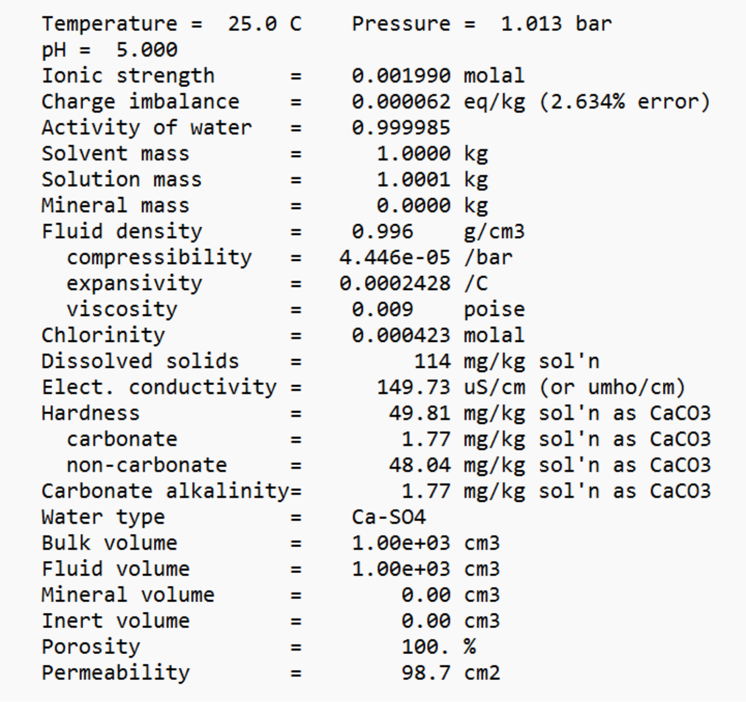
Exercise 1: Hypothetical freshwater

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?

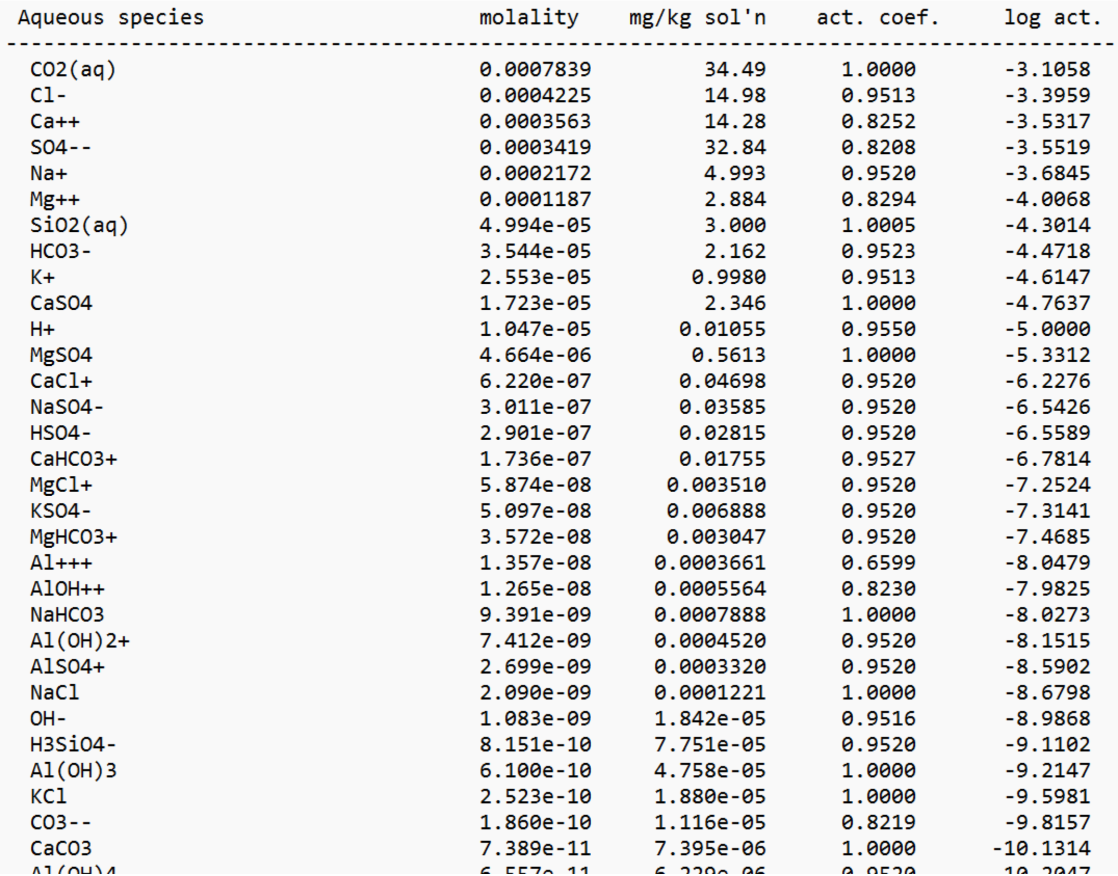
Exercise 1: Solution

Click on View Results on the Results pane to see calculation results in tabular form.



