Geochemical Divides and evaporative concentration of uranium

EMILY NELSON

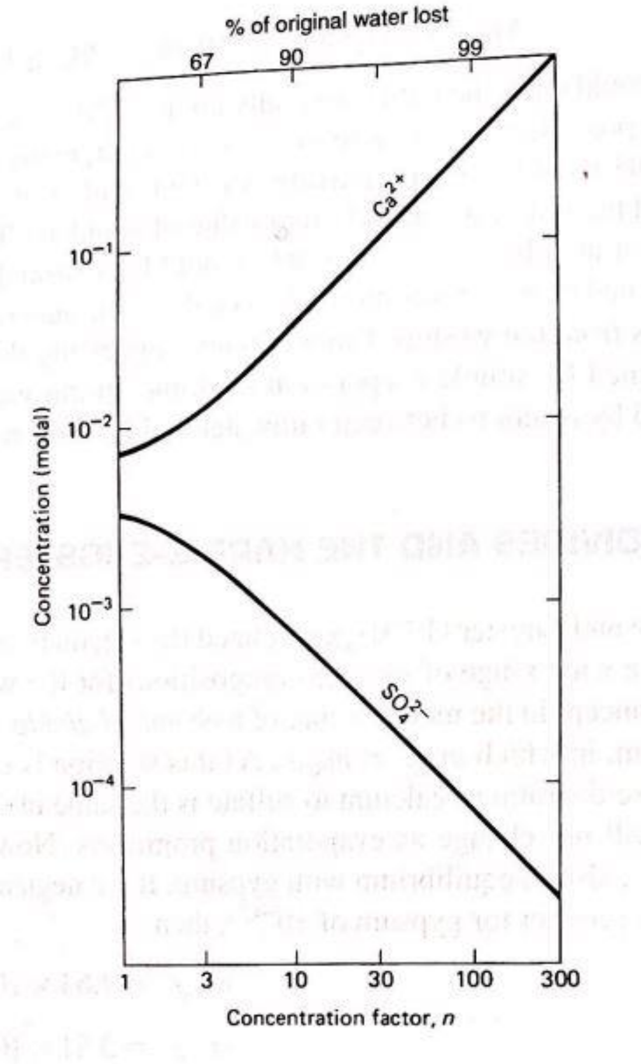
GEOL 428 GEOCHEMISTRY

NDSU 12/10/2020

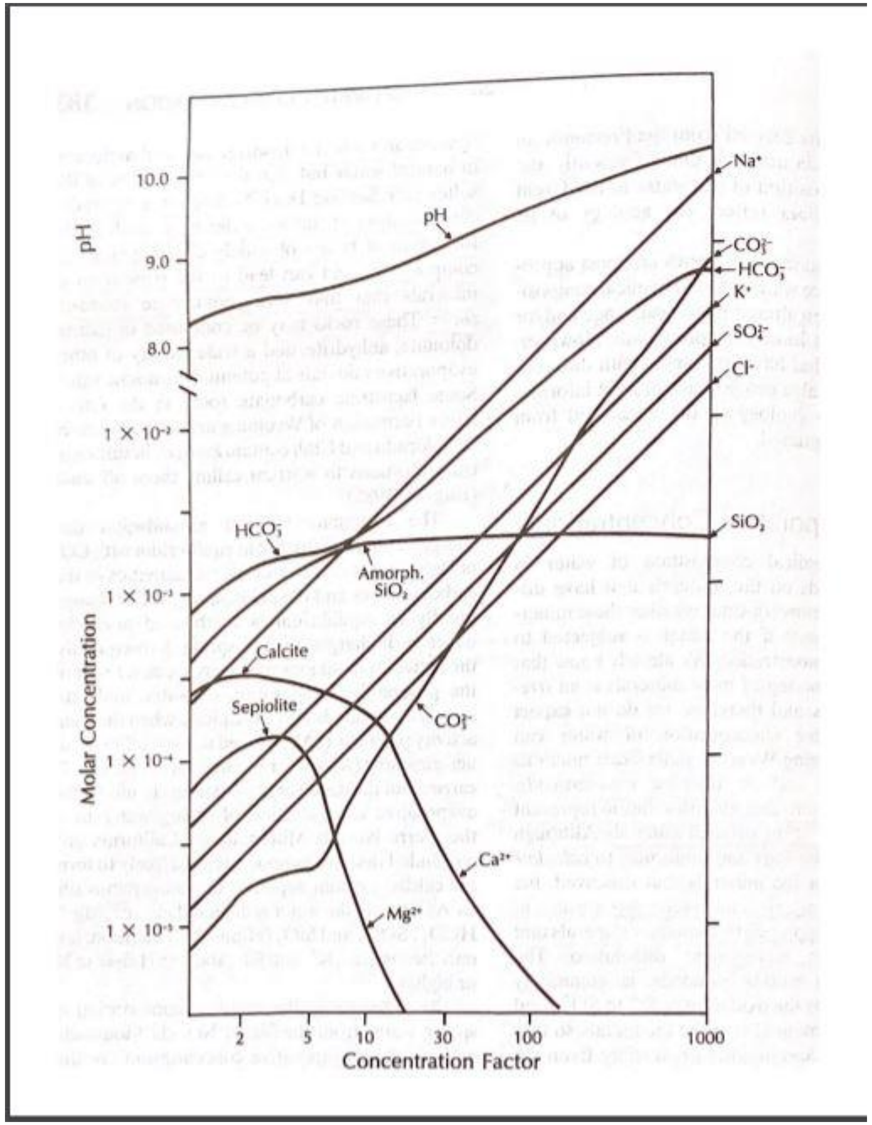
Geochemical Divide:

Occurs when salts that are in equilibrium with an evaporative body of water have differing relative/effective concentrations in solution to the relative concentrations in the precipitating mineral

The ion with the higher initial relative/effective concentration will build-up in the water with further evaporation, while the ion with the lower initial relative/effective concentration will become depleted



Drever Ch 15



Evaporative Concentration

Molar concentrations build-up in evaporative bodies of water until precipitates begin to form

This is where geochemical divides begin to govern the chemistry of the water

Brines of various compositions can form as a result of evaporative concentrations as well as rock deposits of evaporite minerals in non-marine environments

Faure Ch 20

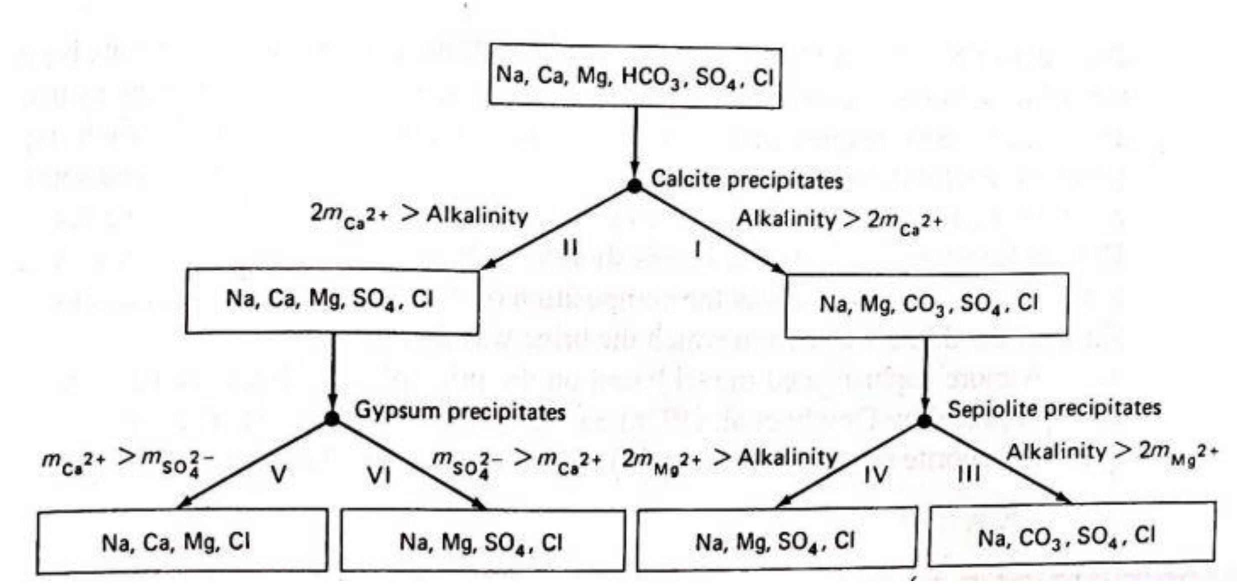
Hardie-Eugster Model

Analyses waters undergoing evaporation through successive models of geochemical divides.

