Evaluation of a High Fluoride Contaminated Fractured Rock Aquifer in South Africa: An Evaporation Case Study

Paper by Elumalai et al.

Presented by Matthew Hughes

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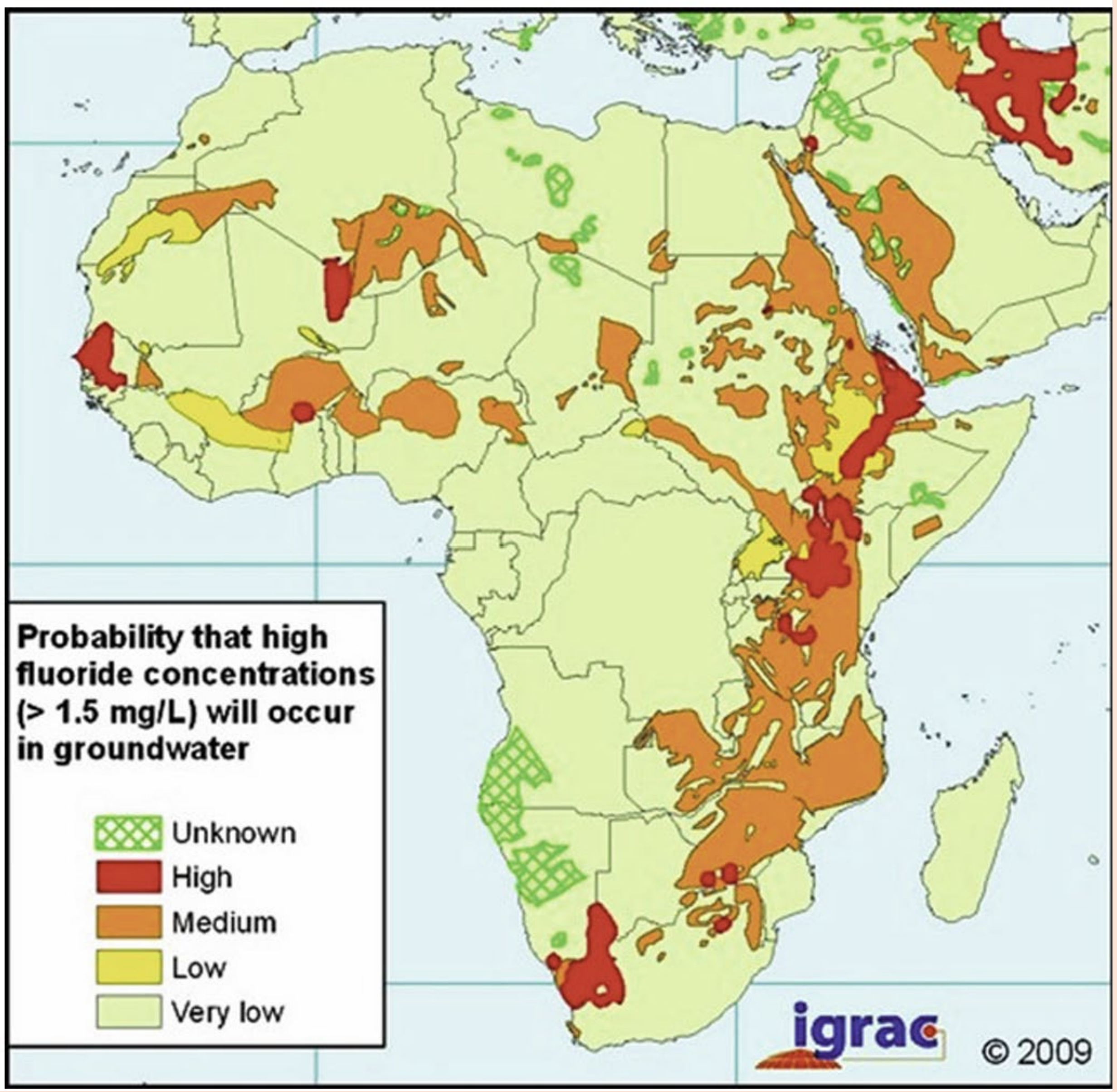
Background

- Groundwater is an important resource for arid communities, 44% of sub-Saharan Africa has limited access to clean water
- A combination of natural and anthropogenic factors determine groundwater quality
- Geologic Processes: rock-water interaction, weathering, precipitation/dissolution and **evaporation**
- Fluoride is beneficial below 1.5 ppm, above is harmful to health causing hypothyroidism, fluorosis and more

Background

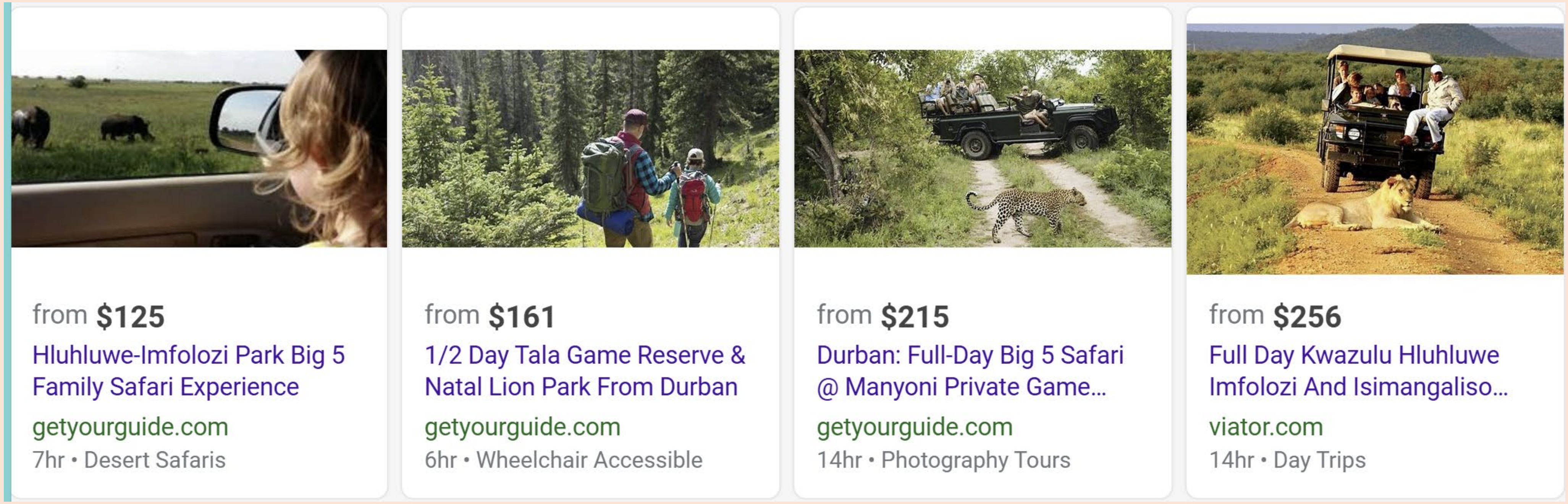
- Several provinces of South Africa have over 4ppm F in water
- Common geologic sources of F include volcanic, gneissic, and granitic minerals, and rocks; fluorite, fluorapatite, hydroxyapatite, cryolite, and hornblende



(IGRAC 2009)

Study Objectives

- Identify the geological mechanisms that lead to high F concentration in Kwazulu-Natal region
- Perform chemometric modeling to show the possibility of high F concentrations
- Spread awareness, get aid for Kwazulu-Natal



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Study area

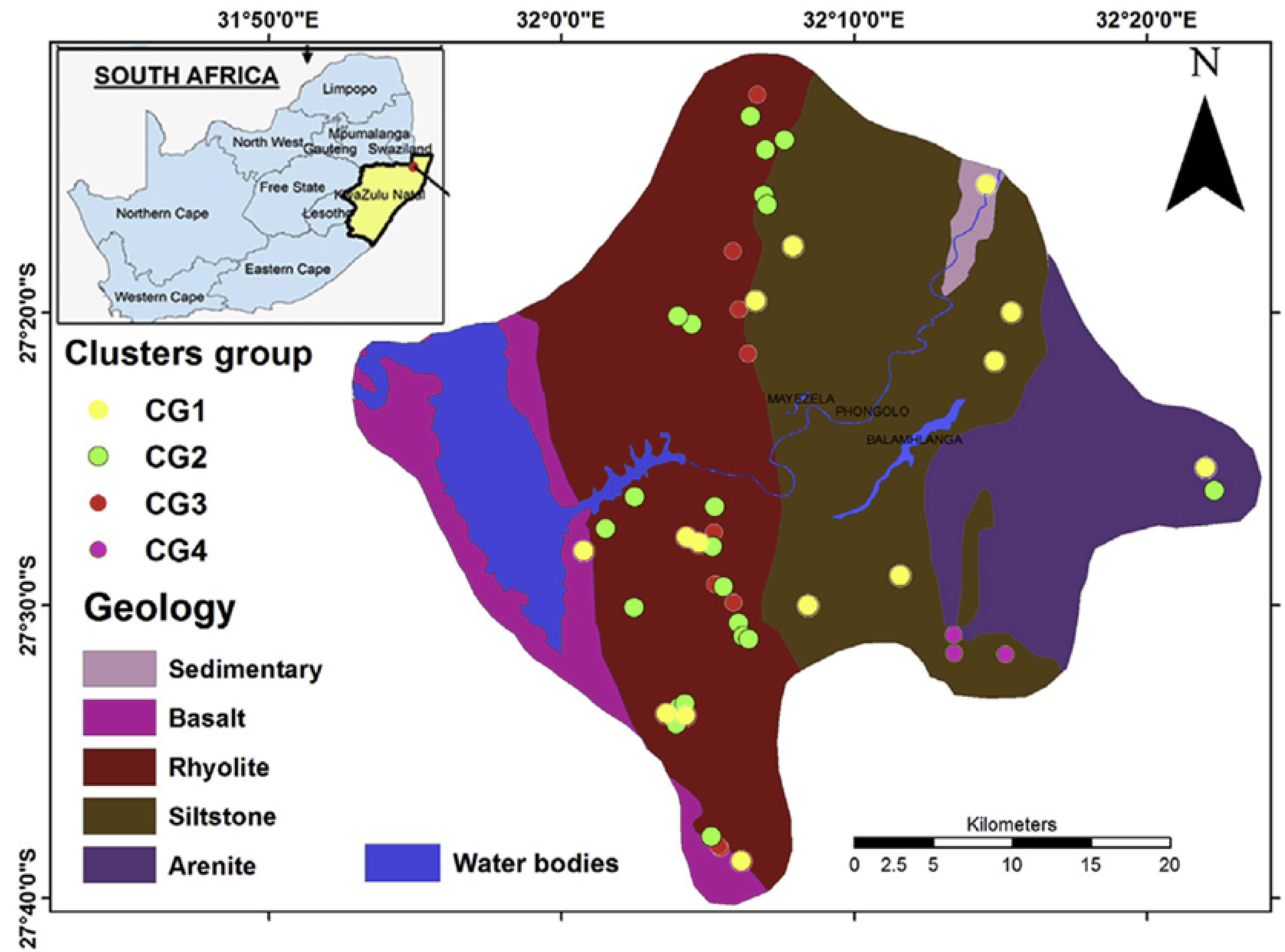
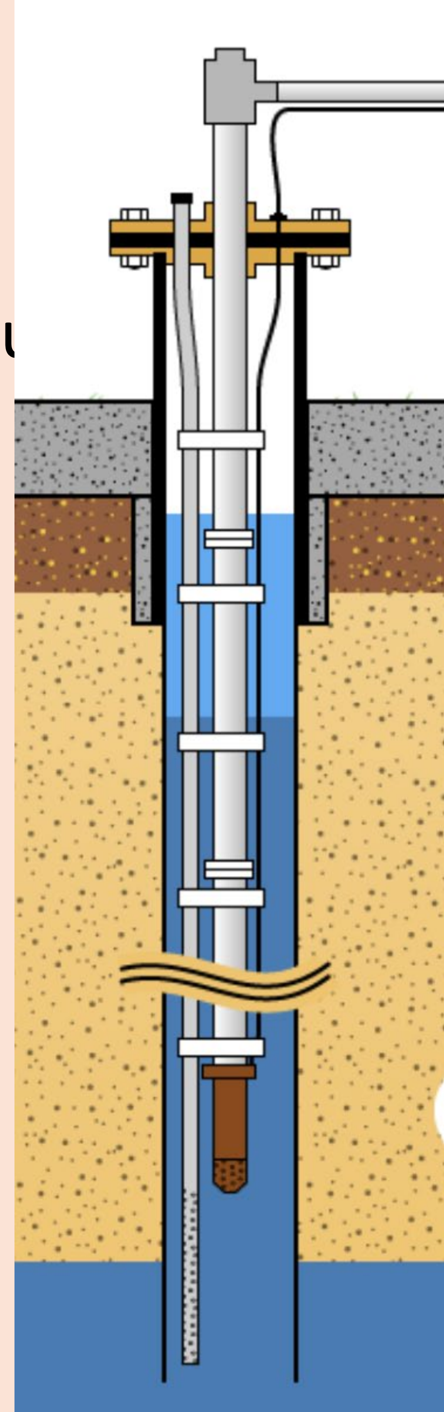


