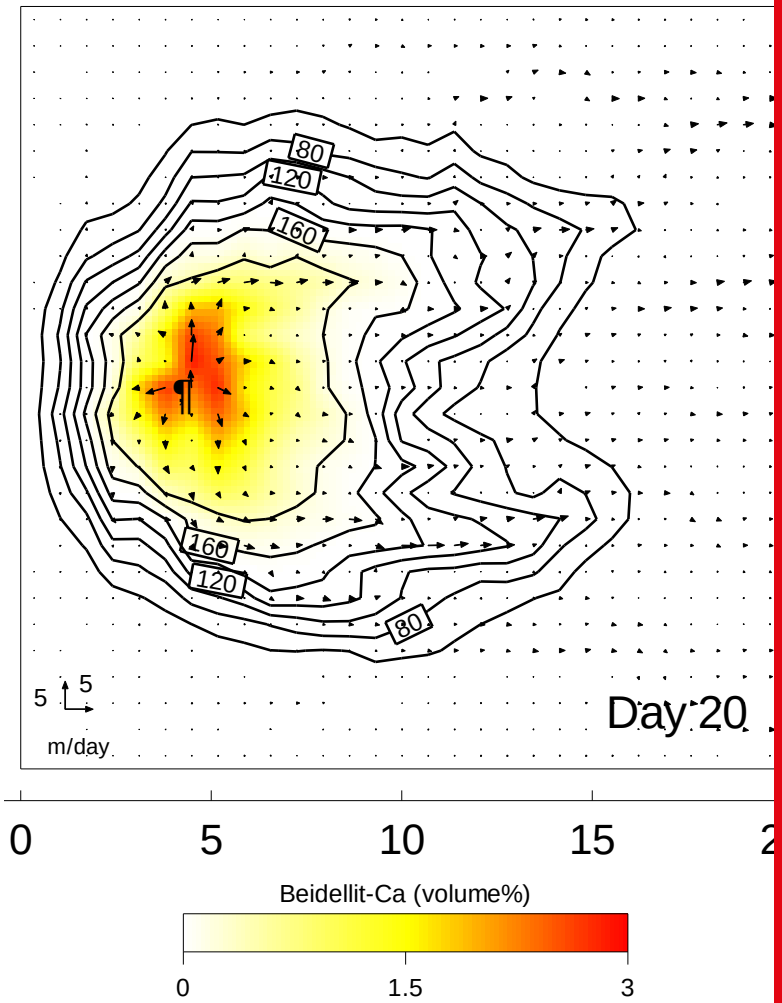


Geochemical modeling

ENV-200 Weeks 9 & 10

Meret Aeppli
meret.aeppli@epfl.ch

Learning objectives

You should be able to

1. explain what geochemical modeling is useful for
2. be familiar with Apps in the Community Edition of the Geochemist's Workbench
3. interpret and plot the output of a simple modeling run
4. describe how you can use geochemical modeling in environmental engineering challenges

Resources

- Geochemist's Workbench Community Edition https://community.gwb.com/community_download.php
- Geochemical and Biogeochemical Reaction Modeling by Craig M. Bethke (Cambridge University Press)
- Many examples that we cover here are from the GWB Essentials Guide (by Craig M. Bethke, Brian Farrell, Sharon Yeakel)

- There are many other geochemical modeling tools available (e.g. PhreeqC, Visual Minteq, CHESS, Reaktoro, etc.)
- A quite extensive list of tools is provided on the USGS website

What is geochemical modeling?

In almost all environmental problems, there is a need for knowledge or predictions of the solute concentrations in space and time.

- Contamination issues
  - Examples:
    - What will happen to a particular toxic chemical component or species in groundwater downstream from a contamination source such as a polluted industrial manufacturing site?
    - How fast will the contaminant progress downstream, and when will it reach a certain point?
    - What processes will slow down its movement (retardation) or immobilize it?
    - Will the concentrations of the contaminant be above regulatory thresholds? Would the remediation methods be effective, i.e., limiting the migration of a contaminant and lowering its concentrations?
  - These questions may also be posed for the history of a site concerning past activities: what has happened at this site in the past?
- Water resources issues
  - Example: Water is clear and uncontaminated, but just how much is there to tap and who is entitled to what proportions? In this case, chemical constituents in groundwater and their movement can help delineate the flow system that hydraulic data alone fail to reveal

Environmental engineering applications

Meret Aeppli

- High-Level Radioactive Waste Disposal
- Mining-related environmental issues
- Landfills
- Geological carbon sequestration
- Deep well injection of hazardous wastes
- Artificial recharge to aquifers

What do we want to accomplish?

Ultimately, we want to describe the complete chemical composition of a system (e.g. a lake, a soil column, an aquifer)

There are two ways to accomplish this:

- **Thermodynamic description**: If a closed system is at equilibrium, its chemical composition is uniquely defined.
- **Kinetic description**: If equilibrium is not attained (slow reactions) or if the system it is continuously perturbed (i.e. biological activity), a kinetic description is necessary.

Here, we will focus on the thermodynamic description.

Natural systems are complex

- We have discussed different chemical reactions in this class:
  - Acid-base reactions
  - Complexation reactions
  - Dissolution/precipitation reactions
  - Redox reactions
- You have learned to predict how a system behaves considering a few reactions that are at equilibrium simultaneously:
  - For example, the carbonate system or reductive dissolution of iron minerals
  - Complex calculations and/or graphical solutions can help solving these systems
- However, in natural systems, many or even all reaction types mentioned above may operate simultaneously, forming extremely complex reaction networks.

How do we deal with complexity?

Meret Aeppli

We could set up a mathematical framework. We already have

- Mass law equations

  $A^{2+} + 2B^{-} = AB_2$

  $K = \frac{\{AB_2\}}{\{A_{2_+}\}\{B_-\}^2}$

- Mass balance equations

  $[B^-] + 2[AB_2] + [CB(s)] = [B]_{tot}$

- Charge balance equations

  $2[A^{2+}] + [B^+] - [B^-] = 0$

Workflow for thermodynamic modeling

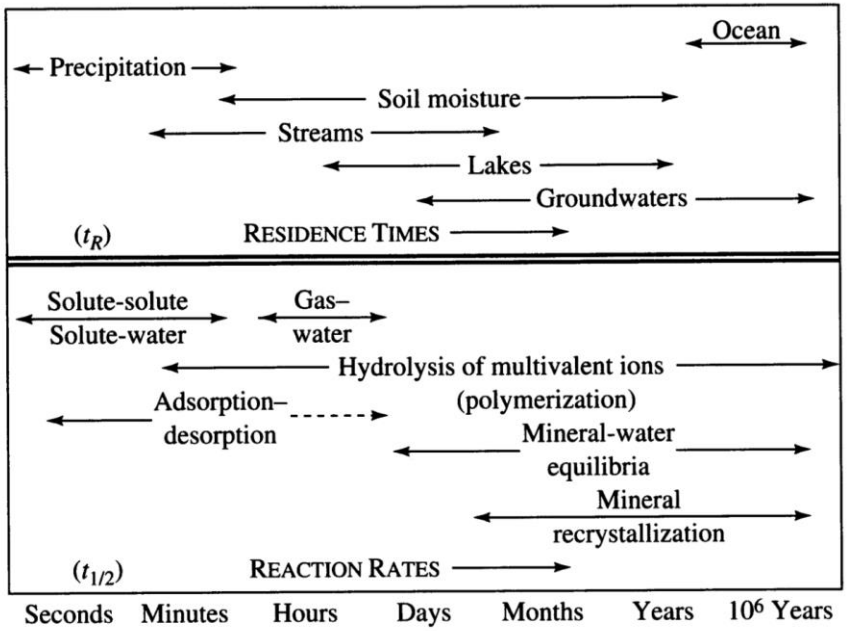
1. Develop a conceptual model: List the processes that likely determine the chemical composition of a system.
2. Make partial equilibrium assumptions: Consider the timeframes in which you wish to understand a system (minutes? years? millions of years?). Decide which of the relevant reactions will reach equilibrium in this timeframe, and which ones will not proceed to any relevant degree.
3. Make sure you have thermodynamic parameters for these reactions.
4. Solve all equations simultaneously with a numerical model.
5. Interpret the output with respect to your conceptual model.
6. Potentially revise the conceptual model and start over.

1. The conceptual model

- A model is a simplified abstraction of nature.
- It is described by a set of mathematical expressions thought to represent natural processes in a particular system.
- The model is built by you! You chose what data to use, which software is appropriate, which results are reasonable.

2. Partial equilibrium assumptions

- Which timeframe is important for the processes you are interested in? Which of the relevant reactions will reach equilibrium in this timeframe?



Langmuir, Mahoney (85)

2. Partial equilibrium assumptions

Meret Aeppli

- Kinetic information can be introduced into equilibrium calculations.
- Partial equilibrium assumptions
  - consider only fast reactions with half-lives much smaller than the reaction time scale we are interested in ($t_{1/2} << t_r$)
  - ignore slow reactions in which half-lives are much larger than reaction times ($t_{1/2} >> t_r$)
- This becomes problematic if reactions with half-lives close to the reaction times are important ($t_{1/2} \approx t_r$). In this case, we would need kinetic modeling.

3. Thermodynamic data

Step no. (Scheme 2)	Substituent	Gaseous phase $\Delta_{r,298}H^\circ$	Gaseous phase $\Delta_{r,298}G^\circ$	Aqueous phase $\Delta_{r,298}G^\circ$
I	2-F	−164.2	−151.3	−43.3
	2-CF$_3$	−167.1	−153.2	−44.1
	2-NO$_2$	−166.0	−153.5	−44.7
	2-OCH$_3$	−162.8	−150.5	−43.0
	2,6-diBr	−165.4	−152.8	−44.2
II	2-F	−190.2	−180.2	−63.1
	2-CF$_3$	−192.9	−182.0	−64.4
	2-NO$_2$	−191.4	−181.1	−64.9
	2-OCH$_3$	−188.9	−178.4	−62.7
	2,6-diBr	−188.0	−178.5	−62.6
III	2-F	−138.4	−125.5	−25.0
	2-CF$_3$	−142.0	−128.2	−26.0
	2-NO$_2$	−135.4	−123.3	−23.0
	2-OCH$_3$	−133.9	−121.0	−22.4
	2,6-diBr	−138.3	−124.9	−25.0
IV	2-F	−156.6	−146.6	−36.7
	2-OCH$_3$	−152.3	−142.1	−34.9
V	2-F	−75.4	−78.0	−51.7
	2-CF$_3$	−86.4	−89.1	−58.8
	2-NO$_2$	−96.3	−99.8	−68.4
	2-OCH$_3$			
	2,6-diBr			
VI	2-F			
	2-CF$_3$			
	2-OCH$_3$			
VII	2-F			
	2-CF$_3$			
	2-OCH$_3$			
VIII	2-F			
	2-CF$_3$			
	2-OCH$_3$			
IX	2-F			
	2-CF$_3$			
	2-NO$_2$			
	2-OCH$_3$			
	2,6-diBr			

Step no. (Scheme 1)	Substituent	Gaseous phase $\Delta_{r,298}H^\circ$	Gaseous phase $\Delta_{r,298}G^\circ$	Aqueous phase $\Delta_{r,298}G^\circ$
X	2-F	−0.1	−24.4	−34.4
	2-CF$_3$	−6.6	−30.9	−39.0
	2-NO$_2$	−1		
	2-OCH$_3$			
	2,6-diBr	−2		
XI	2-F	−7		
	2-CF$_3$	−7		
	2-NO$_2$	−7		
	2-OCH$_3$	−6		
	2,6-diBr	−6		
XII	2-F	2		
	2-CF$_3$	2		
	2-NO$_2$	1		
	2-OCH$_3$	3		
	2,6-diBr			
XIII		−9		
XIV	2-F	−10		
	2-CF$_3$	−10		
	2-OCH$_3$	−10		
XV	2-F	−8		

	JANAF 2 Stull and Prophet (1971)			JANAF 3 Chase et al. (1985)					
Aqueous Species	**Δ_fG° kJ mol^{-1}**	**Δ_fH° kJ mol^{-1}**	**S° J mol^{-1} K^{-1}**	**Δ_fG° kJ mol^{-1}**	**Δ_fH° kJ mol^{-1}**				
H2O(l)				-237.141	-285.830				
Gas Species	**Δ_fG° kJ mol^{-1}**	**Δ_fH° kJ mol^{-1}**	**S° J mol^{-1} K^{-1}**	**Δ_fG° kJ mol^{-1}**	**Δ_fH° kJ mol^{-1}**				
O2(g)	0.000	0.000	205.142	0.	0.				
H2(g)	0.000	0.000	130.684	0.	0.				
H2O(g)	-228.581	-241.827	188.833	-228.582	-241.826				
CO2(g)	-394.405	-393.522	213.795	-394.389	-393.522				
Solid Species	**Δ_fG° kJ mol^{-1}**	**Δ_fH° kJ mol^{-1}**	**S° J mol^{-1} K^{-1}**	**Δ_fG° kJ mol^{-1}**	**Δ_fH° kJ mol^{-1}**				
P(white)	12.012	17.460	41.079	0.	0.	41.077	0.000	0.000	41.087
P(red)	0.000	0.000	22.803	-12.026	-17.460	22.853	-12.134	-17.573	22.845
		.097	228.781	-2723.335	-3009.936	228.781	-2723.357	-3009.970	228.781
		857	41.463	-856.443	-910.857	41.463	-856.637	-910.940	41.840
		.430	53.848	-1192.796	-1271.936	53.953	-1194.312	-1273.484	53.974
		.990	88.743	-968.520	-1093.990	88.743			
		.274	50.936	-1582.275	-1675.692	50.950	-1582.223	-1675.692	50.919
		.072	93.220	-2444.482	-2592.072	93.221	-2442.843	-2590.314	93.776
		503	87.400	-743.523	-825.503	87.400	-742.293	-824.248	87.404
		.894	145.268	-1017.438	-1120.894	145.266	-1015.228	-1118.383	146.147
							-1380.692	-1479.881	151.001
		241	26.945	-568.945	-601.241	26.924	-569.200	-601.492	26.945
		664	63.178	-833.652	-924.664	63.242			
		.689	65.856	-1028.124	-1111.689	65.854	-1029.299	-1113.090	65.103
		.935	95.140	-2057.879	-2176.935	95.140	-2054.944	-2174.006	95.140
				-603.501	-635.089	38.212	-603.459	-635.089	38.074
				-898.421	-986.085	83.387			
							-1129.033	-1207.544	91.713
							-1549.629	-1634.940	82.006
		982	75.040	-379.090	-417.982	75.042	-378.322	-417.145	75.270
		120	72.115	-384.024	-411.120	72.115	-384.062	-411.153	72.132
		171	94.140	-322.094	-363.171	94.140	-301.257	-339.992	102.006
		684	82.555	-408.761	-436.684	82.554	-408.819	-436.747	82.546

