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Geochemistry Research Laboratory Notebook:
Ion Exchange and Sorption Experiments
(03/21/1992 through 12/10/1996)

Geochemistry
Research Lab
Notebook

VOL. GC-06

GC-06

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Research Lab Notebook
VOL. GC-06

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DM Paula Muller student scientist
TD - Todd B. Dietrich, student
James D. Pohl

3/19/92 1000hrs JP

Na^+-H^+ ION EXCHANGE EXPERIMENT Na/H-III

WRITTEN BY: R. T. PABALAN DATE WRITTEN: October 25, 1991
REVISION NO.: Rev. 2 of Na/H-I LAST REVISED: March 16, 1992

OBJECTIVE:

Determine the importance of the ion exchange reaction:

$$H^+ + Na\text{-}Z \rightleftharpoons Na^+ + H\text{-}Z\ .$$

Ion exchange reactions between H^+ and Na^+ 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^+ 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_2(g)

PROCEDURE:

1030hrs 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_2(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_3 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_2O Mass to Use	Measured pH of H_2O	HNO_3 to add to ultrapure water					pH meas'd 24 hrs. after HNO3 addition
			Conc. (m)	Approx. Vol.(ml)	Approx. #Drops	#Drops Added	Approx. Vol HNO_3 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_3 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.

Naf 3/19/92 RJP

03/20/92 1350hrs JP

2. For each mixture given in column 1 of Table 2, pipet 50 ml solution (IS*ph*i*) 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 mixs 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*pH*i*).

PREPARATION:

1. Preclean the glassware and PP bottles to be used by soaking in ~10% HNO_3 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_3 solution. Store in precleaned and appropriately labeled PP bottles.

3. Check calibration of glass droppers, if needed.

03/19/92
1300hrs JP

*Note: Instead of using glass droppers to add HNO_3, microliter pipets and tips were used to add HNO_3 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

TD

3/24/92 1620 hrs

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

3/20/92 1440 hrs JP

3/20/92 1330 hrs JP

3/24/92 1555 hrs JP

3/26/92 0900 hrs JP

TABLE 3.

Soln. Label	Wt. Zeol. Used (gm)	Measured pH of IS*pHi	Measured Final pH/°C	Measured Final Na^+ ppm	Δm_{H+}	Δm_{Na+}
Na/H*III*1a	0.5000	2.00	2.52/21.4°C	154	0.00698	0.0067
Na/H*III*1b	0.5001		2.52/21.7°C	152	0.00698	0.0066
Na/H*III*2a	0.2501		2.36/21.6°C	116	0.00563	0.0050
Na/H*III*2b	0.2500		2.36/21.5°C	117	0.00563	0.0051
Na/H*III*3a	0.2002	2.50	3.08/21.8°C	54.1	0.00233	0.00235
Na/H*III*3b	0.2000		3.08/21.7°C	53.8	0.00233	0.00234
Na/H*III*4a	0.1000		2.91/21.7°C	42.9	0.00193	0.00187
Na/H*III*4b	0.1002		2.90/21.9°C	42.5	0.00190	0.00185
Na/H*III*5a	0.1000	3.01	3.69/22.0°C	20.0	0.000773	0.00087
Na/H*III*5b	0.1001		3.69/21.9°C	19.9	0.000773	0.00087
Na/H*III*6a	0.0502		3.49/21.8°C	16.4	0.0006536	0.000713
Na/H*III*6b	0.0501		3.48/22.0°C	16.8	0.0006461	0.000731
Na/H*III*7a	0.1002	3.51	4.69/21.7°C	7.87	0.0002886	0.0003423
Na/H*III*7b	0.1002		4.68/21.9°C	7.86	0.0002881	0.0003419
Na/H*III*8a	0.0502		4.33/21.9°C	7.37	0.0002622	0.0003206
Na/H*III*8b	0.0503		4.33/22.1°C	7.35	0.0002622	0.0003197
Na/H*III*9a	0.1000	4.00	5.85/21.3°C	2.98	0.0000986	0.0001296
Na/H*III*9b	0.1000		5.86/21.2°C	2.96	0.0000986	0.0001288
Na/H*III*10a	0.0502		5.42/21.3°C	2.80	0.0000962	0.0001218
Na/H*III*10b	0.0503		5.38/21.0°C	2.83	0.0000958	0.0001231
Na/H*III*11a	0.0502	4.97	6.40/21.3°C	1.45	0.0000103	0.0000631
Na/H*III*11b	0.0501		6.49/21.4°C	3.92	0.0000104	0.0001705

3/24/92 1500hrs JP

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

4/23/92 0900hrs JP

Concentration of Ca^{++} and Na^+ in 0.05N $NaNO_3$-$Ca(NO_3)_2$ reference solutions by AA.

Objective - determine the Ca^{++} and Na^+ content of the 0.05N $NaNO_3$-$Ca(NO_3)_2$ reference solutions used in isotherm experiments.

Method - Atomic Absorption analysis

Equipment -
1) Model 3100 AA spectrometer (SN 146109)
2) Na hollow cathode lamp (SN 70625)
3) Ca 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 Ca^{++} and 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 NO_3 in standards was adjusted with HNO_3 to reflect the NO_3 concentration of samples.

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

Results-

Ca^{++}

$X_{Ca,i}$	Expected ppm	Dilution Factor	Measured value (ppm)	Corrected 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

Na^{+}

$X_{Na,i}$	Expected ppm	Dilution factor	Measured value ppm	Corrected value (ppm)
.9	103.4	1/20	~~4.4 ± .0471~~ 4/23/92 5.2 ± .0238	104.0
.8	919.6	1/100	~~9.1 ± .0655~~ 4/23/92 9.4 ± .0471	940.0
.7	804.6	1/100	8.1 ± .0655	810.0
.6	689.7	1/100	6.7 ± .0592	670.0
.5	574.7	1/100	5.6 ± .0610	560.0
.4	459.8	1/100	4.5 ± .0347	450.0
.3	344.8	1/100	3.4 ± .0157	340.0
.2	229.9	1/100	2.2 ± .0102	220.0
.1	114.9	1/20	5.7 ± .0258	114.0
.075	86.2	1/20	4.2 ± .0336	84.0
.05	57.5	1/20	2.9 ± .0262	58.0
.025	28.7	1/20	1.5 ± .0312	30.0

4/24/92 0915 hrs JP

Measure concentration of Ca^{++} and Na^{+} in 0.05N $NaNO_3 - CaCl_2$ reference solutions by AA

Objective: determine the concentration of Ca^{++} and Na^{+} in 0.05N $NaNO_3 - CaCl_2$ 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 Ca^{++} 4, 5, and 10 ppm standards were prepared.

For 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

$X_{Ca,i}$	Dilution Factor Ca^{++}	Dilution Factor Na^{+}
0.1	1/50	JP ~~1/100~~ ~~1/200~~ 4/24/92
0.2	1/50	JP ~~1/100~~ ~~1/200~~ 4/24/92
0.3	1/50	JP ~~1/100~~ ~~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

Ca^{++}

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

Na^{+}

$X_{Ca,i}$	Expected ppm	Measured ppm	Converted Value ppm
0.1	1035	5.1 ± .0232	1020
0.2	920	4.6 ± .0120	920
0.3	805	4.0 ± .0171	800
0.4	690	6.8 ± .1046	680
0.5	575	5.8 ± .0614	580
0.6	460	4.6 ± .0103	460
0.7	345	3.4 ± .0298	340
0.8	230	2.3 ± .0160	230
0.9	115	2.3 ± .0156	115
1.0	0	0 ± .0016	0

4/27/92 1330hrs JP

Measure concentration of Ca^{++} and Na^{+} in 0.05N $NaNO_3$-$CaCl_2$ + clinoptilolite samples by AA

Objective: determine concentrations of Ca^{++} and Na^{+} in 0.05N $NaNO_3$-$CaCl_2$ + 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)
2) 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 Ca^{++} 0.5, 5, + 10 ppm standards were prepared.

