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Scientific Notebook No. 276: Chemistry and Radiochemistry of Nopal I Waters--Analysis of Existing Data (06/18/1998 through 04/17/2006)

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Technical Assistance: Radionuclide Transport KTI

Project Code 20-1402-871

CNWRA
CONTROLLED
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Contents — Page

Chemistry and Radiochemistry of Nopal I Waters – Analysis of Existing DAta

6/18/98 DAP (= David Pickett)

The work documented in this notebook involves analysis and interpretation of chemical and isotopic data on waters collected at the Nopal I natural analog site.

This notebook does not document sample collection or analysis. These activities were performed in previous years as far back as 1995, and are recorded in other notebooks as follows:

CNWRA #	pages	activities
080	299-300	Preparation of sample collection bottles.
117	44-64	Field collection of samples, August 1995. W. Murphy's notes.
121	29-34	Field collection of samples, August 1995. D. Pickett's notes.
126	37-58	Acquisition of chemical and isotopic data and initial analysis of results. Aug 96 to Jan 97.

The purpose of this work is to understand better transport of natural U and Th at the Nopal I analog and apply that understanding to ongoing attempts to model radionuclide transport at the proposed repository at Yucca Mountain. Included is comparison of general chemical features of Nopal I waters with Yucca Mountain (YM) waters. Activities include plots of data using KaleidaGraph; spreadsheet calculations using Microsoft Excel; and thermodynamic calculations using EQ3/6 (run under Windows NT). Chemical data are used to estimate speciation and solubility characteristics of U and Th. U/Th isotopic data are interpreted in terms of mobility and water/rock interaction in the context of available data on U-Th characteristics of the host rocks.

The overall goal of this work is to use the natural analog data to constrain conceptual models of radionuclide transport for PA at YM, but the data may also provide parameters which may affect performance.

The data are of three types:

1. Field collected, including pH, temperature, alkalinity, O_2 content. These are recorded on the attached diskette as Excel file "895 field water.xls".

2. Cation and anion data obtained from SwRI Division 1. These are recorded on the attached diskette as Excel files "Div 1 water chem 996.xls" and "Water chem summary.xls".

3. U-Th isotopic data provided by the Minnesota Isotope Laboratory at University of Minnesota (John Hoff and Larry Edwards). These are recorded on the attached diskette as the ~~fi~~ DAP 6/18/98 Excel file "Minn UTh data.xls".

Again, acquisition of these data is described in previous notebooks (see above).

The diskette is labelled "Nopal Water Data."

Thermodynamic Modeling of Nopal Waters

6/19/98
DAP

These notes represent a compilation of work performed over the past 3½ weeks, concerned with EQ3/6 modeling of Nopal waters, comparison with saturation states of U minerals, and comparison with YM data. Emphasis is on Uranium.

Samples investigated are:

ADIT95-6
ADIT95-9
BH12W95-05
BH12W95-11
WVW95-03

Chemical data (see pp 1-2) are included on the attached diskette, files "Div 1 water chem 996.xls" and "Water chem summary.xls," and "895 field water.xls." These are the only five samples for which U and Th were determined. Data on diskette: "Minn UTh data.xls."

The general procedure for EQ3 speciation runs was:

1. Use laboratory data for cation and anion inputs except as noted below. Cation data are from filtered waters, anion from unfiltered.

2. Redox was set by measured dissolved O_2 (field) for BH12 and ~~ADIT~~ WVW DAP 6/19/98 sample, and to atmospheric $O_2(g)$ for ADIT samples.

3. Temperature for BH12 and WVW was from field measurement. Assumed 26°C for ADIT.

(cont'd)

4. HCO_3^- was set to field alkalinity for BH12 and WVW, lab alkalinity for ADIT.

5. pH for BH12 and WVW was field measurement; assumed 7.0 for ADIT.

On 5/26/98, ran a series of EQ3 calculations for each of the samples listed above.
Problems were encountered because:
- if N were entered as NH_3(aq), Haiweeite and Soddyite would not show up in the mineral saturation state list.
- if N were entered as NO_3^-, no pickup file for EQ6 would be written.
- Runs would not converge without auto basis switching if N entered as NH_3(aq).

Electrical balancing was done with Ca^{++}.

On the following pages are shown photocopies of notes on the runs of 5/26/98. They illustrate the problems listed above.
Note that it was only possible to ① see Haiweeite and Soddyite saturation states and ② create an EQ6 pickup file if N is removed from the input.

The EQ3NR input and output files (*.3i, *.3p, *.3o) are saved to David Pickett's hard drive (machine name Syreen) in directory D:\eq\Nopal and are backed up on a Zip disk.

On the following pages, where a U phase is mentioned and an affinity (kcal) shown, this is the highest affinity U solid.

5/28/98

Look at Nopal EQ3 runs
"ABS" = auto basis switching

BH12W98-05

bh12_05 : - Basis species for all
- ABS on
Balance = Ca^{++} -21 %
UO_2^{++} = 1.015×10^{-14} m
Haiwee, Soddy gone
$CaUO_4$ -5.297 kcal
U all carbonates (aq)

bh1205b : - N, Cu, V, Fe original species (non-basis)
- ABS off
No pickup
Same results as bh12_05, except Haiweeite + Soddy are in list. Haiwee supersat (0.503 kcal)

bh1205c : - N, Cu, V, Fe orig species
- ABS on
No pickup
Same results as bh1205b.

bh1205d : - Basis species for all
- ABS off
Does not converge – goes "sour"

bh1205e : - N, Cu, V, Fe removed
- ABS on
Ca^{+} -22% : Haiwee Soddy present; Essentially same as bh1205b

Note added 10/19/98: run bh1205b w/ HCO3- varying →
bh1205bg → log Q/K Haiweeite = 0.026

/ note : no Cl^- in input

5/28/98
p. 2

WVW95 -03

wvw9503 : - N, Cu, Fe not as basis species (no V)
- ABS off

Balance ⇒ Ca^{++} - 3%

UO_2^{++} = 1.82 ×10^{-16}

No pickup

Haiwee, Soddy precent
↳ -4.325 kcal

U 97% carbonates, 2.6 % $UO_2(OH)_2$ (aq)

wvw953b - N, Cu, Fe removed
- ABS off

Yes pickup

Very similar to wvw9503

wvw953c - N, Cu, Fe as basis species
- ABS off

Does not converge

wvw953d - N, Cu, Fe as basis species
- ABS on

Yes pickup

Same as 1st two, except Haiwee + Soddy gone.

wvw953e - N, Cu, Fe removed
- ABS on

Same results as wvw953b

Yes pickup

→

5/28/98
p. 3

ADIT95 -9

adit959 : - N, Cu, V, Fe not as basis
- ABS off

balance ⇒ Ca^{++} - 13%

UO_2^{++} = 7.19 ×10^{-13} m

Haiwee, Soddy present

Soddyite - 1.967 kcal

U 86% hydrox, 15% carb

No pickup

adit959b : - N, Cu, V, Fe removed
- ABS off

Same as adit959, except pickup is written

adit959c : - N, Cu, V, Fe as basis
- ABS off

Does not converge

adit959d : - N, Cu, V, Fe as basis
- ABS on

No Haiwee, Soddy

Yes pickup

– note: As left out

5/28/98
p. 4

ADIT95-06

adit956 : – N, Cu, V, Fe as non-basis
– ABS off

balance ⇒ Ca^{++} –18%
UO_2^{++} = 6.55×10^{-14} m
Haiwee, Soddy present
U 67% carb, 32% hydrox
Haiwee –0.870 kcal
No pickup

adit956b : – N, Cu, V, Fe removed
– ABS off
Similar to adit956, but yes pickup.

adit956c : – N, Cu, V, Fe as basis
– ABS off
Does not converge

adit956d : – N, Cu, V, Fe as basis
– ABS on
No Haiweeite, Soddy – Otherwise like adit956
Yes pickup.

Note on 10/19/98. Run adit956 w/ HCO3- varying →
adit956g → Haiweeite log Q/K = – 0. 862 (more undersat)

DAP 10/2/03

5/28/98
p. 5

BH12W95-11

bh12_11 : – N, not as basis
– ABS off
Balance Ca^{++} – 19 %
UO_2^{++} = 7.65×10^{-15} m
Haiwee, Soddy present
↳ +0.811 kcal
U 99% carb
No pickup

bh12_11b : – N removed
– ABS off
Very similar to bh12_11, except yes pickup

bh12_11c : – N as basis
– ABS off
Does not converge

bh12_11d : – N as basis
– ABS on
Same as others, but Haiwee + Soddy gone
Yes pickup

Bottom line:

1. Entering N as NH3(aq) results in Soddyite and Haiweeite ~~from~~ DAP 10/2/03 being eliminated from mil. list.
2. Entering N as NO3- result in no pickup.
3. Entering N as NH3(aq) without ABS results in non-convergence.

Note on 10/19/98. Run bh12-11 w/ HCO_3^- varying → bh12-11g → Haiweeite log Q/K = 0.277

On 5/26/98, Bill Murphy (WM) suggested producing a plot of activities which would show graphically the U mineral saturation states relative to water chemistry. YM waters could also be shown.

We could plot the EQ3NR results and then run EQ6 to show the evolution of the waters as U is added by dissolution of uraninite.

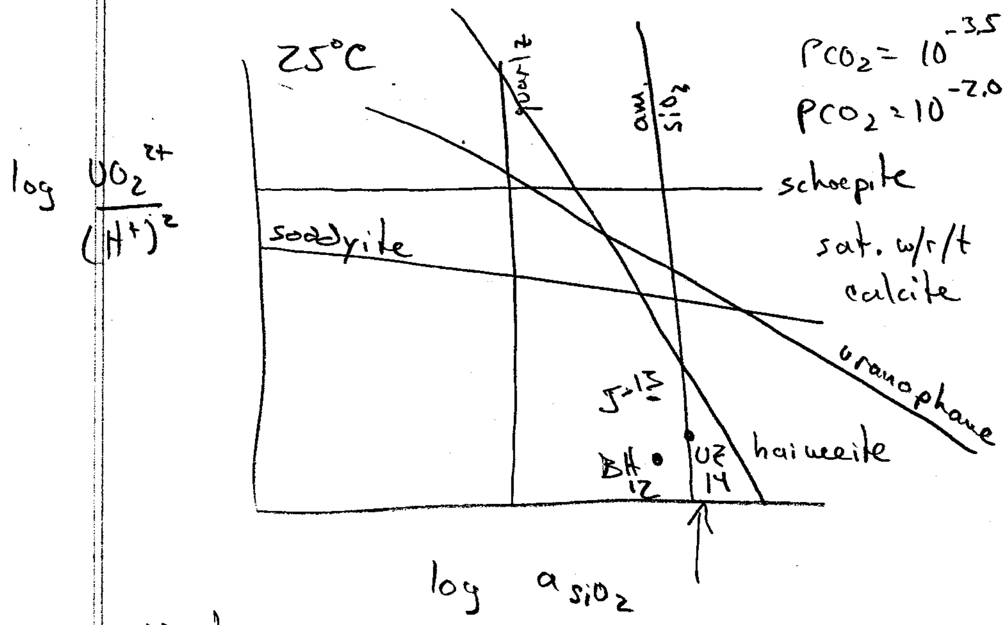
The following pages have photocopies of the notes he provided me outlining the approach.

DAP 6/19/98

WM 5/26/98

✓ schoepite

$UO_3 \cdot 2H_2O + 2H^+ \rightleftarrows UO_2^{2+} + 3H_2O$ log K = 4.8333



$P_{CO_2} = 10^{-3.5}$

$P_{CO_2} = 10^{-2.0}$

sat. w/r/t calcite

✓ soddyite

$(UO_2)_2SiO_4 \cdot 2H_2O + 4H^+ \rightleftarrows 2UO_2^{2+} + SiO_2 + 4H_2O$

log K = 0.392

✓ haiweeite

$Ca(UO_2)_2Si_6O_{15} \cdot 5H_2O + 6H^+ \rightleftarrows Ca^{2+} + 2UO_2^{2+} + 6SiO_2 + 8H_2O$

log K = -7.0413

$$\frac{a_{SiO_2}^{6}\, a_{UO_2^{2+}}^{2}\, a_{Ca^{2+}}}{a_{H^+}^{6}} ; \log \frac{a_{UO_2^{2+}}}{a_{H^+}^{2}} = -3a_{SiO_2} + \left(\log K - \log \frac{a_{Ca^{2+}}}{a_{H^+}^{2}}\right)$$

calcite

$CaCO_3 + 2H^+ \rightleftharpoons$

$Ca^{2+} + CO_{2g} + H_2O$

		log K
$CaCO_3 + H^+ \rightleftharpoons$	$HCO_3^- + Ca^{2+}$	1.8487
$H^+ + HCO_3^- \rightleftharpoons$	$CO_{2g} + H_2O$	7.8136
$CaCO_3 + 2H^+ \rightleftharpoons CO_{2g} + H_2O + Ca^{2+}$		9.6623

$$\log \frac{a_{Ca^{2+}}}{(a_{H^+})^2} = \log K - \log f_{CO_2}$$

uranophane

$Ca(UO_2)_2[SiO_3(OH)]_2 \cdot 5\cancel{H_2O} + 6H^+ \rightleftharpoons$

$Ca^{2+} + 2SiO_2 + 2UO_2^{2+} + 4H_2O$ $\quad \log K = 17.285$

$Ca(UO_2)_2(SiO_3)_2(OH)_2 + 6H^+ \ldots$

$UO_2 + 2H^+ + \frac{1}{2}O_2 \rightarrow$

$UO_2^{2+} + H_2O$

rutherfordine

On 5/28/98, I (DAP) worked on producing the thermodynamic activity plot suggested by WM.

The plot has a vertical axis of ~~$\frac{\log a_{UO_2^{++}}}{\log}$~~ DAP 6/19/98

$$\log \frac{a_{UO_2^{++}}}{(a_{H^+})^2}$$

and a horizontal axis of

$$\log a_{SiO_2(aq)}.$$

The task was to produce curves on this plot corresponding to equilibrium between a specific U mineral and dissolved U; i.e., the solubility curve for the mineral.

I wrote a reaction which included UO_2^{++} in the aqueous phase and the solid in question. (The solids considered were taken from lists of saturation states from EQ3NR results.)

It was found (as predicted by WM) that for many minerals, it was necessary to assume ① calcite present and ② a value for $\log f_{CO_2}$. This is illustrated by the notes reproduced on the following pages. The end product for each U mineral was an equation relating the x and y axis values above for the solubility reaction. (Also, T assumed 25°C)

After the three pages of notes, I have taped a hard copy of file "EQ3 minl calc.xls" (included on attached diskette), which shows plot values at various $\log f_{CO_2}$ values for two values of $\log a_{SiO_2}$.

Note - All log K values for reactions are taken from DATA0. COM from the EQ3/6 version 7.2b package. (File data0.com.R2).

Cross-outs: DAP 10/2/03

5/28/98

U min'l plot work

I have produced EQ3 runs on 5 Nopal UZ waters with U-Th data. Included are EQ6 pickup files.

What do I need for a Murphy plot of $\log \frac{UO_2^{2+}}{(H^+)^2}$ vs $\log a_{SiO_2}$? All calcs at 25°C

Haiweeite

$$\log K = 6\log a_{SiO_2} + 2\log a_{UO_2^{++}} + \log_{Ca^{++}} - 6\log a_{H^+}$$

$$2(\log a_{UO_2^{++}} - \cancel{2}\log a_{H^+}) = \log K - 6\log a_{SiO_2} - \log_{Ca^{++}} + \cancel{2}\log a_{H^+}$$

$$\log \frac{a_{UO_2^{++}}}{(a_{H^+})^2} = \frac{1}{2}\log K - 3\log a_{SiO_2} - \frac{1}{2}\log_{Ca^{++}} + \log a_{H^+}$$

$$= -3\log a_{SiO_2} + \frac{1}{2}(\log K - \log C_{Ca^{++}} + 2\log a_{H^+})$$

$$= -3\log a_{SiO_2} + \frac{1}{2}\left(\log K - \log \boxed{\frac{a_{Ca^{++}}}{(a_{H^+})^2}}\right)$$

Calcite

$$\log K = 9.6623 = \log a_{Ca^{++}} + \log f_{CO_2} - \log (a_{H^+})^2$$

$$\log a_{Ca^{++}} - \log (a_{H^+})^2 = \log K - \log f_{CO_2}$$

$$\cancel{\log}\ \log \frac{a_{Ca^{++}}}{(a_{H^+})^2} = \log K - \log f_{CO_2}$$

$$\log K = 7.8136 = \log f_{CO_2} - \log a_{HCO_3} - \log a_{H^+}$$

$$\log[a_{HCO_3} * a_{H^+}] = \log f_{CO_2} - 7.8136$$

5/28/98
p. 2

Schoepite

$$\log \frac{a_{UO_2^{2+}}}{(a_{H^+})^2} = 4.8333$$

Soddyite $\log K = 0.392$ DAP 10/2/03

$$\log K = 2\log a_{UO_2^{++}} + \log a_{SiO_2} - 4\log a_{H^+}$$

$$\log a_{UO_2^{++}} - 2\log a_{H^+} = \frac{1}{2}\log K - \frac{1}{2}\log a_{SiO_2}$$

$$\log \frac{a_{UO_2^{++}}}{(a_{H^+})^2} = -\frac{1}{2}\log a_{SiO_2} + \frac{1}{2}\log K$$

Uranophane $\log K = 17.2850$

$$\log K = 2\log a_{UO_2^{++}} + 2\log a_{SiO_2} + \log a_{Ca^+} - 6\log a_{H^+}$$

$$2\log a_{UO_2^{++}} - 4\log a_{H^+} = \log K - 2\log a_{SiO_2} - \log a_{Ca^+} + 2\log a_{H}$$

$$\log \frac{a_{UO_2^{++}}}{(a_{H^+})^2} = \frac{1}{2}\log K - \log a_{SiO_2} - \frac{1}{2}\log \frac{a_{Ca^+}}{(a_{H^+})^2}$$

$$= -\log a_{SiO_2} + \frac{1}{2}\left(\log K - \log \frac{a_{Ca^+}}{(a_{H^+})^2}\right)$$

Rutherfordine

$$UO_2CO_3 + H^+ = HCO_3^- + UO_2^{++} \qquad \log K = -4.1064$$

$$\log K = \log a_{UO_2^{++}} + \log a_{HCO_3^-} - \log a_{H^+}$$

$$\log a_{UO_2^{++}} - 2\log a_{H^+} = \log K - \log a_{HCO_3^-} - \log a_{H^+}$$

$$\log \frac{a_{UO_2^{++}}}{(a_{H^+})^2} = \log K - \boxed{\log[(a_{HCO_3^-})(a_{H^+})]}$$

DAP 10/2/03

see previous page

5/28/98
p. 3

CaUO4

$CaUO_4 + 4H^+ = Ca^{++} + UO_2^{++} + 2H_2O$

$\log K = 15.9420 = \log a_{Ca^{++}} + \log a_{UO_2^{++}} - 4 \log a_{H^+}$

$\log a_{UO_2^{++}} - 2 \log a_{H^+} = 15.9420 - \log a_{Ca^{++}} + 2 \log a_{H^+}$

$\log \frac{a_{UO_2^{++}}}{(a_{H^+})^2} = 15.9420 - \underline{\log \frac{a_{Ca^{++}}}{(a_{H^+})^2}}$
see calcite

Quartz

$SiO_2(s) = SiO_2(aq)$ $\log K = a_{SiO_2(aq)} = -3.9993$

~~aq~~ SiO2 (am)

$SiO_2(am) = SiO_2(aq)$ $\log K = a_{SiO_2(aq)} = -2.7136$

DAP 10/2/03

Plot calculations for UO2++/H+2 versus SiO2(aq) activity plot
All assume calcite saturation

logfCO2	log[Ca++/(H+)2]	log[HCO3-XH+]	Soddyite log [UO2++/H+2		Haiweeite log [UO2++/H+2]		Uph log [UO2++/H+2]	
			@logSiO2		@logSiO2		@logSiO2	
			-5	-2	-5	-2	-5	-2
-1	10.6623	-8.8136	2.696	1.196	6.1482	-2.8518	8.31135	5.31135
-1.5	11.1623	-9.3136	2.696	1.196	5.8982	-3.1018	8.06135	5.06135
-2	11.6623	-9.8136	2.696	1.196	5.6482	-3.3518	7.81135	4.81135
-2.5	12.1623	-10.3136	2.696	1.196	5.3982	-3.6018	7.56135	4.56135
-3	12.6623	-10.8136	2.696	1.196	5.1482	-3.8518	7.31135	4.31135
-3.5	13.1623	-11.3136	2.696	1.196	4.8982	-4.1018	7.06135	4.06135
-4	13.6623	-11.8136	2.696	1.196	4.6482	-4.3518	6.81135	3.81135

Plot calculat
All assume c

logfCO2	Ruther log [UO2++/H+2]	CaUO4 log [UO2++/H+2]
	@ all logSiO2	@ all logSiO2
-1	4.7072	5.2797
-1.5	5.2072	4.7797
-2	5.7072	4.2797
-2.5	6.2072	3.7797
-3	6.7072	3.2797
-3.5	7.2072	2.7797
-4	7.7072	2.2797

File "EQ3 U min'l calcs.xls" in attached diskette.
DAP 6/19/98

The results of the spreadsheet on the previous page were fed into the KaleidaGraph application on my Macintosh (app not yet installed on Windows NT machine).