TABLE 4.1 Thermodynamic Data for Inorganic Compounds at 298.15 K (continued)

Substance	ΔH_f° (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})	S_m° (J mol^{-1} K^{-1})	$C_{P,m}$ (J mol^{-1} K^{-1})	Atomic or Molecular Weight (amu)
Silicon					
Si(*s*)	0	0	18.8	20.0	28.09
Si(*g*)	450.0	405.5	168.0	22.3	28.09
$SiCl_4$(*g*)	−662.7	−622.8	330.9	90.3	169.70
SiO_2(*quartz*)	−910.7	−856.3	41.5	44.4	60.09
Silver					
Ag(*s*)	0	0	42.6	25.4	107.87
Ag(*g*)	284.9	246.0	173.0	20.8	107.87
AgCl(*s*)	−127.0	−109.8	96.3	50.8	143.32
$AgNO_2$(*s*)	−44.4	19.8	140.6	93.0	153.88
$AgNO_3$(*s*)	−44.4	19.8	140.9	93.1	169.87
Ag_2SO_4(*s*)	−715.9	−618.4	200.4	131.4	311.80
Ag^+(*aq*)	105.6	77.1	72.7		107.87
Sodium					
Na(*s*)	0	0	51.3	28.2	22.99
Na(*g*)	107.5	77.0	153.7	20.8	22.99
NaCl(*s*)	−411.2	−384.1	72.1	50.5	58.44
NaOH(*s*)	−425.8	−379.7	64.4	59.5	40.00
Na_2SO_4(*s*)	−1387.1	−1270.2	149.6	128.2	142.04
Na^+(*aq*)	−240.1	−261.9	59.0		22.99
Sulfur					
S(*rhombic*)	0	0	32.1	22.6	32.06
SF_6(*g*)	−1220.5	−1116.5	291.5	97.3	146.07
H_2S(*g*)	−20.6	−33.4	205.8	34.2	34.09
SO_2(*g*)	−296.8	−300.1	248.2	39.9	64.06
SO_3(*g*)	−395.7	−371.1	256.8	50.7	80.06
SO_3^{2-}(*aq*)	−635.5	−486.6	−29.3		80.06
SO_4^{2-}(*aq*)	−909.3	−744.5	20.1		96.06
Tin					
Sn(*white*)	0	0	51.2	27.0	118.69
Sn(*g*)	301.2	266.2	168.5	21.3	118.69
SnO_2(*s*)	−577.6	−515.8	49.0	52.6	150.69
Sn^{2+}(*aq*)	−8.9	−27.2	−16.7		118.69
Titanium					
Ti(*s*)	0	0	30.7	25.0	47.87
Ti(*g*)	473.0	428.4	180.3	24.4	47.87
$TiCl_4$(*l*)	−804.2	−737.2	252.4	145.2	189.69
TiO_2(*s*)	−944.0	−888.8	50.6	55.0	79.88

T/K	C_p^0 J K^{-1} mol^{-1}	$H_T^0 - H_{298.15}^0$ J mol^{-1}	S_T^0 J K^{-1} mol^{-1}	$-(G_T^0 - H_{298.15}^0)/T$ J K^{-1} mol^{-1}	Δ_fH^0 kJ mol^{-1}	Δ_fG^0 kJ mol^{-1}
298.15	109.4	0	113.70	113.70	−961.536	−884.475
300	109.8	203	114.38	113.70	−961.512	−883.998
400	108.4	10 823	144.93	117.87	−960.818	−858.275
500	114.6	21 978	169.79	125.84	−960.126	−832.719
600	120.0	33 711	191.17	134.98	−959.359	−807.309
700	124.9	45 959	210.04	144.38	−958.531	−782.033
800	129.3	58 672	227.01	153.67	−957.646	−756.877
900	133.4	71 813	242.48	162.69	−956.698	−731.839
980	136.6	82 614	253.98	169.68	−955.869	−711.977
980	136.6	82 614	253.98	169.68	−960.319	−711.978
1000	137.3	85 353	256.75	171.39	−960.149	−706.820
1100	141.0	99 271	270.01	179.76	−959.071	−681.537
1200	144.6	113 552	282.43	187.80	−957.778	−656.365
1300	148.0	128 183	294.14	195.54	−956.269	−631.302
1360	150.1	137 127	300.87	200.04	−955.260	−616.425
1360	150.1	137 127	300.87	200.04	−959.500	−616.424
1400	151.4	143 157	305.24	202.98	−959.086	−606.242

			S_T^0 J K^{-1} mol^{-1}	$-(G_T^0 - H_{298.15}^0)/T$ J K^{-1} mol^{-1}	Δ_fH^0 kJ mol^{-1}	Δ_fG^0 kJ mol^{-1}
			165.60	165.60	−1386.185	−1284.409
			166.48	165.60	−1386.176	−1283.779
			209.41	171.37	−1385.372	−1249.751
			245.01	182.64	−1384.332	−1215.966
			275.48	195.63	−1383.264	−1182.394
			302.25	208.99	−1382.210	−1149.001
			326.22	222.17	−1381.159	−1115.755
			348.03	234.96	−1380.081	−1082.647
			364.20	244.86	−1379.150	−1056.369
			364.20	244.86	−1385.825	−1056.370
			368.10	247.28	−1385.648	−1049.525
			386.75	259.12	−1384.449	−1015.969
			404.24	270.50	−1382.945	−982.538
			420.73	281.42	−1381.121	−949.236
			430.22	287.78	−1379.872	−929.462
1360	211.71	193 713	430.22	287.78	−1386.232	−929.462
1400	213.74	202 222	436.38	291.94	−1385.785	−915.903
1411	214.29	204 576	438.06	293.07	−1385.713	−912.238
1411	214.29	204 576	438.06	293.07	−1391.353	−912.240
1445	216.01	211 891	443.18	296.54	−1391.195	−900.813
1445	210.90	229 615	455.43	296.53	−1373.471	−900.788
1500	210.90	241 214	463.31	302.50	−1373.337	−882.651
1519	210.90	245 222	465.96	304.53	−1373.442	−876.614
1519	210.90	245 222	465.96	304.53	−1406.442	−876.612
1600	210.90	262 304	476.92	312.98	−1406.393	−848.179
1700	210.90	283 394	489.71	323.00	−1406.499	−813.289
1800	210.90	304 484	501.76	332.60	−1406.651	−778.391

4. Solve equations using a numerical model

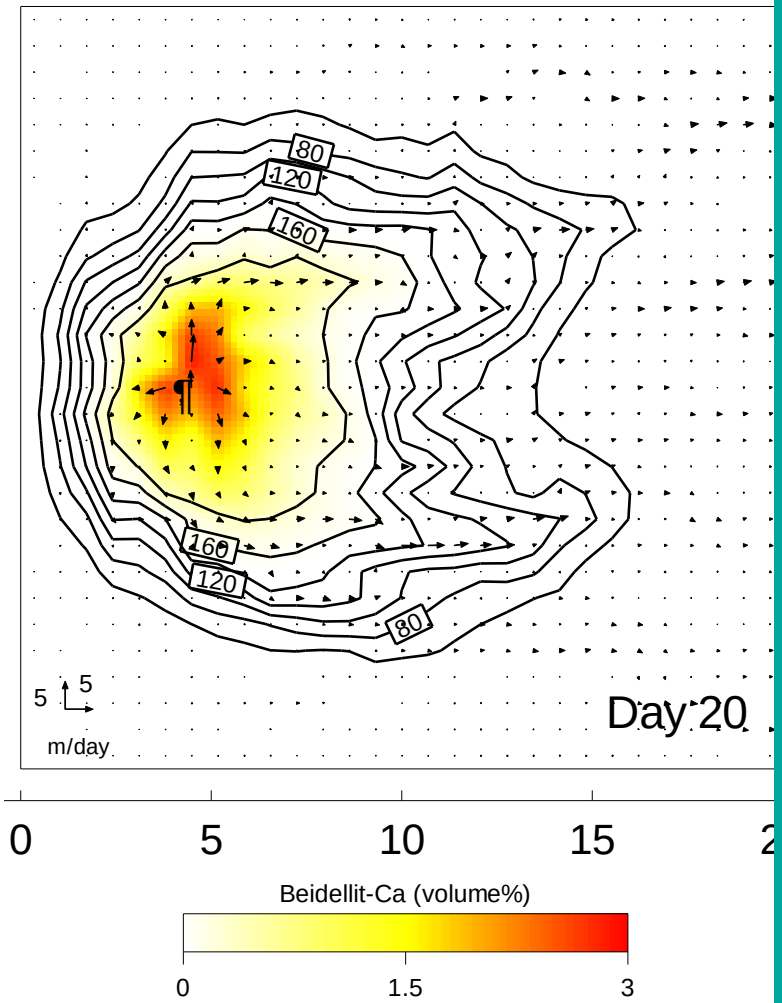
- Here, we are using the Geochemist's Workbench.
- The remainder of the class will focus on how to use this software.

Workflow for thermodynamic modeling

1. Develop a conceptual model: List the processes that likely determine the chemical composition of a system.
2. Make partial equilibrium assumptions: Consider the timeframes in which you wish to understand a system (minutes? years? millions of years?). Decide which of the relevant reactions will reach equilibrium in this timeframe, and which ones will not proceed to any relevant degree.
3. Make sure you have thermodynamic parameters for these reactions.
4. Solve all equations simultaneously with a numerical model.
5. Interpret the output with respect to your conceptual model.
6. Potentially revise the conceptual model and start over.

Meret Aeppli

Geochemist's Workbench Installation guide

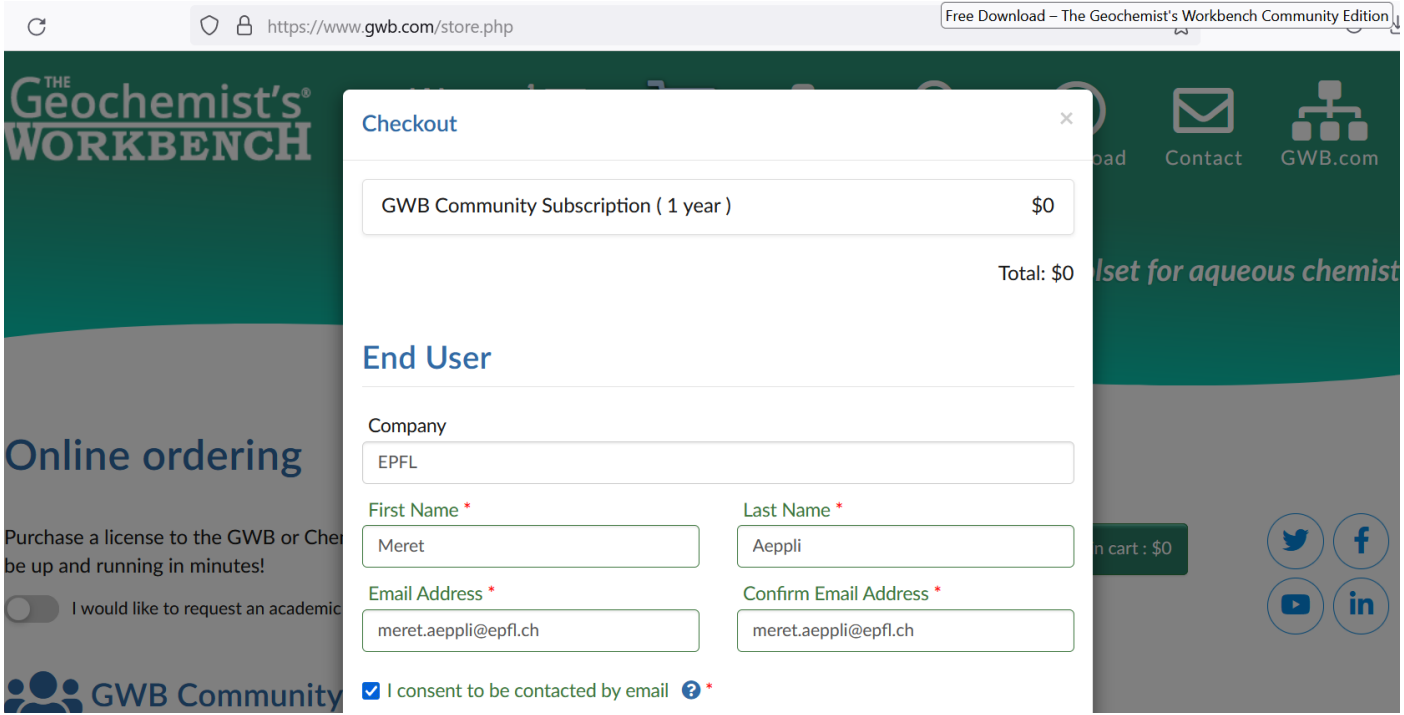


Information

- The Geochemist's Workbench is not available for MacOS or Linux systems
- If you are working with MacOS (or Linux), please find another student whose PC is running on Windows and work together

Installation guide

Go to https.//www.gwb.com/store.php and add GWB community to your chart ($0).



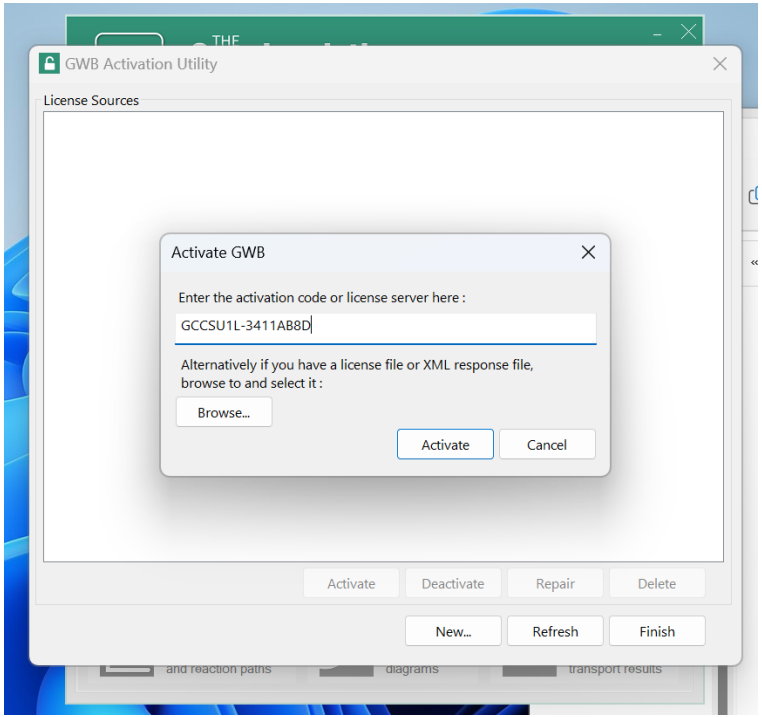
Installation guide

You will receive an email with a link to the download. Download and install following the prompts on the screen.