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

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

Sample No	$X_{Ca,i}$ mmol	Dilution Factor Ca^{++}	Dilution Factor Na^{+}
1	0.1	4/27/92 JP ~~1/500~~ 1/100	JP 4/27/92 ~~1/500~~ 1/500
2	0.1	4/27/92 JP ~~1/500~~ 1/100	JP 4/27/92 ~~1/500~~ 1/500
3	0.2	4/27/92 JP ~~1/500~~ 1/100	JP 4/27/92 ~~1/500~~ 1/500
4	0.2	4/27/92 JP ~~1/500~~ 1/100	JP 4/27/92 ~~1/400~~ 1/500
5	0.2	4/27/92 JP ~~1/50~~ 1/100	JP 4/27/92 ~~1/400~~ 1/500
6	0.3	1/100	JP 4/27/92 ~~1/400~~ 1/500
7	0.4	1/100	JP 4/27/92 ~~1/400~~ 1/500
8	0.4	1/100	JP 4/27/92 ~~1/400~~ 1/500
9	0.5	1/100	JP 4/27/92 ~~1/400~~ 1/500
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, all samples measured following operating instructions outlined in "Running the 3100".

5) Results

Ca^{++}

Sample No	Expected ppm	Measured ppm	Converted ppm value
1	19.8	6.2 ± ~~.0081~~ .0014 JP 4/27/92	20.0
2	33.0	6.3 ± ~~.0023~~ .0015 JP 4/27/92	30.0
3	50.7 4/27/92 JP	~~6.8 ± .0008~~ 0.5 ± .0015	50.0
4	73.4 4/27/92 JP	~~1.0 ± .0018~~ 6.8 ± .0008	80.0
5	89.8 4/27/92 JP	~~1.4 ± .0088~~ 1.0 ± .0018	100.0
6	136.0 4/27/92 JP	~~2.0 ± .0115~~ 1.4 ± .0088	140.0
7	182.0 4/27/92 JP	~~2.5 ± .0079~~ 2.0 ± .0115	200.0
8	216.0 4/27/92 JP	~~2.8 ± .0055~~ 2.5 ± .0079	250.0
9	263.0 4/27/92 JP	~~3.7 ± .0061~~ 2.8 ± .0055	280.0
10	343.0 4/27/92 JP	~~4.~~ 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	4/27/92 JP ~~714~~ 714.0	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^{+}

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 0930hrs JP

Remeasured Ca^{++} concentrations of 0.05N $NaNO_3$-$CaCl_2$ reference solutions using AA.

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

Results:

Ca^{++}

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

4/30/92 0900 TD

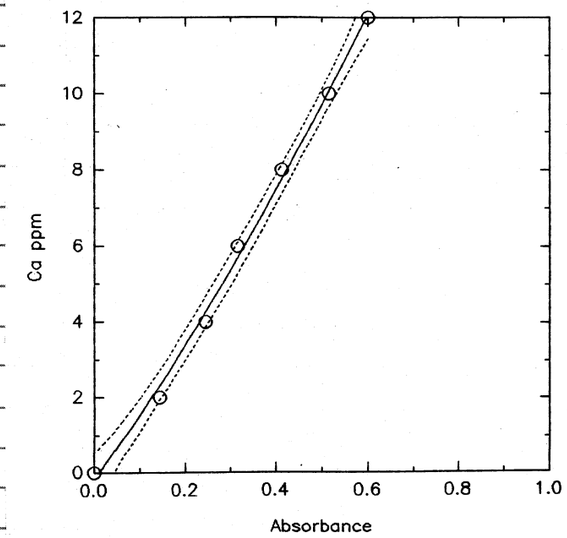
Remeasured Ca^{2+} concentrations of 0.05N $NaNO_3$-$CaCl_2$ reference solutions using AA. Each sample was run twice

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

RESULTS OF Ca^{2+} ANALYSIS

$X_{Ca,i}$	EXPECTED ppm	measured ppm	corrected ppm
0.1	100	1.79 ± .0055	89.5
0.2	200	3.61 ± .0203	180.5
0.3	301	5.56 ± .0144	278
0.4	401	3.79 ± .0098	379
0.5	501	4.69 ± .0047	469
0.6	601	5.87 ± .0090	587
0.7	701	7.06 ± .0250	706
0.8	802	8.21 ± .0371	821
0.9	902	10.71 ± .0327	1071
1.0	1002	9.42 ± .0151	942
0.1	100	1.74 ± .0051	87
0.2	200	3.55 ± .0016	177.5
0.3	301	5.48 ± .0022	274
0.4	401	3.73 ± .0084	373
0.5	501	4.65 ± .0318	465
0.6	601	5.78 ± .0032	578
0.7	701	7.04 ± .0132	704
0.8	802	8.24 ± .0394	824
0.9	902	10.75 ± .0350	1075
1.0	1002	9.36 ± .0160	936

1200 TD AA analysis of Ca^{2+} ($NaNO_3$ - $CaCl_2$, .05N soln)
Prepared 2, 6, 8, 12 ppm Ca^{2+} standards by diluting the appropriate amount of 1000 ppm Standard to 500 ml in a volumetric flask using Ultrapure water. ~0.1% 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.



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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
		0
		0
		0
		0.99832

$E_{Ca,i}$	Abs.(1)	Abs(2)	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	[illegible]	10.17	1017

7/10/92 gp

Measure amount of H_2O in analcime

Objective: determine amount of H_2O in analcime from ASE experiment (see GC-03/237)

Method: gravimetric analysis after drying & heating analcime to drive off H_2O.

Equipment: 1) air tight quartz crucibles - 10 ml
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 ~~AES4~~ 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 0800 hrs 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°C.

5) Weigh 2 quartz crucibles, place ~1.0g of ASH* 450/635 *UC*WA *ASE4*REC in each crucible + record weight.

Weight of qtz crucible 1	=	12.3877 g
+ ASH*...*REC	=	13.3876 g
Wt of ASH*...*REC absorbed	=	.9999 g

Weight of qtz crucible	=	12.5101 g
+ ASH*...*REC	=	13.5102 g
Wt of ASH*...*REC	=	1.0001 g

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

Weight of crucible 1	=	13.3870 g
Previous wt	=	13.3876 g
Wt absorbed H_2O	=	.0006 g

Weight of crucible 2	=	13.5095 g
Previous wt	=	13.5102 g
Wt absorbed H_2O	=	.0007 g

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

8.) Reweigh to get amount of structural water.

Wt of qtz crucible 1	=	~~13.3077~~ 13.3059 g
Previous wt	=	13.3870 g
Wt structural H_2O	=	~~0.0793~~ 0.0811 g

Wt of qtz crucible 2	=	~~13.4302~~ 13.4285 g
Previous wt		13.5095 g
Wt structural H_2O	=	~~0.0793~~ 0.081 g

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 μm.

5 PM 8/14/92

7) A small portion (~ 10 mL) of the < 2μm-containing solution was vacuum-filtered through a 0.45 μm 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 °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 °C for 30 minutes.

"b" was heated in the oven at 550 °C for 30 minutes.
"c" was placed in a dessicator containing ~ 1/2 pint ethylene glycol, + the dessicator put in an oven at 60°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 μm 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~~ clay PM 8/17/92 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 50-mL centrifuge tubes. They were centrifuged at 1300 rpm (checked by tachometer) for two and a quarter minutes. The upper 4/5 of the supernatant was poured off into a large beaker. 8/19/92

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

0957 PM The large beaker was labeled "< 2 μm 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 μm solution was decanted into each of 2 centrifuge tubes, + the tubes were centrifuged for 15 minutes at 3700 rpm. The supernatant was poured off and the accumulated mineral was transfered 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 μm fraction, to cut down on the amount of mineral volume.

A: Removal of Carbonates

Equipment: graduated 50-mL centrifuge tubes / rack
hotplate
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

A1 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
00 PM 8/19/92

03:15 PM 41.50 grams of NaOAc was weighed out and dissolved in an beaker using ultrapure water.

weight used: 41.05 g

The dissolved NaOAc was transfered to the volumetric flask, and 13.5 mLs 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 $NaHCO_3$ solution
8/4/94

8.400 g of $NaHCO_3$ ~~was~~ is weighed out + dissolved in a 100 mL volumetric flask to produce 100 mL of 1M $NaHCO_3$ solution.

weight used: 8.3995 g $NaHCO_3$, lot # 897186A

C3 Preparation of 0.3M sodium citrate solution

88 grams of $Na_3C_6H_5O_7 \cdot 2H_2O$ 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 μm fraction. To try to remove some of this, the <2 μm 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.

