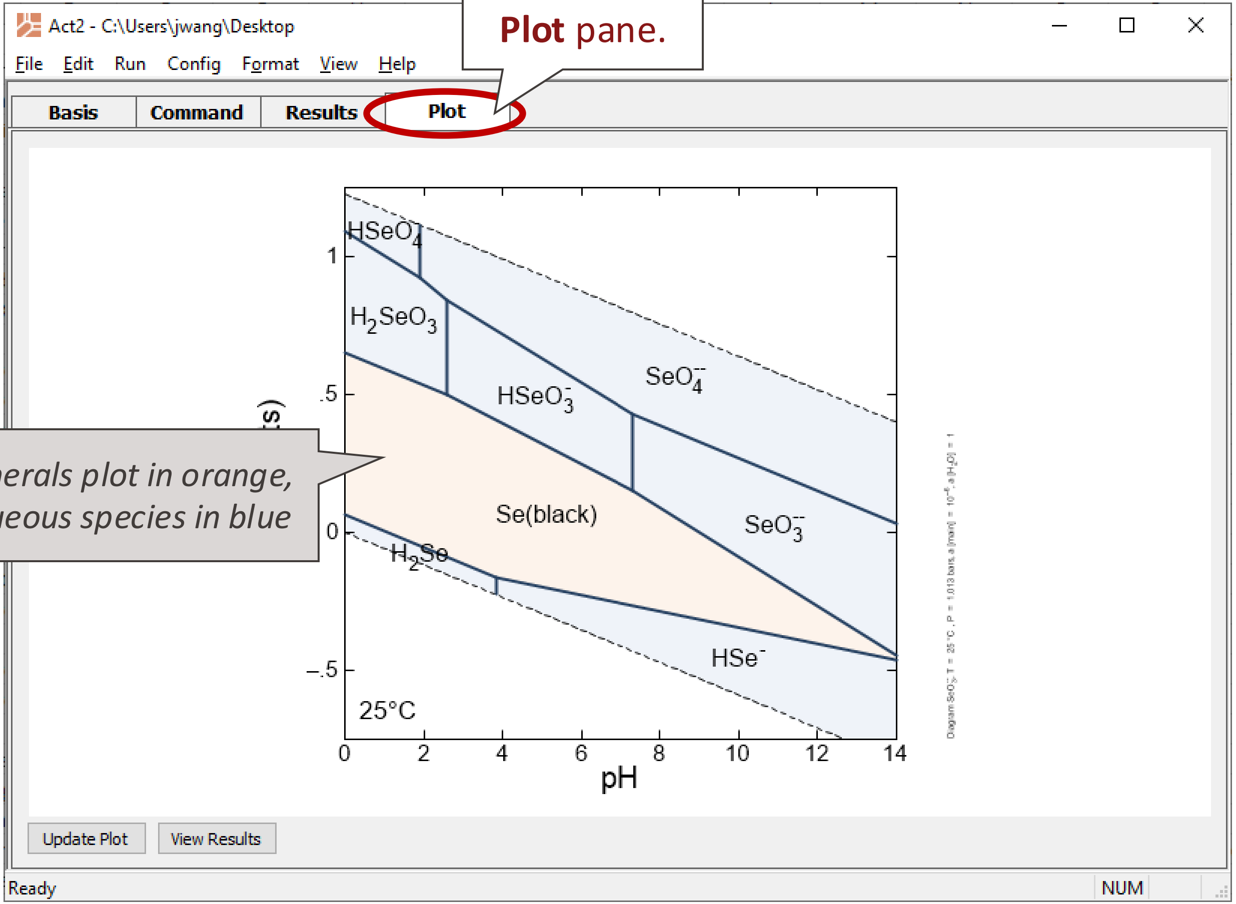
temperature 25.0 C

pressure

Set temperature

Add any background ions

Run → Go
draws the diagram

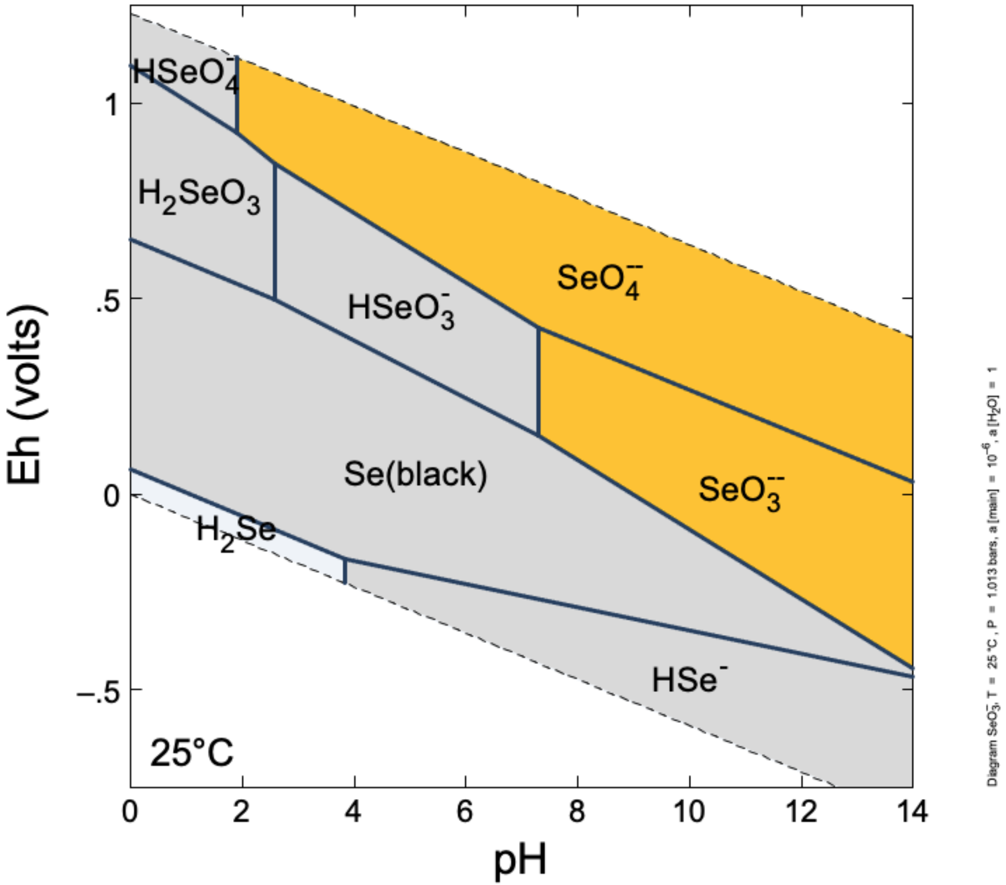


Move to the **Plot** pane.

