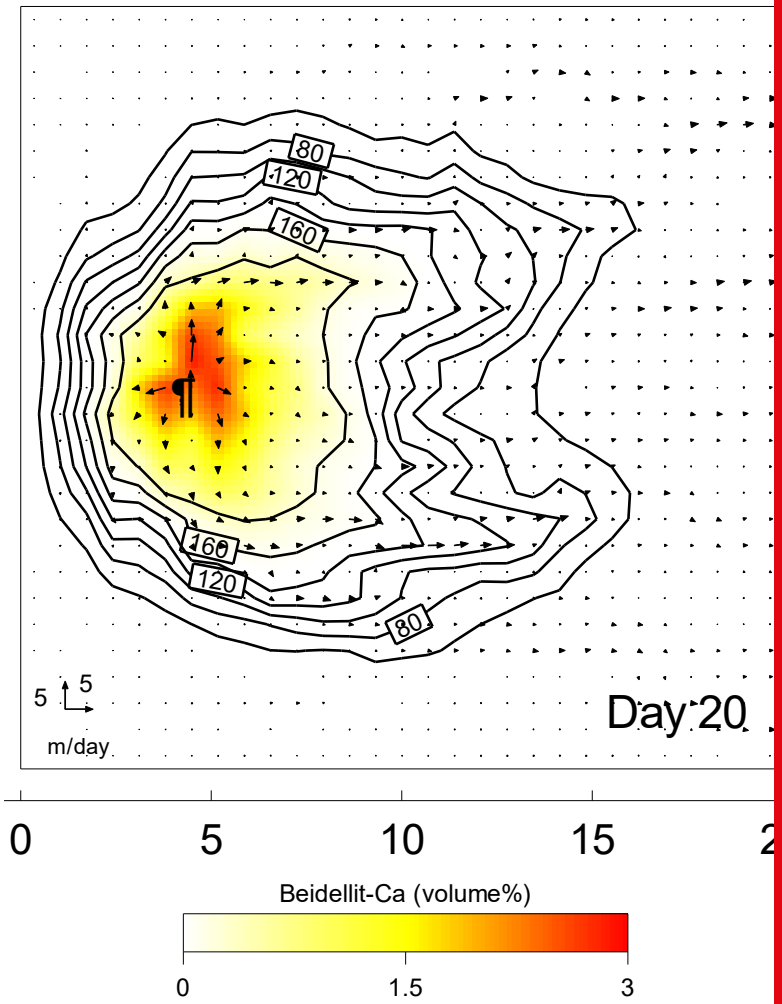

Geochemical modeling I

ENV-200

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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://academy.gwb.com/
- 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)

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
  - Example: 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

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

Environmental engineering challenge

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Waterfall in Dreimühlen (D)

- Water emerges from the subsurface in a karst source just above a waterfall
- In the waterfall, the water equilibrates with the atmosphere and calcite is precipitating

How fast does the waterfall “grow”, i.e., how much calcite is precipitating each year?

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:
  - Remember, for example, the carbonate system or reductive dissolution of iron minerals
  - Complex calculations and/or graphical solutions were required to solve 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?

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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

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

We have a lot of thermodynamic data!

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					
$Ag(g)$	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

	$^{-1}$ mol^{-1}	$H_T^0 - H_{298.15}^0$ J mol^{-1}	S_T^0 J K^{-1} mol^{-1}	$-(G_T^0 - F$ J K^{-1} mol^{-1}		
	.36	0	165.60	165.60		
	.67	264	166.48	165.60		
	.26	15 215	209.41	171.37		
	.75	31 185	245.01	182.64		
	.61	47 911	275.48	195.63		
	.72	65 282	302.25	208.99		
	.42	83 241	326.22	222.17		
	.88	10 1757	348.03	234.96		
	.14	11 6958	364.20	244.86		
	.14	11 6958	364.20	244.86		
	.19	12 0812	368.10	247.28		
	.41	14 0392	386.75	259.12		
	.56	160 490	404.24	270.50	−1382.945	−982.538
	.66	181 102	420.73	281.42	−1381.121	−949.236
	.71	193 713	430.22	287.78	−1379.872	−929.462
	.71	193 713	430.22	287.78	−1386.232	−929.462
	.74	202 222	436.38	291.94	−1385.785	−915.903
	.29	204 576	438.06	293.07	−1385.713	−912.238
	.29	204 576	438.06	293.07	−1391.353	−912.240
	.01	211 891	443.18	296.54	−1391.195	−900.813
	.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

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	−67.2	−69.7	−46.9
	2,6-diBr	−91.7	−94.8	−64.7
VI	**2-F**	−77.2	−78.3	−40.4
	2-CF_3	−80.1	−81.9	−42.7
	2-OCH_3	−72.0	−72.6	−37.6
VII	**2-F**	−93.6	−108.0	−117.7
	2-CF_3	−95.7	−111.0	−117.8
	2-OCH_3	−97.6	−112.0	−118.0
VIII	**2-F**	10.8	2.2	0.4
	2-CF_3	7.7	−0.3	−3.6
	2-OCH_3	16.4	8.1	2.4
IX	**2-F**	−68.0	−68.7	−33.2
	2-CF_3	−69.8	−71.4	−34.5
	2-NO_2	−73.9	−75.4	−34.9
	2-OCH_3	−63.5	−64.7	−32.3
	2,6-diBr	−66.5	−67.4	−35.4