~50 mL of the suspension was poured into each of 4 50 mL centrifuge tubes. The tubes were centrifuged at 1700 rpm (checked by tachometer) for 2½ minutes. The supernatant was poured into a large beaker, + the remainder discarded.

The process was repeated until ~ one liter of supernatant (< 2 μm clay particles) was collected.

8/4/94

The < 2 μm 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 μm 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 °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 ~ 70 °C until a soil-to-water ratio of ~ 1:2 was reached. (The time needed will depend on the amount of water used to transfer the clay).

9/2/92 PM 1320 The suspension was evaporated until the total volume of the soil + water was ~ 40 mL. 10 mL of 50% H_2O_2 was added, 5 mL at a time, with 10 min of stirring allowed between additions. The solution was heated gently (65 °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 ~2.5 g 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 $NaHCO_3$ 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. 0.5 g $Na_2S_2O_4$ 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 NaCl solution (GC-06-28) was added to each tube. The solution was stirred, warmed (~50°C in water bath) and centrifuged for 2 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 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: 41.09 g 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: 88.00 g, lot # 905257A

9/16/92 PM Removal of Carbonates from more <2 μm Montmorillonite

1045 PM 1.15 g of the air-dried <2 μm montmorillonite was weighed into each of 2 50 mL centrifuge tubes.

Nano pure water was poured into a beaker and heated to ~~70~~ 75 PM 9/16/92 °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.

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

1350PM 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.

0834PM 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 ~65 °C with stirring for about five minutes.

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

0902PM 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 ~65°C for the last half hour.

1206PM 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

1332PM 10 mLs 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°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. PM 19 9/18/92

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

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

1422PM The clay was washed once with sodium citrate solution. Then another 10 mLs of sodium citrate + 1 mL of $NaHCO_3$ solution was added to each tube, the tubes heated back up to 75°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~~ PM 9/18/92 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 3 M NaCl for Montmorillonite Ion Exchange

To make certain that all exchangeable sites on the Montmorillonite clay are occupied by Na^+, the clay will be soaked in 3 M 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 liter volumetric flask. The solution was brought to volume with ultrapure water, stirred to mix, + poured into a 1L PP bottle. The bottle was appropriately labeled.

PM 9/21/92

wt used: 175.30 g NaCl, lot # 914193

0925 PM Soaking of Montmorillonite Clay in 3 M NaCl

The $Na_2S_2O_4$-treated sodium citrate solution-washed clay had enough 3M NaCl solution added to allow the clay to be picked up by maxipipet. 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 3 M NaCl solution. The clay will be soaked for four days, with the 3 M 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.

1358 PM 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 ~ 1600 rpm for about 5 minutes. The supernatant was poured off + the rinsing (addition of water, swirling, + centrifugation) repeated 6 times.

1653 PM The supernatant was poured into a beaker and 2 drops of 0.1 M $AgNO_3$ solution (lot # 910644-24) was added. A white cloudy substance formed (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 ~3 minutes to make certain the particles would disperse for thorough rinsing.

The suspension was poured into centrifuge tubes + centrifuged at ~ 1700 rpm for 5 min, but no separation of the phases was seen.

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

0904 PM 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 ~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 $AgNO_3$ solution for formation of AgCl. No reaction was seen, so the excess 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 $AgNO_3$ 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 ~~KI~~ MK1 (renamed 10/26/92) PM

Objective: Determine the time needed for sorption equilibrium between ^{233}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 - ie, pH ~ 6.5. The ionic strength of the solutions will be kept constant at 0.1M $NaNO_3$. Initial pH of the solutions will be set 6.0 and 7.0. Initial pH of the 50 ppb ^{233}U stock solution will be adjusted by addition of $NaHCO_3$. The amount of $NaHCO_3$ to be used is determined by EQ3 calculations.

MK1 PM 8/4/94

Preparation of 0.1M $NaNO_3$ for ~~KI~~ experiments

0932 PM 4 liters of 0.1M $NaNO_3$ solution was made up two liters at a time by weighing out 16.9980 g $NaNO_3$ (lot # 7808 KDJE), transferring it to a 2L volumetric flask, and bringing the solution to volume with NANOpure (> 17 MΩ resistivity) water. The solution was stirred to mix + stored in ~~an~~ two PM 9/30/92 appropriately labeled Polypropylene (PP) bottles. The other 2L was made up in the same manner.

wts used: 16.9953 g $NaNO_3$ (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 ~0.5 g cleaned, <2 micron sample when dry.

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

10/16/92 PM After soaking since Monday in 3M NaCl solution, the clay will be transferred into a beaker, diluted with ~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 rewashed, 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 $AgNO_3$ 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 ($AgNO_3$ droptest - 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 $NaNO_3$; equilibrium with atm 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}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 $NaNO_3$. Initial pH of the solutions will be at 6.0 and 7.0. Initial pH of the 50 ppb ^{233}U stock solution will be adjusted by addition of $NaHCO_3$. The amount of $NaHCO_3$ to be used is determined by EQ3 calculations.

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

- initial ΣU = 50 ppb
- activity of 50 ppb U solution = 0.480 nCi/g
- initial ΣNa = 0.1 + x where 0.1 is from $NaNO_3$ and x is from $NaHCO_3$
- 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 $CO_2(g)$, $pCO_2 = 10^{-3.5}$ 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}U stock solution (in 0.1 M $NaNO_3$ matrix; prepared previously from commercial 50 ppm ^{233}U spike) to a total of 1600 g by carefully taring 0.1 M $NaNO_3$ solution into the plastic bottle on a Mettler 4600 balance.

see GC-06-39 PM 12/28/92

0709 PM Weight of ~~50~~ 500 ppb ^{233}U solution used: 160.15 g (Standard 22A; see Radiochemistry Notebook p111 PM 12/28/92)

JM 10/26/92

Final weight of 50 ppb ^{233}U solution: 1600.2 g

MK1-1-B: Transfer three 500 g aliquots of the ~~100~~ 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.

JM 10/26/92

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.

Reweigh each tube after addition of the sample. Add to each sample using an Eppendorf micropipet 250 µL of 1.0 M HNO_3 solution for later analysis with alpha-spectrometry.

0758PM weight of tube MK1-1*1U*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.

0815PM 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 $NaHCO_3$ to each 500 mL ^{233}U solution. Cover the bottle with a porous material and keep the solution agitated on a gyratory shaker to equilibrate it with atmospheric $CO_2(g)$.

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.

0845PM Weight of $NaHCO_3$ (lot #886728) used:
MK1-1* A 0.0040g
*B 0.0037g
*C 0.0041g

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

10/28/92PM 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 soln
10/28	1403	6.44	5.99	6.18	23.5°C
10/30	1014 11/2/92 PM	6.28	5.96	6.11	21.5
11/2	~~1405~~ 1505	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 JP

Prepared additional reagents for spectrophotometric analysis of SiO_2 and Al in accordance with TOPS 13 and 14.

Reducing agent -
Dissolved 500 mg 1-amino-2-napthol-4-sulfonic acid (lot 904622) and 1g Na_2SO_3 (lot 915208) in 50 ml H_2O.
Dissolved 30g $NaHSO_3$ in 150 ml H_2O.
Mix these solutions & filtered into a PP bottle. Labelled bottle "Reducing agent".

Oxalic Acid Solution -
Dissolve 7.5g oxalic acid (lot 905504) in 100ml H_2O. Transfer to PP bottle and labelled "Oxalic Acid Solution".