The resulting plots are shown the following two pages, for log f_{CO_2} values of -2 and -3.5. The latter value represents equilibrium with air.

The labelled lines represent equilibrium between water with the activities as plotted and the U solid. Calcite saturation assumed.

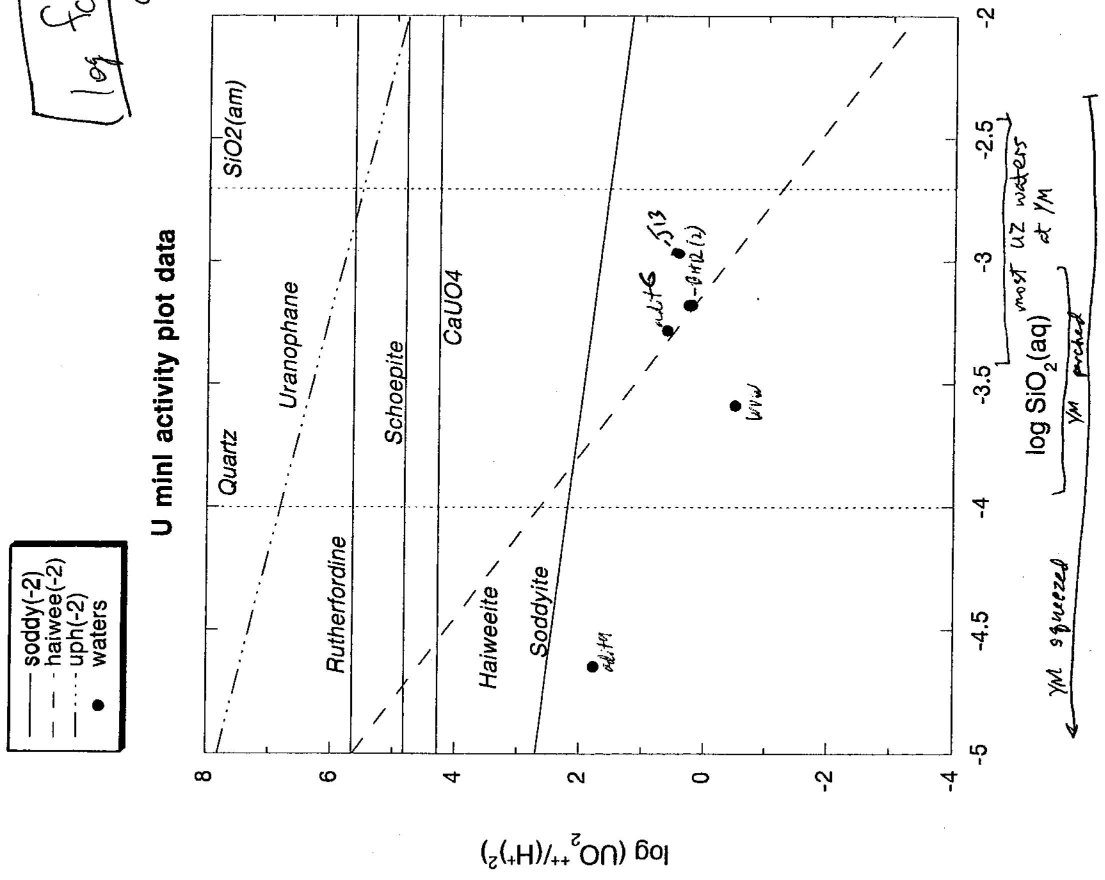
Note that Soddyite and Haiweeite - under equilibrium conditions - are the solubility limiting phases (assuming a direct relationship between total dissolved U and the species UO_2^{++} - not necessarily the case). The other lines do not represent solid-solid reactions - rather they represent equilibrium with water if U is not limited by other phases.

The data points and hand-written notes are explained later.

The Kaleidagraph data file is "U minl activity plot data." Two plot files are: "U minl plot log fCO2 = -2"
"U minl plot log fCO2 = -3.5"

These are not saved to diskette because they can easily be re-created.

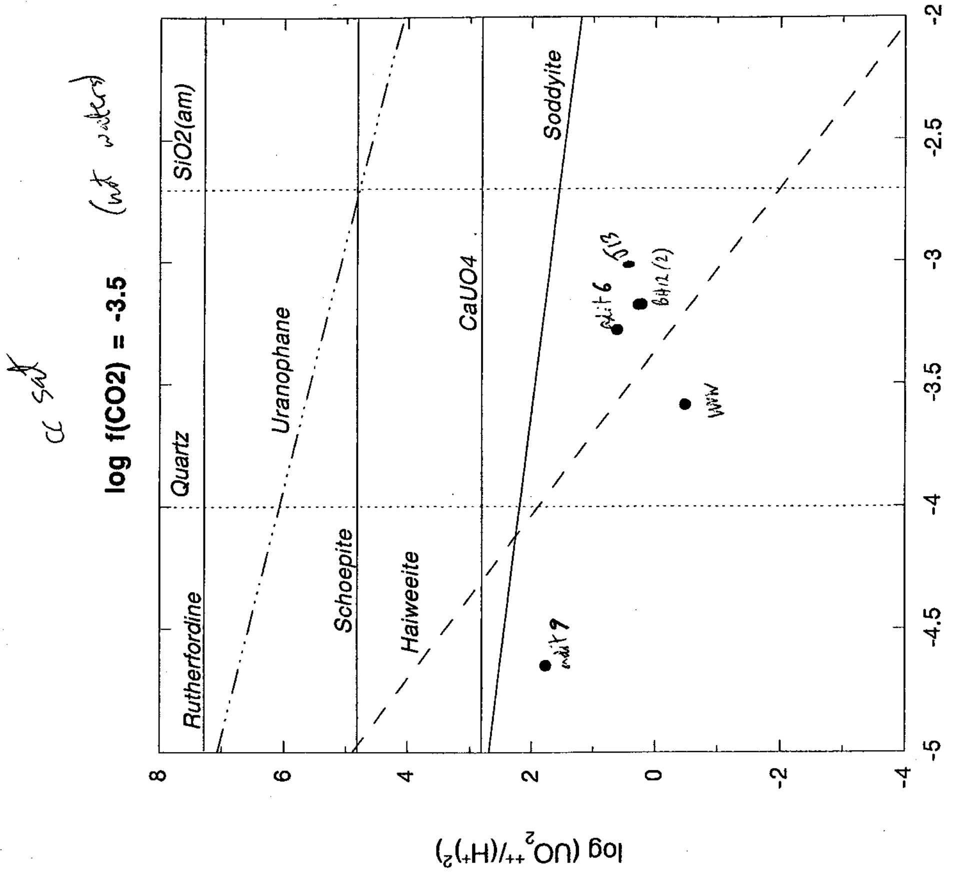
log f_{CO_2} = -2
cc sat



J13 - not at cc sat

Actual log $f_{CO_2(g)}$

BH12	-1.80 -1.73
adit6	-2.30
adit9	-2.89
WW	-2.51



6/22/98
DAP

Continued summary and documentation of Nopal water chemistry modeling.

On 5/29/98, I did "final" EQ3NR runs on the five Nopal waters. I had noticed that the HCO_3^- results in previous runs were significantly lower than measured amounts because the code had taken my input values as total dissolved carbon and re-calculated distribution of C among various species only one of which was HCO_3^-.

Therefore, I ran all five waters (with the letter "f" appended to the file name) with HCO_3^- input as "free molal". This fixes the species concentration of HCO_3^- to my input value. In these runs, charge balance was adjusted with Ca^{++}.

The output files from these EQ3NR runs are:

bh12_11f.30
bh12_05f.30
adit956f.30
adit959f.30
wvw9503f.30

They are saved on the attached diskette labelled "Nopal EQ3/6."

A second set of runs (with the letter "g" appended) took another approach in order to "check" the field alkalinity ($\doteq HCO_3^-$) data. HCO_3^- was input as the measured value, and charge balance was adjusted with HCO_3.

bh12_11g.30
bh12_05g.30
adit956g.30
adit959g.30
wvw9503g.30

On "Nopal EQ3/6" diskette

For each I:

- noted how much Ca^{++} or HCO_3^- had to be adjusted for charge balance. (in percent).
- Noted calculated activities of UO_2^{++}, H^+, and $SiO_2(aq)$ and calculated the x and y axis values discussed on page 13.
- Noted for the "f" runs the saturation state of calcite (in kcal affinity).

I could not evaluate the saturation states of Haiweeite and Soddyite quantitatively because of the aforementioned bug in EQ3NR (see p. 4).

N was entered as basis species NH3(aq) and auto basis switching was on.

On the following pages are reproduced the first pages of the *.3o output files, showing the input data and the values noted above.

Notable:

- the charge adjustment was <10% for all but WVW9503
- Choice of charge adjustment did not significantly affect the pertinent calculated activities.
- Calcite is near saturation in bh12_11, ~~bh~~ 12_05, and wvw9503. Adit samples are undersaturated.

Results were plotted on the activity plots on pages 19 - 20. The bh12 results overlap considerably. The plot on p. 19 is marked with the calculated log f_{CO_2} for the water.

Quartz is oversaturated in all but adit959.
(continued on p. 33)

Dissolved Th is always well above Thorianite solubility.

```
                              bh12_11f.3o

EQ3/6, Version 7.2b (EQ3/6-V7-REL-V7.2b-PC)
EQ3NR Speciation-Solubility Code (EQ3/6-V7-EQ3NR-EXE-R139-P5)
Supported by the EQLIB library (EQ3/6-V7-EQLIB-LIB-R168-P5)

Copyright (c) 1987, 1990-1993, 1995 The Regents of the University of
California, Lawrence Livermore National Laboratory. All rights
reserved.

This work is subject to additional statements and
disclaimers which may be found in the README.txt file
included in the EQ3/6 software transmittal package.


Run  15:48:55  05/28/98


--- Reading the input file ---
|-------------------------------------------------------------------|
|EQ3NR input file name= bh12_11f.3i                                 |
|Description= "Calculate BH12W95-11 water, 5/98"                    |
|Version level= 7.2                                                 |
|Created 05/28/98      Creator= D.A. Pickett                        |
|                                                                   |
|Calculate speciation and conditions in Borehole 12 water based on lab |
|and field chemical data. Sample BH12W95-11.  Set HCO3- to meas. field |
|alkalinity as "free molal."  T, pH, and logfO2 are also field      |
|measurements.  Eliminate Fe because it was undetected.  Auto basis |
|switching is on because run would not otherwise converge.  All are as |
|basis species.                                                     |
|                                                                   |
|-------------------------------------------------------------------|
|Temperature (C)          | 26.00        |Density(gm/cm3)|  1.00000 |
|-------------------------------------------------------------------|
|Total Dissolved Salts    |              | mg/kg | mg/l  |*not used |
|------------------------------------------------------------------------|
|Electrical Balancing on |Ca++                      | code selects| not performed|
|------------------------------------------------------------------------|
| SPECIES               | BASIS SWITCH/CONSTRAINT| CONC/ETC   | UNITS OR TYPE  |
|------------------------------------------------------------------------|
|redox                  |                        |-1.81000    |LogfO2          |
|H+                     |                        | 7.3400     |pH              |
|Cl-                    |                        | 0.0001848  |molality        |
|F-                     |                        | 4.52e-05   |molality        |
|NH3(aq)                |                        | 5.79e-05   |molality        |
|HPO4--                 |                        | 7.88e-06   |molality        |
|SO4--                  |                        | 7.65e-05   |molality        |
|Al+++                  |                        | 1.52e-06   |molality        |
|H2AsO4-                |                        | 1.47e-07   |molality        |
|Ba++                   |                        | 1.09e-07   |molality        |
|B(OH)3(aq)             |                        | 3.24e-06   |molality        |
|Ca++                   |                        | 0.00262    |molality        |
|Cu++                   |                        | 7.87e-08   |molality        |
|Li+                    |                        | 5.04e-06   |molality        |
|Mg++                   |                        | 0.000228   |molality        |
|Mn++                   |                        | 3.44e-05   |molality        |
|MoO4--                 |                        | 2.92e-07   |molality        |
|K+                     |                        | 0.0001527  |molality        |
|SiO2(aq)               |                        | 0.000662   |molality        |
|Na+                    |                        | 0.000826   |molality        |
|Sr++                   |                        | 4.14e-06   |molality        |
|VO++                   |                        | 2.16e-07   |molality        |
|Zn++                   |                        | 1.38e-07   |molality        |
|UO2++                  |                        | 2.43e-08   |molality        |
|Th++++                 |                        | 6.74e-10   |molality        |
|HCO3-                  |                        | 0.005735   |free molal      |
|------------------------------------------------------------------------|
|Input Solid Solutions                                                   |
|------------------------------------------------------------------------|
                              Page 1
```

Ca^{++} -7%

Log activity

UO_2^{++} -14.4022

H^+ -7.34

$SiO_2(aq)$ -3.1804

$\log \frac{UO_2^{++}}{(H^+)^2} = 0.2778$

cc 0.577 kcal

```
                              bh12_11g.3o

EQ3/6, Version 7.2b (EQ3/6-V7-REL-V7.2b-PC)
EQ3NR Speciation-Solubility Code (EQ3/6-V7-EQ3NR-EXE-R139-P5)
Supported by the EQLIB library (EQ3/6-V7-EQLIB-LIB-R168-P5)

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Run  15:51:43  05/28/98


 --- Reading the input file ---
|-------------------------------------------------------------------|
|EQ3NR input file name= bh12_11g.3i                                 |
|Description= "Calculate BH12W95-11 water, 5/98"                    |
|Version level= 7.2                                                 |
|Created 05/28/98     Creator= D.A. Pickett                         |
|                                                                   |
|Calculate speciation and conditions in Borehole 12 water based on lab |
|and field chemical data. Sample BH12W95-11.  Set HCO3- to meas. field |
|alkalinity as "free molal."  T, pH, and logfO2 are also field      |
|measurements.  Eliminate Fe because it was undetected.  Auto basis |
|switching is on because run would not otherwise converge.  All are as |
|basis species.                                                     |
|                                                                   |
|Same as bh12_11f, except balanced on HCO3-.                        |
|                                                                   |
|-------------------------------------------------------------------|
|Temperature (C)         | 26.00          |Density(gm/cm3)|  1.00000 |
|-------------------------------------------------------------------|
|Total Dissolved Salts   |                | mg/kg | mg/l  |*not used |
|------------------------------------------------------------------------|
|Electrical Balancing on |HCO3-                    | code selects| not performed|
|------------------------------------------------------------------------|
| SPECIES                | BASIS SWITCH/CONSTRAINT| CONC/ETC   | UNITS OR TYPE |
|------------------------------------------------------------------------|
|redox                   |                        |-1.81000    |LogfO2         |
|H+                      |                        | 7.3400     |pH             |
|Cl-                     |                        | 0.0001848  |molality       |
|F-                      |                        | 4.52e-05   |molality       |
|NH3(aq)                 |                        | 5.79e-05   |molality       |
|HPO4--                  |                        | 7.88e-06   |molality       |
|SO4--                   |                        | 7.65e-05   |molality       |
|Al+++                   |                        | 1.52e-06   |molality       |
|H2AsO4-                 |                        | 1.47e-07   |molality       |
|Ba++                    |                        | 1.09e-07   |molality       |
|B(OH)3(aq)              |                        | 3.24e-06   |molality       |
|Ca++                    |                        | 0.00262    |molality       |
|Cu++                    |                        | 7.87e-08   |molality       |
|Li+                     |                        | 5.04e-06   |molality       |
|Mg++                    |                        | 0.000228   |molality       |
|Mn++                    |                        | 3.44e-05   |molality       |
|MoO4--                  |                        | 2.92e-07   |molality       |
|K+                      |                        | 0.0001527  |molality       |
|SiO2(aq)                |                        | 0.000662   |molality       |
|Na+                     |                        | 0.000826   |molality       |
|Sr++                    |                        | 4.14e-06   |molality       |
|VO++                    |                        | 2.16e-07   |molality       |
|Zn++                    |                        | 1.38e-07   |molality       |
|UO2++                   |                        | 2.43e-08   |molality       |
|Th++++                  |                        | 6.74e-10   |molality       |
|HCO3-                   |                        | 0.005735   |molality       |
|------------------------------------------------------------------------|
                              Page 1
```