GWB Community Edition 2023

Installation guide

Once installation is complete, open the software. Input the activation code you received by email and click *activate*, then *finish*.

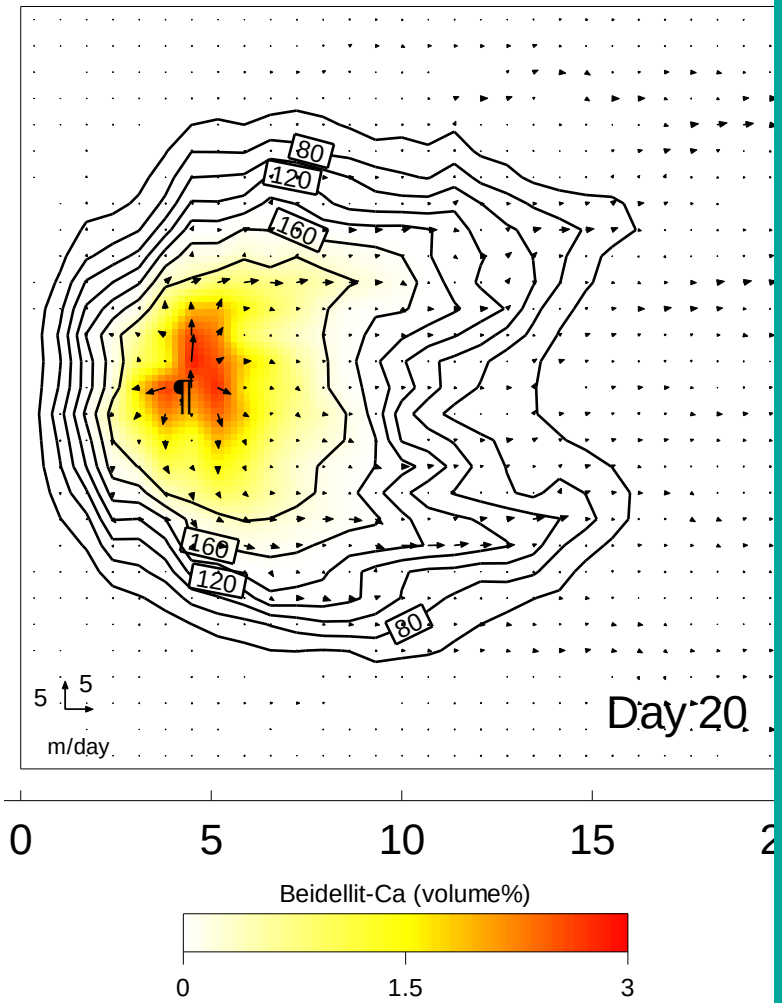


Installation guide

Open Geochemist's Workbench. It should look like this:

Meret Aeppli

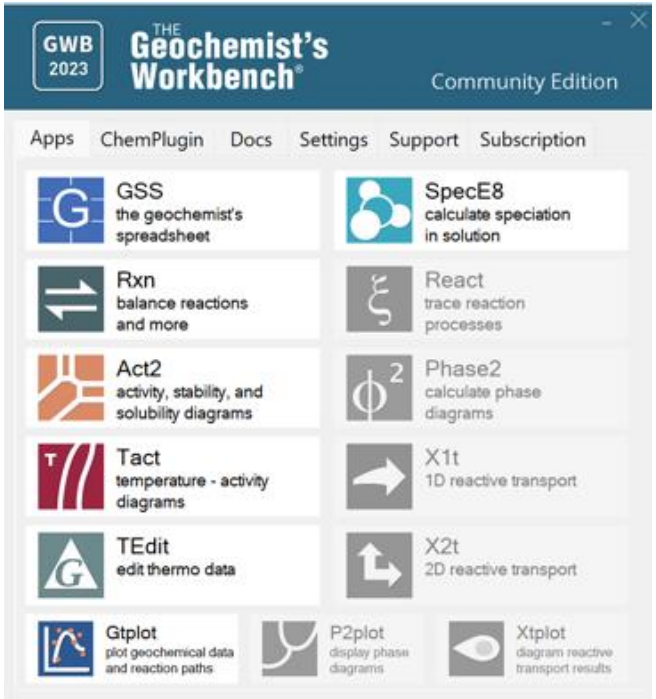
Introduction to the Geochemist's Workbench



The Geochemist's Workbench Essentials

We will use the following Apps here:

- **GSS** is a spreadsheet designed for manipulating and plotting geochemistry data
- **Rxn** balances chemical reactions and calculates equilibrium constants, temperatures, and equations
- **Act2** generates stability diagrams on activity, Eh, pe, pH, and fugacity axes
- **SpecE8** computes the distribution of species, sorption onto surfaces, mineral saturation, gas fugacity, and isotope fractionation in aqueous solutions



GSS: The Geochemist's Spreadsheet

- **GSS** is a spreadsheet designed for geochemists. The program works with the other software tools in The Geochemist's Workbench. You enter, paste, or drag the analyses for your samples into a GSS data sheet.
- You can then convert units, create plots and diagrams, mix samples, compare replicate analyses and check standards, calculate speciation and saturation, and more. You can drag samples into the other GWB apps, and drag calculations results from the other apps into **GSS**.

GSS: The Geochemist's Spreadsheet

Open GSS, go to File → Open and select the file "RiverWaters.gss"

Analytes

Samples

GSS Community Edition - C:\Users\maeppli\OneDrive - epfl.ch\GWB\RiverWaters.gss

File Edit Data Plot Analysis Help

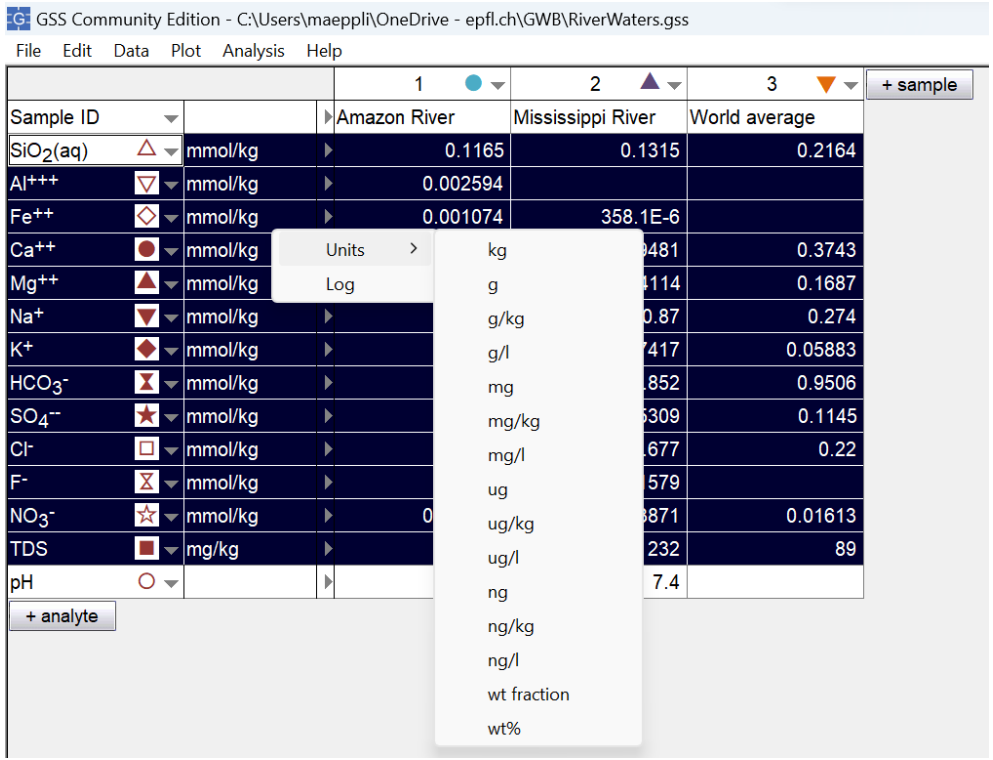
Sample ID		1 Amazon River	2 Mississippi River	3 World average
$SiO_{2(aq)}$	mmol/kg	0.1165	0.1315	0.2164
Al^{+++}	mmol/kg	0.002594		
Fe^{++}	mmol/kg	0.001074	358.1E-6	
Ca^{++}	mmol/kg	0.1073	0.9481	0.3743
Mg^{++}	mmol/kg	0.04526	0.4114	0.1687
Na^{+}	mmol/kg	0.0783	0.87	0.274
K^{+}	mmol/kg		0.07417	0.05883
HCO_3^{-}	mmol/kg	0.3114	1.852	0.9506
SO_4^{--}	mmol/kg	0.03123	0.5309	0.1145
Cl^{-}	mmol/kg	0.05359	0.677	0.22
F^{-}	mmol/kg	0.01053	0.01579	
NO_3^{-}	mmol/kg	0.001613	0.03871	0.01613
TDS	mg/kg	28	232	89
pH		6.5	7.4	

+ sample

+ analyte

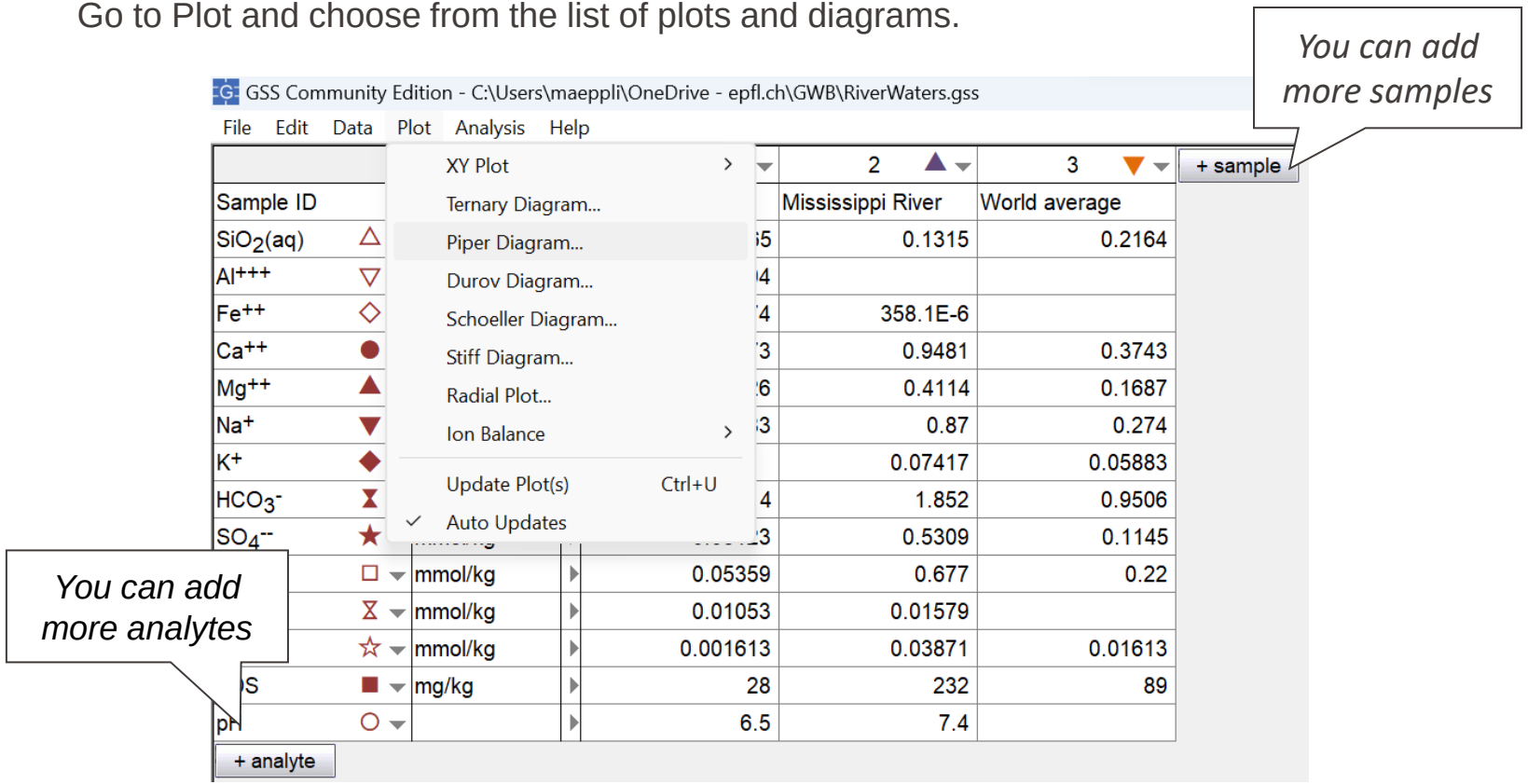
GSS: Converting units

Select one or more analytes, right click in the unit field to show a selection of units.