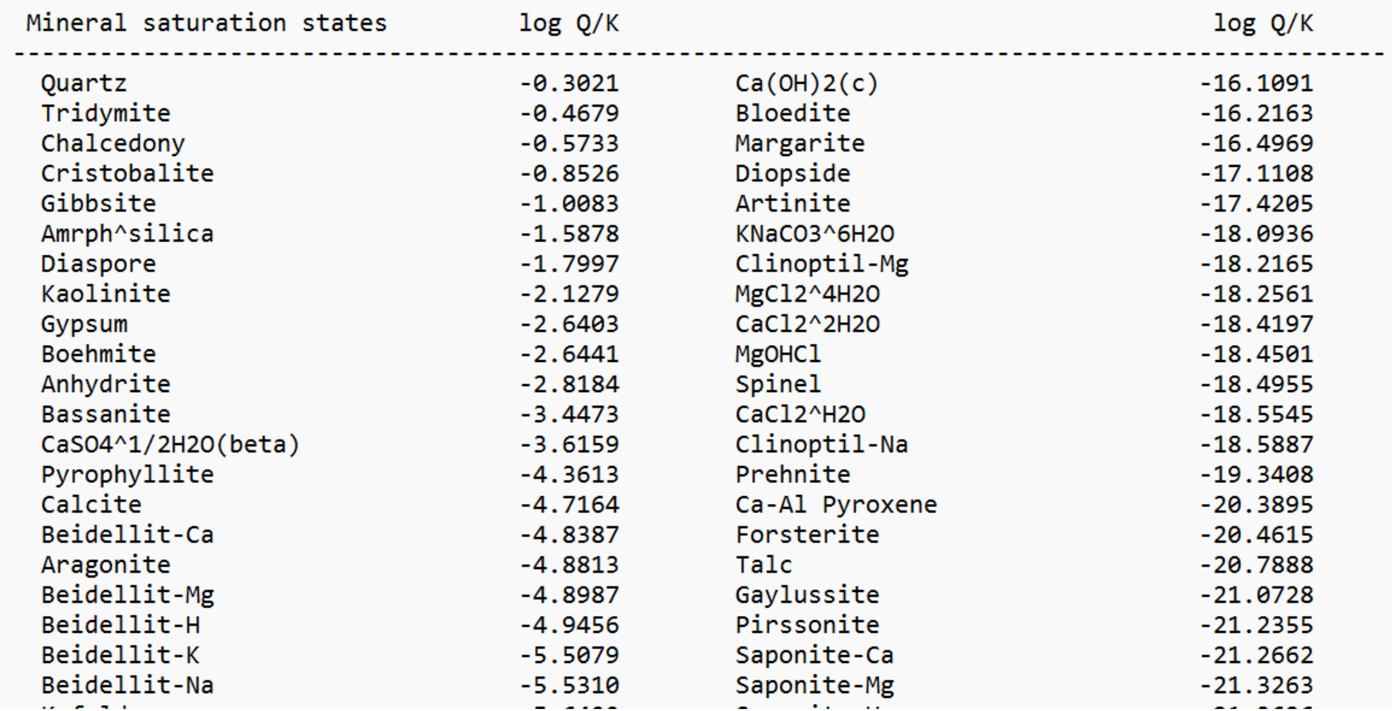
```
Temperature =  25.0 C    Pressure =  1.013 bar
pH =  5.000
Ionic strength         =    0.001990 molal
Charge imbalance       =    0.000062 eq/kg (2.634% error)
Activity of water      =    0.999985
Solvent mass           =      1.0000 kg
Solution mass          =      1.0001 kg
Mineral mass           =      0.0000 kg
Fluid density          =    0.996    g/cm3
  compressibility      =   4.446e-05 /bar
  expansivity          =   0.0002428 /C
  viscosity            =    0.009    poise
Chlorinity             =    0.000423 molal
Dissolved solids       =         114 mg/kg sol'n
Elect. conductivity    =      149.73 uS/cm (or umho/cm)
Hardness               =       49.81 mg/kg sol'n as CaCO3
  carbonate            =        1.77 mg/kg sol'n as CaCO3
  non-carbonate        =       48.04 mg/kg sol'n as CaCO3
Carbonate alkalinity=           1.77 mg/kg sol'n as CaCO3
Water type             =    Ca-SO4
Bulk volume            =    1.00e+03 cm3
Fluid volume           =    1.00e+03 cm3
Mineral volume         =        0.00 cm3
Inert volume           =        0.00 cm3
Porosity               =        100. %
Permeability           =        98.7 cm2
```

