

Report Analysis from Lorah and Herman (1988)

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1 Introduction

The aim of this exercise is to learn how to use PHREEQC in order to analyse real data. We use the data from the paper by Lorah and Herman (1988). The aim of our analysis is to calculate the SI values for Calcite and CO₂(g) along the stream and estimate how much calcite has precipitated between two sampling points along the stream (D3 and F6).

2 Materials and Methods

We use PHREEQC to analyse the data. The input file with which we analysed the data is given in

Lorah and Herman (1988) where they analysed the change in the hydrochemistry along a stream with a 20-m vertical waterfall in Virginia (US). The stream is supersaturated with CO₂ compared to atmospheric level and with calcite based on the saturation index. Due to agitation in the water fall significant degassing occurs. As a result, the stream water becomes so highly supersaturated with respect to calcite that precipitation (as travertine) occurs. Using water samples along the stream these changes can be quantified.

2.1 Analyse the composition of water samples along the stream

The input file I made for this practical is given in listing 1. As you can see I first used SOLUTION_SPREAD in order to load all the data in to PHREEQC. I start with defining the units used for the input data. Because the SOLUTION_MASTER_SPECIES for carbonates is CO₃²⁻, I used the approach “as HCO₃” to tell PHREEQC that HCO₃⁻ used the input file. The names of the compounds should be equal to those found in the first column of the SOLUTION_MASTER_SPECIES section of the PHREEQC database. The key-word SELECTED_OUTPUT allows us to create a file: Travertine01.csv in which we store a summary of the results for each solution (rows) for a number of selected parameters (columns). We choose to switch all defaults off, and then add the parameters we want in the file. Finally we use the key-word END to tell PHREEQC to solve the equilibrium state for all samples in the SOLUTION_SPREAD.

Listing 1: PHREEQC input file for all steps in the analysis of Practical Exercise 3

```
DATABASE C:\Program Files (x86)\USGS\Phreeqc Interactive 3.7.3-15968\database\phreeqc.dat
SOLUTION_SPREAD
  -units      mg/l
  temp        pH      C(4)      Ca      Mg      Na      K      F      Cl      S(6)
                        as HCO3                        as SO4
24.3      7.32      308      165      25.4      5.1      14.2      1      3.3      283
24.6      7.23      316      168      28      3.9      14.8      1.1      3.5      291
24.7      7.2      315      169      26.2      3.9      14.3      1.1      5.8      296
24.3      7.24      310      168      26      3.4      14.2      1.1      3.2      283
23.6      7.43      314      168      26.2      2.8      12.9      1.2      3.5      288
21.4      7.79      312      166      25.6      3.5      13.9      1.2      3.4      286
20.5      8.06      311      164      25.2      3.7      14      1      3.5      283
19.7      8.27      278      160      25.6      3.6      14.3      1      3.8      286
19.6      8.28      273      157      25.5      3.1      14      1.1      3.4      283
18.4      8.37      264      151      25.6      3.2      14.3      1      3.4      283
14.4      8.25      210      122      21.3      3.3      11.4      0.7      4      246
SELECTED_OUTPUT 1
  -file      Tavertine01.csv
  -reset      false
  -solution      true
```

```

    -pH                true
    -temperature       true
    -alkalinity         true
    -ionic_strength     true
    -charge_balance     true
    -percent_error      true
    -totals             C(4)   Ca
    -molalities         Ca+2   HC03-   C03-2
    -equilibrium_phases C02(g)   Calcite
    -saturation_indices C02(g)   Calcite
END

USE solution 5 # from D3 to F1
EQUILIBRIUM_PHASES 3
    CO2(g)    -2.3687    10
    calcite    0.8375    0
end

USE solution 5 #from D3 to F6
EQUILIBRIUM_PHASES 4
    CO2(g)    -3.0296    10
    calcite    0.9286    0
REACTION_TEMPERATURE 1
    14.4
end

USE solution 1 # Equilibrate S1 with atmosphere and calcite...
EQUILIBRIUM_PHASES 5
    CO2(g)    -3.38    10
    calcite    0    0
end

USE solution 5 # Equilibrate D3 with atmosphere and calcite...
EQUILIBRIUM_PHASES 5
    CO2(g)    -3.38    10
    calcite    0    0
end

USE solution 11 # Equilibrate F6 with atmosphere and calcite...
EQUILIBRIUM_PHASES 5
    CO2(g)    -3.38    10
    calcite    0    0
end

