

Geochemistry  
Research Lab  
Notebook  
Vol. GC-06

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Geochemistry  
Research Lab Notebook  
VOL. GC-06

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PM Paula Muller student scientist  
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James D. Fultz JP



3/19/92

1000 hrs JP

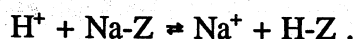
Na<sup>+</sup>-H<sup>+</sup> ION EXCHANGE EXPERIMENT Na/H-III

WRITTEN BY: R. T. PABALAN  
 REVISION NO.: Rev. 2 of Na/H-I

DATE WRITTEN: October 25, 1991  
 LAST REVISED: March 16, 1992

## OBJECTIVE:

Determine the importance of the ion exchange reaction:



Ion exchange reactions between H<sup>+</sup> and Na<sup>+</sup> may affect sorption studies on zeolites at acidic pH's.

## EQUIPMENT:

ORION pH/mV/ISE/°C meter  
 Combination pH electrode  
 Automatic temperature compensator probe  
 Na<sup>+</sup> ion selective glass + reference electrode  
 Analytical balance  
 New Brunswick gyratory shaker

## SUPPLIES:

pH buffer (pH = 1,2,4,6,7)  
 Na electrode ionic strength adjustor  
 Na concentration standards  
 22 15-ml polypropylene (PP) bottles  
 22 50-ml polypropylene bottles  
 6 250-ml PP bottle  
 11 10-ml volumetric pipet  
 6 50-ml volumetric pipet  
 5 glass droppers  
 ultrapure water, preequilibrated with atmospheric CO<sub>2</sub>(g)

## PROCEDURE:

1030 hrs JP

1. Prepare aqueous solutions of initial pH given in Table 1 by taring the amount of ultrapure water (>17 megaohm), which has been preequilibrated with atmospheric CO<sub>2</sub>(g), indicated in column 2 into pre-labeled 250-ml polypropylene bottles. Measure and record the initial pH of the solution (~5.65) and add the appropriate amount of HNO<sub>3</sub> shown in columns 3-5 of Table 1, dropwise, until the expected initial pH given in column 1 is



Table 1.

Initial Solution Label	H <sub>2</sub> O Mass to Use	Measured pH of H <sub>2</sub> O	HNO <sub>3</sub> to add to ultrapure water					pH meas'd 24 hrs. after HNO <sub>3</sub> addition
			Conc. (m)	Approx. Vol. (ml)	Approx. #Drops	#Drops Added	Approx. Vol HNO <sub>3</sub> Added	
IS*pH2.0	250	5.56	2.5	1.105	30		1.1	
IS*pH2.5	250	5.58	2.5	0.340	9		.34	
IS*pH3.0	250	5.58	0.5	0.529	14		.52	
IS*pH3.5	250	5.57	0.1	0.803	22		.8	
IS*pH4.0	250	5.60	0.05	0.501	14		.51	
IS*pH5.0	250	5.62	0.005	0.476	13		.48	

number of drops needed to be added was calculated using a value of 0.037 ml/drop, which is based on the calibration of the glass dropper conducted previously in Kinetic Experiment-IA. If another type of glass dropper is used, calibration will have to be redone. Take care to swirl each bottle by hand between additions of HNO<sub>3</sub> to thoroughly mix the solution and to achieve equilibrium pH.

After the target initial pH indicated in Table 1 has been reached, cover the bottles with a porous material (e.g., kimwipe) and agitate for at least 24 hours using a gyratory shaker set to ~130 rpm. After this period, take a 10-ml aliquot from each solution and remeasure (and record) the pH.

03/20/92 1350 hrs JP

2. For each mixture given in column 1 of Table 2, pipet 50 ml solution (IS\*phi) of initial pH given in column 2 of Table 2 into pre-labeled 50-ml PP bottles. Tare the weights of the zeolite powder (CDV\*100/200\*UC\*WA\*HL\*CPT\*Na/HF) given in column 3 on weighing paper, and carefully transfer the zeolite into the appropriate PP bottle. Place the cover on each bottle, then keep the mixtures agitated on a gyratory shaker. After a period of three days and no more than 5 days, take a 10-ml aliquot from each solution using a volumetric pipet, transfer into appropriately labeled (e.g., Na/H\*III\*1a\*1) 15-ml polypropylene bottles. Add 1 ml of ionic strength adjustor to each bottle and save for later analysis using a sodium ion selective electrode. Then measure and record the pH and temperature of each solution (e.g., Na/H\*III\*1a). Also measure the pH and temperature of the initial solutions (IS\*phi).

NaF 3/19/92 RT

#### PREPARATION:

1. Preclean the glassware and PP bottles to be used by soaking in ~10% HNO<sub>3</sub> overnight and rinsing them at least ten times with ultrapure water.
2. Prepare at least 100 ml each of 2.5, 0.5, 0.1, 0.05, and 0.005 m HNO<sub>3</sub> solution. Store in precleaned and appropriately labeled PP bottles.
3. Check calibration of glass droppers, if needed.

03/19/92  
1300 hrs JP

\*Note: Instead of using glass droppers to add HNO<sub>3</sub>, microliter pipets and tips were used to add HNO<sub>3</sub> in step 1 of the procedure.



TABLE 2.

Soln. Label	Initial pH	Wt. Zeol. to Use (gm)
Na/H*III*1a Na/H*III*1b	2.0	0.50
Na/H*III*2a Na/H*III*2b	2.0	0.25
Na/H*III*3a Na/H*III*3b	2.5	0.20
Na/H*III*4a Na/H*III*4b	2.5	0.10
Na/H*III*5a Na/H*III*5b	3.0	0.10
Na/H*III*6a Na/H*III*6b	3.0	0.05
Na/H*III*7a Na/H*III*7b	3.5	0.10
Na/H*III*8a Na/H*III*8b	3.5	0.05
Na/H*III*9a Na/H*III*9b	4.0	0.10
Na/H*III*10a Na/H*III*10b	4.0	0.05
Na/H*III*11a Na/H*III*11b	5.0	0.05

3/20/92 3/20/92 3/24/92  
14 40 hrs 1330hrs 1555hrs 0900hrs  
JP JP JP

TABLE 3.

Soln. Label	Wt. Zeol. Used (gm)	Measured pH of IS*PHi	Measured Final pH/°C	Measured Final Na <sup>+</sup> ppm	Δm <sub>Na</sub>	Δm <sub>Na</sub>
Na/H*III*1a	0.5000	2.00	2.52/21.4°C	154	0.0067	0.0067
Na/H*III*1b	0.5001		2.52/21.7°C	152	0.0066	0.0066
Na/H*III*2a	0.2501		2.36/21.6°C	116	0.0050	0.0050
Na/H*III*2b	0.2500		2.36/21.5°C	117	0.0051	0.0051
Na/H*III*3a	0.2002	2.50	3.08/21.8°C	54.1	0.00235	0.00235
Na/H*III*3b	0.2000		3.08/21.7°C	53.8	0.00234	0.00234
Na/H*III*4a	0.1000		2.91/21.7°C	42.9	0.00187	0.00187
Na/H*III*4b	0.1002		2.90/21.9°C	42.5	0.00185	0.00185
Na/H*III*5a	0.1000	3.01	3.69/22.0°C	20.0	0.00087	0.00087
Na/H*III*5b	0.1001		3.69/21.9°C	19.9	0.00087	0.00087
Na/H*III*6a	0.0502		3.49/21.8°C	16.4	0.000713	0.000713
Na/H*III*6b	0.0501		3.48/22.0°C	16.8	0.000731	0.000731
Na/H*III*7a	0.1002	3.51	4.69/21.7°C	7.87	0.0003423	0.0003423
Na/H*III*7b	0.1002		4.68/21.9°C	7.86	0.0003419	0.0003419
Na/H*III*8a	0.0502		4.33/21.9°C	7.37	0.0003206	0.0003206
Na/H*III*8b	0.0503		4.33/22.1°C	7.35	0.0003197	0.0003197
Na/H*III*9a	0.1000	4.00	5.85/21.3°C	2.98	0.0001296	0.0001296
Na/H*III*9b	0.1000		5.86/21.2°C	2.96	0.0001288	0.0001288
Na/H*III*10a	0.0502		5.42/21.3°C	2.80	0.0001218	0.0001218
Na/H*III*10b	0.0503		5.38/21.0°C	2.83	0.0001231	0.0001231
Na/H*III*11a	0.0502	4.97	6.40/21.3°C	1.45	0.0000631	0.0000631
Na/H*III*11b	0.0501		6.49/21.4°C	3.92	0.0001705	0.0001705

3/24/92  
1620hrs

Measured  
pH of IS + PHi

1.98/21.7°C

2.50/21.9°C

3.00/22.2°C

3.50/22.1°C

4.00/22.2°C

4.95/21.9°C  
4.88/22.3°C

3/24/92 JP



3/24/92 1500hr JF

10 ml aliquots taken for  $\text{Na}^+$  analysis for ion exchange experiment Na/H III (see step 2 page 3 for explanation).

4/23/92 0900hr JF

Concentration of  $\text{Ca}^{++}$  and  $\text{Na}^+$  in 0.05N  $\text{NaNO}_3$ - $\text{Ca}(\text{NO}_3)_2$  reference solutions by AA.

Objective - determine the  $\text{Ca}^{++}$  and  $\text{Na}^+$  content of the 0.05N  $\text{NaNO}_3$ - $\text{Ca}(\text{NO}_3)_2$  reference solutions used in isotherm experiments.

Method - Atomic Absorption analysis

Equipment -

- 1) Model 3100 AA spectrometer (SN 146109)
- 2) Na hollow cathode lamp (SN 70425)
- 3) Cu hollow cathode lamp (SN 70038)

Supplies -

- 1) Volumetric flasks
- 2) pipets
- 3) plastic + glass beakers
- 4) Ca + Na standards (1000 ppm) (lot C076)

Procedure -

1) Set up Model 3100 for analysis of  $\text{Ca}^{++}$  and  $\text{Na}^+$  in accordance with the standard conditions outlined in "Analytical Methods for Atomic Absorption Spectrophotometry" provided by Perkin-Elmer.

2) Prepared standards and samples

3) Set up and operated Model 3100 in accordance with instructions outlined in "Running the 3100" provided by Perkin Elmer.

\* Note - to minimize matrix interferences the normality of  $\text{NO}_3$  in standards was adjusted with  $\text{HNO}_3$  to reflect the  $\text{NO}_3$  concentration of samples.

Also ~ 0.1% KCl was added to both standards & samples to avoid ionization interferences



## Results-

<u>Ca<sup>++</sup></u>				
$X_{Ca,i}$	Expected ppm	Dilution Factor	Measured Value (ppm)	Converted Value (ppm)
.01	10.02	1/20	0.6	12.0
.025	25.05	1/20	1.2	24.0
.05	50.1	1/20	2.4	48.0
.075	75.15	1/20	3.5	70.0
.1	100.2	1/20	4.7	94.0
.2	200.4	1/20	10.0	200.0
.3	300.6	1/20	15.0	300.0
.4	400.8	1/20	19.9	398.0
.5	501.0	1/20	25.3	506.0
.6	601.2	1/50	11.9	595.0
.7	701.4	1/50	12.4	620.0
.8	801.6	1/50	16.3	815.0
.9	901.8	1/50	17.8	890.0
.925	926.85	1/50	18.6	930.0
.95	951.9	1/50	19.3	965.0
.975	976.95	1/50	19.9	995.0
1.0	1002.0	1/50	20.2	1010.0

<u>Na<sup>+</sup></u>				
$X_{Na,i}$	Expected ppm	Dilution Factor	Measured Value ppm	Converted Value (ppm)
.9	103.4	1/20	$9.4 \pm .0471$ <sup>4123/92</sup>	104.0
.8	919.6	1/100	<del>8.1</del> <sup>4123/52</sup> $9.4 \pm .0471$	940.0
.7	804.6	1/100	$8.1 \pm .0655$	810.0
.6	689.7	1/100	$6.7 \pm .0592$	670.0
.5	574.7	1/100	$5.6 \pm .0610$	560.0
.4	459.8	1/100	$4.5 \pm .0347$	450.0
.3	344.8	1/100	$3.4 \pm .0157$	340.0
.2	229.9	1/100	$2.2 \pm .0102$	220.0
.1	114.9	1/20	$5.7 \pm .0252$	114.0
.075	86.2	1/20	$4.2 \pm .0336$	84.0
.05	57.5	1/20	$2.9 \pm .0262$	58.0
.025	28.7	1/20	$1.5 \pm .0312$	30.0

4/24/92 0915 hr JP

Measure concentration of  $\text{Ca}^{++}$  and  $\text{Na}^+$  in 0.05N  $\text{NaNO}_3$ - $\text{CaCl}_2$  reference solutions by AA

Objective: determine the concentration of  $\text{Ca}^{++}$  and  $\text{Na}^+$  in 0.05N  $\text{NaNO}_3$ - $\text{CaCl}_2$  reference solutions used in isotherm experiments.

Method - Atomic Absorption

Equipment:

- 1) Perkin-Elmer Model 3100 AA spectrometer (SN 146109)
- 2) Na hollow cathode lamp (SN 70625)
- 3) Ca hollow cathode lamp (SN 70038)

Supplies:

- 1) Volumetric flasks
- 2) volumetric pipets
- 3) plastic beakers
- 4) Ca reference standard (1000 ppm) lot C076
- 5) Na reference standard (1000 ppm)
- 6) Eppendorf pipets + tips

Procedure:

- 1) Standards prepared by diluting reference standards to 1000 ml in 1000 ml volumetric flasks.

For  $\text{Ca}^{++}$  4, 5, and 10 ppm standards were prepared.

For  $\text{Na}^+$  0.5, 1, 3, and 10 ppm standards were prepared

- 2) Samples prepared by diluting solutions to 100 ml in 100 ml volumetric flasks.

Dilution factors for solutions are shown in following table

$X_{\text{Ca}, i}$	Dilution Factor	
	$\text{Ca}^{++}$	$\text{Na}^+$
0.1	1/50	JP 7/100 1/200 4/24/92
0.2	1/50	JP 7/100 1/200 4/24/92
0.3	1/50	JP 7/100 1/200 4/24/92
0.4	1/100	1/100
0.5	1/100	1/100
0.6	1/100	1/100
0.7	1/100	1/100
0.8	1/100	1/100
0.9	1/100	1/50
1.0	1/100	1/50

- 3) About 0.1% KCl was added to each standard and sample to eliminate ionization effects.



- 4) Lamps were mounted, wavelengths set, machine calibrated, and samples measured according to operating instructions outlined in "Running the 3100"

- 5) Results of analyses are shown below

$\text{Ca}^{++}$

$X_{\text{Ca},i}$	Expected ppm	Measured ppm	Converted Value ppm
0.1	100	$1.7 \pm .0622$	85
0.2	200	$3.5 \pm .0069$	175
0.3	301	$5.4 \pm .0687$	270
0.4	401	$4.0 \pm .0112$	400
0.5	501	$5.0 \pm .0158$	500
0.6	601	$5.8 \pm .1346$	580
0.7	701	$7.4 \pm .0331$	740
0.8	802	$8.9 \pm .0725$	890
0.9	902	$11.9 \pm .0347$	1190
1.0	1002	$10.2 \pm .0442$	1020

$\text{Na}^+$

$X_{\text{Ca},i}$	Expected ppm	Measured ppm	Converted Value ppm
0.1	1035	$5.1 \pm .0232$	1020
0.2	920	$4.6 \pm .0120$	920
0.3	805	$4.0 \pm .0171$	800
0.4	690	$6.8 \pm .1046$	680
0.5	575	$5.8 \pm .0614$	580
0.6	460	$4.6 \pm .0123$	460
0.7	345	$3.4 \pm .0298$	340
0.8	230	$2.3 \pm .0160$	230
0.9	115	$2.3 \pm .0156$	115
1.0	0	$0 \pm .0016$	0

4/27/92 1330 hrs JP

Measure concentration of  $\text{Ca}^{++}$  and  $\text{Na}^+$   
in 0.05N  $\text{NaNO}_3\text{-CaCl}_2$  + clinoptilolite  
samples by AA

Objective: Determine concentrations of  $\text{Ca}^{++}$   
and  $\text{Na}^+$  in 0.05N  $\text{NaNO}_3\text{-CaCl}_2$   
+ clinoptilolite samples used in  
isotherm experiments.

Method: Atomic Absorption

Equipment:

- 1) Perkin Elmer Model 3100 Atomic  
Absorption Spectrometer (SN 146109)
- 2) Na hollow cathode lamp (SN 70625)
- 3) Ca hollow cathode lamp (SN 70038)

Supplies + Materials:

- 1) Volumetric flasks
- 2) Volumetric pipets
- 3) Eppendorf pipets + tips
- 4) beakers
- 5) Ca reference standard (1000 ppm) lot C076
- 6) Na reference standard (1000 ppm)

Procedure:

- 1) Standards prepared by diluting reference  
standards in 1000 ml volumetric  
flasks.

For  $\text{Ca}^{++}$  0.5, 5, + 10 ppm standards  
were prepared.

For  $\text{Na}^+$  0.5, 1, and 3 ppm standards  
were prepared.

- 2) Samples prepared by diluting samples  
to 100 ml in 100 ml volumetric  
flasks. Dilute factors for samples are  
shown below:

Sample No	$\text{Ca}^{++}$ conc	Dilute Factor	
		$\text{Ca}^{++}$	$\text{Na}^+$
1	0.1	4/27/92 1000/100	4/27/92 1000/500
2	0.1	4/27/92 1000/100	4/27/92 1000/500
3	0.2	4/27/92 1000/100	4/27/92 1000/500
4	0.2	4/27/92 1000/100	4/27/92 1000/500
5	0.2	4/27/92 1000/100	4/27/92 1000/500
6	0.3	1/100	4/27/92 1000/500
7	0.4	1/100	4/27/92 1000/500
8	0.4	1/100	4/27/92 1000/500
9	0.5	1/100	4/27/92 1000/500
10	0.6	1/100	1/250
11	0.7	1/100	1/200
12	0.7	1/100	1/200
13	0.8	1/100	1/200
14	0.9	1/100	1/100
15	1.0	1/100	1/200
16	1.0	1/100	1/200
17	1.0	1/100	1/200
18	1.0	1/100	1/100
19	1.0	1/100	1/100



- 3) About 0.1% KCl was added to standards & samples to eliminate ionization effects
- 4) Lamps were mounted & adjusted, machine calibrated, and samples measured following operating instructions outlined in "Running the 3100".

## 5) Results

Ca <sup>++</sup>			
Sample No.	Expected ppm	Measured ppm	Converted ppm value
1	19.8	6.2 ± .008	20.0
2	33.0	6.3 ± .002	30.0
3	50.7	6.8 ± .008	50.0
4	73.4	6.8 ± .008	80.0
5	89.8	1.0 ± .0018	100.0
6	136.0	1.4 ± .0088	140.0
7	182.0	2.0 ± .0115	200.0
8	216.0	2.5 ± .0079	250.0
9	263.0	2.8 ± .0055	280.0
10	343.0	3.7 ± .0061	370.0
11	441.0	4.8 ± .0153	480.0
12	480.0	5.2 ± .0173	520.0
13	605.0	6.0 ± .0239	600.0
14	732.0	7.4 ± .0321	740.0
15	628.0	6.3 ± .0199	630.0
16	673.0	6.9 ± .0249	690.0
17	744.0	7.3 ± .0215	730.0
18	762.0	7.8 ± .0229	780.0
19	803.0	8.4 ± .0406	840.0
20	825.0	9.0 ± .0625	900.0

Na <sup>+</sup>			
Sample No.	Expected ppm	Measured ppm	Converted ppm value
1	1150	2.29 ± .0054	1145
2	1130	2.20 ± .0091	1100
3	1100	2.16 ± .0166	1080
4	1080	2.10 ± .0004	1050
5	1060	2.02 ± .0100	1010
6	990	1.94 ± .0016	970
7	939	1.84 ± .0149	920
8	924	1.74 ± .0073	870
9	824	1.56 ± .0053	780
10	704	2.75 ± .0026	687
11	577	2.94 ± .0090	588
12	522	2.65 ± .0174	530
13	458	2.30 ± .0192	460
14	315	3.05 ± .0203	305
15	430	2.22 ± .0172	444
16	378	1.89 ± .0176	378
17	321	1.63 ± .0025	326
18	286	2.65 ± .0070	265
19	212	2.19 ± .0130	219
20	167	1.68 ± .0030	168

4/29/92 0930hr JP

Remeasured  $\text{Ca}^{++}$  concentrations of  
0.05N  $\text{NaNO}_3\text{-CaCl}_2$  reference  
solutions using AA.

Equipment, supplies, procedure, and  
dilution factors same as those  
in previous analysis (see pp. 10-12).