GSS: Plotting data

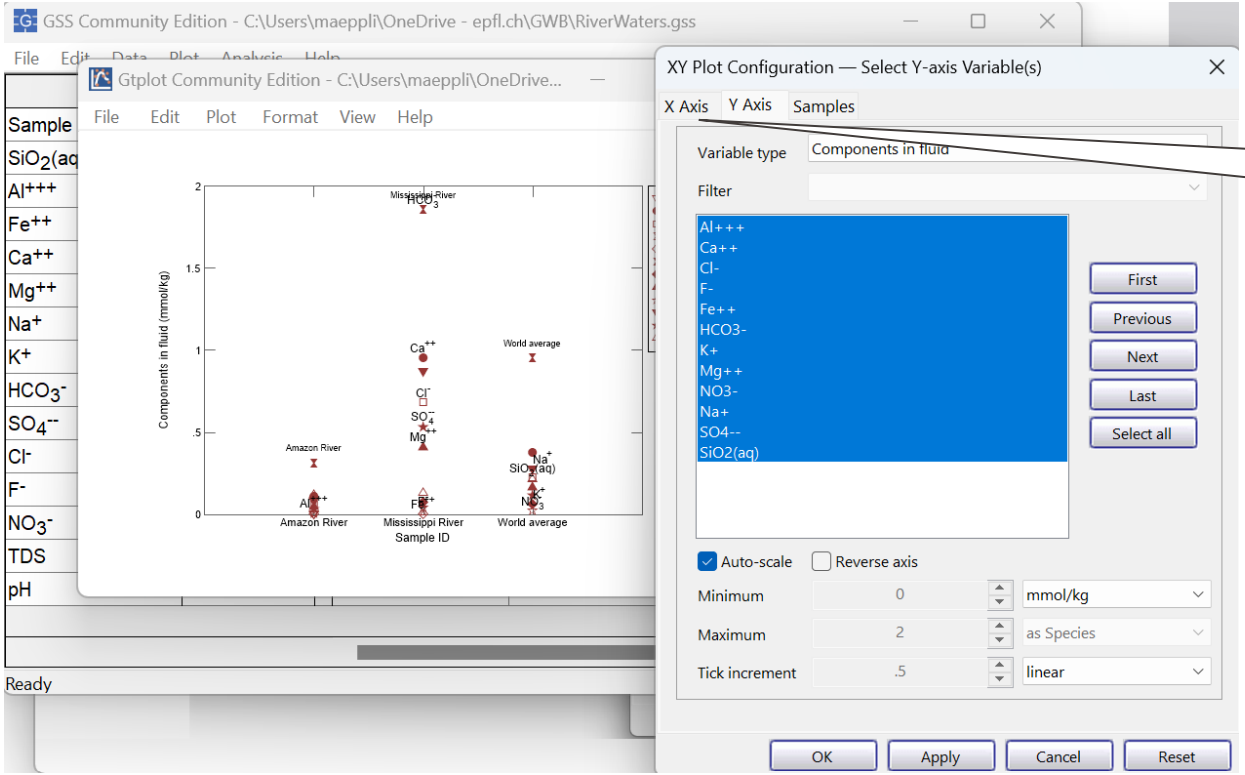
Go to Plot and choose from the list of plots and diagrams.



GSS: Plotting data

Meret Aeppli

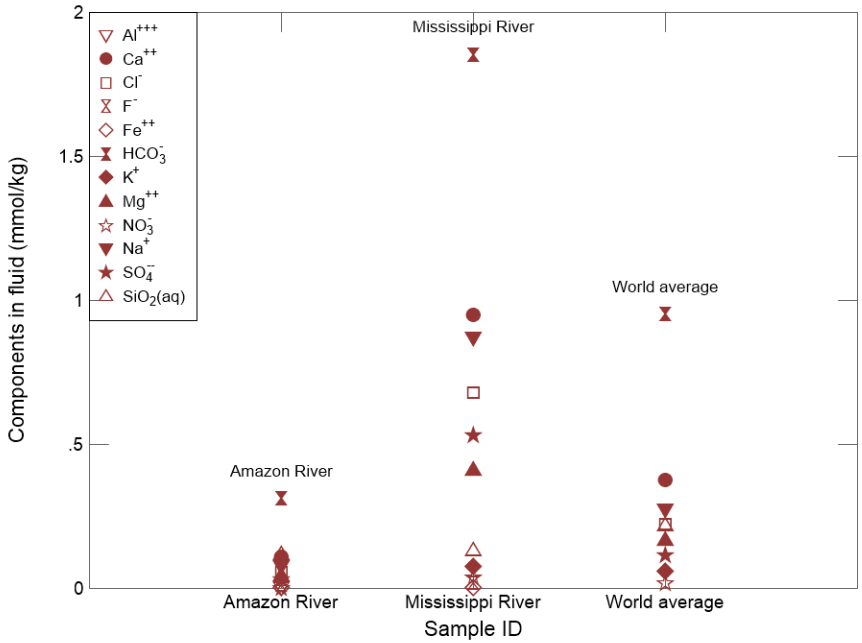
Chose XY Plot → Cross Plot. This will open Gtplot to generate the following:



In Tab X Axis, you can chose which parameter to show on the X axis

GSS: Plotting data

To change the appearance of the plot, go to Format → Appearance



GSS: Calculate water hardness

Go back to the initial GSS table. Click on + analyte → Calculate with SpecE8 → Hardness.
A row with water hardness values is added to the table.

GSS Community Edition - V:\Lectures\GWB Files\RiverWaters.gss

File Edit Data Plot Analysis Help

Sample ID		1 Amazon River	2 Mississippi River	3 World average
$SiO_2(aq)$	mg/l	6.972	7.87	12.95
Al^{+++}	mg/l	0.06972		
Fe^{++}	mg/l	0.05976	0.01992	
Ca^{++}	mg/l	4.283	37.85	14.94
Mg^{++}	mg/l	1.096	9.962	4.084
Na^{+}	mg/l	1.793	19.92	6.275
K^{+}	mg/l		2.889	2.291
HCO_3^{-}	mg/l	18.92	112.6	57.77
SO_4^{--}	mg/l	2.988	50.8	10.96
Cl^{-}	mg/l	1.892	23.91	7.769
F^{-}	mg/l	0.1992	0.2988	
NO_3^{-}	mg/l	0.0996	2.391	0.9961
TDS	mg/kg	28	232	89
pH		6.5	7.4	
Hardness	mmol/l_as_$CaCO_3$	0.152	1.354	0.5408

Ready NUM

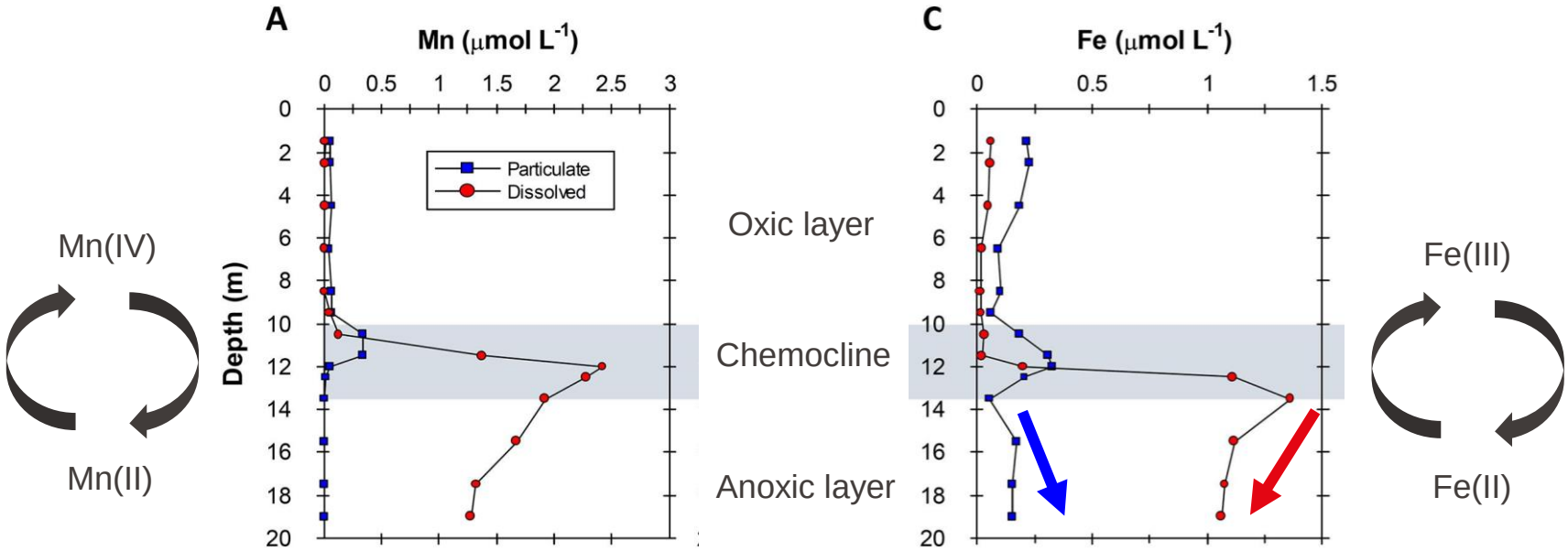
$$Hardness\ in\ mmol\ L^{-1} \approx \frac{[Ca\ in\ mg\ L^{-1}]}{40} + \frac{[Mg\ in\ mg\ L^{-1}]}{24.3}$$

Interpreting the data

Why is the water of the Mississippi River harder than the water of the Amazon River?

Meret Aeppli

Particulate and dissolved Fe and Mn concentrations in Lake Cadagno



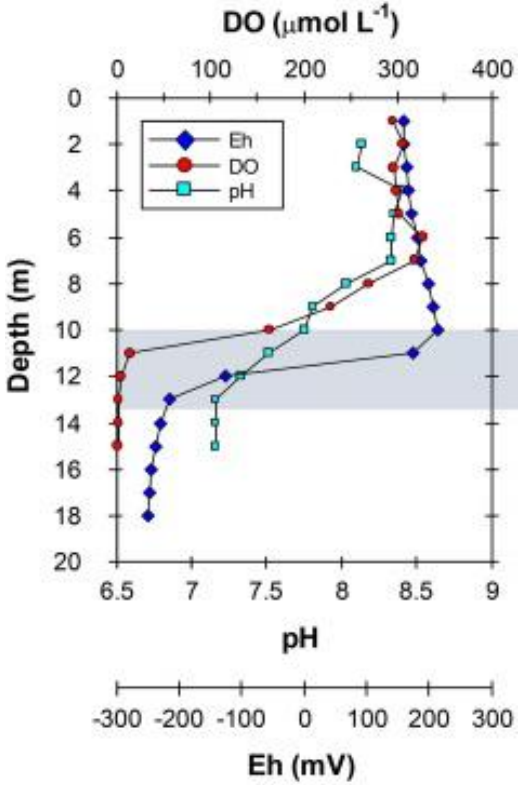
Iron(III) compounds are reductively dissolved in the anoxic zone. Why do we see an increase in particulate iron and decrease in dissolved iron below the chemocline?

*Ellwood, MJ et al., Geochim Cosmochim Acta, **2019**, 255, 205-221.*

Iron redox processes

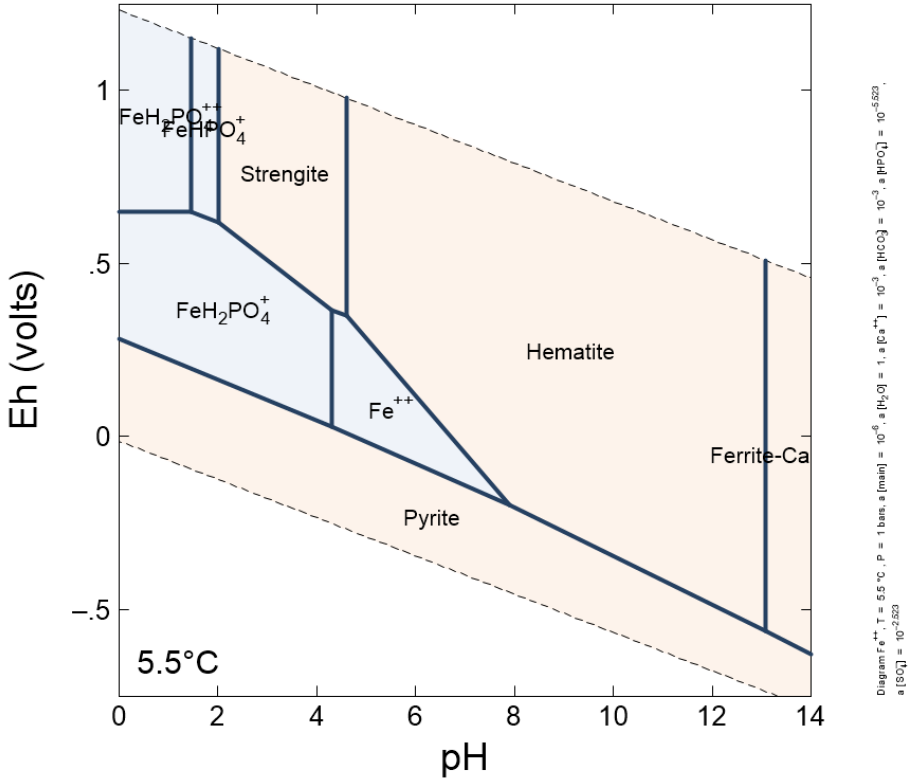
- The decrease in dissolved and increase in particulate Fe concentrations suggest that iron phases are precipitating.
- Which method could you use to figure out which phases are precipitating?

