

TECHNICAL PROGRESS REPORT

Morphological Changes of U-Bearing Precipitates over Time via SEM/EDS

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1.0 INTRODUCTION

Uranium is a key groundwater and vadose zone contaminant beneath the 200 Area located on the Central Plateau at the Hanford Site. Past water leaks from plutonium production and chemical processing released radionuclides and hazardous materials to the ground surface. These leakages influenced the vadose zone sediments by creating potential sources for groundwater contamination and risk to receptors through water uptake from contaminated wells or discharge to surface water. Despite significant progress to reduce the potential for radionuclides migration, uranium groundwater plumes identified in multiple locations around the site still persist after many years. The goal of environmental cleanup activities at Hanford is to protect the Columbia River by reducing the concentration of contaminants entering the river to below levels that can cause harm (DOE/RL-2007-20). One of the innovative testing technologies being investigated to accomplish this mission is the injection of reactive gases such as NH_3 to sequester uranium in the subsurface, thereby minimizing the potential for uranium mobilization in vadose zone environments contaminated with radionuclides. The injection of a NH_3 gaseous mixture causes the formation of NH_4OH and a subsequent increase in pH, leading to silica and aluminum dissolution from soil minerals. The subsequent decrease in the pH to ambient conditions would trigger the co-precipitation process of U(VI) with mobilized Si and other constituencies released from soil minerals to pore water. These chemical reactions can potentially control the mobility of uranyl cations in soil systems since co-precipitated contaminants are less available for migration. This subtask is focusing on the assessment of uranium-bearing precipitates to evaluate their mineralogical and morphological characteristics. There is no single method that would help in the characterization of solid phases. Hence, the mineralogical and morphological characteristics of precipitates were examined by means of scanning electron microscope energy-dispersive spectroscopy (SEM-EDS), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and X-ray photoelectron spectroscopy (XPS). Preliminary results on these assessments were presented in the Project 2 2011 Year End Report. This progress report presents a summary of the SEM/EDS analysis performed during the reporting period starting May 2012. The SEM/EDS analysis shows the structure and composition of dried uranium-bearing precipitates that were created after NH_3 gas was injected into the synthetic solutions mimicking pore water composition and then kept over time in the “mother solution.” The objectives of the study also included an evaluation of the effect of sample preparation procedures on the morphology of precipitates to observe if any crystalline structures could be developed over time.

2.0 MATERIALS AND METHODS

The experimental approach to conduct these studies involved preparation of appropriate sets of samples with and without Ca; containing the desired Si, Al, and HCO_3^- concentrations; and amended with 200 ppm of U(VI). Sample preparation procedures for the characterization studies of the U(VI)-bearing precipitates followed the same routine as for the U(VI) removal experiments outlined in the Project 2 2011 Year End Report. The concentrations of the elements used in preparation of the solutions are presented in Table 1.

Table 1. Stock Solutions for SEM/EDS Analysis of 200 ppm U

Stock Solution	Stock Solution Concentration (mM)	Concentration (mM)	
		100 mM Si + 3 mM HCO_3^- + 5 mM Al + 200 ppm U	100 mM Si + 50 mM HCO_3^- + 5 mM Al + 200 ppm U
KHCO_3	400	3	50
$\text{Al}(\text{NO}_3)_3$	422.24	5	5
$\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$	50	100	100
$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	4.2	0.84	0.84
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	147.01	5	5
HNO_3		Used to adjust pH of the mixture solution to 8	
5% NH_3 + 95% N_2 GAS		adjusted in each case to reach pH 11	

Three batches were prepared for these experiments. The 1st batch consisted of identical multiples of each sample prepared to analyze over time in a sacrificial mode. The first sample was taken for precipitate drying after 2 days (set #1) of being prepared and kept in the “mother solution” on the shaker; the next samples were taken after being kept in the “mother solution” for 2 weeks (set #2), 1 month (set #3), 1.5 months (set #4), 2 months (set #5), 3 months (set #6) and 4 months (set #7). All the samples were placed on the shaker at 100 rpm and kept at a constant temperature of 25°C for future SEM-EDS analysis. The increase in U(VI) concentration to 200 ppm helped to raise the atomic percentage of U(VI) in the sample and to determine if any crystalline U-bearing phases could be observed over time. Each sample set consisted of two samples precipitated out of the following solutions: a) 100 mM Si, 5 mM Al, 3 mM HCO_3^- , and 200 ppm U(VI); and b) 100 mM Si, 5 mM Al, 50 mM HCO_3^- , and 200 ppm U(VI). At certain time intervals, the sample precipitate from each set was extracted by centrifugation followed by decantation of the supernatant. Gel precipitates were then placed in the incubator for drying in preparation for the SEM/EDS. A total of 14 sample test tubes of 5 mL were prepared. Supernatant solutions were kept for U(VI) analysis via kinetic phosphorescence analyzer (KPA).