Results:

$X_{\text{Ca},i}$	$\text{Ca}^{++}$ Expected ppm	Measured ppm	Converted ppm Value
0.1	100	$2.01 \pm .0056$	100.5
0.2	200	$3.63 \pm .0705$	181.5
0.3	301	$6.13 \pm .0385$	306.5
0.4	401	$4.24 \pm .0222$	424
0.5	501	$5.26 \pm .0065$	526 4/29/92
0.6	601	$6.46 \pm .0315$	646 4/29/92
0.7	701	$7.70 \pm .0467$	770
0.8	802	$8.93 \pm .0107$	893
0.9	902	$12.05 \pm .0952$	1205
1.0	1002	$10.38 \pm .0240$	1038

4/30/92 0900 TD

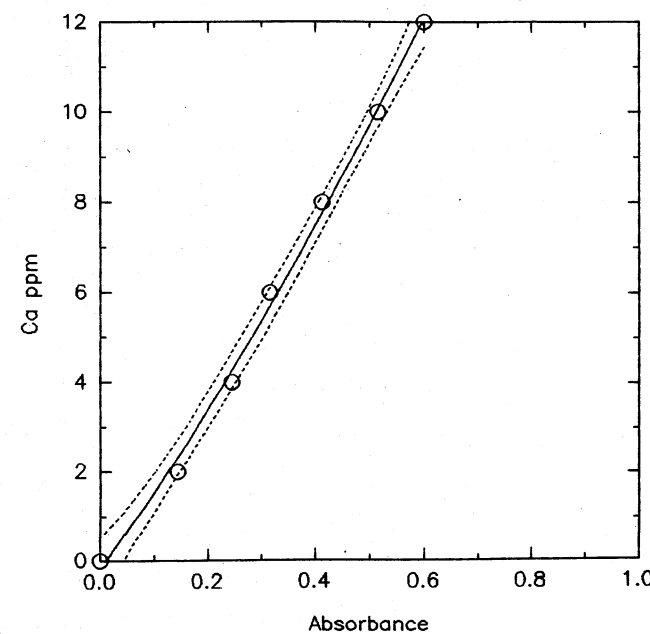
Remeasured  $\text{Ca}^{2+}$  concentrations of 0.05N  
 $\text{NaNO}_3\text{-CaCl}_2$  reference solutions using AA.  
Each sample was run twice

Equipment, supplies, procedure, and dilution  
factors were the same as those in the previous  
analyses (p. 10-12)

RESULTS OF  $\text{Ca}^{2+}$  ANALYSIS

$X_{\text{Ca},i}$	EXPECTED ppm	measured ppm	corrected ppm
0.1	100	$1.79 \pm .0055$	89.5
0.2	200	$3.61 \pm .0203$	180.5
0.3	301	$5.56 \pm .0144$	278
0.4	401	$3.79 \pm .0098$	379
0.5	501	$4.69 \pm .0047$	469
0.6	601	$5.87 \pm .0090$	587
0.7	701	$7.06 \pm .0250$	706
0.8	802	$8.21 \pm .0371$	821
0.9	902	$10.77 \pm .0327$	1071
1.0	1002	$9.42 \pm .0151$	942
0.1	100	$1.74 \pm .0051$	87
0.2	200	$3.55 \pm .0016$	177.5
0.3	301	$5.48 \pm .0022$	274
0.4	401	$3.73 \pm .0084$	373
0.5	501	$4.65 \pm .0318$	465
0.6	601	$5.78 \pm .0032$	578
0.7	701	$7.04 \pm .0132$	704
0.8	802	$8.24 \pm .0394$	824
0.9	902	$10.75 \pm .0350$	1075
1.0	1002	$9.36 \pm .0160$	936

1200 TO AA analysis of  $\text{Ca}^{2+}$  ( $\text{NaNO}_3$  -  $\text{CaCl}_2$  .05N soln)  
 Prepared 2, 6, 8, 12 ppm  $\text{Ca}^{2+}$  standards by diluting  
 the appropriate amount of 1000 ppm Standard  
 to 500 ml in a Volumetric flask using Ultrapure water.  
 No. 1% KCl was added to eliminate ionization  
 in the AA. The 4 and 10 ppm standards used earlier  
 were also used here. The absorbances of the standards  
 were recorded and a calibration curve was plotted.  
 This curve was used to determine the concentrations  
 of the samples.



Ca ppm 1	Absorbance 2	Regress 3
0	0	-0.18742
2	0.143	16.679
4	0.244	6.2982
6	0.315	0
8	0.412	0
10	0.515	0
12	0.6	0
		0.99832

$E_{\text{Ca}}$	Abs. (1)	Abs. (2)	$\text{Ca}^{2+}$ conc (ppm)	Adjusted conc (ppm)
0.1	.096	.097	1.48	74
0.2	.192	.189	3.22	161
0.3	.297	.287	5.22	261
0.4	.219	.219	3.78	378
0.5	.267	.272	4.77	477
0.6	.331	.334	6.06	606
0.7	.394	.395	7.38	738
0.8	.460	.454	8.75	875
0.9	.584	.570	11.53	1153
1.0	.524	.511	10.17	1017

7/10/92

JP

## Measure amount of $\text{H}_2\text{O}$ in analcime

Objective: determine amount of  $\text{H}_2\text{O}$  in  
 analcime from ASE experiment  
 (see GC-03/237)

Method: gravimetric analysis after  
 drying + heating analcime to  
 drive off  $\text{H}_2\text{O}$ .

Equipment: 1) air tight quartz crucibles - 10ml  
 2) Mettler AE 240 balance accurate  
 to 0.1 mg (SN 101237)  
 3) Fisher muffle furnace Model 184A  
 (SN 91100314)  
 4) Filter paper (Whatman 5)  
 5) Blue M drying oven

### Procedure

1410 gp 1) Filter analcime from sample ASE4  
 (ASH # 450/635\*UC\*WA) and let  
 air dry. Filtered liquid into a  
 1L plastic bottle and saved for  
 later analysis. Bottle labeled  
 ASE4a.

2) Allowed analcime to air dry.

7/13/92

0300h gp

3) Transfer air dried analcime to glass  
 beaker + label ASH # 450/635\*UC\*WA\*ASE4\*REC

4) Bring drying oven up to temperature  
 of  $105^\circ\text{C}$ .



- 5) Weigh 2 quartz crucibles, place ~1.0g of ASH\*450/635\*UC\*WA\*AE4\*REC in each crucible + record weight.

$$\begin{aligned} \text{Weight of qty crucible 1} &= 12.3877 \text{ g} \\ + \text{ASH*...*REC} &= 13.3876 \text{ g} \\ \text{Wt of ASH*...*REC} &= .9999 \text{ g} \end{aligned}$$

$$\begin{aligned} \text{Weight of qty crucible} &= 12.5101 \text{ g} \\ + \text{ASH*...*REC} &= 13.5102 \text{ g} \\ \text{Wt of ASH*...*REC} &= 1.0001 \text{ g} \end{aligned}$$

- 6) Reweigh to get amount of absorbed water after heating at 105°C for ~2 hrs.

$$\begin{aligned} \text{Weight of crucible 1} &= 13.3870 \text{ g} \\ \text{Previous wt} &= 13.3876 \text{ g} \\ \text{Wt absorbed H}_2\text{O} &= .0006 \text{ g} \end{aligned}$$

$$\begin{aligned} \text{Weight of crucible 2} &= 13.5095 \text{ g} \\ \text{Previous wt} &= 13.5102 \text{ g} \\ \text{Wt absorbed H}_2\text{O} &= .0007 \text{ g} \end{aligned}$$

- 7) Place crucibles in muffle furnace at 900°C for ~2 hrs.

- 8) Reweigh to get amount of structural water.

$$\begin{aligned} \text{Wt of qty crucible 1} &= 13.3059 \text{ g} \\ \text{Previous wt} &= 13.3077 \text{ g} \\ \text{Wt structural H}_2\text{O} &= 0.0018 \text{ g} \end{aligned}$$

$$\begin{aligned} \text{Wt of qty crucible 2} &= 13.4285 \text{ g} \\ \text{Previous wt} &= 13.4302 \text{ g} \\ \text{Wt structural H}_2\text{O} &= 0.0017 \text{ g} \end{aligned}$$

### 8/14/92 PM X-ray Diffraction Identification of Montmorillonite (oriented mineral slides)

Na-form montmorillonite from Otay, CA was received from Ward's (API #24). XRD analyses will be made on the mineral to determine its composition.

- 1) The mineral was crushed using mortar + pestle.
- 2) The crushed mineral was milled for ~10 minutes.
- 3) Four grams of the milled mineral was weighed into a 600 mL beaker.
- 4) 5.01 grams of sodium metaphosphate (lot #720373) was weighed out + dissolved using ultrapure water in a 2000 mL volumetric flask. This solution will be used as a dispersing agent. The solution is stored in two 1000 mL labeled polypropylene bottles.
- 5) The beaker containing the four grams of mineral was filled to the 500 mL mark with the sodium metaphosphate solution.

The mineral/sodium metaphosphate suspension was cleaned by ultrasound for 10 minutes to disperse the sample.

6) About 180 mL of the supernatant was poured into centrifuge tubes, and centrifuged at 1300 rpm for about two minutes. The particles remaining in suspension will be  $< 2 \mu\text{m}$ .

5 PM 8/14/92

7) A small portion ( $\sim 10 \text{ mL}$ ) of the  $< 2 \mu\text{m}$ -containing solution was vacuum-filtered through a  $0.45 \mu\text{m}$  filter. The solution should be filtered by adding very small amounts of solution in succession, or else the solution will not be pulled through at a reasonable rate.

8) The filtered sample was carefully transferred from the filter paper onto a slide. The slide was heated in an oven at  $400^\circ\text{C}$  for 30 minutes, + labelled "a".

9) Three more slides were prepared in the same manner as above. They were labelled "b", "c", + "d". They were NOT heated in the oven at  $400^\circ\text{C}$  for 30 minutes.

"b" was heated in the oven at  $550^\circ\text{C}$  for 30 minutes.

"c" was placed in a desiccator containing  $\sim 1/2$  pint ethylene glycol, + the desiccator put in an oven at  $60^\circ\text{C}$  for an hour.

"d" was simply air-dried.

All 4 slides will be analyzed by X-ray diffraction.

8/17/92 PM X-ray Diffraction Identification of Montmorillonite (Unoriented Sample slide)

More of the previously ground and milled montmorillonite will be checked by XRD to see how much quartz and feldspar remains in the  $< 2 \mu\text{m}$  fraction.

1045 PM 2 grams of the milled montmorillonite were weighed into a 250 mL glass beaker. The beaker was filled to the 250 mL mark with the 2.5 g/l sodium metaphosphate solution prepared earlier. The beaker was placed in the ultrasonic cleaner + cleaned for 10 minutes.

1100 PM Approximately 30 mL of the suspended sample was poured into each of 4 centrifuge tubes + the solution was centrifuged at 1300 rpm for 2.25 minutes. The upper  $2/3$  of the supernatant was poured into a beaker + the beaker allowed to settle. Settling will probably take a couple of days.

8/19/92 PM 0915 The settled sample from 8/17 was looked at. There wasn't enough mineral settling out to make a slide, so a new batch of montmorillonite will be prepared to remedy this. (The 8/17 sample will be discarded).

0920 PM Preparation of 2.5 g/l Sodium Metaphosphate

2.50 grams of sodium metaphosphate (lot #720373) was weighed into a beaker. Nanopure water was added to the beaker, the contents swirled, + the upper portion of the beaker's contents poured into a 1000 mL volumetric flask. The sodium

metaphosphate was dissolved in this manner, & the flask made up to volume with ultrapure water.

Four grams of previously crushed and milled montmorillonite were weighed into each of two 600 mL beakers. The beakers were filled to the 500 mL mark with the 2.5 g/L sodium metaphosphate solution.

The ultrasonic cleaner was used for ten minutes on both beakers to disperse the montmorillonite.

About 45 mL of the suspension was poured into each of the ~~four~~ <sup>two</sup> 50 mL centrifuge tubes. They were centrifuged at 1300 rpm (checked by tachometer) for two and a quarter minutes. The upper  $\frac{4}{5}$  of the supernatant was poured off into a large beaker.

Three more sets of suspended material were centrifuged and decanted in the same manner as above.

0957 PM The large beaker was labeled "< 2  $\mu$ m montmorillonite", covered with a watch glass, and set aside.

When enough mineral has settled to the bottom of the beaker, the mineral will be separated from the supernatant and the mineral air-dried. The dried sample will be used to make an unoriented XRD-mount to determine if this method of separation will remove a sufficient amount of quartz and feldspar present in the montmorillonite.

1120 PM To cut down on waiting time, 45 mL of the < 2  $\mu$ m solution was decanted into each of 2 centrifuge tubes, & the tubes were centrifuged for 15 minutes at 5700 rpm. The supernatant was poured off, and the accumulated mineral was transferred to a weighing paper. The mineral was dried under a drying lamp & prepared for XRD analysis as an unoriented slide.

### Cleaning montmorillonite -

The montmorillonite received from Wards will be chemically treated to remove carbonates, organics & iron oxides. The treatments will be performed on the < 2  $\mu$ m fraction, to cut down on the amount of mineral volume.

### A: Removal of Carbonates

Equipment: graduated 50-mL centrifuge tubes / rack  
hot plate  
600 mL beaker  
thermometer up to 80°C (at least)

Solutions: 1 N NaOAc @ pH = 5.0 - see A1  
ultrapure water

### A1 : Preparation of 1 N NaOAc @ pH 5.0

Equipment: 500 mL PP bottle  
500 mL volumetric flask  
glass eye dropper  
glass electrode / pH meter  
pH buffer 5.0  
analytical balance



NaOAc  
glacial acetic acid

0315 PM 8/19/92  
41.50 grams of NaOAc was weighed out  
and dissolved in a beaker using ultrapure  
water.

weight used: 41.05 g

The dissolved NaOAc was transferred to the volumetric  
flask, and 13.5 mL of glacial acetic acid  
were added to the volumetric flask. The flask  
was brought to volume with nanopure water.  
The pH of the solution is adjusted to 5.0 with  
glacial acetic acid as necessary.

1N NaOAc buffer pH: 4.8

The adjusted buffer solution was poured into  
the 500 mL PP bottle, and the bottle labeled.

8/20/92 Cleaning montmorillonite - continued.

C1 Preparation of saturated NaCl solution

C1 equipment: NaCl (lot # 912763)  
balance  
beaker  
nanopure water

0940 PM ~100 mL of nanopure water was poured  
into a beaker + the beaker + water tared off  
on the balance. 29.5 grams of NaCl were added  
to the beaker, + the solution stirred to mix. The  
solution was poured into a labeled PP bottle.

C2 Preparation of 1M  $\text{NaHCO}_3$  solution

8.400 g of  $\text{NaHCO}_3$  <sup>is 8.3995 g</sup> was weighed out +  
dissolved in a 100 mL volumetric flask  
to produce 100 mL of 1M  $\text{NaHCO}_3$  solution.

weight used: 8.3995 g  $\text{NaHCO}_3$ , lot # 897186A

C3 Preparation of 0.3M sodium citrate solution

88 grams of  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$  is weighed out  
and dissolved in a 1 L volumetric flask. The  
solution is brought to volume with ultrapure  
water.

weight used: 88.00 g, lot # 905257A

1125 PM Another 2000 mL of 2.5 g/L sodium metaphosphate  
solution (lot # 720373) was made up as described  
on page 23.

weight used: 5.00 grams

1304 PM The XRD for the unoriented slide showed a very  
small amount of quartz remaining in the  $< 2 \mu\text{m}$   
fraction. To try to remove some of this, the  $< 2 \mu\text{m}$   
fraction will be obtained by using a different  
r.p.m. centrifugation for a longer time.

5 grams of the milled montmorillonite was  
weighed into a 600 mL beaker. The beaker was  
filled to the 500 mL mark with the 2.5 g/L  
sodium metaphosphate solution prepared today.  
The beaker/mineral/solution was ultrasonically  
cleaned for 10 minutes to disperse the clay.

~50ml of the suspension was poured into each of 4 50 ml centrifuge tubes. The tubes were centrifuged at 1700 rpm (checked by tachometer) for  $2\frac{1}{2}$  minutes. The supernatant was poured into a large beaker, + the remainder discarded.

The process was repeated until ~ one liter of supernatant ( $< 2\mu\text{m}$  clay particles) was collected.

4/4/94  
The  $< 2\mu\text{m}$  suspension was centrifuged at ~ 3450 rpm for 25-30 minutes, the supernatant discarded, + the clay remaining in the tubes removed with a spatula + allowed to air dry.

The preparation of the milled montmorillonite to get the  $< 2\mu\text{m}$  clay was continued until approximately 5 grams of the clay was separated + air dried.

8/31/92 PM Removal of Carbonates continued (see p. 27-28)

A2: 2.3 g of the  $< 2$  micron montmorillonite was weighed into each of 2 centrifuge tubes.

Nanopure water was heated in the beaker + maintained at  $65^\circ\text{C}$  (checked by a thermometer suspended in the water) to make a water bath.

0950 PM 25 ml of the buffer NaOAc solution (GC-06-27,28) was poured into each of the centrifuge tubes. The tubes will be heated for 30 minutes.

1025 PM The tubes were centrifuged at 2800 rpm for 20 minutes. The supernatant was poured off and the tubes refilled to the 25 ml mark

with NaOAc. The contents were stirred with a glass stirring rod + the tubes put in the ultrasonic cleaner for a few minutes to redisperse the clay.

1115 PM The tubes were centrifuged at 2800 rpm for 5 minutes (clear supernatant resulting). Another portion of NaOAc was used to wash the clay in the same manner. The tubes were centrifuged for 5 minutes at 2300 (clear supernatant resulting).

1150 PM Because of the high rpm level used in the first 2 centrifugations, the clay may not have dispersed properly in the following washes. So a fourth wash/centrifugation (5 minutes at 2300 rpm) will be run.

1330 PM The washed clay was transferred to a 150-ml beaker with a minimum of nanopure water, + the suspension evaporated at  $\sim 70^\circ\text{C}$  until a soil-to-water ratio of  $\sim 1:2$  was reached. (The time needed will depend on the amount of water used to transfer the clay).

9/2/92 PM The suspension was evaporated until the total volume of the soil + water was  $\sim 40\text{ml}$ . 10 ml of 50%  $\text{H}_2\text{O}_2$  was added, 5 ml at a time with 10 min of stirring allowed between additions. The solution was heated gently ( $65^\circ\text{C}$ ) + then another 10 ml were added, stirred, + heated in the same manner. A watch glass was used to cover the beaker, + the solution allowed to sit for 2 hours.

1555 PM The suspension was transferred into 4 centrifuge tubes, and NaOAc buffer solution was used

to wash the mineral twice (~5 min at 2650 rpm after the mineral + buffer were stirred together). The supernatant (clear) was discarded. The clay was also washed twice with 95% + 99% methanol.

9/14/92 PM C: Removal of Free Iron Oxides from the Clay Mineral

0830 ~2.5g of the clay was in each tube (weight is VERY approximate, due to the swelling nature of the clay). 10 mL of the 0.3M Sodium Citrate solution (GC-06-29) was added to each test tube and 2.5 mL of 1N  $\text{NaHCl}$  was added as well (graduated cylinder). The tubes were placed in a water bath at ~75°C which was watched to make sure the temperature would not exceed 80°C. 0.5g  $\text{Na}_2\text{S}_2\text{O}_4$  was added to each tube. The solutions were stirred constantly for one minute, then occasionally for the next fourteen minutes.

5 mL of the saturated  $\text{NaCl}$  solution (GC-06-28) was added to each tube. The solution was stirred, warmed (~50°C in water bath) and centrifuged for 12 minutes at 2200 rpm.

The resulting supernatant was clear, + the clay left was light army green.

The clay was washed three times with the 0.3M sodium citrate solution.

1240 PM The iron oxide removal process was repeated, with the additional step of 5 mL's acetone added immediately following the 5 mL saturated  $\text{NaCl}$  solution to help flocculation.

Again, the resulting supernatant was clear, + the clay light army green.

1440 PM The clay was washed 3 times with the sodium citrate solution.

9/14/92 PM Prep of more NaOAc Buffer

Another 500 mL of ~5.0 pH NaOAc buffer was made up as described on GC-06-28.

wt used: 41.09g NaOAc, lot # 905630  
NaOAc buffer pH: 4.9

1550 PM Prep of more 0.3M Sodium Citrate Solution

Another liter of 0.3M sodium citrate solution was made up as described on GC-06-29.

wt used: 88.00g, lot # 905257A

9/16/92 PM Removal of Carbonates from more <2  $\mu\text{m}$  Montmorillonite

1045 PM 1.15g of the air-dried <2  $\mu\text{m}$  montmorillonite was weighed into each of 2 50 mL centrifuge tubes.

Nano pure water was poured into a beaker and heated to ~75°C (checked by thermometer) to make a water bath.

~15 mL of the acetate buffer prepared above was poured into each of the tubes containing the montmorillonite. The clay/buffer was stirred to suspend the



clay particles, and the tubes were placed in the water bath.

1315 PM The tubes were kept in the water bath and the contents intermittently stirred for 30 minutes.

1350 PM The tubes were centrifuged at 1300 rpm for 4 minutes + the supernatant discarded. The clay was washed twice more with the acetate buffer, and the clay remaining left in the tubes. The tubes will be kept capped until the organic matter in the clay is removed.

9/18/92 PM Removal of Organic Matter

Preparation of 30%  $H_2O_2$

60 mL of 50%  $H_2O_2$  was poured into a 150 mL beaker (marked at 10 mL intervals). Nanopure water was poured in until the liquid level stood at the 100 mL mark. The solution was swirled to mix + poured into an appropriately labeled 125-mL polypropylene bottle.

0834 PM The clay remaining in the centrifuge tubes was carefully removed with a narrow-tipped spatula into a beaker. No water was used to transfer the clay this time because too much water is absorbed. 5 mL of the 30%  $H_2O_2$  was added to the clay, + the clay was stirred + watched for excessive bubbling (which was not observed). The beaker with the clay/hydrogen peroxide was then gently heated in a water bath maintained at  $\sim 65^\circ C$  with stirring for about five minutes.

The addition of 5 mL of the  $H_2O_2$  followed by heating was repeated.

0902 PM 10 mL of the  $H_2O_2$  was added to the clay, the beaker

containing the clay covered with a watch glass + the beaker left to sit for 3 hours. The beaker was kept heated in the water bath at  $\sim 65^\circ C$  for the last half hour.

1206 PM The clay was put into 2 centrifuge tubes + washed 3 times with NaOAc buffer + centrifuged after each washing.

The clay was then washed twice with 99% methanol, lot # 920369.

Removal of free iron oxides

1332 PM 10 mL of sodium citrate solution (6C-06-33) and 1 mL of  $NaHCO_3$  (6C-06-29) was added to each centrifuge tube. The clay/citrate/carbonate solutions in the tubes were heated to  $75^\circ C$  in the water bath. 0.5 g of  $Na_2S_2O_4$  (lot # 912722) was added to each tube, the contents were stirred constantly for one minute, then stirred occasionally for 14 minutes. The clay in one tube turned greenish, the other remained tan. 19 9/14/92

5 mL saturated NaCl solution (NaCl lot # 914913) was added to each tube.