Generally:

The first mineral to precipitate is calcite

Followed by magnesium bearing minerals



Drever Ch 15

Issues with Mg^{2+}

SEPIOLITE

$$Mg^{2+} + 2HCO_3{}^- + 3H_4SiO_4 = MgSi_3O_6(OH)_2 + 2CO_2 + 6H_2O$$

This Mg-rich smectite is the one used in the Hardie-Eugster model, but it is not accurate for all-natural waters.

DOLOMITE

$$Mg^{2+} + 2HCO_3{}^- + CaCO_3 = CaMg(CO_3)_2 + CO_2 + H_2O$$

Notice that the net products of this dolomite reaction and the sepiolite reaction are very similar. The ratio of Mg^{2+} to alkalinity removed is equal in both. Therefore, there is not a great difference in terms of the chemical divide calculation between these two.

$$2CaCO_3 + Mg^{2+} = CaMg(CO_3)_2 + Ca^{2+}$$

However, when dolomitization occurs without the presence of bicarbinate, calcium can build up in the solution or gypsum can precipitate. This will lead to a solution of different composition to what is expected from the Hardie-Eugster model. Eugster and Hardie (1978) describe how to alter their model to account for both high-Mg calcite and dolomite.

Drever Ch 15

Other Processes to Consider

OXIDATION/REDUCTION

$8SO_4^{2-+}2Fe_2O_3 + 15(C) + 7H_2O = 4FeS_2 + 14HCO_3^{-} + CO_3^{2-}$

The reduction of sulfate to sulfide can remove sulfate from natural water as well as evaporation.

In this reaction, (C) is organic carbon and Fe_2O_3 are iron bearing minerals within the sediments that contact the water. Based on this reaction, sulfate and bicarbonate (alkalinity) have an inverse relationship.

ADSORPTION

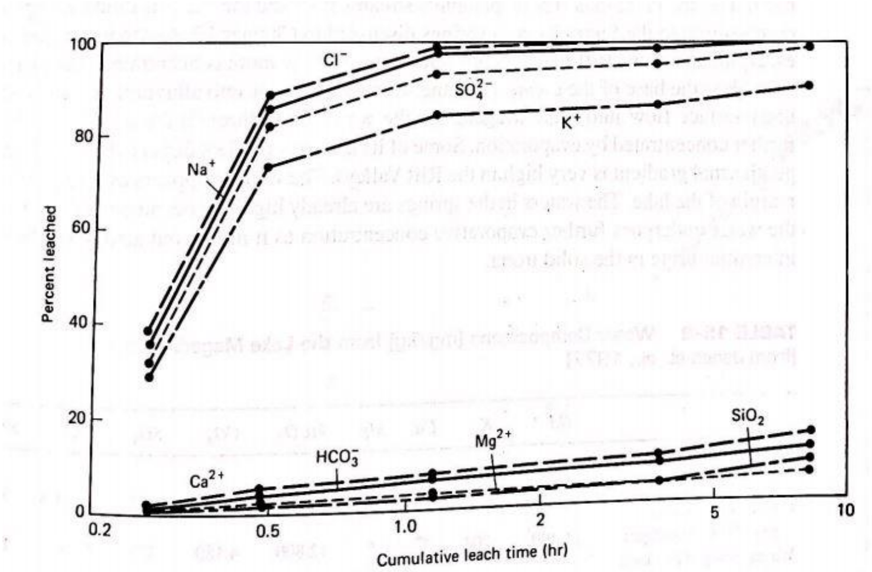
Potassium and sodium, in general, are assumed to build up in natural waters since potassium does not form salts except in high concentrations and sodium is highly soluble. However, potassium is often found as a depleted ion if the waters flowed underground. This occurs as the potassium is favored in the ion exchange compared to other ions such as calcium and sodium, which then likely precipitate from solution within the rock and sediment.

Drever Ch 15

Other Processes to Consider

BIOLOGIC ACTIVITY

Biologic activity can remove ions from solution as well, including potassium. This seems to be a less impactful process in depleting ion concentrations in natural waters.



WET/DRY CYCLING

As the initial water evaporates, the solutes are deposited as mineral phases generally according to the Hardie-Eugster model.

The following wetting cycle will only dissolve the highly-soluble salts previously precipitated.

This leads to a solution that is depleted in gypsum, amorphous silica, and sepiolite even though it has clearly already lost calcium, silica, and magnesium.

Drever Ch 15

Base Research

I will be presenting and building from research on the evolution of uranium-rich closed basins through geochemical divides.

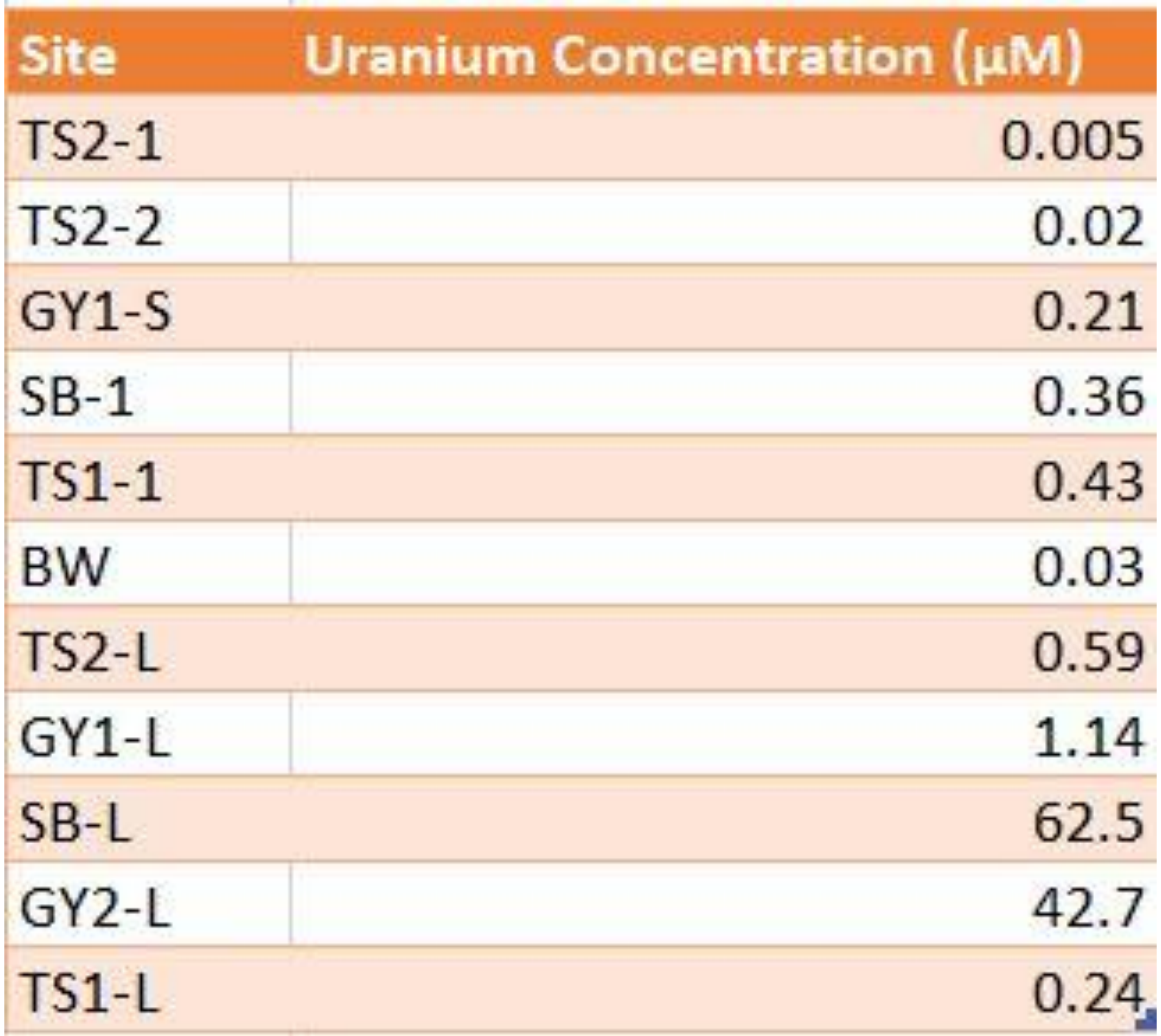
The water in the sodic lakes of Eastern Mongolia are sourced from carbonate-rich groundwater and undergo constant evaporation.