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	−13.9	−38.5	−47.6
	2-OCH_3	2.3	−21.8	−30.9
	2,6-diBr	−20.2	−44.2	−45.8
XI	**2-F**	−70.3	−56.0	−15.7
	2-CF_3	−72.6	−58.0	−16.8
	2-NO_2	−75.3	−61.7	−21.1
	2-OCH_3	−64.4	−50.9	−12.2
	2,6-diBr	−66.7	−51.0	−14.2
XII	**2-F**	24.7	10.2	−3.7
	2-CF_3	24.4	9.8	−8.4
	2-NO_2	15.8	1.9	−13.1
	2-OCH_3	31.5	18.6	−2.7
	2,6-diBr	8.4	−6.3	−18.7
XIII		−94.2	−116.3	−118.6
XIV	**2-F**	−103.1	−104.1	−58.7
	2-CF_3	−105.3	−106.9	−60.8
	2-OCH_3	−100.9	−102.2	−58.2
XV	**2-F**	−88.4	−103.0	−82.9
	2-OCH_3	−84.5	−99.1	−80.0
XVI	**2-F**	−66.3	−80.1	−51.6
	2-CF_3	−74.5	−89.2	−57.9
	2-NO_2	−85.4	−99.6	−66.8
	2-OCH_3	−59.5	−72.5	−47.1
	2,6-diBr	−81.5	−95.4	−63.7
XVII	**2-F**	−92.2	−105.8	−69.9
	2-CF_3	−99.6	−114.2	−76.0
	2-NO_2	−116.0	−129.7	−88.5
	2-OCH_3	−88.4	−102.0	−67.6
	2,6-diBr	−108.6	−123.2	−82.8
XVIII		−93.7	−104.1	−106.2

Workflow for thermodynamic modeling

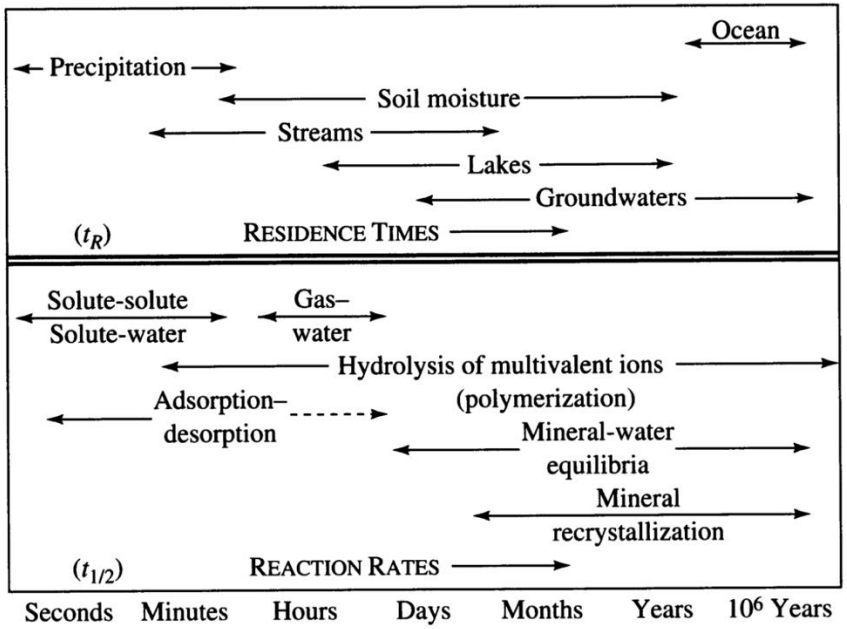
1. Develop a conceptual model: List the processes that likely determine the chemical composition of a system.
2. Make partial equilibrium assumptions: Consider the timeframes in which you wish to understand a system (minutes? years? millions of years?). Decide which of the relevant reactions will reach 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.
- You already build conceptual models
  - Remember, the carbonate system?

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

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- 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.

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3. Thermodynamic data

Step no. (Scheme 2)	Substituent	Gaseous phase $\Delta_{r,298}H°$	Gaseous phase $\Delta_{r,298}G°$	Aqueous phase $\Delta_{r,298}G°$
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 $\Delta_{r,298}H°$	Gaseous phase $\Delta_{r,298}G°$	Aqueous phase $\Delta_{r,298}G°$
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		

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

Substance	ΔHf (kJ mol^{-1})	ΔGf (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_4^{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

	JANAF 2 Stull and Prophet (1971)			Chase et al. (1985),	JANAF 3,
Aqueous Species	$\Delta_f G°$ kJ mol^{-1}	$\Delta_f H°$ kJ mol^{-1}	$S°$ J mol^{-1} K^{-1}	$\Delta_f G°$ kJ mol^{-1}	$\Delta_f H°$ kJ mol^{-1}
H2O(l)				-237.141	-285.830
Gas Species	$\Delta_f G°$ kJ mol^{-1}	$\Delta_f H°$ kJ mol^{-1}	$S°$ J mol^{-1} K^{-1}	$\Delta_f G°$ kJ mol^{-1}	$\Delta_f H°$ 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	$\Delta_f G°$ kJ mol^{-1}	$\Delta_f H°$ kJ mol^{-1}	$S°$ J mol^{-1} K^{-1}	$\Delta_f G°$ kJ mol^{-1}	$\Delta_f H°$ kJ mol^{-1}
P(white)	12.012	17.460	41.079	0.	0.
P(red)	0.000	0.000	22.803	-12.026	-17.460

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}	$\Delta_f H^0$ kJ mol^{-1}	$\Delta_f G^0$ 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