Fig. 1. Sampling wells as cluster groups, geology and other features of the Study area.

Method overview

- Groundwater samples taken from 49 Bore Holes in Northern Kwazu Natal
- Electrical conductivity (EC) and pH were measured in field with meters
- Ion chromatography for major and minor Ion analyses
- Titration for bicarbonate and carbonate evaluation
- Various software for interpretation/chemometric modeling
- ArcGIS for mapping
- PHREEQC for Saturation indices



Concentration Data

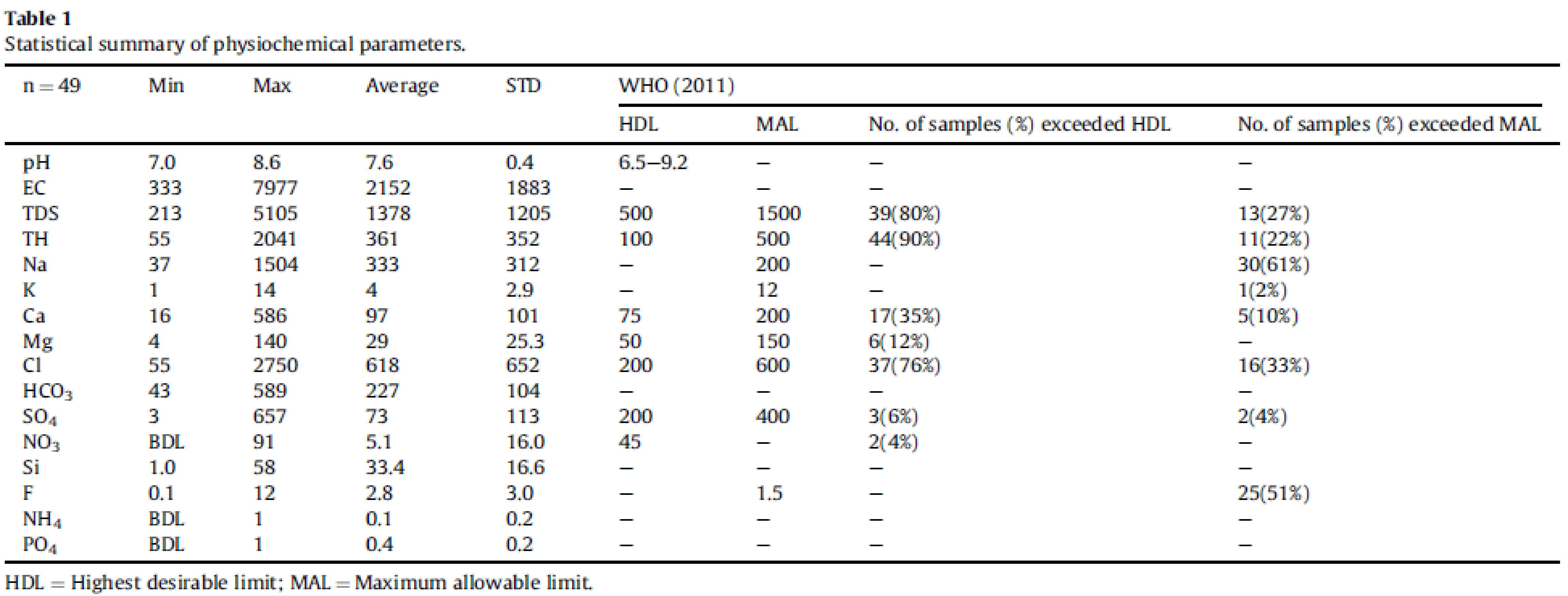


Table 1

Statistical summary of physiochemical parameters.

n = 49	Min	Max	Average	STD	WHO (2011)			
					HDL	MAL	No. of samples (%) exceeded HDL	No. of samples (%) exceeded MAL
pH	7.0	8.6	7.6	0.4	6.5–9.2	–	–	–
EC	333	7977	2152	1883	–	–	–	–
TDS	213	5105	1378	1205	500	1500	39(80%)	13(27%)
TH	55	2041	361	352	100	500	44(90%)	11(22%)
Na	37	1504	333	312	–	200	–	30(61%)
K	1	14	4	2.9	–	12	–	1(2%)
Ca	16	586	97	101	75	200	17(35%)	5(10%)
Mg	4	140	29	25.3	50	150	6(12%)	–
Cl	55	2750	618	652	200	600	37(76%)	16(33%)
HCO_3	43	589	227	104	–	–	–	–
SO_4	3	657	73	113	200	400	3(6%)	2(4%)
NO_3	BDL	91	5.1	16.0	45	–	2(4%)	–
Si	1.0	58	33.4	16.6	–	–	–	–
F	0.1	12	2.8	3.0	–	1.5	–	25(51%)
NH_4	BDL	1	0.1	0.2	–	–	–	–
PO_4	BDL	1	0.4	0.2	–	–	–	–

HDL = Highest desirable limit; MAL = Maximum allowable limit.

Study Conclusions Overview

- High concentrations of fluoride associated with NaCl water.
- Mineral weathering, evaporation and wastewater infiltration control the water chemistry
- Calcite precipitation and groundwater fluoride concentrations control fluorite solubility
- Statistical analyses show that mineral weathering, evaporation, longer residence time, wastewater, nitrification, and ion exchange influenced the water chemistry
- **Geochemical and chemometric methods showed that fluoride concentrations are driven by evaporation**