During the winter, these lakes freeze solid causing extra water loss from freeze concentration and sublimation. These processes allow carbonate minerals to precipitate during the winter months as well.

The Soda lakes being researched in Mongolia also have exceptionally high uranium concentrations.

Linhoff et. al. (2009)

Uranium Concentrations



Site	Uranium Concentration (µM)
TS2-1	0.005
TS2-2	0.02
GY1-S	0.21
SB-1	0.36
TS1-1	0.43
BW	0.03
TS2-L	0.59
GY1-L	1.14
SB-L	62.5
GY2-L	42.7
TS1-L	0.24

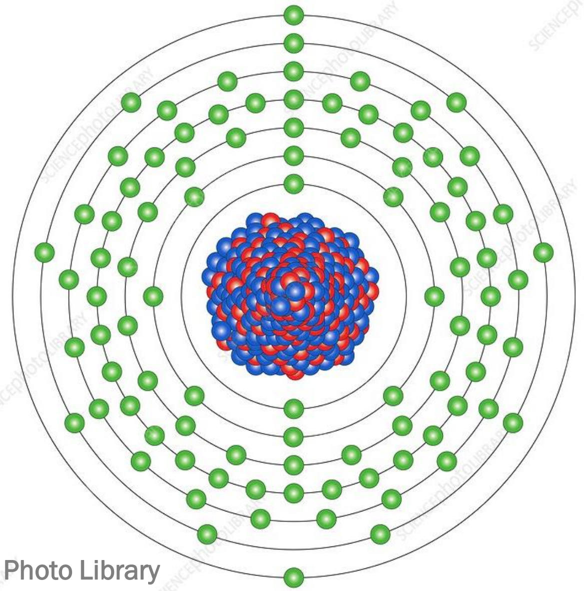
Springer (2020)

Potential Source(s) of Uranium

Several uranium deposits of past or present economic value are located north of the study site. While these deposits are not located within the lakes’ catchment systems, it is possible that the uranium from these deposits was included into and transported by groundwater. This is supported by the presence of coffinite and other uranium phases in the aquifer sediments.

Linhoff et. al. (2009)

Geochemistry of Uranium

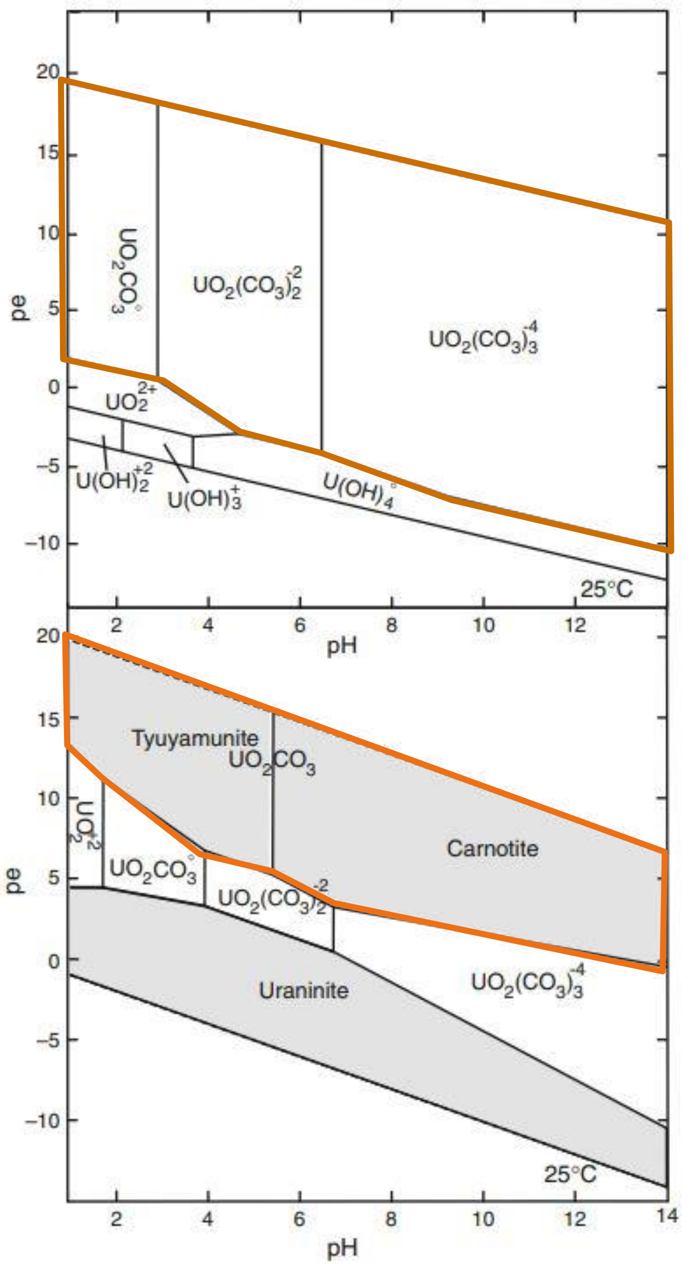

Science Photo Library

Uranium occurs as either U^{4+} or U^{6+} with only the oxidized state having impactful mobility.

U^{4+} will form oxide and silicate minerals that are soluble in acidic solutions under surficial conditions.

U^{6+} is generally more mobile than U^{4+} when in the ionic complex UO_2^{2+} .

Linhoff et. al. (2009)



Geochemistry of Uranium

Uranium mobility is sensitive to the presence of vanadium in a solution.