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

Stock Dye Solution
Dissolve 150 mg of Eriochrome cyanine R (lot K5501, CH-9470 Buchs) in 50ml H_2O
Dilute 5ml glacial acetic acid (lot 893419) to 10ml with H_2O in a 10ml volumetric flask
Adjust pH of Eriochrome solution to about 2.9 with acetic acid solution. Transfer solution to a 100ml volumetric flask & dilute to 100 ml. Transfer to a PP bottle and labelled "Stock Dye Solution".

11/2/92 PM 0900 Separation of the <2micron Montmorillnite
The rest of the previously crushed and milled montmorillnite (Na-form "Otay", API # 24 - see GC-06-23) was treated to separate the <2 micron fraction from the rest. PM 11/2/92

5 grams of the ~90 grams of milled montmorillnite was taken at a time. The 5 grams was placed in a 600 mL beaker. 500 mL of 25g/L sodium metaphosphate solution (lot # 720373) 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. PM 11/2/92

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 MΩ 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 bottom a hotplate. 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 40.85 g

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_2O_2 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_2O_2 solution was added. The clay/H_2O_2 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_2O_2 was added to the clay (out of the water bath) and the stirring + reheating was repeated.

1132PM 10 mL of the H_2O_2 solution was added to the clay. The beaker was loosely covered with a filled 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 into the NaOAc wash between centrifugations.

The centrifuge tubes were capped after the last wash.

11/8/92 PM 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.

10mL of 0.3M sodium citrate solution and 1mL of 1M $NaHCO_3$ solution (GC-06-33 29) was added to each tube; and the tubes heated in the water bath.

0.5g $Na_2S_2O_4$ (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.

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

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

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

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

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

75°C in the water bath. 0.3g $Na_2S_2O_4$ (lot #912722) was added to each tube (quickly) + the contents stirred constantly for the first minute + then occasionally for the next fourteen.

5mL 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 Na^+

1145PM The clay was mixed with a minimum of 3M NaCl solution to allow the clay to be picked up by maxipipet. The clay was injected into dialysis tubing (knotted at both ends). The tubing was put in a beaker + covered with 3M NaCl solution.

11/13/92PM Expt. MK1-1 continued

~~0902~~ 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 250µL of 1.0 M HNO_3 solution for later analysis with alpha-spectrometry.

	wt tube	wt dig
MK1-1*A*I1	11.0909	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

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
MK1-1*A .4996g
MK1-1*B .5001
time 1117
room temp 67.8°F
gyratory shaker set at ~125 rpm

MK1-1-E: At Δtime 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^2 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 disposible tip.

Reweigh each centrifuge tube after addition of the sample. Add to each sample using an Eppendorf micropipet 250µL of 1.0 M HNO_3 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 Δtime (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.

	date	solution	pH	soln temp.	time
sample 1	11/13	MK1-1*A	6.27	20.5	1233 JM
	11/13	*B	6.04	20.5	1239
	11/13	*C	6.14	20.6	1246
sample 2	11/13	MK1-1*A	6.26	20.8	1326 JM
	11/13	*B	6.07	20.9	1332
	11/13	*C	6.15	20.9	1337
3	11/13	MK1-1*A	6.27	21.6	1535 JM
	11/13	*B	6.05	21.6	1542
	11/13	*C	6.13	21.6	1548
4	11/13	MK1-1*A	6.20	20.2	2243 JM
	11/13	*B	5.98	20.2	2249
	11/13	*C	6.02	20.2	2256
5	11/14	MK1-1*A	6.22	19.2	1111 JM
	11/14	*B	6.03	19.3	1117
	11/14	*C	6.07	19.3	1123

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

	Sample	wt tube	wt aliquot	time
JM	MK1-1*A*1a	10.3338	5.2951	1219
	B*1a	11.0992	5.1312	1223
	C*1a	11.0949	5.0731	1226
JM	MK1-1*A*2a	11.0072	4.9112	JM 11/18/92 1314
	B*2a	10.7578	4.9471	1317
	C*2a	10.6382	4.7732	1320
JM	MK1-1*A*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
JM	MK1-1*A*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
MK1-1XAX5a	10.7205	4.9235	1100 JM
BX5a	10.7115	5.0852	1103
CX5a	10.7042	5.0299	1105
MK1-1XAX6a	10.7219	4.8838	1658 JM
AX6b	10.8743	5.2538	1701
BX6a	10.7266	4.9020	1703
BX6b	10.7407	5.2542	1705
CX6a	10.3364	5.0356	1708
CX6b	10.7276	5.0388	1710
MK1-1XAX7a	10.7423	5.1548	2133 JM
XBX7a	10.7000	4.6868	2136
XCX7a	10.7636	5.0601	2139
MK1-1XAX8a	10.7015	5.0693	0848
XBX8a	10.8279	4.9524	0851
XCX8a	10.7236	5.0353	0854
MK1-1XAX9a	10.7309	4.9755	1433 JM
AX9b	10.7306	5.0664	1435
BX9a	10.7597	4.9370	1438
BX9b	10.8747	5.1270	1441
CX9a	10.7664	5.0353	1443
CX9b	10.8202	5.0395	1446
MK1-1XAX10a	10.7202	4.9983	~~1348~~ 1248 JM
BX10a	10.8186	5.0382	~~1350~~ 1250 11/14/92
CX10a	10.7600	5.0404	1254
MK1-1XAX11a	10.7371	4.9243	1112
BX11a	10.7245	5.0822	1115
CX11a	10.9372	5.0468	1117

11/18/92
1130 JM

MK1-1-F: After the last samples have been taken, take 2 5-mL aliquots of solution MK1-1*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 µL of 1.0 M HNO_3 for later analysis using alpha-spectrometry. Label the bottles MK1-1*FU*a or *b.

11/18/92 PM

Sample	tube wt (g)	aliquot wt (g)	time
MK1-1XFUKa	10.7613	5.0285	1141
Xb	10.7016	5.0593	1143

90 JM 11/18/92

11/23/92 PM Prep. of more 0.1 M $NaNO_3$ solution

0945 PM 4 Liters of 0.1 M $NaNO_3$ was prepared by twice weighing out 17.00 g $NaNO_3$ (lot # 7808 KDJE) transfering the 17.00 g to a 2 L volumetric flask and bringing the solution to volume with ultrapure (> 17 MΩ resistivity) water. The solutions were stirred to mix + stored in 1L polypropylene bottles.
JM 11/23/92

1401 PM Prep of ~~3~~ Na-form 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 maxipipetter. 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 watchglass.

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

a stirbar 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 $AgNO_3$ added to a portion of the rinse did not result in the formation of a whitish precipitate. ($AgNO_3$ lot # 910644-24). Formation of precipitate shows there's still enough free Na^+ in solution to form $NaNO_3$ when $AgNO_3$ is added.

11/53 PM The 3M NaCl solution soaking the clay was replaced with fresh solution.

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

11/24/92 1011PM 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 3500rpm, about a third of the clay is left in suspension + is lost between washings.

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

11/29/92 1730PM 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 $AgNO_3$ solution.

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

12/02/92 080PM The 3M NaCl solution was replaced again.

0851PM 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 $NaNO_3$; equilibrium with atm 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}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 $NaNO_3$. Initial pH of the solutions will be at 6.0 and 7.0. Initial pH of the 50 ppb ^{233}U stock solution will be adjusted by addition of $NaHCO_3$. The amount of $NaHCO_3$ to be used is determined by EQ3 calculations.

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

- initial ΣU = 50 ppb
- activity of 50 ppb U solution = 0.480 nCi/g
- initial ΣNa = 0.1 + x where 0.1 is from $NaNO_3$ and x is from $NaHCO_3$
- 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 $CO_2(g)$, $pCO_2 = 10^{-3.5}$ 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}U stock solution (in 0.1 M $NaNO_3$ matrix; prepared previously from commercial 50 ppm ^{233}U spike) to a total of 1600 g by carefully taring 0.1 M $NaNO_3$ solution into the plastic bottle on a Mettler 4600 balance.

1340PM weight of 500ppb ^{233}U solution used: 159.88g
(Standard 23A: see Radiochemistry Notebook, p. 150 PM 12/28/92)
weight of 50 ppb ^{233}U solution prepared: 1600.2g

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.