The contents were mixed, warmed, + centrifuged @ 1800 rpm for 12 minutes.

1422 PM The clay was washed once with sodium citrate solution. Then another 10 mL of sodium citrate + 1 mL of  $NaHCO_3$  solution was added to each tube, the tubes heated back up to  $75^\circ C$  in the water bath, and 0.25 g  $Na_2S_2O_4$  was added to each tube. The contents were stirred as before, and within about three minutes both the clay in both tubes was green. Heating + stirring was

continued for the full 15 minutes.

The clay was then washed with sodium citrate solution 3 times with stirring followed by centrifugation, and the test tubes capped.

9/21/92 PM Preparation of 3M NaCl for Montmorillonite  
1M Exchange

To make certain that all exchangeable sites on the Montmorillonite clay are occupied by  $\text{Na}^+$ , the clay will be soaked in 3M NaCl solution.

Preparation of 3M NaCl solution

175 g of NaCl was weighed into a beaker, the NaCl dissolved with Nanopure water, and the beaker repeatedly rinsed into a 1 L PP 1/2 liter volumetric flask. The solution was brought to volume with ultrapure water, stirred to mix, & poured into a 1 L PP bottle. The bottle was appropriately labeled.

wt used: 175.30g NaCl, lot # 914193

0925PM Soaking of Montmorillonite Clay in 3M NaCl

The  $\text{Na}_2\text{S}_2\text{O}_4$ -treated, sodium citrate solution-washed clay had enough 3M NaCl solution added to allow the clay to be picked up by max pipet. The clay was injected into water-soaked dialysis tubing (12,000-14,000 MWCO) which was knotted at one end. The top was twisted & the tubing immersed in a beaker containing 3M NaCl solution. The clay will be soaked for four days, with the 3M NaCl solution changed daily.

9/23/92 PM 1330 The NaCl solution was replaced with fresh solution.

9/25/92 PM 0807 The 3M NaCl solution was replaced.

1358PM The dialysis tubing containing the Na-form clinoptilolite was rinsed on the outside with nanopure water. The tubes were emptied into a clean beaker and nanopure water added to the clay suspension until the volume was about a third again greater. The clay was swirled to mix. The suspension was poured into 4 50-ml centrifuge tubes, and the clay suspension centrifuged at  $\sim 1600\text{rpm}$  for about 5 minutes. The supernatant was poured off & the rinsing (addition of water, swirling, & centrifugation) repeated 6 times.

1653PM The supernatant was poured into a beaker, and 2 drops of 0.1 M  $\text{AgNO}_3$  solution (lot # 910644-24) was added. A white cloudy substance formed ( $\text{AgCl}$ ) which showed that the clay needs further rinsing to free it from excess NaCl.

9/28/92 PM 0756 The clay suspension was put (in a beaker) in the ultrasonic cleaner for  $\sim 3$  minutes to make certain the particles would disperse for thorough rinsing.

The suspension was poured into centrifuge tubes & centrifuged at  $\sim 1700\text{rpm}$  for 5 min, but no separation of the phases was seen.

0825PM About 30 ml of the suspension was put in each of four centrifuge tubes & centrifuged at 3500 rpm for 25 minutes.

0904PM The supernatant was cloudy-greenish & the clay was reddish at the bottom & greenish at the top.

The clay was repeatedly washed (3 times) with nanopure water, and the clay was dispersed by ultrasound treatment between washings. The resulting suspension was centrifuged at  $\sim 3000$  rpm for about 25 minutes each time. The supernatant was slightly cloudy each washing. On the third wash, the supernatant was tested with 2 drops of 0.1M  $\text{AgNO}_3$  solution for formation of  $\text{AgCl}$ . No reaction was seen, so the excess  $\text{NaCl}$  should be washed out by now.

1148 PM The clay was washed with nanopure water one more time and the supernatant checked again with 0.1M  $\text{AgNO}_3$  solution. The test was again negative (no precipitate).

The clay was taken over to Div. 1 where it will be freeze-dried to avoid collapsing the clay.

9/30/92 PM Kinetics Experiment ~~K4~~ MK1 (renamed 10/26/92) (PM)

Objective: Determine the time needed for sorption equilibrium between  $^{233}\text{U}$  solutions and the clay mineral montmorillonite.

Notes: Maximum sorption of uranium on montmorillonite is expected to occur at a pH similar to that obtained with clinoptilolite - i.e.,  $\text{pH} \sim 6.5$ . The ionic strength of the solutions will be kept constant at 0.1M  $\text{NaNO}_3$ . Initial pH of the solutions will be at 6.0 and 7.0. Initial pH of the 50 ppb  $^{233}\text{U}$  stock solution will be adjusted by addition of  $\text{NaHCO}_3$ . The amount of  $\text{NaHCO}_3$  to be used is determined by EQ 3 calculations.

MK1 PM 8/4/94

Preparation of 0.1M  $\text{NaNO}_3$  for K4 experiments.

0932 PM 4 liters of 0.1M  $\text{NaNO}_3$  solution was made up two liters at a time by weighing out 16.9980 g  $\text{NaNO}_3$  (lot # 7808 KDJF), transferring it to a 2L volumetric flask, and bringing the solution to volume with NANOpure ( $> 17 \text{ M}\Omega$  resistivity) water. The solution was stirred to mix + stored in <sup>two PM 9/30/92</sup> appropriately labeled Polypropylene (PP) bottles. Another 2L was made up in the same manner.

wt's used: 16.9953 g  $\text{NaNO}_3$  (first 2L)  
16.9931 g (second 2L)

1400 PM The freeze-dried clay was received back from Div. 1. The clay was weighed and the amount (0.903 g) is insufficient to begin the kinetics experiment. More clay will be cleaned and dried.

Again, removal of carbonates (GC-06-33), removal of organic matter (GC-06-34), and removal of free iron oxides (GC-06-35) was done to crushed + milled clay, montmorillonite, after the  $< 2$  micron clay fraction was obtained by centrifugation (GC-06-29, 30) + air-dried.

Roughly 35 g of the milled montmorillonite is needed to yield  $\sim 0.5$  g cleaned,  $< 2$  micron sample when dry.

10/12/92 PM The cleaned clay was soaked in 3M  $\text{NaCl}$  solution as described in GC-06-36. The solution will be changed daily.

10/16/92 PM After soaking since Monday in 3M  $\text{NaCl}$  solution, the clay will be transferred into a beaker, diluted with  $\sim 25$  mL ultrapure water, divided into



4 50-mL centrifuge tubes, & washed by centrifugation with ultrapure water. RPM used was ~1600, time was ~5 min.

1050 PM As the clay is re-washed, the clay flocculates less & less & the phases (solid & liquid) become more difficult to separate. After 4 washes, the rpm is raised to ~3500 rpm for a period of ~25 minutes.

1502 PM The murky green supernatant is discarded as it won't clear up after 2 30 min centrifugations at ~3500 rpm. Washing is continued on the clay remaining.

1704 PM After 3 washings, the supernatant is tested using dropwise addition of  $\text{AgNO}_3$  solution (0.1N lot # 910644-24). A white cloudy precipitate formed, so excess NaCl is still present. Washing will be continued.

10/19/92 PM

1042 The clay has been washed free of extraneous NaCl solution ( $\text{AgNO}_3$  drop test - see above) and then rinsed once more. The wet clay will be freeze-dried in the recently received LABCONCO Freeze drier.

10/23/92 PM

0958 Freeze-drying of the clay has been delayed due to a malfunctioning pump, but with another pump attached to the freeze dryer, the system should work.

1432 PM The clay is freeze-drying, and will be taken off-line at ~1900 today.

10/26/92 PM Experiment MK1 actually started (see GC-06-38, 39)

0702 PM

# Kinetics Experiment MK1

Initial pH approx. 6.0, 7.0; 0.1 M  $\text{NaNO}_3$ ; equilibrium with atm  $\text{CO}_2$

Based on Kinetics Experiment K3 by R. T. Pabalan  
Adapted Aug. 25, 1992  
Revised Oct. 23, 1992

## OBJECTIVE:

Determine the time needed for sorption equilibrium between  $^{233}\text{U}$  solutions and the clay mineral montmorillonite.

## NOTES:

Maximum sorption of uranium on montmorillonite is expected to occur at a pH similar to that obtained with clinoptilolite, i.e., pH approximately equal to 6.5. The ionic strength of the solutions will be kept constant at 0.1 M  $\text{NaNO}_3$ . Initial pH of the solutions will be at 6.0 and 7.0. Initial pH of the 50 ppb  $^{233}\text{U}$  stock solution will be adjusted by addition of  $\text{NaHCO}_3$ . The amount of  $\text{NaHCO}_3$  to be used is determined by EQ3 calculations.

MK1-1: Solution MK1-1 (2 bottles)

- initial  $\Sigma\text{U}$  = 50 ppb
- activity of 50 ppb U solution = 0.480 nCi/g
- initial  $\Sigma\text{Na}$  = 0.1 + x where 0.1 is from  $\text{NaNO}_3$  and x is from  $\text{NaHCO}_3$
- initial pH = 6.0
- initial solution mass = 500 g
- weight clay used = 0.5 g Otay montmorillonite supplied by Wards, <2 micron, carbonate pretreatment (also removal of organics and free iron oxides), sodium form
- equilibrium with atmospheric  $\text{CO}_2(\text{g})$ ,  $p\text{CO}_2 = 10^{-3.5}$  bar

MK1-1-A: In a pre-cleaned 4 liter plastic bottle, prepare 1600 g of 50 ppb U solution by diluting 160 g (carry in 500 mL glass beaker) of a 500 ppb  $^{233}\text{U}$  stock solution (in 0.1 M  $\text{NaNO}_3$  matrix; prepared previously from commercial 50 ppm  $^{233}\text{U}$  spike) to a total of 1600 g by carefully taring 0.1 M  $\text{NaNO}_3$  solution into the plastic bottle on a Mettler 4600 balance.

500 PM 10/26/92  
0709 PM Weight of 50 ppb  $^{233}\text{U}$  solution used: 160.15 g  
(Standard 22A; see Radiochemistry Notebook)  
Final weight of 50 ppb  $^{233}\text{U}$  solution: 1600.2 g

50 PM 10/26/92  
MK1-1-B: Transfer three 500 g aliquots of the 50 ppb solution into three 500-mL polypropylene (PP) bottles labeled MK1-1\*A, MK1-1\*B, and MK1-1\*C. Transfer the remaining 50 ppb solution into a 125-mL bottle labeled MK1-1\*1U. The bottles will need radiation stickers and a listing of the measured radiation level, isotope and chemical solution contained, estimate of the activity of the solution, and the date.

Take 2 5-mL aliquots of solution MK1-1\*1U using an adjustable pipettor with disposable tips. Transfer the aliquots into prelabeled and pre-weighed 50-mL centrifuge tubes. The labels will be MK1-1\*1U\*a or \*b.

Reweight each tube after addition of the sample. Add to each sample using an Eppendorf micropipet 250  $\mu\text{L}$  of 1.0 M  $\text{HNO}_3$  solution for later analysis with alpha-spectrometry.

SEC  
GC-06-39  
PM 12/29/92  
p111  
PK  
12/28/92

0758 PM weight of tube MK1-1X10x a 11.0911g  
 \* b 10.7242g

weight of aliquots \* a 4.9761g  
 \* b 4.9544g

MK1-1-C: Measure and record the initial pH of solutions MK1-1\*A, MK1-1\*B and MK1-1\*C (approximately 4.2 calculated using EQ3) using a combination glass microelectrode. The automatic temperature compensator (ATC) probe should be immersed in water in a separate container.

0815 PM Initial pH of solution MK1-1\*A 4.17 @ 20.7°C  
 \* B 4.14  
 \* C 4.14

pH buffers used to calibrate: Fisher 3, 4, 7, 9, + 10  
 lot #s 910886.24, 910359.24, 910943.24, 910944.24,  
 + 910870.24

Carefully add 0.0036 g of  $\text{NaHCO}_3$  to each 500 mL  $^{233}\text{U}$  solution. Cover the bottle with a porous material and keep the solution agitated on a gyratory shaker to equilibrate it with atmospheric  $\text{CO}_2(\text{g})$ .

Measure the pH of the solutions periodically until a constant value is reached. This step may take at least 10 days. Then proceed to the next step.

0845 PM Weight of  $\text{NaHCO}_3$  (lot # 886728) used:  
 MK1-1\*A 0.0040g  
 \* B 0.0037g  
 \* C 0.0041g

0905 PM Bottles set on gyratory shaker at ~110 rpm.

10/28/92 PM pH measurement of MK1-1 solutions

The microelectrode and ATC used earlier will be used for all measurements. Fresh portions of the 3, 4, 7, 9, + 10 buffers listed above will be used for calibrating the meter.

Date	time	pH MK1-1*A	* B	* C	temp °C
10/28	1403	6.44	5.99	6.18	23.5°C
10/30	1014	6.28	5.96	6.11	21.5
11/2	1405	6.46	6.09	6.28	22.5
11/4	0905	6.40	6.16	6.35	20.1
11/6	1445	6.42	6.04	6.22	20.1
11/9	1335	6.30	6.17	6.37	21.6
11/11	1335	6.43	6.01	6.38	21.6
* 11/11	1415	6.36	5.98	6.10	21.7
11/13	0928	6.39	6.14	6.26	18.8
* 11/13	0956	6.32	6.04	6.14	19.0

\* means the pH was measured using a Ross glass electrode (calibrated using the same pH buffers used for the microelectrode).

11/2/92 0830hrs JF

Prepared additional reagents for spectrophotometric analysis of  $\text{SiO}_2$  and Al in accordance with TOPS 13 and 14.

## Reducing agent -

Dissolved 500 mg 1-amino-2-naphthol-4-sulfonic acid (lot 904672) in 50 ml  $\text{H}_2\text{O}$ .  
 Dissolved 30 g  $\text{NaHSO}_3$  (lot 913268) in 150 ml  $\text{H}_2\text{O}$ .  
 Mix these solutions & filtered into a PP bottle. Labelled bottle "Reducing agent".

## Oxalic Acid Solution -

Dissolve 7.5 g oxalic acid (lot 905504) in 100 ml  $\text{H}_2\text{O}$ . Transfer to PP bottle and labelled "Oxalic Acid Solution".

## Ammonium Molybdate Reagent

Place 10 g ammonium molybdate (lot 901533) in a 100 ml beaker. Dissolve by stirring and warming gently. Dilute to 100 ml and adjust pH to 7-8 with 6M NaOH. Transfer solution of PP bottle & label "Ammonium Molybdate Reagent".

## Stock Dye Solution

Dissolve 150 mg of Eriochrome cyanine R (lot K5501, CH-9410 Buchs) in 50 ml  $\text{H}_2\text{O}$ . Dilute 5 ml glacial acetic acid (lot 893419) to 10 ml with  $\text{H}_2\text{O}$  in a 100 ml volumetric flask. Adjust pH of Eriochrome solution to about 2.9 with acetic acid solution. Transfer

solute to a 100 ml volumetric flask & dilute to 100 ml. Transfer to a PP bottle and labelled "Stock Dye Solution".

11/2/92 PM Separation of the <2 micron Montmorillonite  
 0900 The rest of the previously crushed and milled montmorillonite (Na-form "Otaj", API # 924 - see GC-06-23) was treated to separate the <2 micron fraction from the rest.

5 grams of the ~ 90 grams of milled montmorillonite was taken at a time. The 5 grams was placed in a 600 ml beaker. 500 ml of 25 g/L sodium metaphosphate solution (lot # 720 373) was added to the montmorillonite. The suspension was swirled to mix and put in the ultrasonic cleaner for 10 minutes.

~45 mL of the ultrasonicated suspension was poured into each of 6 50-ml centrifuge tubes & the tubes centrifuged at 1700 rpm (checked by tachometer) for 3 minutes. The supernatant was saved in a large beaker, and the material left in the tubes was discarded. The supernatant contains the <2 micron clay fraction, and the remainder is mostly quartz & feldspar impurities.

The <2 micron clay fraction suspension was centrifuged at ~3450 rpm for 30 minutes. This was done on 45 mL aliquots in 50-ml centrifuge tubes. The resultant supernatant was discarded and the clay remaining in the tubes was removed with a spatula and air-dried.

The separation process will be repeated as described above until all of the crushed and milled montmorillonite has had the <2 micron fraction separated out.



11/6/92 PM Removal of carbonates from the <2 micron Montmorillonite.

0802PM 1.05 grams of the air-dried clay was measured into each of six 50-ml centrifuge tubes.

A water bath was prepared by pouring about 75 ml of ultrapure water (>17 M $\Omega$  resistivity) into a 1000 ml beaker, adding a small stir bar to discourage bumping, pouring about 50 ml ultrapure water into a 600 ml beaker, placing the smaller beaker inside the larger and heating them both on a hot plate. The inner beaker is maintained at 75°C (checked with thermometer suspended in the beaker).

More pH 5.0 NaOAc buffer was made up as described on GC-06-27,28.

weight NaOAc 40.85g

15 ml of the NaOAc buffer was added to each clay-containing centrifuge tube. The contents were stirred to suspend the clay and the tubes put in the bath. The suspensions were warmed and stirred for half an hour.

0943PM The suspensions were centrifuged at 1300 rpm for five minutes and the supernatant discarded. Another 15 ml of the buffer was added to each tube & a vortex mixer used to mix the buffer & clay. The tubes were centrifuged again & the process repeated so the clay is washed three times.

1015PM Removal of Organic Matter.

More 30% H<sub>2</sub>O<sub>2</sub> was prepared as described on

GC-06-34.

The NaOAc buffer-washed clay was removed from the centrifuge tubes using a glass rod with a rubber policeman into a 100-ml beaker. 5 ml of the 30% H<sub>2</sub>O<sub>2</sub> solution was added. The clay/H<sub>2</sub>O<sub>2</sub> was stirred for five minutes. No excess bubbling was seen so the beaker was heated in the water bath to 65°C, and heated and stirred for five minutes.

Another 5 ml H<sub>2</sub>O<sub>2</sub> was added to the clay (out of the water bath) and the stirring & reheating was repeated.

1132PM 10 ml of the H<sub>2</sub>O<sub>2</sub> solution was added to the clay. The beaker was loosely covered with a tilted watchglass & heated at 45°C for three hours. The clay puffs up, but does not actually dry out at any time.

1432PM The clay was still bubbling quite a lot, so the clay was left in the bath for another hour. The clay will be removed from heat & put back into six centrifuge tubes at the end of the hour.

1605PM The clay was washed three times with the 5.0 pH NaOAc buffer. The vortex mixer and a glass rod w. rubber policeman was used to stir the clay in to the NaOAc wash between centrifugations.

The centrifuge tubes were capped after the last wash.

11/8/92PM Removal of Free Iron Oxides

1115PM The water bath (GC-06-46) was again

heated to 75°C

The clay in the tubes was washed twice with 99% methanol, lot # 920369.

10 mL of 0.3 M sodium citrate solution and 1 mL of 1 M  $\text{NaHCO}_3$  solution (GC-06-33, 29) was added to each tube, and the tubes heated in the water bath.

0.5 g  $\text{Na}_2\text{S}_2\text{O}_4$  (lot # 912722) was added to each tube (not in the water bath). The first two tubes were allowed to sit a little too long without stirring (about 45 sec) so when they were stirred the contents boiled up + over the sides of the tubes. The tubes were hastily wiped off, all contents stirred, + the tubes returned to the bath.

The tubes were heated and stirred for fourteen minutes. The clay in 3 of the tubes turned greenish, while the others remained tan.

5 mL saturated NaCl solution (see GC-06-35) was added to each tube.

The contents were vortex mixed, warmed, + centrifuged for 12 minutes at 1800 rpm.

1310 PM The clay was washed once with sodium citrate solution and the centrifuge tubes were capped.

11/9/92 PM Removal of Free Iron Oxides - Continued

0821 PM Another 10 mL of sodium citrate solution and 1 mL of sodium bicarbonate solution was added to each test tube containing clay. The tubes were heated to

75°C in the water bath. 0.3 g  $\text{Na}_2\text{S}_2\text{O}_4$  (lot # 912722) was added to each tube (quickly) + the contents stirred constantly for the first minute + then occasionally for the next fourteen.

5 mL saturated NaCl solution was added to each tube. The solutions were mixed, warmed, + centrifuged.

The clay is then washed four times with sodium citrate solution.

Saturation of montmorillonite exchange sites with  $\text{Na}^+$

1155 PM The clay was mixed with a minimum of 3 M NaCl solution to allow the clay to be picked up by max pipet. The clay was injected into dialysis tubing (knotted at both ends). The tubing was put in a beaker + covered with 3 M NaCl solution.

11/13/92 PM

Expt. MK1-1 continued

0902 PM  
1002

MK1-1-D: Take 2 5-mL aliquots of MK1-1\*A, MK1-1\*B, and MK1-1\*C using an adjustable pipettor with disposable tips. Transfer the aliquots into prelabeled and pre-weighed 50-mL centrifuge tubes. The labels will be MK1-1\*A\*I1 or \*I2. Reweigh each tube after addition of the sample. Add to each sample using an Eppendorf micropipet 250  $\mu\text{L}$  of 1.0 M  $\text{HNO}_3$  solution for later analysis with alpha-spectrometry.

	wt tube	wt elg
MK1-1*A*I1	11.0909 g	5.0269
I2	10.3378	5.0278
*B*I1	10.3444	5.0188
I2	11.0720	5.0273
*C*I1	10.6986	5.0169
I2	10.6260	5.0205

1040 PM

Then into bottles MK1-1\*A and MK1-1\*B (NOT to MK1-1\*C), add 0.5 g of Na-montmorillonite which was previously tared onto weighing paper. Record the time and room temperature. Solution MK1-1\*C is the control experiment to determine uranium losses to the container walls. Keep the solutions agitated on a gyratory shaker (note the approximate rpm of the shaker on the notebook).

wt montmorillonite used

MK1-1XA 1.4996g

MK1-1XB 1.5001

time 1117

room temp 67.8°F

gyratory shaker set at ~125 rpm

MK1-1-E: At a time approximating the values listed below, take one 5-mL sample from MK1-1\*A, MK1-1\*B, and MK1-1\*C with a 10 cc sterile syringe in the following manner: connect the 10 cc syringe to a Dynagard polypropylene filter (0.2 micrometer pore rating, 3.9 cm<sup>2</sup> surface area). Withdraw 8 mLs of solution through the filter. Eject 3 mLs of the solution back into the sample bottle to wash clay back out of the filter paper. Remove the filter from the syringe, add 5 mL of the withdrawn solution to a pre-weighed 50-mL centrifuge tube, replace the filter, and put the rest of the withdrawn solution back in the solution bottle. The filter is to keep the montmorillonite out of the sample aliquot. (The syringe and filters are disposed of). The MK1-1\*C sample can be taken with an Oxford pipet with a 5-mL disposable tip.