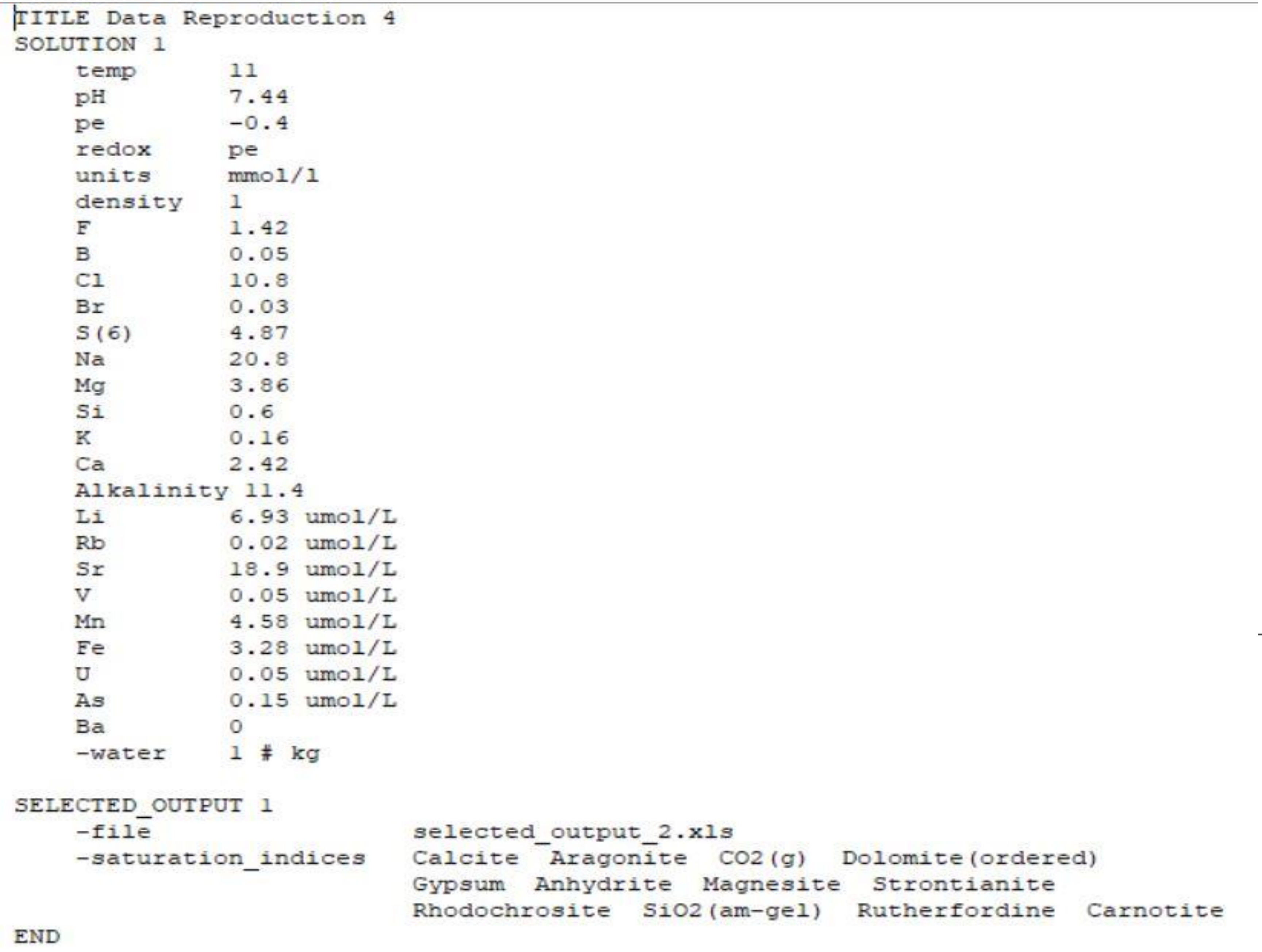
This diagram shows the change in uranium phase stabilities with the addition of vanadium (bottom portion).

Linhoff et. al. (2009)

Uranium Phases and Concentrations

- Rutherfordine: UO_2CO_3
- Carnotite: $K_2(UO_2)_2(VO_4)_2$
- Tyuyamunite: $Ca(UO_2)_2(VO4)_2$
- Uraninite: UO_2
- $UO_2(CO_3)_{(1, 2, 3)}$

Initial Data Reproduction Input

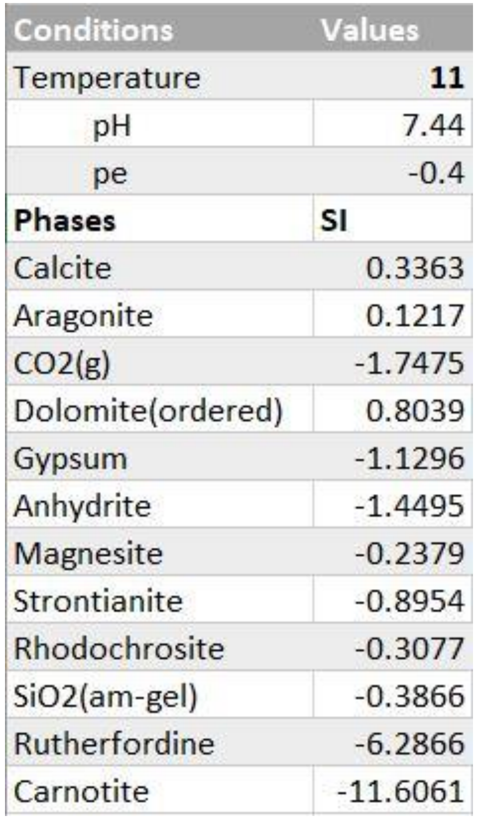


```
TITLE Data Reproduction 4
SOLUTION 1
    temp      11
    pH        7.44
    pe        -0.4
    redox     pe
    units     mmol/l
    density   1
    F         1.42
    B         0.05
    Cl        10.8
    Br        0.03
    S(6)      4.87
    Na        20.8
    Mg        3.86
    Si        0.6
    K         0.16
    Ca        2.42
    Alkalinity 11.4
    Li        6.93 umol/L
    Rb        0.02 umol/L
    Sr        18.9 umol/L
    V         0.05 umol/L
    Mn        4.58 umol/L
    Fe        3.28 umol/L
    U         0.05 umol/L
    As        0.15 umol/L
    Ba        0
    -water    1 # kg

SELECTED_OUTPUT 1
    -file                 selected_output_2.xls
    -saturation_indices   Calcite  Aragonite  CO2(g)  Dolomite(ordered)
                          Gypsum  Anhydrite  Magnesite  Strontianite
                          Rhodochrosite  SiO2(am-gel)  Rutherfordine  Carnotite
END
```

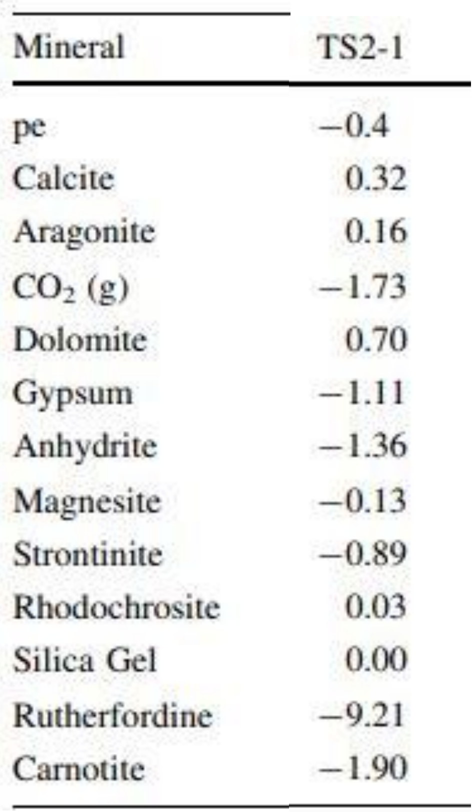
Data Reproduction Results

MY RESULTS



Conditions	Values
Temperature	**11**
pH	7.44
pe	-0.4
Phases	**SI**
Calcite	0.3363
Aragonite	0.1217
CO2(g)	-1.7475
Dolomite(ordered)	0.8039
Gypsum	-1.1296
Anhydrite	-1.4495
Magnesite	-0.2379
Strontianite	-0.8954
Rhodochrosite	-0.3077
SiO2(am-gel)	-0.3866
Rutherfordine	-6.2866
Carnotite	-11.6061