Exercise 1: Solution



```
 Aqueous species                     molality    mg/kg sol'n   act. coef.    log act.
---------------------------------------------------------------------------------------
  CO2(aq)                            0.0007839         34.49      1.0000      -3.1058
  Cl-                                0.0004225         14.98      0.9513      -3.3959
  Ca++                               0.0003563         14.28      0.8252      -3.5317
  SO4--                              0.0003419         32.84      0.8208      -3.5519
  Na+                                0.0002172         4.993      0.9520      -3.6845
  Mg++                               0.0001187         2.884      0.8294      -4.0068
  SiO2(aq)                           4.994e-05         3.000      1.0005      -4.3014
  HCO3-                              3.544e-05         2.162      0.9523      -4.4718
  K+                                 2.553e-05        0.9980      0.9513      -4.6147
  CaSO4                              1.723e-05         2.346      1.0000      -4.7637
  H+                                 1.047e-05       0.01055      0.9550      -5.0000
  MgSO4                              4.664e-06        0.5613      1.0000      -5.3312
  CaCl+                              6.220e-07       0.04698      0.9520      -6.2276
  NaSO4-                             3.011e-07       0.03585      0.9520      -6.5426
  HSO4-                              2.901e-07       0.02815      0.9520      -6.5589
  CaHCO3+                            1.736e-07       0.01755      0.9527      -6.7814
  MgCl+                              5.874e-08      0.003510      0.9520      -7.2524
  KSO4-                              5.097e-08      0.006888      0.9520      -7.3141
  MgHCO3+                            3.572e-08      0.003047      0.9520      -7.4685
  Al+++                              1.357e-08     0.0003661      0.6599      -8.0479
  AlOH++                             1.265e-08     0.0005564      0.8230      -7.9825
  NaHCO3                             9.391e-09     0.0007888      1.0000      -8.0273
  Al(OH)2+                           7.412e-09     0.0004520      0.9520      -8.1515
  AlSO4+                             2.699e-09     0.0003320      0.9520      -8.5902
  NaCl                               2.090e-09     0.0001221      1.0000      -8.6798
  OH-                                1.083e-09     1.842e-05      0.9516      -8.9868
  H3SiO4-                            8.151e-10     7.751e-05      0.9520      -9.1102
  Al(OH)3                            6.100e-10     4.758e-05      1.0000      -9.2147
  KCl                                2.523e-10     1.880e-05      1.0000      -9.5981
  CO3--                              1.860e-10     1.116e-05      0.8219      -9.8157
  CaCO3                              7.389e-11     7.395e-06      1.0000     -10.1314
  Al(OH)4                            6.557e-11     6.229e-06      0.9520      10.2047
```

Exercise 1: Solution



```
 Mineral saturation states         log Q/K                                           log Q/K
--------------------------------------------------------------------------------------------------
  Quartz                           -0.3021        Ca(OH)2(c)                        -16.1091
  Tridymite                        -0.4679        Bloedite                          -16.2163
  Chalcedony                       -0.5733        Margarite                         -16.4969
  Cristobalite                     -0.8526        Diopside                          -17.1108
  Gibbsite                         -1.0083        Artinite                          -17.4205
  Amrph^silica                     -1.5878        KNaCO3^6H2O                       -18.0936
  Diaspore                         -1.7997        Clinoptil-Mg                      -18.2165
  Kaolinite                        -2.1279        MgCl2^4H2O                        -18.2561
  Gypsum                           -2.6403        CaCl2^2H2O                        -18.4197
  Boehmite                         -2.6441        MgOHCl                            -18.4501
  Anhydrite                        -2.8184        Spinel                            -18.4955
  Bassanite                        -3.4473        CaCl2^H2O                         -18.5545
  CaSO4^1/2H2O(beta)               -3.6159        Clinoptil-Na                      -18.5887
  Pyrophyllite                     -4.3613        Prehnite                          -19.3408
  Calcite                          -4.7164        Ca-Al Pyroxene                    -20.3895
  Beidellit-Ca                     -4.8387        Forsterite                        -20.4615
  Aragonite                        -4.8813        Talc                              -20.7888
  Beidellit-Mg                     -4.8987        Gaylussite                        -21.0728
  Beidellit-H                      -4.9456        Pirssonite                        -21.2355
  Beidellit-K                      -5.5079        Saponite-Ca                       -21.2662
  Beidellit-Na                     -5.5310        Saponite-Mg                       -21.3263
```