1400PM weight of aliquot in bottle MK1A-1*A : 500.20
*B : 499.96
*C : 500.70
*1U : [illegible]

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.

Reweigh each tube after addition of the sample. Add to each sample using an Eppendorf micropipet 250 µL of 1.0 M HNO_3 solution for later analysis with alpha-spectrometry.

1423PM weight of tube MK1A-1*1U*a : 10.8302
*b : 10.7283
weight of aliquot in MK1A-1*1U*a : 5.0302
*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 MK1A-1*A : 4.29 @ 21.1°C
*B : 4.32
*C : 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 $NaHCO_3$ to each 500 mL ^{233}U solution. Cover the bottle with a porous material and keep the solution agitated on a gyratory shaker to equilibrate it with atmospheric CO_2(g).

weight of $NaHCO_3$ (lot#886728) added:
1450PM MK1A-1*A : 0.0035
*B 0.0036
*C 0.0038

1505PM The bottles were put on the gyratory shaker at ~125 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.

date	time	pH MK1A-1*A		*B	*C	temp soln, °C
12/4/92	0828	6.89		6.74	6.96	20.4
12/7/92	0822	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 12/14/92	6.70	6.91	17.7
12/16/92	0902	~~6.90~~	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 PM The ~5g portions of Na-exchanged 'Chelo' clay washed 11/25, 11/26, 11/29, + 12/02 (see GC-OB-53, 54, 55) were put in plastic vials labeled "Chelo Montmorillonite SA2-1 date" + the clays sent to Texas Tech for chemical analysis.

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

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

12/14/92 0804 PM The Na-montmorillonite was rinsed until its wash water formed no precipitate when 0.1 N $AgNO_3$ was added. (0.1 N $AgNO_3$ lot #910644-24) PH 12/14/92 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 0535PM The MK1A solutions' pHs have equilibrated, ~~sot~~ and the clay is freeze-dried, so Expt MK1A 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 250µL of 1.0 M HNO_3 solution for later analysis with alpha-spectrometry.

PM 1120

weight of

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	:	5.0340
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	:	.5012 g
room temp	:	64.8°F @ 1138
rpm	:	125

MK1-1-E: At Δtime 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^2 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 disposible tip.

Reweigh each centrifuge tube after addition of the sample. Add to each sample using an Eppendorf micropipet 250µL of 1.0 M HNO_3 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* <u>*every third*</u> *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 Δtime (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
12/18	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
12/19	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
12/20	6	MK1A-1*A	6.95	18.1	0938
	6	*B	6.92	18.1	0944
	6	*C	6.98	18.2	0952
12/21	7	MK1A-1*A	6.96	~~18.~~ 16.2	0833
	7	*B	6.90	16.2	0840
	7	*C	6.95	16.3	0846

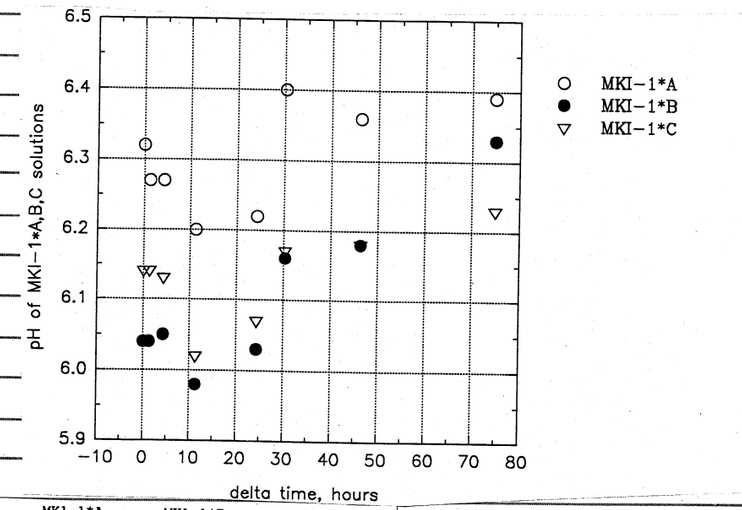
date	sample	wt tube g	wt aliquot g	time	Δtime minutes
12/18/92	MK1A-1*AK1a	10.8705	4.9424	1332	114
	B*K1a	10.9310	4.9799		
	C*K1a	10.6463	5.0534		
12/18/92	MK1A-1*AK2a	10.7430	5.0607	1528	230
	B*K2a	10.7299	5.0984		
	C*K2a	10.7349	5.0462		
12/18/92	MK1A-1*AK3a	10.7283	4.9374	2037	539
	*K3b	10.7440	4.9003		
	B*K3a	10.7922	4.8331		
	*K3b	10.8743	5.0462		
	C*K3a	10.7403	5.0556		
	*K3b	10.7404	5.0250		
12/19/92	MK1A-1*AK4a	10.7600	4.9479	0839	1261
	B*K4a	10.6516	4.9654		
	C*K4a	10.6461	5.0515		
	A*K5a	10.8713	4.8972	1632	1734
	B*K5a	10.7193	4.9716		
	C*K5a	10.8470	5.0343		
12/20/92	MK1A-1*AK6a	10.7422	4.8639	0918	2740
	A*K6b	10.9263	4.9893		
	B*K6a	10.7588	4.8116		
	B*K6b	10.7398	5.0262		
	C*K6a	10.7336	5.0441		
	C*K6b	10.7381	5.0530		
12/21/92	MK1A-1*AK7a	10.7263	4.8859	0814	4116
	B*K7a	10.6466	4.9390		
	C*K7a	10.7286	5.0606		

1028PM The last samples were taken, 2 from MK1A-1* 1V by Oxford pipet:

	wt tube, g	wt aliquot g	time
MK1A-1*FU*a	10.8720	5.0519	1032
*b	10.7254	5.0541	

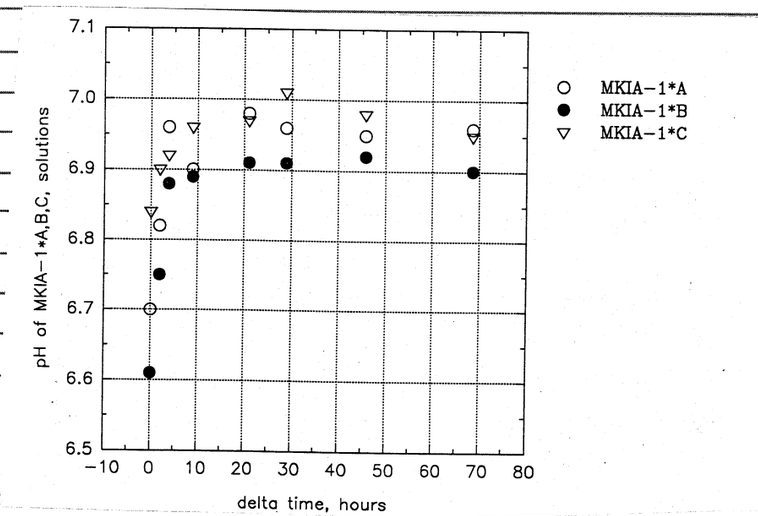
12/21/92 1045PM The plots of Δtime vs pH for Expts MK1-1 + MKA-1 are

shown (reduced from SIGMAPLOT print outs) for comparison.



MK1-1

	sample # 1	MK1-1*A 2	MK1-1*B 3	MK1-1*C 4	time, min 5	time, hours 6
1	0	6.32	6.04	6.14	0	0
2	1	6.27	6.04	6.14	75	1.3
3	3	6.27	6.05	6.13	255	4.3
4	4	6.2	5.98	6.02	675	11.3
5	5	6.22	6.03	6.07	1455	24.3
6	6	6.4	6.16	6.17	1815	30.3
7	8	6.36	6.18	6.18	2775	46.3
8	10	6.39	6.33	6.23	4495	74.9



MKIA-1

MKIAPLT.SP5: Mon, 21-Dec-92

	delta hours 1	MKIA*A 2	MKIA*B 3	MKIA*C 4
1	0	6.7	6.61	6.84
2	1.9	6.82	6.75	6.9
3	3.8	6.96	6.88	6.92
4	9	6.9	6.89	6.96
5	21	6.98	6.91	6.97
6	28.9	6.96	6.91	7.01
7	45.7	6.95	6.92	6.98

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 'Cheto' 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 1000PM Prep. of more Na-'Cheto' Montmorillonite

Another 50g of the 'Cheto' clay from the Source Clay Repository was weighed out, ultrapure 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.