.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

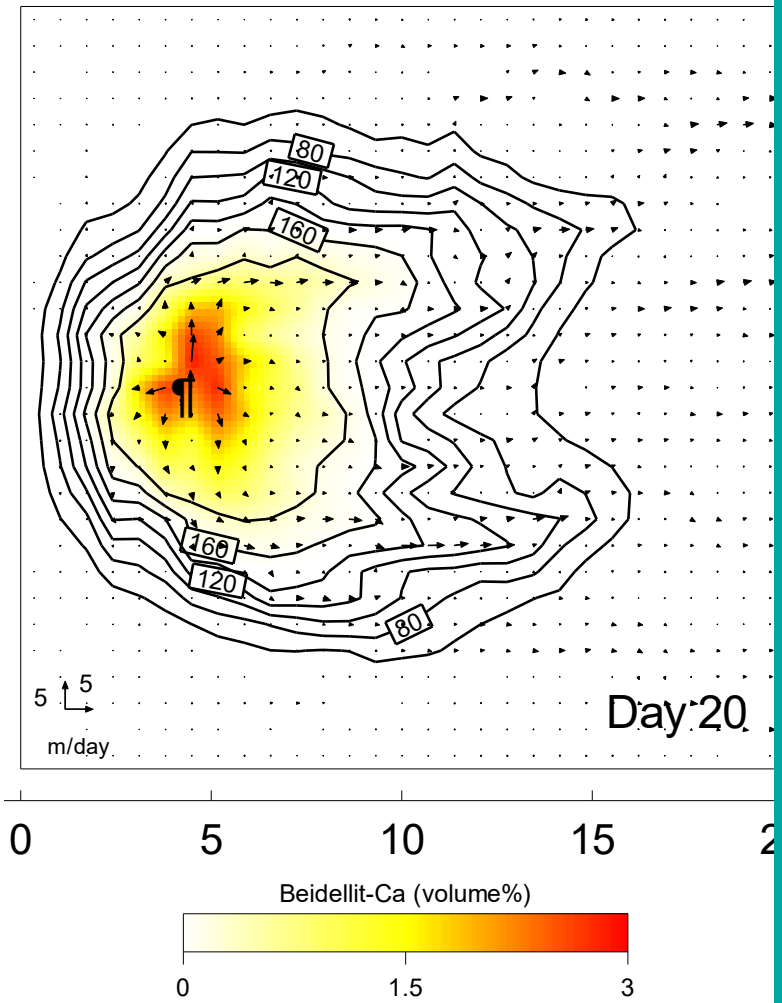
1360	211.71	193 713	430.22	287.78	−1386.232	−929.462
1400	213.74	202 222	436.38	291.94	−1385.785	−915.903
1411	214.29	204 576	438.06	293.07	−1385.713	−912.238
1411	214.29	204 576	438.06	293.07	−1391.353	−912.240
1445	216.01	211 891	443.18	296.54	−1391.195	−900.813
1445	210.90	229 615	455.43	296.53	−1373.471	−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.