Minerals plot in orange, aqueous species in blue

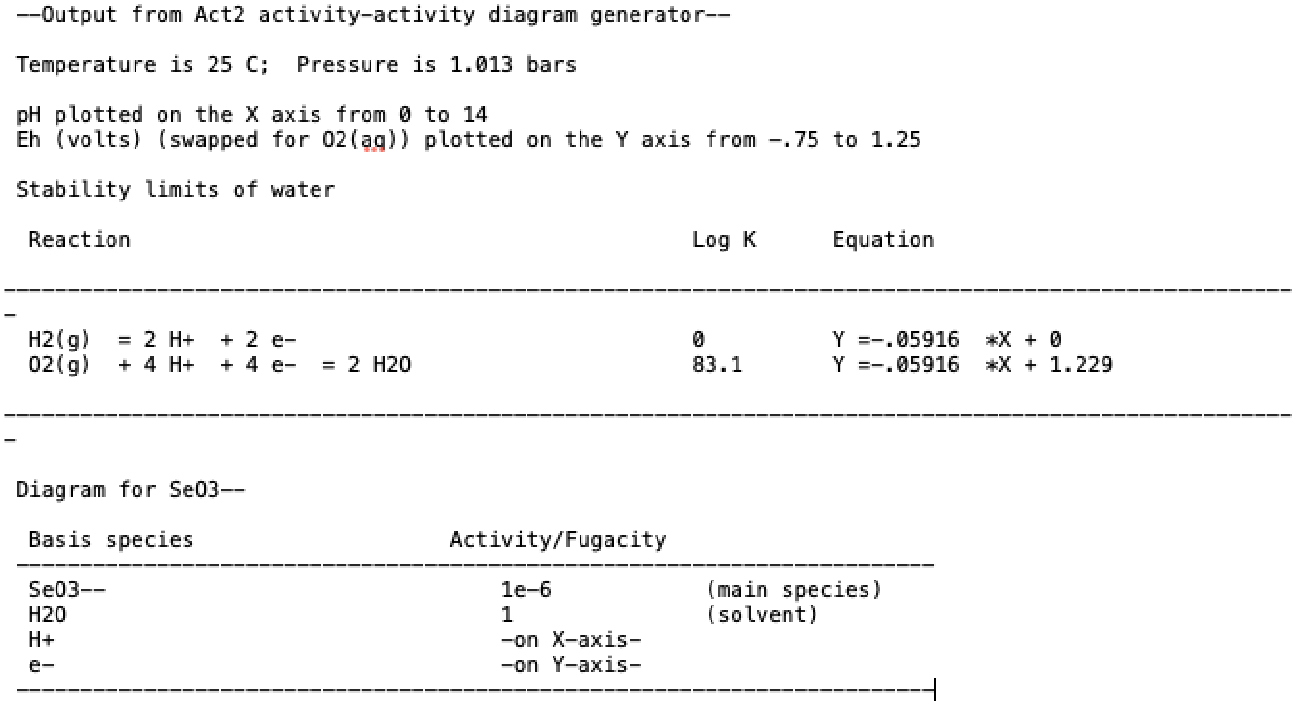
Act2: Export plots

You can copy your plot and paste it into your documents, including Microsoft Word, Excel, and PowerPoint, or Adobe Illustrator. First, select Edit → Copy. Then, paste into PowerPoint as an Enhanced Metafile. Ungroup the image to enable editing



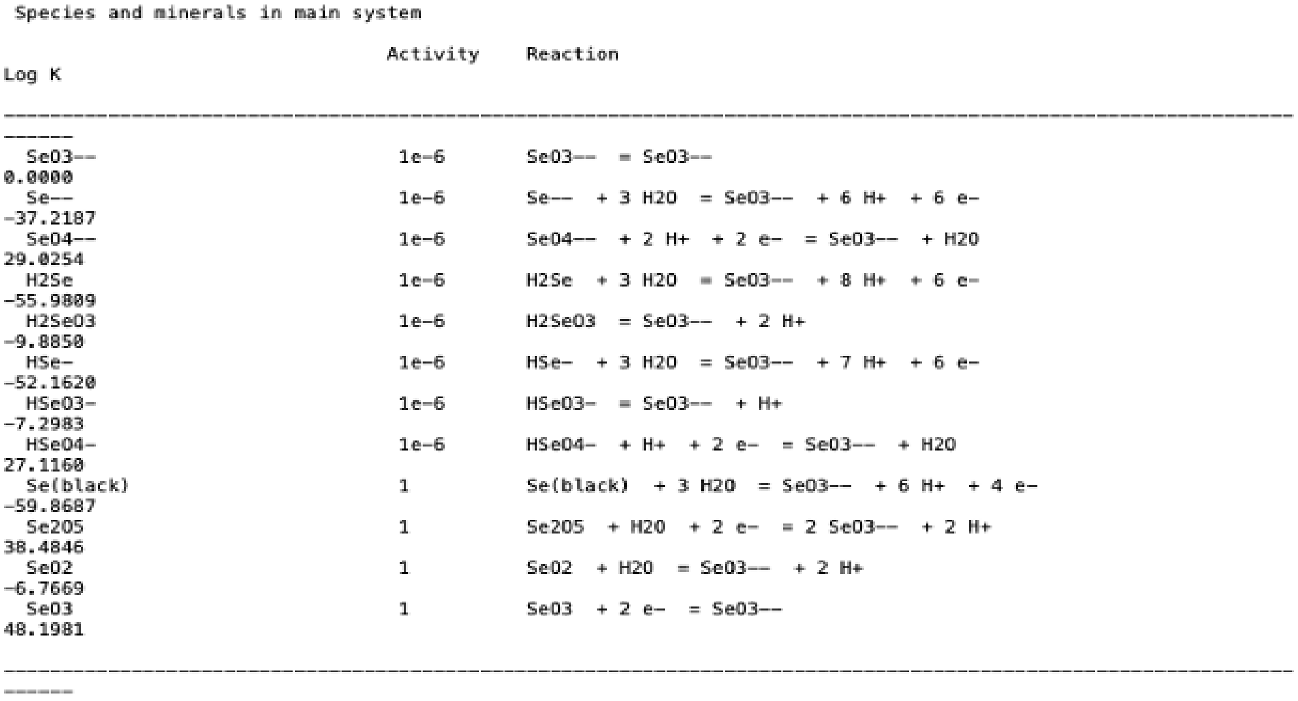
Act2: Output

Go to Results pane and click “View Results” to see the output:



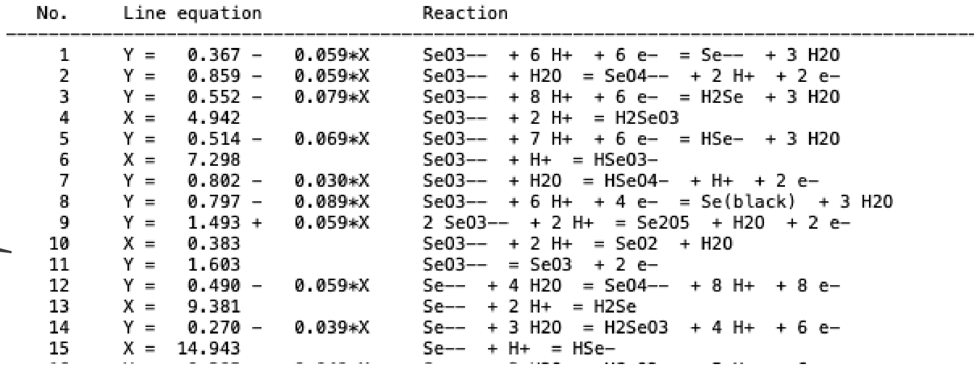
```
 --Output from Act2 activity-activity diagram generator--

 Temperature is 25 C;  Pressure is 1.013 bars

 pH plotted on the X axis from 0 to 14
 Eh (volts) (swapped for O2(aq)) plotted on the Y axis from -.75 to 1.25

 Stability limits of water

  Reaction                                                    Log K      Equation

--------------------------------------------------------------------------------------------------------
-
  H2(g)   = 2 H+   + 2 e-                                     0          Y =-.05916  *X + 0
  O2(g)   + 4 H+   + 4 e-   = 2 H2O                           83.1       Y =-.05916  *X + 1.229

--------------------------------------------------------------------------------------------------------
-

 Diagram for SeO3--

  Basis species                    Activity/Fugacity
 -------------------------------------------------------------------------
  SeO3--                               1e-6             (main species)
  H2O                                  1                (solvent)
  H+                                   -on X-axis-
  e-                                   -on Y-axis-
 -------------------------------------------------------------------------
```

Act2: Output



```
 Species and minerals in main system

                                Activity    Reaction
Log K

----------------------------------------------------------------------------------------------------------------
------
  SeO3--                         1e-6        SeO3--   = SeO3--
0.0000
  Se--                           1e-6        Se--   + 3 H2O   = SeO3--   + 6 H+   + 6 e-
-37.2187
  SeO4--                         1e-6        SeO4--   + 2 H+   + 2 e-   = SeO3--   + H2O
29.0254
  H2Se                           1e-6        H2Se   + 3 H2O   = SeO3--   + 8 H+   + 6 e-
-55.9809
  H2SeO3                         1e-6        H2SeO3   = SeO3--   + 2 H+
-9.8850
  HSe-                           1e-6        HSe-   + 3 H2O   = SeO3--   + 7 H+   + 6 e-
-52.1620
  HSeO3-                         1e-6        HSeO3-   = SeO3--   + H+
-7.2983
  HSeO4-                         1e-6        HSeO4-   + H+   + 2 e-   = SeO3--   + H2O
27.1160
  Se(black)                      1           Se(black)   + 3 H2O   = SeO3--   + 6 H+   + 4 e-
-59.8687
  Se2O5                          1           Se2O5   + H2O   + 2 e-   = 2 SeO3--   + 2 H+
38.4846
  SeO2                           1           SeO2   + H2O   = SeO3--   + 2 H+
-6.7669
  SeO3                           1           SeO3   + 2 e-   = SeO3--
48.1981

----------------------------------------------------------------------------------------------------------------
------
```