THEIR RESULTS



Mineral	TS2-1
pe	−0.4
Calcite	0.32
Aragonite	0.16
CO_2 (g)	−1.73
Dolomite	0.70
Gypsum	−1.11
Anhydrite	−1.36
Magnesite	−0.13
Strontinite	−0.89
Rhodochrosite	0.03
Silica Gel	0.00
Rutherfordine	−9.21
Carnotite	−1.90

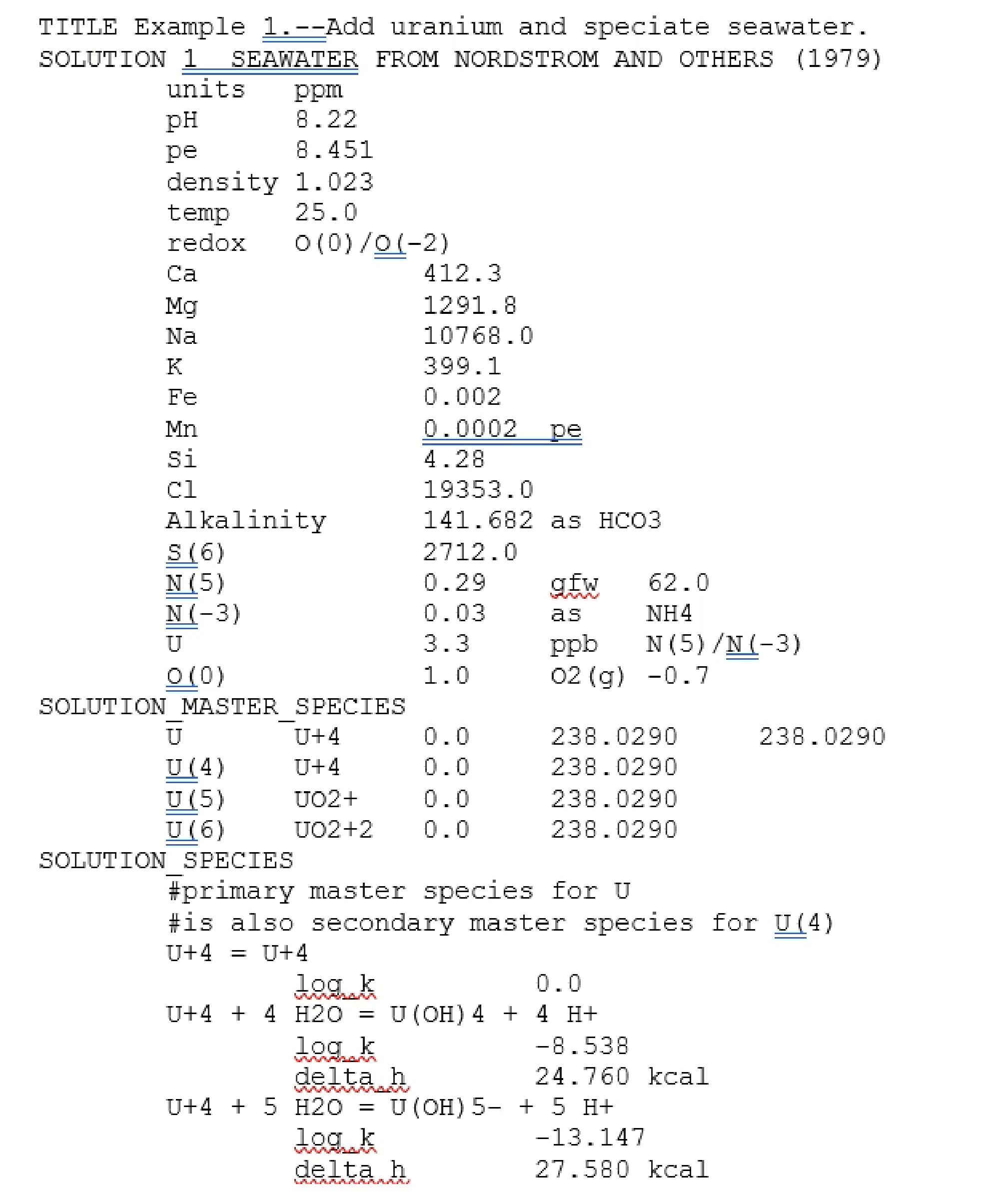
Linhoff et. al. (2009)

Adding Elements to a Database

There are two ways to add elements to a database:

1. You can follow example one in the user manual to add them directly into your input file.
   - Use the key phrases SOLUTION_MASTER_SPECIES, SOLUTION_SPECIES, and PHASES to define your input data

2. You can alter the database file before importing it to PHREEQC.
   - Must save the entire database folder to another location on your laptop because you cannot alter files located on your C-drive
   - Must make sure to add element information, aqueous species reactions, and all phases that you wish to appear on your output
   - Pay attention to formatting, K values, delta G values, etc. as you are adding information to a database



```
TITLE Example 1.--Add uranium and speciate seawater.
SOLUTION 1  SEAWATER FROM NORDSTROM AND OTHERS (1979)
        units   ppm
        pH      8.22
        pe      8.451
        density 1.023
        temp    25.0
        redox   O(0)/O(-2)
        Ca              412.3
        Mg              1291.8
        Na              10768.0
        K               399.1
        Fe              0.002
        Mn              0.0002  pe
        Si              4.28
        Cl              19353.0
        Alkalinity      141.682 as HCO3
        S(6)            2712.0
        N(5)            0.29    gfw   62.0
        N(-3)           0.03    as    NH4
        U               3.3     ppb   N(5)/N(-3)
        O(0)            1.0     O2(g) -0.7
SOLUTION_MASTER_SPECIES
        U       U+4     0.0     238.0290     238.0290
        U(4)    U+4     0.0     238.0290
        U(5)    UO2+    0.0     238.0290
        U(6)    UO2+2   0.0     238.0290
SOLUTION_SPECIES
        #primary master species for U
        #is also secondary master species for U(4)
        U+4 = U+4
                log_k          0.0
        U+4 + 4 H2O = U(OH)4 + 4 H+
                log_k          -8.538
                delta_h        24.760 kcal
        U+4 + 5 H2O = U(OH)5- + 5 H+
                log_k          -13.147
                delta_h        27.580 kcal
```

PHREEQ Examples

Geochemists Workbench Modeling

Linhoff et. al. did a lot of modeling with geochemists work bench to monitor the concentration of various phases through continuous evaporation of a solution.