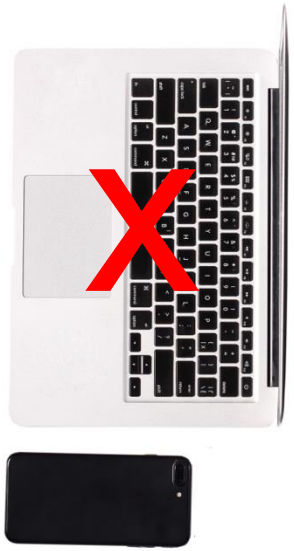
Meret Aeppli

Geochemist's Workbench Installation guide



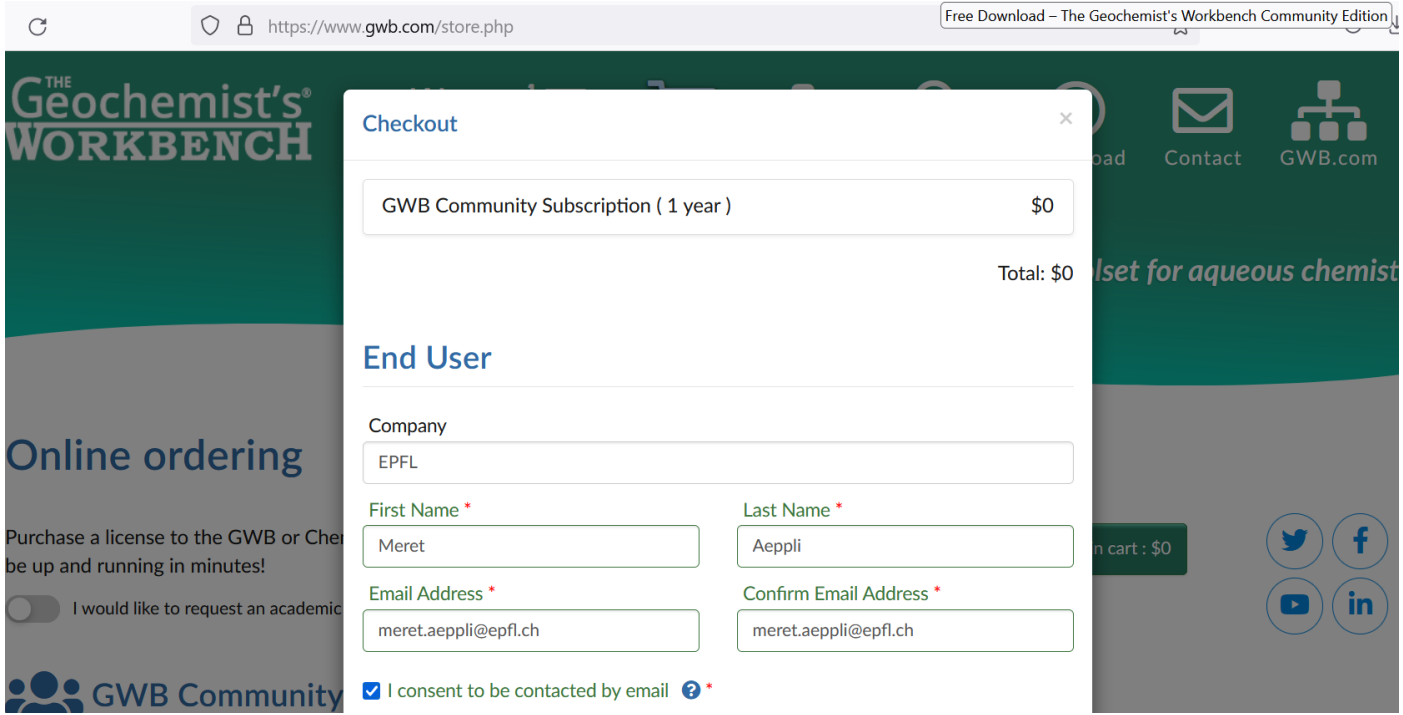
Information

- 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.