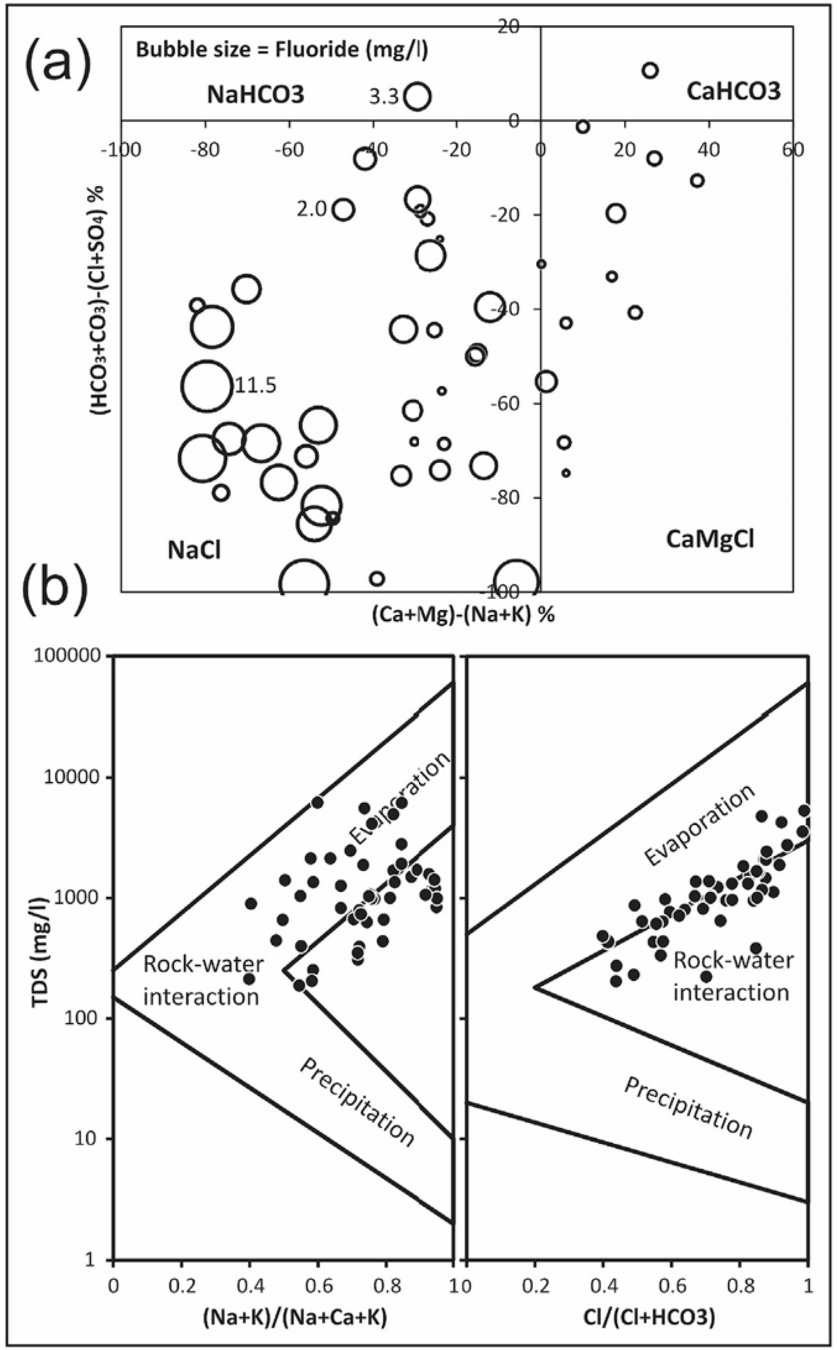


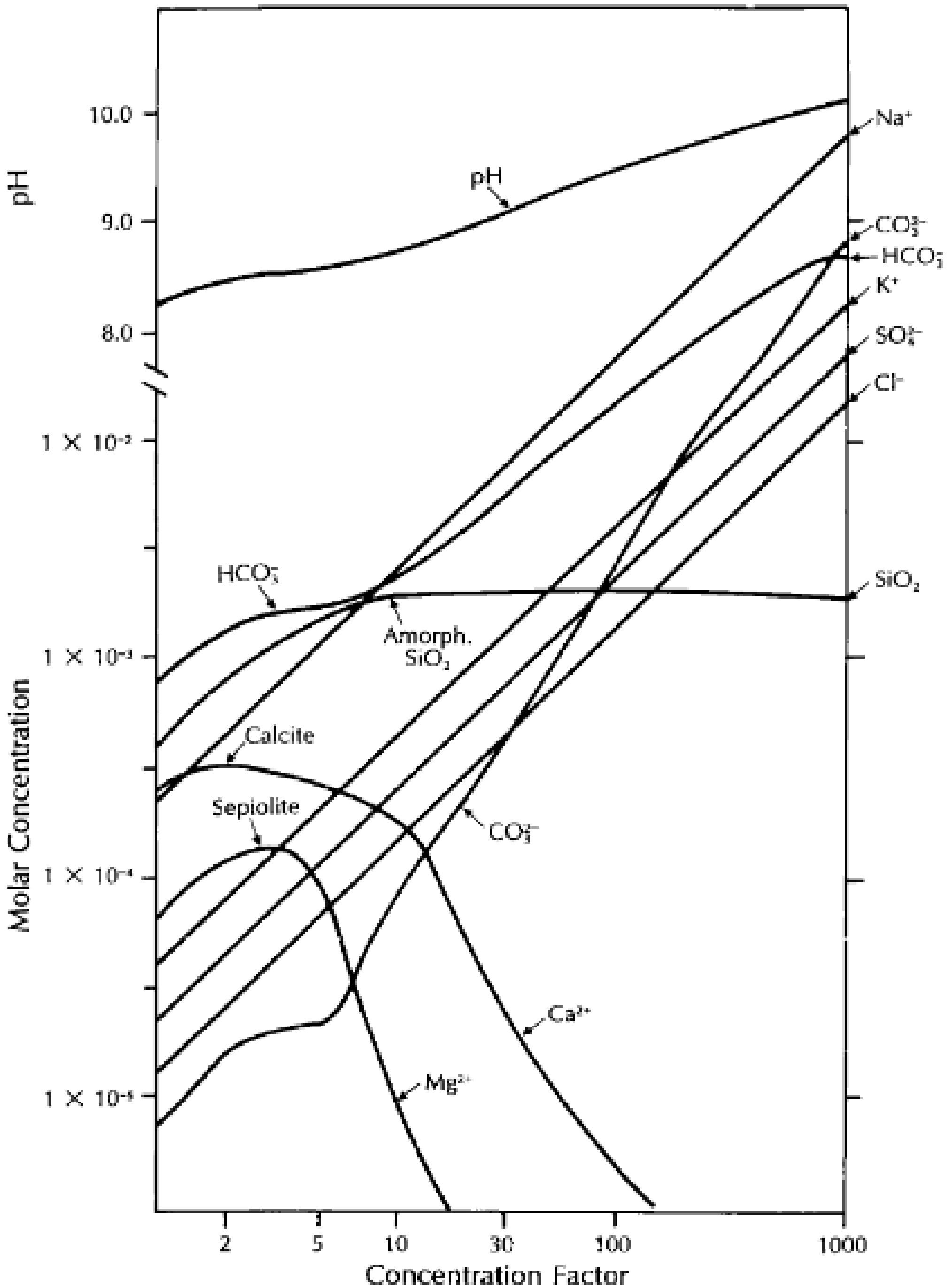
Fig. 2. Modified Chadha diagram explains water types and fluoride concentration and Gibbs plots explain dominance processes.

Evaporation Bootcamp: Faure 18.3

- When water evaporates the minerals that stay behind become more concentrated
- If two elements ex; X and Y don't react or form solids their concentrations increase together in a linear relationship
- If X or Y precipitates the other element will continue to rise in concentration
- If both X and Y precipitate in a fixed ratio their concentrations decrease
- This process acts as a geochemical divide and influences changes in water chemistry due to evaporation

$m = (Y)/(X)$

$(X)_f = g(X)_i$



Faure Fig 20.4

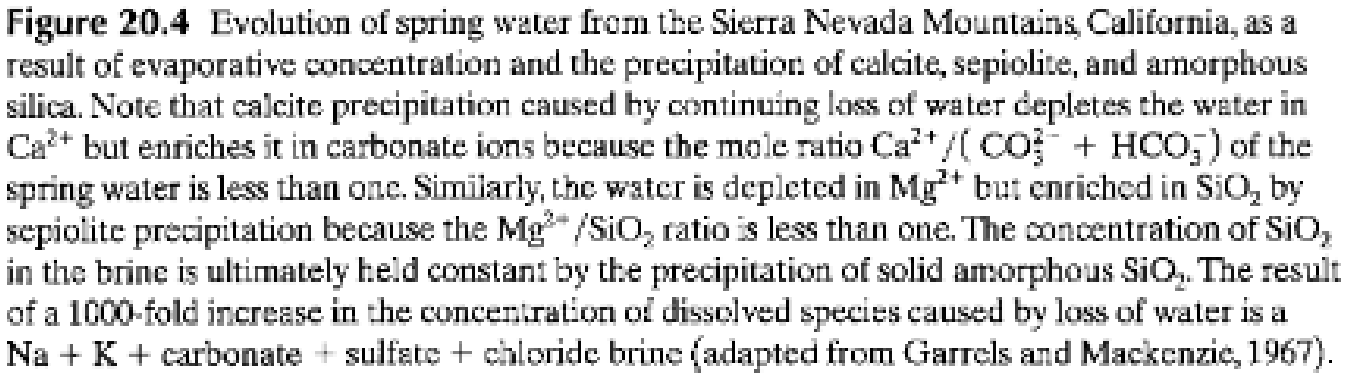
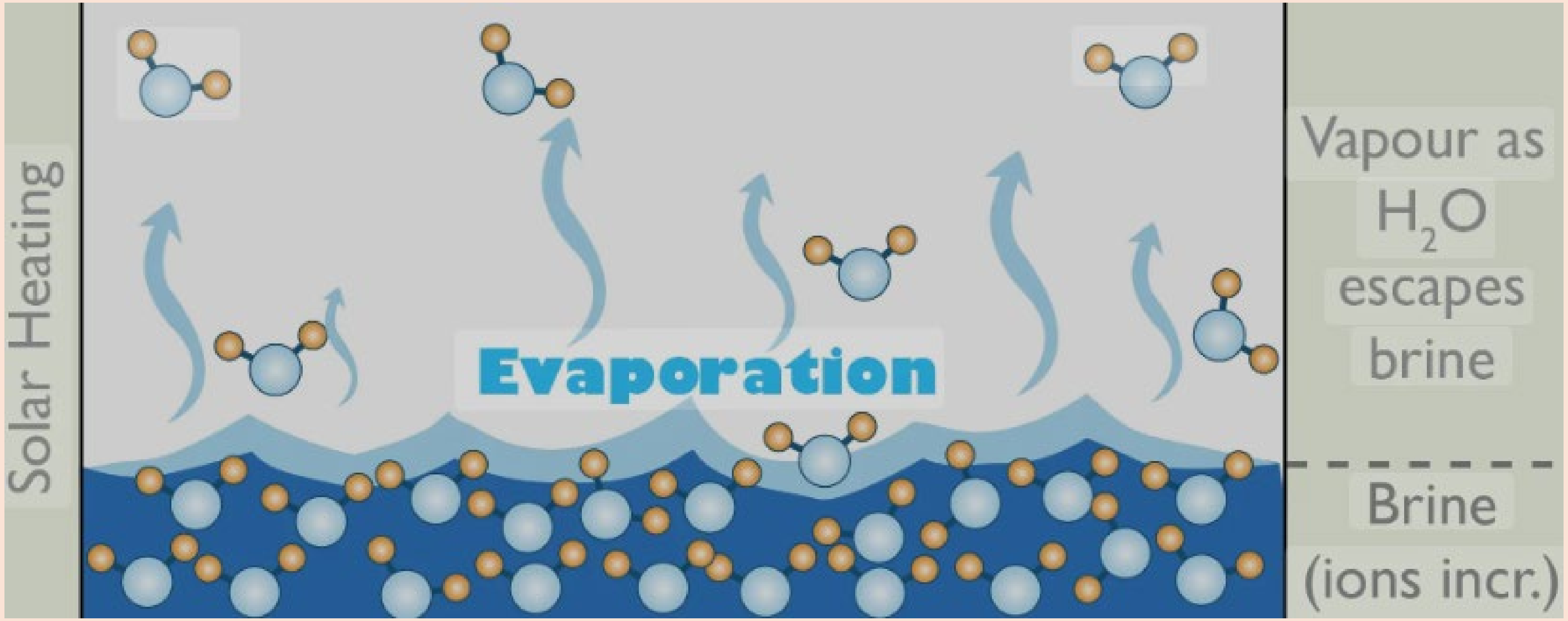


Figure 20.4 Evolution of spring water from the Sierra Nevada Mountains, California, as a result of evaporative concentration and the precipitation of calcite, sepiolite, and amorphous silica. Note that calcite precipitation caused by continuing loss of water depletes the water in Ca^{2+} but enriches it in carbonate ions because the mole ratio $Ca^{2+}/(CO_3^{2-} + HCO_3^-)$ of the spring water is less than one. Similarly, the water is depleted in Mg^{2+} but enriched in SiO_2 by sepiolite precipitation because the Mg^{2+}/SiO_2 ratio is less than one. The concentration of SiO_2 in the brine is ultimately held constant by the precipitation of solid amorphous SiO_2. The result of a 1000-fold increase in the concentration of dissolved species caused by loss of water is a Na + K + carbonate + sulfate + chloride brine (adapted from Garrels and Mackenzie, 1967).