Reweigh each centrifuge tube after addition of the sample. Add to each sample using an Eppendorf micropipet 250μL of 1.0 M HNO<sub>3</sub> solution for later analysis with alpha-spectrometry. Label the samples MK1-1\*A\*ia, where i is the sampling time number (1,2,3,...).

Take two 5-mL samples from MK1-1\*A, \*B, \*C every third sampling time. Label the second sample MK1-1\*A\*ib or \*B\*ib or \*C\*ib.

In addition, measure the pH of each solution. Record the pH and solution temperature.

Use the following a time (hours): 1, 2, 4, 12, 24, 30, 36, 42, 48. These may be changed if necessary. The solutions are expected to reach equilibrium in roughly 24 hours.

sample	date	solution	pH	soln. Temp.	time
1	"/13	MK1-1XA	6.27	20.5	1233 PM
	"/13	*B	6.04	20.5	1239
	"/13	*C	6.14	20.6	1246
2	"/13	MK1-1XA	6.26	20.8	1326 PM
	"/13	*B	6.07	20.9	1332
	"/13	*C	6.15	20.9	1337
3	"/13	MK1-1XA	6.27	21.6	1535 PM
	"/13	*B	6.05	21.6	1542
	"/13	*C	6.13	21.6	1548
4	"/13	MK1-1XA	6.20	20.2	2243 PM
	"/13	*B	5.98	20.2	2249
	"/13	*C	6.02	20.2	2256
5	"/14	MK1-1XA	6.22	19.2	1111 PM
	"/14	*B	6.03	19.3	1117
	"/14	*C	6.07	19.3	1123

sample	date	solution	pH	soln. Temp.	time
6	"/14	MK1-1XA	6.40	20.8	1717 PM
	"/14	*B	6.16	20.8	1723
	"/14	*C	6.17	20.8	1729
7	"/14	MK1-1XA	6.53	20.1	2145 PM
	"/14	*B	6.29	20.1	2148
	"/14	*C	6.24	20.1	2153
8	"/15	MK1-1XA	6.36	18.4	0903 PM
	"/15	*B	6.18	18.5	0908
	"/15	*C	6.18	18.6	0914
9	"/15	MK1-1XA	6.39	20.4	1452
	"/15	*B	6.23	20.4	1501
	"/15	*C	6.17	20.4	1507
10	"/16	MK1-1XA	6.39	20.2	1258
	"/16	*B	6.33	21.3	1303
	"/16	*C	6.23	21.3	1307
11	"/18	MK1-1XA	6.40	21.4	1120
	"/18	*B	6.30	21.4	1127
	"/18	*C	6.27	21.4	1129

sample	wt tube	wt aliquot	time
PM MK1-1XA * 1a	10.3338	5.2951	1219
B * 1a	11.0992	5.1312	1223
C * 1a	11.0949	5.0731	1226
PM MK1-1XA * 2a	11.0072	4.9112	1314
B * 2a	10.7578	4.9471	1317
C * 2a	10.6382	4.7732	1320
PM MK1-1XA * 3a	10.6420	5.0075	1514
A * 3b	10.3381	5.2748	1516
B * 3a	11.0906	4.7770	1519
B * 3b	10.7696	4.8193	1523
C * 3a	10.7874	5.0101	1525
C * 3b	11.0971	5.0095	1528
PM MK1-1XA * 4a	10.7647	4.8589	2231
B * 4a	10.8747	4.7830	2233
C * 4a	10.8677	5.0301	2236

sample	wt. tube (g)	wt. aliquot (g)	time
MKI-1XAX5a	10.7205	4.9235	1100 AM
BX5a	10.7115	5.0852	1103
CK5a	10.7042	5.0299	1105
MKI-1XAX6a	10.7219	4.9838	1658 PM
AK6b	10.8743	5.2538	1701
BX6a	10.7266	4.9020	1703
BX6b	10.7407	5.2542	1705
CK6a	10.3364	5.0356	1708
CK6b	10.7276	5.0388	1710
MKI-1XAX7a	10.7423	5.1548	2133 PM
XB7a	10.7000	4.6868	2136
XCK7a	10.7636	5.0601	2139
MKI-1XAX8a	10.7015	5.0693	0848
XB8a	10.8279	4.9524	0851
XCK8a	10.7236	5.0353	0854
MKI-1XAX9a	10.7309	4.9755	1433 PM
AX9b	10.7306	5.0664	1435
BX9a	10.7597	4.9370	1438
BX9b	10.8747	5.1270	1441
CK9a	10.7664	5.0353	1443
CK9b	10.8202	5.0395	1446
MKI-1XAX10a	10.7202	4.9983	1348/1248 PM
BX10a	10.8186	5.0382	1350/1250 PM
CK10a	10.7600	5.0404	1254
MKI-1XAX11a	10.7371	4.9243	1112
BX11a	10.7245	5.0822	1115
CK11a	10.9372	5.0468	1117

11/18/92

1130 AM

MKI-1-F: After the last samples have been taken, take 2 5-mL aliquots of solution MKI-1\*1U using a 10 cc syringe with filter as described previously. Transfer the aliquots into pre-weighed 50-mL centrifuge tubes. Reweigh the tubes after addition of the sample. Add to each sample using an Eppendorf micropipet 250  $\mu$ L of 1.0 M HNO<sub>3</sub> for later analysis using alpha-spectrometry. Label the bottles MKI-1\*FU\*a or \*b.

11/18/92 PM

sample	tube wt (g)	aliquot wt (g)	time
MKI-1XFKa	10.7613	5.0285	1141
Xb	10.7016	5.0593	1143

11/23/92 PM Prep. of more 0.1 M NaNO<sub>3</sub> solution

0945 PM 4 Liters of 0.1 M NaNO<sub>3</sub> was prepared by twice weighing out 17.00g NaNO<sub>3</sub> (lot # 7808 KDJE), transferring the 17.00g to a 2 L volumetric flask and bringing the solution to volume with ultra pure (> 17 M $\Omega$  resistivity) water. The solutions were stirred to mix + stored in 1L polypropylene bottles.

PM 11/23/92

1401 PM Prep of 3M NaCl from SAz-1 Montmorillonite

50 grams of Cheto Montmorillonite from the source Clays Repository were weighed out. Nanopure water was added to the clay until it could be picked up by max pipettor. The clay was injected into water rinsed dialysis tubing + the tubing knotted at both ends. The clay in tubing was placed in a 600 mL beaker + covered with 3M NaCl solution (lot # 912763). The beaker is kept covered with a watch glass.

11/24/92

0725 PM More 3M NaCl solution was made up from lot # 912763. The solution in the tubing-containing beaker was changed out.

11/25/92

0840 PM About 5g (wet) of the 3M NaCl soaked clay was transferred into a water-rinsed dialysis tube + rinsed. The rinsing was accomplished by putting the tubing containing the clay into a beaker with



a stir bar and filling the beaker with ultrapure water. The water was stirred for ~ 5 min + the water changed for fresh water. This was repeated until 0.1 N  $\text{AgNO}_3$  added to a portion of the rinse did not result in the formation of a whitish precipitate. ( $\text{AgNO}_3$  lot # 910644-24). Formation of precipitate shows there's still enough free  $\text{Na}^+$  in solution to form  $\text{NaNO}_3$  when  $\text{AgNO}_3$  is added.

1153 PM The 3M NaCl solution soaking the clay was replaced with fresh solution.

11/26/92 1142 PM The 3M NaCl solution was replaced again.

11/26/92 1011 PM The 3M NaCl solution was replaced again.

A ~ 5g portion of the NaCl-soaked clay was removed from the tubing and repeatedly washed with ultrapure water. Washing was done by vortexing + centrifugation. As the lab centrifuges only go up to about 3500 rpm, about a third of the clay is left in suspension + is lost between washings.

11/28/92 1350 PM The 3M NaCl solution was replaced again.

11/29/92 1730 PM The 3M NaCl solution was replaced.

A ~ 5g portion of the NaCl-soaked clay was repeatedly washed using vortexing + centrifugation. This was repeated until no precipitate was formed by addition of  $\text{AgNO}_3$  solution.

11/30/92 0845 PM The 3M NaCl solution was replaced again.

12/02/92 0801 PM The 3M NaCl solution was replaced again.

0851 PM A ~ 5g portion of the 3M-soaked clay was washed repeatedly in ultrapure water to remove excess NaCl.

### Kinetics Experiment MK1A

Initial pH approx. 6.0; 0.1 M  $\text{NaNO}_3$ ; equilibrium with atm  $\text{CO}_2$

Based on Kinetics Experiment K3 by R. T. Pabalan  
Adapted Aug. 25, 1992  
Revised Dec. 2, 1992

#### OBJECTIVE:

Determine the time needed for sorption equilibrium between  $^{233}\text{U}$  solutions and the clay mineral montmorillonite from the Source Clay Repository.

#### NOTES:

Previous experiment MK11 did not reach equilibrium within the expected time (24 hours). This may be due to the mineral having contaminants in it that were not removed by cleaning. This experiment will duplicate experiment MK11 except for the montmorillonite clay used. This time, SAZ-1 ("Cheto", Ca-form montmorillonite will be used.) Maximum sorption of uranium on montmorillonite is expected to occur at a pH similar to that obtained with clinoptilolite, i.e., pH approximately equal to 6.5. The ionic strength of the solutions will be kept constant at 0.1 M  $\text{NaNO}_3$ . Initial pH of the solutions will be at 6.0 and 7.0. Initial pH of the 50 ppb  $^{233}\text{U}$  stock solution will be adjusted by addition of  $\text{NaHCO}_3$ . The amount of  $\text{NaHCO}_3$  to be used is determined by EQ3 calculations.

#### MK1A-1: Solution MK1A-1 (2 bottles)

- initial  $\Sigma\text{U}$  = 50 ppb
- activity of 50 ppb U solution = 0.480 nCi/g
- initial  $\Sigma\text{Na}$  = 0.1 + x where 0.1 is from  $\text{NaNO}_3$  and x is from  $\text{NaHCO}_3$
- initial pH = 6.0
- initial solution mass = 500 g
- weight clay used = 0.5 g Cheto montmorillonite supplied by the Clay Mineral Repository, treated with 3 M NaCl to prepare the Na-form clay
- equilibrium with atmospheric  $\text{CO}_2(\text{g})$ ,  $p\text{CO}_2 = 10^{-3.5}$  bar

**MK1A-1-A:** In a pre-cleaned 4 liter plastic bottle, prepare 1600 g of 50 ppb U solution by diluting 160 g (carry in 500 mL glass beaker) of a 500 ppb  $^{233}\text{U}$  stock solution (in 0.1 M  $\text{NaNO}_3$  matrix; prepared previously from commercial 50 ppm  $^{233}\text{U}$  spike) to a total of 1600 g by carefully taring 0.1 M  $\text{NaNO}_3$  solution into the plastic bottle on a Mettler 4600 balance.

1340 PM weight of 500 ppb  $^{233}\text{U}$  solution used: 159.88g  
(Standard 23A: see Radiochemistry Notebook, p. 150)

weight of 50 ppb  $^{233}\text{U}$  solution prepared: 1600.2g  
PR 12/28/92

**MK1A-1-B:** Transfer three 500 g aliquots of the 50 ppb solution into three 500-mL polypropylene (PP) bottles labeled MK1A-1\*A, MK1A-1\*B, and MK1A-1\*C. Transfer the remaining 50 ppb solution into a 125-mL bottle labeled MK1A-1\*1U. The bottles will need radiation stickers and a listing of the measured radiation level, isotope and chemical solution contained, estimate of the activity of the solution, and the date.

1400 PM weight of aliquot in bottle MK1A-1\*A : 500.20

\*B : 499.96

\*C : 500.70

\*1U : 125.00

Take 2 5-mL aliquots of solution MK1A-1\*1U using an adjustable pipettor with disposable tips. Transfer the aliquots into prelabeled and pre-weighed 50-mL centrifuge tubes. The labels will be MK1A-1\*1U\*a or \*b.

Reweight each tube after addition of the sample. Add to each sample using an Eppendorf micropipet 250  $\mu\text{L}$  of 1.0 M  $\text{HNO}_3$  solution for later analysis with alpha-spectrometry.

1423PR	weight of tube MKIA-1*10* $\alpha$ : 10.8302
	$\times b$ : 10.7283
	weight of aliquot in MKIA-1*10* $\alpha$ : 5.0302
	$\times b$ : 5.0265

**MK1-1-C:** Measure and record the initial pH of solutions MK1A-1\*A, MK1A-1\*B and MK1A-1\*C (approximately 4.2 calculated using EQ3) using a combination glass microelectrode. The automatic temperature compensator (ATC) probe should be immersed in water in a separate container.

Initial pH of solution MKIA-1KA : 4.29 @ 21.1°C  
KB : 4.32  
KC : 4.31

pH buffers used to calibrate: Fisher 2, 4, 7, + 10  
(Lot #s 910358-24, 910359-24, 921733-24,  
+ 910870-24)

Carefully add 0.0036 g of  $\text{NaHCO}_3$  to each 500 mL  $^{233}\text{U}$  solution. Cover the bottle with a porous material and keep the solution agitated on a gyratory shaker to equilibrate it with atmospheric  $\text{CO}_2(\text{g})$ .

	weight of $\text{NaHCO}_3$ (lot # 886728) added:
1450PAC MIRA	1 KA 0.0035
	KB 0.0036
	KC 0.0038

1505 PM The bottles were put on the gyratory shaker at  $\sim 125 \text{ rpm}$ .

Measure the pH of the solutions periodically until a constant value is reached. This step may take at least 10 days. Then proceed to the next step.

The Ross glass pH electrode + Fisher buffers 2, 4, 7, + 10 will be used to measure pH.

<u>date</u>	<u>time</u>	<u>pH MK1A-1XH</u>	<u>*B</u>	<u>*C</u>	<u>temp. solus, °C</u>
12/4/92	0828	6.89	6.74	6.96	20.4
12/7/92	0922	7.00	6.73	7.00	15.5
12/9/92	0752	6.78	6.73	6.96	16.6
12/14/92	0824	6.77	PM 12/4/92 6.70	6.91	17.7
12/16/92	0902	<del>6.90</del> 6.83	6.73	6.96	16.1
12/17/92	0855	6.80	6.66	6.90	15.7
12/18/92	1045	6.70	6.61	6.84	17.1

12/02/92 1604 P/R The ~5g portions of Na-exchanged 'Cheto' clay washed 11/25, 11/26, 11/29, + 12/02 (see GC-00-53, 54, 55) were put in plastic vials labeled "Cheto Montmorillonite, SAZ-1, date" + the clays sent to Texas Tech for chemical analysis.

12/7/92 0845 For The 3M NaCl solution was changed out again

12/11/92 0715 PM The remaining Na-O soaked materialite was repeatedly washed with ultra pure water. The lightest-weight solid obtained was peach colored, + the heaviest was black.

12/14/92 0804 PM The Na-montmorillonite was rinsed until it ~~3 to~~ <sup>PH 12.14/92</sup> wash water formed no precipitate when 0.1 N  $\text{AgNO}_3$  was added. (0.1 N  $\text{AgNO}_3$  lot # 910644-24)  
The black portion was separated from the rest by centrifugation, + will be analyzed by XRD.

1414 PM The washed Na-montmorillonite was taken to Michael Miller in Div. 1 For Freeze-drying.

12/18/92 0935PM The MKIA solutions' pH's have equilibrated, so and the clay is freeze-dried, so Expt MKIA will continue today.

**MK1-1-D:** Take 2 5-mL aliquots of MK1A-1\*A, MK1A-1\*B, and MK1A-1\*C using an adjustable pipettor with disposable tips. Transfer the aliquots into prelabeled and pre-weighed 50-mL centrifuge tubes. The labels will be MK1A-1\*A\*I1 or \*I2. Reweigh each tube after addition of the sample. Add to each sample using an Eppendorf micropipet 250 $\mu$ L of 1.0 M HNO<sub>3</sub> solution for later analysis with alpha-spectrometry.

*PM 1120*

weights  
 MK1A-1\*A I1 tube: 10.7402 sample: 5.0479  
 A I2 : 10.6499 : 5.0409  
 B I1 : 10.7246 : 5.0445  
 B I2 : 10.7655 : 5.0383  
 C I1 : 10.7658 : 5.0390  
 C I2 : 10.7392 : 5.0390

Then into bottles MK1A-1\*A and MK1A-1\*B (NOT to MK1A-1\*C), add 0.5 g of Na-montmorillonite which was previously tared onto weighing paper. Record the time and room temperature. Solution MK1A-1\*C is the control experiment to determine uranium losses to the container walls. Keep the solutions agitated on a gyratory shaker (note the approximate rpm of the shaker on the notebook).

*PM 1132* wt Na-montmorillonite added to  
 MK1A-1\*A : 5.008 g  
 MK1A-1\*B : 5.012 g  
 room temp : 64.8°F @ 1138  
 rpm : 125

**MK1-1-E:** At time approximating the values listed below, take one 5-mL sample from MK1A-1\*A, MK1A-1\*B, and MK1A-1\*C with a 10 cc sterile syringe in the following manner: connect the 10 cc syringe to a Dynagard polypropylene filter (0.2 micrometer pore rating, 3.9 cm<sup>2</sup> surface area). Withdraw 8 mLs of solution through the filter. Eject 3 mLs of the solution back into the sample bottle to wash clay back out of the filter paper. Remove the filter from the syringe, add 5 mL of the withdrawn solution to a pre-weighed 50-mL centrifuge tube, replace the filter, and put the rest of the withdrawn solution back in the solution bottle. The filter is to keep the montmorillonite out of the sample aliquot. (The syringe and filters are disposed of). The MK1A-1\*C sample can be taken with an Oxford pipet with a 5-mL disposable tip.

Reweigh each centrifuge tube after addition of the sample. Add to each sample using an Eppendorf micropipet 250 $\mu$ L of 1.0 M HNO<sub>3</sub> solution for later analysis with alpha-spectrometry. Label the samples MK1A-1\*A\*ia, where *i* is the sampling time number (1,2,3...).

Take two 5-mL samples from MK1A-1\*A, \*B, \*C every third sampling time. Label the second sample MK1A-1\*A\*ib or \*B\*ib or \*C\*ib.

In addition, measure the pH of each solution. Record the pH and solution temperature.