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

1050PM 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 0909PM Calibration of glass droppers for Upcoming S1 Sorption Experiment

Glass droppers were labeled "1.0", ".1" and ".02". 1.0 M HNO_3 solution (5 Aug 92, GC-07-149), 0.1 M HNO_3 solution (2 Dec 92, GC-08-23) + 0.02 M HNO_3 solution (6 Aug 92, GC-07) was added dropwise to ~~10~~ 5 mL volumetric flasks + the # drops noted. 5PM 12/28/92

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

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

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

0945PM 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:
Kd vs pH; Equilibrium with atmospheric pCO_2; 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*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_3 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_3)
- 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^+-montmorillonite
- reagent grade $NaHCO_3$
- 500 ppb U stock solution prepared from 50 ppm ^{233}U commercial spike
- 2 L 0.1 M $NaNO_3$ stock solution
- 1000 mL stock solution of 1.0 M HNO_3
- 1000 mL stock solution of 0.1 M HNO_3
- 1000 mL stock solution of 0.02 M HNO_3
- ultrapure water

PROCEDURE:

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

- -Initial ΣU = 50 ppb
- -Initial pH = 2.0 to 9.0, every 0.25 pH unit; adjustments made with HNO_3 or $NaHCO_3$
- -Initial volume = 50 mL
- -Ionic strength = 0.1 M $NaNO_3$
- -Wt. zeolite to use = 0.100±0.001 g
- -Initial $[Na^+]$ = 0.1 M $NaNO_3$ + $[NaHCO_3]$ added
- -pCO_2 = atmospheric = $10^{-3.48}$ 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 $NaNO_3$ matrix; prepared previously from commercial 50 ppm ^{233}U spike) to a total of 2050 g by carefully taring 0.1 M $NaNO_3$ solution into the plastic bottle on a Mettler 4600 balance.

The 500 ppb stock solution used is 23A - see Radiochemistry Notebook, p 150. The 0.1M $NaNO_3$ solution prep. is found on GC-06-53.

0810PM weight of 500 ppb ^{233}U solution used: 205.10 g

weight of 50 ppb ^{233}U solution prepared: 2050.9 g

b) Into each of 29 50-mL centrifuge tubes labeled S-I*pH*i* [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 ^{233}U solution added to tube:

S-I*pH 2.0 = 46.2~~050~~ 601 12/29/92 tube wt: 10.7~~379~~ 642

2.25 = 46.~~2969~~ 0784 12/29/92 10.7~~453~~ 690

tube	wt ^{233}U (50 ppb) soln:	tube wt:
S-I*pH 2.50	46.~~3009~~ 2409 12/29/92	10.~~8200~~ 8200
2.75	46.3~~571~~ 205	10.~~7686~~ 8186
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*pH*i**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 ^{233}U soln
S-I-C*pH 2*a	10.7667	46.1485
b	10.8177	46.1889
4*a	10.7699	46.0044
b	10.8262	46.0076

tube	wt tube	wt 50ppb ^{233}U soln
S-I-C*pH6*a	10.7229	46.0224
b	10.7055	46.0201
8*a	10.7601	46.1475
b	10.7661	46.0422
95*a	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_3. Swirl each tube and save for later analysis of uranium concentration by alpha-spectrometry.

wt tube + 0.02 M HNO_3	wt solution from S-I*IU
S-I-11*a : 15.6042	: 5.0247
*b : 15.5558	: 5.0208

Table S-I-1. Amount of reagent grade HNO_3 or $NaHCO_3$ to add to 50 ml 0.1 m $NaNO_3$ 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_2(g).

Solution pH	Volume of HNO_3 Needed, Drops (0.0394 mL/drop)	Molarity of 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 (.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 $NaHCO_3$ 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	0.00029
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 probed lite than .000259 12/29/92

table S-I-1 continued:

Solution pH	Amount of $NaHCO_3$ 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*pH*i* and S-I-C*pH*i*, 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
S-I*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
S-I*pH 4.00	4.18	21.6	1150
S-I-C*pH2*a	4.18	21.6	1154
b	4.17	"	1159
4*a	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_3 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 #s 910358-24, 910886-24, 910359-24 + 913827R-24) were used to calibrate. pH buffers 4, 7, 9 + 10 are used for the next section c) 2. 5 + 7 12/29/92 JPL

Solution Label	# Drops Added	Conc. HNO_3	pH measured	Soln.Temp. °C
S-I*pH2.00	15	1.0	1.94	21.4
S-I*pH2.25	8 ~~9~~	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 ~~15~~	0.1	3.03	21.5
S-I*pH3.25	7 ~~9~~	0.1	3.24	"
S-I*pH3.50	5	0.1	3.45	"
S-I*pH3.75	2 ~~3~~	0.1	3.64	21.6
S-I*pH4.00	1 ~~2~~	0.1	3.86	"
S-I-C*pH2*a	14 ~~15~~	1.0	1.97	21.6
S-I-C*pH2*b	14 ~~15~~	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

12/08 RM

2. For each solution S-I*pH*i* and S-I-C*pH*i*, 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*pH 8.50	"	"	1358

solution	pH	temp of solution	time
S-I*pH 8.75	4.15	22.3	1400
9.00	"	"	1402
S-I-C*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 $NaHCO_3$ 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_2(g). This equilibration process may take at least twelve days.

see GC-06-66 table 2 for amounts RM 01/04/93

Solution Label	g $NaHCO_3$ 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	0.16468

7/06 RM

1758PM All S1 sample tubes are on the gyratory shaker at ~125rpm.

12/30/92 PM 0755 The pH of all S1 sample tubes will be monitored. The pH buffers used to calibrate are pH 2, 4, 7, 9 + 10.

solution	pH	temp
S-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

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

0926PM All S1 tubes were put back on the shaker.

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

01/02/93 PM Expt S1 continued - pH monitoring

solution	pH	temp
12 ~~PM~~ S-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	3.89	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	pH 1/2/93 ~~7.13~~ 7.58	16.3
8.0	pH 1/2/93 ~~7.58~~ 8.00	~~16.3~~ 17.0
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-1 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/~~93~~ PM
1022 The 3M NaCl solution covering the montmorillonite was replaced.

More 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.

1259PM - electrode maintainance -
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 kpH 2.0	1.95	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	7.27	"
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
S-I* 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
S-I-C* pH 2* a	2.00	20.2
b	1.93	"
4* a	3.89	"
b	3.86	"
6* a	6.06	"
b	6.18	"
8* a	7.92	20.3
b	8.03	20.2
9.5* a	9.15	"
b	9.10	"

1/5/93 PM Prep of More Na-'Cheto' Montmorillonite continued
1114 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 5th rinse shows no precipitate formation when it is placed in a beaker + 0.1 N $AgNO_3$ solution is added dropwise.