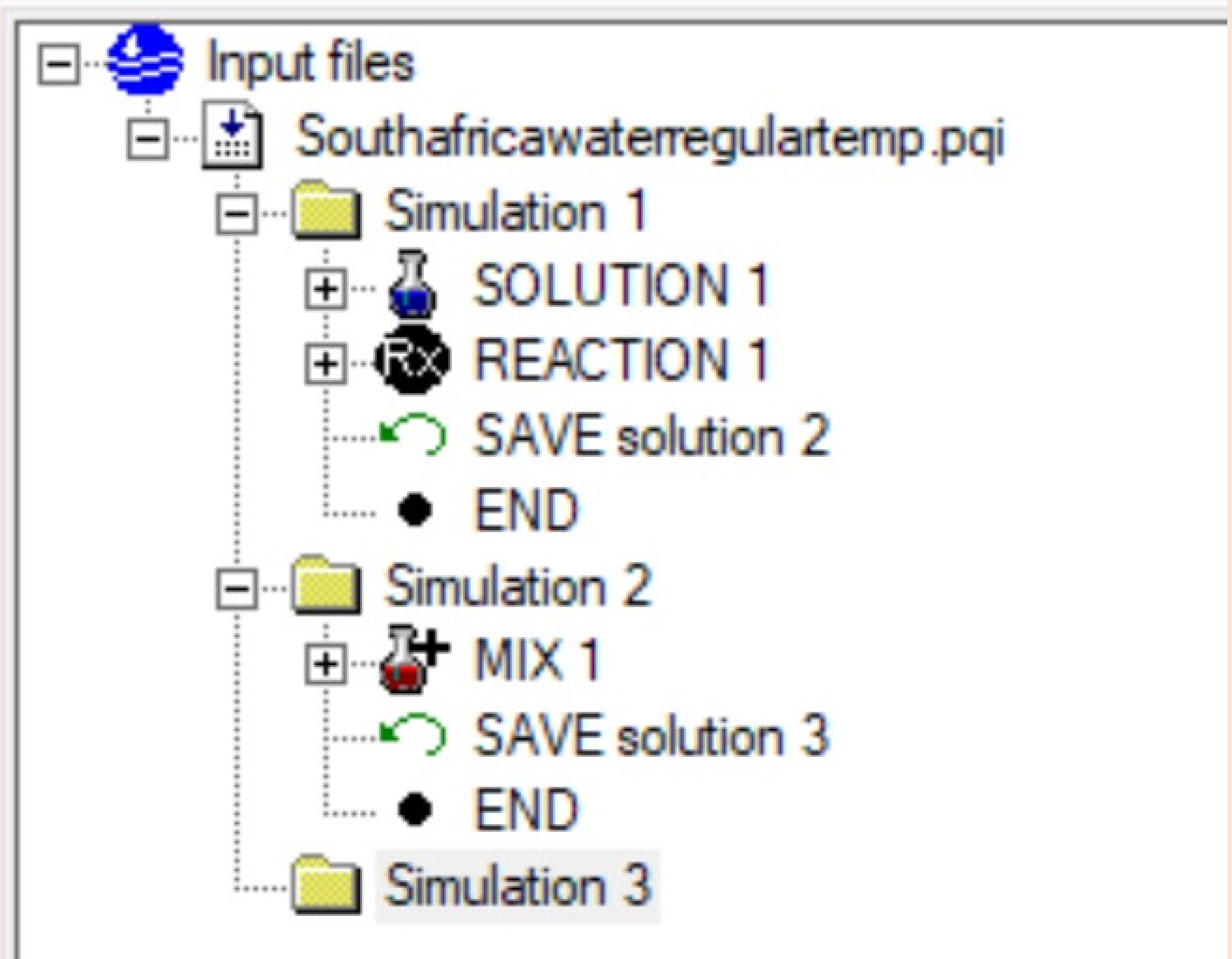
My Evaporation Analyses Objectives

- Use PHREEQC to see how evaporation changes concentrations and SI's in Kwazulu-Natal water
- See what happens to concentration and SI data if the temperature is increased to the maximum temp recorded in the study, 30 °C

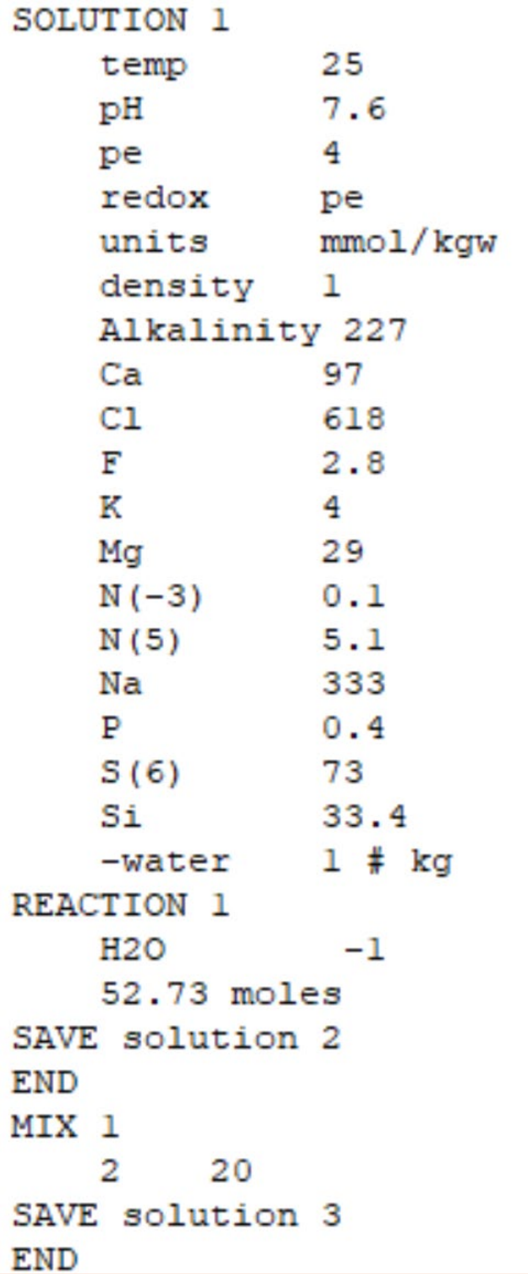


(Guerra, n.d.)

PHREEQC input



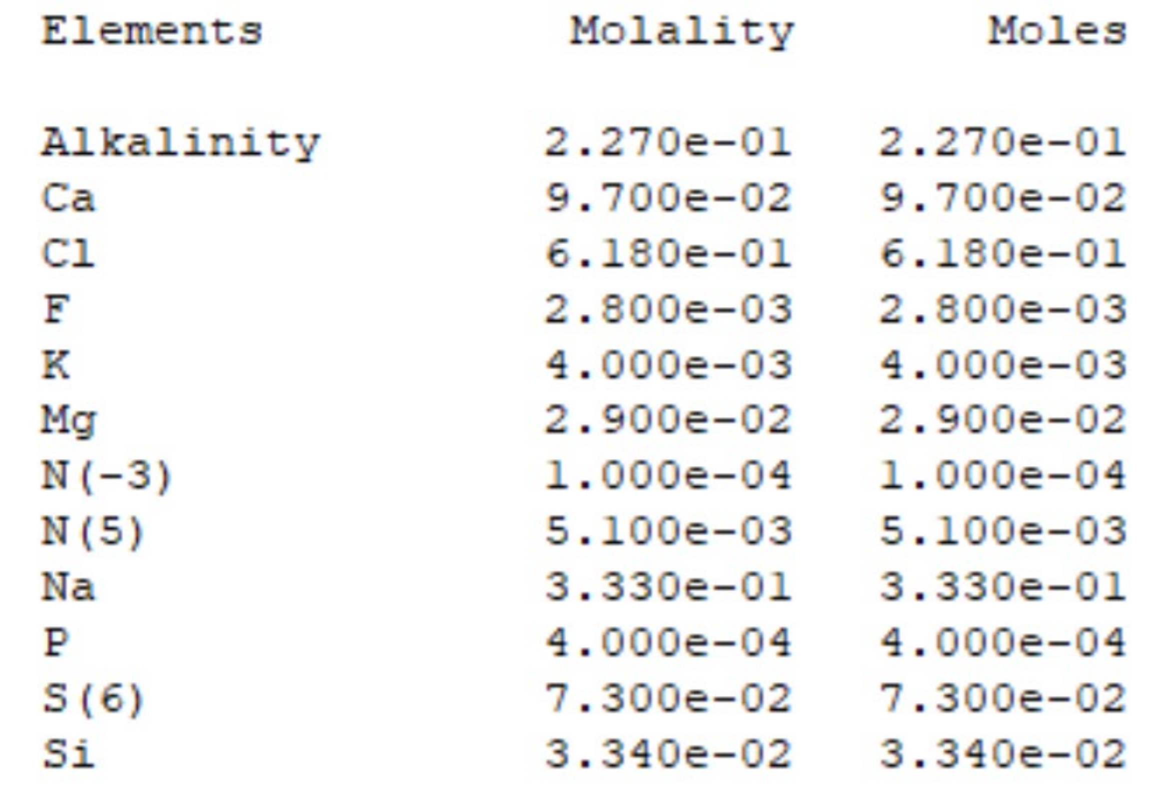
Input files
Southafricawaterregulartemp.pqi
Simulation 1
SOLUTION 1
REACTION 1
SAVE solution 2
END
Simulation 2
MIX 1
SAVE solution 3
END
Simulation 3



```
SOLUTION 1
    temp      25
    pH        7.6
    pe        4
    redox     pe
    units     mmol/kgw
    density   1
    Alkalinity 227
    Ca        97
    Cl        618
    F         2.8
    K         4
    Mg        29
    N(-3)     0.1
    N(5)      5.1
    Na        333
    P         0.4
    S(6)      73
    Si        33.4
    -water    1 # kg
REACTION 1
    H2O        -1
    52.73 moles
SAVE solution 2
END
MIX 1
    2    20
SAVE solution 3
END
```