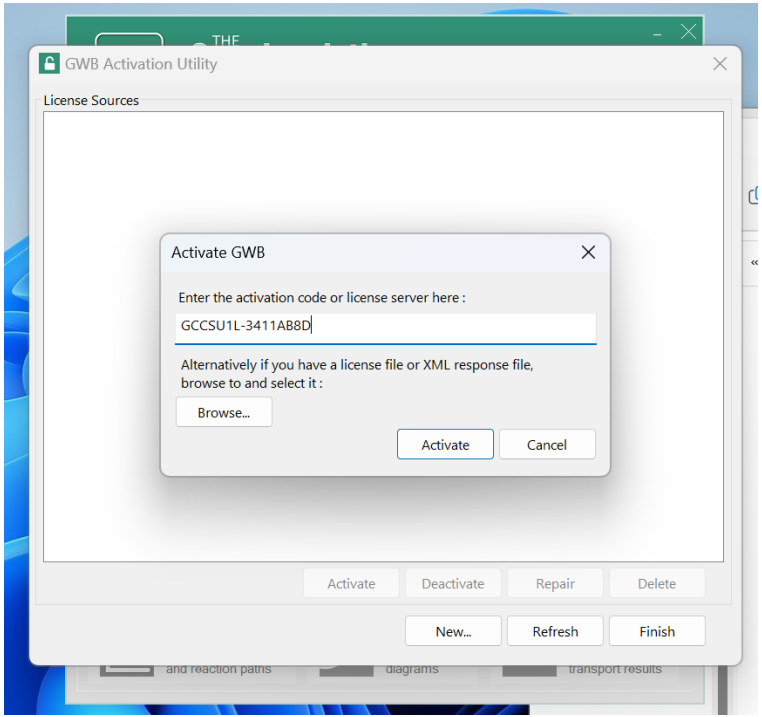
GWB Community Edition 2023

Installation guide

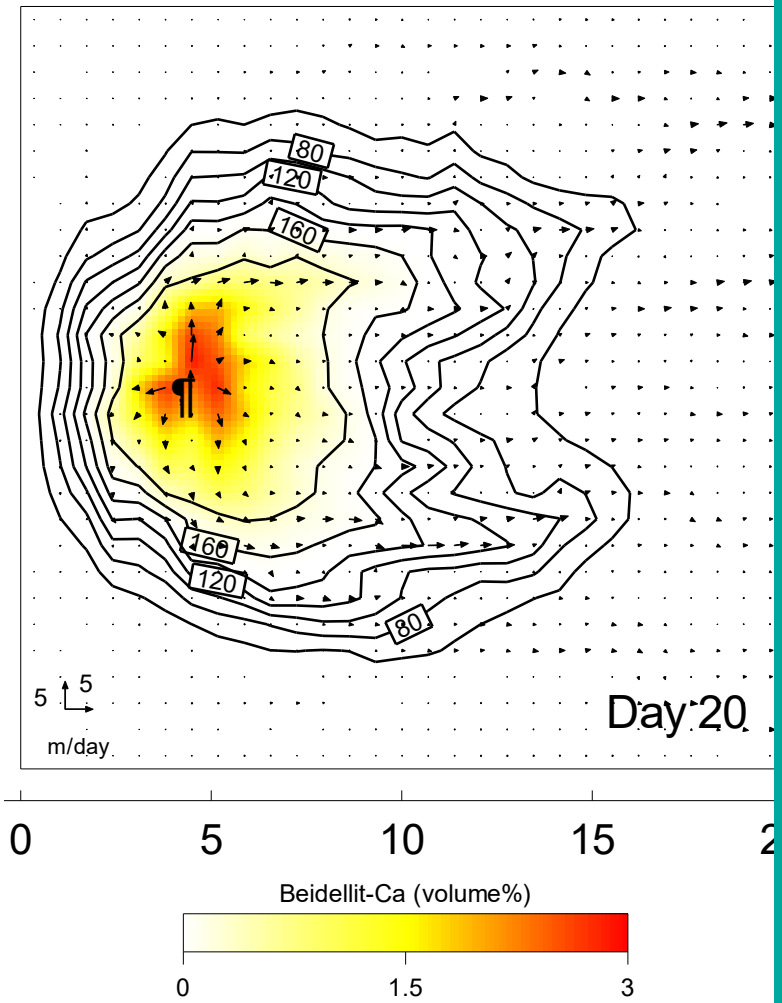
GWB Community Edition 2023

Installation guide

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



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

Meret Aeppli

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

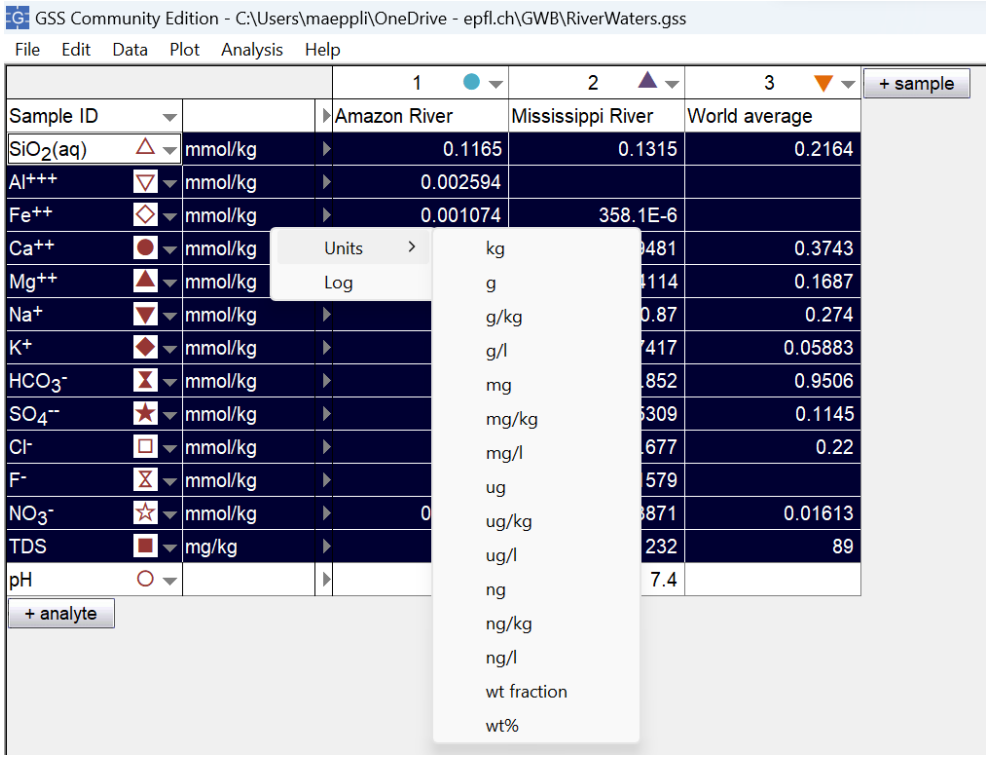
File Edit Data Plot Analysis Help

		1	2	3	+ sample
Sample ID		Amazon River	Mississippi River	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		

+ analyte

GSS: Converting units

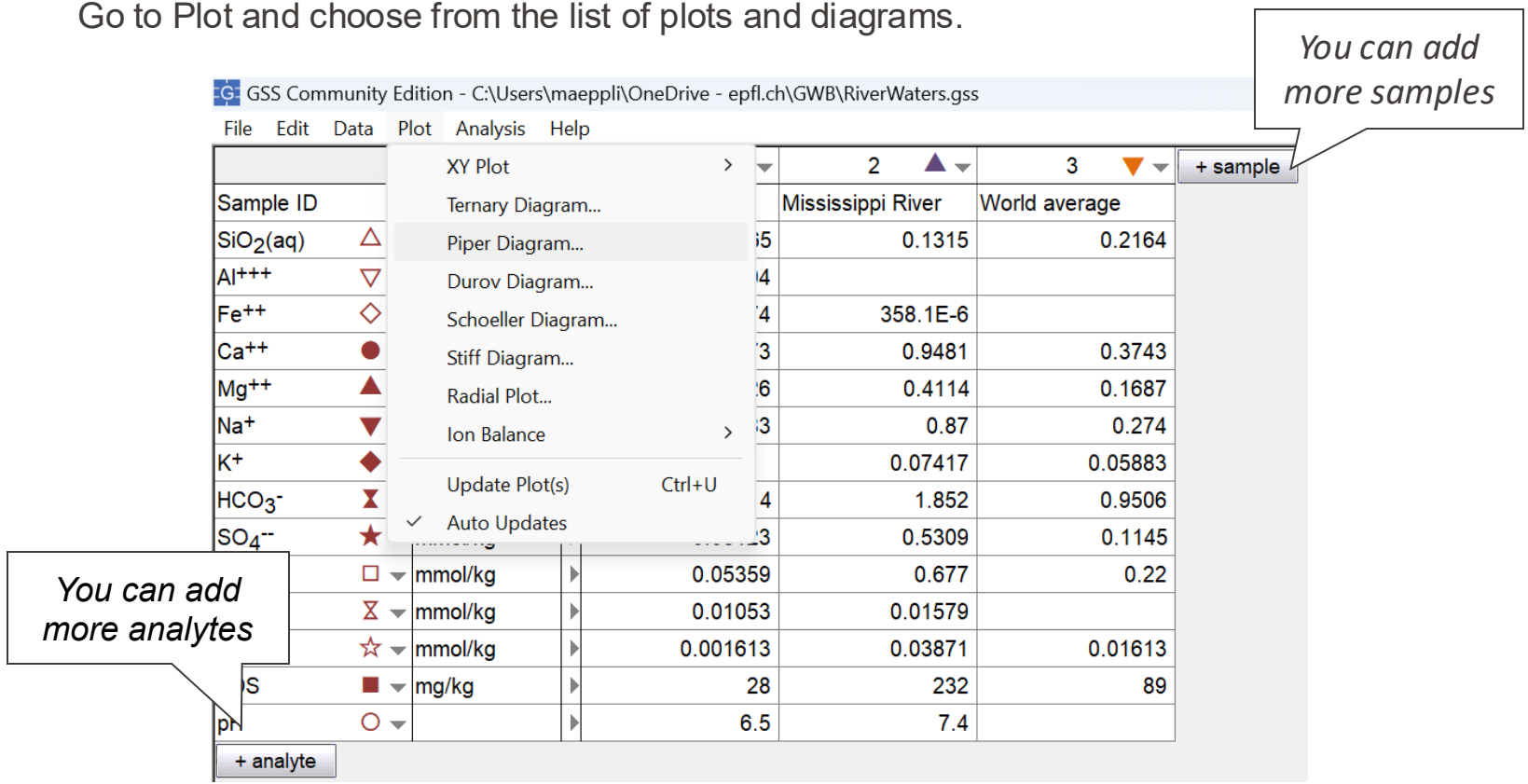
Select one or more analytes, right click in the unit field to show a selection of units.