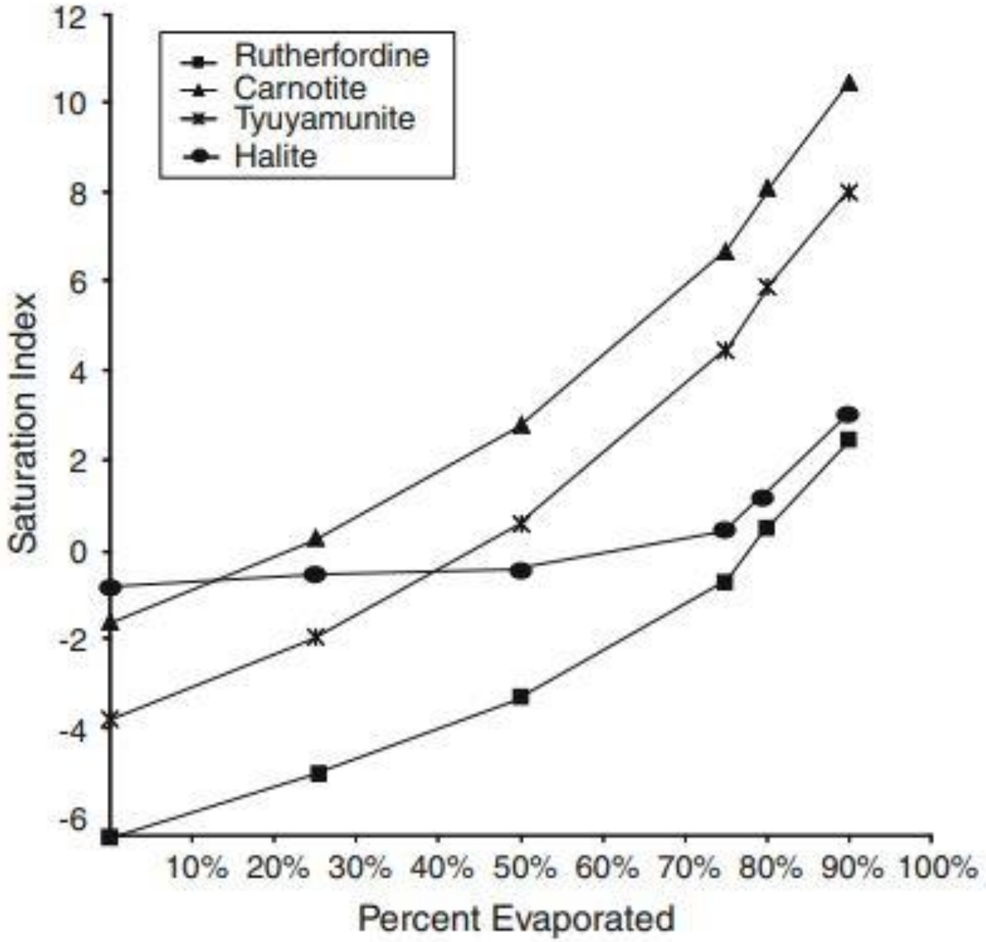


Fig. 3 Saturation indexes of three uranium minerals and halite modeled using PHREEQC during the evaporation of Shar Burdiin Lake

Linhoff et. al. (2009)

Calculation Methods

DEBYE-HÜCKEL EQUATION

$$\ln \gamma_{\pm} = -\frac{A|z_1 z_2|\sqrt{I}}{1 + B\mathring{a}\sqrt{I}}$$

where γ± is the mean ionic activity coefficient, A and B are physical constants, z_1 and z_2 are the electronic charges on the cation and anion respectively, å is the “effective distance of closest approach”, notionally related to the diameter of the solvated ions, and $I = \frac{1}{2}\sum m_i z_i^2$ is the stoichiometric molality based ionic strength.

PITZER EQUATION

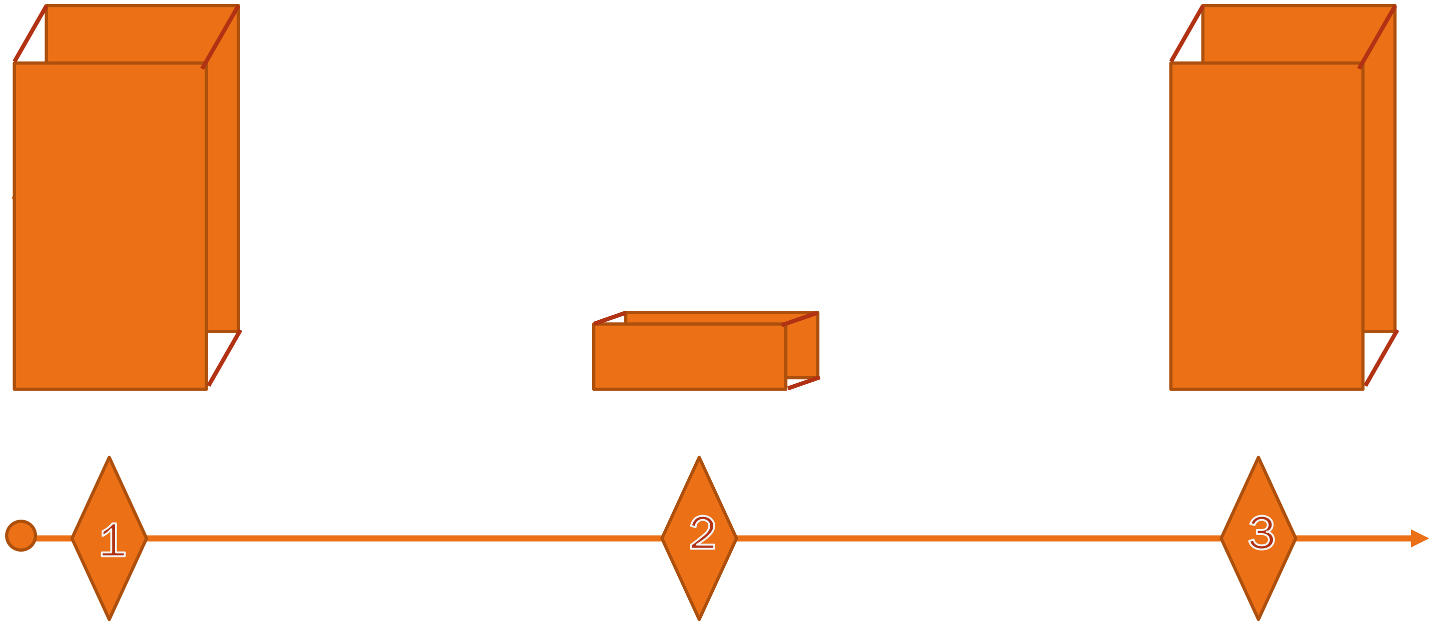
$$\ln \gamma_{\pm} = -\frac{A|z_1 z_2|\sqrt{I}}{1 + B\mathring{a}\sqrt{I}} + Cm + Dm^2$$

$$G^{EXm} = RT\left(w_w f(I) + \left(\frac{1}{w_w}\right)\sum_{ij}\lambda_{ij}(I)n_i n_j + \left(\frac{1}{w_w^2}\right)\sum_{ijk}\mu_{ijk}n_i n_j n_k\right)$$

To be comparable the Hückel equations, the Pitzer equations must include second-order and third-order terms in molality. The second term is still a function of ionic strength, making it theoretical and empirical, while third is completely empirical meaning that certain parameters must be met before it is used.