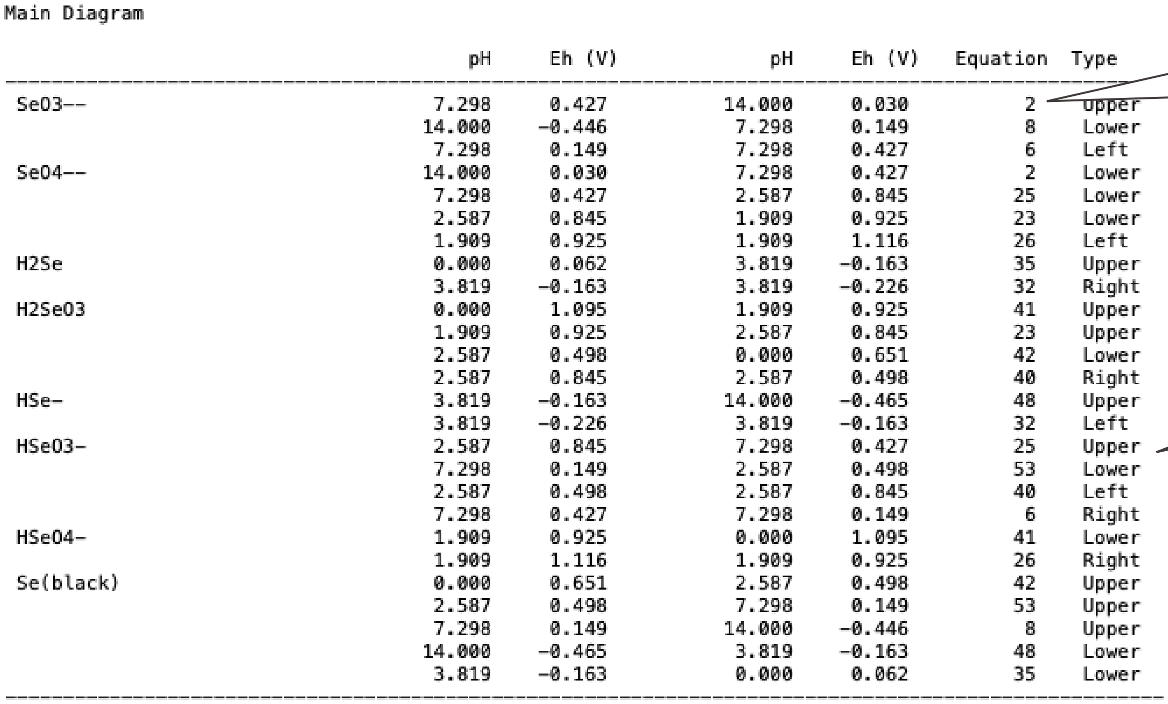
Act2: Output



```
 No.     Line equation                Reaction
-----------------------------------------------------------------------------------------
   1     Y =   0.367 -   0.059*X      SeO3--  + 6 H+  + 6 e-  = Se--  + 3 H2O
   2     Y =   0.859 -   0.059*X      SeO3--  + H2O  = SeO4--  + 2 H+  + 2 e-
   3     Y =   0.552 -   0.079*X      SeO3--  + 8 H+  + 6 e-  = H2Se  + 3 H2O
   4     X =   4.942                  SeO3--  + 2 H+  = H2SeO3
   5     Y =   0.514 -   0.069*X      SeO3--  + 7 H+  + 6 e-  = HSe-  + 3 H2O
   6     X =   7.298                  SeO3--  + H+  = HSeO3-
   7     Y =   0.802 -   0.030*X      SeO3--  + H2O  = HSeO4-  + H+  + 2 e-
   8     Y =   0.797 -   0.089*X      SeO3--  + 6 H+  + 4 e-  = Se(black)  + 3 H2O
   9     Y =   1.493 +   0.059*X      2 SeO3--  + 2 H+  = Se2O5  + H2O  + 2 e-
  10     X =   0.383                  SeO3--  + 2 H+  = SeO2  + H2O
  11     Y =   1.603                  SeO3--  = SeO3  + 2 e-
  12     Y =   0.490 -   0.059*X      Se--  + 4 H2O  = SeO4--  + 8 H+  + 8 e-
  13     X =   9.381                  Se--  + 2 H+  = H2Se
  14     Y =   0.270 -   0.039*X      Se--  + 3 H2O  = H2SeO3  + 4 H+  + 6 e-
  15     X =  14.943                  Se--  + H+  = HSe-
```

All possible reaction equations are reported

The reaction equations used in the diagram are given

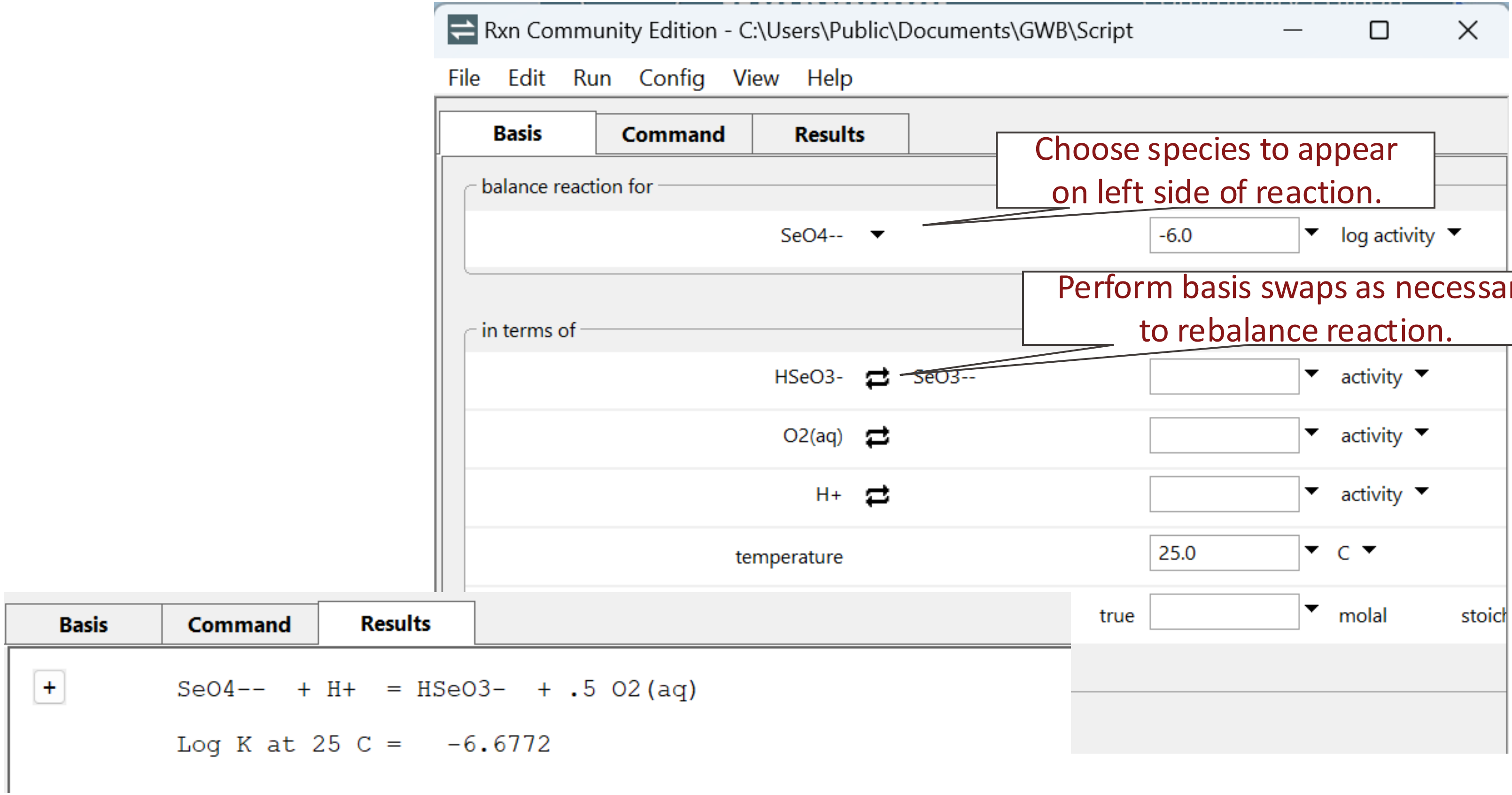


```
Main Diagram

                              pH      Eh (V)        pH      Eh (V)   Equation  Type
--------------------------------------------------------------------------------------
 SeO3--                     7.298     0.427      14.000     0.030        2     Upper
                           14.000    -0.446       7.298     0.149        8     Lower
                            7.298     0.149       7.298     0.427        6     Left
 SeO4--                    14.000     0.030       7.298     0.427        2     Lower
                            7.298     0.427       2.587     0.845       25     Lower
                            2.587     0.845       1.909     0.925       23     Lower
                            1.909     0.925       1.909     1.116       26     Left
 H2Se                       0.000     0.062       3.819    -0.163       35     Upper
                            3.819    -0.163       3.819    -0.226       32     Right
 H2SeO3                     0.000     1.095       1.909     0.925       41     Upper
                            1.909     0.925       2.587     0.845       23     Upper
                            2.587     0.498       0.000     0.651       42     Lower
                            2.587     0.845       2.587     0.498       40     Right
 HSe-                       3.819    -0.163      14.000    -0.465       48     Upper
                            3.819    -0.226       3.819    -0.163       32     Left
 HSeO3-                     2.587     0.845       7.298     0.427       25     Upper
                            7.298     0.149       2.587     0.498       53     Lower
                            2.587     0.498       2.587     0.845       40     Left
                            7.298     0.427       7.298     0.149        6     Right
 HSeO4-                     1.909     0.925       0.000     1.095       41     Lower
                            1.909     1.116       1.909     0.925       26     Right
 Se(black)                  0.000     0.651       2.587     0.498       42     Upper
                            2.587     0.498       7.298     0.149       53     Upper
                            7.298     0.149      14.000    -0.446        8     Upper
                           14.000    -0.465       3.819    -0.163       48     Lower
                            3.819    -0.163       0.000     0.062       35     Lower
--------------------------------------------------------------------------------------
```