GSS: Plotting data

Meret Aeppli

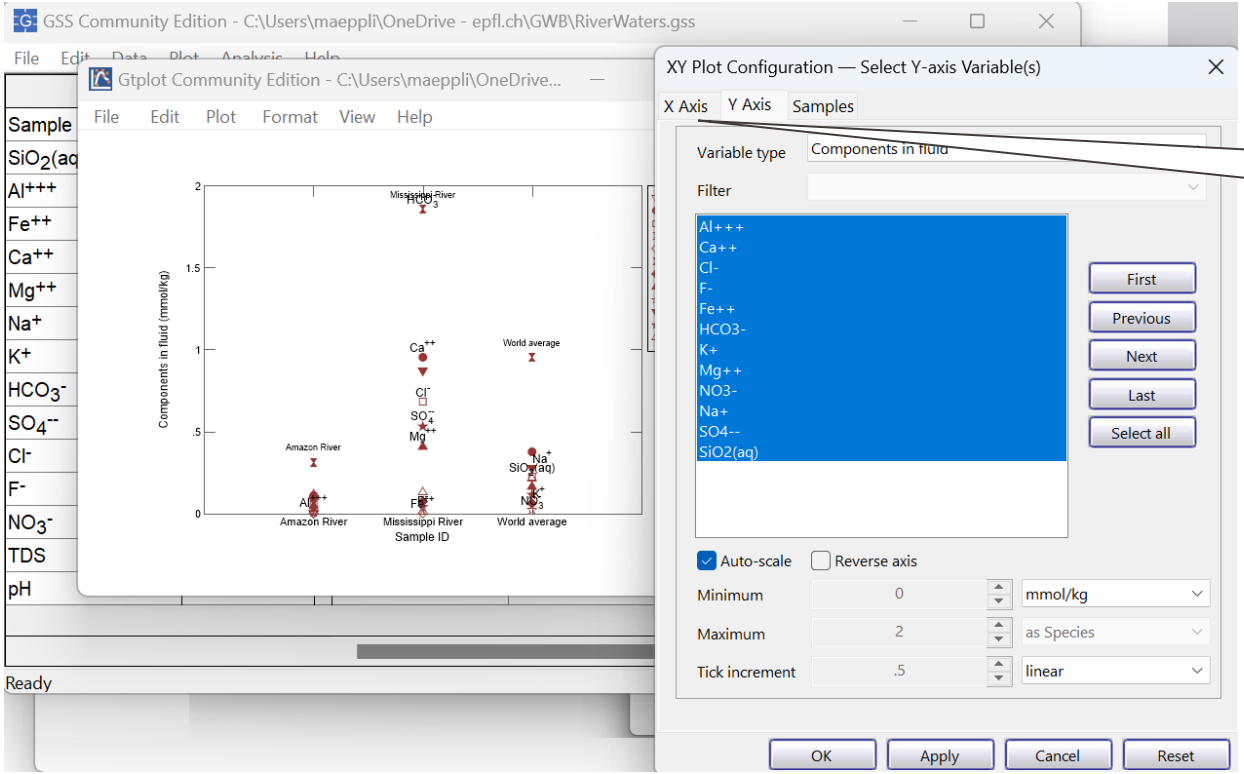
Go to Plot and choose from the list of plots and diagrams.