HCO_3^- + 6%

<u>log activity</u>

UO_2^{++} -14.4744

H^+ -7.3400

$SiO_2(aq)$ -3.1804

$\log \frac{UO_2^{++}}{(H^+)^2} = 0.2056$

$\log f CO_2 = -1.7785$

cc ssatd 0.650 kcal

0.650 kcal

DAP 8/25/00

```
                              bh12_05f.3o

EQ3/6, Version 7.2b (EQ3/6-V7-REL-V7.2b-PC)
EQ3NR Speciation-Solubility Code (EQ3/6-V7-EQ3NR-EXE-R139-P5)
Supported by the EQLIB library (EQ3/6-V7-EQLIB-LIB-R168-P5)

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Run  11:10:26  05/28/98


 --- Reading the input file ---
|-------------------------------------------------------------------|
|EQ3NR input file name= bh12_05f.3i                                 |
|Description= "Calculate BH12W95-05 water, 5/98"                    |
|Version level= 7.2                                                 |
|Created 01/21/97     Creator= D.A. Pickett                         |
|                                                                   |
|Calculate speciation and conditions in Borehole 12 water based on lab |
|and field chemical data. Sample BH12W95-05.  Set HCO3- to meas. field |
|alkalinity.  Re-run on 5/28/98 on PC with output settings changed. |
|Also, I changed species designations for N, Cu, and V so that      |
|EQ6 pickup file could be written.  Eliminate Fe because it was     |
|not detected and does not affect U.  Auto basis switching is turned on|
|because it would not converge with it off.  Also, changed bicarbonate |
|input to free molal.                                               |
|                                                                   |
|-------------------------------------------------------------------|
|Temperature (C)         | 25.60          |Density(gm/cm3)|  1.00000 |
|-------------------------------------------------------------------|
|Total Dissolved Salts   |                | mg/kg | mg/l  |*not used |
|------------------------------------------------------------------------|
|Electrical Balancing on |Ca++                     | code selects| not performed|
|------------------------------------------------------------------------|
| SPECIES                | BASIS SWITCH/CONSTRAINT| CONC/ETC   | UNITS OR TYPE |
|------------------------------------------------------------------------|
|redox                   |                        |-1.81000    |LogfO2         |
|H+                      |                        | 7.2600     |pH             |
|Cl-                     |                        | 0.0001927  |molality       |
|F-                      |                        | 4.71e-05   |molality       |
|NH3(aq)                 |                        | 5.31e-05   |molality       |
|HPO4--                  |                        | 8.03e-06   |molality       |
|SO4--                   |                        | 7.39e-05   |molality       |
|Al+++                   |                        | 1.22e-06   |molality       |
|H2AsO4-                 |                        | 1.33e-07   |molality       |
|Ba++                    |                        | 1.09e-07   |molality       |
|B(OH)3(aq)              |                        | 3.42e-06   |molality       |
|Ca++                    |                        | 0.00262    |molality       |
|Cu++                    |                        | 7.87e-08   |molality       |
|Li+                     |                        | 5.04e-06   |molality       |
|Mg++                    |                        | 0.000229   |molality       |
|Mn++                    |                        | 3.71e-05   |molality       |
|MoO4--                  |                        | 2.71e-07   |molality       |
|K+                      |                        | 0.000153   |molality       |
|SiO2(aq)                |                        | 0.000666   |molality       |
|Na+                     |                        | 0.000835   |molality       |
|Sr++                    |                        | 4.14e-06   |molality       |
|VO++                    |                        | 1.77e-07   |molality       |
|Zn++                    |                        | 6.12e-08   |molality       |
|UO2++                   |                        | 2.01e-08   |molality       |
|Th++++                  |                        | 1.16e-09   |molality       |
|HCO3-                   |                        | 0.005735   |free molal     |
|------------------------------------------------------------------------|
                              Page 1
```

Ca^{++} -8%

<u>log activity</u>

UO_2^{++} -14.2925

H^+ -7.26

$SiO_2(aq)$ -3.1775

$\log \frac{UO_2^{2+}}{(H^+)^2} = 0.2275$

CC 0457 kcal

```
                                    bh12_05g.3o

EQ3/6, Version 7.2b (EQ3/6-V7-REL-V7.2b-PC)
EQ3NR Speciation-Solubility Code (EQ3/6-V7-EQ3NR-EXE-R139-P5)
Supported by the EQLIB library (EQ3/6-V7-EQLIB-LIB-R168-P5)

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Run  11:18:16  05/28/98


--- Reading the input file ---
|-------------------------------------------------------------------|
|EQ3NR input file name= bh12_05g.3i                                 |
|Description= "Calculate BH12W95-05 water, 5/98"                    |
|Version level= 7.2                                                 |
|Created 01/21/97     Creator= D.A. Pickett                         |
|                                                                   |
|Calculate speciation and conditions in Borehole 12 water based on lab |
|and field chemical data. Sample BH12W95-05.  Set HCO3- to meas. field |
|alkalinity.  Re-run on 5/28/98 on PC with output settings changed.    |
|Also, I changed species designations for N, Cu, and V so that      |
|EQ6 pickup file could be written.  Eliminate Fe because it was     |
|not detected and does not affect U.  Auto basis switching is turned on|
|because it would not converge with it off.  Also, changed bicarbonate |
|input to free molal.                                               |
|                                                                   |
|This run is identical to bh12_05f, except that electrical balancing |
|is done on HCO3- as a check on field data.                         |
|                                                                   |
|-------------------------------------------------------------------|
|Temperature (C)         | 25.60        |Density(gm/cm3)|  1.00000  |
|-------------------------------------------------------------------|
|Total Dissolved Salts   |              | mg/kg | mg/l  |*not used  |
|------------------------------------------------------------------------|
|Electrical Balancing on |HCO3-                   | code selects| not performed|
|------------------------------------------------------------------------|
| SPECIES                | BASIS SWITCH/CONSTRAINT| CONC/ETC   | UNITS OR TYPE |
|------------------------------------------------------------------------|
|redox                   |                        |-1.81000    |LogfO2        |
|H+                      |                        | 7.2600     |pH            |
|Cl-                     |                        | 0.0001927  |molality      |
|F-                      |                        | 4.71e-05   |molality      |
|NH3(aq)                 |                        | 5.31e-05   |molality      |
|HPO4--                  |                        | 8.03e-06   |molality      |
|SO4--                   |                        | 7.39e-05   |molality      |
|Al+++                   |                        | 1.22e-06   |molality      |
|H2AsO4-                 |                        | 1.33e-07   |molality      |
|Ba++                    |                        | 1.09e-07   |molality      |
|B(OH)3(aq)              |                        | 3.42e-06   |molality      |
|Ca++                    |                        | 0.00262    |molality      |
|Cu++                    |                        | 7.87e-08   |molality      |
|Li+                     |                        | 5.04e-06   |molality      |
|Mg++                    |                        | 0.000229   |molality      |
|Mn++                    |                        | 3.71e-05   |molality      |
|MoO4--                  |                        | 2.71e-07   |molality      |
|K+                      |                        | 0.000153   |molality      |
|SiO2(aq)                |                        | 0.000666   |molality      |
|Na+                     |                        | 0.000835   |molality      |
|Sr++                    |                        | 4.14e-06   |molality      |
|VO++                    |                        | 1.77e-07   |molality      |
|Zn++                    |                        | 6.12e-08   |molality      |
|UO2++                   |                        | 2.01e-08   |molality      |
                                         Page 1
```

DAP 8/25/00

HCO_3^- + 7 %

log activity

UO_2^{++} -14.3683

H^+ -7.26

$SiO_2(aq)$ -3.1775

$\log \frac{UO_2^{2+}}{(H^+)^2} = 0.1517$

cc ssatd 0.535 kcal

cc ssatd 0.535 kcal

DAP 8/25/00

```
                                    adit956f.3o

EQ3/6, Version 7.2b (EQ3/6-V7-REL-V7.2b-PC)
EQ3NR Speciation-Solubility Code (EQ3/6-V7-EQ3NR-EXE-R139-P5)
Supported by the EQLIB library (EQ3/6-V7-EQLIB-LIB-R168-P5)

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Run  15:26:00  05/28/98


--- Reading the input file ---
|-------------------------------------------------------------------|
|EQ3NR input file name= adit956f.3i                                 |
|Description= "Calculate ADIT95-6 water, 5/98"                      |
|Version level= 7.2                                                 |
|Created 05/28/98     Creator= D.A. Pickett                         |
|                                                                   |
|Calculate speciation and conditions in ADIT95-6 water based on lab |
|chemical data. Set HCO3- to meas. lab alkalinity as "free molal."  pH |
|set to 7, T set.  All as basis species (including N).  Remove      |
|undetected elements (except Al).  Auto basis switching on because run |
|would not otherwise converge.  Arsenic is added; it was neglected  |
|earlier.                                                           |
|                                                                   |
|-------------------------------------------------------------------|
|Temperature (C)         | 26.00        |Density(gm/cm3)|  1.00000  |
|-------------------------------------------------------------------|
|Total Dissolved Salts   |              | mg/kg | mg/l  |*not used  |
|------------------------------------------------------------------------|
|Electrical Balancing on |Ca++                    | code selects| not performed|
|------------------------------------------------------------------------|
| SPECIES                | BASIS SWITCH/CONSTRAINT| CONC/ETC   | UNITS OR TYPE |
|------------------------------------------------------------------------|
|redox                   |                        |-0.68000    |LogfO2        |
|H+                      |                        | 7.0000     |pH            |
|Cl-                     |                        | 2.71e-05   |molality      |
|F-                      |                        | 0.000117   |molality      |
|NH3(aq)                 |                        | 1.87e-05   |molality      |
|SO4--                   |                        | 0.000195   |molality      |
|H2AsO4-                 |                        | 6.01e-07   |molality      |
|Al+++                   |                        | 1.00e-20   |molality      |
|Ca++                    |                        | 0.000531   |molality      |
|Li+                     |                        | 8.64e-07   |molality      |
|Mg++                    |                        | 3.33e-06   |molality      |
|MoO4--                  |                        | 9.59e-07   |molality      |
|K+                      |                        | 3.71e-05   |molality      |
|SiO2(aq)                |                        | 0.000523   |molality      |
|Na+                     |                        | 0.000304   |molality      |
|Sr++                    |                        | 5.48e-07   |molality      |
|VO++                    |                        | 3.14e-07   |molality      |
|Zn++                    |                        | 4.59e-08   |molality      |
|UO2++                   |                        | 8.27e-10   |molality      |
|Th++++                  |                        | 1.90e-12   |molality      |
|HCO3-                   |                        | 0.000799   |free molal    |
|------------------------------------------------------------------------|
|Input Solid Solutions   |                        |            |               |
|------------------------------------------------------------------------|
| none                   |                        |            |               |
|------------------------------------------------------------------------|
|SUPPRESSED SPECIES   (suppress,replace,augmentk,augmentg)   value |
|-------------------------------------------------------------------|
| none                   |              |          |                |
                                         Page 1
```

Ca^{++} -5 %

log activity

UO_2^{++} -13.3802

H^+ -7.0

$SiO_2(aq)$ -3.2820

$\log \frac{UO_2^{2+}}{(H^+)^2} = 0.6198$

cc -1.840 kcal

```
                              adit956g.3o

EQ3/6, Version 7.2b (EQ3/6-V7-REL-V7.2b-PC)
EQ3NR Speciation-Solubility Code (EQ3/6-V7-EQ3NR-EXE-R139-P5)
Supported by the EQLIB library (EQ3/6-V7-EQLIB-LIB-R168-P5)

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Run  15:27:57  05/28/98


 --- Reading the input file ---
|-----------------------------------------------------------------------|
|EQ3NR input file name= adit956g.3i                                     |
|Description= "Calculate ADIT95-6 water, 5/98"                          |
|Version level= 7.2                                                     |
|Created 05/28/98      Creator= D.A. Pickett                            |
|                                                                       |
|Calculate speciation and conditions in ADIT95-6 water based on lab     |
|chemical data. Set HCO3- to meas. lab alkalinity as "free molal."  pH  |
|set to 7, T set.  All as basis species (including N).  Remove          |
|undetected elements (except Al).  Auto basis switching on because run  |
|would not otherwise converge.  Arsenic is added; it was neglected      |
|earlier.                                                               |
|                                                                       |
|Same as adit956f, except balanced on HCO3-.                            |
|                                                                       |
|-----------------------------------------------------------------------|
|Temperature (C)         | 26.00         |Density(gm/cm3)|  1.00000     |
|-----------------------------------------------------------------------|
|Total Dissolved Salts   |               | mg/kg | mg/l  |*not used     |
|-----------------------------------------------------------------------------|
|Electrical Balancing on |HCO3-                   | code selects| not performed|
|-----------------------------------------------------------------------------|
| SPECIES                | BASIS SWITCH/CONSTRAINT| CONC/ETC    | UNITS OR TYPE |
|-----------------------------------------------------------------------------|
|redox                   |                        |-0.68000     |Logf02         |
|H+                      |                        | 7.0000      |pH             |
|Cl-                     |                        | 2.71e-05    |molality       |
|F-                      |                        | 0.000117    |molality       |
|NH3(aq)                 |                        | 1.87e-05    |molality       |
|SO4--                   |                        | 0.000195    |molality       |
|H2AsO4-                 |                        | 6.01e-07    |molality       |
|Al+++                   |                        | 1.00e-20    |molality       |
|Ca++                    |                        | 0.000531    |molality       |
|Li+                     |                        | 8.64e-07    |molality       |
|Mg++                    |                        | 3.33e-06    |molality       |
|MoO4--                  |                        | 9.59e-07    |molality       |
|K+                      |                        | 3.71e-05    |molality       |
|SiO2(aq)                |                        | 0.000523    |molality       |
|Na+                     |                        | 0.000304    |molality       |
|Sr++                    |                        | 5.48e-07    |molality       |
|VO++                    |                        | 3.14e-07    |molality       |
|Zn++                    |                        | 4.59e-08    |molality       |
|UO2++                   |                        | 8.27e-10    |molality       |
|Th++++                  |                        | 1.90e-12    |molality       |
|HCO3-                   |                        | 0.000799    |molality       |
|-----------------------------------------------------------------------------|
|Input Solid Solutions   |                        |             |               |
|-----------------------------------------------------------------------------|
| none                   |                        |             |               |
|-----------------------------------------------------------------------------|
|SUPPRESSED SPECIES   (suppress,replace,augmentk,augmentg)   value    |
                              Page 1
```

HCO_3^- + 6%

log activity

UO_2^{++} -13.4194

H^+ -7.0

$SiO_2(aq)$ -3.2820

$\log \frac{UO_2^{++}}{(H^+)^2} = 0.5806$

cc -1.777 kcal

```
                              adit959f.3o

EQ3/6, Version 7.2b (EQ3/6-V7-REL-V7.2b-PC)
EQ3NR Speciation-Solubility Code (EQ3/6-V7-EQ3NR-EXE-R139-P5)
Supported by the EQLIB library (EQ3/6-V7-EQLIB-LIB-R168-P5)

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Run  15:15:26  05/28/98


 --- Reading the input file ---
|-----------------------------------------------------------------------|
|EQ3NR input file name= adit959f.3i                                     |
|Description= "Calculate ADIT95-9 water, 5/98"                          |
|Version level= 7.2                                                     |
|Created 05/28/98      Creator= D.A. Pickett                            |
|                                                                       |
|Calculate speciation and conditions in ADIT95-9 water based on lab     |
|chemical data. Set HCO3- to meas. lab alkalinity as "free molal."  pH  |
|set to 7, T set.  Delete elements not detected (e.g., Fe, V).  All are|
|as basis species (including N).  Auto basis switching is on because    |
|run would not otherwise converge.                                      |
|                                                                       |
|-----------------------------------------------------------------------|
|Temperature (C)         | 26.00         |Density(gm/cm3)|  1.00000     |
|-----------------------------------------------------------------------|
|Total Dissolved Salts   |               | mg/kg | mg/l  |*not used     |
|-----------------------------------------------------------------------------|
|Electrical Balancing on |Ca++                    | code selects| not performed|
|-----------------------------------------------------------------------------|
| SPECIES                | BASIS SWITCH/CONSTRAINT| CONC/ETC    | UNITS OR TYPE |
|-----------------------------------------------------------------------------|
|redox                   |                        |-0.68000     |Logf02         |
|H+                      |                        | 7.0000      |pH             |
|Cl-                     |                        | 1.96e-05    |molality       |
|F-                      |                        | 1.31e-05    |molality       |
|NH3(aq)                 |                        | 6.68e-06    |molality       |
|SO4--                   |                        | 0.000133    |molality       |
|Al+++                   |                        | 7.78e-07    |molality       |
|Ba++                    |                        | 9.47e-08    |molality       |
|Ca++                    |                        | 0.000207    |molality       |
|Mg++                    |                        | 6.38e-06    |molality       |
|Mn++                    |                        | 5.46e-08    |molality       |
|K+                      |                        | 5.32e-05    |molality       |
|SiO2(aq)                |                        | 2.25e-05    |molality       |
|Na+                     |                        | 3.98e-05    |molality       |
|Sr++                    |                        | 3.20e-07    |molality       |
|Zn++                    |                        | 1.45e-06    |molality       |
|UO2++                   |                        | 3.72e-09    |molality       |
|Th++++                  |                        | 5.31e-12    |molality       |
|HCO3-                   |                        | 0.000200    |free molal     |
|-----------------------------------------------------------------------------|
|Input Solid Solutions   |                        |             |               |
|-----------------------------------------------------------------------------|
| none                   |                        |             |               |
|-----------------------------------------------------------------------------|
|SUPPRESSED SPECIES   (suppress,replace,augmentk,augmentg)   value    |
|-----------------------------------------------------------------------|
| none                   |              |          |                    |
|-----------------------------------------------------------------------|
|OPTIONS                                                                |
|-----------------------------------------------------------------------|
                              Page 1
```