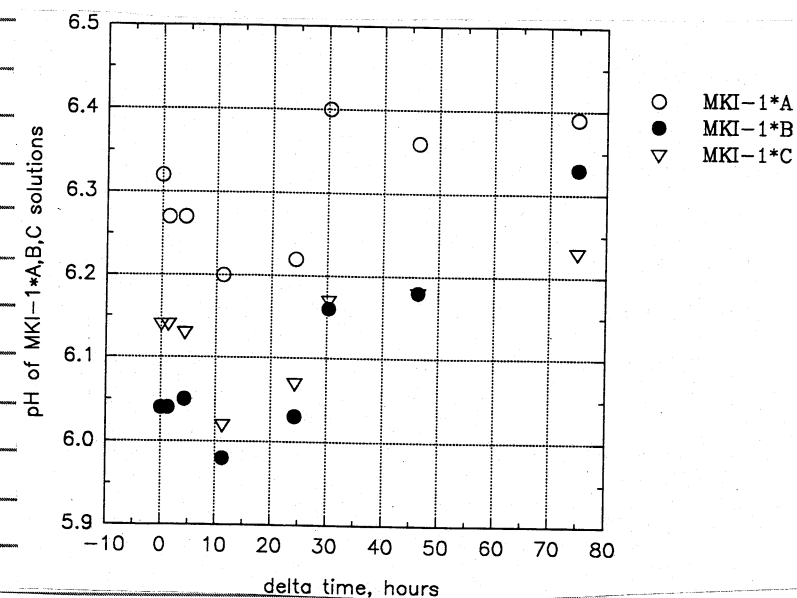
Use the following  $\Delta$ time (hours): 2, 4, 12, 24, 30, 36, 42, 48. These may be changed if necessary. The solutions are expected to reach equilibrium in roughly 24 hours.

date	sample #	solution	pH	soln temp °C	time
4/18	1	MK1A-1*A	6.82	19.2	1347
	1	*B	6.75	19.3	1352
	1	*C	6.90	19.3	1359
	2	*A	6.96	19.9	1539
	2	*B	6.88	19.9	1546
	2	*C	6.92	19.9	1552
	3	*A	6.90	20.1	2053
	3	*B	6.89	20.2	2105
	3	*C	6.96	20.2	2110
4/19	4	MK1A-1*A	6.98	20.3	0855
	4	*B	6.91	20.3	0902
	4	*C	6.97	20.3	0908
	5	MK1A-1*A	6.96	21.1	1648
	5	*B	6.91	21.1	1655
	5	*C	7.01	21.2	1702
4/20	6	MK1A-1*A	6.95	18.1	0938
	6	*B	6.92	18.1	0944
	6	*C	6.98	18.2	0952
4/21	7	MK1A-1*A	6.96	16.2	0833
	7	*B	6.90	16.2	0840
	7	*C	6.95	16.3	0846

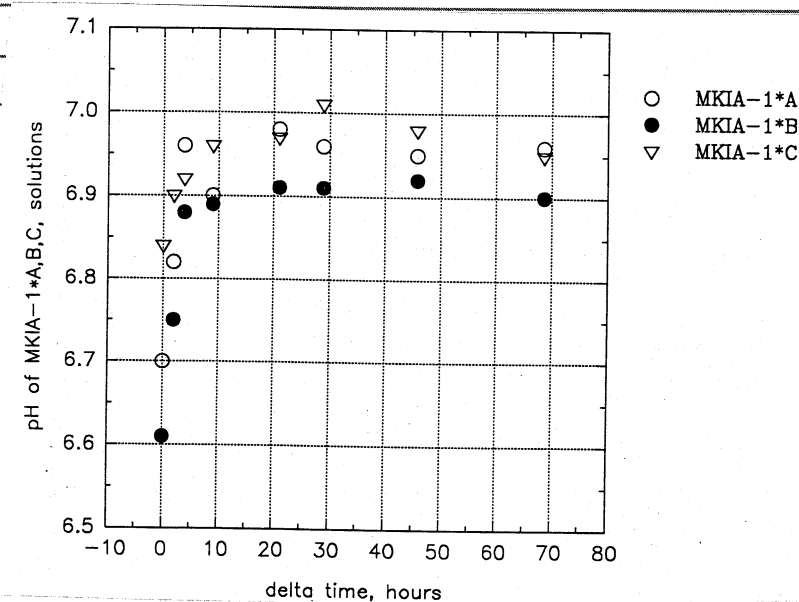
date	sample	wt tube, g	wt aliquot, g	time	time minutes
12/18/92	MKIA-1KAK1a	10.8205	4.9424	1332	114
	BK1a	10.9310	4.9799		
	CK1a	10.6463	5.0534		
12/18/92	MKIA-1KAK2a	10.7430	5.0607	1528	230
	BK2a	10.7299	5.0984		
	CK2a	10.7349	5.0462		
12/18/92	MKIA-1KAK3a	10.7283	4.9374	2037	539
	BK3a	10.7922	4.8331		
	CK3a	10.7403	5.0556		
12/19/92	MKIA-1KAX4a	10.7600	4.9479	0839	1261
	BK4a	10.6516	4.9054		
	CK4a	10.6461	5.0515		
	AK5a	10.8713	4.8972	1632	1734
	BK5a	10.7193	4.9716		
	CK5a	10.8470	5.0343		
12/20/92	MKIA-1KAX6a	10.7422	4.8639	0918	2740
	AK6a	10.9263	4.9893		
	BK6a	10.7588	4.8116		
	BK6b	10.7398	5.0262		
	CK6a	10.7336	5.0441		
	CK6b	10.7381	5.0530		
12/21/92	MKIA-1KAK7a	10.7263	4.8859	0814	4116
	BK7a	10.6466	4.9390		
	CK7a	10.7286	5.0606		
1028PM	The last samples were taken, 2 from MKIA-1K 1U by Oxford pipet:				
	MKIA-1KFXa	10.8720	5.0519	1032	
	BKb	10.7254	5.0541		

12/21/92 1045PM The plots of  $\Delta$ time vs pH for Expts MKI-1 + MKA-1 are

shown (reduced from SIGMAPLOT print out) For comparison.



sample #	MKI-1*A	MKI-1*B	MKI-1*C	time, min	time, hours
1	0	6.32	6.04	0	0
2	1	6.27	6.04	75	1.3
3	3	6.27	6.05	255	4.3
4	4	6.2	5.98	675	11.3
5	5	6.22	6.03	1455	24.3
6	6	6.24	6.16	1815	30.3
7	8	6.36	6.18	2775	46.3
8	10	6.39	6.33	4495	74.9



delta hours	MKIA*A	MKIA*B	MKIA*C
1	0	6.7	6.61
2	1.9	6.82	6.75
3	3.8	6.96	6.88
4	9	6.9	6.89
5	21	6.98	6.91
6	28.9	6.96	6.91
7	45.7	6.95	6.92
8	55.7	6.95	6.92



Only MKI-1 data from samples taken at ~ the same time interval as those from MKIA-1 were plotted, to make comparison easier. The pH values in MKI-1 are more widely scattered than those in MKIA. The pH values for MKIA level off at about 6.93 after about 24 hours. The montmorillonite used for the MKIA experiment was contacted with 3M NaCl but had no other chemical treatment, and was obtained from the Source Clays Repository of the Clay Mineral Society (clay is SAz-1 U'Cheto, a Ca form montmorillonite). The clay previously prepared in this way and freeze-dried will be used to begin sorption experiments. About 6 grams more will be needed to complete 3 sorption experiments, and this will be prepared as before - see GC-06-53.

12/22/92 1000 PM Prep. of more Na-'Cheto' Montmorillonite

Another 50g of the 'Cheto' clay from the Source Clay Repository was weighed out, ultra pure water was added so the clay could be picked up by maxi-pipet, & the clay was injected into water-washed dialysis tubing which was knotted at the bottom. After injection, the tubing was tied at the top as well. The tubes of clay were placed in a 600 mL glass beaker.

1038 PM - 175.3g of NaCl (lot # 912763) was weighed out and diluted in a 1000 mL beaker to prepare a ~ 3 M NaCl solution.

1050 PM The clay tubes were covered with 3M NaCl solution & the beaker covered with a watch glass to keep dust out. The remaining 3M NaCl solution was poured into a clean 1000 mL PP bottle & a 500 mL wash bottle.

12/29/92 0907 PM Calibration of glass droppers for upcoming 51 Sorption Experiment

Glass droppers were labeled ".10" ".1" and ".02".  
1.0 M HNO<sub>3</sub> solution (5 Aug 92, GC-07-149) 0.1 M HNO<sub>3</sub> solution (2 Dec 92, GC-88-23) + 0.02 M HNO<sub>3</sub> solution (6 Aug 92, GC-07) was added dropwise to 10 mL volumetric flasks & the # drops noted.

$$1.0M: \frac{132 \text{ drops}}{5 \text{ mL}} = \frac{1 \text{ drop}}{x \text{ mL}} \quad x = 0.038 \text{ mL/drop}$$

$$0.1M: \frac{125 \text{ drops}}{5 \text{ mL}} = \frac{1 \text{ drop}}{x \text{ mL}} \quad x = 0.04 \text{ mL/drop}$$

$$0.02M: \frac{129 \text{ drops}}{5 \text{ mL}} = \frac{1 \text{ drop}}{x \text{ mL}} \quad x = 0.039 \text{ mL/drop}$$

0945 PM Na-Montmorillonite prep continued from p 62  
The 3M NaCl solution was replaced with more NaCl solution prepared previously.

12/29/92 PM

#### URANIUM SORPTION EXPERIMENT S-I: K<sub>d</sub> vs pH; Equilibrium with atmospheric pCO<sub>2</sub>; Initial ΣU = 50 ppb

Based on Uranium Sorption Experiment B-I by R. T. Pabalan  
Adapted Nov. 4, 1992  
Revised Dec 22, 1992

#### OBJECTIVE:

To investigate the importance of uranium sorption on the clay mineral montmorillonite as a function of solution pH and total uranium concentration. Experimental data will be correlated with uranium aqueous speciation.

To investigate reversibility and reproducibility of uranium sorption reactions.

#### EQUIPMENT:

Gyratory shaker or constant temperature shaker bath  
EG&G alpha-spectrometer  
ORION pH/mV/ISE/°C meter  
Combination pH electrode  
Automatic temperature compensator probe  
Analytical balance

## SUPPLIES:

pH buffer (pH = 2, 4, 7, 9, 10)  
 1 125-mL bottle (to contain S-I\*U)  
 39 50-mL centrifuge tubes (to contain experimental mixtures and control solutions)  
 82 50-mL centrifuge tubes (to contain samples for U analysis)  
 1 50-mL volumetric pipet (to pipet 50 ppb U solution into PP bottles)  
 1 5-mL volumetric pipet (to pipet 0.02 M HNO<sub>3</sub> into 50-mL centrifuge tubes)  
 1 4000-mL plastic bottle (for preparation of 50 ppb U solution)  
 3 glass droppers (for adjusting pH by addition of HNO<sub>3</sub>)  
 weighing paper  
 1 Oxford adjustable pipet (for taking 5-mL samples) with disposable tips  
 10 cc syringes (for taking samples with clay in them)  
 0.2 micron Dynaguard polypropylene membrane filters  
 Na<sup>+</sup>-montmorillonite  
 reagent grade NaHCO<sub>3</sub>  
 500 ppb U stock solution prepared from 50 ppm <sup>233</sup>U commercial spike  
 2 L 0.1 M NaNO<sub>3</sub> stock solution  
 1000 mL stock solution of 1.0 M HNO<sub>3</sub>  
 1000 mL stock solution of 0.1 M HNO<sub>3</sub>  
 1000 mL stock solution of 0.02 M HNO<sub>3</sub>  
 ultrapure water

## PROCEDURE:

Solution S-I (1 centrifuge tube for each pH value)

-Initial  $\Sigma U = 50$  ppb  
 -Initial pH = 2.0 to 9.0, every 0.25 pH unit; adjustments made with HNO<sub>3</sub> or NaHCO<sub>3</sub>  
 -Initial volume = 50 mL  
 -Ionic strength = 0.1 M NaNO<sub>3</sub>  
 -Wt. zeolite to use = 0.100 $\pm$ 0.001 g  
 -Initial [Na<sup>+</sup>] = 0.1 M NaNO<sub>3</sub> + [NaHCO<sub>3</sub>] added  
 -pCO<sub>2</sub> = atmospheric = 10<sup>-3.48</sup> bar

a) In a pre-cleaned 4 liter plastic bottle, prepare 2050 g of 50 ppb U solution by diluting 205 g of a 500 ppb stock solution (in 0.1 M NaNO<sub>3</sub> matrix; prepared previously from commercial 50 ppm <sup>233</sup>U spike) to a total of 2050 g by carefully taring 0.1 M NaNO<sub>3</sub> solution into the plastic bottle on a Mettler 4600 balance.

The 500 ppb stock solution used is 23A - see Radiochemistry Notebook, p 50. The 0.1M NaNO<sub>3</sub> solution prep is found on GC-06-53.

08/09/11 weight of 500 ppb <sup>233</sup>U solution used: 205.10g

weight of 50 ppb <sup>233</sup>U solution prepared: 2050.9g

b) Into each of 29 50-mL centrifuge tubes labeled S-I\* $\phi$ Hi [where i is the approximate initial pH of the solution (see below)], tare 50 g of the 50 ppb uranium solution.

i = 2.0 2.25 2.50 2.75 ... 8.75 9.0

weight of 50 ppb <sup>233</sup>U solution added to tube: 642  
 S-I\* $\phi$ Hi 2.0 = 46.2856 12/29/92 tube wt: 10.7379  
 2.25 = 46.2969 10.7453  
 0784 690

tube	wt <sup>233</sup> U (50 ppb) soln:	tube wt:
S-I* $\phi$ Hi 2.50	46.3609	10.8200
2.75	46.3577	10.7686
3.00	46.1433	10.7249
3.25	46.1281	10.7246
3.50	46.3571	10.7681
3.75	46.2050	10.7379
4.00	46.2969	10.7652
4.25	46.0166	10.9315
4.50	46.0331	10.7306
4.75	46.1730	10.7020
5.00	46.1098	10.7437
5.25	46.1920	10.7374
5.50	46.0564	10.7604
5.75	46.2969	10.7453
6.00	46.1188	10.7225
6.25	46.0532	10.7221
6.50	46.0824	10.8721
6.75	46.1011	10.8791
7.00	46.0823	10.7256
7.25	46.1755	10.6506
7.50	46.0796	10.7417
7.75	46.3009	10.8200
8.00	46.0191	10.8233
8.25	46.0718	10.8290
8.50	45.9968	10.7305
8.75	46.1403	10.7383
9.00	46.0136	10.7264

Into each of 10 50-mL centrifuge tubes labeled S-I-C\* $\phi$ Hi\*a (or b) [where i is 2, 4, 6, 8, or 9.5, representing the approximate initial pH of the solution], tare 50 g of the 50 ppb uranium solution. These are control solutions to determine uranium loss to the container walls as a function of pH.

tube	weight tube	weight 50 ppb <sup>233</sup> U soln
S-I-C* $\phi$ Hi 2Ka	10.7667	46.1485
b	10.8177	46.1889
4Ka	10.7699	46.0044
b	10.8262	46.0076

tube	wt tube	wt 50ppb <sup>233</sup> U soln
5-1-CKpH6Ka	10.7229	46.0224
b	10.7055	46.0201
8Ka	10.7601	46.1475
b	10.7661	46.0422
95Ka	10.8767	46.0020
b	10.7363	46.0099

1028 PM

Transfer the remaining solution into a 125-mL PP bottle labeled S-I\*IU. Take two 5-mL samples from S-I\*IU with an Eppendorf pipet, transfer into pre-labeled [e.g., S-I-IU\*a (or b)] and pre-weighed 50-mL centrifuge tubes containing 5 g of 0.02 M HNO<sub>3</sub>. Swirl each tube and save for later analysis of uranium concentration by alpha-spectrometry.

wt tube + 0.02 M HNO <sub>3</sub>	wt solution from S-I*IU
5-1-11Ka : 15.6042	: 5.0247
8b : 15.5558	: 5.0208

**Table S-I-1.** Amount of reagent grade HNO<sub>3</sub> or NaHCO<sub>3</sub> to add to 50 ml 0.1 m NaNO<sub>3</sub> solution containing 50 ppb U to result in pH values given in column-1. The amount of reagent to be added was estimated using EQ3 calculations and assuming the solutions are in equilibrium with atmospheric CO<sub>2</sub>(g).

Solution pH	Volume of HNO <sub>3</sub> Needed, Drops (0.0394 mL/drop)	Molarity of HNO <sub>3</sub> Used
2.00	15 (0.605 mL)	1.0
2.25	9 (0.34 mL)	1.0
2.50	5 (0.19 mL)	1.0
2.75	3 (0.105 mL)	1.0
3.00	15 (.605 mL)	0.1
3.25	9 (0.34 mL)	0.1
3.50	5 (0.19 mL)	0.1
3.75	3 (0.11 mL)	0.1
4.00	2 (0.06 mL)	0.1
Solution pH	Amount of NaHCO <sub>3</sub> Needed, Grams	
4.25	0.000051	0.00008 ✓
4.50	0.000176	0.000129 ✓
4.75	0.000246	0.00025 ✓
5.00	0.000287	0.00027 ✓
5.25	0.000312	0.00031 ✓
5.50	0.000329	0.00032 ✓
5.75	0.000344	0.00035 ✓
6.00	0.000361	0.00036 ✓
6.25	0.000386	0.00038 ✓
6.50	0.000429	0.00046 ✓
6.75	0.000503	0.00053 ✓
7.00	0.000635	0.00057 ✓
7.25	0.000869	0.00090 ✓
7.50	0.001287	0.00126 ✓
7.75	0.002036	0.00190 ✓

might be better if  
I added 1 liter of water  
than 1000 g  
12/29/92

table S-T-1 continued:

Solution pH	Amount of NaHCO <sub>3</sub> Needed, Grams	
8.00	0.003387	0.00346 ✓
8.25	0.005846	0.00562 ✓
8.50	0.010409	0.01047 ✓
8.75	0.019135	0.01965 ✓
9.00	0.036664	0.03719 ✓
[9.25]	[0.074694]	
[9.50]	[0.167773]	

1112 PM

c) 1. For each solution S-I\*pHi and S-I-C\*pHi, where  $i \leq 4.2$ :

Measure and record the initial pH (-4.2, based on EQ3 calculation). The automatic temperature compensator (ATC) probe should be immersed in water in a separate container.

solution	pH	temp of solution	time
5-Ix pH 2.0	4.16	21.4	1113
2.25	4.15	"	1118
2.50	4.14	"	1123
2.75	4.16	"	1128
3.00	4.19	21.5	1134
3.25	4.15	"	1138
3.50	4.15	"	1142
3.75	4.15	"	1145
5-Ix pH 4.00	4.18	21.6	1150
5-T-CKpH2Ka	4.18	21.6	1154
b	4.17	"	1159
4Ka	4.16	"	1203
b	4.17	"	1208

Adjust the pH to the value of  $i$  of each solution by adding dropwise with a glass dropper HNO<sub>3</sub> solution, the concentration and approximate amount of which is given in Table S-I-1. Swirl the solutions by hand. Record the number of drops and concentration of solution added. Also record the attained pH. Cover the bottles with a kimwipe and place on the gyratory shaker set to ~120 rpm. Monitor the pH periodically, together with the centrifuge tubes prepared in step 2 below.

pH buffers 2, 3, 4, & 5 (Fisher lot #5 910358-24, 910886-24, 910359-24 + 913827R-24) were used to calibrate. pH buffers 4, 7, 9 & 10 are used for the next section. (12/29/92) JML

Solution Label	# Drops Added	Conc. HNO <sub>3</sub>	pH measured	Soln. Temp. °C
S-I*PH2.00	15	1.0	1.94	21.4
S-I*PH2.25	8.5	1.0	2.19	"
S-I*PH2.50	4.5	1.0	2.52	"
S-I*PH2.75	3	1.0	2.67	"
S-I*PH3.00	13.5	0.1	3.03	21.5
S-I*PH3.25	7.5	0.1	3.24	"
S-I*PH3.50	5	0.1	3.45	"
S-I*PH3.75	2.5	0.1	3.64	21.6
S-I*PH4.00	1.2	0.1	3.86	"
S-I-C*PH2*a	14.5	1.0	1.97	21.6
S-I-C*PH2*b	14.5	1.0	1.92	"
S-I-C*PH4*a	1.2	0.1	3.86	"
S-I-C*PH4*b	1.2	0.1	3.85	21.7

12.10 PM

2. For each solution S-I\*PH<sub>i</sub> and S-I-C\*PH<sub>i</sub>, where  $i > 4.2$ :

Measure and record the initial pH (-4.2, based on EQ3 calculation).

solution	pH	temp of solution	time
S-I*PH4.25	4.15	22.1	1333
4.50	"	"	1334
4.75	"	"	1336
5.00	"	"	1337
5.25	"	"	1338
5.50	4.16	22.2	1340
5.75	4.15	"	1342
6.00	"	"	1343
6.25	"	"	1345
6.50	"	"	1346
6.75	4.16	"	1348
7.00	4.15	"	1349
7.25	"	"	1351
7.50	"	"	1352
7.75	"	"	1354
8.00	"	"	1355
8.25	"	22.3	1357
S-I*PH8.50	"	"	1358

solution	pH	temp of solution	time
S-I*PH8.75	4.15	22.3	1400
9.00	"	"	1402
S-I-CK*PH6*a	4.16	22.3	1404
*b	4.15	"	1406
8*a	4.11	"	1408
*b	4.15	"	1409
9.5*a	"	"	1410
*b	"	"	1412

Tare onto weighing paper reagent grade NaHCO<sub>3</sub> in the amounts listed in Table S-I-1 and transfer into the respective centrifuge tubes. Swirl the solutions by hand. Cover the tubes with a kimwipe and place on gyratory shaker set to -120 rpm. Monitor the pH periodically until the pH becomes constant and in equilibrium with atmospheric CO<sub>2</sub>(g). This equilibration process may take at least twelve days.

see  
66-06-66  
table 2 for  
amounts

PM  
01/04/93

Solution Label	g NaHCO <sub>3</sub> Added
S-I*PH4.25	
S-I*PH4.50	
S-I*PH4.75	
S-I*PH5.00	
S-I*PH5.25	
S-I*PH5.50	
S-I*PH5.75	
S-I*PH6.00	
S-I*PH6.25	
S-I*PH6.50	
S-I*PH6.75	
S-I*PH7.00	
S-I*PH7.25	
S-I*PH7.50	
S-I*PH7.75	
S-I*PH8.00	
S-I*PH8.25	
S-I*PH8.50	
S-I*PH8.75	
S-I*PH9.00	
S-I-C*PH6*a	0.00039
S-I-C*PH6*b	0.00038
S-I-C*PH8*a	0.00340
S-I-C*PH8*b	0.00352
S-I-C*PH9.5*a	0.16738
S-I-C*PH9.5*b	0.16668

736 PM



1158PM All SI sample tubes are on the gyratory shaker at ~125rpm

12/30/92 PM 0755 The pH of all SI sample tubes will be monitored.  
The pH buffers used to calibrate are pH 2, 4, 7, 9, & 10.

<u>solution</u>	<u>pH</u>	<u>temp</u>
5-I * pH 2.0	1.98	21.3
2.25	2.22	21.3
2.5	2.55	21.3
2.75	2.68	21.3
3.0	3.10	21.3
3.25	3.26	21.3
3.5	3.47	21.3
3.75	3.66	21.3
4.0	3.86	21.3
4.25	4.26	21.3
→ 4.5	7.18	21.3
4.75	4.42	21.3
5.0	4.72	21.3
5.25	4.78	21.3
5.5	5.17	21.3
5.75	5.05	21.2
6.0	5.96	21.2
6.25	6.36	21.2
6.5	6.52	21.2
6.75	6.38	21.2
7.0	6.71	21.2
7.25	7.05	21.2
7.5	7.24	21.2
7.75	7.55	21.2
8.0	7.90	21.2
8.25	7.95	21.1
8.5	8.01	21.1
8.75	8.09	21.1
9.0	8.11	21.1

<u>solution</u>	<u>pH</u>	<u>temp</u>
5-I-C * pH 2Ka	1.98	21.1
b	1.94	21.1
4Ka	3.86	21.1
b	3.84	21.1
6Ka	6.13	21.1
* b	6.18	21.1
8Ka	7.89	21.1
b	7.88	21.1
9.5a	8.16	21.1
b	8.17	21.1

0926PM All SI tubes were put back on the shaker.

0930PM The 3M NaCl soln was changed out for the montmorillonite being changed to Na-form.