Equation number refers to the table above

Type describes the position relative to the stability area

Finding equilibrium equations using Rxn



balance reaction for
SeO4-- -6.0 log activity

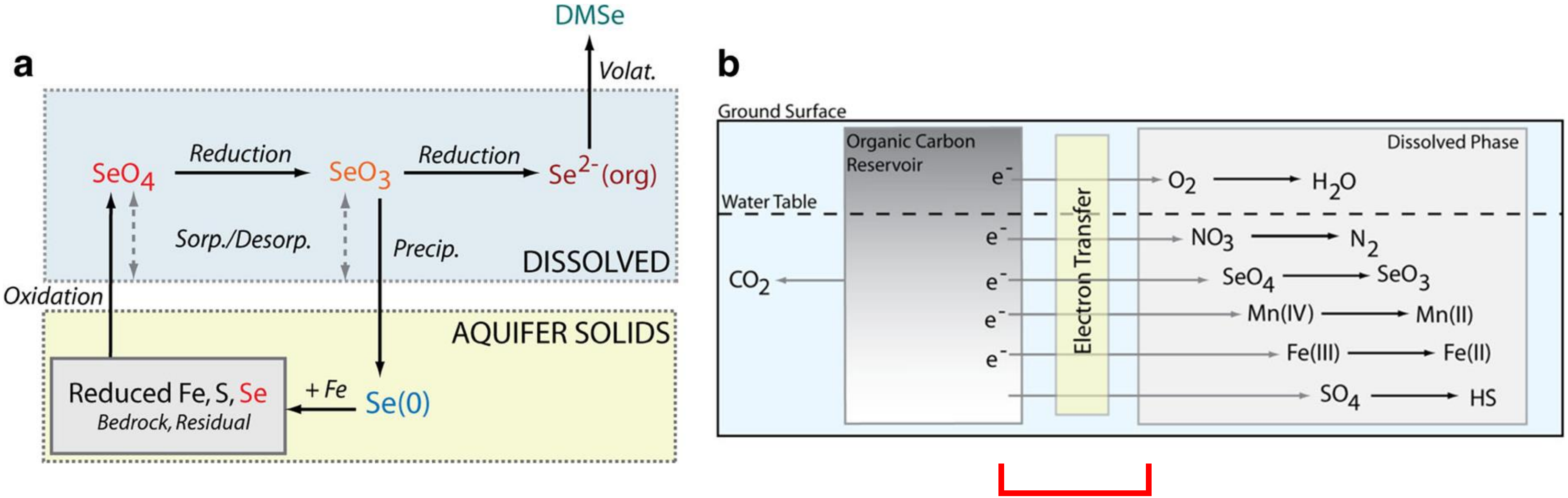
in terms of
HSeO3- ⇄ SeO3-- activity
O2(aq) ⇄ activity
H+ ⇄ activity
temperature 25.0 C
true molal stoich

Choose species to appear on left side of reaction.

Perform basis swaps as necessary to rebalance reaction.

```
SeO4--  + H+  = HSeO3-  + .5 O2(aq)

Log K at 25 C =   -6.6772
```

Context: Selenium speciation in alluvial aquifers

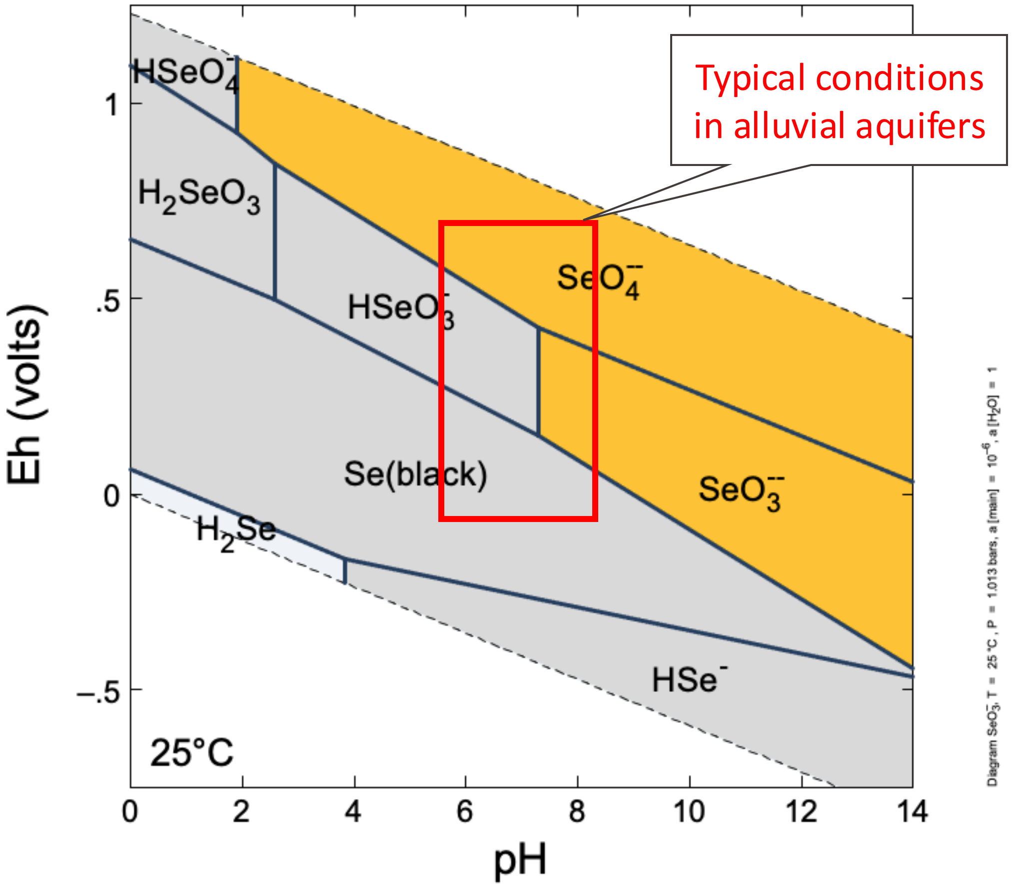


Se movement in soil and aquifer systems is governed by redox reactions which control speciation and sorption processes.

Bailey, RT, Hydrogeol J, ***2017****, 25:1191-1217.*

Selenium speciation in alluvial aquifers

- What are typical Eh and pH conditions for alluvial aquifers?
- Which species do you expect to be present under those condition?
- You find Se(0) and organic Se^{2-} under aerated conditions. Why?