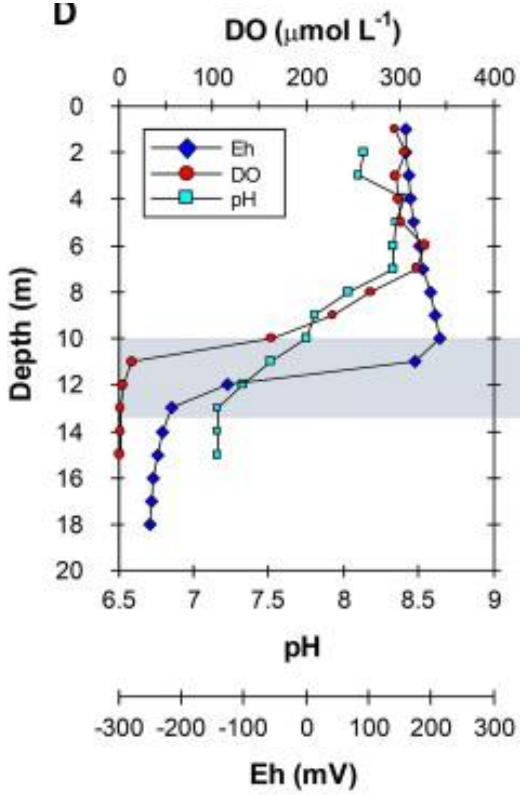
=> Eh-pH diagram



Ellwood, MJ et al., Geochim Cosmochim Acta, ***2019****, 255, 205-221.*

E_H-pH stability diagram



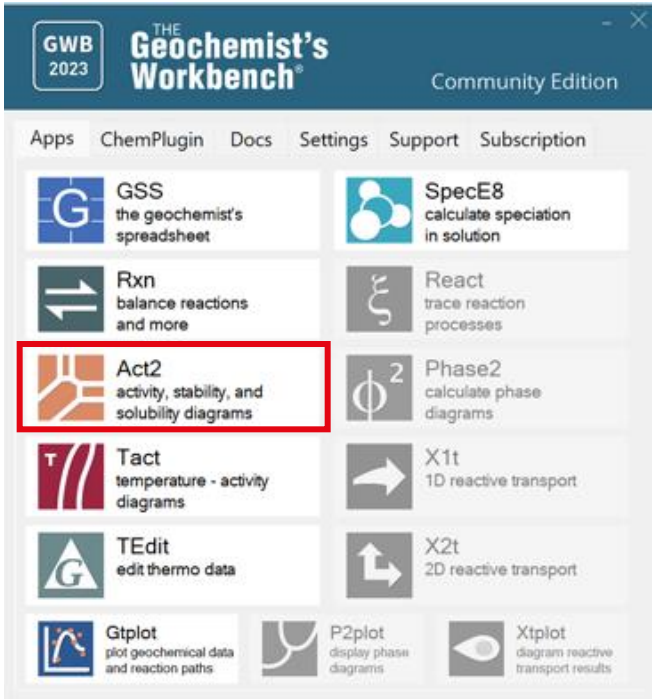


Meret Aeppli

Meret Aeppli

Act2: Create stability diagrams

- Open the Act2 App in the GWB Software
- Enter the input parameters

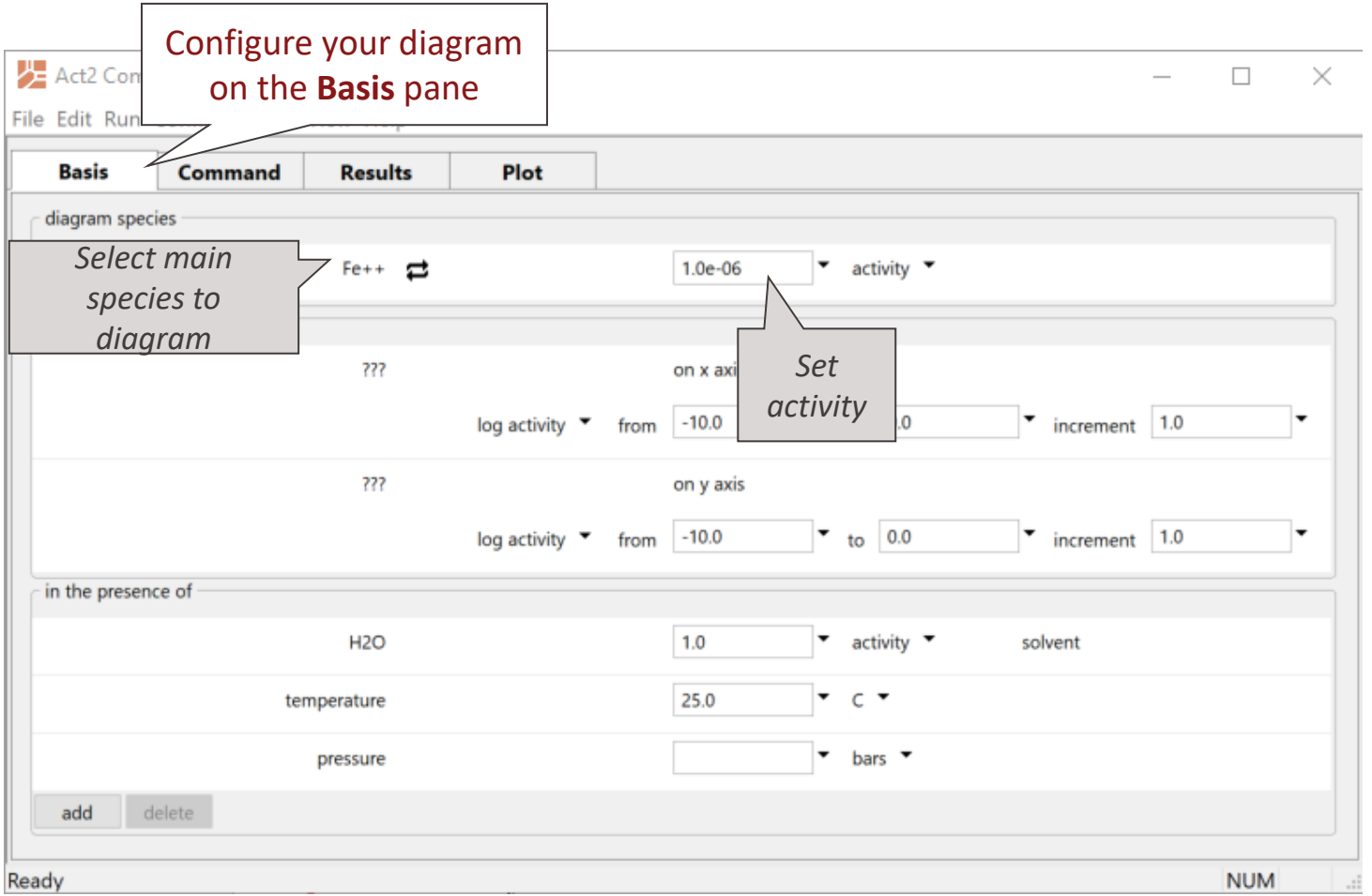


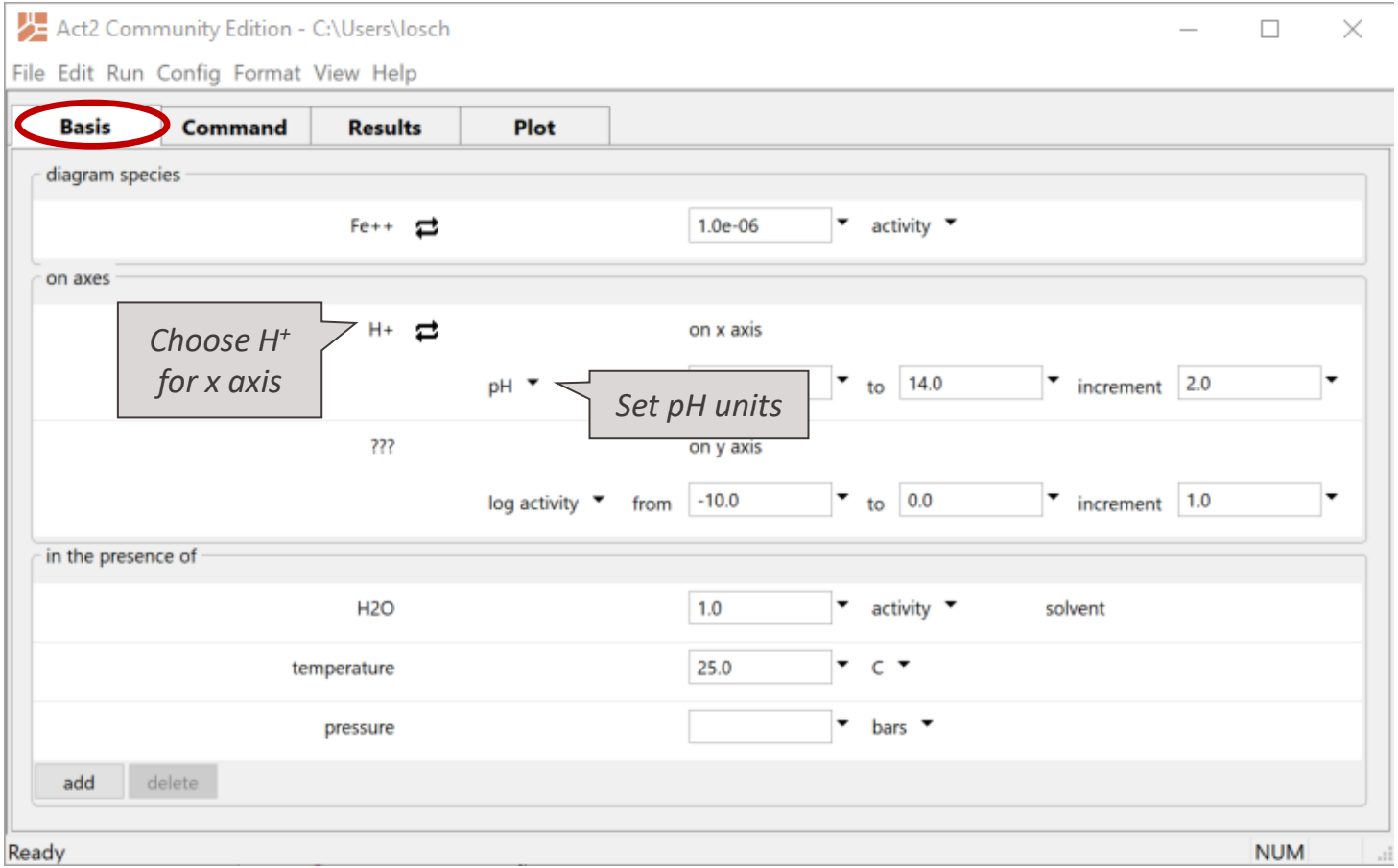
E_H-pH stability diagram

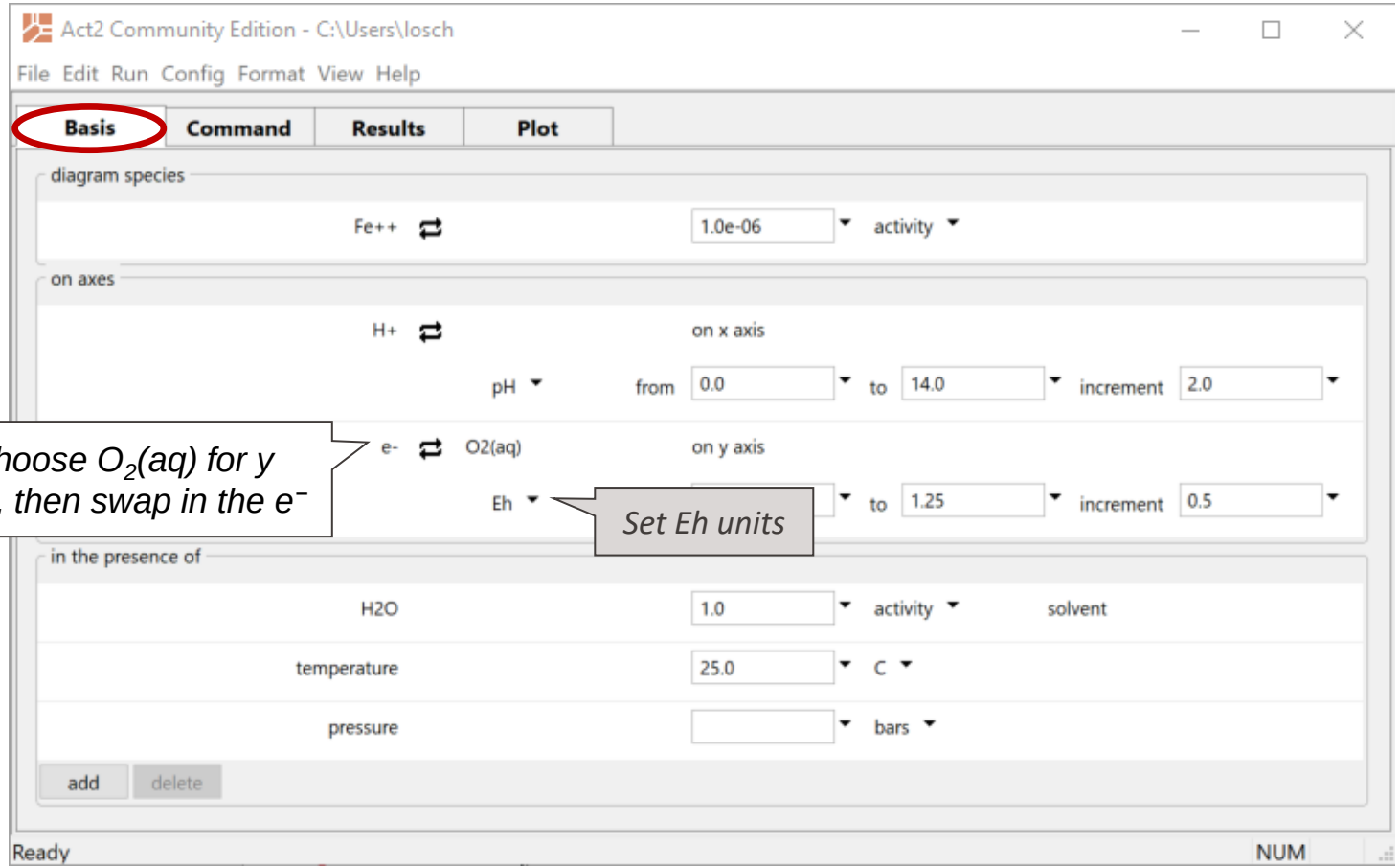
Which parameters do you need? (These are given in the paper referenced below)

- Temperature: 5.5 °C
- Pressure: 1 bar
- Total iron concentration: 1 µmol/L
- Bicarbonate: 1 mmol/L
- Calcium: 1 mmol/L
- Sulfate: 3 mmol/L
- Phosphate: 3 µmol/L