25°C PHREEQC Output: Solution Composition

Before Evaporation

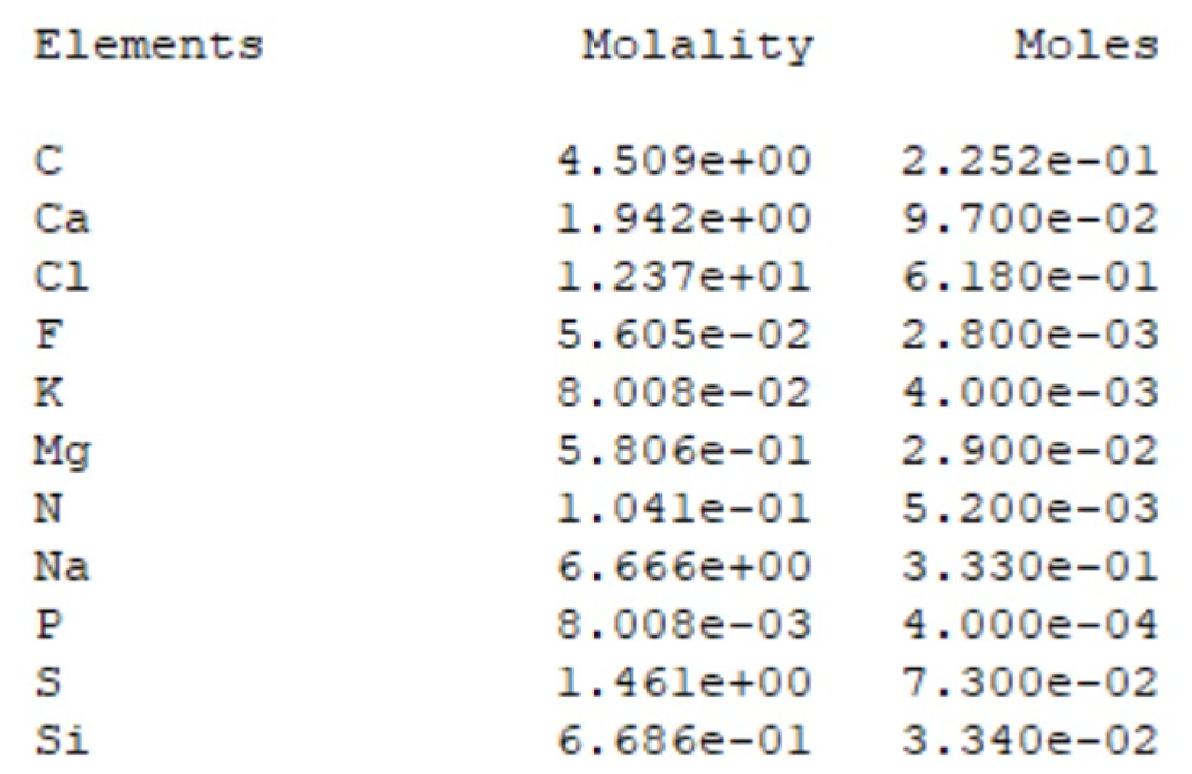


```
Elements                 Molality       Moles

Alkalinity              2.270e-01   2.270e-01
Ca                      9.700e-02   9.700e-02
Cl                      6.180e-01   6.180e-01
F                       2.800e-03   2.800e-03
K                       4.000e-03   4.000e-03
Mg                      2.900e-02   2.900e-02
N(-3)                   1.000e-04   1.000e-04
N(5)                    5.100e-03   5.100e-03
Na                      3.330e-01   3.330e-01
P                       4.000e-04   4.000e-04
S(6)                    7.300e-02   7.300e-02
Si                      3.340e-02   3.340e-02
```

VS

After Evaporation

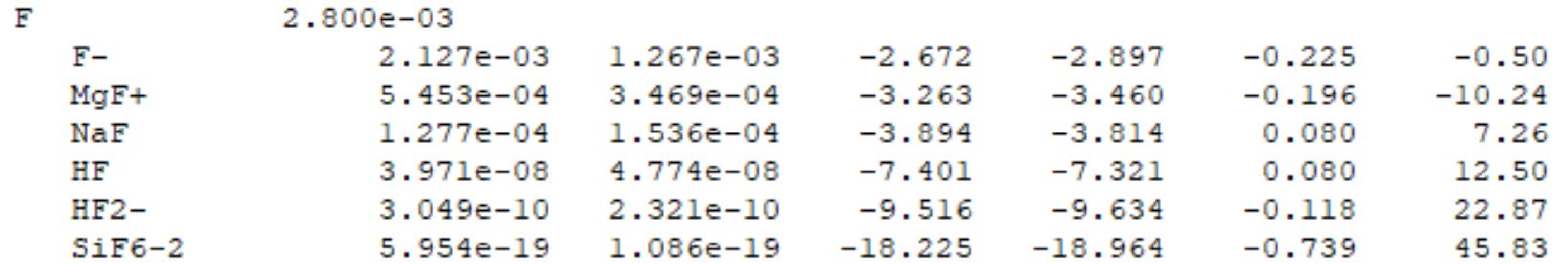


```
Elements                 Molality       Moles


C                       4.509e+00   2.252e-01
Ca                      1.942e+00   9.700e-02
Cl                      1.237e+01   6.180e-01
F                       5.605e-02   2.800e-03
K                       8.008e-02   4.000e-03
Mg                      5.806e-01   2.900e-02
N                       1.041e-01   5.200e-03
Na                      6.666e+00   3.330e-01
P                       8.008e-03   4.000e-04
S                       1.461e+00   7.300e-02
Si                      6.686e-01   3.340e-02
```

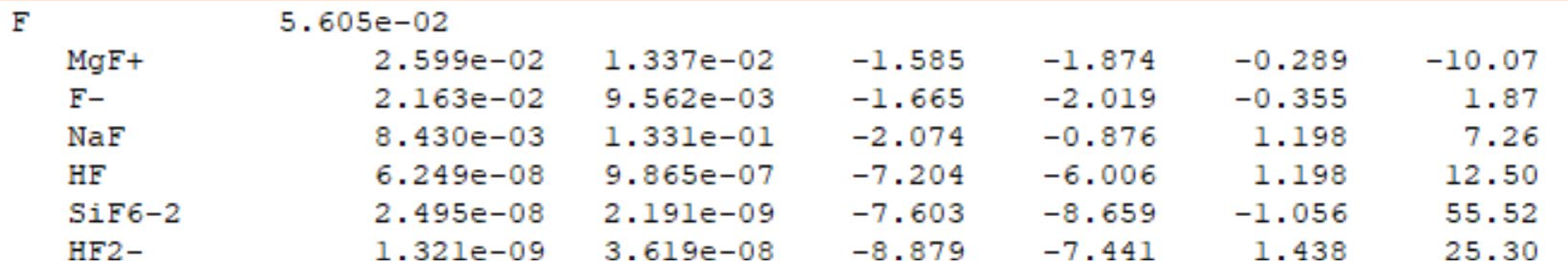
25°C PHREEQC Output: F speciation

Before Evaporation



```
F               2.800e-03
   F-                  2.127e-03   1.267e-03    -2.672    -2.897    -0.225    -0.50
   MgF+                5.453e-04   3.469e-04    -3.263    -3.460    -0.196   -10.24
   NaF                 1.277e-04   1.536e-04    -3.894    -3.814     0.080     7.26
   HF                  3.971e-08   4.774e-08    -7.401    -7.321     0.080    12.50
   HF2-                3.049e-10   2.321e-10    -9.516    -9.634    -0.118    22.87
   SiF6-2              5.954e-19   1.086e-19   -18.225   -18.964    -0.739    45.83
```

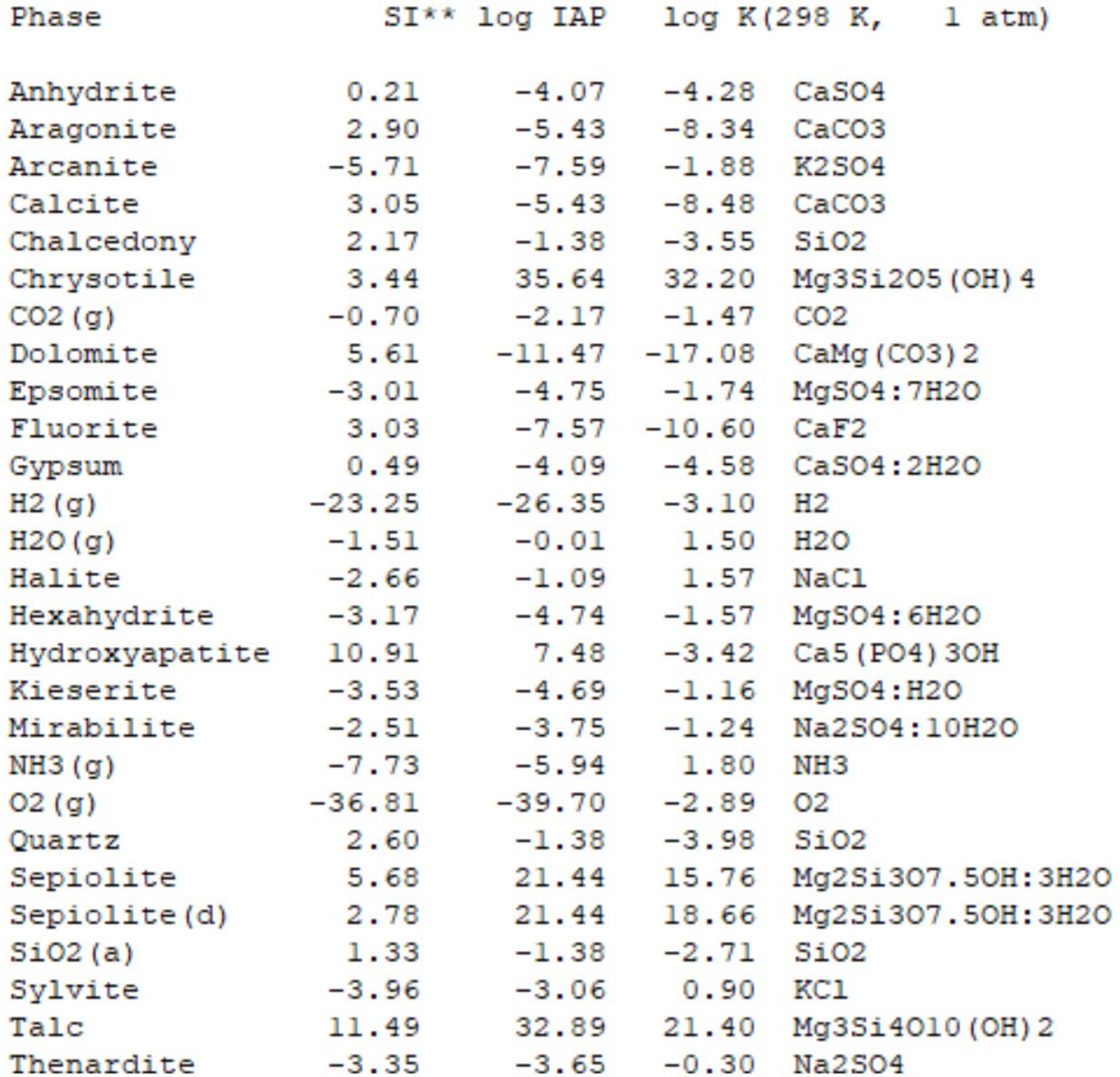
After Evaporation



```
F               5.605e-02
   MgF+                2.599e-02   1.337e-02    -1.585    -1.874    -0.289   -10.07
   F-                  2.163e-02   9.562e-03    -1.665    -2.019    -0.355     1.87
   NaF                 8.430e-03   1.331e-01    -2.074    -0.876     1.198     7.26
   HF                  6.249e-08   9.865e-07    -7.204    -6.006     1.198    12.50
   SiF6-2              2.495e-08   2.191e-09    -7.603    -8.659    -1.056    55.52
   HF2-                1.321e-09   3.619e-08    -8.879    -7.441     1.438    25.30
```