Typical conditions in alluvial aquifers

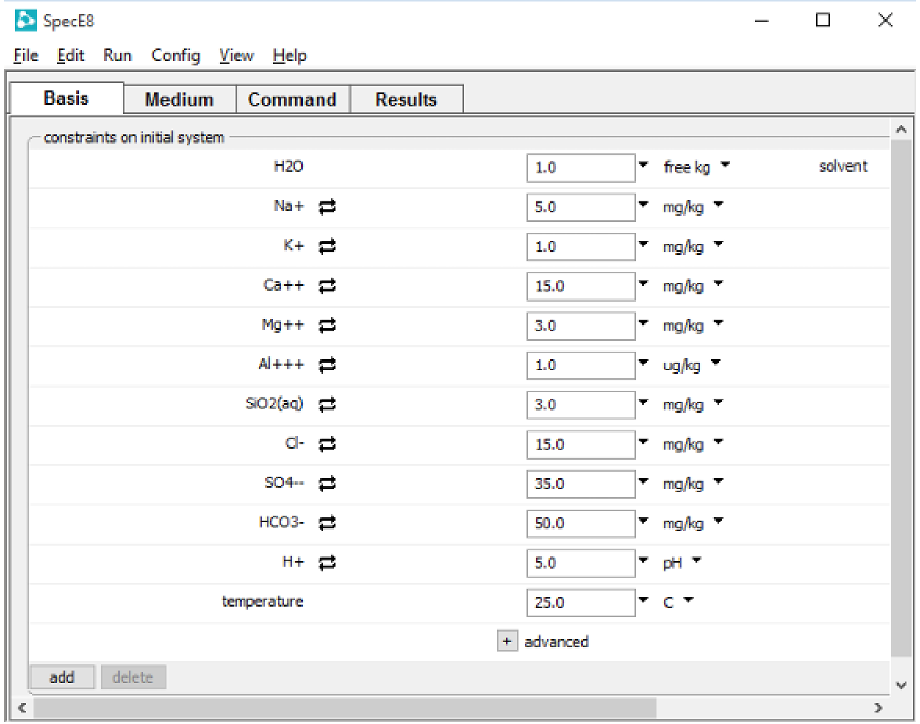
*Bailey, RT, Hydrogeol J, **2017**, 25:1191-1217.*

SpecE8: Speciation calculations

SpecE8 calculates the equilibrium distribution of aqueous species in a fluid, the fluid’s saturation state with respect to minerals, the sorption of aqueous species onto various types of surfaces, and the fugacity and partial pressure of gases dissolved in the fluid.

SpecE8: Speciation calculations

The input file “Freshwater.sp8” equilibrates a hypothetical water sample at 25°C. Double-click the file to launch SpecE8, then move to the Basis pane to see the compositional constraints on the hypothetical water.



constraints on initial system

H2O	1.0	free kg	solvent
Na+	5.0	mg/kg	
K+	1.0	mg/kg	
Ca++	15.0	mg/kg	
Mg++	3.0	mg/kg	
Al+++	1.0	ug/kg	
SiO2(aq)	3.0	mg/kg	
Cl-	15.0	mg/kg	
SO4--	35.0	mg/kg	
HCO3-	50.0	mg/kg	
H+	5.0	pH	
temperature	25.0	C	

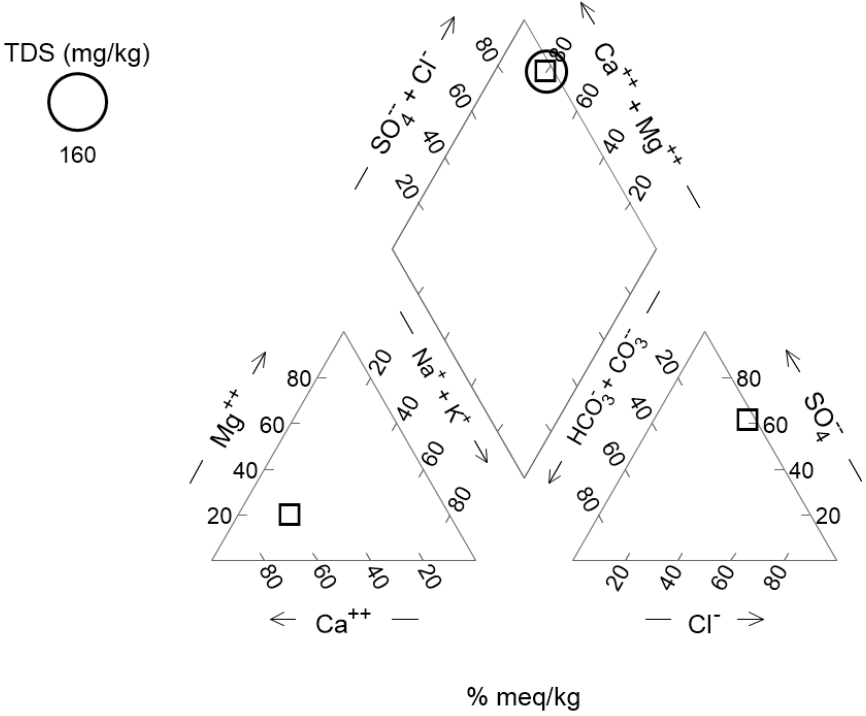
+ advanced

Exercise 1: Hypothetical freshwater

Press the Run button on the Results pane to calculate the equilibrium species distribution in the water. SpecE8 produces as output a dataset “SpecE8_output.txt”. Examine the output file. Do you expect any minerals to precipitate in this water? If so, which ones?

SpecE8: Speciation calculations

The run also produced a dataset "SpecE8_plot.gtp" that passes more complete information to the graphics program Gtplot. Click on "Plot Results". Create a Piper diagram from the data.



SpecE8: Speciation calculations

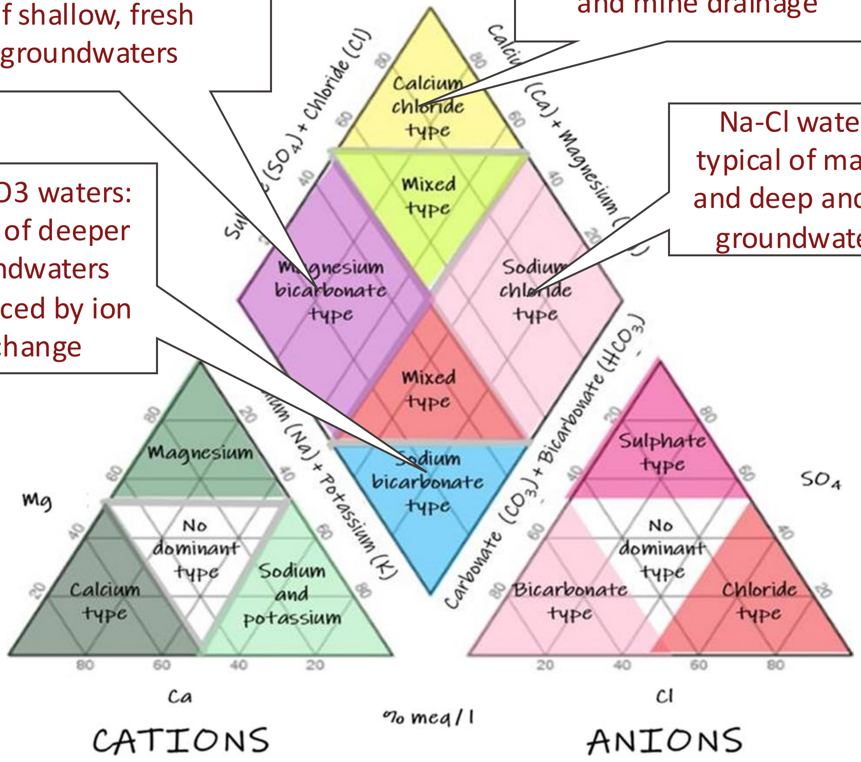
A piper diagram segregates concentrations of the most abundant cations and anions to understand the sources of dissolved constituents in water.

Advantages

- Many water analyses can be plotted on the same diagram
- Can be used to classify waters
- Can be used to identify mixing of waters

Disadvantages

- Concentrations are renormalized
- Cannot easily accommodate waters in which other cations or anions are significant