01/02/93 PM Expt SI continued - pH monitoring

<u>solution</u>	<u>pH</u>	<u>temp</u>
12 PM 5-I * pH 2.0	2.13	16.7
2.25	2.36	16.7
2.5	2.66	16.7
2.75	2.79	16.7
3.0	3.11	16.7
3.25	3.31	16.7
3.5	3.51	16.8
3.75	3.69	16.8
4.0	3.89	16.4
4.25	4.27	16.5
→ 4.5	7.28	16.5
4.75	4.38	16.6
5.0	4.75	16.6
5.25	4.80	16.6
5.5	5.18	16.6
5.75	5.04	16.6
6.0	5.87	16.0
6.25	6.31	16.0

	pH	temp
* pH 6.5	6.36	16.1
6.75	6.34	16.1
7.0	6.73	16.1
7.25	7.12	16.2
7.5	7.32	16.2
7.75	7.13	16.3
8.0	7.58	16.3
8.25	8.22	17.1
8.5	8.58	17.1
8.75	8.81	17.2
9.0	9.02	17.2

2a	2.14	16.8
b	2.09	16.9
4a	3.90	16.9
b	3.88	16.9
6a	6.07	16.9
b	6.18	16.9
8a	7.95	17.0
b	7.99	17.0
9.5a	9.14	17.0
b	9.08	17.0

1354PM The S-I solutions were put back on the gyratory shaker.

1359PM The 3M NaCl solution covering the montmorillonite being changed to Na-form was replaced.

12/04/93  
01/04/94

1022 The 3M NaCl solution covering the montmorillonite was replaced.

Now 3M NaCl solution was prepared by weighing out 175.3 g NaCl (lot # 912763) and putting it in a 1000 ml beaker and diluted dissolved in ultrapure water to the 1000 ml mark.

water to the 1000 ml mark.

1259PM - electrode maintenance -  
The filler solution in the Ross glass pH electrode was replaced.

1304PM The pH electrode/meter is being calibrated with fresh portions of Fisher buffers 2, 4, 7, 9, + 10 (lots 910358-24, 910359-24, 921733-24, 910065-24, + 910870-24).

1320PM Expt S-I continued -

solution	pH	temp. soln
S-I pH 2.0	1.85	20.2
2.25	2.19	"
2.5	2.54	"
2.75	2.69	"
3.0	3.06	"
3.25	3.25	"
3.5	3.45	"
3.75	3.66	"
4.0	3.84	20.1
4.25	4.23	"
4.5	4.27	"
4.75	4.34	"
5.0	4.70	"
5.25	4.77	20.2
5.5	5.14	"
5.75	4.99	"
6.0	5.90	20.0
6.25	6.30	20.0

solution	pH	temp
5-I-X pH 6.5	6.39	20.0
6.75	6.34	"
7.0	6.71	"
7.25	7.12	"
7.5	7.30	20.1
7.75	7.59	"
8.0	7.99	20.2
8.25	8.19	"
8.5	8.48	"
8.75	8.75	20.3
9.0	8.95	"

	pH	temp
5-I-X pH 2Ka	2.00	20.2
b	1.93	"
4Ka	3.89	"
b	3.86	"
6Ka	6.06	"
b	6.18	"
8Ka	7.92	20.3
b	8.03	20.2
9Ka	9.15	"
b	9.10	"

1/5/93 PM Prep of More Na-'Cheto' Montmorillonite continued  
 11/4 The clay in the tubes was removed from the tubing and put into a beaker. The clay was then repeatedly washed in 50 mL centrifuge tubes with nanopure water. The clay separates into peach, brown, off-white, + black fractions as it's rinsed. The black portion is heaviest + is removed + saved for later XRD analysis. Rinsing will continue until the clay's 1st rinse shows no precipitate formation when it is placed in a beaker + 0.1 N  $\text{HNO}_3$  solution is added dropwise.

01/06/93 Expt 51-continued pH monitoring

solution	pH	sdn. temp
0959 PM 5-I-X pH 2.0	2.08	16.8
2.25	2.31	"
2.5	2.61	"
2.75	2.74	16.9
3.0	3.14	"
3.25	3.31	"
3.5	3.49	"
3.75	3.66	"
4.0	3.86	16.7
4.25	4.24	"
4.5	7.28	"
4.75	4.35	"
5.0	4.71	"
5.25	4.77	16.8
5.5	5.13	"
5.75	4.99	"
6.0	5.84	16.4
6.25	6.29	16.5
6.5	6.39	"
6.75	6.35	"
7.0	6.70	"
7.25	7.11	16.6
7.5	7.30	"
7.75	7.60	"
8.0	7.94	16.9
8.25	8.18	17.0
8.5	8.52	"
8.75	8.77	"
9.0	9.00	"

5-I-X pH 2Ka	2.12	17.0
b	2.06	17.1

<u>solution</u>	<u>pH</u>	<u>soln temp</u>
S-1-CX pH 4Ka	3.86	12.1
b	3.86	"
pH 6Ka	6.07	"
b	6.17	12.2
pH 8Ka	7.92	"
b	8.02	"
9.5Ka	9.29	12.2
b	9.26	"

1130PM The S-1 solutions were put back on the gyratory shaker.

01/05/93 Expt S-1 continued pH monitoring

<u>solution</u>	<u>pH</u>	<u>soln temp °C</u>
S-1 CX pH 2.0	1.92	19.7
2.25	2.16	"
2.5	2.49	"
2.75	2.63	"
3.0	2.98	19.8
3.25	3.20	"
3.5	3.41	"
3.75	3.60	"
4.0	3.83	19.6
4.25	4.21	19.7
4.5	7.30	"
4.75	4.32	"
5.0	4.68	"
5.25	4.74	"
5.5	5.10	"
5.75	4.97	"
6.0	5.87	19.6
6.25	6.34	"
6.5	6.39	"
6.75	6.35	"

<u>solution</u>	<u>pH</u>	<u>soln temp</u>
S-1 CX pH 7.0	6.75	19.6
7.25	7.17	"
7.5	7.35	"
7.75	7.62	"
8.0	7.96	19.8
8.25	8.18	"
8.5	8.45	"
8.75	8.70	"
9.0	8.93	19.9

<u>solution</u>	<u>pH</u>	<u>soln temp</u>
S-1-CX pH 2Ka	1.94	19.9
*b	1.88	"
4Ka	3.82	"
*b	3.81	"
6Ka	6.40	"
*b	6.29	"
8Ka	7.95	"
*b	7.97	"
9.5Ka	9.24	"
*b	9.24	"

1144PM The S-1 solutions were returned to the gyratory shaker.

01/11/93 Expt S-1 continued pH monitoring

0811PM - The filler solution in the pH electrode was replaced -

<u>solution</u>	<u>pH</u>	<u>soln temp °C</u>
S-1 CX pH 2.0	1.90	15.9
2.25	2.19	"
2.5	2.50	"
2.75	2.70	"
3.0	3.02	"
3.25	3.27	"
3.5	3.45	"
3.75	3.62	"

16.0 PM 8/4/94  
16



<u>solution</u>	<u>pH</u>	<u>soln temp °C</u>
5-1KpH4.0	3.83	16.0
4.25	4.22	"
4.5	7.24	"
4.75	4.34	"
5.0	4.73	"
5.25	4.76	"
5.5	5.10	"
5.75	5.04	"
6.0	5.91	15.7
6.25	6.35	"
6.5	6.38	15.8
6.75	6.35	"
7.0	6.74	"
7.25	7.13	"
7.5	7.32	"
7.75	7.60	15.9
8.0	7.93	16.0
8.25	8.22	16.1
8.5	8.51	"
8.75	8.79	"
9.0	9.02	"

<u>solution</u>	<u>pH</u>	<u>soln temp °C</u>
5-1-CKpH2Ka	1.96	16.1
b	1.89	"
4Ka	3.85	16.2
b	3.84	"
6Ka	6.07	"
b	6.21	"
8Ka	7.97	"
b	8.08	"
9.5Ka	9.38	"
b	9.35	"

1027 PM The 5-1 solutions were put back in the gyratory shaker.

01/13/93 Expt 5-1 continued - pH monitoring

<u>solution</u>	<u>pH</u>	<u>soln temp °C</u>
0730 PM 5-1KpH2.0	1.88	16.7
2.25	2.12	"
2.5	2.45	"
2.75	2.64	"
3.0	3.04	"
3.25	3.23	"
3.5	3.45	"
3.75	3.65	"
4.0	3.84	16.8
4.25	4.27	"
4.5	7.28	"
4.75	4.36	16.8 o.k. 7M. 1/13/93
5.0	4.75	"
5.25	4.77	"
5.5	5.14	"
5.75	5.06	"
6.0	5.91	"
6.25	6.34	16.9
6.5	6.36	"
6.75	6.37	"
7.0	6.75	"
7.25	7.17	"
7.5	7.38	"
7.75	7.64	"
8.0	7.98	"
8.25	8.27	"
8.5	8.55	17.0
8.75	8.91	"

<u>solution</u>	<u>pH</u>	<u>soln temp °C</u>
S-I * pH 9.0	9.04	17.0

<u>solution</u>	<u>pH</u>	<u>soln temp °C</u>
S-I-C * pH 2 Ka	1.95	17.0
b	1.92	"
4 Ka	3.85	"
b	3.88	"
6 Ka	6.06	17.1
b	6.24	"
8 Ka	7.97	"
b	8.06	"
9.5 Ka	9.42	"
b	9.39	"

0942 PM The S-I solutions were put back on the gyratory shaker.

The solutions have had 15 days to equilibrate, + the experiment will continue with additions of the Na-form montmorillonite.

1155 PM d) Tare 0.100±0.001 g of Na-montmorillonite onto weighing paper, and carefully transfer into each of the S-I \* pH (not the S-I-C \* pH) centrifuge tubes. Swirl each tube by hand, replace the cover, then place on the shaker.

<u>solution</u>	<u>amt Na-montmorillonite, g</u>
S-I * pH 2.0	0.1005
2.25	0.1003
2.5	0.1002
2.75	0.1003
3.0	0.1001
3.25	0.1005
3.5	0.1002
3.75	0.1004
4.0	0.1001
4.25	0.1004
4.5	0.1004

<u>solution</u>	<u>amt Na-montmorillonite, g</u>
S-I * pH 4.75	0.1001
5.0	0.1000
5.25	0.1004
5.5	0.1002
5.75	0.1007
6.0	0.1001
6.25	0.1006
6.5	0.1007
6.75	0.1006
7.0	0.1004
7.25	0.1003
7.5	0.1006
7.75	0.1005
8.0	0.1005
8.25	0.1002
8.5	0.1006
8.75	0.1005
9.0	0.1003

1320 PM The solutions were put back on the shaker

01/08/93 PM Expt S-I continued; - sample taking after day has time to equilibrate

e) After equilibrium is reached (at least 2 days), take two 5-mL samples from each tube S-I \* pH and S-I-C \* pH with a 10 cc syringe in the following manner: connect the 10 cc syringe to a disposable Dynaguard polypropylene (0.2 micrometer pore rating, 3.9 cm<sup>2</sup> surface area) membrane filter. Withdraw 8 mLs of solution through the filter. Eject 3 mLs of the solution back into the sample centrifuge tube to wash the clay back out of the filter. Remove the filter from the syringe, add 5 mL of the withdrawn solution to a pre-labeled [e.g., S-I-pH \* a (or b) and pre-weighed 50-mL centrifuge tube that contains 5 g of 0.02 M HNO<sub>3</sub>, replace the filter, and put the rest of the withdrawn solution back in the solution bottle. The filter is to keep the montmorillonite out of the sample aliquot. (The syringe and filter are disposed of). The S-I-C \* pH samples can be taken with the Oxford pipettor.

At the end of the experiment, two samples are taken from solution S-I \* IU and put in preweighed test tubes marked FS-I \* a or b and containing 5 g of 0.02 M HNO<sub>3</sub>.

Swirl each tube and save for later analysis of uranium concentration by alpha-spectrometry.

sample	wt tube + 5 mL 0.02 M HNO <sub>3</sub>	wt U aliquot
1045 PM 5-IX pH 2.0 ka	15.5976 g	5.0392 g
kb	15.6338 g	5.0752 g
2.25 ka	15.6953	5.1208
kb	15.7711	5.1111
2.5 ka	15.6913	4.9706
kb	15.8522	4.9813
2.75 ka	15.9049	5.0044
kb	15.7297	5.0076
3.0 ka	15.7369	4.9620
kb	15.6297	4.8179
3.25 ka	15.8165	5.0313
kb	15.6367	4.9491
3.50 ka	15.7349	5.0796
kb	15.9306	4.9671
3.75 ka	15.7423	4.9325
kb	15.7021	4.9797
4.0 ka	15.8494	5.0089
kb	15.9444	4.9174
4.25 ka	15.7931	4.9933
kb	15.7130	4.9630
4.5 ka	15.6814	4.8415
kb	15.7839	4.8402
4.75 ka	15.6894	4.9821
kb	15.7289	4.9877
5.0 ka	15.7515	5.1265
kb	15.8354	5.1720
5.25 ka	15.7118	5.0011
kb	15.6368	4.8603
5.5 ka	15.8433	5.0890
kb	15.6501	4.9578
5.75 ka	15.7959	4.6031
kb	15.7805	4.8691
6.0 ka	15.7714	5.0919
kb	15.7535	5.0364

sample	wt tube + 5 mL 0.02 M HNO <sub>3</sub>	wt U aliquot
5-IX pH 6.25 ka	15.7361	5.1096
kb	15.7169	5.0332
6.5 ka	15.7585	5.0517
kb	15.6993	5.0056
6.75 ka	15.7995	5.1815
kb	15.7054	4.9248
7.0 ka	15.7865	5.0223
kb	15.8101	4.7936
7.25 ka	15.6349	5.0375
kb	15.7021	4.8781
7.5 ka	15.7243	4.7134
kb	15.7722	5.1189
7.75 ka	15.9167	5.2457
1250 PM kb	15.7290	5.0227
1340 PM 8.0 ka	15.7284	4.9271
kb	15.8840	4.9618
8.25 ka	15.7357	4.860
kb	15.7895	4.7776
8.5 ka	15.7878	4.9844
kb	15.7654	4.8222
8.75 ka	15.8332	4.8421
kb	15.7706	4.9816
9.00 ka	15.6672	4.9444
kb	15.7623	4.9117
5-I-CK pH 2 ka1	15.8851	5.0016
ka2	15.7755	4.9879
kb1	15.7765	4.9856
kb2	15.7608	4.9971
5-I-CK pH 4 ka1	15.7399	4.9850
ka2	15.8260	4.9766
kb1	15.7285	4.9774
kb2	15.7809	4.9808
FS-1 ka	15.7467	5.0484
kb	15.7116	5.0167

sample	wt tubet 5mL 0.02M HNO <sub>3</sub>	wt Ualignot
5-1-Ck pH 6xal	15.7750	4.9721
ka2	15.9617	4.9713
kb1	15.7874	4.9759
kb2	15.7616	4.9744
5-I-Ck pH 8xal	15.6854	4.9490
ka2	15.9393	4.9689
kb1	15.7331	4.9662
kb2	15.7331	4.9735
5-I-Ck pH 9.5xal	15.7372	4.9879
ka2	15.7436	4.9956
kb1	15.7336	4.9870
1445PM kb2	15.8015	4.9939

The pH of the solutions 5-1X + 5-1-CX were read once more.

solution	pH	soln temp °C
1505PM 5-1X pH 2.0	1.92	22.3
2.25	2.19	"
2.5	2.58	"
2.75	2.76	"
3.0	3.29	"
3.25	3.70	"
3.5	4.11	"
3.75	4.47	"
4.0	5.01	"
4.25	6.12	"
4.5	7.45	"
4.75	6.35	"
5.0	6.67	22.4
5.25	6.67	"
5.5	6.81	"
5.75	6.78	"
6.0	6.93	"

solution	pH	soln temp °C
5-1X pH 6.25	7.00	22.4
6.5	6.98	"
6.75	7.02	"
7.0	7.11	"
7.25	7.41	"
7.5	7.54	"
7.75	7.74	22.5
8.0	8.02	"
8.25	8.21	22.4
8.5	8.47	"
8.75	8.72	"
9.0	8.95	"

5-1X Ck pH 2a	1.89	22.4
2b	1.83	"
4a	3.76	22.5
4b	3.75	"
6a	5.98	"
6b	6.14	"
8a	7.97	"
8b	8.00	"
9.5a	9.34	"
9.5b	9.34	"

1644PM The 5-1X solutions were put back on the gyratory shaker.

see 6.06-1201  
for 5-1 analysis copy  
1.0 and 3.0 in 11/10/5  
3/6/93

The samples will be analyzed for U content by alpha-spectrometry. Afterwards, reversibility tests may be run by changing the pH of the solutions back and allowing the solutions to reequilibrate at the new pH values.



01/20/93 *PK*

# URANIUM SORPTION EXPERIMENT S-II: Kd vs pH; Equilibrium with atmospheric pCO<sub>2</sub>; Initial ΣU = 500 ppb

Based on Uranium Sorption Experiment B-I by R. T. Pabalan  
Adapted Dec. 16, 1992  
Revised Dec. 22, 1992

## OBJECTIVE:

To investigate the importance of uranium sorption on the clay mineral montmorillonite as a function of solution pH and total uranium concentration. Experimental data will be correlated with uranium aqueous speciation.

To investigate reversibility and reproducibility of uranium sorption reactions.

## EQUIPMENT:

Gyratory shaker or constant temperature shaker bath  
EG&G alpha-spectrometer  
ORION pH/mV/ISE/°C meter  
Combination pH electrode  
Automatic temperature compensator probe  
Analytical balance

## SUPPLIES:

pH buffer (pH = 2, 4, 7, 9, 10)  
1 125-mL bottle (to contain S-II\*IU)  
39 50-mL centrifuge tubes (to contain experimental mixtures and control solutions)  
82 50-mL centrifuge tubes (to contain samples for U analysis)  
1 50-mL volumetric pipet (to pipet 50 ppb U solution into PP bottles)  
1 5-mL volumetric pipet (to pipet 0.02 M HNO<sub>3</sub> into 50-mL centrifuge tubes)  
3 glass droppers (for adjusting pH by addition of HNO<sub>3</sub>)  
weighing paper  
1 Oxford adjustable pipet (for taking 5-mL samples) with disposable tips  
10 cc syringes (for taking samples with clay in them)  
0.2 micron Dynaguard polypropylene membrane filters  
Na<sup>+</sup>-montmorillonite  
reagent grade NaHCO<sub>3</sub>  
500 ppb U stock solution prepared from 50 ppm <sup>235</sup>U commercial spike  
1000 mL stock solution of 1.0 M HNO<sub>3</sub>  
1000 mL stock solution of 0.02 M HNO<sub>3</sub>  
ultrapure water

## PROCEDURE:

Solution S-II (1 centrifuge tube for each pH value)

-Initial ΣU = 500 ppb  
-Initial pH = 2.0 to 9.0, every 0.25 pH unit; adjustments made with HNO<sub>3</sub> or NaHCO<sub>3</sub>  
-Initial volume = 50 mL  
-Ionic strength = 0.1 M NaNO<sub>3</sub>  
-Wt. zeolite to use = 0.100±0.001 g  
-Initial [Na<sup>+</sup>] = 0.1 M NaNO<sub>3</sub> + [NaHCO<sub>3</sub>] added  
-pCO<sub>2</sub> = atmospheric = 10<sup>-3.48</sup> bar

a) Into each of 29 50-mL centrifuge tubes labeled S-II\*pHi [where *i* is the approximate initial pH of the solution (see below)], tare 50 g of the 500 ppb uranium solution.

The 500 ppb U stock solution is from dilution 23-A  
(Radiochemistry Notebook, 150).

i.e. 2.0, 2.25, ..., 8.75, 9.0

tube label	wt tube, g	wt U soln added, g
08257M S-II* <i>pH</i> 2.0	10.9540	46.1371
2.25	10.9500	46.1332
2.5	10.7648	46.0933
2.75	10.7779	46.0658
3.0	10.6377	46.1328
3.25	10.7433	46.0614
3.5	10.9544	46.0072
3.75	10.7373	46.0173
4.0	10.8032	46.1385
4.25	10.6925	46.0237
4.5	10.7999	46.0819
4.75	10.7357	46.0504
5.0	10.7813	46.0603
5.25	10.7926	46.0547
5.5	10.9071	46.0081
5.75	10.7513	46.1286
6.0	10.7654	46.1321
6.25	10.6945	46.0719
6.5	10.9068	46.0329
6.75	10.7647	46.0948
7.0	10.7423	46.1192
7.25	10.7380	46.0734
7.5	10.7519	46.0914
7.75	10.9247	46.1031
8.0	10.7597	46.0073
8.25	10.7242	46.0235
8.5	10.7754	46.0679
8.75	10.7579	46.0185
9.0	10.7598	46.0106

Into each of 10 50-mL centrifuge tubes labeled S-II-C\*pHi\*a (or b) [where *i* is 2, 4, 6, 8, or 9.5, representing the approximate initial pH of the solution], tare 50 g of the 500 ppb uranium solution. These are control solutions to determine uranium loss to the container walls as a function of pH.

tube label	wt tube, g	wt U soln added, g
S-II-C* <i>pH</i> 2Ka	10.9116	46.0203
b	10.7775	46.1138

tube label	wt tube, g	wt U soln added, g
S-II-C *pH 4ka	10.7378	46.1133
b	10.8010	46.1271
6ka	10.8574	46.1061
b	10.7699	46.1537
8ka	10.7937	46.1561
b	10.9113	46.1632
9.5ka	10.7919	46.1618
1028PM b	10.7784	46.1273

b). Take two 5-mL samples from the 500 ppb stock solution (for this purpose called S-II\*IU) with an Oxford pipet, transfer into pre-labeled [e.g., S-II-IU\*a (or b)] and pre-weighed 50-mL centrifuge tubes containing 5 g of 0.02 M HNO<sub>3</sub>. Swirl each tube and save for later analysis of uranium concentration by alpha-spectrometry.

wt tube + HNO <sub>3</sub> , g	wt sample taken, g
S-II-IUka: 15.80318	5.0096
b: 15.8298	5.0040

c) 1. For each solution S-II\*pHi and S-II-C\*pHi, where  $i \leq 3.2$ :

Measure and record the initial pH (~3.2, based on EQ3 calculation). The automatic temperature compensator (ATC) probe should be immersed in water in a separate container.

solution	pH	soln temp °C
S-II-kpH 2.0	3.17	18.7
2.25	3.14	"
2.5	3.15	18.8
2.75	"	"
3.0	"	18.9
S-II-C *pH 2ka	3.16	19.0
*b	3.18	

The pH meter/electrode was calibrated using Fisher pH buffer solutions 2, 3, & 4 (lot #s 910958-24, 910886-24, & 913914-24).