Ca^{++} -4%

log activity

UO_2^{++} -12.2210

H^+ -7.0

$SiO_2(aq)$ -4.6483

$\log \frac{UO_2^{++}}{(H^+)^2} = 1.779$

cc -3.164 kcal

```
                                 adit959g.3o
 EQ3/6, Version 7.2b (EQ3/6-V7-REL-V7.2b-PC)
 EQ3NR Speciation-Solubility Code (EQ3/6-V7-EQ3NR-EXE-R139-P5)
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 Run  15:17:35  05/28/98


 --- Reading the input file ---
|----------------------------------------------------------------------|
|EQ3NR input file name= adit959g.3i                                    |
|Description= "Calculate ADIT95-9 water, 5/98"                         |
|Version level= 7.2                                                    |
|Created 05/28/98     Creator= D.A. Pickett                            |
|                                                                      |
|Calculate speciation and conditions in ADIT95-9 water based on lab    |
|chemical data. Set HCO3- to meas. lab alkalinity as "free molal."  pH |
|set to 7, T set.  Delete elements not detected (e.g., Fe, V).  All are|
|as basis species (including N).  Auto basis switching is on because   |
|run would not otherwise converge.                                     |
|                                                                      |
|Same as adit959f, except balanced on HCO3-.                           |
|                                                                      |
|----------------------------------------------------------------------|
|Temperature (C)        | 26.00        |Density(gm/cm3)|  1.00000      |
|----------------------------------------------------------------------|
|Total Dissolved Salts  |              | mg/kg | mg/l  |*not used      |
|----------------------------------------------------------------------------|
|Electrical Balancing on |HCO3-                    | code selects| not performed|
|----------------------------------------------------------------------------|
| SPECIES               | BASIS SWITCH/CONSTRAINT| CONC/ETC  | UNITS OR TYPE |
|----------------------------------------------------------------------------|
|redox                  |                        |-0.68000   |LogfO2         |
|H+                     |                        | 7.0000    |pH             |
|Cl-                    |                        | 1.96e-05  |molality       |
|F-                     |                        | 1.31e-05  |molality       |
|NH3(aq)                |                        | 6.68e-06  |molality       |
|SO4--                  |                        | 0.000133  |molality       |
|Al+++                  |                        | 7.78e-07  |molality       |
|Ba++                   |                        | 9.47e-08  |molality       |
|Ca++                   |                        | 0.000207  |molality       |
|Mg++                   |                        | 6.38e-06  |molality       |
|Mn++                   |                        | 5.46e-08  |molality       |
|K+                     |                        | 5.32e-05  |molality       |
|SiO2(aq)               |                        | 2.25e-05  |molality       |
|Na+                    |                        | 3.98e-05  |molality       |
|Sr++                   |                        | 3.20e-07  |molality       |
|Zn++                   |                        | 1.45e-06  |molality       |
|UO2++                  |                        | 3.72e-09  |molality       |
|Th++++                 |                        | 5.31e-12  |molality       |
|HCO3-                  |                        | 0.000200  |molality       |
|----------------------------------------------------------------------------|
|Input Solid Solutions  |                        |           |               |
|----------------------------------------------------------------------------|
| none                  |                        |           |               |
|----------------------------------------------------------------------------|
|SUPPRESSED SPECIES   (suppress,replace,augmentk,augmentg)    value |
|-------------------------------------------------------------------|
| none                  |               |          |                 |
|-------------------------------------------------------------------|
                                 Page 1
```

HCO_3^- + 8%

log activity

UO_2^{++} −12.2331

H^+ −7.0

$SiO_2(aq)$ −4.6483

$\log \frac{UO_2^{++}}{(H^+)^2} = 1.7669$

cc −3.093 kcal

cc = −3.093 kcal

DAP 8/25/00

```
                                 wvw9503f.3o
 EQ3/6, Version 7.2b (EQ3/6-V7-REL-V7.2b-PC)
 EQ3NR Speciation-Solubility Code (EQ3/6-V7-EQ3NR-EXE-R139-P5)
 Supported by the EQLIB library (EQ3/6-V7-EQLIB-LIB-R168-P5)

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 Run  11:58:34  05/28/98


 --- Reading the input file ---
|----------------------------------------------------------------------|
|EQ3NR input file name= wvw9503f.3i                                    |
|Description= "Calculate WVW95-03 water, 5/98"                         |
|Version level= 7.2                                                    |
|Created 05/28/97     Creator= D.A. Pickett                            |
|                                                                      |
|Calculate speciation and conditions in aquifer water near Nopal based |
|on lab and field chemical data. Set HCO3- to meas. field alkalinity as|
|"free molal."  All as basis species (including N).  Eliminate Fe as it|
|was not detected.  Auto basis switching is on because run would not   |
|converge otherwise.   Cl- is added; it was neglected earlier.         |
|                                                                      |
|----------------------------------------------------------------------|
|Temperature (C)        | 29.40        |Density(gm/cm3)|  1.00000      |
|----------------------------------------------------------------------|
|Total Dissolved Salts  |              | mg/kg | mg/l  |*not used      |
|----------------------------------------------------------------------------|
|Electrical Balancing on |Ca++                     | code selects| not performed|
|----------------------------------------------------------------------------|
| SPECIES               | BASIS SWITCH/CONSTRAINT| CONC/ETC  | UNITS OR TYPE |
|----------------------------------------------------------------------------|
|redox                  |                        |-1.60000   |LogfO2         |
|H+                     |                        | 7.7200    |pH             |
|Cl-                    |                        | 0.0001647 |molality       |
|Br-                    |                        | 2.18e-06  |molality       |
|F-                     |                        | 5.05e-05  |molality       |
|NH3(aq)                |                        | 2.23e-05  |molality       |
|SO4--                  |                        | 0.0001343 |molality       |
|Al+++                  |                        | 9.64e-07  |molality       |
|Ba++                   |                        | 5.17e-07  |molality       |
|B(OH)3(aq)             |                        | 4.53e-06  |molality       |
|Ca++                   |                        | 0.000803  |molality       |
|Cu++                   |                        | 6.29e-08  |molality       |
|Li+                    |                        | 1.30e-06  |molality       |
|Mg++                   |                        | 0.000314  |molality       |
|Mn++                   |                        | 2.06e-06  |molality       |
|MoO4--                 |                        | 3.44e-07  |molality       |
|K+                     |                        | 0.000111  |molality       |
|SiO2(aq)               |                        | 0.000260  |molality       |
|Na+                    |                        | 0.000465  |molality       |
|Sr++                   |                        | 4.47e-06  |molality       |
|Zn++                   |                        | 1.38e-07  |molality       |
|UO2++                  |                        | 7.13e-10  |molality       |
|Th++++                 |                        | 6.05e-13  |molality       |
|HCO3-                  |                        | 0.002498  |free molal     |
|----------------------------------------------------------------------------|
|Input Solid Solutions  |                        |           |               |
|----------------------------------------------------------------------------|
| none                  |                        |           |               |
|----------------------------------------------------------------------------|
|SUPPRESSED SPECIES   (suppress,replace,augmentk,augmentg)    value |
                                 Page 1
```

Ca^{++} + 16 %

log activity

UO_2^{++} −15.9177

H^+ −7.72

$SiO_2(aq)$ −3.5882

$\log \frac{UO_2^{2+}}{(H^+)^2} = -0.4777$

cc 0.186 kcal

```
                                        wvw9503g.3o

EQ3/6, Version 7.2b (EQ3/6-V7-REL-V7.2b-PC)
EQ3NR Speciation-Solubility Code (EQ3/6-V7-EQ3NR-EXE-R139-P5)
Supported by the EQLIB library (EQ3/6-V7-EQLIB-LIB-R168-P5)

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Run  12:00:56  05/28/98


 --- Reading the input file ---
|----------------------------------------------------------------------|
|EQ3NR input file name= wvw9503g.3i                                    |
|Description= "Calculate WVW95-03 water, 5/98"                         |
|Version level= 7.2                                                    |
|Created 05/28/97    Creator= D.A. Pickett                             |
|                                                                      |
|Calculate speciation and conditions in aquifer water near Nopal based |
|on lab and field chemical data. Set HCO3- to meas. field alkalinity as|
|"free molal."  All as basis species (including N).  Eliminate Fe as it|
|was not detected.  Auto basis switching is on because run would not   |
|converge otherwise.   Cl- is added; it was neglected earlier.         |
|                                                                      |
|Same as wvw9503f, except that electrical balancing is done on HCO3-.  |
|                                                                      |
|----------------------------------------------------------------------|
|Temperature (C)         | 29.40          |Density(gm/cm3)|  1.00000   |
|----------------------------------------------------------------------|
|Total Dissolved Salts   |                | mg/kg | mg/l  |*not used   |
|---------------------------------------------------------------------------|
|Electrical Balancing on |HCO3-                  | code selects| not performed|
|---------------------------------------------------------------------------|
| SPECIES                | BASIS SWITCH/CONSTRAINT| CONC/ETC   | UNITS OR TYPE |
|---------------------------------------------------------------------------|
|redox                   |                        |-1.60000    |Logfo2        |
|H+                      |                        | 7.7200     |pH            |
|Cl-                     |                        | 0.0001647  |molality      |
|Br-                     |                        | 2.18e-06   |molality      |
|F-                      |                        | 5.05e-05   |molality      |
|NH3(aq)                 |                        | 2.23e-05   |molality      |
|SO4--                   |                        | 0.0001343  |molality      |
|Al+++                   |                        | 9.64e-07   |molality      |
|Ba++                    |                        | 5.17e-07   |molality      |
|B(OH)3(aq)              |                        | 4.53e-06   |molality      |
|Ca++                    |                        | 0.000803   |molality      |
|Cu++                    |                        | 6.29e-08   |molality      |
|Li+                     |                        | 1.30e-06   |molality      |
|Mg++                    |                        | 0.000314   |molality      |
|Mn++                    |                        | 2.06e-06   |molality      |
|MoO4--                  |                        | 3.44e-07   |molality      |
|K+                      |                        | 0.000111   |molality      |
|SiO2(aq)                |                        | 0.000260   |molality      |
|Na+                     |                        | 0.000465   |molality      |
|Sr++                    |                        | 4.47e-06   |molality      |
|Zn++                    |                        | 1.38e-07   |molality      |
|UO2++                   |                        | 7.13e-10   |molality      |
|Th++++                  |                        | 6.05e-13   |molality      |
|HCO3-                   |                        | 0.002498   |molality      |
|---------------------------------------------------------------------------|
|Input Solid Solutions   |                        |            |              |
|---------------------------------------------------------------------------|
| none                   |                        |            |              |
                                   Page 1
```

HCO_3^- - 10 %

log activity

UO_2^{++} -15.8116

H^+ -7.72

$SiO_2(q)$ -3.5882

$\log \frac{UO_2^{2+}}{(H^+)^2} = -0.3716$

$\log fCO_2 = -2.56$

cc satd: 0.047 kcal

Want to compare these data with YM waters.

J-13 Use cation/anion chemistry from Ogard + Kerrisk (1984) and ~~U th data~~ DAP 6/22/94 U data from Laul + Maiti (1990).

The EQ3NR output file is j13dap.3o, and is saved on the "Nopal EQ3/6" diskette.

The first page of the file is shown on p. ~~33~~34.
DAP 6/22/98

From the output file:

$\log a_{SiO_2(aq)} = -2.9712$ (supersaturated)

$\log a_{UO_2^{++}} = -13.5687$

$\log a_{H^+} = -7.0000$

Note: See copy of notes on pp 37-38.

$\log \frac{a_{UO_2^{++}}}{(a_{H^+})^2} = 0.4313$

plotted by hand on the plots on pp 19-20.
Not very different from BH12 and ADIT 956.

YM Unsaturated Zone

Checked two Yang et al references:

1. USGS Water-Resources Investigations Report 96-4058
2. Un-numbered USGS Water-Resources Investigations Report (Yang, Yu, Rattray, Thorstenson) for DOE Level 3 Milestone 3 GUH607M.

I could find no U data from perched waters or "squeezed" waters.

Inspection of SiO_2 data resulted in the ranges shown on the p. 19 plot for "most UZ waters," "YM perched," and "YM squeezed." The latter is a very wide range.

A copy of notes on YM UZ water SiO_2 contents is on p. 37.

DAP 6/22/98

~~EQ6 Runs - BH12W95-11~~

```
                                  j13dap.3o

EQ3/6, Version 7.2b (EQ3/6-V7-REL-V7.2b-PC)
EQ3NR Speciation-Solubility Code (EQ3/6-V7-EQ3NR-EXE-R139-P5)
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Run  16:13:22  05/29/98


--- Reading the input file ---
|------------------------------------------------------------------|
|EQ3NR input file name= j13dap.3i                                  |
|Description= "Calculate J-13 water, 5/98"                         |
|Version level= 7.2                                                |
|Created 05/29/98     Creator= D.A. Pickett                        |
|                                                                  |
|Calculate speciation and conditions in J-13 water with uranium.   |
|Use J-13 chemistry from Ogard & Kerrisk (1984) as reported by Efurd et|
|al. (1997): LANL Milestone SP34FAM4, "Neptunium Redox Behavior and |
|Solubility in J-13 Conditions."  Use uranium concentration data from |
|Laul & Maiti, 1990, HLRWM Volume 1, "Natural radionuclides in     |
|groundwater from J-13 well at the Nevada Test Site."              |
|                                                                  |
|Auto basis switching on because did not otherwise converge.       |
|                                                                  |
|------------------------------------------------------------------|
|Temperature (C)        | 25.00       |Density(gm/cm3)|  1.00000   |
|------------------------------------------------------------------|
|Total Dissolved Salts  |             | mg/kg | mg/l  |*not used   |
|------------------------------------------------------------------------|
|Electrical Balancing on |Ca++                 | code selects| not performed|
|------------------------------------------------------------------------|
| SPECIES               | BASIS SWITCH/CONSTRAINT| CONC/ETC   | UNITS OR TYPE  |
|------------------------------------------------------------------------|
|redox                  |                     | 0.700      |eh              |
|H+                     |                     | 7.0000     |pH              |
|Cl-                    |                     | 0.00018    |molarity        |
|F-                     |                     | 0.00011    |molarity        |
|NH3(aq)                |                     | 0.00016    |molarity        |
|SO4--                  |                     | 0.00019    |molarity        |
|Al+++                  |                     | 1.00e-06   |molarity        |
|Ca++                   |                     | 0.00029    |molarity        |
|Li+                    |                     | 9.00e-06   |molarity        |
|Mg++                   |                     | 7.20e-05   |molarity        |
|Mn++                   |                     | 2.00e-08   |molarity        |
|K+                     |                     | 0.000136   |molarity        |
|SiO2(aq)               |                     | 0.00107    |molarity        |
|Na+                    |                     | 0.00196    |molarity        |
|UO2++                  |                     | 2.31e-09   |molarity        |
|Fe++                   |                     | 8.00e-07   |molarity        |
|HCO3-                  |                     | 0.00228    |molarity        |
|------------------------------------------------------------------------|
|Input Solid Solutions                                                   |
|------------------------------------------------------------------------|
| none                  |                     |            |                |
|------------------------------------------------------------------------|
|SUPPRESSED SPECIES   (suppress,replace,augmentk,augmentg)    value |
|------------------------------------------------------------------|
| none                  |                 |           |              |
|------------------------------------------------------------------|
|OPTIONS                                                           |
                                Page 1
```

EQ6 Modeling - BH12W95-11

Want to see what happens to U water chemistry as U is added by uraninite dissolution; e.g. minl saturation states, limits on dissolved U.

Use EQ6 reaction path modeling. (Note - this work is still in progress).

For input use bh12_11f.3p file. (See ~~also~~ DAP 6/22/98 p. 23). Set EQ6 to dissolve uraninite.

Input file bh12-11f.6i is on the "Nopal EQ3/6" diskette.

Results: $\log a_{UO_2^{++}} = -11.8989$

$\log a_{H^+} = -7.0473$

$\log a_{SiO_2(aq)} = -3.9993$ set by quartz.

$$\log \frac{a_{UO_2^{++}}}{(a_{H^+})^2} = 2.1957$$

$\log f_{CO_2} = -1.5782$.

Haiweeite is undersatured. Soddyite controls U dissolved. Because of $\log f_{CO_2}$, compare position on plot on p. 19. It is essentially at the intersection of the Quartz and Soddyite.

Therefore, addition of U by uraninite leads to saturation in and precipitation of Haiweeite and Soddyite according to thermodynamic calculations!

These calculations will be further developed and refined.

Nopal Water U-Th Data.

6/22/98
DAP

These data were first discussed in notebook 126, pp 56-58. Shown there is a hard copy of the isotopic data as delivered by the Univ. of Minnesota (file "Minn UTh data.xls" in attached diskette "Nopal Water Data." Also shown is a plot of $^{234}U/^{238}U$ versus 1/[U], showing a linear correlation among Nopal UZ waters. The WW carbonate aquifer appears completely unrelated.

[U] higher in BH-12 than in adit waters. 234/238 lower.

These data will be investigated further.

Look for any patterns relating to effect of host rocks.

See if can constrain at all the amount of U that could have been removed from the deposit based on 234/238 of waters and lack of change in deposits 234/238 of unity.

On 6/19/98, the information on these pages (1 - 36) was incorporated into an abstract titled "Unsaturated Zone Waters from the Nopal I Natural Analog, Chihuahua, Mexico – Implications for Radionuclide Mobility at Yucca Mountain" and submitted to the Fall 1998 MRS meeting.

Notes on - YM UZ SiO_2 (see p. 33)
- J-13 EQ3 calculations (p. 33)

YM UZ water SiO_2 (aq) 5/29/98

From Turner's Excel file

Lowest porewater
3.329×10^{-6} M UE-25 UZ-N2 30.10 m
log a_{SiO_2} = -5.4777

Highest porewater
5.858×10^{-3} M USW UZ-1K 644.33 m
log = -2.2323

Lowest perched
1.282×10^{-4} M USW UZ-14 390.75 m
log = -3.8921

highest perched
1.068×10^{-3} M USW SD-9/TS 453.85 m
log -2.9714

overall avg	1.216×10^{-3} M	log a = -2.9151
Perched avg	6.675×10^{-4} M	log = -3.1755

EQ3 run j13 dap. 3i

$\Rightarrow$ log $a_{UO_2^{++}}$ = -13.5687
log a_{H^+} = -7.0
log $a_{SiO_2(aq)}$ = -2.9712

log $\frac{UO_2^{++}}{(H^+)^2}$ = 0.4313

(note: cc not sat, charge balance required lg change in Ca^{++})

with all haul data
log $a_{UO_2^{++}}$ = -13.5113
log a_{H^+} = -7.0
log a_{SiO_2} = -2.9794
(Ca^{++} changed a lot)

log $\frac{UO_2^{++}}{(H^+)^2}$ = 0.4887

continued.

5/29/98
p. 2

Again in these J13 runs, Haiweeite + Soddyite are excluded.

Run j13haiw → set U by Haiweeite.
(My plot shows it should be sat — except I assume cc sat.)
Total U → 1.95×10^{-9} molal (versus 2.31×10^{-9} molal in Laul)

So, J-13 is oversat w.r.t. Haiweeite! (very slightly)

Both Soddyite + Haiweeite are now in minl sat list (Soddyite undersat)
$\log a_{UO_2^{++}} = -13.5852$

9/8/98

Summary of previous EQ6 modeling of BH12-11 water dissolving uraninite.
<u>All</u> use bh12-11f.3p as pickup file from EQ3NR.