```

2.2 How much Calcite will have precipitated between sampling point D-3 and sampling point F-6?

The next simulation in the file is to estimate the amount of calcite that has precipitated between sampling points D-3 and F-6. There are different approaches to do this.

1. One way is to equilibrate Solution 5 with the calculated SI values for Solution 11 (please note, I first solved the initial solutions and then by looking at the output in the CSV file I included follow-up reactions). The delta calcite in output file (d_Calcite) gives the amount of calcite that has precipitated or that has dissolved. Please note that it is important to ensure that the final temperature in the reaction is equal to the temperature of the sample of F6 which is equal to 14.5 °C. This is achieved using the key word REACTION_TEMPERATURE. My simulation gives a result of 0.726 mmol/liter precipitation of calcite.
2. The other approach is to equilibrate both samples with the same atmospheric condition while forcing it in to equilibrium with calcite. This approach is given in the last two blocks of the simulation. I used the key-word EQUILIBRIUM_PHASES and set the SI of calcite to 0 and assuming no calcite to be initially present. For CO₂ I equilibrate with a partial pressure of 0.000413 atm (SI = -3.5) (<https://www.co2.earth/daily-co2>) and assume a large amount of CO₂ present in the gas phase. I do this for both samples (solution 5 and solution 11). The results are written to the Travertine01.csv file. The amount of calcite that has precipitated between the two samples is the difference between the calcite precipitated for solution 5 and solution 11. You could also estimate this value from the difference in the total amounts of Ca-species in solution. You should not use the Ca²⁺ concentration because this is only part of the total amount of Ca in solution. I get 0.794 mmol/liter

precipitation of calcite. This number is slightly different than in approach 1 and is most likely due to the fact that the final acidity is different due the different partial CO₂ pressures. The solubility product (and therefore the SI) depends on both the Ca⁺² and the CO₃⁻² concentrations. But the two results are close enough, about 1 mmol/liter.

3 Results

The results are given in table 1. We can compare the SI values calculated with PHREEQC to those reported by Lorah and Herman. Those from the paper are higher than ours, but the trend along the samples is similar. The results in rows 12 to 16 are simulated values where I allow the samples to react with gas and calcite to achieve the SI values calculated for other samples. The last three simulations equilibrate the samples with atmosphere and calcite. The amount of calcite precipitating between D3 and F6 is given in the last column of row 13 or can be calculated by subtracting the values in the last columns of rows 15 and 16. According to the last calculation 0.000779 moles of calcite precipitates between samples D3 and F6.

4 References

Lorah, Michelle M. & Herman Janet, S., 1988, The chemical evolution of a travertine-depositing stream: geochemical processes and mass transfer reactions, Water Resources Research, Volume 24(9), 1541-1552