Minerals will not precipitation because all saturation states are negative (remember: Q is the ion activity product, when assuming activity = 1 for mineral phases; K is the solubility product. Hence, if log Q/K is negative, IAP < K)

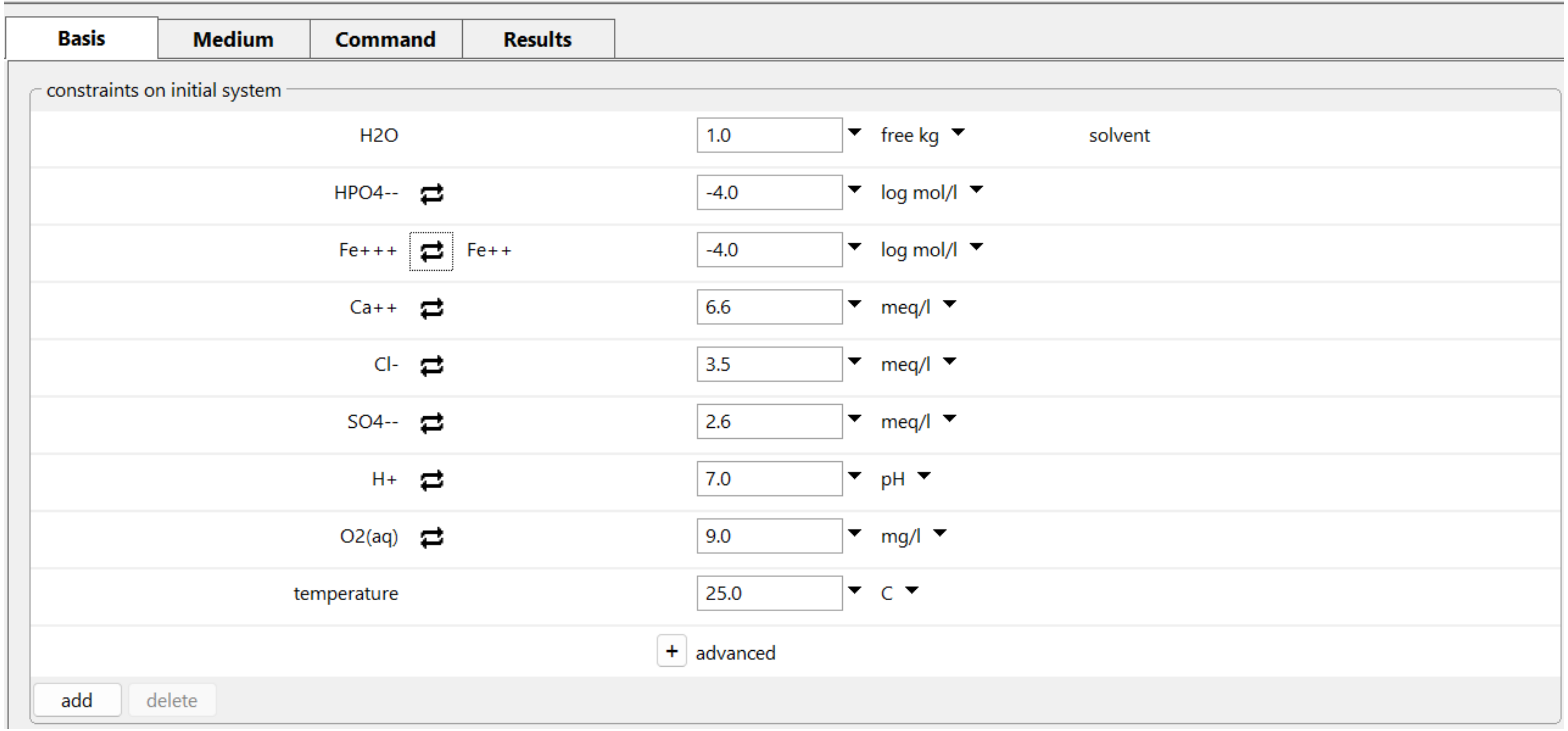
Exercise 2: Iron precipitation

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.