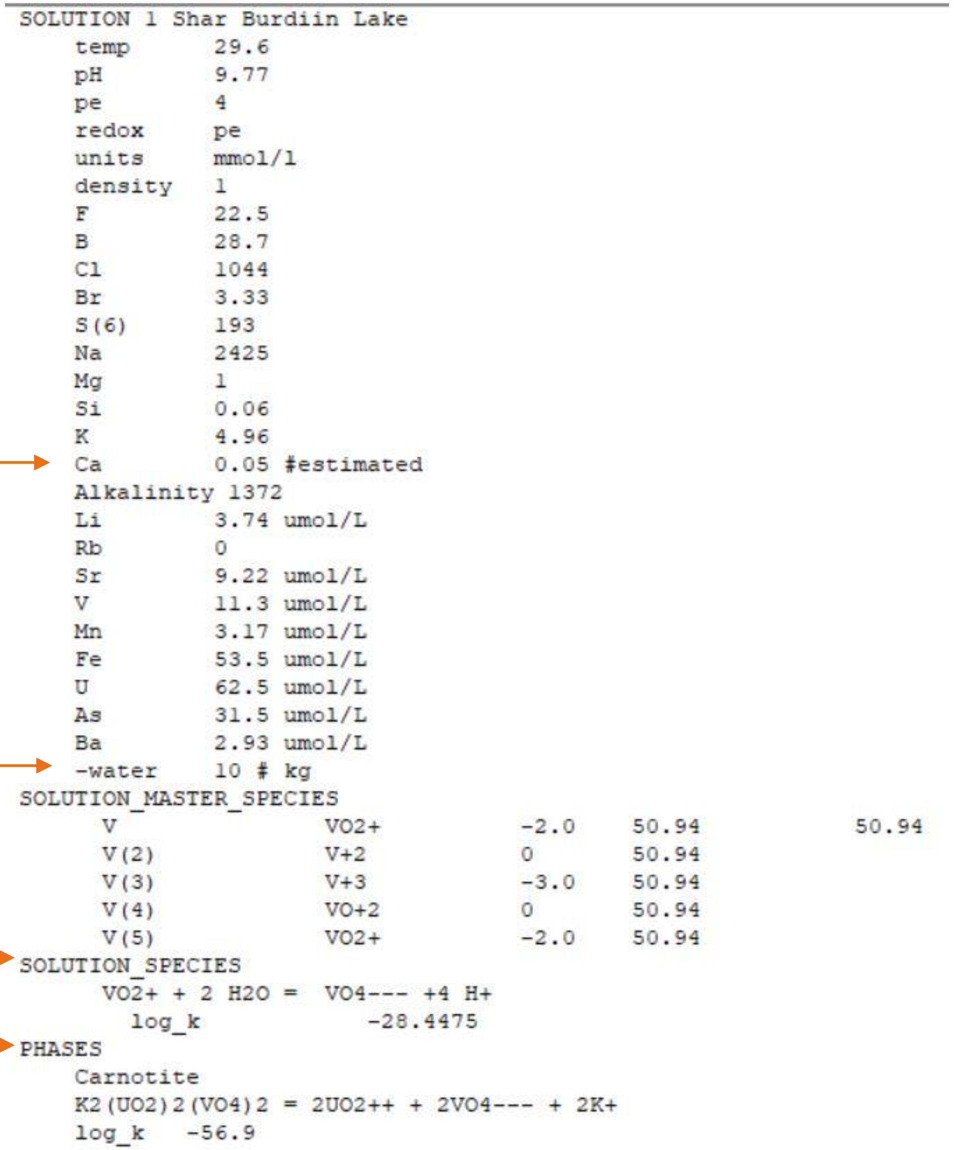
Northwestern University (2015) Rowland and May (2015)

Modelling Evaporation in PHREEQC

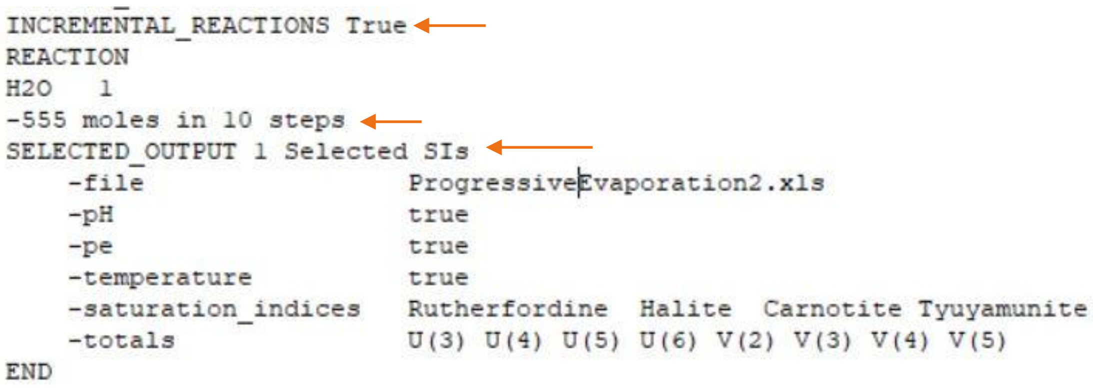


1. Start with 1 L solution of composition x
2. “Evaporate” the solution by subtracting 95% (or your goal %) of the water. This leaves a solution of concentrated composition xc since all the original ions in solution are still present but only 5% of the original water is.
3. Lastly, you multiple the concentrated solution by 20 to return to a 1 L volume of solution.

Faure Ch 20



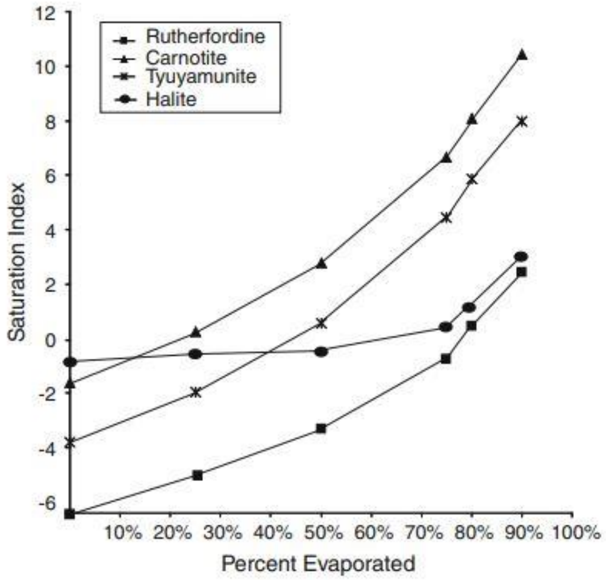
```
SOLUTION 1 Shar Burdiin Lake
    temp      29.6
    pH        9.77
    pe        4
    redox     pe
    units     mmol/l
    density   1
    F         22.5
    B         28.7
    Cl        1044
    Br        3.33
    S(6)      193
    Na        2425
    Mg        1
    Si        0.06
    K         4.96
    Ca        0.05 #estimated
    Alkalinity 1372
    Li        3.74 umol/L
    Rb        0
    Sr        9.22 umol/L
    V         11.3 umol/L
    Mn        3.17 umol/L
    Fe        53.5 umol/L
    U         62.5 umol/L
    As        31.5 umol/L
    Ba        2.93 umol/L
    -water    10 # kg
SOLUTION_MASTER_SPECIES
      V                VO2+          -2.0    50.94            50.94
      V(2)             V+2           0       50.94
      V(3)             V+3           -3.0    50.94
      V(4)             VO+2          0       50.94
      V(5)             VO2+          -2.0    50.94
SOLUTION_SPECIES
      VO2+ + 2 H2O =   VO4--- +4 H+
        log_k             -28.4475
PHASES
    Carnotite
    K2(UO2)2(VO4)2 = 2UO2++ + 2VO4--- + 2K+
    log_k   -56.9
```



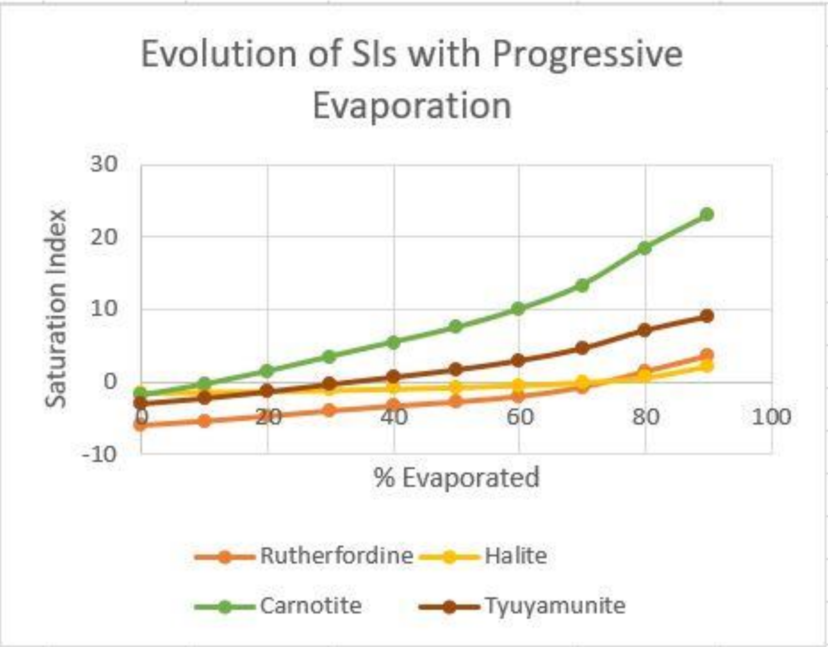
```
INCREMENTAL_REACTIONS True
REACTION
H2O   1
-555 moles in 10 steps
SELECTED_OUTPUT 1 Selected SIs
    -file                  ProgressiveEvaporation2.xls
    -pH                    true
    -pe                    true
    -temperature           true
    -saturation_indices    Rutherfordine  Halite  Carnotite Tyuyamunite
    -totals                U(3) U(4) U(5) U(6) V(2) V(3) V(4) V(5)
END
```