<u>EQ6 file</u>	<u>notes</u>	$\log \frac{[UO_2^{++}]}{[H^+]^2}$	$\log(SiO_{2(aq)})$	<u>Product U phases</u>	<u>CC sat?</u>
bh12_11f	Closed	2.20	-4.00	Soddy	Y
bh1211f2	Open	1.62	-4.57	$UO_{2.25}$, Soddy (undersat)	Y
bh1211f3	Closed. Suppress all Si-containing minls.	4.36	-3.18	Tyuyam, $UO_{2.667}$	Y
bh1211f4	Closed. Suppress <u>except</u> Soddy, Haiw, Schoep, CC (?)	2.20	-4.00	Soddy	Y
bh1211f5	Closed. Suppress Qz in pick-up portion.	2.11	-3.83	Soddy	Y
bh1211f6	Closed. Suppress Qz, Trid, Stilb in pick-up portion.	2.06	-3.73	Haiw, Soddy	Y
bh1211f7	Closed. Add Kaolinite to Suppress list for bh1211f6.	2.06	-3.73	"	Y
bh1211f8	Closed. bh1211f7, but also Suppress all Al-containing.	2.06	-3.73	"	Y

Effects of Kaolinite and other Al-containing phases is negligible.

Now, go back and suppress only the three silica phases Quartz, Tridymite, & Chalcedony.
(it was very close to satd in —6, —7, and —8.)
→ bh1211f9

For bh1211f9, $\log \frac{[UO_2^{++})}{(H^+)^2} = 2.06$ and ↙ activities
$\log [SiO_2(aq)] = -3.73$. So, chalcedony is not controlling SiO_2.

Wait! Look at page 19 — the intersection between Haiweeite + Soddyite is probably at this point at $\log f_{CO_2} = -1.8$ (figure is at −2.0). So the U phases are controlling SiO_2.

bh121f9b → Same as bh1211fd, except use the "titration" model.
→ Same results as at top of page for bh1211fd.

bh121f9c → same, except use "open" model.

$\log \frac{\{UO_2^{++})}{(H^+)^2} = 1.62$ $\log [SiO_2(aq)] = -3.84$

U products → $\underbrace{\text{Soddy, Haiw}}_{\text{not satd}}$, $\underset{\uparrow\ \text{satd}}{UO_{2.25}}$

Note - final log f_{O_2} is much lower here (−52) compared to bh1211f9 (−19) and bh121f9b (−19). It drops drastically near the end with very little reaction progress. Is this when soddyite and/or haiweeite saturation is reached? Not exactly....

9/9/98
DAP

Look at bh121f9c to try and understand drop in f_{O_2} (see previous page).

On output file, seems to coincide with the removal of Pyrolusite (MnO_2) from the assemblage in order to allow convergence. (after step # 149). After this:
- Log f_{O_2} drops to −44.2; was −7.7 after previous printed interval (after # 118 step?)
- Dissolved Mn^{++} goes from $10^{-10.0}$ molal to $10^{-7.3}$ m.

i.e., Pyrolusite is removed from the system. I note that some was dissolved because in the "Grand Summary of Solid Phases," Pyrolusite volume drops a little.

Pyrolusite solubility reaction is
$$\text{Pyrolusite} + 2H^+ = \tfrac{1}{2}O_2(g) + H_2O + Mn^{++}$$

So, driving the reaction to the right should increase f_{O_2}. (Mn is reduced.) ?

Test the effect of Mn phases by doing a run with Mn phases suppressed → bh121f9d. Still see a drop; final value is −52.7 for log f_{O_2}.
∴ Mn phases *not* responsible.

So, what happens? Keep looking at bh121f9d.
After step 130 (Log z_i = ~~−3.770~~ DAP 9/9/98 −3.739), Log f_{O_2} = −9.177. $[U] = 9.97 \times 10^{-7}$ m, $\{UO_2^{++}] = 1.64 \times 10^{-12}$ m, Haiw undersat, Soddy satd.

After step 151 (Log z_i = −3.737), Log f_{O_2} = −46.197, $[U] = 9.99 \times 10^{-7}$ m, $[UO_2^{++}] = 1.64 \times 10^{-12}$ m, Haiw + Soddy same.
So — U phases don't appear responsible.

What about Cu? Cuprite was oversaturated in steps before the big drop in fO_2. But Cuprite solub reaction is not a redox reaction.

bh121f9e.6i — same as ~~bh121f9d~~, ~~[illegible]~~ DAP 9/3/98 bh121f9d.6i, ~~but~~ replace Mn with Cu. Same thing!

Is there a change in solid assemblage? Look at bh121f9e.

		After step 150
After step 118:	Log Zi = -4.00	-3.83
	Log fO_2 = -7.73	-44.2
	[U] = 8.6×10^{-7} m	9.4×10^{-7} m
	Log $a_{UO_2^{++}}$ = -11.9618	-11.9489
	dvol Uranin 0.05 cc	0.07
	dVol Soddy 65.5 cc	-131
	Solid phases: CC, Cristobal, Dolo, Fluorap, Haiw, Pyrolus, Soddy, Still, Thor, Wither	Same
	dvol Pyrolus -4.96×10^{-4}	
	"Just precip phases": same as → except + pyrolusite	Fluorap, Soddy, Still, Thor, Wither

bh121f9f — Suppress both Cu and Mn phases. It happens again, though later in progress.

I'll just accept it as a continued exhaustion of O_2 due to Uraninite dissolution. Remember - this is Log scale.

Summarize bh1211f9 and bh121f9* runs

	notes	$\log\frac{[UO_2^{++}]}{[H^+]^2}$	$\log(SiO_{2(aq)})$	Pred. U phases
bh1211f9	Closed. Suppress Qz, Trid, Chalc	2.06	-3.73	Haiw, Soddy
bh121f9b	Titration. Suppress Qz, Trid, Chalc	"	"	"
bh121f9c	Open. Suppress Qz, Trid, Chalc	1.62	-3.84	Haiw, Soddy, $UO_{2.25}$
bh121f9d	Open. Suppress Qz, Trid, Chalc, Mn	1.32	-3.89	" " "
bh121f9e	Open. Suppress Qz, Trid, Chalc, Cu	1.84	-3.84	" " "
bh121f9f	Open Suppress Qz, Trid, Chalc, Cu, Mn	1.32	-3.89	" " "

Now, I want to impose oxygen fugacity, so that it is not changed by the reactions. Reasonable for the unsaturated zone. Use the Log fO_2 used in EQ3NR (measured). For BH-12-11, this is -1.81. (Have to input 1 mole, because 0.5 mole wasn't enough.)

→ bh121f9g.6i "open," Log fO_2 = -1.81, Qz, Trid, chalc suppressed.

Result: Uraninite is completely dissolved.
U Products are Soddyite, Haiweeite, Tyuyamunite, $UO_3 \cdot 2H_2O$.
↑ satd ↑ unsatd ↑ satd ↑ satd

[U] = 5.75×10^{-4}

Calcite unsat.

$\log \frac{UO_2^{++}}{H^{+2}} = 4.8335$

$\log SiO_{2(aq)} = -9.2747$

i.e., Use up Si! rather than O_2.

bh121f9h — Same as bh121f9g, but Closed.
U products : Soddy, Tyuya, $UO_3:2H_2O$, $CaUO_4$
Uraninite is not completely disolved
[U] = 6.4×10^{-4} m

Log $\frac{UO_2^{++}}{H^{+2}}$ = 4.8335 Log $SiO_2(aq)$ = −9.2747

Same point, except $CaUO_4$ is also satd. Also, Haiweeite is gone because closed system.

slightly

Note: Calcite unsat. This is probably because the U being added to solution is taking up $CO_3^{=}$. The chief U aqueous species is $UO_2(CO_3)_2^{--}$, and the next three species down in abundance are also carbonate or hydroxycarbonate.

A thought on how to proceed with other waters: Perform four EQ6 calculations:
- Closed with no fO_2 constraint.
- Open " " "
- Closed with fO_2 fixed.
- Open " " "

For all, suppress the three silica phases Qz, Tridymite, + Chalcedony. Remember to carefully choose the EQ3NR pick up file. Experiment with allowing reaction to progress further.

Change print constraints in input file:
- show only species > 10^{-20} molal
- print gas species

9/10/98
DAP

More EQ6 — All waters from Nopal

BH12-11 Re-do. This time, use bh12_11g.3p for pickup file. In that run, charge was balanced on HCO_3^-. It was adjusted upward only 6 ~~7~~ % DAP 9/10/98 (see page 24). See page 44 for other parameters (e.g. suppressed phases)

bh1211_1 Closed, no fO_2 constraint
U + Si results very similar to bh1211f9 (p. 43)
Log fO_2 = −44.8 Log fCO_2 = −1.51 CC satd Aff = 0.000

bh1211_2 Open, no fO_2 constraint.
U + Si results very similar to bh121f9c (p. 43)
Log fO_2 = −51.9 Log fCO_2 = −1.51 CC satd −0.003

bh1211_3 Closed, fO_2 = −1.81
U + Si results identical to bh121f9h (p. 44)
Log fCO_2 = −1.50 CC a little undersatd −0.077

bh1211_4 Open, fO_2 = −1.81
U + Si results identical to bh121f9g (p. 43)
Log fCO_2 = −1.45 CC unsatd −0.263

bh1211_5 Closed, fO_2 = −1.81, fCO_2 = −1.78 fixed. → EQ3 result.
Results identical to bh1211_3. CC unsatd −0.455

bh1211_6 Open, fO_2 = −1.81, fCO_2 = −1.78 fixed.
Results identical to bh1211_4, except add $CaUO_4$. cc unsatd −0.455

bh1211_7 Closed, with atmospheric Log fO_2 (−0.68) + Log fCO_2 (−3.5) fixed.
Log $\frac{UO_2^{++}}{H^{+2}}$ = ~~4.8337~~ 3.9717 DAP 9/10/98 Log $SiO_2(aq)$ = −7.5512

Calcite not saturated. Aff = −1.626
U phases : Soddy ~~is all~~ DAP 9/10/98, $CaUO_4$

6h1211-8 Open, with atmos O_2 + CO_2 as in 6h1211-7.

$\text{Log} \frac{UO_2^{++}}{H^{+2}} = 4.8333$ $\text{Log } SiO_2(aq) = -9.2746$

$[U] = 4 \times 10^{-5}$ m   Cc unsatd (-2.802)

U product phases: $CaUO_4$, Carnotite, Haiweeite, Soddy, $UO_3:2H_2O$. (Haiw unsat.)

9/11/98
DAP

Digression to look at Moll et al (1986) Soddyite solubility data.

(reference Radiochimica Acta, v. 74, p3-7, 1996)

In the paper, they calculate a Log K_{sp} for the reaction

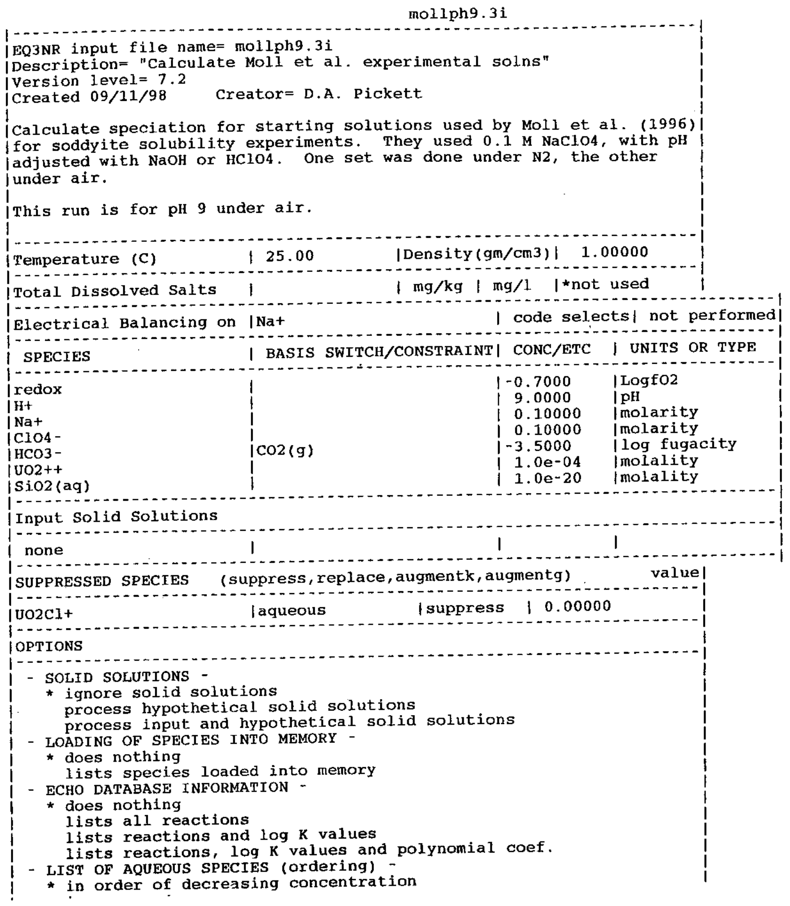
$$(UO_2)_2SiO_4 \cdot 2H_2O + 4H^+ \rightleftharpoons 2UO_2^{2+} + SiO_2(aq) + 4H_2O$$

from their results at pH 3. They do not attempt to calculate LogK_{sp} at any other pH values because of U complexation at higher pH. I am curious if their results are consistent with the determined Log K_{sp} — look just at experiments in air. LogK_{sp} (pH 3) = 6.15.

I will calculate - using EQ3 - the U speciation in solution at pH 3, 4, 5, 6, 8, 9 under their experimental conditions:

0.1 M $NaClO_4$
in air
pH adjusted with NaOH or $HClO_4$.

On the following page is an example input file. It doesn't much matter what U concentration I use, as long as I can see what the UO_2^{2+} concentration is in the result. SiO_2(aq) also needs to be included for calculating the Log Ksp. (not really)



```
                              mollph9.3i
|-----------------------------------------------------------------------|
|EQ3NR input file name= mollph9.3i                                      |
|Description= "Calculate Moll et al. experimental solns"                |
|Version level= 7.2                                                     |
|Created 09/11/98     Creator= D.A. Pickett                             |
|                                                                       |
|Calculate speciation for starting solutions used by Moll et al. (1996)|
|for soddyite solubility experiments.  They used 0.1 M NaClO4, with pH |
|adjusted with NaOH or HClO4.  One set was done under N2, the other     |
|under air.                                                             |
|                                                                       |
|This run is for pH 9 under air.                                        |
|                                                                       |
|-----------------------------------------------------------------------|
|Temperature (C)        | 25.00         |Density(gm/cm3)|  1.00000      |
|-----------------------------------------------------------------------|
|Total Dissolved Salts  |               | mg/kg | mg/l  |*not used      |
|------------------------------------------------------------------------------|
|Electrical Balancing on |Na+                        | code selects| not performed|
|------------------------------------------------------------------------------|
| SPECIES               | BASIS SWITCH/CONSTRAINT| CONC/ETC   | UNITS OR TYPE |
|------------------------------------------------------------------------------|
|redox                  |                        |-0.7000     |LogfO2         |
|H+                     |                        | 9.0000     |pH             |
|Na+                    |                        | 0.10000    |molarity       |
|ClO4-                  |                        | 0.10000    |molarity       |
|HCO3-                  |CO2(g)                  |-3.5000     |log fugacity   |
|UO2++                  |                        | 1.0e-04    |molality       |
|SiO2(aq)               |                        | 1.0e-20    |molality       |
|------------------------------------------------------------------------------|
|Input Solid Solutions                                                         |
|------------------------------------------------------------------------------|
| none                  |                        |            |               |
|------------------------------------------------------------------------------|
|SUPPRESSED SPECIES   (suppress,replace,augmentk,augmentg)           value|
|-----------------------------------------------------------------------|
|UO2Cl+                 |aqueous         |suppress   | 0.00000          |
|-----------------------------------------------------------------------|
|OPTIONS                                                                |
|-----------------------------------------------------------------------|
| - SOLID SOLUTIONS -                                                   |
|   * ignore solid solutions                                            |
|     process hypothetical solid solutions                              |
|     process input and hypothetical solid solutions                    |
| - LOADING OF SPECIES INTO MEMORY -                                    |
|   * does nothing                                                      |
|     lists species loaded into memory                                  |
| - ECHO DATABASE INFORMATION -                                         |
|   * does nothing                                                      |
|     lists all reactions                                               |
|     lists reactions and log K values                                  |
|     lists reactions, log K values and polynomial coef.                |
| - LIST OF AQUEOUS SPECIES (ordering) -                                |
|   * in order of decreasing concentration
```

What I will do is:

1. Estimate the total U concentration at each pH value from the tables and figures in Moll et al. (just air experiments
2. Calculate $[UO_2^{2+}]$ at each point based on the U speciation calculated by EQ3. ~~at~~ DAP 9/11/98
3. Assume stoichiometry, so that $[SiO_2(aq)]$ is one half of $[UO_2^{2+}]$ — Remember, this results from dissolution of soddyite. May have to adjust for other Si species.
4. Calculate Log K_{sp} at each pH.

pH 3 (Sample AII)

U is 99.7% UO_2^{2+} ⇒ 1.95×10^{-2} M

This is given on page 5, along with the $SiO_2(aq)$ conc of 1.00×10^{-2} M.

$$\text{Log } K_3 = \text{Log}\left[\frac{(0.0195)^2(0.01)}{(10^{-3})^4}\right] = 6.58$$ (they say 6.60)

Ionic strength adjustments brings this down to $\boxed{6.15}$, according to page 5 of Moll et al. I'll use this same adjustment in the other calculations, because "I" is similar in all.

pH 4 (Sample ~~A~~BII)

U is 97.0% UO_2^{2+}

Figs 2 and 3 → $[U] \simeq 1.58 \times 10^{-3}$ M

⇒ $[UO_2^{2+}] \simeq 1.54 \times 10^{-3}$ M

→ $[SiO_2(aq)] \simeq 7.7 \times 10^{-4}$ M $SiO_2(aq) = 100\%$

$$\text{Log } K_4 = \text{Log } \frac{(1.58 \times 10^{-3})^2 (7.7 \times 10^{-4})}{(10^{-4})^4} = 7.28$$

⇝ $\text{Log } K_{4_0} \cong 6.8$

~~pH 5 (Sample ~~B~~ DAP 9/21/98 C II)~~

~~U is 67.95% UO_2^{2+}~~

~~Figs 2+3 → $[U] \simeq 2 \times 10^{-4}$ M~~ DAP 9/21/98

~~→ $[UO_2^{2+}] \simeq 1.4 \times 10^{-4}$ M~~

~~→ $[SiO_2(aq)] \simeq 7 \times 10^{-5}$ M~~

~~$\text{Log } K_5 = \text{Log } \frac{(1.4 \times 10^{-4})^2 (7 \times 10^{-5})}{(10^{-5})^4} =$~~

Problem — Because we assume stoichiometric dissolution of Soddyite, the total U molality must be twice the total Si molality. Therefore, total Si dissolved should be calculated from total U, and both then speciated according to EQ3. Doesn't affect pH 3 and 4 results, because

UO_2^{2+} and $SiO_2(aq)$ are essentially 100% species.