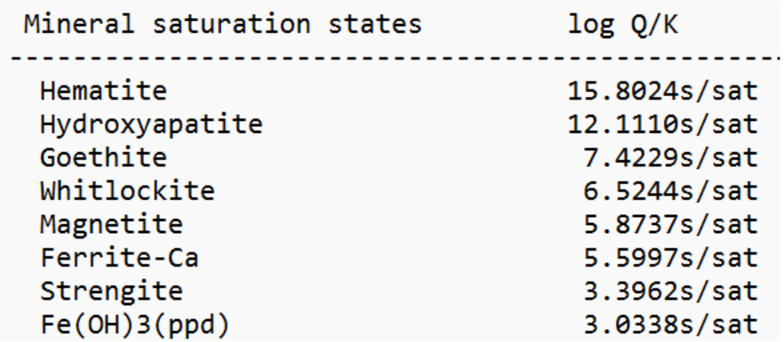
Exercise 2: Solution



constraints on initial system

H2O			1.0	free kg	solvent
HPO4--	⇄		-4.0	log mol/l	
Fe+++	⇄	Fe++	-4.0	log mol/l	
Ca++	⇄		6.6	meq/l	
Cl-	⇄		3.5	meq/l	
SO4--	⇄		2.6	meq/l	
H+	⇄		7.0	pH	
O2(aq)	⇄		9.0	mg/l	
temperature			25.0	C	

Exercise 2: Solution



```
Mineral saturation states           log Q/K
-----------------------------------------------
  Hematite                         15.8024s/sat
  Hydroxyapatite                   12.1110s/sat
  Goethite                          7.4229s/sat
  Whitlockite                       6.5244s/sat
  Magnetite                         5.8737s/sat
  Ferrite-Ca                        5.5997s/sat
  Strengite                         3.3962s/sat
  Fe(OH)3(ppd)                      3.0338s/sat
```

Strengite has a higher saturation state and is therefore expected to form preferentially compared to $Fe(OH)_3$

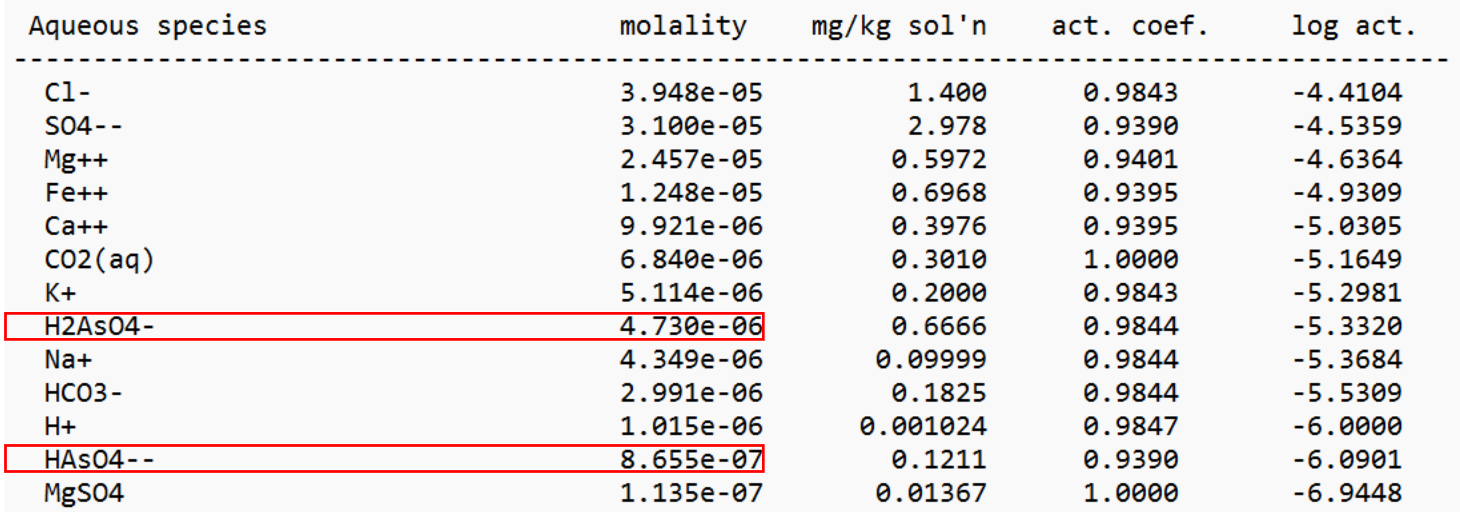
Exercise 3: Redox disequilibrium

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?