Ca-HCO3 waters: typical of shallow, fresh groundwaters

Ca-SO4 waters: typical of gypsum ground waters and mine drainage

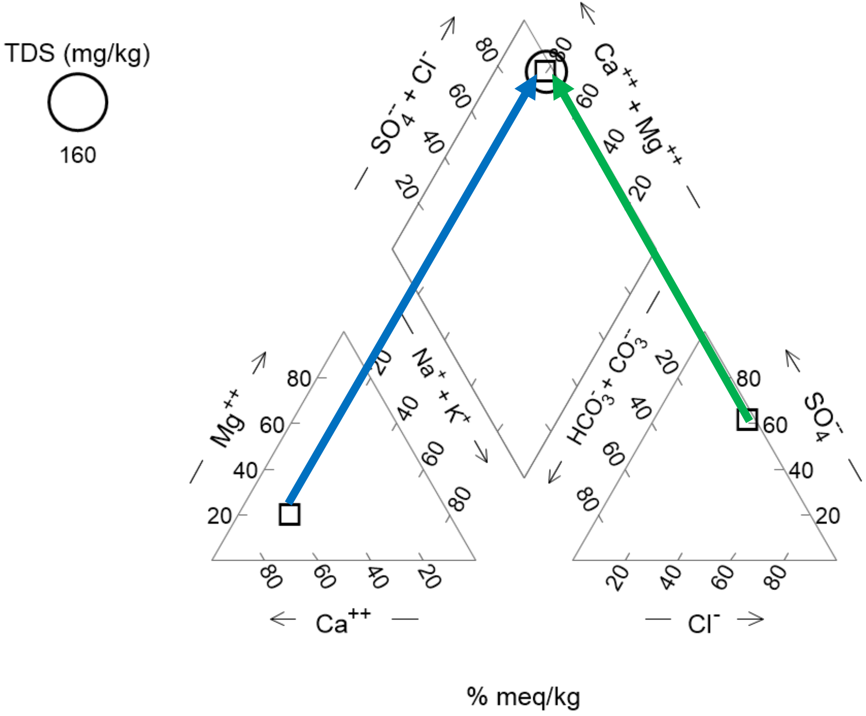
Na-HCO3 waters: typical of deeper groundwaters influenced by ion exchange

Na-Cl waters: typical of marine and deep ancient groundwaters

SpecE8: Speciation calculations

$Ca^{2+} + Mg^{2+}$ = 60 meq/kg + 20 meq/kg
= 80 meq/kg

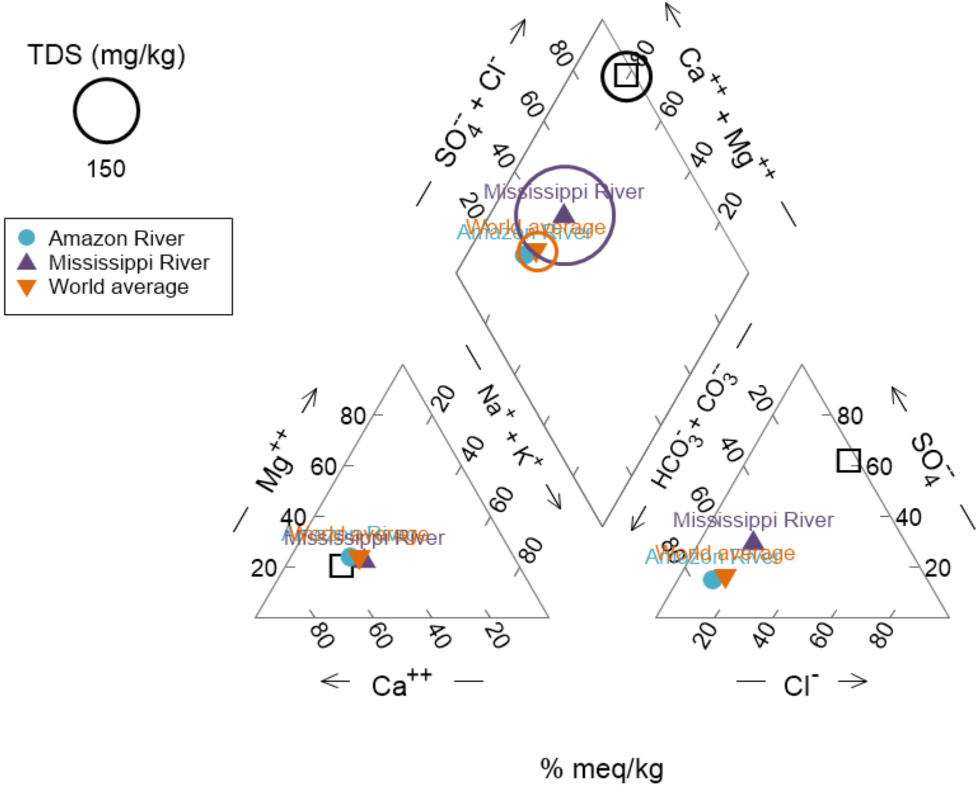
$SO_4^{2-} + Cl^-$ = 60 meq/kg + 40 meq/kg =
100 meq/kg



SpecE8: Speciation calculations

We can add the river data for Mississippi and Amazon from last week: Simply drag and drop the file RiverWaters.gss into Gtplog

What is the main chemical difference between our hypothetical freshwater and the river waters?



TDS = total dissolved solids

Typical tap water concentrations: 150-400

Exercise 2: Iron precipitation

Let's re-examine exercise 1 from Homework 4: A wastewater contains 10^{-4} M phosphate. Fe(III) is added to the system to precipitate phosphate. Is $FePO_4$(s) or $Fe(OH)_3$(s) precipitated at pH=7?

Use SpecE8 to answer this question. The following information is useful:

- Assume an oxic system (O2(aq) at saturation: 9 mg/L)
- Assume an Fe(III) concentration of 10^{-4} M.
- Assume typical wastewater concentrations of
  - Ca^{2+}= 6.6 meq/L
  - Cl^- = 3.5 meq/L
  - SO_4^{2-} = 2.6 meq/L
- Strengite is a $FePO_4$ mineral.

SpecE8: Redox disequilibrium

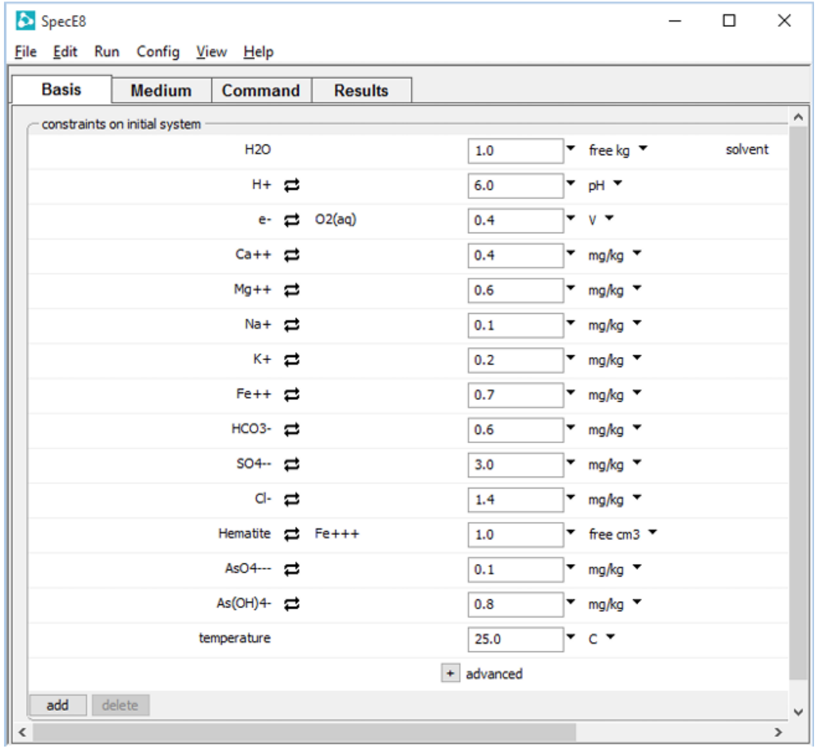
Redox reactions in natural waters, especially at low temperatures, cannot always be assumed to be at thermodynamic equilibrium.

For example, the photo shows part of a river in the Rocky Mountains where waters containing reduced iron encounter oxygen-containing waters. As a result, iron is oxidized and iron minerals are precipitating as evidenced from the orange color.

In our modeling efforts, we therefore want to calculate a scenario in which redox reactions are in a state of disequilibrium. Let's see how this works in SpecE8!

SpecE8: Redox disequilibrium

Double-click the “Redox.sp8” input file to launch SpecE8, then move to the basis pane. The input configures a model of a fluid of a certain pH, Eh, and major ion composition.