pH 5 (Sample C II)

Figs 2 and 3 → $[U] \simeq 2 \times 10^{-4}$ M

⇒ $[UO_2^{++}] \simeq 1.4 \times 10^{-4}$ M } 67.95%

→ $[Si] \simeq 1.0 \times 10^{-4}$ M (and $SiO_2(aq)$ is 100%)

$$\text{Log } K_5 = \text{Log}\left[\frac{(1.4 \times 10^{-4})^2 (1.0 \times 10^{-4})}{(10^{-5})^4}\right] = 8.29$$

$\text{Log } K_{5_0} \sim 7.9$

pH 6 (Sample DII)

Figs 2+3 → $[U] \simeq 8 \times 10^{-6}$ M

$UO_2^{2+} \sim 4.56\%$ ⇒ $[UO_2^{2+}] \simeq 3.7 \times 10^{-7}$ M

$SiO_2(aq) \sim 100\%$ → $[SiO_2(aq)] \simeq 4 \times 10^{-6}$ M

$$\text{Log } K_6 = \text{Log } \frac{(3.7 \times 10^{-7})^2 (4 \times 10^{-6})}{(10^{-6})^4} = 5.74$$

$\text{Log } K_{6_0} \sim 5.3$

pH 8 (Sample EII)

Figs 2+3 → $[U] \simeq 1 \times 10^{-4}$ M

$UO_2^{2+} \sim \frac{2.45 \times 10^{-11}}{2.94 \times 10^{-5}} \times 58.85\%$ ⇝ 4.9×10^{-5} % of U

conc. most abundant U species   % for most abundant U species

⇒ $[UO_2^{2+}] \simeq 4.9 \times 10^{-11}$ M

$SiO_2(aq) = 94.97\%$ of Si

→ $[SiO_2(aq)] \simeq (1 \times 10^{-4})(\frac{1}{2})(0.9497) \simeq 4.7 \times 10^{-5}$ M

$$\text{Log } K_8 = \text{Log } \frac{(4.9 \times 10^{-11})^2 (4.7 \times 10^{-5})}{(10^{-8})^4} = 7.05$$

$\text{Log } K_{8_0} \sim 6.6$

See Moll fig 2

Note - not steady-state.

pH 9 (Sample F II)

Figs 2 + 3 → [U] ≈ 4×10^{-4} M

$UO_2^{2+} \approx \frac{8.77 \times 10^{-17}}{9.96 \times 10^{-5}} \times 99.61\% \approx 8.77 \times 10^{-11}\ \%$

(see pH 8)

$\simeq 3.5 \times 10^{-16}$ M

$SiO_2(aq)$ is 64.27 % of Si

↳ $\simeq (4 \times 10^{-4})(\frac{1}{2})(0.6427) \simeq 1.3 \times 10^{-4}$ M

$$\text{Log } K_9 = \text{Log } \frac{(3.5 \times 10^{-16})^2 (1.3 \times 10^{-4})}{(10^{-9})^4} = 1.20$$

$\text{Log } K_{90} \simeq 0.8$

To summerize: My calculated $\text{Log } K_{sp,0}$ from Moll's data and U + Si speciations by EQ 3:

pH	3	6.2
	4	6.8
	5	7.9
	6	5.3
	8	6.6
	9	0.8

Not too bad, except for pH 9.

What should [U] have been at pH 9?

$UO_2^{2+} = (8.77 \times 10^{-13})\, U$

$SiO_2(aq) = (0.32)\, U$

Assume Log K = 7

$$7 = \text{Log } \frac{(8.77 \times 10^{-13})^2 U^2 (0.32) U}{10^{-36}}$$

$$= \text{Log } \left(\frac{U^3}{4.1 \times 10^{-12}} \right)$$

$U^3 = 10^7 \times 4.1 \times 10^{-12}$

$U = \underline{3.4 \times 10^{-2}\ M}$

But - maybe another U phase(s) comes into play.

Do an EQ3 run for these pH 9 conditions.
U input as UO_2^{++} (basis) at 3.4×10^{-2} molal
Si input as $SiO_2(aq)$ (basis) at 1.7×10^{-2} molal
Otherwise like previous pH 9 input (e.g. air for O_2 + CO_2). Name mollpH9x.
Soddyite is the only ssatd U phase. & SiO_2 (am) is ssatd.
Note that the SiO_2 speciation is different.
$SiO_2(aq)$ is 45 %, not 64.
And U speciation is quite different. I should have done the EQ3 calcs with the appropriate U + Si !.

Do all pH runs again, appending "x" to file name. Input U and Si according to estimated U from Moll et al figures, and Si = ½U.
~~No need to do this for~~ DJP 9/11/98
Speciation is not simply a function of pH, but also of relative concentrations of other aqueous species. For

DJP 9/14/98

~~pH 3~~
~~$UO_2^{2+} = 1.75 \times 10^{-2}$ m~~
~~$SiO_2(aq) = 1.00 \times 10^{-2}$ m~~
~~ssatd U phases = Soddyite~~

$\text{Log } K_{30} =$ ~~6.1~~ 6.5 DJP 9/11/98

~~pH 4~~
~~$UO_2^{2+} = 1.21 \times 10^{-3}$ m~~
~~$SiO_2(aq) = 7.9 \times 10^{-4}$ m~~
ssatd U phases = Soddyite

$\text{Log } K_{40} = 7.1$

9/14/98 The above two calculations are incorrect — Should use the calculated <u>activities</u> of the ions for calculating Log Ko.
But - I am not doing an ionic strength calculation.

Recall: these are for air.

pH 3
$\text{Log } a_{UO2++} = -2.2625$
$\text{Log } a_{SiO2(aq)} = -2.0000$
$\text{Log } a_{H^+} = -3.0000$
$\text{Log } K_{30} = 2(-2.2625) + (-2) - 4(-3) = 5.48$ by concs = 6.5 see above

pH 4

Log a_{UO2++} = -3.3591
Log $a_{SiO2(aq)}$ = -3.1024
Log K_4 = 6.18 by concs → 7.1

pH 5

Log a_{UO2++} = -4.7265
Log $a_{SiO2(aq)}$ = -4.0000
Log K_5 = 6.55 by concs → 7.1
ssatd U phases: Schoepite, Soddyite, three uranyl hydrates

pH 6

Log a_{UO2++} = -6.9967
Log $a_{SiO2(aq)}$ = -5.3982
Log K_6 = 4.61 by concs → 5.2
ssatd U phases: Same as pH 5.

pH 8

Log a_{UO2++} = -11.0497
Log $a_{SiO2(aq)}$ = -4.3235
Log K_8 = 5.58 by concs → 6.1
ssatd U phases: $Na_2U_2O_7$, Schoepite, Soddyite, 2 uranyl hydrates

pH 9 (mollph9y.3i)

Log a_{UO2++} = -15.9222
Log $a_{SiO2(aq)}$ = -3.8921
Log K_9 = 0.26 by concs → 0.8
ssatd U phases: none

Summary of new Log K calcs (using actually concentrations and activities.)

pH	3	5.5	6.5 by concentrations rather than activities
	4	6.2	7.1
	5	6.6	7.1
	6	4.6	5.2
	8	5.6	6.1
	9	0.3	0.8

mean of 1st 5 = 5.7

Re-run a few of the BHR-11 EQ6 runs from page 45.
The following runs did not appear to reach a steady state [U] and/or did not completely dissolve the uraninite. Previously had a maximum of 200 steps

bh1211_1 Re-run allowing 400 steps as bh1211#1.
bh1211_2 " " " " " bh1211#2.
bh1211_7 " " " " " bh1211#7.

bh1211#1 : Now quits when uraninite saturation is reached.
Final U phases: Haiweeite, $UO_{2.25}$, Uraninite - all satd.
cc satd. Log fCO_2 = -1.51
Log $\frac{(UO2++)}{(H^+)^2}$ = 1.3191 Log $((SiO_2(aq)))$ = -3.4760

bh1211#2 : Also quits at uraninite saturation.
Final U phases: Soddyite, Haiweeite, $UO_{2.25}$, Uraninite - only the latter two are satd.
cc satd. Log fCO_2 = -1.51
Log $\frac{\{UO2++\}}{[H^+]^2}$ = 1.3192 Log $[SiO_2(aq)]$ = -3.8323

bh1211#7: Quits when uraninite is used up - [Si] and [U] converge before this (at ~ Zi = 0.01)
Final U phases: $CaUO_4$, Soddyite, $UO3:2H2O$ - all satd.
cc undersatd. Log fCO_2 = -3.5 (fixed)
Log $\frac{[UO2++]}{[H^+]^2}$ = 4.8333 Log $[SiO_2(aq)]$ = -9.2746.

Summarize final round of BH12-11 EQ6 runs

activity→	Log $\frac{[UO_2^{++}]}{[H^+]^2}$	Log [SiO_2(aq)]	Uraninite termination	Notes	
bh1211#1	1.3191	−3.4760	sat		
bh1211#2	1.3192	−3.8323	sat	Path similar to #1	
bh1211-3	4.8335	−9.2747	used	cc slightly unsatd.	
bh1211-4	4.8335	−9.2747	used	Path similar to _3. cc more unsatd.	
bh1211-5	4.8335	−9.2747	used	cc more unsatd	Similar to 3+4, except [U] is 1/2. (lower CO_2?)
bh1211-6	4.8334	−9.2747	used	Path similar to _5.	
bh1211#7	4.8333	−9.2746	used	similar paths; also like 5+6, less [U]. More gradual.	
bh1211-8	4.8333	−9.2746	almost used	cc highly unsatd	

9/15/98 DAP

Note: under the conditions of Runs 3,5,6,7,8, CaUO4 and Schoepite (or UO_3:$2H_2O$) coincide on my plot at Log $\frac{[UO_2^{++}]}{(H^+)^2}$ = 4.8334. This is also the reaction end point.

For a more detailed look at the reaction progress, it is probably worth only looking at 1 or 2, and 7 or 8. Open versus closed doesn't affect the path of aqueous chemistry much, and 3,4,5, and 6 are a lot like 7 and 8.

Note: Cristobalite is present + oversaturated initially. Run again, with Cristobalite added to the suppressed list:

bh1211@1.6i – Doesn't affect final results.
bh1211@2.6i – Does affect final SiO_2 (aq)

Wait – Coesite is controlling SiO_2 (aq) to just

below the starting concentration.

Re-do these, + 7+8, with Coesite suppression added.

bh1211c1 Closed, determined O_2 + CO_2.
bh1211c2 Open, determined O_2 + CO_2.
bh1211c7 Closed, atmos O_2 + CO_2
bh1211c8 Open, atmos O_2 + CO_2

Take the *.6t ~~ouptu~~ DAP 9/15/98 output files and translate to Excel workbooks. Note – it was necessary to input some data (e.g. UO_2^{++}) manually.

bh1211c1.xls
bh1211c2.xls
bh1211c7.xls
bh1211c8.xls

9/16/98 DAP

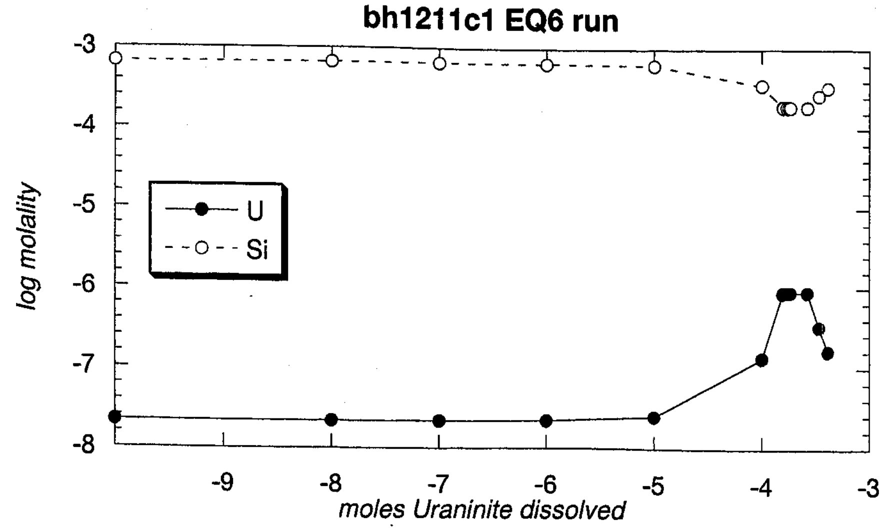
Move some of the data from the above Excel files into KaleidaGraph data files and plot up for each EQ6 run:

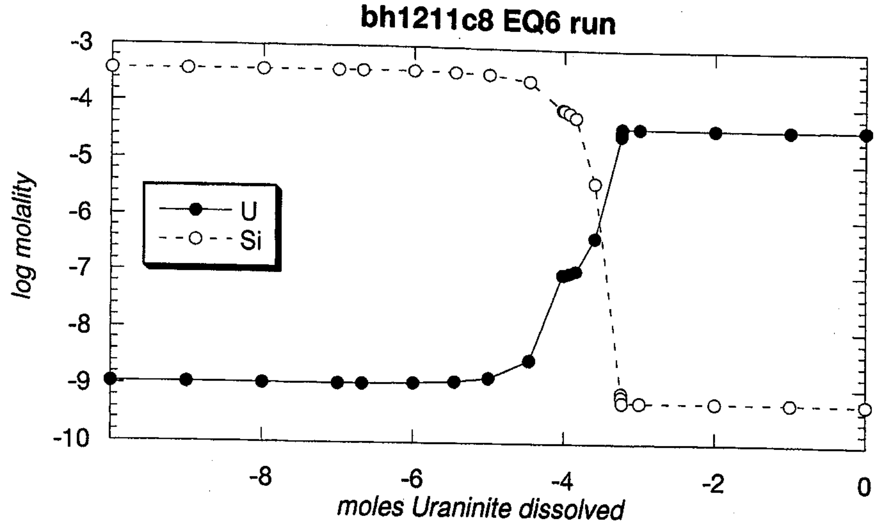
- U + Si molality
- cumulative moles of Uranium minerals

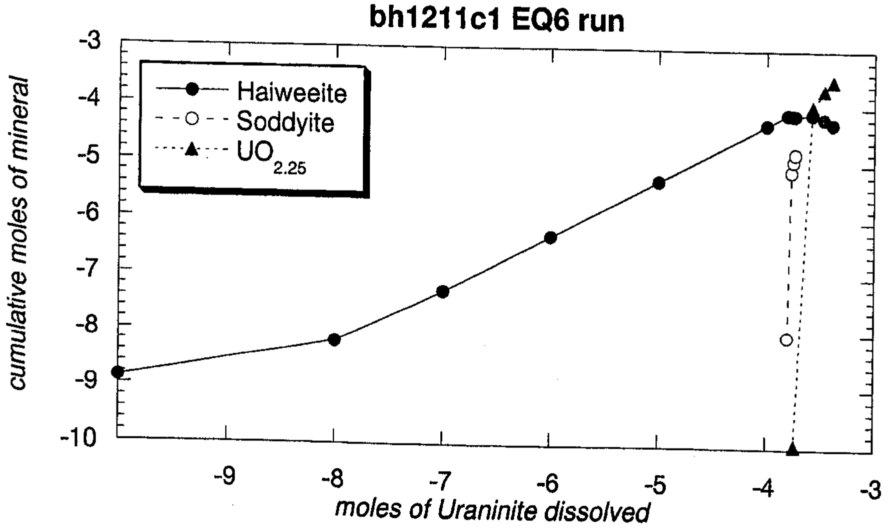
Plotted against moles Uraninite dissolved.
Plots for bh1211c1 and bh1211c8 are shown on the following pages. Results for bh1211c2 are similar to bh1211c1, and bh1211c7 is similar to bh1211c8.

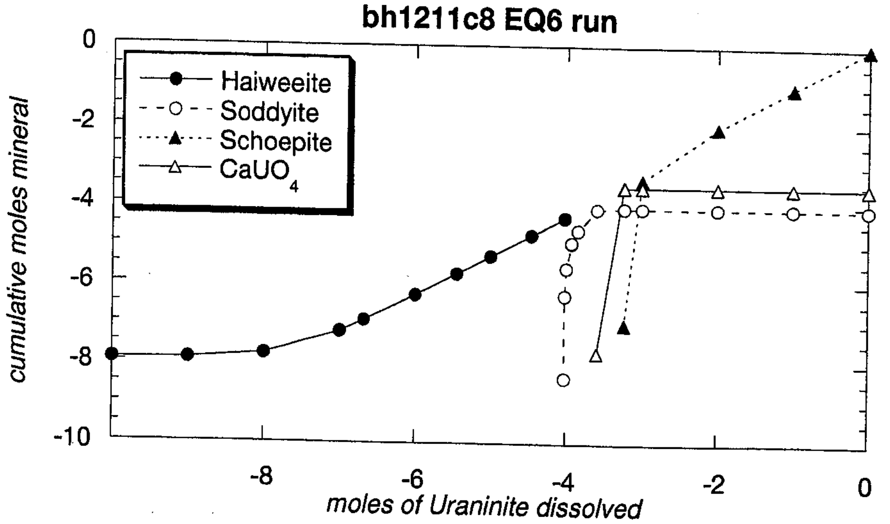
Notes: – Downturn in U in #1 is due to reducing conditions, as is appearance of $UO_{2.25}$. O_2 is used up in closed system.
– Air conditions (#8) allow complete Uraninite dissolution and higher U – controlled by Schoepite solubility. Solub. of Haiweeite and Soddyite don't matter.
– 1 and 2 ended with Uraninite saturation (low fO_2)
– 7 and 8 ended with Uraninite exhaustion.