25°C PHREEQC Output: Saturation Indices

Before Evaporation

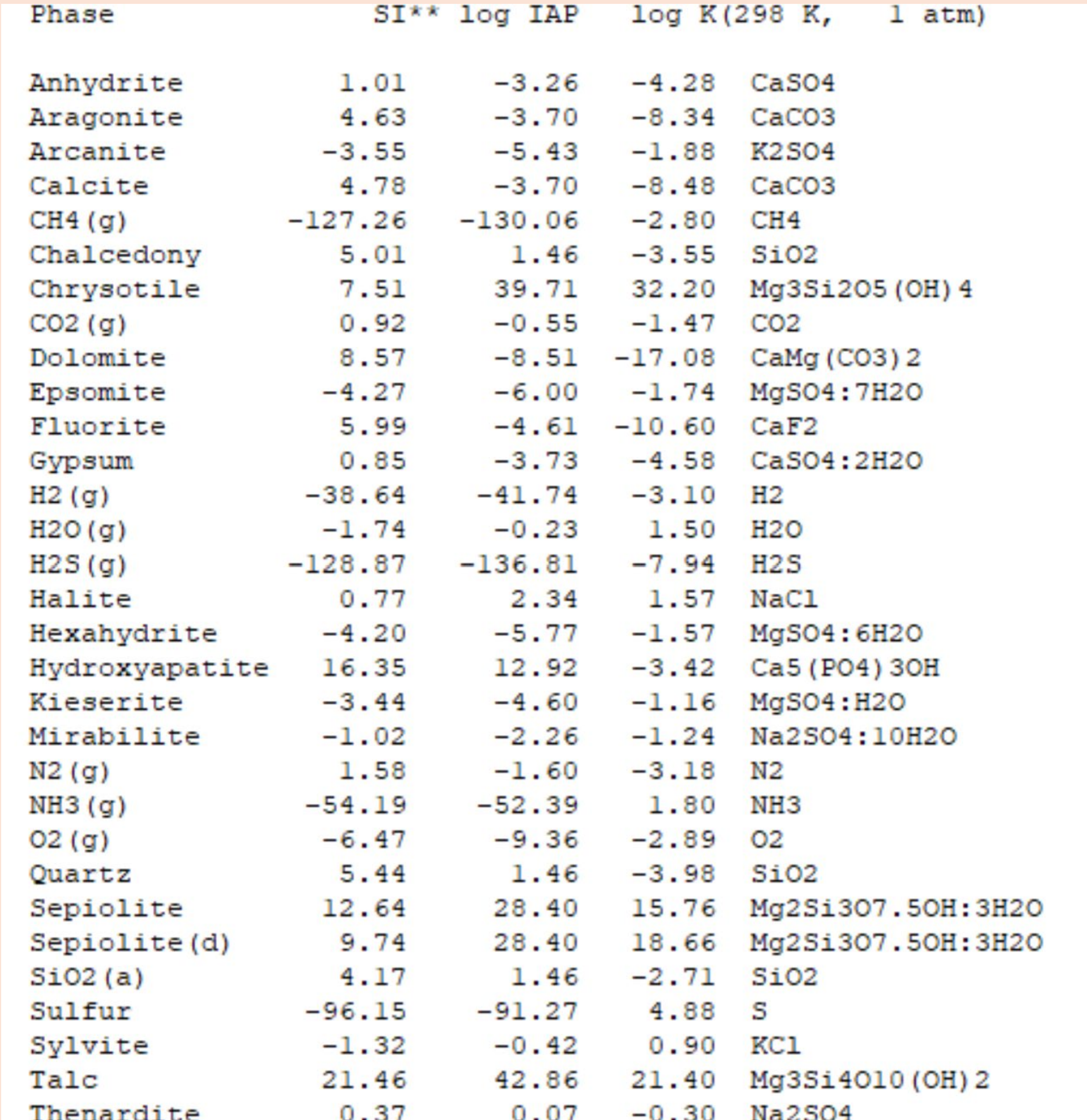


```
Phase               SI** log IAP   log K(298 K,   1 atm)

Anhydrite           0.21     -4.07   -4.28  CaSO4
Aragonite           2.90     -5.43   -8.34  CaCO3
Arcanite           -5.71     -7.59   -1.88  K2SO4
Calcite             3.05     -5.43   -8.48  CaCO3
Chalcedony          2.17     -1.38   -3.55  SiO2
Chrysotile          3.44     35.64   32.20  Mg3Si2O5(OH)4
CO2(g)             -0.70     -2.17   -1.47  CO2
Dolomite            5.61    -11.47  -17.08  CaMg(CO3)2
Epsomite           -3.01     -4.75   -1.74  MgSO4:7H2O
Fluorite            3.03     -7.57  -10.60  CaF2
Gypsum              0.49     -4.09   -4.58  CaSO4:2H2O
H2(g)             -23.25    -26.35   -3.10  H2
H2O(g)             -1.51     -0.01    1.50  H2O
Halite             -2.66     -1.09    1.57  NaCl
Hexahydrite        -3.17     -4.74   -1.57  MgSO4:6H2O
Hydroxyapatite     10.91      7.48   -3.42  Ca5(PO4)3OH
Kieserite          -3.53     -4.69   -1.16  MgSO4:H2O
Mirabilite         -2.51     -3.75   -1.24  Na2SO4:10H2O
NH3(g)             -7.73     -5.94    1.80  NH3
O2(g)             -36.81    -39.70   -2.89  O2
Quartz              2.60     -1.38   -3.98  SiO2
Sepiolite           5.68     21.44   15.76  Mg2Si3O7.5OH:3H2O
Sepiolite(d)        2.78     21.44   18.66  Mg2Si3O7.5OH:3H2O
SiO2(a)             1.33     -1.38   -2.71  SiO2
Sylvite            -3.96     -3.06    0.90  KCl
Talc               11.49     32.89   21.40  Mg3Si4O10(OH)2
Thenardite         -3.35     -3.65   -0.30  Na2SO4
```

25°C PHREEQC Output: Saturation Indices

After Evaporation

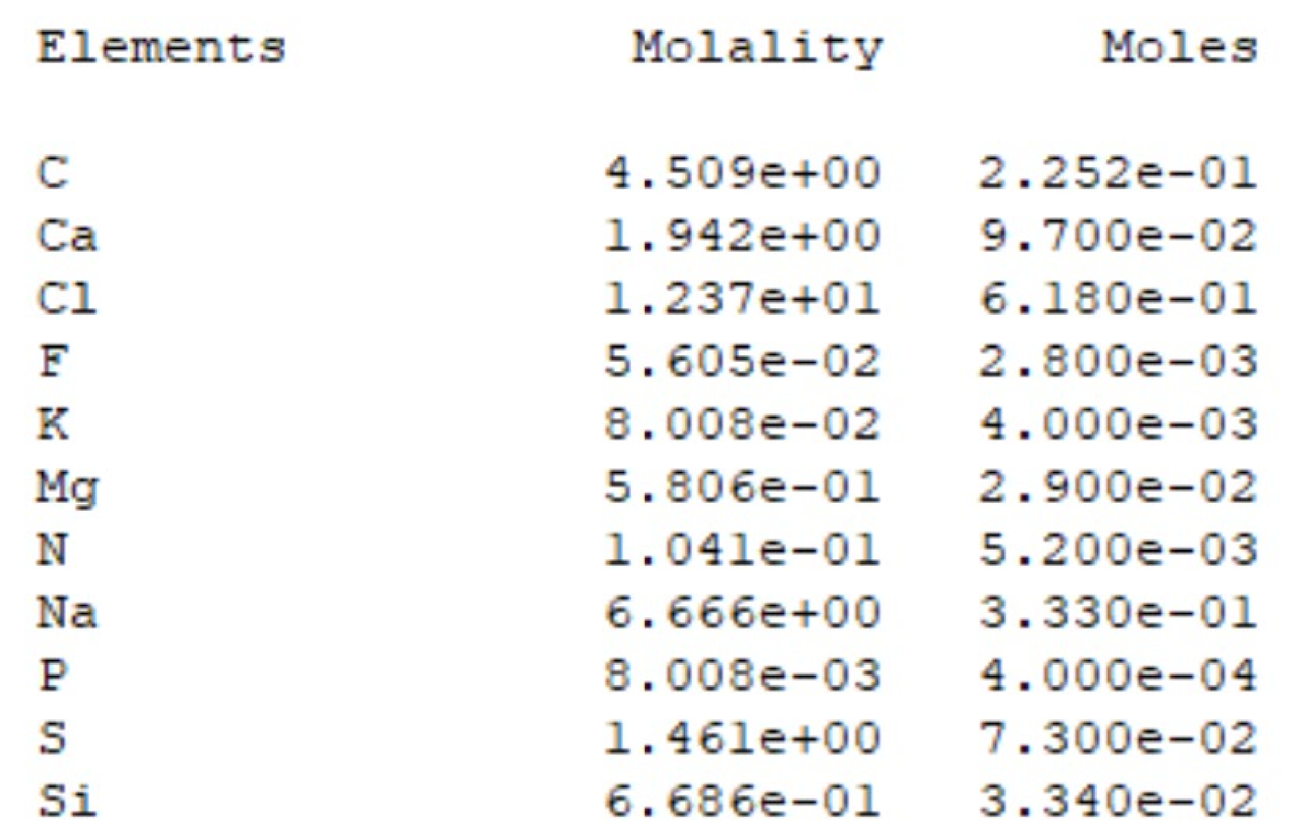


```
Phase               SI** log IAP   log K(298 K,   1 atm)

Anhydrite           1.01    -3.26   -4.28  CaSO4
Aragonite           4.63    -3.70   -8.34  CaCO3
Arcanite           -3.55    -5.43   -1.88  K2SO4
Calcite             4.78    -3.70   -8.48  CaCO3
CH4(g)           -127.26  -130.06   -2.80  CH4
Chalcedony          5.01     1.46   -3.55  SiO2
Chrysotile          7.51    39.71   32.20  Mg3Si2O5(OH)4
CO2(g)              0.92    -0.55   -1.47  CO2
Dolomite            8.57    -8.51  -17.08  CaMg(CO3)2
Epsomite           -4.27    -6.00   -1.74  MgSO4:7H2O
Fluorite            5.99    -4.61  -10.60  CaF2
Gypsum              0.85    -3.73   -4.58  CaSO4:2H2O
H2(g)             -38.64   -41.74   -3.10  H2
H2O(g)             -1.74    -0.23    1.50  H2O
H2S(g)           -128.87  -136.81   -7.94  H2S
Halite              0.77     2.34    1.57  NaCl
Hexahydrite        -4.20    -5.77   -1.57  MgSO4:6H2O
Hydroxyapatite     16.35    12.92   -3.42  Ca5(PO4)3OH
Kieserite          -3.44    -4.60   -1.16  MgSO4:H2O
Mirabilite         -1.02    -2.26   -1.24  Na2SO4:10H2O
N2(g)               1.58    -1.60   -3.18  N2
NH3(g)            -54.19   -52.39    1.80  NH3
O2(g)              -6.47    -9.36   -2.89  O2
Quartz              5.44     1.46   -3.98  SiO2
Sepiolite          12.64    28.40   15.76  Mg2Si3O7.5OH:3H2O
Sepiolite(d)        9.74    28.40   18.66  Mg2Si3O7.5OH:3H2O
SiO2(a)             4.17     1.46   -2.71  SiO2
Sulfur            -96.15   -91.27    4.88  S
Sylvite            -1.32    -0.42    0.90  KCl
Talc               21.46    42.86   21.40  Mg3Si4O10(OH)2
Thenardite          0.37     0.07   -0.30  Na2SO4
```