*Ellwood, MJ et al., Geochim Cosmochim Acta, **2019**, 255, 205-221.*

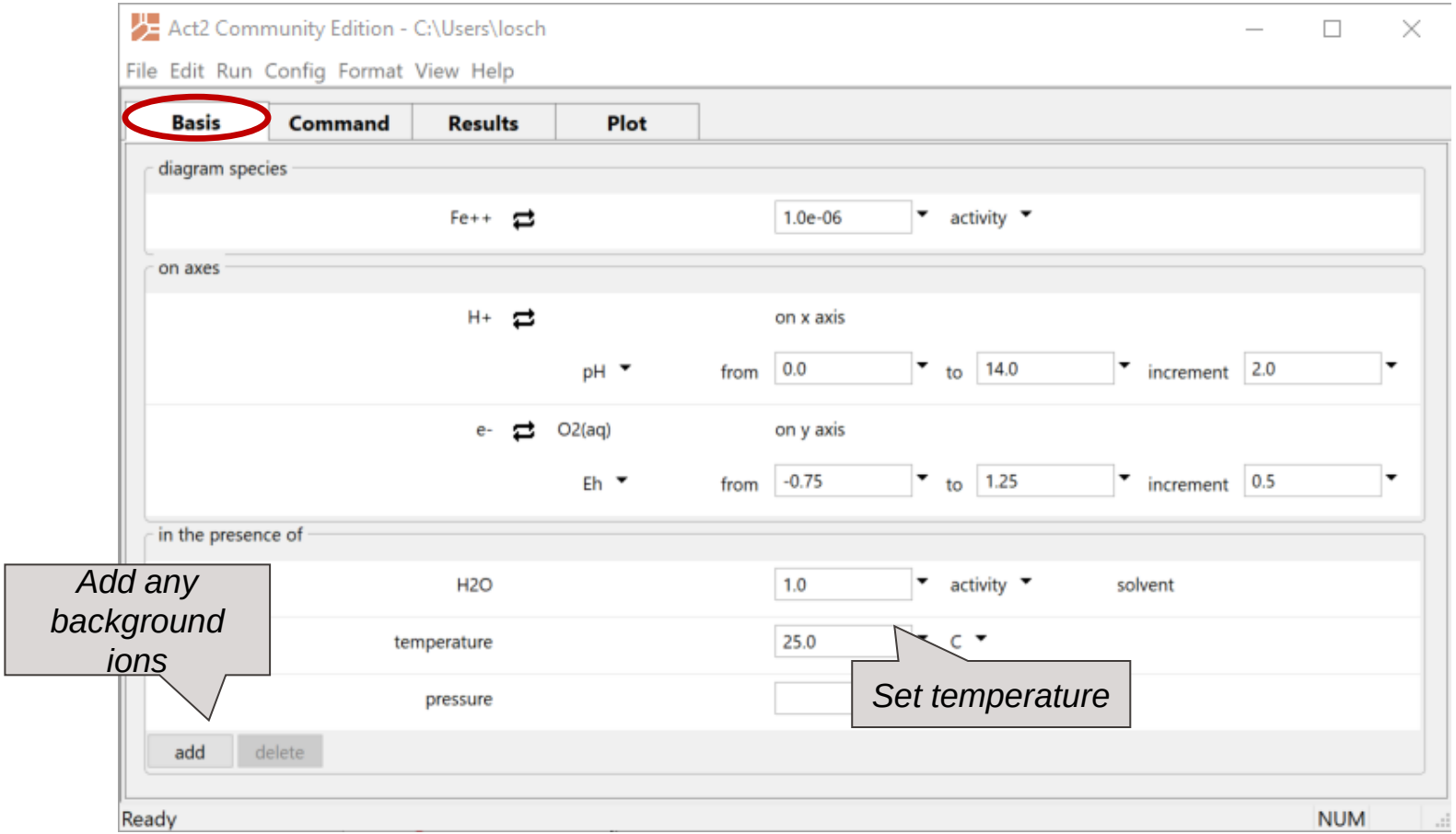

Configure your diagram on the **Basis** pane
Act2 Con
File Edit Run
Basis
Command
Results
Plot
diagram species
Select main species to diagram
Fe++
1.0e-06
activity
Set activity
???
on x axi
log activity
from
-10.0
increment
1.0
???
on y axis
log activity
from
-10.0
to
0.0
increment
1.0
in the presence of
H2O
1.0
activity
solvent
temperature
25.0
C
pressure
bars
add
delete
Ready
NUM

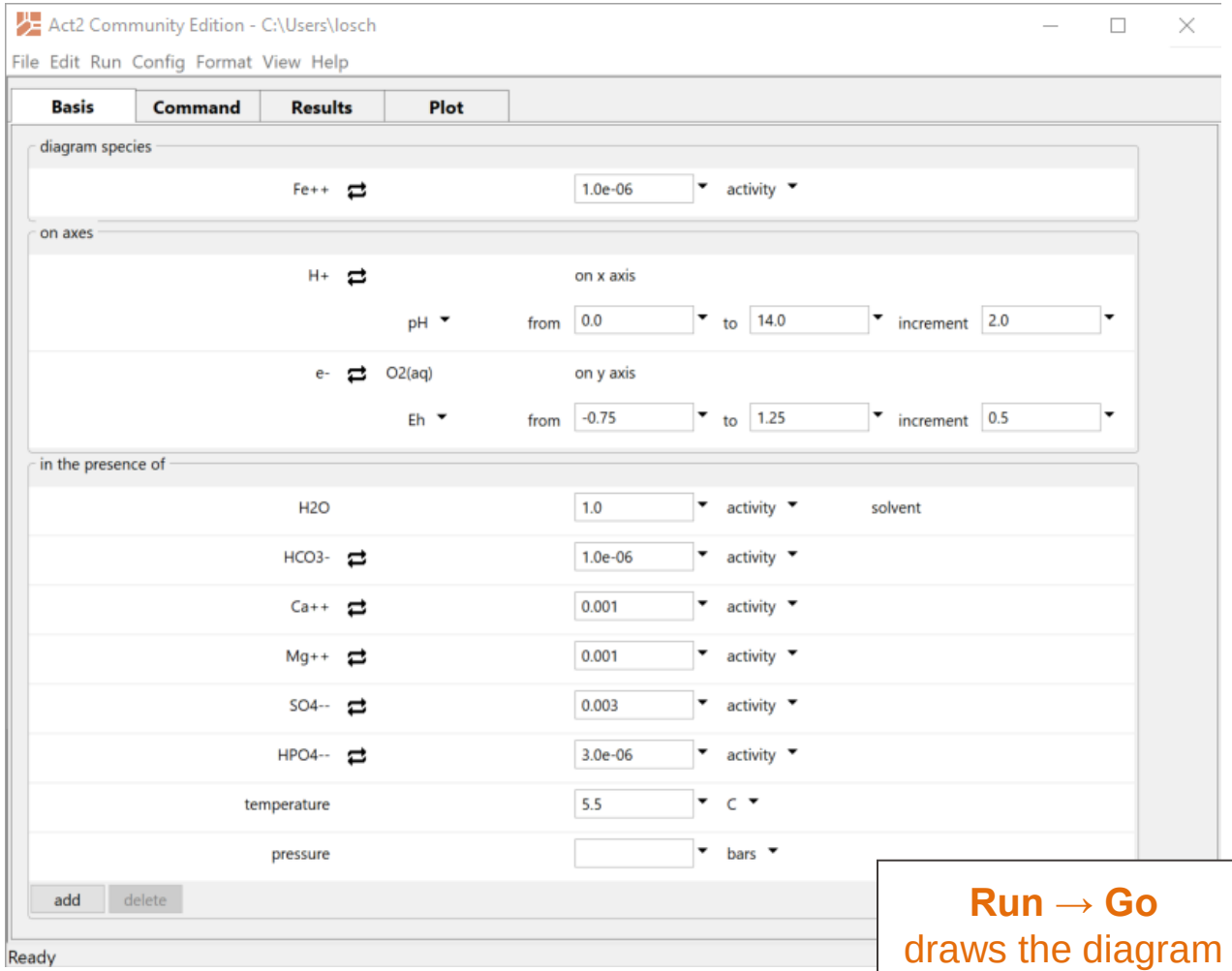

Act2 Community Edition - C:\Users\losch
File Edit Run Config Format View Help
Basis
Command
Results
Plot
diagram species
Fe++
1.0e-06
activity
on axes
Choose H+ for x axis
H+
on x axis
pH
Set pH units
to
14.0
increment
2.0
???
on y axis
log activity
from
-10.0
to
0.0
increment
1.0
in the presence of
H2O
1.0
activity
solvent
temperature
25.0
C
pressure
bars
add
delete
Ready
NUM



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

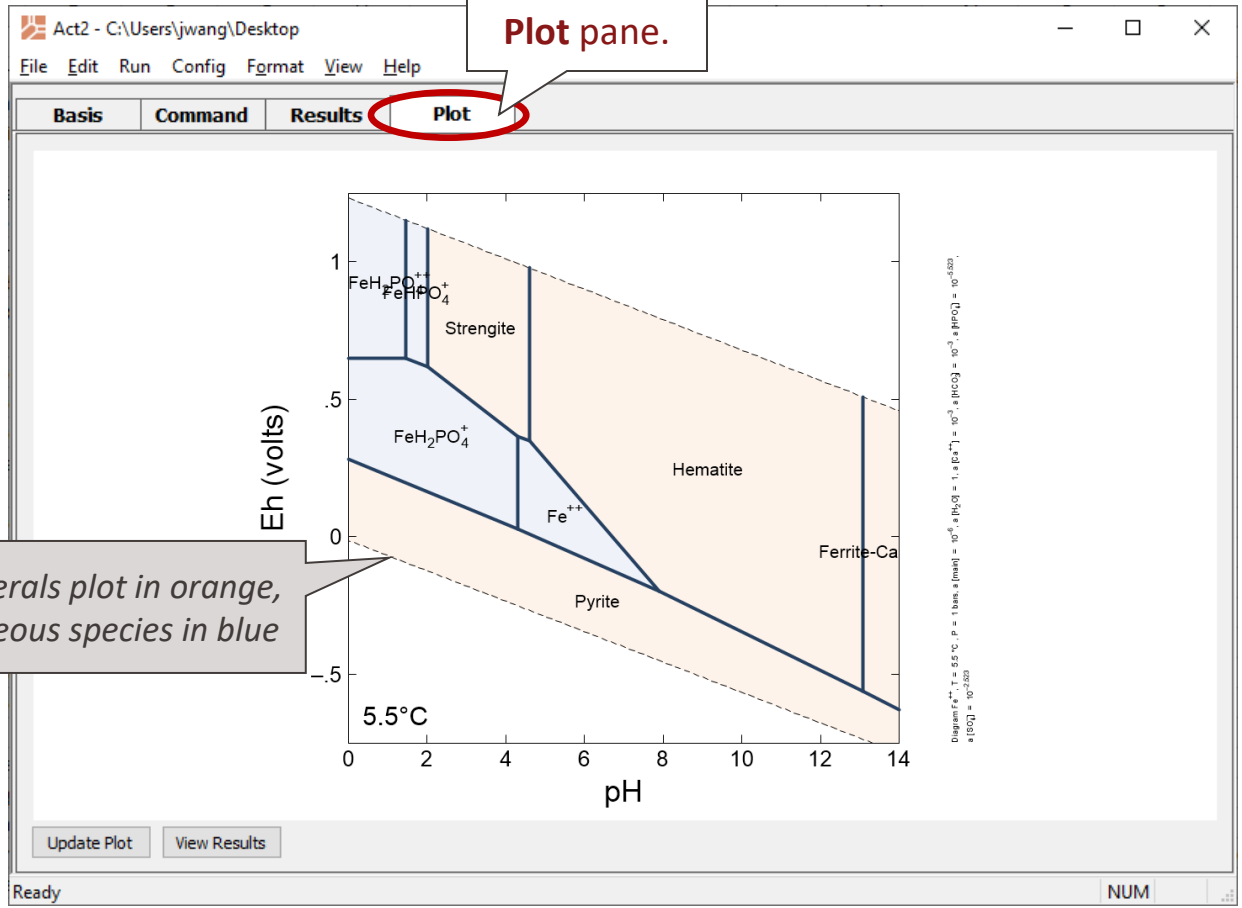
Set Eh units


Act2 Community Edition - C:\Users\losch
File Edit Run Config Format View Help
Basis
Command
Results
Plot
diagram species
Fe++
1.0e-06
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
add
delete
Ready
NUM
Add any background ions
Set temperature



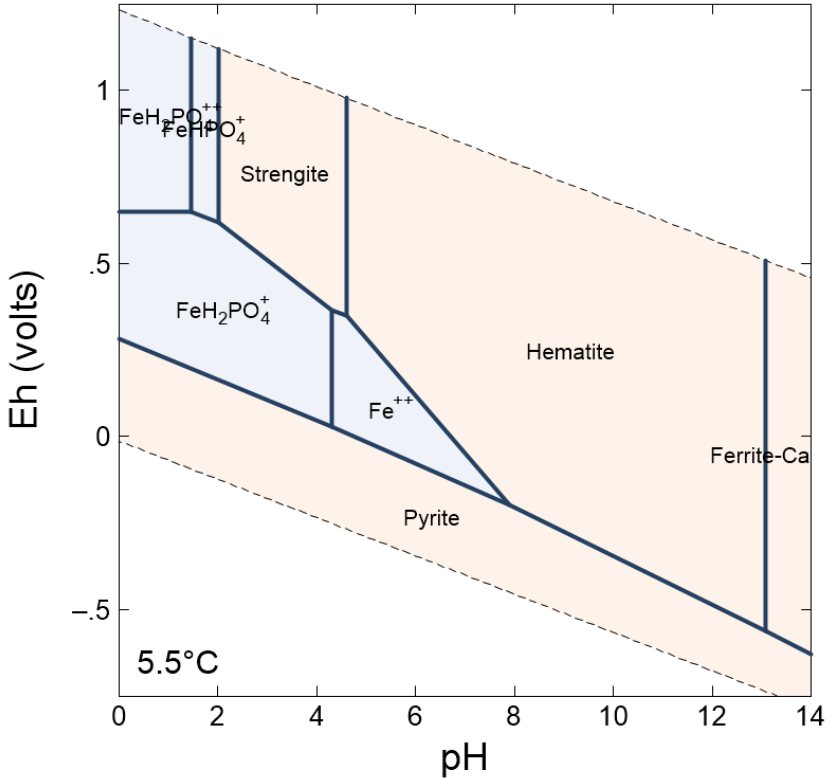
Run → Go
draws the diagram

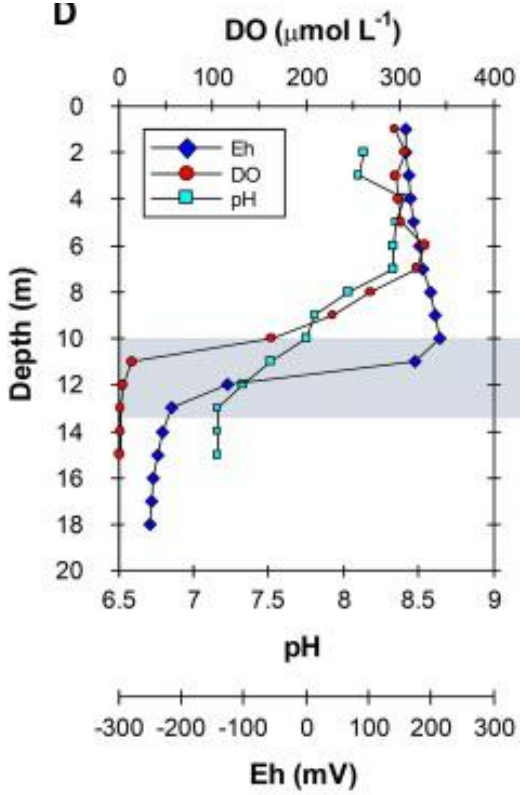
Move to the **Plot** pane.