01/06/93 Expt 51- continued pH monitoring

solution	pH	soln. temp
0959 S-I* 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	"
S-I-C* pH 2* a	2.12	17.0
b	2.06	17.1

solution	pH	soln temp
S-1-C*pH 4*a	3.86	17.1
b	3.85	"
pH 6*a	6.07	"
b	6.17	17.2
pH 8*a	7.92	"
b	8.02	"
9.5*a	9.29	17.2
b	9.26	"

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

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

1020PM

solution	pH	soln temp °C
S-I*pH2.0	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	"

solution	pH	soln temp
S-I*pH7.0	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

solution	pH	soln temp
S-1-C*pH2*a	1.94	19.9
*b	1.88	"
4*a	3.82	"
*b	3.81	"
6*a	6.40	"
*b	6.29	"
8*a	7.95	"
*b	7.97	"
9.5*a	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 –

0834PM

solution	pH	soln temp °C
S-I*pH2.0	1.90	19.9
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 16

8/4/94

solution	pH	soln. temp °C
S-1*pH 4.0	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	"

solution	pH	soln. temp. °C
S-1-C*pH 2*a	1.96	16.1
b	1.89	"
4*a	3.85	16.2
b	3.84	"
6*a	6.07	"
b	6.21	"
8*a	7.97	"
b	8.08	"
9.5*a	9.38	"
b	9.35	"

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

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

	solution	pH	soln. temp °C
0730 PM	S-I*pH 2.0	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. PM 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	"

solution	pH	soln temp °C
S-I*pH9.0	9.04	17.0

solution	pH	soln temp °C
S-I-C*pH2*a	1.95	17.0
b	1.92	"
4*a	3.85	"
b	3.88	"
6*a	6.06	17.1
b	6.24	"
8*a	7.97	"
b	8.06	"
9.5*a	9.42	"
b	9.39	"

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

The solutions have had 15 days to equilibrate, + the experiment will continue with addition 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*i* (**not** the S-I-C*pH*i*) centrifuge tubes. Swirl each tube by hand, replace the cover, then place on the shaker.

solution	amt Na-montmorillonite, g
S-I*pH2.0	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

solution	amt Na-montmorillonite, g
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

1220PM The solutions were put back on the shaker

01/08/93 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*i* and S-I-C*pH*i* 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^2 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*i**a (or b) and pre-weighed 50-mL centrifuge tube that contains 5 g of 0.02 M HNO_3, 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*i* 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_3.

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

	sample	wt tube + 5mL 0.02M HNO_3	wt U aliquot
1045 PM	S-I pH 2.0 ka	15.5976 g	5.0392 g
	kb	15.6338	5.0752
	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 a	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 + 5mL 0.02M HNO_3	wt U aliquot
	S-I pH 6.25 ka	15.7361	5.1076
	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	4.9274
	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
	S-I-CK pH 2 ka1	15.8851	5.0016
	ka2	15.7755	4.9879
	kb1	15.7765	4.9856
	kb2	15.7608	4.9971
	S-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 tube + 5mL 0.02M HNO_3	wt U aliquot
S-I-C pH 6 a1	15.7750	4.9721
a2	15.9617	4.9713
b1	15.7874	4.9759
b2	15.7616	4.9744
S-I-C pH 8 a1	15.6854	4.9490
a2	15.9393	4.9689
b1	15.7331	4.9662
b2	15.7331	4.9735
S-I-C pH 9.5 a1	15.7372	4.9879
a2	15.7436	4.9956
b1	15.7336	4.9870
1445PM b2	15.8015	4.9939

The pH of the solutions S-I-X + S-I-C-X were read once more.

	Solution	pH	soln temp. °C
1502PM	S-I-X 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
S-I-X 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	"
S-I-X-C 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 S-I-X solutions were put back on the gyratory shaker.

See C06-1204 for S-1 analysis by liq. and scintillation 3/5/93 PM

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 JPM

URANIUM SORPTION EXPERIMENT S-II:
Kd vs pH; Equilibrium with atmospheric pCO_2; 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_3 into 50-mL centrifuge tubes)
3 glass droppers (for adjusting pH by addition of HNO_3)
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^+-montmorillonite
reagent grade $NaHCO_3$
500 ppb U stock solution prepared from 50 ppm ^{233}U commercial spike
1000 mL stock solution of 1.0 M HNO_3
1000 mL stock solution of 0.02 M HNO_3
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_3 or $NaHCO_3$
-Initial volume = 50 mL
-Ionic strength = 0.1 M $NaNO_3$
-Wt. zeolite to use = 0.100±0.001 g
-Initial $[Na^+]$ = 0.1 M $NaNO_3$ + $[NaHCO_3]$ added
-pCO_2 = atmospheric = $10^{-3.48}$ bar

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

The 500ppb ^{233}U stock solution is from dilution 23-A (Radiochemistry Notebook, 150).

i = 2.0, 2.25, ..., 8.75, 9.0

	tube label	wt tube, g	wt U soln added, g
082574	S-II*pH2.0	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*pH*i**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.

[redacted] label	wt tube, g	wt U soln added, g
S-II-CkpH2*a	10.9116	46.0203
b	10.7775	46.1138

tube label	wt tube, g	wt U soln added, g
S-II-C*pH4*a	10.7378	46.1133
b	10.8010	46.1271
6*a	10.8574	46.1061
b	10.7699	46.1537
8*a	10.7937	46.1561
b	10.9113	46.1632
9.5*a	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_3. Swirl each tube and save for later analysis of uranium concentration by alpha-spectrometry.

	wt tube + HNO_3, g	wt sample taken, g
S-II-IU*a:	15.8318	5.0096
b:	15.8298	5.0040

c) 1. For each solution S-II*pH*i* and S-II-C*pH*i*, 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*pH 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*pH2*a	3.16	19.0
*b	3.18	

The pH meter/electrode was calibrated using Fisher pH buffer solutions 2, 3, + 4 (lot #s 910358-24, 910886-24, + 913914-24).

Adjust the pH to the value of *i* of each solution by adding *dropwise* with a glass dropper HNO_3 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_3 solution was prepared 5 Aug 92 by Todd Dutrich from lot #910962. The 0.1 M HNO_3 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_3 or $NaHCO_3$ to add to 50 ml 0.1 m $NaNO_3$ 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_2(g).

Solution pH	Volume of HNO_3 Needed, Drops (0.0394 mL/drop)	Molarity of HNO_3 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 $NaHCO_3$ 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 $NaHCO_3$ 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_3]	# 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*i* and S-II-C*pH*i*, where *i* > 3.2:

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

	solution S-II*pHi	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*pHi	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
1212 PM	9.5b	3.20	"

Tare onto weighing paper reagent grade $NaHCO_3$ 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_2(g). This equilibration process may take at least twelve days.

$NaHCO_3$ used is lot # 886728.

	Solution label	amt $NaHCO_3$ 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

solution label	ant. $NaHCO_3$ added, g.
S-II* pH 8.0	0.00634
8.25	0.00882
8.5	0.01310
8.75	0.02244
9.0	0.03949
S-II-C* 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

1605PM The S-II solutions were covered with kim wipes & placed on a gyratory shaker at ~ 125rpm.

01/22/93 Expt S-11 continued pH monitoring

	solution	pH	temp of soln, °C
0749PM	S-II* 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	"

solution	pH	temp of soln, °C
S-II* 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* 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

0938PM The S-II solutions were put back on the gyratory shaker.

01/25/93 Expt S-11 continued pH monitoring

	solution	pH	°C soln
1032PM	S-II* pH 2.0	2.060	16.2
	2.25	2.25	"

solution	pH	°C soln
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	8.74	"
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.

solution	pH	°C soln
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.

1/27/93 PM Expt S-II continued: pH monitoring

solution	pH	°C solution
0224 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

solution	pH	°C solution
S-II*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
S-II-C*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

1130 PM The S-II ~~samples~~ solutions were put back on the gyratory shaker. 1/27 PM

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

	solution	pH	solution temp. °C
1014 PM	S-II*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	"

solution	pH	solution temp. °C
S-II*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
S-II-C*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	"

1148 PM The S-II solutions were put back on the gyratory shaker.

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

	soln	pH	temp soln °C	soln	pH	temp soln °C
1324 PM	S-11 pH 2.0	1.96	19.9	S-11 pH 2a	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	"			

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

02/03/93 PM Expt MK1 continued - U-233 Alpha Spectrometry Analysis Procedure (see GC-066-53)

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_2O 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 ^{232}U and ^{233}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 (^{232}U and ^{233}U) present in concentrations C_{232U} and C_{233U} with maximum permissible concentrations MPC_{232U} and MPC_{233U}: $(C_{232U}/MPC_{232U}) + (C_{233U}/MPC_{233U}) \leq 1$. Note that the limits for MPC_{232U} and MPC_{233U} 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_4), which readily converts to nitrate) or acid and require liberal dilution prior to and during disposal via the sink.

1002 PM 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 (O_2(g)) + 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 partway 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.

1012PM Drying was started.