Max Temp PHREEQC Output: Solution Composition

After Evaporation at 25 C = After Evaporation at 30.3 C

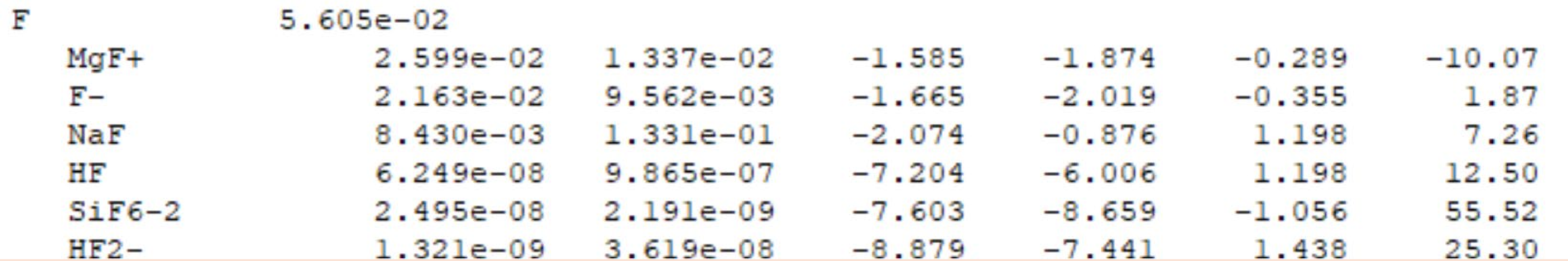


```
Elements             Molality       Moles

C                   4.509e+00   2.252e-01
Ca                  1.942e+00   9.700e-02
Cl                  1.237e+01   6.180e-01
F                   5.605e-02   2.800e-03
K                   8.008e-02   4.000e-03
Mg                  5.806e-01   2.900e-02
N                   1.041e-01   5.200e-03
Na                  6.666e+00   3.330e-01
P                   8.008e-03   4.000e-04
S                   1.461e+00   7.300e-02
Si                  6.686e-01   3.340e-02
```

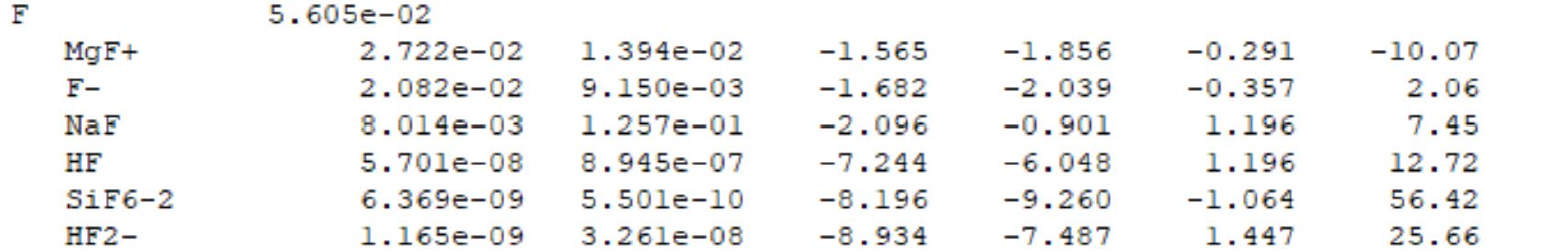
Max Temp PHREEQC Output: F speciation

After Evaporation at 25°C



```
F             5.605e-02
   MgF+                2.599e-02   1.337e-02    -1.585    -1.874    -0.289    -10.07
   F-                  2.163e-02   9.562e-03    -1.665    -2.019    -0.355      1.87
   NaF                 8.430e-03   1.331e-01    -2.074    -0.876     1.198      7.26
   HF                  6.249e-08   9.865e-07    -7.204    -6.006     1.198     12.50
   SiF6-2              2.495e-08   2.191e-09    -7.603    -8.659    -1.056     55.52
   HF2-                1.321e-09   3.619e-08    -8.879    -7.441     1.438     25.30
```

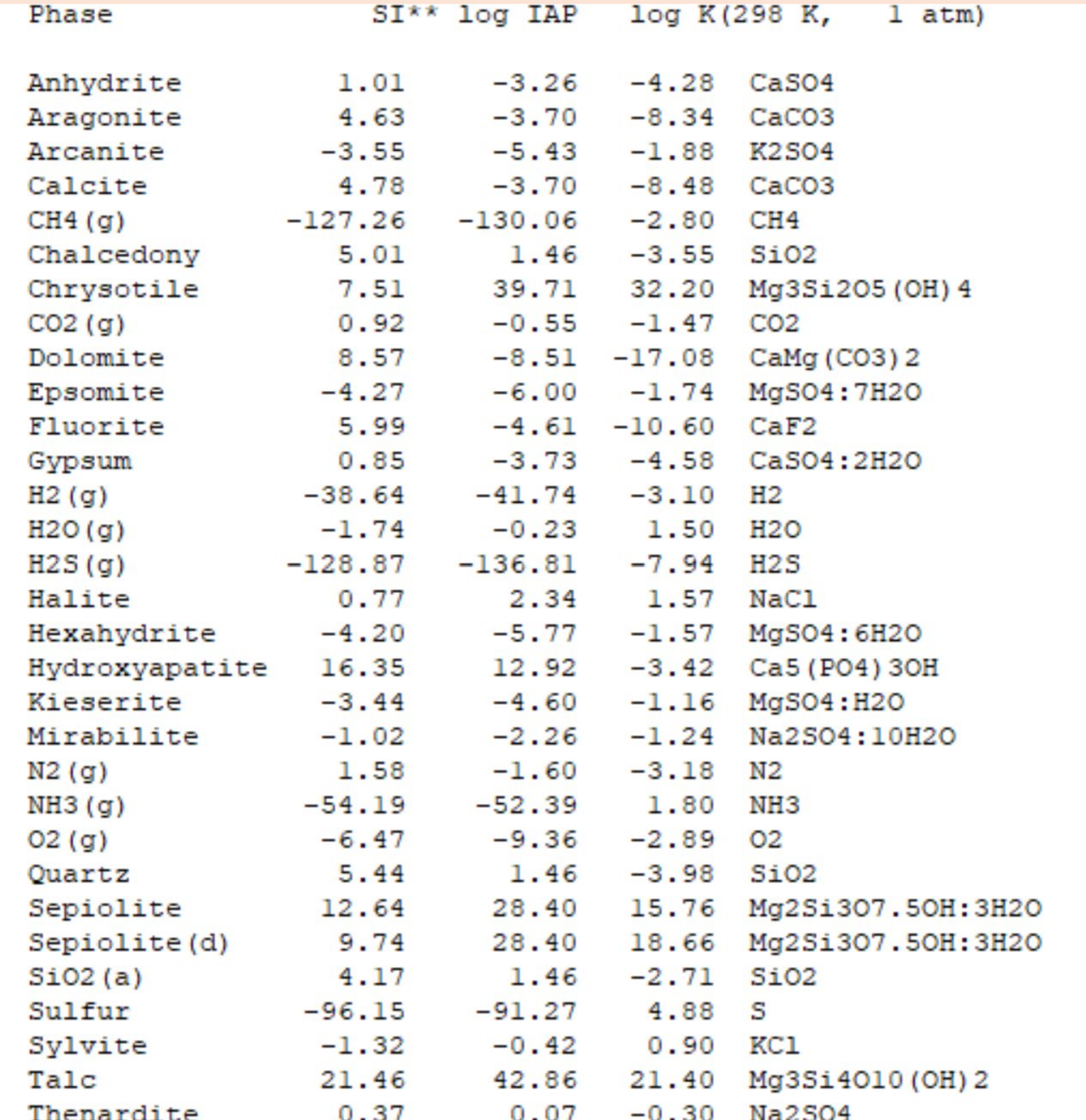
After Evaporation at 30.3°C



```
F             5.605e-02
   MgF+                2.722e-02   1.394e-02    -1.565    -1.856    -0.291    -10.07
   F-                  2.082e-02   9.150e-03    -1.682    -2.039    -0.357      2.06
   NaF                 8.014e-03   1.257e-01    -2.096    -0.901     1.196      7.45
   HF                  5.701e-08   8.945e-07    -7.244    -6.048     1.196     12.72
   SiF6-2              6.369e-09   5.501e-10    -8.196    -9.260    -1.064     56.42
   HF2-                1.165e-09   3.261e-08    -8.934    -7.487     1.447     25.66
```