Minerals plot in orange, aqueous species in blue

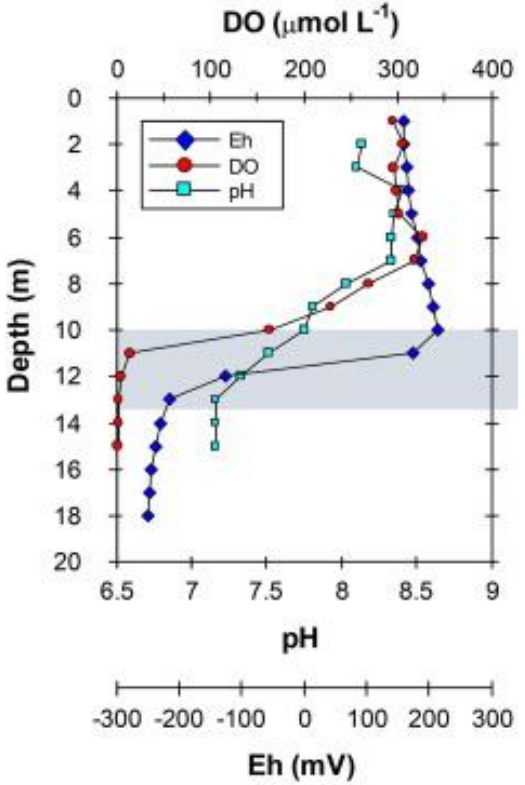
E_H-pH stability diagram: Solution





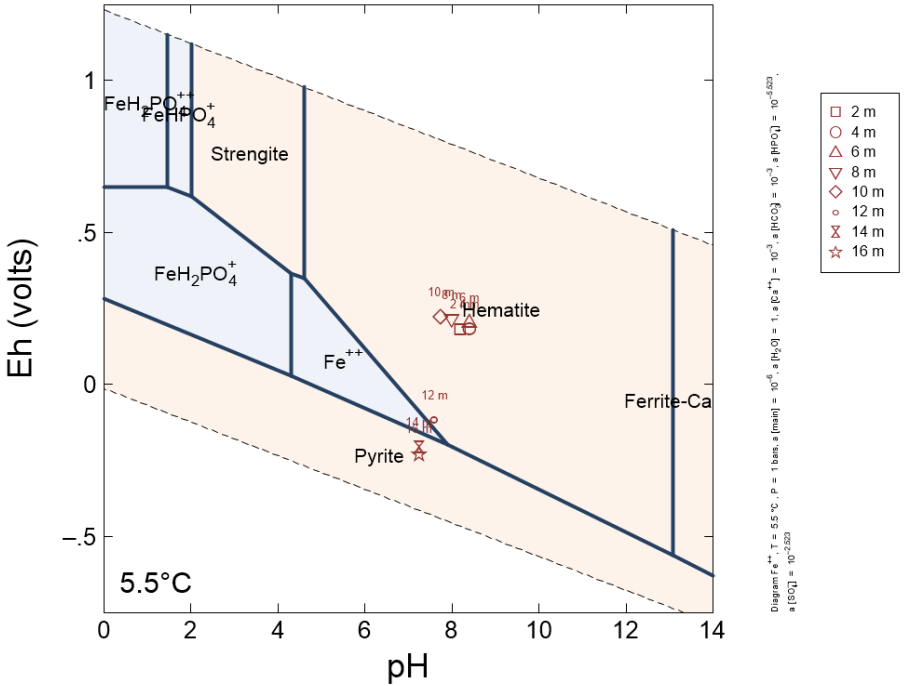
E_H-pH stability diagram: Solution

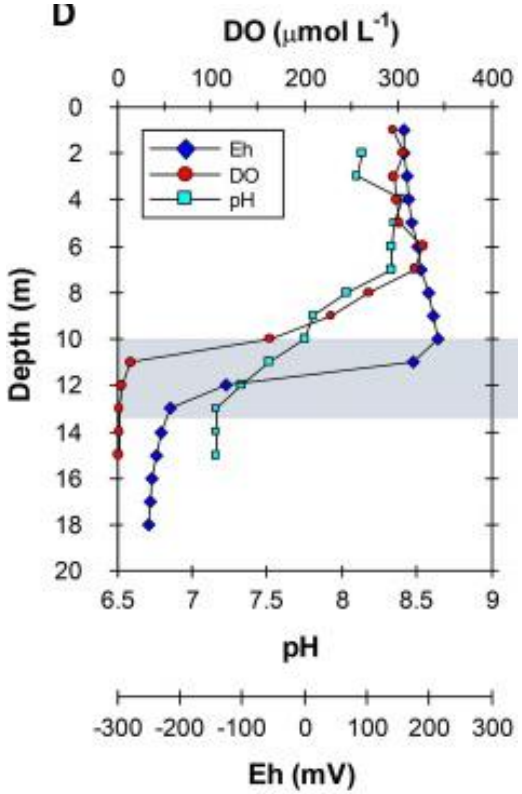
- Now add the data from the figure on the right into your E_H-pH diagram.
- To do so, create a GSS file, add the data, and then drag and drop it into your E_H-pH diagram.



Ellwood, MJ et al., Geochim Cosmochim Acta, ***2019****, 255, 205-221.*

E_H-pH stability diagram: Solution

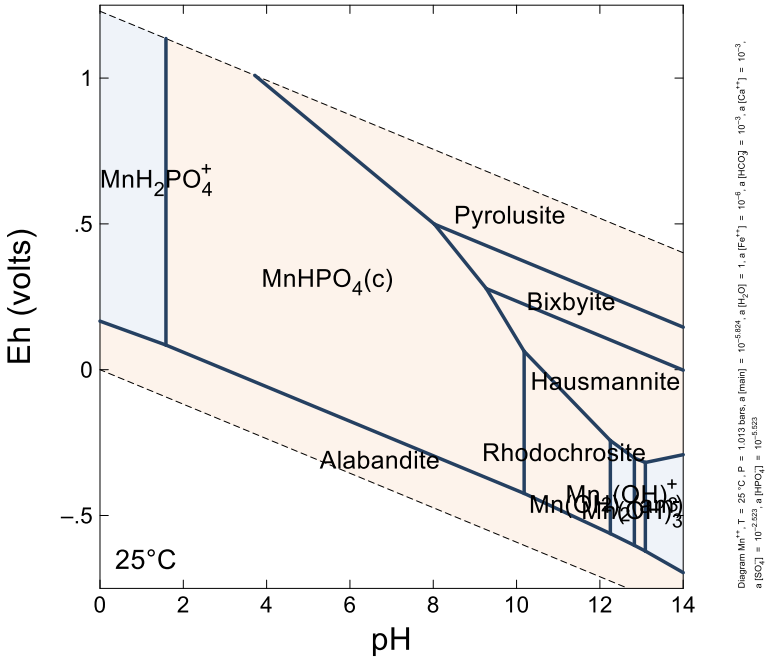


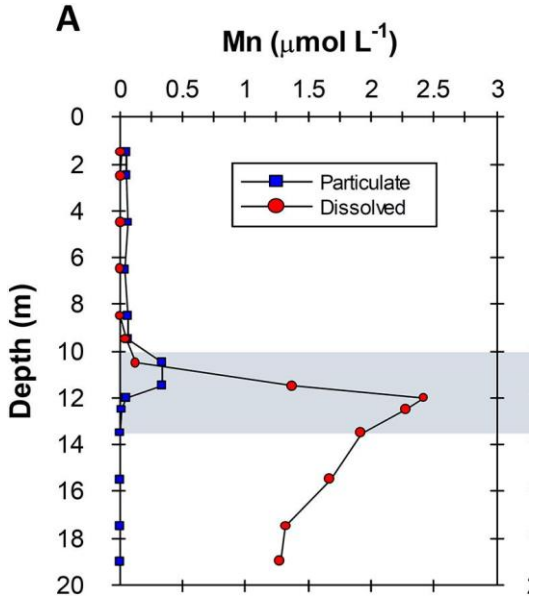


FeS is expected to precitipate in the anoxic zone and likely causes the increase in particulate concentrations we observed.

Meret Aeppli

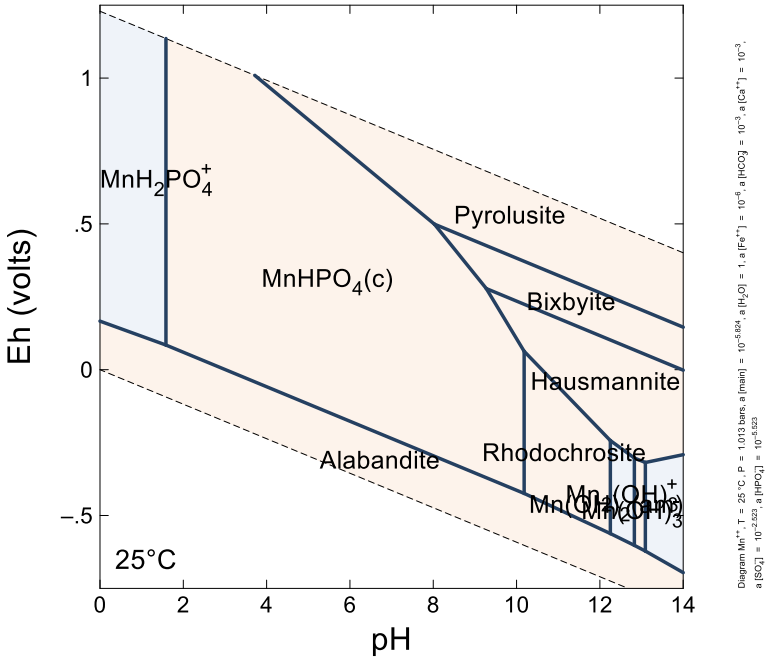
E_H-pH stability diagram: Solution?





Why is there no increase in particulate Mn?

E_H-pH stability diagram: Solution?

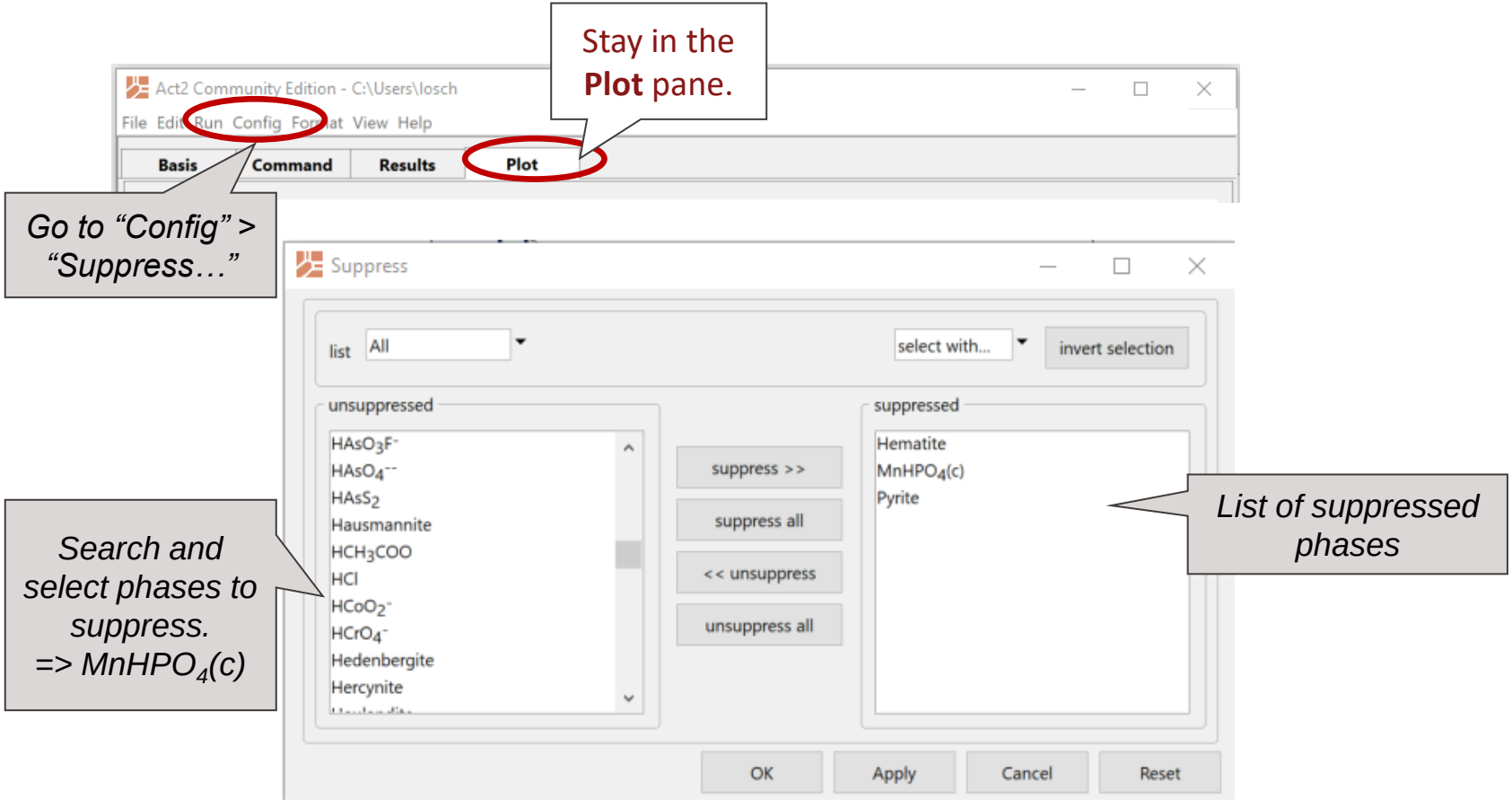


Why is there no increase in particulate Mn?