GSS: Plotting data

Meret Aeppli

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

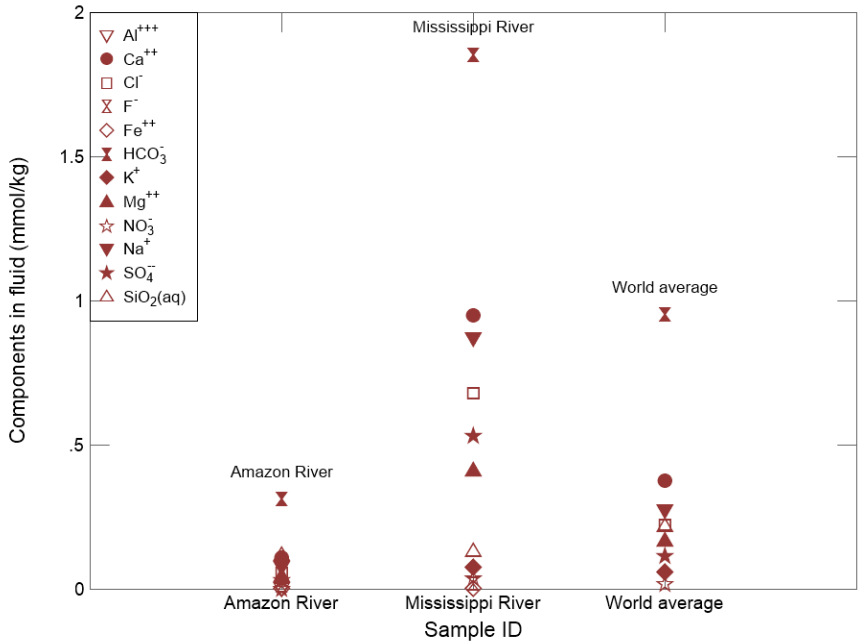


In Tab X Axis, you can chose which parameter to show on the X axis

GSS: Plotting data

Meret Aeppli

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 (carbonate). A row with water hardness values is added to the table.

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

File Edit Data Plot Analysis Help

		1	2	3	+ sample
Sample ID		Amazon River	Mississippi River	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		
Hardness	mg/kg_as_CaC	15.27	136.1	54.35	

+ analyte

Interpreting the data

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

Reaction balancing with Rxn

Meret Aeppli

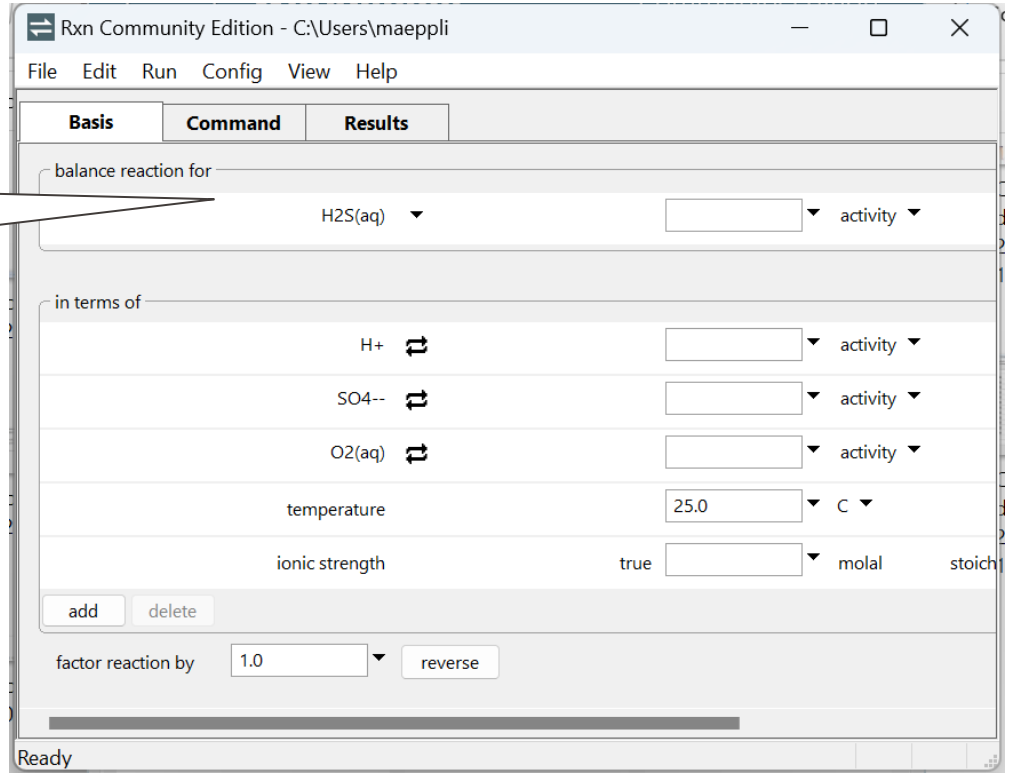
- Consider the oxidation of $H_2S(aq)$ to sulfate (SO_4^{2-}). To balance this reaction, we can use the Rxn App.
- To balance a reaction with Rxn, first set a species, mineral, etc., to appear on the left side of the reaction. Then, swap the basis to pull in the various species you want to appear in the reaction.

Rxn: Reaction balancing

Meret Aeppli

Start Rxn and move to the Basis pane. Under “balance reaction for”, select “???”→ Aqueous… → H2S(aq). Set “temperature” to 25 °C