Adjust the pH to the value of  $i$  of each solution by adding dropwise with a glass dropper HNO<sub>3</sub> solution, the concentration and approximate amount of which is given in Table S-II-1. Swirl the solutions by hand. Record the number of drops and concentration of solution added. Also record the attained pH. Cover the bottles with a kimwipe and place on the gyratory shaker set to ~120 rpm. Monitor the pH periodically, together with the centrifuge tubes prepared in step 2 below.

The 1.0 M HNO<sub>3</sub> solution was prepared 5 Aug 92 by Todd Dutich from lot #910962. The 0.1 M HNO<sub>3</sub> solution was prepared 2 Dec 92 by Jim Prikryl from the same lot.

The glass droppers used were calibrated previously - see GC-06-63.

Table S-II-1. Amount of reagent grade HNO<sub>3</sub> or NaHCO<sub>3</sub> to add to 50 ml 0.1 m NaNO<sub>3</sub> solution containing 500 ppb U to result in pH values given in column-1. The amount of reagent to be added was estimated using EQ3 calculations and assuming the solutions are in equilibrium with atmospheric CO<sub>2</sub>(g).

Solution pH	Volume of HNO <sub>3</sub> Needed, Drops (0.0394 mL/drop)	Molarity of HNO <sub>3</sub> Used
2.00	14 (0.561 mL)	1.0
2.25	9 (0.34 mL)	1.0
2.50	5 (0.191 mL)	1.0
2.75	3 (0.108 mL)	1.0
3.00	2 (0.061 mL)	1.0
Solution pH	Amount of NaHCO <sub>3</sub> Needed, Grams	
3.25	0.000497	
3.50	0.001743	
3.75	0.002443	
4.00	0.002837	
4.25	0.003059	
4.50	0.003185	
4.75	0.003256	
5.00	0.003299	
5.25	0.003327	
5.50	0.003347	
5.75	0.003364	
6.00	0.003384	
6.25	0.003410	
6.50	0.003454	
6.75	0.003529	
7.00	0.003661	
7.25	0.003896	
7.50	0.004317	
7.75	0.005073	

Solution pH	Amount of NaHCO <sub>3</sub> Needed, Grams	
8.00	0.006438	
8.25	0.008906	
8.50	0.013476	
8.75	0.022214	
9.00	0.039767	
[9.25]	[0.077855]	
[9.50]	[0.171074]	

	target pH	pH attained	soln temp °C	[HNO <sub>3</sub> ]	# drops
(S-II * pH)	2.0	1.99	18.7	1.0M	12
	2.25	2.26	18.8	"	6
	2.5	2.48	"	"	3
	2.75	2.66	"	"	2
	3.00	2.98	18.9	0.1M	4
(S-II - C * pH)	2 a	2.02	19.0	1.0M	11
	2 b	1.99	"	"	11

1130 PM

2. For each solution S-II \* pH<sub>i</sub> and S-II-C \* pH<sub>i</sub>, where  $i > 3.2$ :

Measure and record the initial pH (~3.2, based on EQ3 calculation).

	solution S-II * pH <sub>i</sub>	pH measured	temp soln, °C
i =	3.25	3.14	19.1
	3.5	"	"
	3.75	3.15	"
	4.0	3.16	"
	4.25	3.17	19.2
	4.5	"	"
	4.75	"	"
	5.0	"	"
	5.25	"	"
	5.5	"	19.3
	5.75	3.16	"
	6.0	"	"
	6.25	"	"
	6.5	3.17	"
	6.75	3.16	"
	7.0	"	"
	7.25	3.17	19.4
	7.5	"	"
	7.75	3.18	"
	8.0	3.16	"
	8.25	3.17	"
	8.5	3.16	"
	8.75	3.17	19.5
	9.0	"	"

	solution S-II-C * pH <sub>i</sub>	pH measured	temp soln °C
i =	4a	3.20	19.5
	4b	3.19	"
	6a	3.21	19.6
	6b	3.19	"
	8a	3.21	"
	8b	3.19	"
	9.5a	3.22	19.7
	9.5b	3.20	"

1212 PM

Tare onto weighing paper reagent grade NaHCO<sub>3</sub> in the amounts listed in Table S-II-1 and transfer into the respective centrifuge tubes. Swirl the solutions by hand. Cover the tubes with a kimwipe and place on gyratory shaker set to ~120 rpm. Monitor the pH periodically until the pH becomes constant and in equilibrium with atmospheric CO<sub>2</sub>(g). This equilibration process may take at least twelve days.

NaHCO<sub>3</sub> used is lot # 886728.

	solution label	amt NaHCO <sub>3</sub> added, g.
1325 PM	S-II * pH 3.25	0.00067
	3.5	0.00160
	3.75	0.00253
	4.0	0.00281
	4.25	0.00305
	4.5	0.00314
	4.75	0.00320
	5.0	0.00326
	5.25	0.00329
	5.5	0.00334
	5.75	0.00336
	6.0	0.00339
	6.25	0.00343
	6.5	0.00345
	6.75	0.00351
	7.0	0.00362
	7.25	0.00388
	7.5	0.00425
	7.75	0.00491

<u>solution label</u>	<u>amt. <math>\text{NaHCO}_3</math> added, g.</u>
S-II x pH 8.0	0.00634
8.25	0.00882
8.5	0.01310
8.75	0.02244
9.0	0.03949
S-II-C x pH 4a	0.00278
b	0.00277
6a	0.00335
b	0.00339
8a	0.00649
b	0.00650
9.5a	0.17097
b	0.17088

11:05 PM The S-II solutions were covered with the kim wipes  
+ placed in a gyratory shaker at ~125 rpm.

01/22/93 Expt S-II continued pH monitoring

<u>solution</u>	<u>pH</u>	<u>temp of soln, °C</u>
07:49 PM S-II x pH 2.0	2.00	17.5
2.25	2.25	"
2.5	2.46	"
2.75	2.64	"
3.0	2.96	"
3.25	3.22	"
3.5	3.42	"
3.75	3.90	"
4.0	3.99	"
4.25	4.48	"
4.5	4.66	"
→ 4.75	6.25	"
5.0	6.54	"
5.25	6.51	"

<u>solution</u>	<u>pH</u>	<u>temp of soln, °C</u>
S-II x pH 5.5	6.84	17.5
5.75	6.86	17.6
6.0	6.76	"
6.25	6.85	"
6.5	6.87	"
6.75	6.98	"
7.0	7.08	17.7
7.25	7.25	"
7.5	7.46	"
7.75	7.66	17.8
8.0	7.93	17.9
8.25	8.18	"
8.5	8.40	"
8.75	8.50	"
9.0	8.20	"

S-II-C x pH 2a	2.00	18.0
b	2.02	"
4a	4.11	18.1
b	4.17	"
6a	6.89	"
b	7.01	"
8a	8.45	"
b	8.35	"
9.5a	8.71	"
b	8.61	18.2

09:38 PM The S-II solutions were put back in the gyratory shaker.

01/25/93 Expt S-II continued pH monitoring

<u>solution</u>	<u>pH</u>	<u>°C soln</u>
10:52 PM S-II x pH 2.0	2.060	17.5
2.25	2.25	"



<u>solution</u>	<u>pH</u>	<u>°C soln</u>
S-II * pH 2.5	2.46	16.3
2.75	2.64	"
3.0	3.02	"
3.25	3.30	"
3.5	3.46	"
3.75	3.97	16.4
4.0	4.07	"
4.25	4.54	"
4.5	4.76	"
4.75	6.42	"
5.0	6.82	"
5.25	6.70	16.5
5.5	6.88	"
5.75	7.05	"
6.0	6.86	"
6.25	7.01	"
6.5	6.88	"
6.75	7.00	16.6
7.0	7.16	"
7.25	7.26	"
7.5	7.49	"
7.75	7.73	"
1202 PM 8.0	7.90	18.1
* 1403 PM 8.25	8.15	"
8.5	8.49	18.2
8.75	8.76	"
9.0	8.90	"

S-II-C * pH 2a	2.02	18.3
b	2.02	18.5
4a	4.09	18.6
b	4.15	18.7
6a	6.89	18.8
b	6.95	18.9

\* The meter/electrode was recalibrated using the same pH buffers.

<u>solution</u>	<u>pH</u>	<u>°C soln</u>
S-II-C * pH 8a	8.04	19.0
b	8.01	19.1
9.5a	9.12	19.2
b	9.13	19.3

1002 PM The S-II solutions were put back on the gyratory shaker at ~125 rpm.

11/27/93 PM Expt 3-II continued: pH monitoring

<u>solution</u>	<u>pH</u>	<u>°C solution</u>
0522 PM S-II * pH 2.0	1.97	15.8
2.25	2.24	"
2.5	2.44	"
2.75	2.62	"
3.0	2.93	"
3.25	3.20	15.9
3.5	3.40	"
3.75	3.88	"
4.0	4.03	"
4.25	4.53	"
4.5	4.70	"
4.75	6.27	16.0
5.0	6.61	"
5.25	6.60	"
5.5	6.84	16.1
5.75	6.89	"
6.0	6.77	16.2
6.25	6.83	"
6.5	6.93	16.3
6.75	7.05	"
7.0	7.19	16.4
7.25	7.32	"
7.5	7.49	16.5

<u>solution</u>	<u>pH</u>	<u>°C solution</u>
5-II-K pH 7.75	7.69	16.6
8.0	8.03	"
8.25	8.23	16.7
8.5	8.56	16.8
8.75	8.84	"
9.0	9.01	16.9
5-II-CK pH 2a	2.02	16.9
b	2.03	17.0
4a	4.09	17.1
b	4.18	17.2
6a	7.03	"
b	7.06	17.3
8a	8.15	17.5
b	8.20	"
9.5a	9.30	17.6
b	9.30	17.7

11:30 PM The 5-II solutions 1/27 PM  
 samples were put back on the gyratory shaker.

01/29/92 PM Expt 5-II continued: pH monitoring

<u>solution</u>	<u>pH</u>	<u>solution temp, °C</u>
1014 PM 5-II-K pH 2.0	1.93	19.2
2.25	2.16	"
2.5	2.40	19.3
2.75	2.59	"
3.0	2.91	"
3.25	3.18	"
3.5	3.38	"
3.75	3.86	"
4.0	4.00	"
4.25	4.50	"
4.5	4.66	19.4
4.75	6.28	"

<u>solution</u>	<u>pH</u>	<u>solution temp, °C</u>
5-II-K pH 5.0	6.61	19.4
5.25	6.55	"
5.5	6.84	19.5
5.75	6.87	"
6.0	6.80	"
6.25	6.91	19.6
6.5	6.92	"
6.75	7.05	"
7.0	7.13	19.7
7.25	7.28	"
7.5	7.50	"
7.75	7.69	19.8
8.0	7.96	"
8.25	8.20	"
8.5	8.45	"
8.75	8.70	"
9.0	8.92	19.9

5-II-CK pH 2a	1.93	19.9
b	1.89	"
4a	3.94	"
b	4.02	"
6a	6.85	"
b	6.90	20.0
8a	8.02	"
b	7.97	"
9.5a	9.18	"
b	9.21	"

11:48 PM The 5-II solutions were put back on the gyratory shaker.

02/01/93PM Expt. 5-11 continued: pH monitoring

soln	pH	temp soln °C	soln	pH	temp soln °C
1324PM 5-TL pH 20	1.96	19.9	5-TL pH 20	1.95	20.6
2.25	2.20	"	2b	1.97	"
2.5	2.44	"	4a	4.01	"
2.75	2.62	"	4b	4.05	"
3.0	2.94	"	6a	6.86	20.7
3.25	3.20	20.0	6b	6.96	"
3.5	3.40	"	8a	8.07	"
3.75	3.87	"	8b	8.04	"
4.0	4.01	"	9.5a	9.33	20.8
4.25	4.50	"	9.5b	9.35	"
4.5	4.68	"			
4.75	6.30	"			
5.0	6.58	20.1			
5.25	6.56	"			
5.5	6.81	"			
5.75	6.86	20.2			
6.0	6.80	"			
6.25	6.91	"			
6.5	6.89	20.3			
6.75	7.02	"			
7.0	7.14	20.4			
7.25	7.30	"			
7.5	7.48	"			
7.75	7.67	20.5			
8.0	7.96	"			
8.25	8.19	"			
8.5	8.45	"			
8.75	8.74	"			
9.0	8.96	"			

1516PM The 5-11 solutions were returned to the gyratory shaker.

02/03/93PM Expt MKI continued - U-233 Alpha Spectrometry  
Analysis Procedure (see GC-060/-53)**Preparation:**

1. All glass should be washed in a hot acid bath (4 liter beaker with cover glass) of fuming nitric acid over night (> 4 hours). Once the temperature of the acid bath is near room temperature, the acid washed glass should be quickly inserted into nanopure H<sub>2</sub>O in another large beaker inside the fumehood. Two pairs of gloves and goggles should be used during this operation as there is a possibility of splashing and nitric acid is a real hazard. The rinsed glassware should then be rinsed at least three more times in the sink with nanopure water. The rinsed dishes can either be air dried on a covered tray or placed in the drying oven.

**Waste Disposal:**

1. Used ion exchange resins will be stored in nonbreakable, screw-top containers. Containers will be clearly labelled. Radioisotope storage containers will be labelled with the following information: a) radioisotope; b) physical form; c) type of emission; d) activity in Curies; and e) dose rate at container surface. The exchange resins will be regenerated to reduce the level of radioactivity and to reduce the volume that will be disposed. Responsibility for regeneration and disposal of the ion exchange resins will be assumed by the RPC.
2. Disposal of the solutions containing several isotopes (i.e. solutions containing both <sup>232</sup>U and <sup>233</sup>U) down the sewer is restricted by the release limits set forth in TRC 21.303 Appendix 21-A (Note 1). This note states that the release is limited so that the sum of the the ratios in the solution to that of the limiting concentration for each isotope in the solution will be < 1. For example, in the case of two isotopes (<sup>232</sup>U and <sup>233</sup>U) present in concentrations C<sub>232U</sub> and C<sub>233U</sub> with maximum permissible concentrations MPC<sub>232U</sub> and MPC<sub>233U</sub>:  

$$(C_{232U}/MPC_{232U}) + (C_{233U}/MPC_{233U}) \leq 1.$$
Note that the limits for MPC<sub>232U</sub> and MPC<sub>233U</sub> are 0.8 nCi/ml and 0.9 nCi/ml, respectively.
3. All waste solutions derived during ion exchange column manipulations either contain high concentrations of N (nitrate and ammonium (NH<sub>4</sub>), which readily converts to nitrate) or acid and require liberal dilution prior to and during disposal via the sink.

1002PM Prep of more Na-montmorillonite continued - (see p 74)

The rinsed Na-form clay is being freeze dried in the following manner:

Dry ice was obtained from Al Dominguez (Div. 2) and put in the LABONCO freeze-dryer's reservoir.

Acetone was added to the reservoir until the liquid level was almost at the top. Because the apparatus (drier + vacuum containers + pump) is too bulky to be moved in and out of the fume hood and copious (co<sub>2</sub>) + acetone fumes are generated, this was done on the lab bench by the lab door to the outside with the door propped open. The washed clay was vortexed + more nano pure water was added as needed to unclump the clay. The clay (~170 g wet) was divided among a 300 mL vacuum container + two 120 mL containers.

After a filter paper was placed at the opening of each container + the proper glass converter was attached, each container was rotated while partially submerged in the reservoir. This was done to freeze the clay in a more or less even layer on the sides + bottom of the containers. The containers were then attached to the freeze drier, their spigot indicators turned to 'vac' + the others left on 'vent' and the pump attached to the dryer switched on. Drying (if successful) should take several (~7) hours.

10:12 PM Drying was started.

12:10 PM Expt MK1 - Alpha Spec cont:

### Analytical Procedure:

#### A. Spiking and co-precipitation

1. Spike all samples in a rack requiring the same spike at one time (i.e. all spike 25 C at same time). Use the centrifuge tube stand in glass beaker to hold the tube being spiked. Use the syringe stand to hold the pasteur pipet between sample spikings. Tare a pre-folded sample boat (plastic) on balance. Using a pasteur pipet (a new one for each time a series of samples will be spiked with a different <sup>232</sup>U solution) and a small rubber bulb add predetermined mass of spike solution to sample boat and record weight. Error in spike mass should be to the

low side. Dispose of pasteur pipet in special radioactive wastebasket after samples have been spiked.

Identification	Spike #	Wt (g)	Wt (g) weighed:	Finals (mL)
MK1-1*IUa	25A	0.167	1.636	~10
MK1-1*IUb	25B	1.672	1.630	
MK1-1*A*I1	25A	0.167	1.630	
MK1-1*A*I2	25B	1.672	1.6640	
MK1-1*B*I1	25A	0.167	1.643	
MK1-1*B*I2	25B	1.672	1.6707	
MK1-1*C*I1	25A	0.167	1.654	
MK1-1*C*I2	25B	1.672	1.6625	
MK1-1*A*1a	25A	0.162	1.592	
MK1-1*B*1a	25B	1.622	1.6233	
MK1-1*C*1a	25A	0.165	1.643	
MK1-1*A*2a	25B	1.572	1.5706	
MK1-1*B*2a	25A	0.157	1.527	
MK1-1*C*2a	25A	0.165	1.646	
MK1-1*A*3a	25B	1.170	1.1666	
MK1-1*A*3b	25B	1.170	1.1665	
MK1-1*B*3a	25B	1.170	1.1699	
MK1-1*B*3b	25B	1.170	1.1642	
MK1-1*C*3a	25A	0.165	1.652	
MK1-1*C*3b	25A	0.165	1.652	
MK1-1*A*4a	25B	0.836	0.8341	
MK1-1*B*4a	25B	0.836	0.8334	
MK1-1*C*4a	25A	0.165	1.647	
MK1-1*A*5a	25B	0.502	0.8304	error on high side
MK1-1*B*5a	25B	0.502	0.5023	
MK1-1*C*5a	25A	0.165	1.644	
MK1-1*A*6a	25B	0.334	0.3288	
MK1-1*A*6b	25B	0.334	0.3303	
MK1-1*B*6a	25B	0.334	0.3321	
MK1-1*B*6b	25B	0.334	0.3332	
MK1-1*C*6a	25A	0.165	1.632	
MK1-1*C*6b	25A	0.165	1.639	
MK1-1*A*7a	25B	0.251	0.2502	
MK1-1*B*7a	25B	0.251	0.2508	
MK1-1*C*7a	25A	0.165	1.628	
MK1-1*A*8a	25B	0.201	0.2015	
MK1-1*B*8a	25B	0.201	0.2032	
MK1-1*C*8a	25A	0.164	1.629	
MK1-1*A*9a	25B	0.167	1.667	
MK1-1*A*9b	25B	0.167	1.616	
MK1-1*B*9a	25B	0.167	1.648	
MK1-1*B*9b	25B	0.167	1.635	



Identification	Spike #	Wt (g)	wt g (weighed)
MK1-1*C*9a	25A	0.164	.1640
MK1-1*C*9b	25A	0.164	.1628
MK1-1*A*10a	25C	0.836	.8322
MK1-1*B*10a	25C	0.836	.8318
MK1-1*C*10a	25A	0.164	.1616
MK1-1*A*11a	25C	0.167	.1624
MK1-1*B*11a	25C	0.167	.1633
MK1-1*C*11a	25A	0.164	.1629
MK1-1*FU*a	25A	0.164	.1643
MK1-1*FU*b	25A	0.164	.1631

SUM 25A 3.62  
Sum 25B 20.15  
Sum 25C 2.01

25A is 2.051 nCi/g  
25B is 204.88 pCi/g  
25C is 20.477 pCi/g

2. Transfer spike quantitatively to sample centrifuge tube using squirt bottle of 0.1 N HNO<sub>3</sub>. Use enough of 0.1 N HNO<sub>3</sub> during each spike transfer (~ 5 ml) to obtain roughly equal volumes in the centrifuge tubes. Dispose of sample boat into special radioactive wastebasket.

- 1538 PM 3. Homogenize sample after addition of spike by replacing lid and swirling the centrifuge tube. Allow spike to equilibrate at least 24 hours before next step.

1100 PM Clay freeze-drying continued -  
The clay is still wet, and the dry ice has evaporated.  
The clay will be dried again on Friday with only the  
two 120 mL containers & ~ 100g wet clay total  
on line.

02/05/83 PM Clay freeze-drying continued -  
0858 PM The ~100g of clay was re-added to the freeze-  
drier & drying continued.

Expt 5-II continued: pH monitoring

soln	5-II pH	pH	soln temp °C	soln 5-II-C pH	pH	°C
0858 PM	2.0	1.97	17.5	2a	1.94	17.8
	2.25	2.18	"	2b	1.90	17.9
	2.5	2.40	"	4a	3.98	"
	2.75	2.60	"	4b	4.03	"
	3.0	2.92	"	6a	6.82	"
	3.25	3.19	"	6b	6.90	"
	3.5	3.39	"	8a	8.06	"
	3.75	3.87	"	8b	7.98	"
	4.0	4.01	17.6	9.5a	9.35	"
	4.25	4.50	"	9.5b	9.38	"
	4.5	4.67	"			
	4.75	6.32	"			
	5.0	6.62	"			
	5.25	6.55	"			
	5.5	6.83	"			
	5.75	6.90	"			
	6.0	6.78	17.7			
	6.25	6.90	"			
	6.5	6.93	"			
	6.75	7.03	"			
	7.0	7.13	"			
	7.25	7.29	17.8			
	7.5	7.53	"			
	7.75	7.69	"			
	8.0	7.96	"			
	8.25	8.22	"			
	8.5	8.50	"			
	8.75	8.74	"			
	9.0	8.97	"			

1115 PM The 5-II soln trays were placed back in the gyrotory shaker

- Expt MK1 - Alpha Spec continued -

- 13/5/91 4. Add carrier to one row of tubes in a rack at a time. Add 1 ml of Fe carrier using Eppendorf fixed volume pipet and disposable tips. Homogenize sample after addition of carrier by replacing lid and swirling the centrifuge tube. Allow sample to equilibrate for 24 hours.