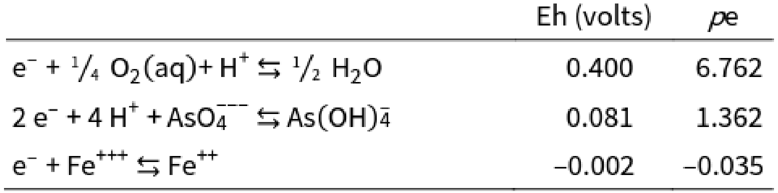
Exercise 3: Solution

As occurs predominantly as $H_2AsO_4^-$ and $HAsO_4^{2-}$:



```
 Aqueous species              molality    mg/kg sol'n    act. coef.    log act.
---------------------------------------------------------------------------------
  Cl-                         3.948e-05       1.400        0.9843       -4.4104
  SO4--                       3.100e-05       2.978        0.9390       -4.5359
  Mg++                        2.457e-05      0.5972        0.9401       -4.6364
  Fe++                        1.248e-05      0.6968        0.9395       -4.9309
  Ca++                        9.921e-06      0.3976        0.9395       -5.0305
  CO2(aq)                     6.840e-06      0.3010        1.0000       -5.1649
  K+                          5.114e-06      0.2000        0.9843       -5.2981
  H2AsO4-                     4.730e-06      0.6666        0.9844       -5.3320
  Na+                         4.349e-06     0.09999        0.9844       -5.3684
  HCO3-                       2.991e-06      0.1825        0.9844       -5.5309
  H+                          1.015e-06    0.001024        0.9847       -6.0000
  HAsO4--                     8.655e-07      0.1211        0.9390       -6.0901
  MgSO4                       1.135e-07     0.01367        1.0000       -6.9448
```

The redox state of As is therefore +V (in $As(OH)_4^-$, As has redox state +III). This makes sense because the system Eh is higher than the Eh of the As redox couple in the previous example. When equilibrating the solution to higher Eh, As(III) oxidizes to As(V).



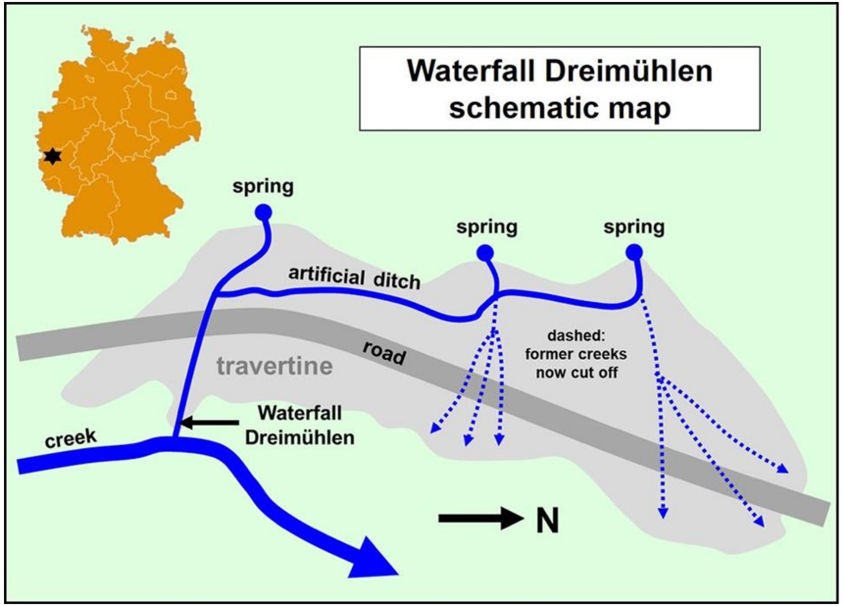
	Eh (volts)	*pe*
$e^- + \frac{1}{4}\,O_2(aq) + H^+ \leftrightharpoons \frac{1}{2}\,H_2O$	0.400	6.762
$2\,e^- + 4\,H^+ + AsO_4^{---} \leftrightharpoons As(OH)_4^-$	0.081	1.362
$e^- + Fe^{+++} \leftrightharpoons Fe^{++}$	−0.002	−0.035

Environmental engineering challenge

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

*Schmidkonz, B, J Chem Educ, **2022**, 99, 3323-3331.*

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:

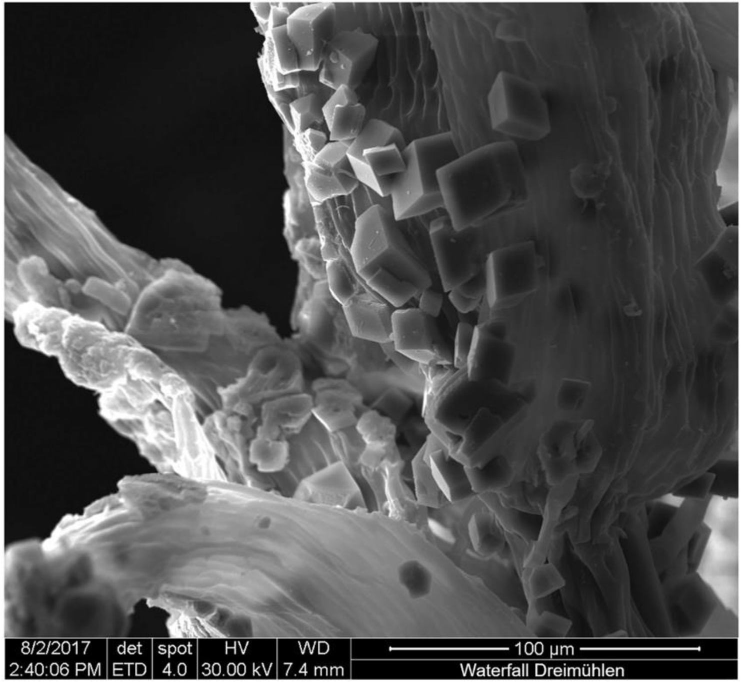
$CaCO_3(s) + H_2O + CO_2(g) \rightleftharpoons Ca^{2+}(aq) + 2HCO_3^-(aq)$

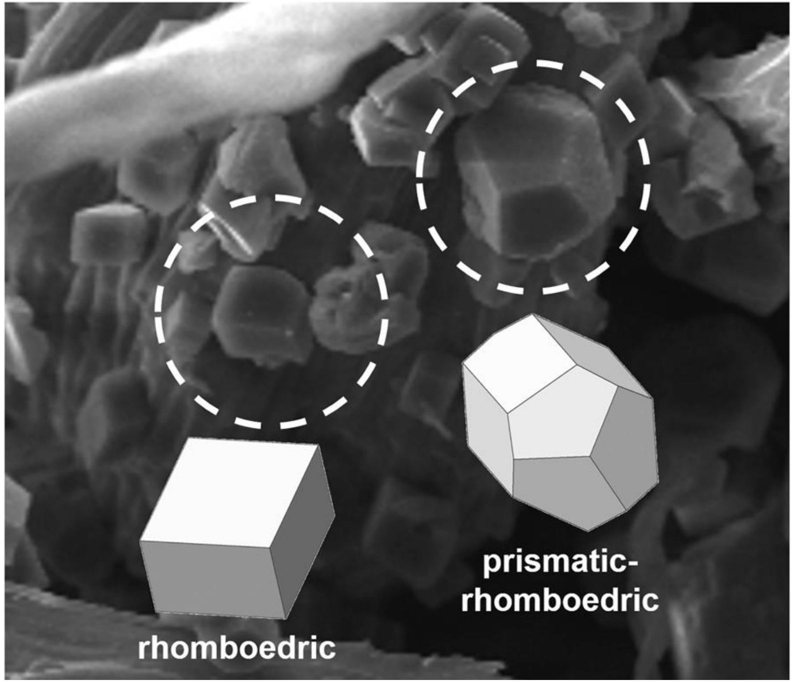
In the underground, high partial pressure of CO_2 (>> 400 ppm) shifts the equilibrium position to the right

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.

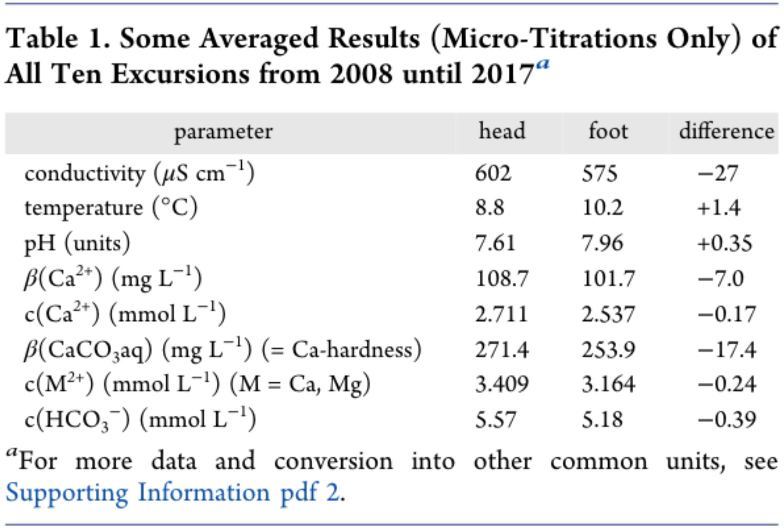

Table 1. Some Averaged Results (Micro-Titrations Only) of All Ten Excursions from 2008 until 2017[a]