Left side of reaction

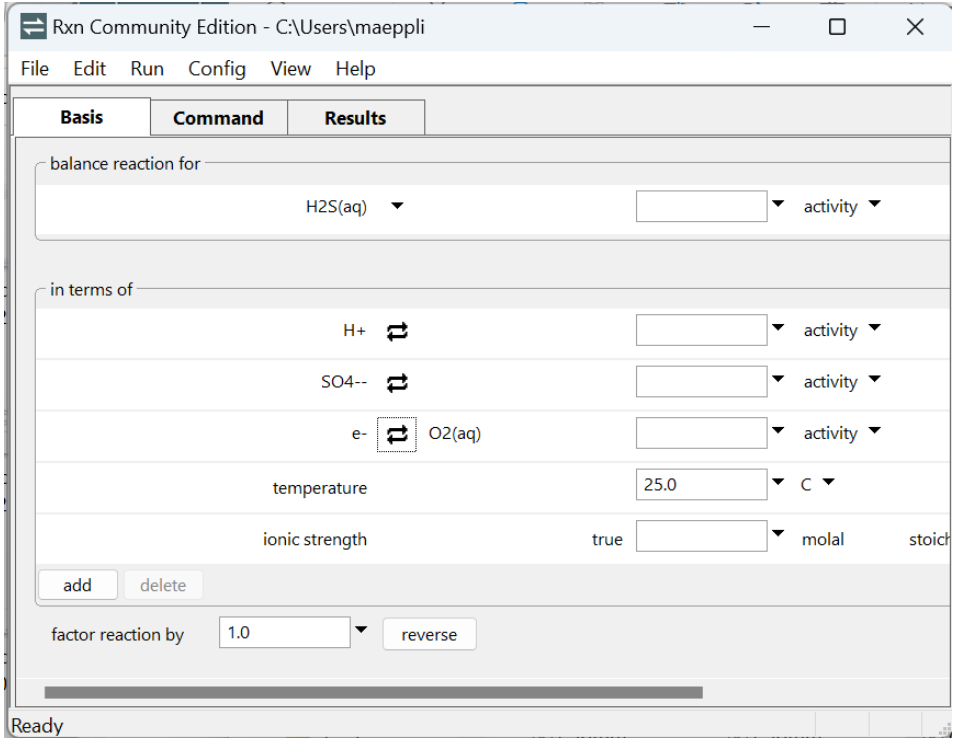


Rxn: Reaction balancing

- Move to the Results pane and click *Run*. What chemical reaction does the program give? What is its log K?

Rxn: Reaction balancing

Now let's balance the corresponding half-cell reaction. Click on the swap button next to the basis entry for "O2(aq)" and select Aqueous… → e−



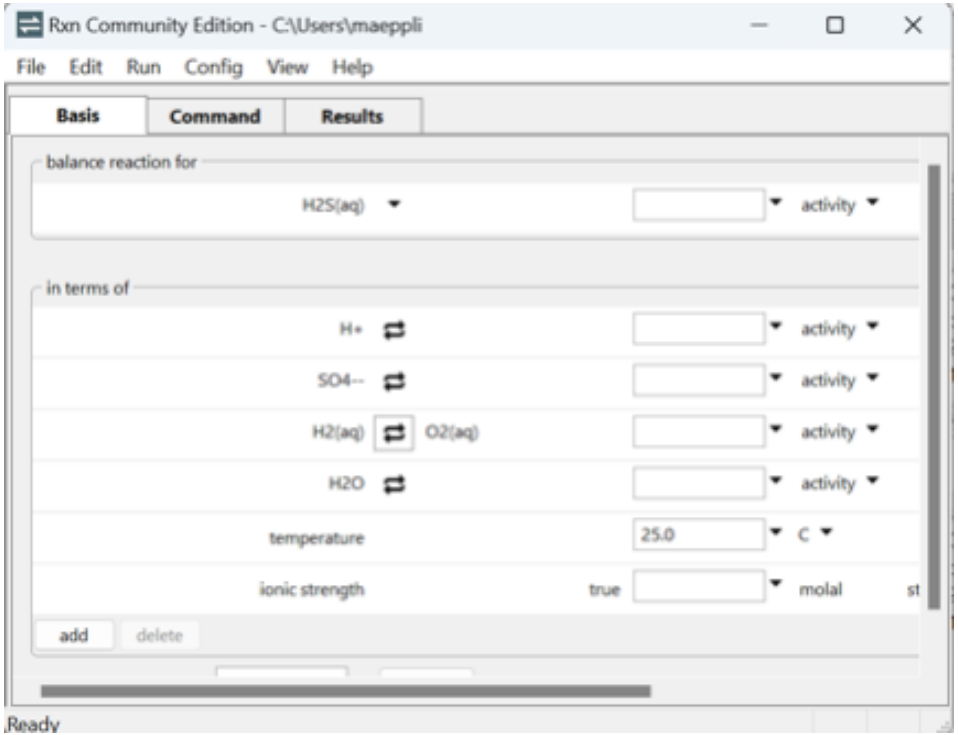
Rxn: Reaction balancing

- Move to the Results pane and click *Run*. How has the reaction changed?

Rxn: Reaction balancing

Meret Aeppli

To recast the reaction to liberate dihydrogen, once again click on the swap button next to the basis entry for “O2(aq)” and select Aqueous… → “H2(aq)”



Rxn: Reaction balancing

- Move to the Results pane and click *Run*. How has the reaction changed?

Meret Aeppli

Exercise 1: Iron oxidation

Dissolved ionic iron exists in anoxic (i.e., in the absence of oxygen) ground water as the reduced species Fe^{2+}. When such waters are used from drinking water supplies and the water becomes exposed to the atmosphere, the Fe^{2+} is oxidized by O_2 to Fe^{III} (ferric iron), which is insoluble at neutral pH and precipitates as $Fe(OH)_3(s)$.

Write the balanced equation for the oxidation of Fe^{2+} to $Fe(OH)_3(s)$ by O_2 with the help of Rxn.

What is the log K value for the reaction?

This is Exercise 2 from the Redox I class

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 calculate speciation and saturation. (We will talk more about this when discussing the SpecE8 app!)
4. We can use the Rxn app in the Geochemist's Workbench to balance reactions.