Note - all are log values


bh1211c1 EQ6 run


bh1211c8 EQ6 run


bh1211c1 EQ6 run


bh1211c8 EQ6 run

9/17/98
DAP

The KaleidaGraph files ~~for~~ the preceding are

data file: BH12-11 data by Zi.QDA

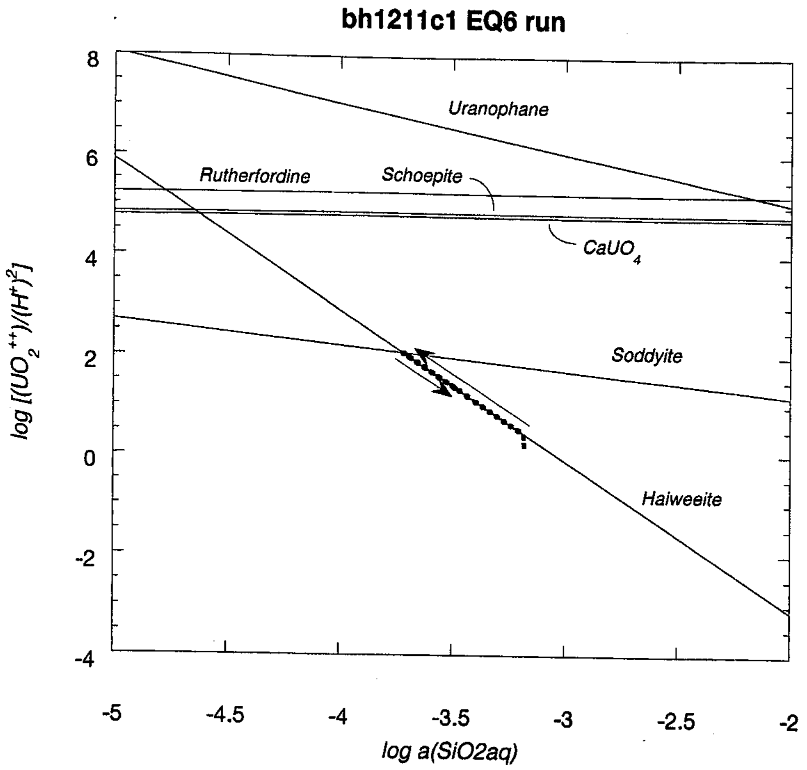
plot files: bh1211c1 U and Si.QPC
. . . . . 2 " " "
. . . . . 7 " " "
. . . . . 8 " " "
bh1211c1 minls.QPC
. . . . 2 " "
. . . . 7 " "
. . . . 8 " "

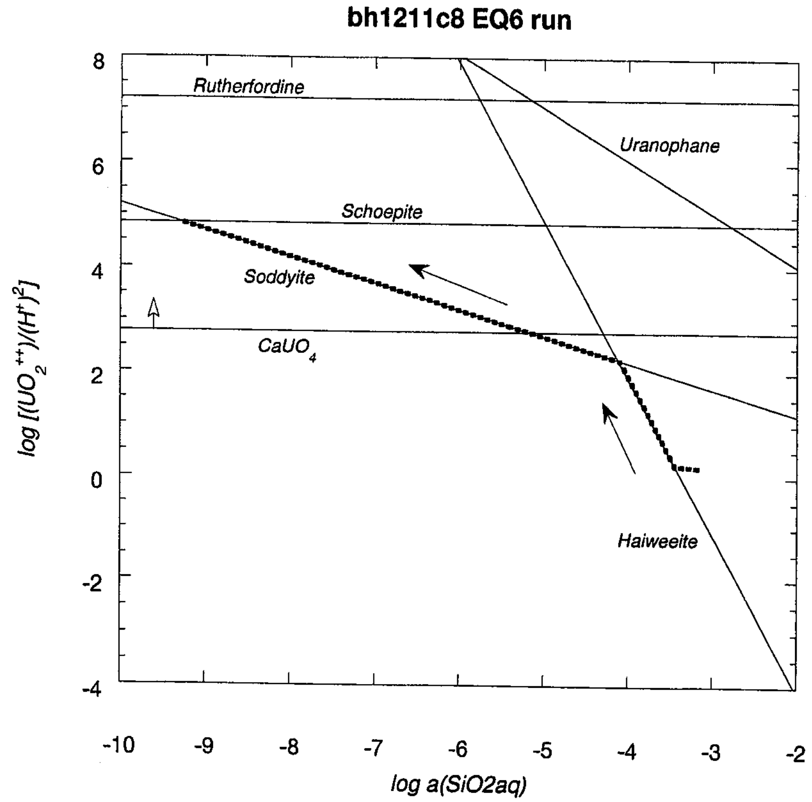
Now plot the reaction path of water chemistry on the activity plot discussed on pages 10 to 20.

data file: BH12-11 data.QDA
plot files: bh1211c1 progress.QPC
. . . . 8 " "

Shown on next page. Note different x axes.
The positions of the mineral saturation lines are different because of the different log fCO₂ for the two simulations:
bh1211c1 - calculated at ~ -1.51 throughout
bh1211c8 - fixed at -3.5
This only affects Ca-containing phases (Uranoph, Ruther, CaUO₄, Haiwee).
Note also that these positions assume calcite saturation, which is not the case ~~throught both simulations.~~ DAP 9/17/98 throughout bh1211c8 – calcite is undersaturated through almost the entire run. Soddyite + Schoepite lines are unaffected, and Haiweeite only slightly ✱ The CaUO₄ line moves up (arrow) during the run, as calcite becomes increasingly undersaturated. Therefore, CaUO₄ is not supersaturated – as it may appear.

✱ when it is involved





What if use Nguyen et al (1992) Log K_{sp} for Soddyite?? → (J. Chem Thermo, 24, p. 359)

Re-do bh1211c1 and bh1211c8.
First, do a new EQ3 run with the LogK for Soddyite changed to 5.74.

→ bh12_11h.3i (edit of bh12-11g)

Then use the pickup file for EQ6 runs:

bh1211h1.6i
bh1211h8.6i

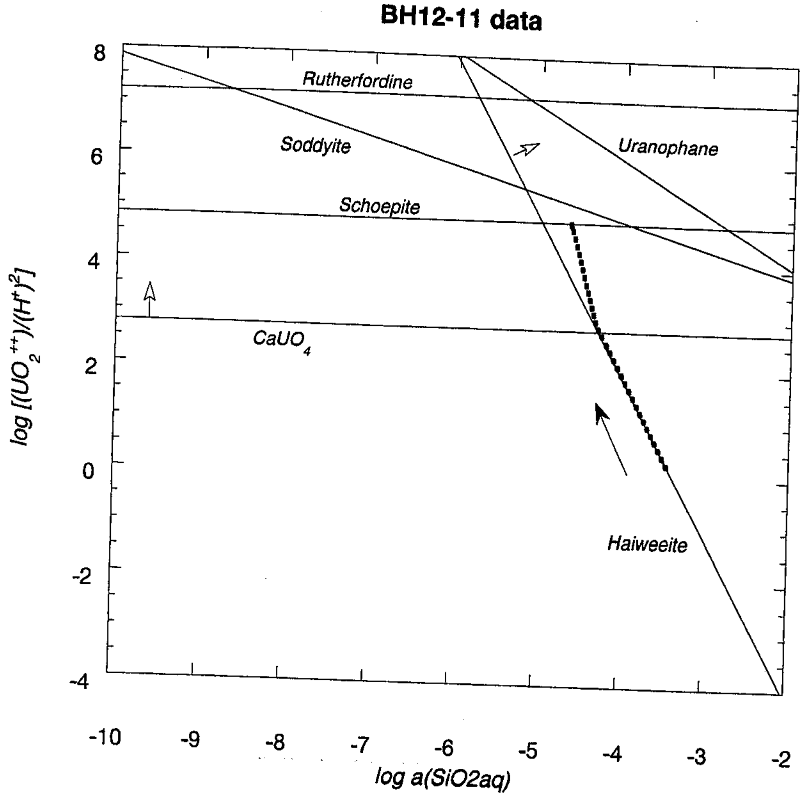
(Still suppressing SiO_2 phases as before.)

<u>bh1211h1.6i</u>
Water goes up Haiweeite line, past former intersection with Soddyite line, but stalls a little past here.
Highest U (log molal) = −5.468
highest Log $\frac{UO_2{++}}{H^{+2}}$ = 2.6319
Lowest Log $SiO_2(aq)$ = −3.9123

Of course Soddyite does not precipitate.
With reference to the top figure on p 60, the Soddyite line is 2.7 log units higher (at same slope).
Again, $UO_{2.25}$ precipitates at very end, at low fO_2.

<u>bh1211h8.6i</u>
U still ends up at Schoepite saturation, with 9.8 ppm. 4×10^{-5} m
However, as shown on the next page, it follows a different path than bh1211c8.
Once the water ~~hits $CaUO_4$~~ DSB 9/17/98 is unsaturated in Calcite, the lines for $CaUO_4$ and Haiweeite begin moving in the direction of the arrows?.

BH12-11 data



So, the water moves with the intersection of Haiweeite and $CaUO_4$, up, until it reaches the Schoepite line. Again, the curves can move because Calcite is not saturated. (Note: Uranophane and Rutherfordine move, too.)

ADIT95-9 Modelling

Using adit959g.3p as a pickup file (see p. 30), do two EQ6 calculations:

adi959c1.6i closed
adi959c8.6i open, atmos $O_2 + CO_2$

In both, again suppress Qz, Trid, Chalce, Cristob, and Coesite.

adi959c1

First, note that in the starting and final solutions, calcite is quite undersaturated. The activity plot should be modified accordingly. According to pages 14-16, the variables sensitive to calcite saturation state are $\log \frac{a_{Ca^{++}}}{(a_{H^+})^2}$ and $\log[(a_{HCO_3^-})(a_{H^+})]$.

Calculate these from the ~~ept~~ DAP 9/17/98 output file.

At zi	$\log \frac{a_{Ca^{++}}}{(a_{H^+})^2}$	$\log[(a_{HCO_3^-})(a_{H^+})]$
0	10.2755	-10.6888
10^{-4}	10.2541	-10.6922
2×10^{-3} (end)	10.4407	-10.7583

These differences are minor in terms of positions of U minerals on the activity plot. Use the zi = 0 values to plot Ca-sensitive phases.

9/18/98 Calculation of mineral saturation lines on activity plot for adi959:

Haiweeite See p. 14.

$$\log \frac{(UO_2^{++})}{\cancel{SiO_2(aq)}\,(H^+)^2} = -3 \log(SiO_2) + \tfrac{1}{2}(-7.0413 - 10.2755)$$

DAP 9/18/98 ↖ activities ↗

$$\log \frac{(UO_2^{++})}{(H^+)^2} = -3 \log(SiO_2(aq)) - 8.6584$$

Uranophane see p. 15

$$\log \frac{(UO_2^{++})}{(H^+)^2} = -\log(SiO_2(aq)) + \tfrac{1}{2}(17.2850 - 10.2755)$$

$$= -\log(SiO_2(aq)) + 3.5048$$

Rutherfordine see p. 15

$$\log \frac{(UO_2^{++})}{(H^+)^2} = -4.1064 - (-10.6888) = 6.5824$$

CaUO4 see p. 16

$$\log \frac{(UO_2^{++})}{(H^+)^2} = 15.9420 - 10.2755 = 5.6665$$

Note - On all previous plots of EQ6 results, included may or may not be the initial water chemistry. It may not be included if the zi = 0 concentrations are different from the starting values.
Go back and add data points, if needed to KaleidaGraph files and plots!

~~bh1211c1 - OK~~
~~bh1211c2 - OK~~ DAP 9/18/98
~~" 7 = OK~~
~~" 8 - OK~~

except bh1211h8 - fix

bh1211 "Progress" plots OK. Note that position of starting water relative to Haiwee line can be misleading, due to dependence of Haiwee on log fCO_2.
bh1211 "U and Si" plots
fix bh1211c1 not fixed because values very close.
fix bh1211c8 ✓
adi959 progress - fixed (slight difference)

adi959c8

Again, calcite undersaturated. Will again calculate U mineral saturation lines for conditions of run (see p. 62 discussion of adi959c1).

Zi	$\text{Log } \frac{a_{Ca^{++}}}{(a_{H^+})^2}$	$\text{Log}[(a_{HCO_3^-})(a_{H^+})]$
0	11.5189	-11.3136
10^{-5}	11.5189	-11.3136
10^{-4}	11.1086	-11.3136
1	11.1087	-11.3136

9/21/98

Use the above calculated mineral lines to construct the reaction progress plots shown on the next page.

As for BH12-11, the closed system model (...c1) ends with reducing conditions and uraninite saturation. The open system (...c8) ends with all uraninite dissolved, replaced mostly by schoepite.

On the following pages (p. 66-67) are plots of U and Si, and mole minerals, versus moles uraninite dissolved.

Pertinent computer files:

Excel: adi959c1.xls adi959c8.xls

Kaleidagraph data: ~~adi959c1 data.QDA~~ ~~adi959c8 data.QDA~~

→ ADIT95-9 data.QDA

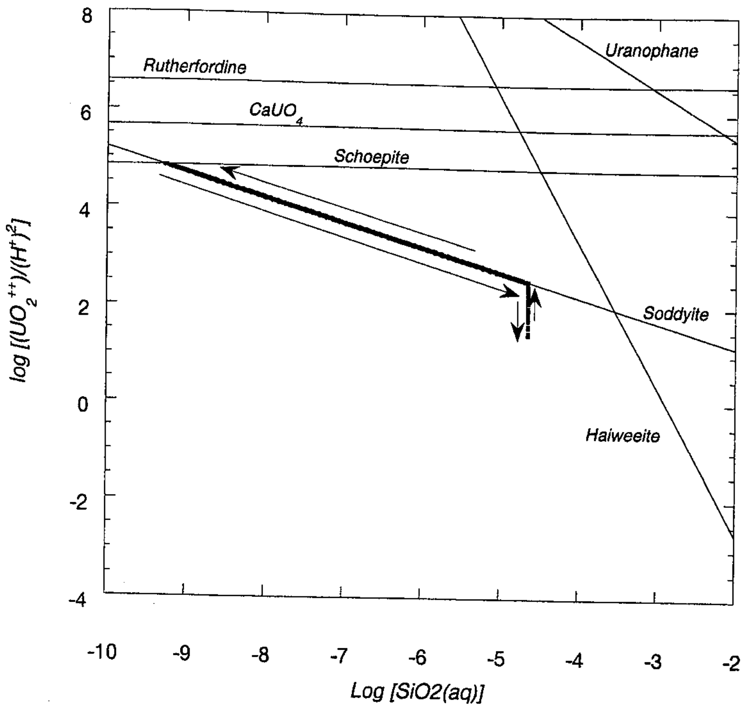
ADIT95-9 data by zi.QDA

KaleidaGraph plots: adi959c1 progress.QPC adi959c8 progress.QPC

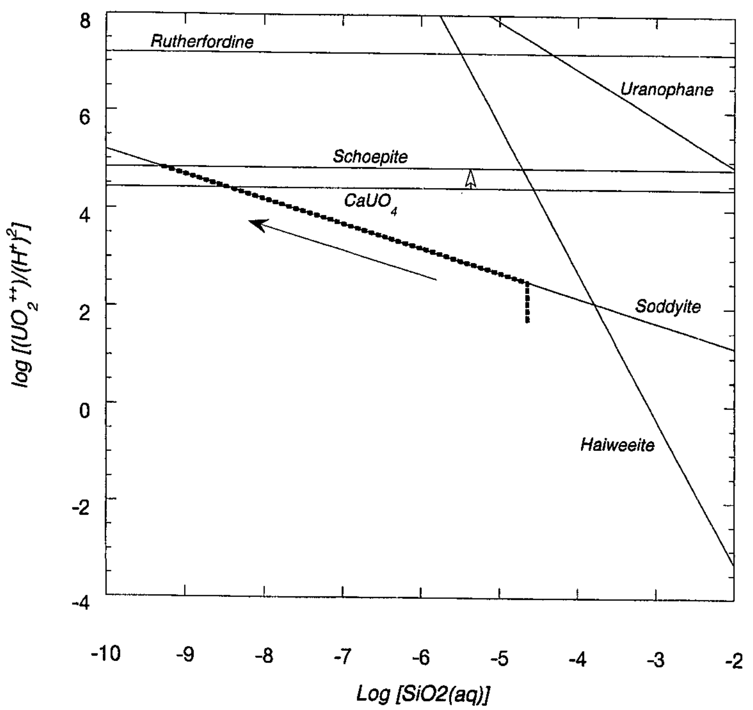
adi959c1 minls.QPC adi959c8minls.QPC

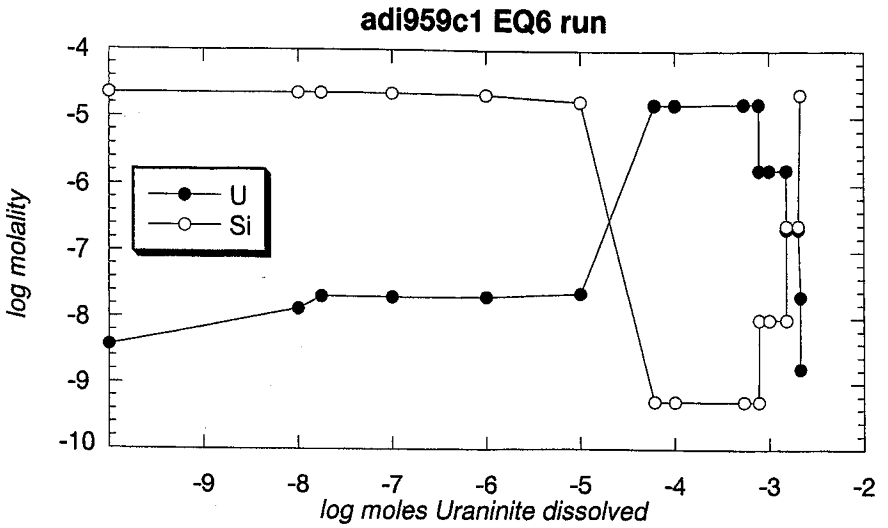
adi959c1 U and Si.QPC adi959c8 U and Si.QPC