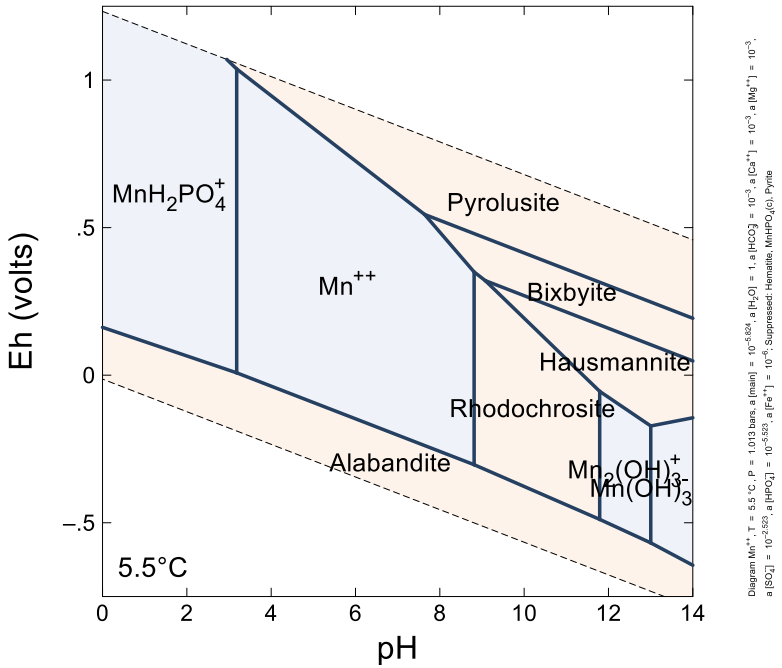
Minerals may not precipitate even if the conditions (Eh, pH) are within their thermodynamic stability field:

- **Kinetic factors**: Activation energy, temperature dependence
- **Nucleation barriers**: Achieving a stable nucleus in solution is energetically unfavourable for some minerals, often there is also a certain degree of supersaturation necessary
- **Solution chemistry**: complexation and ligand effects, competing reactions that are not all represented in this conceptual model

E_H-pH stability diagram: Solution



E_H-pH stability diagram: Solution



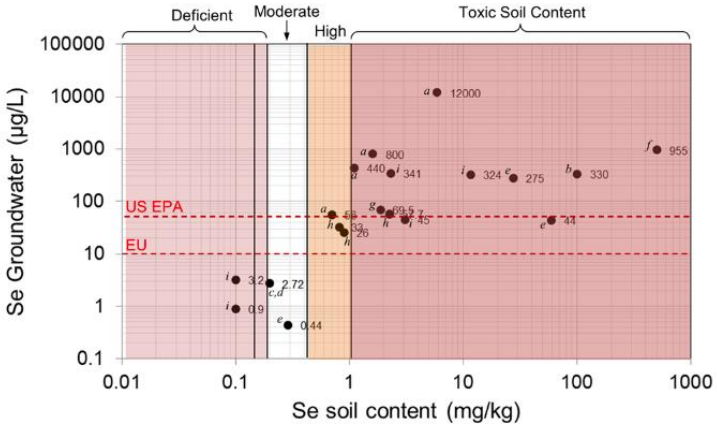
Why is there no increase in particulate Mn?

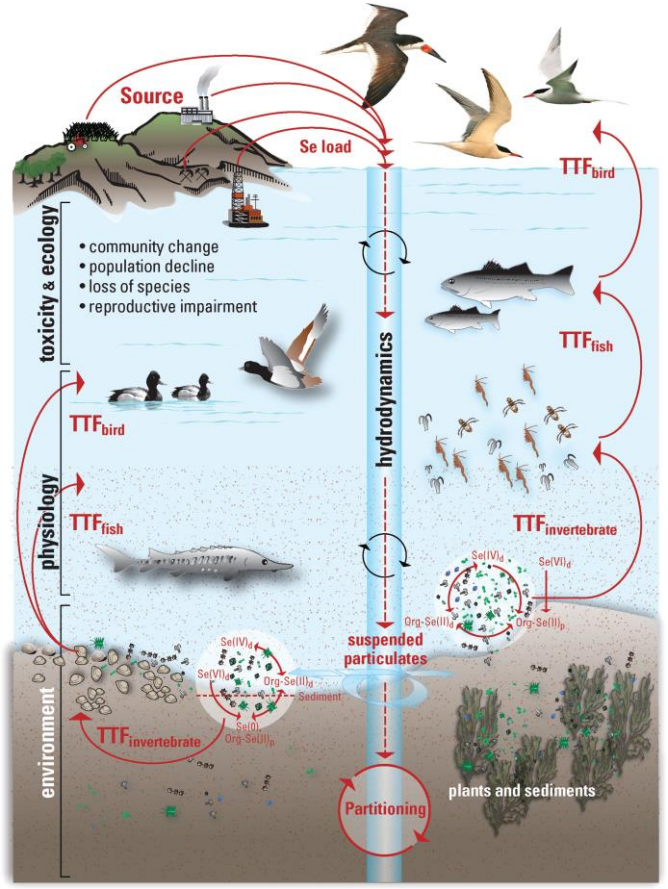
Minerals may not precipitate even if the conditions (Eh, pH) are within their thermodynamic stability field:

- **Kinetic factors**: Activation energy, temperature dependence
- **Nucleation barriers**: Achieving a stable nucleus in solution is energetically unfavourable for some minerals, often there is also a certain degree of supersaturation necessary
- **Solution chemistry**: complexation and ligand effects, competing reactions that are not all represented in this conceptual model

Selenium ecotoxicology

- 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.*

Meret Aeppli

Create an E_H-pH diagram with Act2

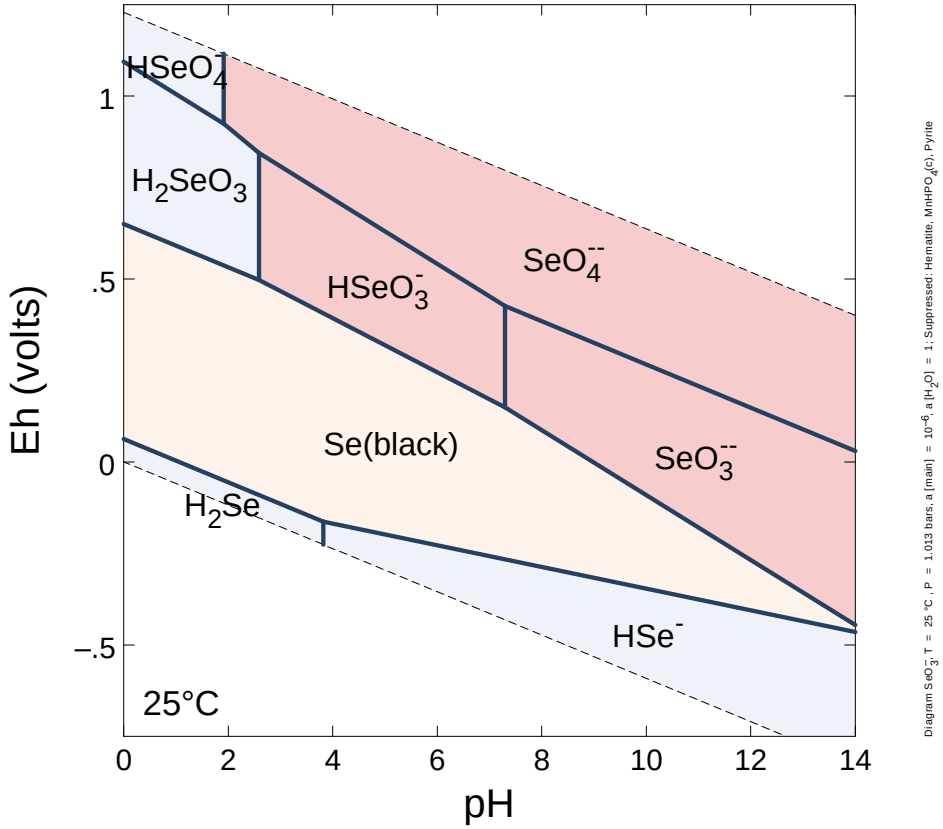
Start the program and move to the Basis pane:

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**”.

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

Meret Aeppli

Species and minerals in main system

	Activity	Reaction	Log K
Se03--	1e-6	Se03-- = Se03--	0.0000
Se--	1e-6	Se-- + 3 H20 = Se03-- + 6 H+ + 6 e-	-37.2187
Se04--	1e-6	Se04-- + 2 H+ + 2 e- = Se03-- + H20	29.0254
H2Se	1e-6	H2Se + 3 H20 = Se03-- + 8 H+ + 6 e-	-55.9809
H2Se03	1e-6	H2Se03 = Se03-- + 2 H+	-9.8850
HSe-	1e-6	HSe- + 3 H20 = Se03-- + 7 H+ + 6 e-	-52.1620
HSe03-	1e-6	HSe03- = Se03-- + H+	-7.2983
HSe04-	1e-6	HSe04- + H+ + 2 e- = Se03-- + H20	27.1160
Se(black)	1	Se(black) + 3 H20 = Se03-- + 6 H+ + 4 e-	-59.8687
Se205	1	Se205 + H20 + 2 e- = 2 Se03-- + 2 H+	38.4846
Se02	1	Se02 + H20 = Se03-- + 2 H+	-6.7669
Se03	1	Se03 + 2 e- = Se03--	48.1981

Act2: Output

All possible reaction equations are reported

The reaction equations used in the diagram are given

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-

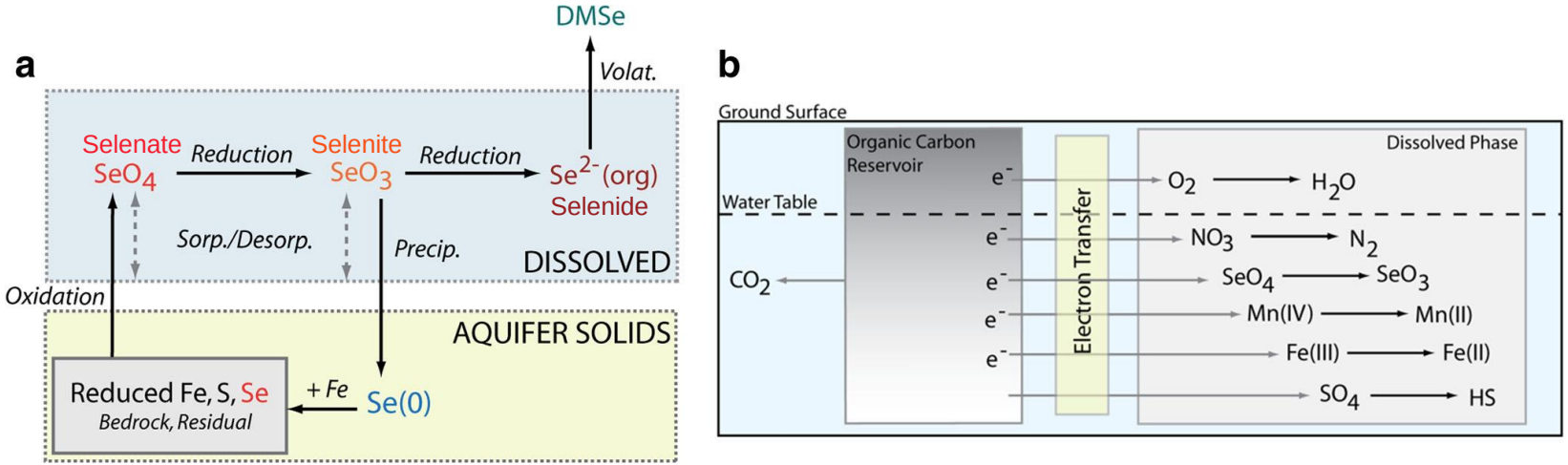
Main Diagram

	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

Context: Selenium speciation in alluvial aquifers

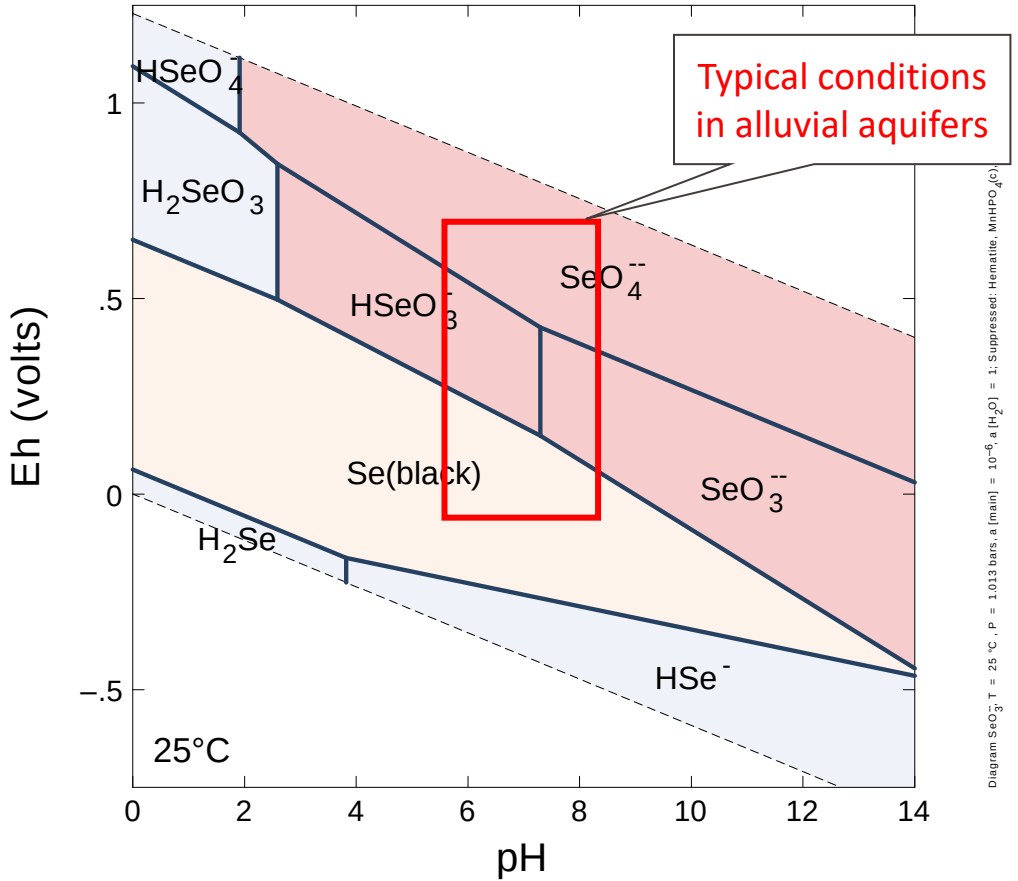


Se movement in soil and aquifer systems is governed by redox reactions which control speciation and sorption processes.

*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?
- Researchers found Se(0) and organic Se^{2-} under aerated conditions. Why?



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

Summary

1. Geochemical modeling is used to obtain information on solute concentrations in space and time.
2. The model is always a simplification of a complex real system. We therefore need to be careful with our assumptions and interpretation of the modeling output.
3. The GSS spreadsheet in the Geochemist's Workbench can be used to convert units, create plots and combined with other GWB apps. (We will talk more about this when discussing the SpecE8 app!)
4. 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.