25°C PHREEQC Output: Saturation Indices

After Evaporation

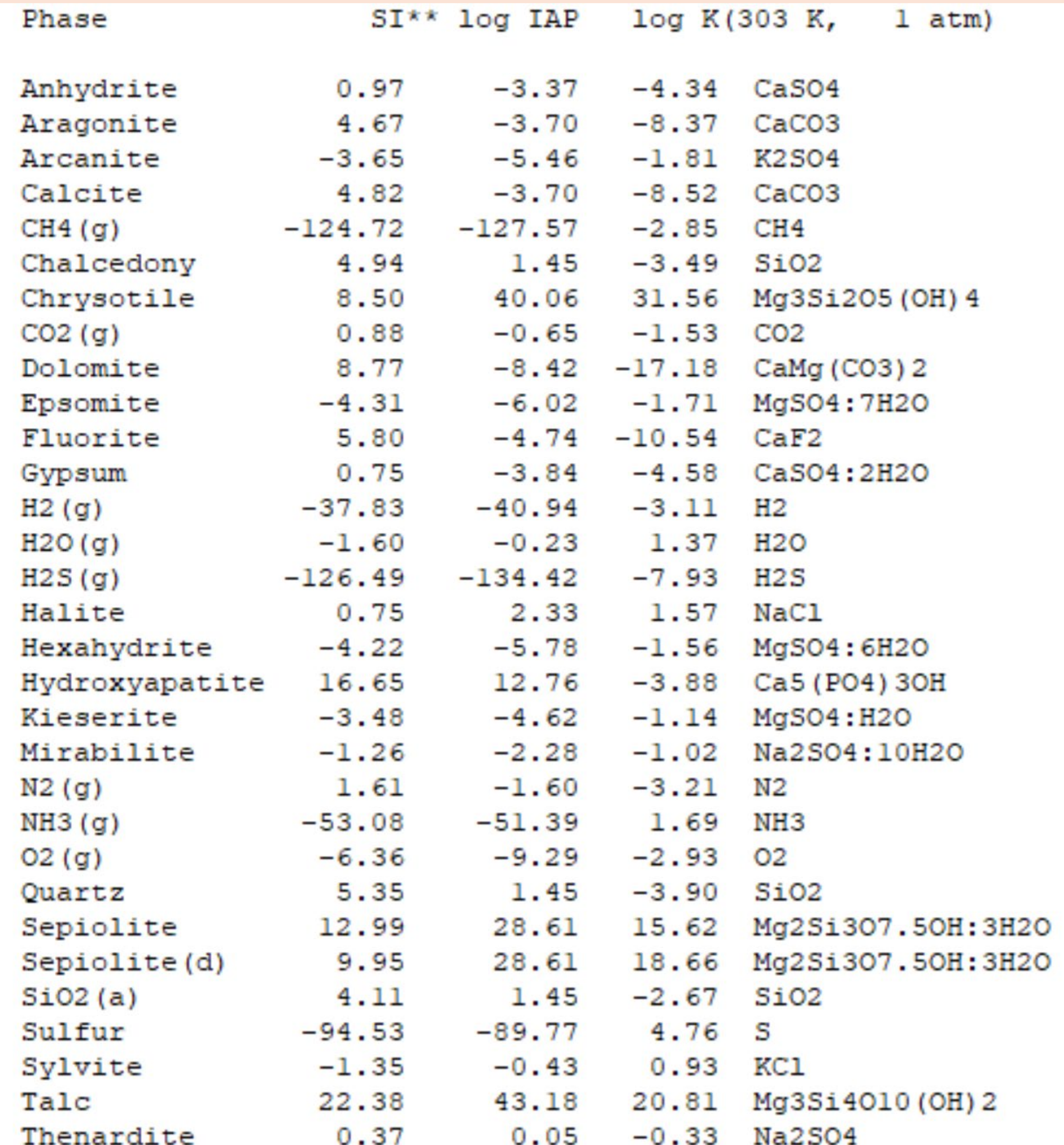


```
Phase               SI** log IAP   log K(298 K,   1 atm)

Anhydrite           1.01    -3.26   -4.28  CaSO4
Aragonite           4.63    -3.70   -8.34  CaCO3
Arcanite           -3.55    -5.43   -1.88  K2SO4
Calcite             4.78    -3.70   -8.48  CaCO3
CH4(g)           -127.26  -130.06   -2.80  CH4
Chalcedony          5.01     1.46   -3.55  SiO2
Chrysotile          7.51    39.71   32.20  Mg3Si2O5(OH)4
CO2(g)              0.92    -0.55   -1.47  CO2
Dolomite            8.57    -8.51  -17.08  CaMg(CO3)2
Epsomite           -4.27    -6.00   -1.74  MgSO4:7H2O
Fluorite            5.99    -4.61  -10.60  CaF2
Gypsum              0.85    -3.73   -4.58  CaSO4:2H2O
H2(g)             -38.64   -41.74   -3.10  H2
H2O(g)             -1.74    -0.23    1.50  H2O
H2S(g)           -128.87  -136.81   -7.94  H2S
Halite              0.77     2.34    1.57  NaCl
Hexahydrite        -4.20    -5.77   -1.57  MgSO4:6H2O
Hydroxyapatite     16.35    12.92   -3.42  Ca5(PO4)3OH
Kieserite          -3.44    -4.60   -1.16  MgSO4:H2O
Mirabilite         -1.02    -2.26   -1.24  Na2SO4:10H2O
N2(g)               1.58    -1.60   -3.18  N2
NH3(g)            -54.19   -52.39    1.80  NH3
O2(g)              -6.47    -9.36   -2.89  O2
Quartz              5.44     1.46   -3.98  SiO2
Sepiolite          12.64    28.40   15.76  Mg2Si3O7.5OH:3H2O
Sepiolite(d)        9.74    28.40   18.66  Mg2Si3O7.5OH:3H2O
SiO2(a)             4.17     1.46   -2.71  SiO2
Sulfur            -96.15   -91.27    4.88  S
Sylvite            -1.32    -0.42    0.90  KCl
Talc               21.46    42.86   21.40  Mg3Si4O10(OH)2
Thenardite          0.37     0.07   -0.30  Na2SO4
```

30.3°C PHREEQC Output: Saturation Indices

After Evaporation



```
Phase               SI** log IAP   log K(303 K,   1 atm)

Anhydrite         0.97     -3.37   -4.34  CaSO4
Aragonite         4.67     -3.70   -8.37  CaCO3
Arcanite         -3.65     -5.46   -1.81  K2SO4
Calcite           4.82     -3.70   -8.52  CaCO3
CH4(g)         -124.72   -127.57   -2.85  CH4
Chalcedony        4.94      1.45   -3.49  SiO2
Chrysotile        8.50     40.06   31.56  Mg3Si2O5(OH)4
CO2(g)            0.88     -0.65   -1.53  CO2
Dolomite          8.77     -8.42  -17.18  CaMg(CO3)2
Epsomite         -4.31     -6.02   -1.71  MgSO4:7H2O
Fluorite          5.80     -4.74  -10.54  CaF2
Gypsum            0.75     -3.84   -4.58  CaSO4:2H2O
H2(g)           -37.83    -40.94   -3.11  H2
H2O(g)           -1.60     -0.23    1.37  H2O
H2S(g)         -126.49   -134.42   -7.93  H2S
Halite            0.75      2.33    1.57  NaCl
Hexahydrite      -4.22     -5.78   -1.56  MgSO4:6H2O
Hydroxyapatite   16.65     12.76   -3.88  Ca5(PO4)3OH
Kieserite        -3.48     -4.62   -1.14  MgSO4:H2O
Mirabilite       -1.26     -2.28   -1.02  Na2SO4:10H2O
N2(g)             1.61     -1.60   -3.21  N2
NH3(g)          -53.08    -51.39    1.69  NH3
O2(g)            -6.36     -9.29   -2.93  O2
Quartz            5.35      1.45   -3.90  SiO2
Sepiolite        12.99     28.61   15.62  Mg2Si3O7.5OH:3H2O
Sepiolite(d)      9.95     28.61   18.66  Mg2Si3O7.5OH:3H2O
SiO2(a)           4.11      1.45   -2.67  SiO2
Sulfur          -94.53    -89.77    4.76  S
Sylvite          -1.35     -0.43    0.93  KCl
Talc             22.38     43.18   20.81  Mg3Si4O10(OH)2
Thenardite        0.37      0.05   -0.33  Na2SO4
```

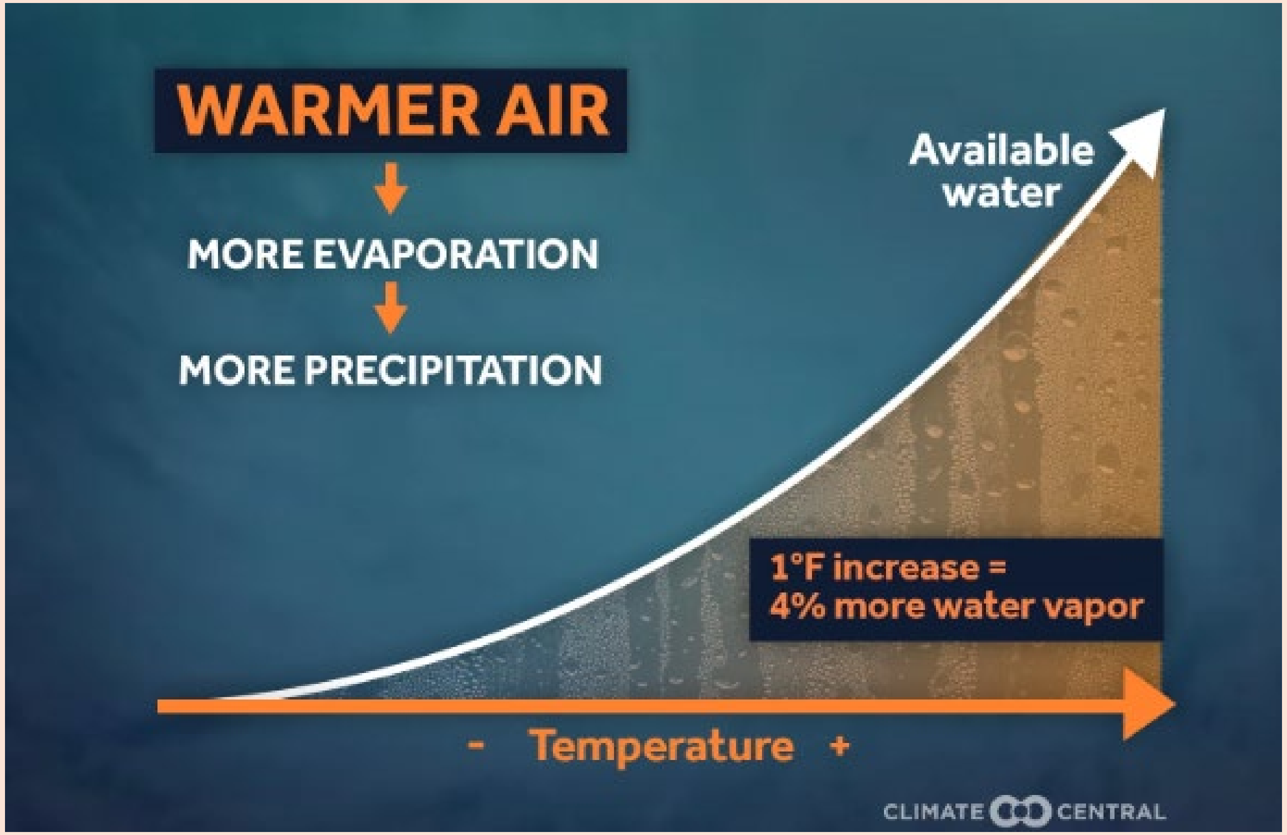
Summary of Results

- Evaporation increases the concentration of fluoride ions
- Evaporation changes the solubility indices of essentially all minerals
- Evaporation changes F speciation, making MgF^+ the dominant F species
- 30° C evaporation creates equal concentration of fluoride, but different species distribution than 25°C
- Temperature changes the solubility indices of each mineral independently, no overarching trend, but higher temperature did make fluorite more soluble.

(OEHHA, 2025)

Key takeaways

- Evaporation is a driving force in how geology impacts water quality
- As the effects of climate change continue to grow, the fluoride concentration/water quality of the groundwater will continue to change



(Abbot et al., 2025)

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