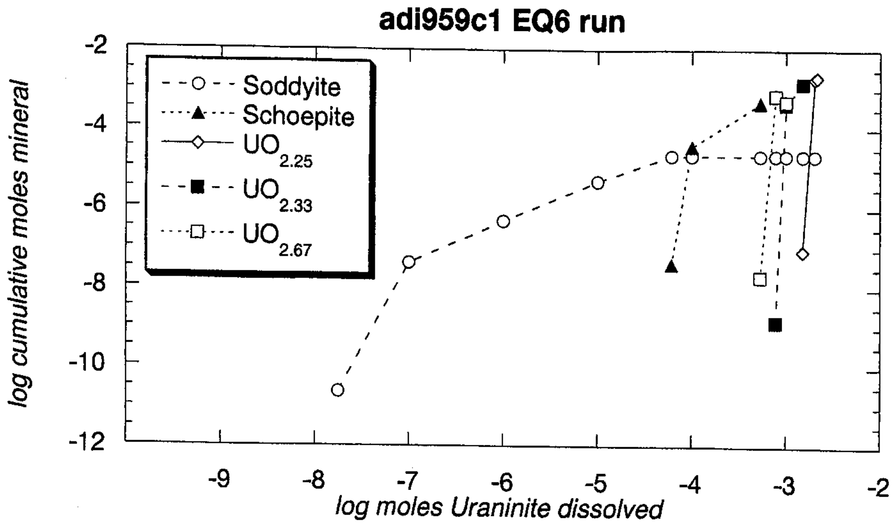
adi959c1 EQ6 run

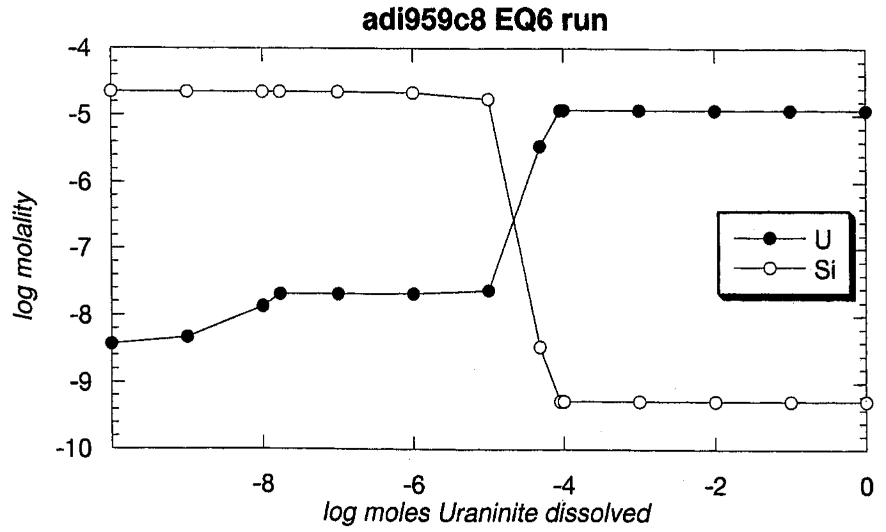


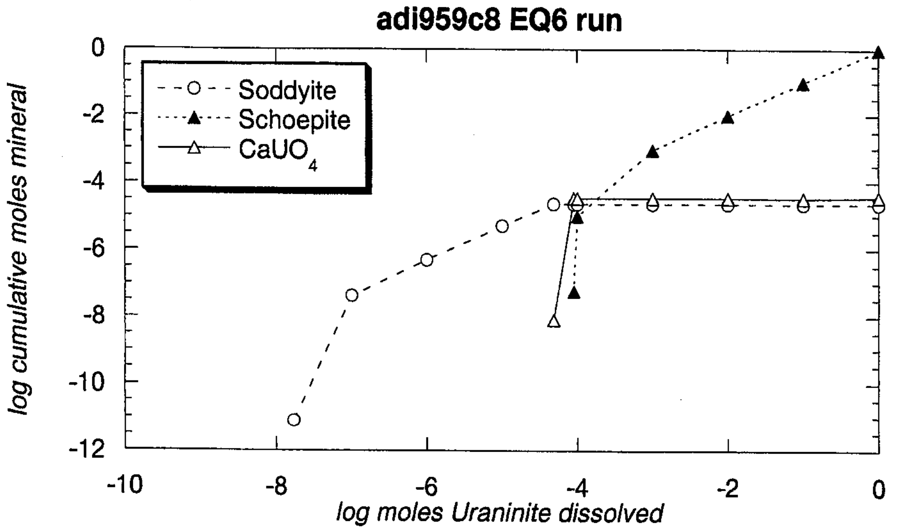
adi959c8 EQ6 run




adi959c1 EQ6 run
log molality
-4
-5
-6
-7
-8
-9
-10
U
Si
-9
-8
-7
-6
-5
-4
-3
-2
log moles Uraninite dissolved


adi959c1 EQ6 run
log cumulative moles mineral
-2
-4
-6
-8
-10
-12
Soddyite
Schoepite
UO2.25
UO2.33
UO2.67
-9
-8
-7
-6
-5
-4
-3
-2
log moles Uraninite dissolved


adi959c8 EQ6 run
log molality
-4
-5
-6
-7
-8
-9
-10
U
Si
-8
-6
-4
-2
0
log moles Uraninite dissolved


adi959c8 EQ6 run
log cumulative moles mineral
0
-2
-4
-6
-8
-10
-12
Soddyite
Schoepite
CaUO4
-10
-8
-6
-4
-2
0
log moles Uraninite dissolved

9/22/98
DAP

WVW 95-03 EQ6

This is from the carbonate aquifer east of Nopal I.

Use wvw9503g.3p as pick up. (p. 32)

wvw953c1.6i closed, as before.

Final log $\frac{UO2++}{(H^+)^2}$ = 1.3191 log($SiO_2(aq)$) = -3.5915

↑ same as other ...c1 runs.

Uraninite reaches saturation. (reducing)

Travels up to Haiweeite curve, then to intersection with Soddyite then comes back down.

Max [U] = 1.5×10^{-7} molal

Calcite initially is near saturation, but ends up undersatd. (-0.363 log Q/K).

Log fCO_2 starts at -2.56, but immediatly changed to -2.3; ends at -2.34.

wvw953c8.6i open with atmospheric O_2 + CO_2.

Final log $\frac{UO2++}{(H^+)^2}$ = 4.8334 (Schoepite, as before)

Final log $SiO_2(aq)$ = -9.2746. Like other c8 runs.

Calcite initially saturated but then under.

Final (and highest) U = 18×10^{-5} m

Back to ADIT95-9

Use Nguyen et al soddyite data (see p. 60).

This time, just add the log K adjustment to the pickup file portion of the *.6i files.

adi959h1.6i

Goes straight up to Schoepite line, not touching Soddyite and Haiweeite. Then comes back down when reducing. Max U = 1.6×10^{-5} m.

adi959h8.6i

Precipitates $CaUO_4$, then Schoepite, then Haiweeite (all three satd at end).

I suspect $CaUO_4$ line moves up, but why would Haiwee come into the picture?

Zi	Log $\frac{a_{Ca^{++}}}{(a_{H^+})^2}$	Log$[(a_{HCO_3^-})(a_{H^+})]$
0	11.5189	-11.3136
10^{-6}	11.5173	-11.3136
10^{-4}	11.1087	-11.3136
1	11.1087	-11.3136

Essentially the same as adi959c8 (p. 64).

for adi959h1:

Zi	Log $\frac{a_{Ca^{++}}}{(a_{H^+})^2}$	Log$[(a_{HCO_3^-})(a_{H^+})]$
0	10.2755	-10.6888
10^{-6}	10.2749	-10.6892
10^{-4}	10.2535	-10.6919
$10^{-2.67}$ (end)	10.4407	-10.7583

Essentially the same as adi959c1 (p. 62).

11/4/98 R.C. Ewing reports a calculated $\Delta G^\circ_{f,298}$ for soddyite in an annual progress report to DOE of -3651.8 kJ/mol. This is within Nguyen et al's uncertainty range. (See p. 60). What is log Ksp for this value?

$\Delta G_{sp} = -RT \ln K_{sp}$.

~~Ewing calc from Nguyen data -3655.7. If have -3651.8 instead,~~

DAP 11/4/98

This means ~~Ewing has~~ ΔG^*_{sp} $\Delta G_{sp} = -RT \ln K_{sp} = -33313.6$

Use Ewing's ΔG° for soddyite, this becomes -33313.6 + 3655.7 + 3651.8

= -333~~07.7~~ 17.5

→ $\ln K_{sp} = 13.218$ $\log K_{sp} = 5.74$ Same DAP 11/4

8/16/00
DAP

See notebook # 172, p. 11-12 for information on a new water sample from Nopal I.

4/29/03
DAP

Preparation for Nopal Field Trip

Part of the work during the upcoming trip to Nopal will be to sample for Radium. DOE is drilling three holes through the Nopal I uranium deposit and nearby, and we will collect some samples, including for radium analysis.

In preparation for this, must prepare Mn-impregnated filters. Take eight "Spun-Polypropylene Sediment Filter Cartridges," USFilter model P5-478. Will follow the preparation procedure shown in Luo et al (2000), Geochim Cosmochim Acta v. 64 pp 867-881. (p. 869)
Note: will not purify the $KMnO_4$.

Take 4 L of Nanopure water and add slightly more than 1 tablespoon Alconox detergent. Heat in Pyrex beaker on hot plate until warm.

Place 4 filter cartridges in each of two 4-L Pyrex beakers.

Pour warm Alconox solution into each; add ~0.5 L Nanopure water. Hold cartridges under solution for a few minutes. Decant solution and rinse twice with Nanopure water.

In 4L beaker, combine 2700 ml Nanopure water + 300 ml 10 M NaOH; mix. Add 2 L to one of the beakers with filters. Add 900 ml water + 100 ml 10 M NaOH to beaker; mix. Add to other beaker of filters.

Note: filters float in solution. After 5-10 mins, turn filters over so that other half gets soaked.

Note: This step is 1 M NaOH.

Rinse filter beakers twice with Nanopure water.

In 4L beaker, combine 3300 ml water + 300 ml conc HCl → 3600 ml 1 M HCl.

Add ~½ to each beaker of filters. Let soak ~15 mins.

Note - now wedging a small beaker into the gap in the middle of 4 filters to hold them under liquid surface.

Rinse filters twice with Nanopure water.

4/30/03
DAP

Weigh 198 g of $KMnO_4$ powder into 4 L Pyrex beaker and bring volume up to 2.5 L with Nanopure water. Will not dissolve at room temperature, despite vigorous stirring. (CRC says solubility should be only ~150 g in 2.5 L.) Heat on hot plate, stirring occasionally.

This gives 2.5 L of 0.5 M $KMnO_4$ soln.

When dissolved, pour over filters in one beaker. Have more soln than needed, so make less for 2nd beaker.

Weigh 158 g $KMnO_4$ into ~1.5 L water in beaker; bring up to 2 L → 0.5 M soln. Heat and stir until dissolved.

At 10:00 AM, turn on hot bath with one of the filter beakers in ~~it~~ DAP 4/30/03 it. Set to 80°C.

At 10:30, place 2nd filter beaker in bath.

10:45, bath temperature is still just 50°C.

At 18:40 turn off bath. Temperature remained at ~70°C since 13:00. (61°C at 11:40) Even though set to ~90°.

Can see the upper parts of the filters in one beaker by pulling up "spacer beaker" with rod. Can see that coverage is spotty. Procedure appears incomplete.

Leave overnight with bath temperature off.

5/1/03
DAP

Filters still have spotty coverage.

At 08:30 set to 95°C. Top off water in bath.

13:15 69°C. Turn up.

Never goes above ~70°C.

15:00 Turn off heat and begin rinsing one beaker by decanting and re-filling with Nanopure water. It is becoming clear that the rinses are still highly concentrated in $KMnO_4$ and it will take many rinses to get clear water.

Leave first beaker with water in it, and 2nd beaker with original $KMnO_4$ solution, overnight at room temperature.

5/2/03
DAP

Rinse 2nd beaker once with Nanopure water.

Note: we are preserving all $KMnO_4$ solution for proper disposal at Safety department's hazardous waste collection facility.

Rinse 2nd beaker a 2nd time with Nanopure water. Place all filters in water in individual beakers to soak for a few hours.

Now, one at a time, rinse Mn-impregnated filters by placing in the sink on an inverted funnel and squirting with Nanopure water from a wash bottle. Rinse water is dilute enough in $KMnO_4$ that OK to put down drain. Soak all filters one more time for ~30 min. in individual beakers to get last vestiges of $KMnO_4$ out.

Store filters in zip-loc bags.

5/16/03
DAP

We ended up with about 12 liters of waste $KMnO_4$ solution for disposal. Bradley took over to facility.

5/20/03
DAP

The Mn-impregnated filters were not used on the field trip to Nopal, May 6-8, recorded in notebook # 121. They will be retained for possible future use.

9/2/05
DAP

Recall of some EQ3 results on Nopal Waters

Bill Murphy has asked that I extract some species activity results from earlier EQ3 runs on Nopal waters. The purpose is to provide points to plot with newly calculated uranium mineral stability fields.

Activities are needed for the following species:

Ca^{++}
H^+
$Si(OH)_4$

so a plot of $\text{Log}\ \frac{a_{Ca^{++}}}{a_{H^+}}$ vs $\text{Log}\ a_{Si(OH)_4}$

can be constructed.

EQ3/6 reports the neutral species $SiO_2(aq)$ instead of $Si(OH)_4(aq)$, but I can substitute one for the other. In the solubility reactions for Soddyite and Uranophane (the two uranyl silicate phases being plotted) in the EQ3/6 database, all species have the same stoichiometry as in Murphy's reactions, except for the number of OH in the uranium phase and the Si aqueous species. Therefore, the $SiO_2(aq)$ and $Si(OH)_4(aq)$ species activities are interchangeable for plotting purposes.

During EQ6 modeling work (pp 35 - 69), I used both the *f.3p and *g.3p pickup files. So I will now look at both *f.30 and *g.30 results (pp 21-32).
DAP 9/2/05

BH12W95-11 All are Log activities, read from files on hard drive. (*.30)

	Ca^{++}	H^+	Ca^{++}/H^+ calculated	$SiO_2(aq)$
bh12_11f	-2.8008	-7.3400	4.5392	-3.1804
bh12_11g	-2.7730	-7.3400	4.5670	-3.1804

BH12W95_05

	Ca^{++}	H^+	Ca^{++}/H^+	$SiO_2(aq)$
bh12_05f	-2.8025	-7.2600	4.4575	-3.1775
bh12_05g	-2.7724	-7.2600	4.4876	-3.1775

ADIT95-6 (recall that pH was assumed)

adit956f	-3.3915	-7.0000	3.6085	-3.2820
adit956g	-3.3717	-7.0000	3.6283	-3.2820

ADIT95-9 (pH assumed)

adit959f	-3.7647	-7.0000	3.2353	-4.6483
adit959g	-3.7474	-7.0000	3.2526	-4.6483

As mentioned above, for the two ADIT95 waters pH had to be assumed. It was not measured in the field. For the *f.30 runs, charge balance was achieved in EQ3 by adjusting Ca^{++}. For *g.30, it was done by adjusting HCO_3^-.

Now perform new calculations that adjust charge balance with H^+ - this may give an idea of the range of possible results for Log ($a_{Ca^{++}}/a_{H^{+2}}$).

adit956z - edit adit956f.3i by merely changing the charge balance species to H^+

Ca^{++}	H^+	Ca^{++}/H^+	$SiO_2(aq)$
-3.3773	-8.3623	4.9850	-3.2936

adit959z - edit adit959f.3i by merely changing the charge balance species to H^+.

Ca^{++}	H^+	Ca^{++}/H^+	$SiO_2(aq)$
-3.7502	-8.5903	4.8401	-4.6676

Like related files, inputs and outputs are located on my PC (SYREEN) in D:\eq\Nopal.

4/17/06
DAP

~~ARCGIS~~
ArcGIS
DAP 4/17/06

John Roseberry and Kevin Smart produced an ARC-compatible map of the adit located on Level +00 at Nopal I. The map was produced in ArcGIS ~~ARCView~~ version 9. A CD containing this directory's contents is now contained in the pocket on the back of this notebook. The CD is labelled "Nopal Adit Map 2006."
The directory was also copied onto the hard drive of David Pickett's computer ("SYREEN") in the directory D:\Documents\Nopal.

A copy of this CD will be taken to NRC headquarters and given to Bret Leslie for inclusion in the ADAMS database.

GEOSCIENCES AND ENGINEERING DIVISION

SCIENTIFIC NOTEBOOK REVIEW CHECKLIST RECORD

Scientific Notebook No.: 276 Date Turned In: 9/29/2006

Accomplished

☑ 1. Initial entries per QAP-001

☑ 2. Dating of entries

☑ 3. Corrections (crossed out, one line through w/initials/date)

☑ 4. No White out used

☑ 5. Page number visible on copy or original notebook

☑ 6. In process entries per QAP-001

☑ 7. Figure information present

☑ 8. Text readable

☐ NA 9. Copyrighted material is identified

☑ 10. Permanent ink or type only

☑ 11. Signing of entries (not required on each page)

☑ 12. Electronic media in the scientific notebook properly labeled

☑ 13. NRC Supplementary Scientific Notebook Questions are addressed. (send completed form to P. Mackin)

Any discrepancies must be resolved before notebook closeout.

==

I have reviewed this scientific notebook and find it in agreement with QAP-001.

E. C. 9/29/2006

Manager's Signature Date

ADDITIONAL INFORMATION FOR SCIENTIFIC NOTEBOOK NO. 276

Document Date:	04/27/2001
Availability:	Southwest Research Institute® Center for Nuclear Waste Regulatory Analyses 6220 Culebra Road San Antonio, Texas 78228
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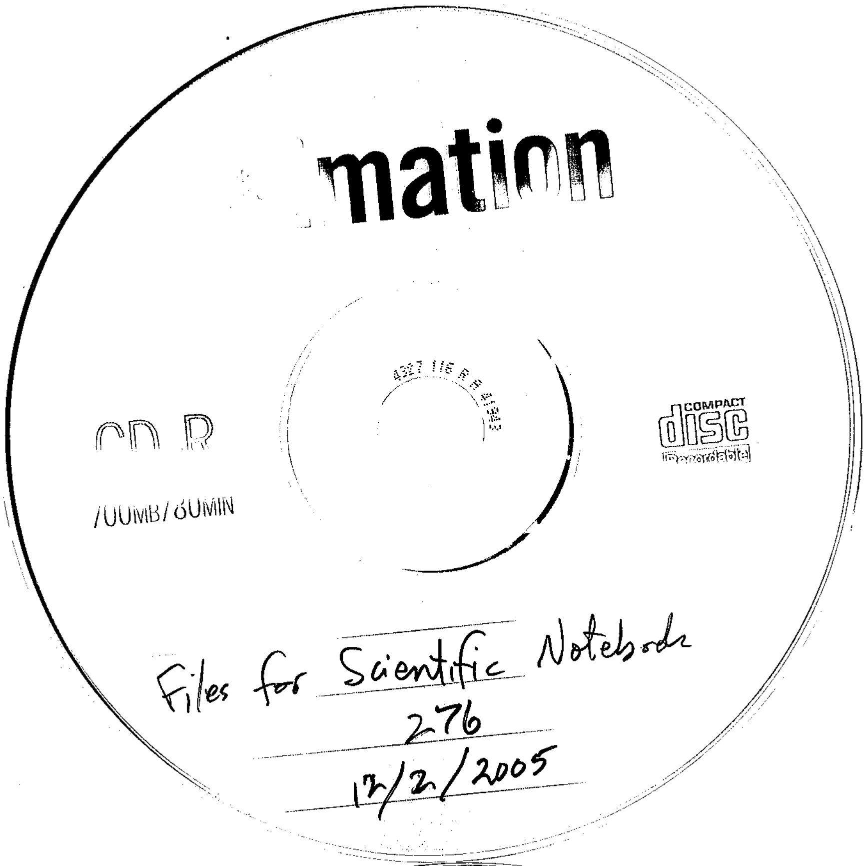
Application Used: (including version number)	Unknown
Media Type: (CDs, 3 1/2, 5 1/4 disks, etc.)	2 CDs
File Types: (.exe, .bat, .zip, etc.)	Excel, QPC, 6XT, 6I, 6O, XML Doc, DBR, LYR, SBN, SBX, SHP
Remarks: (computer runs, etc.)	Media contains: data files for scientific notebook

12/2005 Disketts replaced with CD
containing all relevant data files.



Files for Scientific Notebook
276
12/2/2005

Nopal Adit Map 2006

Files from folder
S:\JRoseberry\+00 Adits\

ArcGIS