Comparison of Evaporation Modeling Results

LINHOFF ET. AL. RESULTS FROM GEOCHEMISTS WORKBENCH

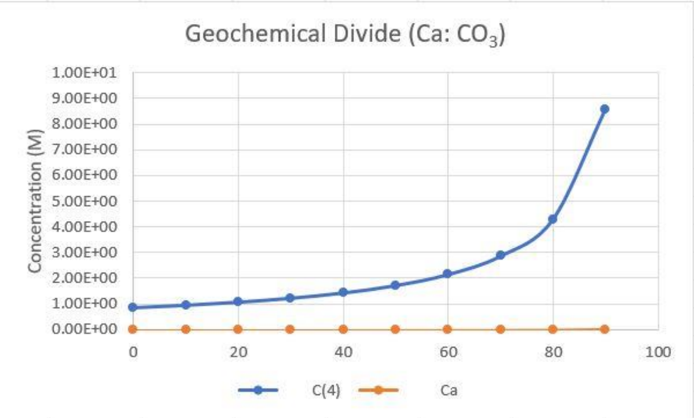


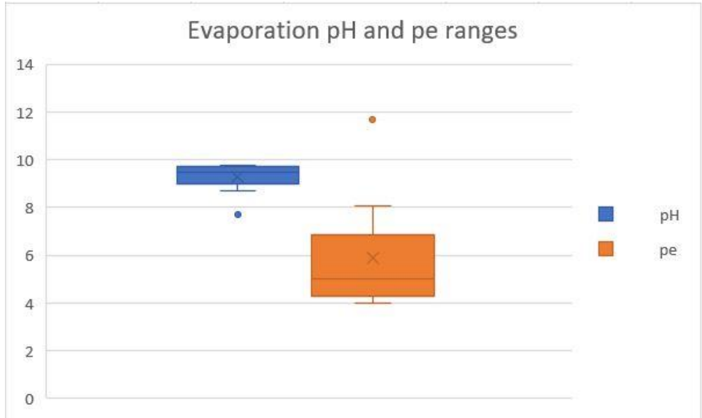
MY RESULTS FROM PHREEQC

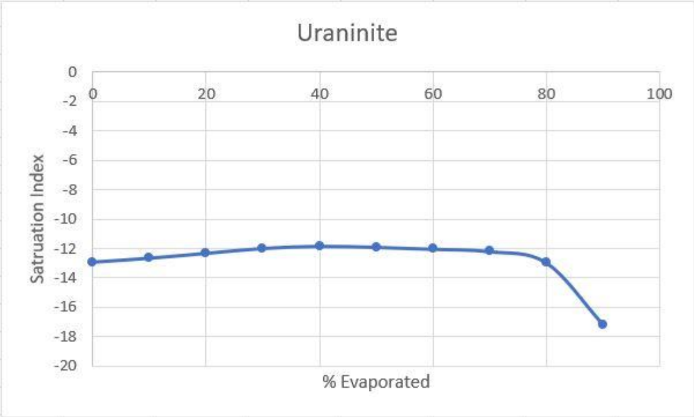


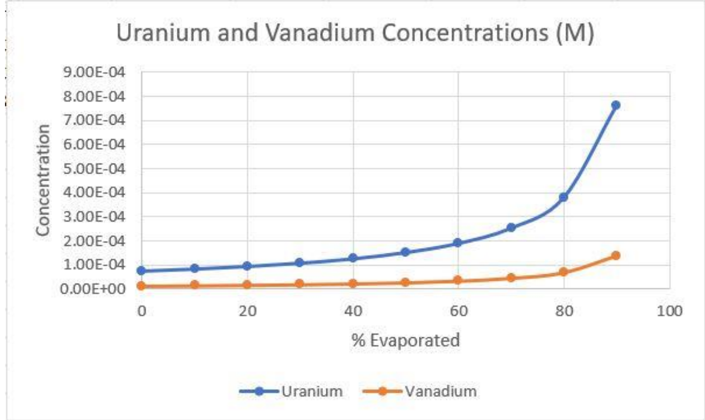
Linhoff et. al. (2009)

More Results









Discussion

- Given the high presence of vanadium in this groundwater (11.3 $\frac{\mu M}{L}$) uranium is precipitating primarily as carnotite, and the system is severly undersaturated in uraninite.
- There are multiple geochemical divides that cause a loss of Ca, Mg, and Si between the groundwaters and the lake waters. As this water starts to evaporate, calcium is the first to be used up leading to a decrease in the SI of uraninite. At this point the solution is enriched in Na, CO_3, Cl, U, and V. This leads to the increase in SI for halite, tyuyamunite, rutherfordine, and carnotite.
- There are very clear trends showing the increase in concentration of U and V in the lakes through progressive evaporation as the saturation indexes of representative phases continue to increase.

Implications

Two lakes in this study alone exceed the WHO limit for U (0.062 $\frac{mM}{L}$) in drinking water. Based on this and the wide distribution of uranium deposits throughout Mongolia, it is likely that more lakes are contaminated with uranium.

When these lakes reach a point of complete evaporation, the precipitated uriniferous salts pose an airborne threat to humans and livestock.

References

Drever, James I. 1982. Geochemistry of Natural Waters. *Prentice-Hall Inc.* Ed. 3. Ch 15.

Faure, Gunther. 1998. Principles and Applications of Geochemistry. *Prentice-Hall Inc.* Ed. 2. Ch 20.

Linhoff, Benjamin, et. al. 2011. Geochemical evolution of uriniferous soda lakes in Eastern Mongolia*.* *Environmental Earth Science.* v. 62, p. 171-183.

Northwestern University. Activity Coefficients of Aqueous Species. http://www.civil.northwestern.edu/EHE/COURSES/D68/Activities_EQ3.pdf

Parkhurst, D.L., and Appelo, C.A.J., 2013, Description of input and examples for PHREEQC version 3—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Techniques and Methods, book 6, chap. A43, 497 p., available only at http://pubs.usgs.gov/tm/06/a43/.

References Continued

Rowland, Darren, and Peter M. May. 2015. Comparison of the Pitzer and Hückel Equation Frameworks for Activity Coefficients, Osmotic Coefficients, and Apparent Molar Relative Enthalpies, Heat Capacities, and Volumes of Binary Aqueous Strong Electrolyte Solutions at 25 °C. *Journal of Chemical & Engineering Data.* V. 60. p. 2090-2097.

Science Photo Library. 2020. Uranium, atomic structure. https://www.sciencephoto.com/media/460793/view/uranium-atomic-structure

Springer, Jon. 2020. What Investors Should Know About Uranium in Mongolia. *Seeking Alpha*

Witherow, Rebecca A., and W. Berry Lyons. 2011. *The fate of minor alkali elements in the chemical evolution of salt lakes.* and Lyons. *Saline Systems. v. 7.*