1210PM Expt MK1- AlphaSpec 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 ^{232}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:	final v (mL)
MK1-1*IUa	25A	0.167	.1636 M 2/3/93	~10
MK1-1*IUb	25B	1.672	~~.1630~~ 1.6600	
MK1-1*A*I1	25A	0.167	.1630	
MK1-1*A*I2	25B	1.672	1.6640	
MK1-1*B*I1	25A	0.167	.1643	
MK1-1*B*I2	25B	1.672	1.6707	
MK1-1*C*I1	25A	0.167	.1654	
MK1-1*C*I2	25B	1.672	1.6625	
MK1-1*A*1a	25A	0.162	.1592	
MK1-1*B*1a	25B	1.622	1.6233	
MK1-1*C*1a	25A	0.165	.1643	
MK1-1*A*2a	25B	1.572	1.5706	
MK1-1*B*2a	25A	0.157	.1527	
MK1-1*C*2a	25A	0.165	.1646	
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	.1652	
MK1-1*C*3b	25A	0.165	.1652	
MK1-1*A*4a	25B	0.836	.8341	
MK1-1*B*4a	25B	0.836	.8334	
MK1-1*C*4a	25A	0.165	.1647	
MK1-1*A*5a	25B	0.502	.8304 ← error on high side	
MK1-1*B*5a	25B	0.502	.5023	
MK1-1*C*5a	25A	0.165	.1644	
MK1-1*A*6a	25B	0.334	.3288	
MK1-1*A*6b	25B	0.334	.3303	
MK1-1*B*6a	25B	0.334	.3321	
MK1-1*B*6b	25B	0.334	.3332	
MK1-1*C*6a	25A	0.165	.1637	
MK1-1*C*6b	25A	0.165	.1639	
MK1-1*A*7a	25B	0.251	.2502	
MK1-1*B*7a	25B	0.251	.2508	
MK1-1*C*7a	25A	0.165	.1628	
MK1-1*A*8a	25B	0.201	.2015	
MK1-1*B*8a	25B	0.201	.2032	
MK1-1*C*8a	25A	0.164	.1629	
MK1-1*A*9a	25B	0.167	.1667	
MK1-1*A*9b	25B	0.167	.1616	
MK1-1*B*9a	25B	0.167	.1648	
MK1-1*B*9b	25B	0.167	.1635	

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	~12
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_3. Use enough of 0.1 N HNO_3 during each spike transfer (~ 5 ml) to obtain roughly equal volumes in the centrifuge tubes. Dispose of sample boat into special radioactive wastebasket.

1538PM 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.

1160 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.

02/05/93PM Clay freeze-drying continued -
0858PM The ~100g of clay was re-attached to the freeze-dryer + drying continued.

Expt S-II continued : pH monitoring

	soln S-II×pH i	pH	soln temp °C	soln S-II-C×pH i	pH	°C
0858PM	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 S-II solutions were placed back on the gyratory shaker.

- Expt MK1 - Alpha Spec continued -

1305PM 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.

1403PM 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 ½ dry (very dry about the edges, still wet in the middle). The containers will be covered with kim wipes + left for the clay to air-dry.

02/02/93 ~~Expt MK1 - Alpha Spec continued~~

0810PM 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 NH_4OH from the reagent bottle using 6 to 7 drops from the plastic pipet attached to the NH_4OH reagent bottle. This is strongly exothermic and the solution should be gently swirled during the addition of the base. Note that the NH_4OH should be from a closed reagent container (*eg.* new 2 l bottle) since this will ensure that minimal CO_2 will be present in the base which would lower yield. This step precipitates about 2.5 ml of $Fe(OH)_3$.

Note: only samples MK1-1 #10a & b were started today. TM 2/8/93

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

7. The $Fe(OH)_3$ 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 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.

0532PM - 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.

TM 02/12/93 Expt S-II continued: pH monitoring

	soln	pH	temp °C	soln	pH	temp °C
0530PM	S-II-pH2.0	1.94	16.0	S-II-CKpH2a	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	14.2			
	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 PM

3. The samples will be lowered to pH =1 using 250 µl of 1.0 N HNO_3 and diluting to 5.0 ml with 0.1 N HNO_3 using squirt bottle. Make sure $Fe(OH)_3$ 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 NH_4NO_3 - 0.1 N 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 NH_4CSN 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 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 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 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±0.001 g of Na-montmorillonite onto weighing paper, and carefully transfer into each of the S-II*pH*i* (**not** the S-II-C*pH*i*) 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 AM S-II * pH 2.0	0.1003	S-II * pH 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	0.0995
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		

1122 PM The S-II samples were put back on the gyratory shaker at ~125 rpm.

02/17/93 - Prep of 0.02 M HNO_3 for S-II samples -

1100 AM 10 mL of 1.0 M 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 nano pure water + stirred to mix. This will be used in the S-II samples

URANIUM SORPTION EXPERIMENT S-III:
Kd vs pH; Equilibrium with atmospheric pCO_2; 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_3 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_3)
- 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^+-montmorillonite
- reagent grade $NaHCO_3$
- 500 ppb U stock solution prepared from 50 pp_m ^{233}U commercial spike
- 2 L 0.1 M $NaNO_3$ stock solution
- 1000 mL stock solution of 1.0 M HNO_3
- 1000 mL stock solution of 0.1 M HNO_3
- 1000 mL stock solution of 0.02 M HNO_3
- 1000 mL stock solution of 0.01 M HNO_3
- 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_3 or $NaHCO_3$
- Initial volume = 50 mL
- Ionic strength = 0.1 M $NaNO_3$
- Wt. zeolite to use = 0.100±0.001 g
- Initial $[Na^+]$ = 0.1 M $NaNO_3$ + $[NaHCO_3]$ added
- pCO_2 = atmospheric = $10^{-3.48}$ 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 $NaNO_3$ matrix; prepared previously from commercial 50 ppm ^{233}U spike) to a total of 2050 g by carefully taring 0.1 M $NaNO_3$ solution into the plastic bottle on a Mettler 4600 balance.

1158PM 4L of 0.1M $NaNO_3$ solution was prepared by weighing out 16.9980g of $NaNO_3$ (lot #7808 KDJE), transferring it into a 2 liter volumetric flask, bringing the solution to volume with DANTO pure water, + shaking to mix. This was repeated once, + the resulting solution (4L) was stored in labeled PP bottles.

weights $NaNO_3$ used: 17.0059g (first 2L)
16.9904g (second 2L)

The 500 ppb ^{233}U stock solution is from dilution 23-A - see Radiochemistry Notebook, p150.

weight of 500 ppb ^{233}U soln used: 20.57g
final solution wt : 2057.0g

b) Into each of 29 50-mL centrifuge tubes labeled S-III*pH*i* [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*pH*i**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-X pH 2.0	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	10.9055	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*pH 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_3. 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
1550 PM b	15.9414	5.0046

Expt S-III continued

c) 1. For each solution S-III*pH*i* and S-III-C*pH*i*, 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
PM 0830	S-III*pH 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*pH2*a	5.26	16.1
	*b	5.21	"
	4*a	5.21	16.2
	*b	5.25	"

The pH meter was calibrated using pH buffers 2, 4, +7 (Fisher, lot #s 910358-24, 913914-24, + 921733-24).

Adjust the pH to the value of *i* of each solution by adding *dropwise* with a glass dropper HNO_3 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_3 solution is the one prepared 6 Aug 92 by Todd Dietrich.

Table S-III-1. Amount of reagent grade HNO_3 or $NaHCO_3$ to add to 50 ml 0.1 m $NaNO_3$ 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 CO_2(g).

Solution	Volume HNO_3 Needed, Drops (.0394 mL/drop)	Molarity of 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 $NaHCO_3$ 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 $NaHCO_3$ 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	$[HNO_3]$	# 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	$[HNO_3]$	# 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-C*	pH 2ka	2.00	16.1	0.1	14
	kb	2.03	"	"	13
	4ka	4.06	16.2	0.1, 0.01	1, 2
1028 PM	kb	4.07	"	"	"

2. For each solution S-I*pH*i* and S-I-C*pH*i*, 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	"			