Table 1: Summary of results for Practical 3

	soln	pH	temp	Alk	mu	charge	pct_err	C(4)	Ca	m_Ca+2	m_HCO3-	CO ₂ (g)	d_CO2(g)	Calcite	d_Calcite	si_CO2(g)	si_Calcite
S-1	1	7.32	24.3	0.00464621	0.0158173	0.000228116	1.23412	5.05E-03	4.12E-03	3.47E-03	4.45E-03	6.18E-06	0.00E+00	0.00E+00	0.00E+00	-1.9079	0.3865
S-3	2	7.23	24.6	0.0046748	0.0162009	0.000349025	1.84937	5.18E-03	4.20E-03	3.52E-03	4.49E-03	5.11E-06	0.00E+00	0.00E+00	0.00E+00	-1.8136	0.3087
S-2	3	7.2	24.7	0.00462556	0.0161979	0.000118131	0.625946	5.17E-03	4.22E-03	3.54E-03	4.44E-03	4.73E-06	0.00E+00	0.00E+00	0.00E+00	-1.7872	0.2777
D-1	4	7.24	24.3	0.00459445	0.0159198	0.000402671	2.17323	5.08E-03	4.20E-03	3.54E-03	4.41E-03	5.09E-06	0.00E+00	0.00E+00	0.00E+00	-1.8325	0.3099
D-3	5	7.43	23.6	0.004832	0.0160868	4.31E-06	0.022943	5.15E-03	4.20E-03	3.52E-03	4.62E-03	8.16E-06	0.00E+00	0.00E+00	0.00E+00	-2.0067	0.5065
F-1	6	7.79	21.4	0.005019	0.016064	-0.000231436	-1.22807	5.12E-03	4.15E-03	3.47E-03	4.74E-03	1.83E-05	0.00E+00	0.00E+00	0.00E+00	-2.3687	0.8375
F-3	7	8.06	20.5	0.00512439	0.0159236	-0.000388173	-2.07457	5.10E-03	4.10E-03	3.41E-03	4.76E-03	3.34E-05	0.00E+00	0.00E+00	0.00E+00	-2.6429	1.0877
F-4	8	8.27	19.7	0.00466473	0.0155746	-0.000163147	-0.90157	4.56E-03	4.00E-03	3.30E-03	4.23E-03	4.71E-05	0.00E+00	0.00E+00	0.00E+00	-2.908	1.2239
F-5	9	8.28	19.6	0.00458337	0.0153548	-0.000200803	-1.12692	4.48E-03	3.92E-03	3.24E-03	4.16E-03	4.71E-05	0.00E+00	0.00E+00	0.00E+00	-2.926	1.2181
F-2	10	8.37	18.4	0.00446269	0.015074	-0.000354285	-2.02871	4.33E-03	3.77E-03	3.11E-03	4.01E-03	5.42E-05	0.00E+00	0.00E+00	0.00E+00	-3.0382	1.258
F-6	11	8.25	14.4	0.00348307	0.0128093	-0.000477336	-3.23364	3.44E-03	3.05E-03	2.58E-03	3.24E-03	2.94E-05	0.00E+00	0.00E+00	0.00E+00	-3.0296	0.92
D3 - F1	5	7.77915	23.6	0.00475523	0.0159397	4.31E-06	0.0232126	4.84E-03	4.16E-03	3.47E-03	4.48E-03	1.77E-05	1.00E+01	3.84E-05	3.84E-05	-2.3687	0.8375
D3 - F6	5	8.23276	14.4	0.00337974	0.0143703	4.31E-06	0.0264588	3.34E-03	3.47E-03	2.91E-03	3.13E-03	2.77E-05	1.00E+01	7.26E-04	7.26E-04	-3.0296	0.9286
S1 to Atm	1	7.98868	24.3	0.000727001	0.0108271	0.000228116	1.97582	7.29E-04	2.16E-03	1.81E-03	6.88E-04	4.22E-06	1.00E+01	1.96E-03	1.96E-03	-3.38	0
D3 to Atm	5	7.99362	23.6	0.000742529	0.010895	4.31E-06	0.0372673	7.45E-04	2.15E-03	1.80E-03	7.03E-04	4.30E-06	1.00E+01	2.04E-03	2.04E-03	-3.38	0
F6 to Atm	11	8.06815	14.4	0.000982044	0.00967473	-0.000477336	-4.56949	9.88E-04	1.80E-03	1.53E-03	9.41E-04	5.40E-06	1.00E+01	1.25E-03	1.25E-03	-3.38	0