14/03/91 freeze drying of clay cont.

the clay was taken off line as all the dry ice is gone. One of the containers' clay is about 1/2 dry (very dry about the edges, still wet in the middle). The containers will be covered with kum wipes + left for the clay to air-dry.

02/08/93 Expt MK1 - Alpha Spec continued

- 08/10/91 5. Start step B1 now and continue with step B2 simultaneously with the following steps of A (A5 - A7) so that once you have completed step A7 you can immediately proceed with step B3. Bring the pH up to 7 with the addition of concentrated  $\text{NH}_4\text{OH}$  from the reagent bottle using 6 to 7 drops from the plastic pipet attached to the  $\text{NH}_4\text{OH}$  reagent bottle. This is strongly exothermic and the solution should be gently swirled during the addition of the base. Note that the  $\text{NH}_4\text{OH}$  should be from a closed reagent container (eg. new 2 l bottle) since this will ensure that minimal  $\text{CO}_2$  will be present in the base which would lower yield. This step precipitates about 2.5 ml of  $\text{Fe}(\text{OH})_3$ .

Note: only samples MK1-1 x 10 a + b were started today.

- 07/10/93 6. The solution can then be centrifuged (labeled 50 ml centrifuge tubes) and the supernate is discarded into a waste beaker.

7. The  $\text{Fe}(\text{OH})_3$  precipitates are washed with about 10 ml of ultrapure water and agitated using the hand homogenizer, centrifuged and washings discarded. This step is repeated once. This is necessary to get rid of the excess  $\text{NH}_4$ .

## B. Uranium-thorium separation

1. Prepare a labeled (Sample ID) anion ion exchange column (8 - 10 cm high, 1 cm diameter) by placing a glass wool plug in the bottom of the column and adding a slurry (in ultrapure water) of Dowex 1 x 8 100-200 mesh chloride form ion exchange resin. Use the teflon column holders and collect the waste liquid in a plastic beaker (100 ml of greater).
2. Add 30-40 ml of 8 N Ammonium Nitrate - 0.1 N Nitric acid into anion exchange column and elute into plastic waste beaker.

07/32 PM - prep. of more Na-form montmorillonite continued -

The mostly-dried clay in the one 125ml freeze-drying container was put in a dessicator to help remove the last of the moisture.

02/12/93 Expt 5-II continued: pH monitoring

sln	pH	temp °C	sln	pH	temp °C
098 PM 5-II pH 2.0	1.94	16.0	5-II-(KPH2a)	1.97	16.6
2.25	2.18	"	2b	1.98	16.7
2.5	2.40	"	4a	4.04	16.8
2.75	2.58	"	4b	4.02	16.9
3.0	2.92	16.1	6a	6.86	"
3.25	3.22	"	6b	6.94	17.0
3.5	3.40	"	8a	8.16	"
3.75	3.86	"	8b	8.05	"
4.0	4.00	"	9.5a	9.48	17.1
4.25	4.51	"	9.5b	9.51	17.2
4.5	4.68	"			
4.75	6.32	"			
5.0	6.65	"			
5.25	6.58	"			
5.5	6.86	"			
5.75	6.90	16.2			
6.0	6.84	"			
6.25	6.91	"			
6.5	6.95	"			
6.75	7.05	16.3			
7.0	7.17	"			
7.25	7.32	16.4			
7.5	7.55	"			
7.75	7.72	"			
8.0	8.17	"			
8.25	8.29	16.5			
8.5	8.65	"			
8.75	8.89	16.6			

## Expt MK1 Alpha Spec Continued

02/08/93 PM  
Work done on  
8th JMK

3. The samples will be lowered to pH = 1 using 250  $\mu$ l of 1.0 N  $\text{HNO}_3$  and diluting to 5.0 ml with 0.1 N  $\text{HNO}_3$  using squirt bottle. Make sure  $\text{Fe}(\text{OH})_3$  is entirely dissolved (agitate) prior to adding the ammonium nitrate. Next, saturate the solution with 5.9 g of ammonium nitrate and shake until all is dissolved. This reaction is highly endothermic.

4. Add the sample onto the column and allow to drain into 100 ml plastic beaker. Elute Fe into the beaker using 80 ml, added in 20 ml increments using squirt bottle, of 8 N  $\text{NH}_4\text{NO}_3$  - 0.1 N  $\text{HNO}_3$ . Rinse the centrifuge tube with the 20

ml aliquot and pour onto column and mark the level of the fluid. Test for the presence of Fe after 70 to 80 ml have drained by placing a drop of  $\text{NH}_4\text{CSN}$  on the convex side of watch glass and allowing a drop of the eluate to come in contact with ammonium cyanide. If Fe is present then the solution will turn red. Continue to eluate the Fe until there is no red upon testing for Fe. Empty the contents of the 100 ml plastic beaker into a waste beaker.

5. Next add 100 ml, in 20 ml aliquots, of 8 N HCL acid and elute the thorium into the same beaker. Dispose of solution in beaker down the sink with liberal flushing.

6. Using a squirt bottle, add no more than 5 ml of 0.1 N nitric acid to the column and allow to drain into waste beaker. The column changes color slightly from orange to slightly yellow. Next, add 50 ml of 0.1 N nitric acid in 10 ml increments and drain the uranium into a labeled and acid washed cleaned 100 ml glass beaker.

Note: the process was stopped + the beakers covered with Parafilm.

02/12/93 PM

0802 PM

(The solution is then placed on a hot plate to reach just to dryness. Allow beaker to cool moderately and then immediately proceed with step C1. As long as the beaker is slightly warm and 0.001 N  $\text{HNO}_3$  is added the U is more easily put into solution and the pH is closer to the desired pH.

## C. Solvent extraction and plating

1. A total of 4 pasteur pipets are used in the following steps and it is imperative to keep them separate by labeling the rubber bulbs used with them. The dried U eluate is taken up with two ml of 0.001 N  $\text{HNO}_3$  (pH 3) issued from a squirt bottle. Using a new pasteur pipet (W on bulb) carefully and completely wash the beaker with the acid. Transfer the acid solution to a labeled glass 12 ml centrifuge tube. Repeat this step twice more with 0.5 - 1 ml of the acid.
2. Add two drops of Methyl Orange indicator solution using a pasteur pipet (MO on bulb) to solution in centrifuge tube. Bring pH up to 3.0 with dilute 0.1 N NaOH solution using a pasteur pipet (NaO on bulb) by adding a few drops at a time and homogenizing the contents of the tube with pasteur pipet used to transfer the U eluate (W on bulb). The color should change from pink to slightly orange. The colors can be seen in test tube set which covers the pH range. If steps in B were done properly the total volume should be 5-6 ml.
3. Add 1-2 ml of the 0.4 M TTA in benzene solution to the centrifuge tube.
4. Homogenize and extract the U using the same pasteur pipet used in step C1 (W on bulb). The TTA solution should be red or orange (depending on U concentration) and this should be quickly evident (within 30 seconds to 1 minute).
5. Solution is centrifuged for 1-2 minutes, making sure that the tube is covered with Parafilm.
6. Carefully clean a stainless steel planchet and label it with a sharp pointed object. The label should have sample ID, date, initials of the person plating and U. Label a glassine stamp envelope with the same information. The mounting ring should be on the hot plate and the hot plate should be set to red mark (~3). Place the plate, labeled side down, on the mounting ring just prior to next step.
7. The TTA solution is carefully separated using a clean pasteur pipet (P on bulb), taking care not to include any of the  $\text{HNO}_3$  solution. This is most easily accomplished by slightly tilting the tube so that the TTA bulges on top of the acid. A total of two aliquots using the pasteur pipet (P on bulb) are used to retrieve all the TTA.
8. The TTA is evaporated drop-wise (vertically) on heated steel plates that have been placed on mounting ring, making sure that spattering is avoided.
9. Remove the plate from the mounting ring and repeat the TTA extraction (Steps 3 - 8).
10. Pass the plate through the flame of a propane flame inside the fume hood to burn off the organic deposit. Allow the plate to cool on the edge of the hot plate.
11. Place plates in labeled glassine stamp envelopes and count samples ASAP after plating, recording the channel in which the sample is counted on the envelope.

1732 PM Plates started counting.

2/13/93

## Expt S-II continued

- d) Tare 0.100 $\pm$ 0.001 g of Na-montmorillonite onto weighing paper, and carefully transfer into each of the S-II\*pHi (not the S-II-C\*pHi) centrifuge tubes. Swirl each tube by hand, replace the cover, then place on the shaker.

soln	amt clay added, g	soln	amt clay added, g
1102 PM S-II KpH 2.0	0.1005	S-II KpH 6.25	0.1004
2.25	0.1009	6.5	0.1001
2.5	0.0992	6.75	0.1002
2.75	0.1004	7.0	0.0998
3.0	0.1002	7.25	0.1005
3.25	0.0999	7.5	0.1003
3.5	0.1001	7.75	0.1007
3.75	0.0999	8.0	0.1000
4.0	0.1005	8.25	0.0986
4.25	0.0995	8.5	0.1008
4.5	0.1005	8.75	0.0999
4.75	0.0997	9.0	0.1009
5.0	0.0991		
5.25	0.0996		
5.5	0.1003		
5.75	0.1009		
6.0	0.1004		

1722 PM The S-II samples were put back on the gyrostary shaker at ~125 rpm.

02/17/93 - Prep of 0.02 M  $\text{HNO}_3$  for S-II samples -

1102 PM 10 mL of 1.0 M  $\text{HNO}_3$  (prep TD 5 Aug 92 lot # 910962) was taken by volumetric pipet + put in a 500 ml volumetric flask. The flask was brought to volume with deionized water + stored to mix. This will be used in the S-II samples

**URANIUM SORPTION EXPERIMENT S-III:**  
Kd vs pH; Equilibrium with atmospheric pCO<sub>2</sub>; Initial ΣU = 5 ppb

Based on Uranium Sorption Experiment B-I by R. T. Pabalan  
Adapted Dec 16, 1992  
Revised Dec 17, 1992

**OBJECTIVE:**

To investigate the importance of uranium sorption on the clay mineral montmorillonite as a function of solution pH and total uranium concentration. Experimental data will be correlated with uranium aqueous speciation.

To investigate reversibility and reproducibility of uranium sorption reactions.

**EQUIPMENT:**

Gyratory shaker or constant temperature shaker bath  
EG&G alpha-spectrometer  
ORION pH/mV/ISE/°C meter  
Combination pH electrode  
Automatic temperature compensator probe  
Analytical balance

**SUPPLIES:**

pH buffer (pH = 2, 4, 7, 9, 10)  
1 125-mL bottle (to contain S-III\*IU)  
39 50-mL centrifuge tubes (to contain experimental mixtures and control solutions)  
78 50-mL centrifuge tubes (to contain samples for U analysis)  
1 50-mL volumetric pipets (to pipet 5 ppb U solution into PP bottles)  
1 5-mL volumetric pipet (to pipet 0.02 M HNO<sub>3</sub> into 50-mL centrifuge tubes)  
1 4000-mL plastic bottle (for preparation of 5 ppb U solution)  
3 glass droppers (for adjusting pH by addition of HNO<sub>3</sub>)  
weighing paper  
1 Oxford adjustable pipet (for taking 5-mL samples) with disposable tips  
10 cc syringes (for taking samples with clay in them)  
0.2 micron Dynaguard polypropylene membrane filters  
Na<sup>+</sup>-montmorillonite  
reagent grade NaHCO<sub>3</sub>  
500 ppb U stock solution prepared from 50 ppm <sup>233</sup>U commercial spike  
2 L 0.1 M NaNO<sub>3</sub> stock solution  
1000 mL stock solution of 1.0 M HNO<sub>3</sub>  
1000 mL stock solution of 0.1 M HNO<sub>3</sub>  
1000 mL stock solution of 0.02 M HNO<sub>3</sub>  
1000 mL stock solution of 0.01 M HNO<sub>3</sub>  
ultrapure water

**PROCEDURE:**

Solution S-III (1 centrifuge tube for each pH value)

- Initial ΣU = 5 ppb
- Initial pH = 2.0 to 9.0, every 0.25 pH unit; adjustments made with HNO<sub>3</sub> or NaHCO<sub>3</sub>
- Initial volume = 50 mL
- Ionic strength = 0.1 M NaNO<sub>3</sub>
- Wt. zeolite to use = 0.100±0.001 g
- Initial [Na<sup>+</sup>] = 0.1 M NaNO<sub>3</sub> + [NaHCO<sub>3</sub>] added
- pCO<sub>2</sub> = atmospheric = 10<sup>-3.48</sup> bar

a) In a pre-cleaned 4 liter plastic bottle, prepare 2050 g of 5 ppb U solution by diluting 20.5 g of a 500 ppb stock solution (in 0.1 M NaNO<sub>3</sub> matrix; prepared previously from commercial 50 ppm <sup>233</sup>U spike) to a total of 2050 g by carefully taring 0.1 M NaNO<sub>3</sub> solution into the plastic bottle on a Mettler 4600 balance.

1158PM 4L of 0.1M NaNO<sub>3</sub> solution was prepared by weighing out 16.9980g of NaNO<sub>3</sub> (lot #7808 KODJF), transferring it into a 2 liter volumetric flask, bringing the solution to volume with NADP pure water, + stirring to mix. This was repeated once, + the resulting solution (4L) was stored in labeled PP bottles.

weights NaNO<sub>3</sub> used: 17.0059g (first 2L)  
16.9904g (second 2L)

The 500 ppb <sup>233</sup>U stock solution is from dilution 23-A - see Radiocchemistry Notebook, p150.

weight of 500 ppb <sup>233</sup>U soln used: 20.57g  
final solution wt : 2057.0g

b) Into each of 29 50-mL centrifuge tubes labeled S-III\*pHi [where i is the approximate initial pH of the solution (see below)], tare 50 g of the 5 ppb uranium solution.

Into each of 10 50-mL centrifuge tubes labeled S-III-C\*pHi\*a (or b) [where i is 2, 4, 6, 8, or 9.5, representing the approximate initial pH of the solution], tare 50 g of the 5 ppb uranium solution. These are control solutions to determine uranium loss to the container walls as a function of pH.

tube label	wt tube g	wt U soln g
1350PM S-III-XpH2.0	10.7000	46.0344
2.25	10.9071	46.0441
2.5	10.9515	46.0189
2.75	10.8011	46.0715
3.0	10.7627	46.1013
3.25	10.7759	46.0210
3.5	10.9053	46.0121
3.75	10.7637	46.0317
4.0	10.7727	46.0543
4.25	10.7368	46.0917
4.5	10.9485	46.0447
4.75	10.8563	46.1002
5.0	10.7934	46.0774



Tube label	wt tube, g	wt U soln, g
S-III-KpH 5.25	10.7730	46.0892
5.5	10.7765	46.0861
5.75	10.7274	46.0296
6.0	10.7789	46.0261
6.25	10.7954	46.0259
6.5	10.7760	46.0779
6.75	10.7812	46.0459
7.0	10.7373	46.0375
7.25	10.8560	46.1796
7.5	10.7970	46.0420
7.75	10.8564	46.0387
8.0	10.7742	46.0246
8.25	10.7722	46.1270
8.5	10.7706	46.0631
8.75	10.9059	46.1219
9.0	10.7532	46.0279
S-III-C pH 2a	10.9488	46.0251
2b	10.7813	46.1096
4a	10.7469	46.0268
4b	10.9078	46.0372
6a	10.7825	46.0638
6b	10.9089	46.0461
8a	10.8035	46.0854
8b	10.9559	46.1139
9.5a	10.9518	46.0424
9.5b	10.7740	46.1407

Transfer the remaining solution into a 125-mL PP bottle labeled S-III\*IU. Take two 5-mL samples from S-III\*IU with an Eppendorf pipet, transfer into pre-labeled [e.g., S-III-IU\*a (or b)] and pre-weighed 50-mL centrifuge tubes containing 5 g of 0.02 M HNO<sub>3</sub>. Swirl each tube and save for later analysis of uranium concentration by alpha-spectrometry.

	wt tube + acid	wt U soln
S-III-IU*a	15.9690	4.9985
1550PM b	15.9414	5.0046

## Expt S-III continued

c) 1. For each solution S-III\*pHi and S-III-C\*pHi, where  $i \leq 5.1$ :

Measure and record the initial pH (~5.1, based on EQ3 calculation). The automatic temperature compensator (ATC) probe should be immersed in water in a separate container.

	solution	pH	soln temp, °C
46.0830	S-III-KpH 2.0	5.16	15.5
	2.25	5.14	"
	2.5	5.17	"
	2.75	5.14	15.6
	3.0	5.20	"
	3.25	5.19	15.7
	3.5	5.21	"
	3.75	5.21	"
	4.0	5.22	15.8
	4.25	5.23	"
	4.5	5.22	15.9
	4.75	5.26	16.0
	5.0	5.27	"
	S-III-C pH 2ka	5.26	16.1
	kb	5.21	"
	4ka	5.21	16.2
	kb	5.25	"

The pH meter was calibrated using pH buffers 2, 4, +7 (Fisher, lot #s 910338-24, 913914-24, +921733-24).

Adjust the pH to the value of  $i$  of each solution by adding dropwise with a glass dropper HNO<sub>3</sub> solution, the concentration and approximate amount of which is given in Table S-III-1. Swirl the solutions by hand. Record the number of drops and concentration of solution added. Also record the attained pH. Cover the bottles with a kimwipe and place on the gyratory shaker set to ~120 rpm. Monitor the pH periodically, together with the centrifuge tubes prepared in step 2 below.

The acid+droppers used are the same ones listed on GC-06-89, plus the 0.01 M HNO<sub>3</sub> solution is the one prepared 6 Aug 92 by Todd Dietrich.

**Table S-III-1.** Amount of reagent grade  $\text{HNO}_3$  or  $\text{NaHCO}_3$  to add to 50 ml 0.1 m  $\text{NaNO}_3$  solution containing 5 ppb U to result in pH values given in column-1. The amount of reagent to be added was estimated using EQ3 calculations and assuming the solutions are in equilibrium with atmospheric  $\text{CO}_2(\text{g})$ .

Solution	Volume $\text{HNO}_3$ Needed, Drops (.0394 mL/drop)	Molarity of $\text{HNO}_3$ Used
2.00	15 (0.605 mL)	1.0
2.25	9 (0.34 mL)	1.0
2.50	5 (0.19 mL)	1.0
2.75	3 (0.105 mL)	1.0
3.00	15 (0.605 mL)	0.1
3.25	9 (0.34 mL)	0.1
3.50	5 (0.19 mL)	0.1
3.75	3 (0.105 mL)	0.1
4.00	2 (0.06 mL)	0.1
4.25	9 (0.34 mL)	0.01
4.50	5 (0.19 mL)	0.01
4.75	3 (0.105 mL)	0.01
5.00	2 (0.055 mL)	0.01
Solution pH	Amount of $\text{NaHCO}_3$ to be Added, Grams	
5.25	0.000011	
5.50	0.000027	
5.75	0.000042	
6.00	0.000059	
6.25	0.000084	
6.50	0.000127	
6.75	0.000201	
7.00	0.000332	
7.25	0.000566	
7.50	0.000984	

Solution pH	Amount of $\text{NaHCO}_3$ to be Added, Grams
7.75	0.001732
8.00	0.003082
8.25	0.00554
8.50	0.010102
8.75	0.018827
9.00	0.036353
[9.25]	[0.074378]
[9.50]	[0.167443]

target pH	pH attained	temp, °C	$[\text{HNO}_3]$	# drops
S-III * pH 2.0	2.00	15.5	1.0	14
2.25	2.23	"	"	8
2.5	2.55	15.6	"	4
2.75	2.83	"	"	2

target pH	pH attained	temp, °C	$[\text{HNO}_3]$	# drops
S-III * pH 3.0	3.02	15.6	0.1	13
3.25	3.25	15.7	"	8
3.5	3.54	"	"	4
3.75	3.77	"	0.1, 0.01	2, 4
4.0	4.03	15.8	0.1, 0.01	1, 3
4.25	4.26	15.9	0.01	8
4.5	4.54	"	"	4
4.75	4.76	16.0	"	2
5.0	4.95	"	"	1
S-III * pH 2Ka	2.00	16.1	0.1	4
4a	2.03	"	"	13
4Ka	4.06	16.2	0.1, 0.01	1, 2
1028 PM * 6	4.07	"	"	"

2. For each solution S-I\* $\text{pHi}$  and S-I-C\* $\text{pHi}$ , where  $i > 5.1$ :

Measure and record the initial pH (~5.1, based on EQ3 calculation).

1030 PM  
(The electrode/meter was  
recalibrated as before.)

solution	pH	temp, °C	solution	pH	temp, °C
S-III * pH 5.25	5.23	16.4	S-III-C * pH 6a	5.25	16.9
5.5	5.24	"	b	"	"
5.75	5.19	"	8a	5.22	"
6.0	5.20	16.5	b	5.24	17.0
6.25	5.23	"	9.5a	5.25	"
6.5	5.19	"	1205 PM b	5.24	17.1
6.75	5.21	"			
7.0	5.22	16.6			
7.25	5.22	"			
7.5	5.20	"			
7.75	5.20	"			
8.0	5.16	16.7			
8.25	5.20	"			
8.5	5.23	"			
8.75	5.22	16.8			
9.0	5.22	"			