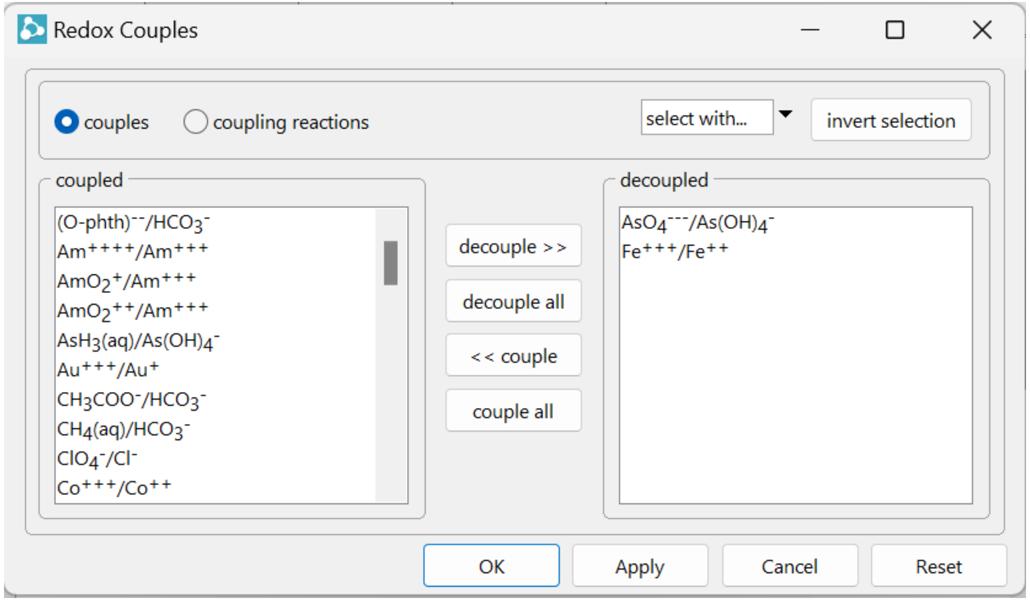


constraints on initial system

H2O		1.0	free kg	solvent
H+		6.0	pH	
e-	O2(aq)	0.4	V	
Ca++		0.4	mg/kg	
Mg++		0.6	mg/kg	
Na+		0.1	mg/kg	
K+		0.2	mg/kg	
Fe++		0.7	mg/kg	
HCO3-		0.6	mg/kg	
SO4--		3.0	mg/kg	
Cl-		1.4	mg/kg	
Hematite	Fe+++	1.0	free cm3	
AsO4---		0.1	mg/kg	
As(OH)4-		0.8	mg/kg	
temperature		25.0	C	

SpecE8: Redox disequilibrium

Open the Config → Redox couples… dialog and note the decoupled redox pairs. Disabling the redox couples between ferric and ferrous iron and between trivalent and pentavalent arsenic [i.e., basis species AsO_4--- and As(OH)4-] causes the program to consider that oxidized and reduced iron and arsenic species exist in quantities not related to the value entered for Eh. Other redox couples, such as between HS- and SO4--, remain enabled and will reflect the specified Eh.



● couples ○ coupling reactions

coupled

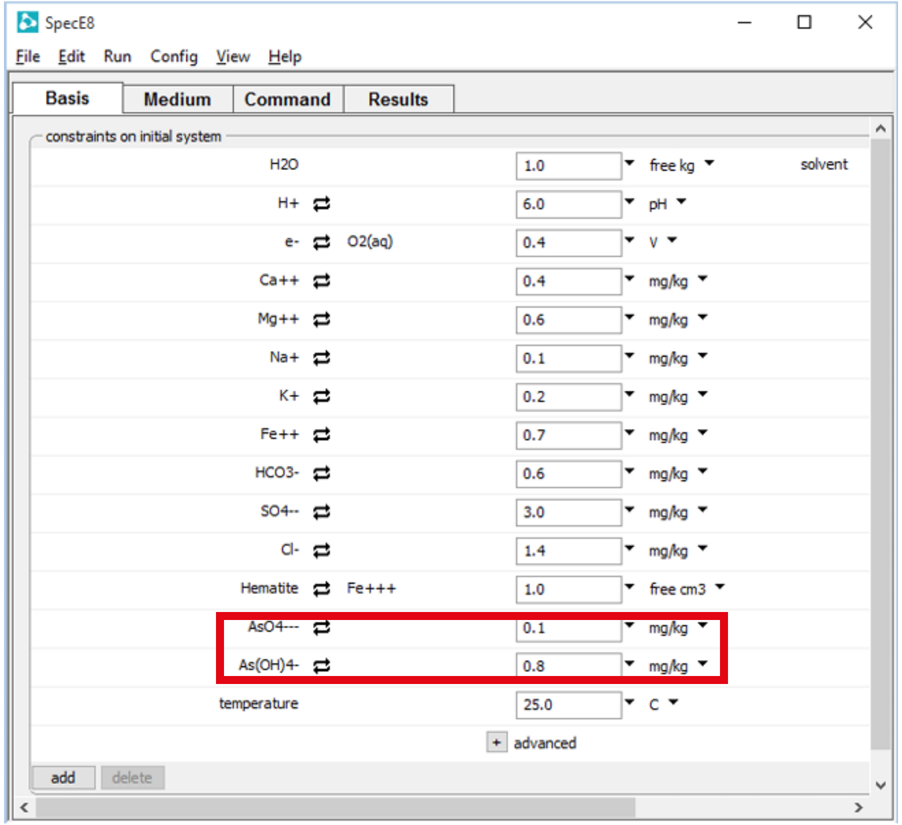
$(O\text{-}phth)^{--}/HCO_3^-$
Am^{++++}/Am^{+++}
AmO_2^+/Am^{+++}
AmO_2^{++}/Am^{+++}
$AsH_3(aq)/As(OH)_4^-$
Au^{+++}/Au^+
CH_3COO^-/HCO_3^-
$CH_4(aq)/HCO_3^-$
ClO_4^-/Cl^-
Co^{+++}/Co^{++}

decoupled

$AsO_4^{---}/As(OH)_4^-$
Fe^{+++}/Fe^{++}

SpecE8: Redox disequilibrium

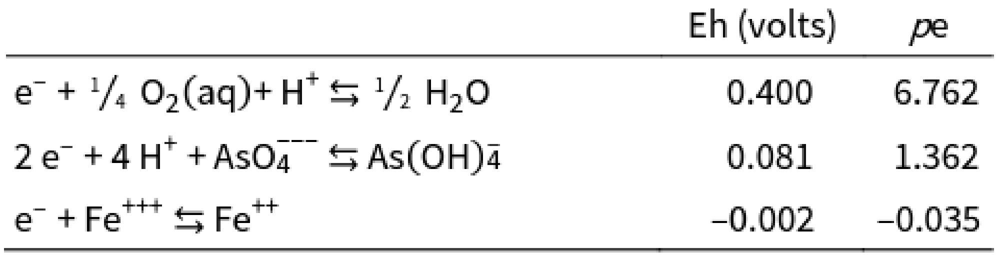
By nature, you need more information to constrain a model of a fluid in redox disequilibrium than you do for an equilibrium model. As you can see on the Basis pane, separate constraints are required for the oxidized and reduced forms of iron and arsenic (i.e., we give the model different concentrations for each redox species).



H2O		1.0	free kg	solvent
H+ ⇄		6.0	pH
e- ⇄	O2(aq)	0.4	V
Ca++ ⇄		0.4	mg/kg
Mg++ ⇄		0.6	mg/kg
Na+ ⇄		0.1	mg/kg
K+ ⇄		0.2	mg/kg
Fe++ ⇄		0.7	mg/kg
HCO3- ⇄		0.6	mg/kg
SO4-- ⇄		3.0	mg/kg
Cl- ⇄		1.4	mg/kg
Hematite ⇄	Fe+++	1.0	free cm3
AsO4--- ⇄		0.1	mg/kg
As(OH)4- ⇄		0.8	mg/kg
temperature		25.0	C

SpecE8: Redox disequilibrium

Whenever there are two or more independent redox couples in a run, SpecE8 reports in “SpecE8_output.txt” the theoretical oxidation state of each couple. In this example, the couples and corresponding Nernst Eh and pe values are:



	Eh (volts)	*pe*
$e^- + \frac{1}{4} O_2(aq) + H^+ \leftrightarrows \frac{1}{2} H_2O$	0.400	6.762
$2\,e^- + 4\,H^+ + AsO_4^{---} \leftrightarrows As(OH)_4^-$	0.081	1.362
$e^- + Fe^{+++} \leftrightarrows Fe^{++}$	–0.002	–0.035

The first line reflects the Eh specified as an input constraint. The second and third lines show the oxidation states calculated from the activities of arsenic and iron species. The differences in oxidation state reflect the extent of redox disequilibrium in the solution.

Exercise 3: Redox disequilibrium

We just discussed the example on redox disequilibrium. In what speciation would As occur if it equilibrated with the solution at the specified potential of Eh = 0.4 V?

Use the input file Redox.sp8 and remove the As redox couple from the list of decoupled redox couples. Then, examine the output file. What is the redox state of As and why?

Environmental engineering challenge

Waterfall Dreimühlen (D): How fast does the waterfall “grow”, i.e., how much calcite is precipitating each year?