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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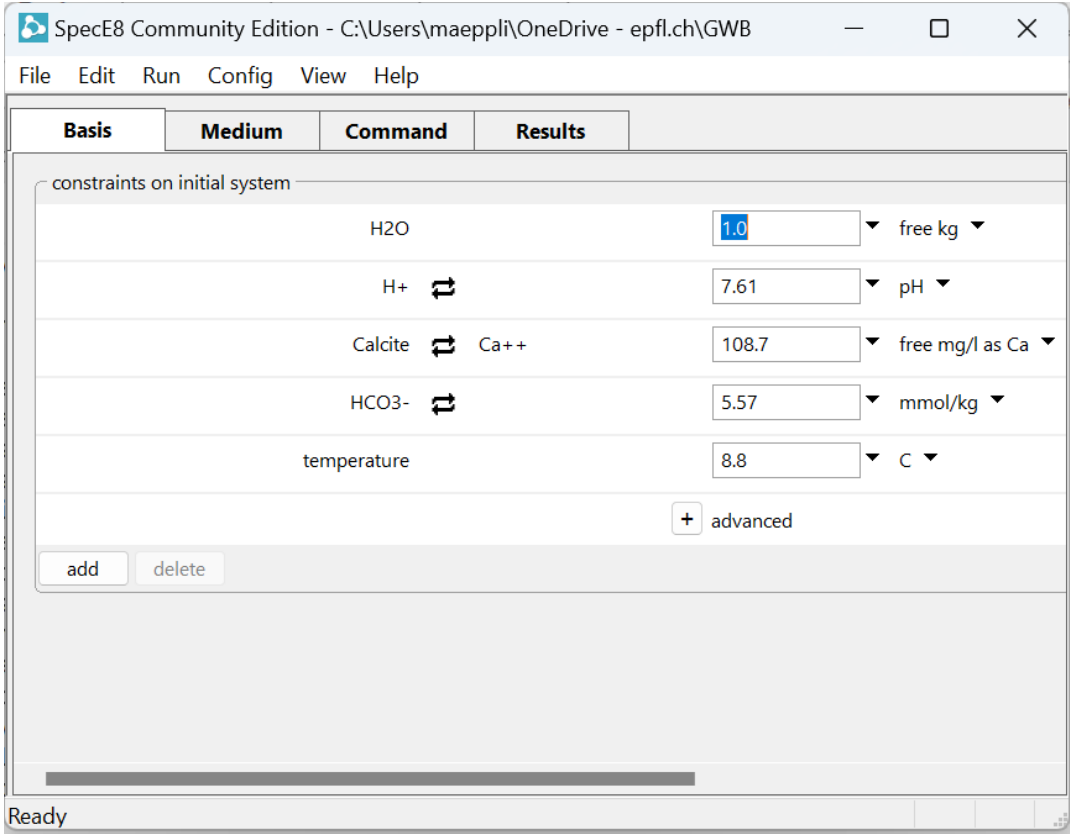
Dreumühlen waterfall: Solution

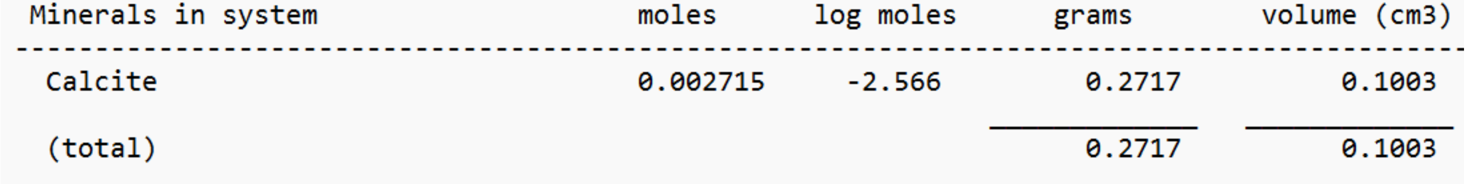
Meret Aeppli



constraints on initial system

H2O		1.0	free kg
H+		7.61	pH
Calcite ⇄	Ca++	108.7	free mg/l as Ca
HCO3-		5.57	mmol/kg
temperature		8.8	C

Dreimühlen waterfall: Solution



```
 Minerals in system                      moles      log moles      grams      volume (cm3)
-------------------------------------------------------------------------------------------
  Calcite                               0.002715     -2.566       0.2717          0.1003
                                                                ________       _________
  (total)                                                         0.2717          0.1003
```

0.2717 g/L calcite are precipitating

Using a flow rate of 60 L/s, we obtain 16.302 g/s

16.302 g/s * 60 s/min * 60 min/h * 24 h/d * 365 d/y = 514’100 kg/y