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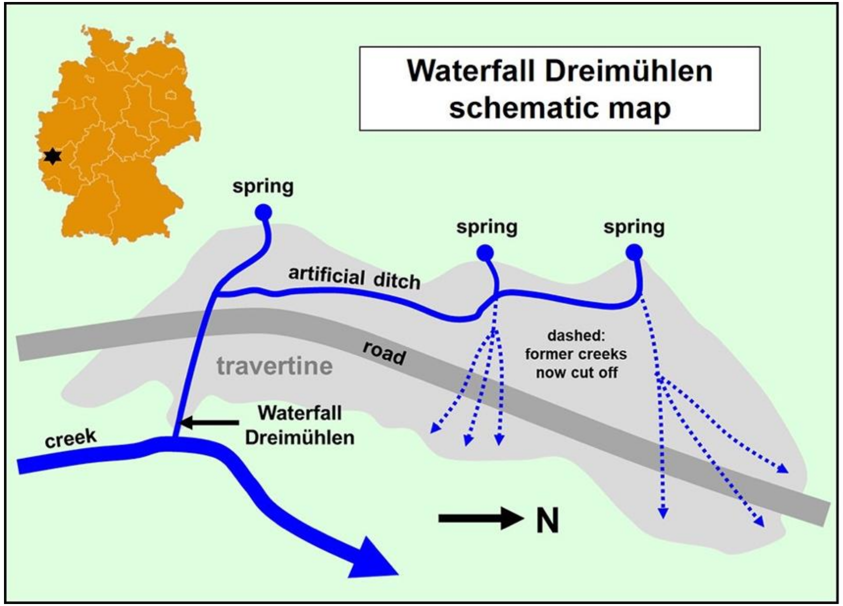
Dreimühlen waterfall



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Geology is dominated by limestone

Travertine is a dense, banded rock composed of calcite ($CaCO_3$)

Relevant chemical reaction:

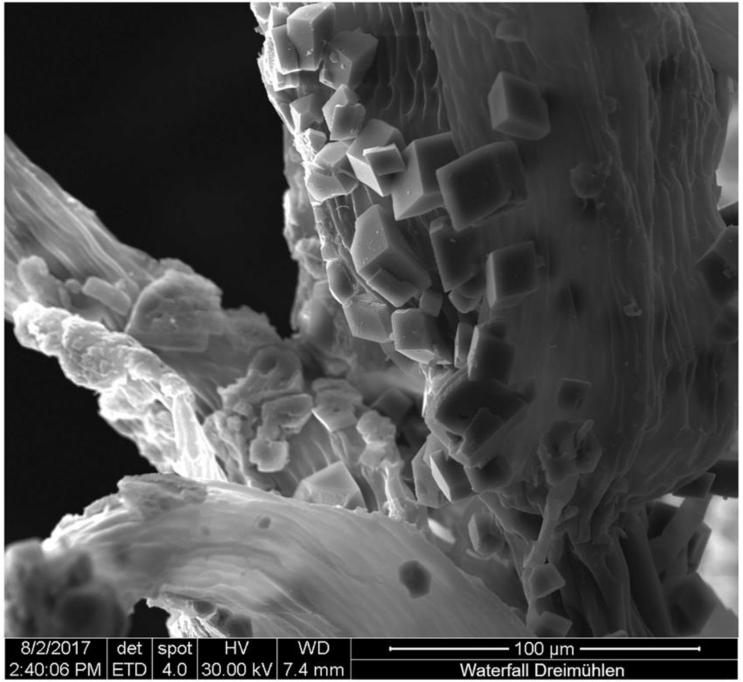
$CaCO_3(s) + H_2O + CO_2(g) \rightleftharpoons Ca^{2+}(aq) + 2HCO_3^-(aq)$

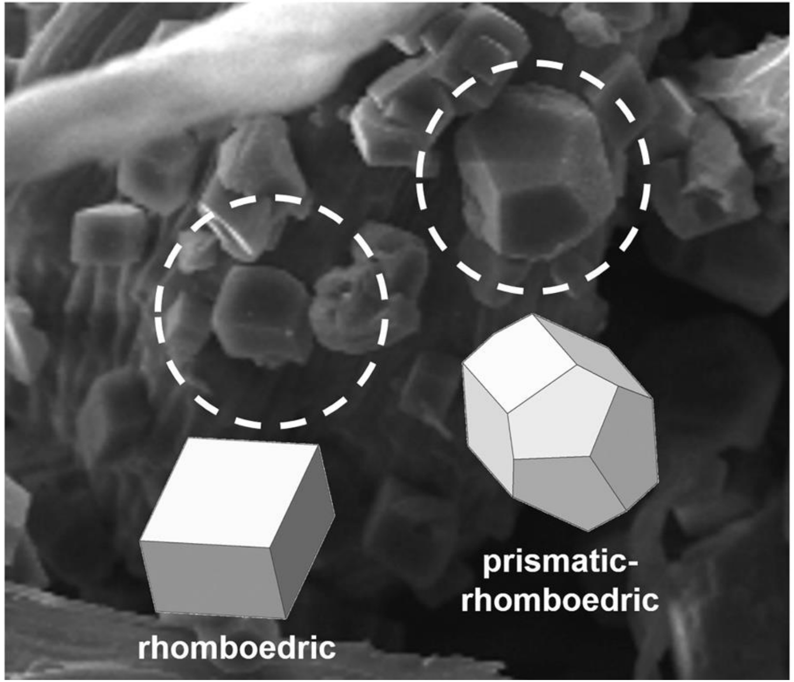
In the underground, high partial pressure of CO_2 (>> 400 ppm) shifts the equilibrium position to the right

When water emerges from the underground, it is oversaturated with dissolved lime (lower partial pressure of CO_2), causing calcite to precipitate

Dreimühlen waterfall

Calcite precipitates as observed under a scanning electron microscope:





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Dreimühlen waterfall

How many kgs of calcite are precipitating each year?

On your field trip, you measured a flowrate of 60 L/s and the parameters in the table below. Use SpecE8 to calculate the amount of calcite precipitating.

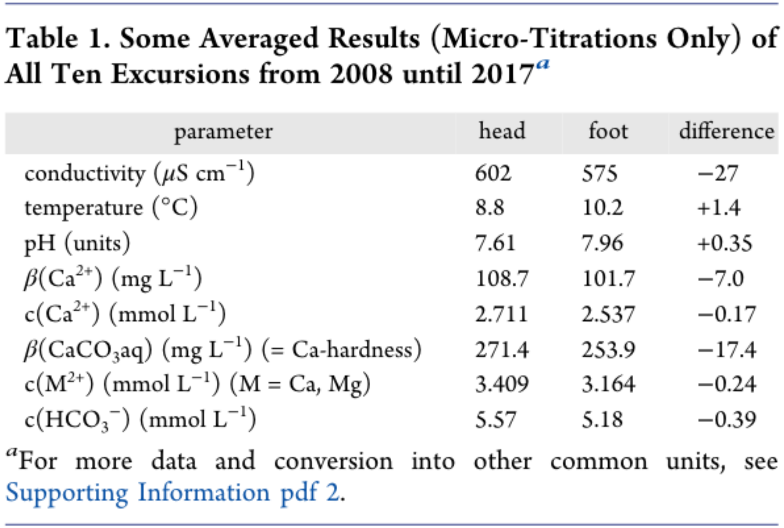

Table 1. Some Averaged Results (Micro-Titrations Only) of All Ten Excursions from 2008 until 2017[a]

parameter	head	foot	difference
conductivity (μS cm^{-1})	602	575	−27
temperature (°C)	8.8	10.2	+1.4
pH (units)	7.61	7.96	+0.35
β(Ca^{2+}) (mg L^{-1})	108.7	101.7	−7.0
c(Ca^{2+}) (mmol L^{-1})	2.711	2.537	−0.17
β(CaCO$_3$aq) (mg L^{-1}) (= Ca-hardness)	271.4	253.9	−17.4
c(M^{2+}) (mmol L^{-1}) (M = Ca, Mg)	3.409	3.164	−0.24
c(HCO$_3^-$) (mmol L^{-1})	5.57	5.18	−0.39

[a] For more data and conversion into other common units, see Supporting Information pdf 2.

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Summary

1. Using the Act2 app in the Geochemist's Workbench, you can create stability diagrams in an easy and fast manner. These diagrams can help you get a quick grasp on the prevailing conditions in the environmental system of interest.
2. The SpecE8 app is a versatile tool for speciation calculations. Successful implementation of speciation calculations requires a good understanding of the system of interest.
3. Geochemical models are always simplifications of natural systems. They can still provide meaningful clues to understand the functioning and complexities of natural systems.