A 2nd batch of samples for the study characterization of uranium-containing precipitates over time was prepared with and without calcium in the solution composition. Samples of these sets were not centrifuged to prepare gel precipitates for drying. This batch consisted of 4 larger sets, one of 100 mM Si, 5 mM Al, 3 mM HCO₃⁻, and 200 ppm U, and the second one of 100 mM Si, 5 mM Al, 50 mM HCO₃⁻, and 200 ppm U. Samples from each of the first 2 sets had 5 mM Ca added. Sets three and four were prepared similarly but without Ca addition. These 4 larger sets were subdivided into the sets that were assessed over time for precipitate characterization: 2 days (#1), 2 weeks (#2), 1 month (#3), 2 months (#4) and 3 months (#5) after sample preparation and being kept in the “mother solution.” For the start of these new sets, the stock solutions of Si, Al, HCO₃⁻, Ca were prepared and then mixed into the test solutions containing the appropriate concentrations. Nitric acid was injected into the solutions to lower their pH to 8, and then ammonia gas was sparged to increase pH to 11. Lastly, the uranium addition completed the sample solutions formulations. A total of 20 samples were prepared and placed in the incubator/shaker at 25°C and 100 rpm. At certain time intervals, samples were extracted, decanted and the gel precipitate was placed in the incubator for drying in preparation for SEM/EDS analysis. Supernatant solutions were kept for U(VI) analysis via KPA.

The 3rd batch was organized differently from the first 2 batches in the sense that two primary solutions were prepared from which, when the time came, smaller samples were extracted, decanted, and precipitates set to dry. Two smaller samples of 15 mL and 5 mL were taken each time from the primary solution and transferred into the separate 15-mL polystyrene tubes. The tubes with 5 mL of sample were centrifuged for 2 min at 2000 rpm, decanted, and the precipitates were then set to dry. The 15-mL tubes were carefully decanted once the sample had settled and the precipitates were then set to dry without preliminary centrifugation. The purpose of this batch was to extract samples over time from the same aging source instead of preparing separate sacrificial samples for each aging time. An additional purpose was to compare sample preparation procedures with and without centrifugation. In order to ensure that each extraction was homogeneous, tubes with primary solutions were vortexed before the extraction. The variation between the two primary solutions was the bicarbonate concentration: one primary solution was of 100 mM Si, 5 mM Al, 3 mM HCO₃, 5 mM Ca, and 238 ppm U and another one was of 100 mM Si, 5 mM Al, 50 mM HCO₃, 5 mM Ca, and 238 ppm U. The uranium concentration in this 3rd batch was slightly higher, 238ppm, in an attempt to increase the uranium atomic percentage present in the sample composition.

2.1 Scanning Electron Microscope-Energy Dispersive Spectroscopy

The samples' surface composition was analyzed after precipitate solidification via scanning electron microscopy and energy-dispersive-spectrometry (SEM-EDS). Two instruments were employed for this analysis. The uranium-containing dry precipitate samples were mounted on aluminum stubs with double-sided sticky carbon tape and then coated for 30 seconds with a thin layer of gold to increase conductivity.

For batch #1, the surface composition of gold-coated samples (Pelco SC-7, Auto sputter coater) was analyzed using a JOEL, JSM-6330F SEM SEM-Energy-Dispersive-Spectrometry (SEM-EDS) Noran System Six Model 200 at 15 kV at magnifications of 2000-5000. For batches #2 and #3, electron microscopy was performed using a JEOL-5910-LV with accelerative potentials between 10 kV and 20 kV. For conduction purposes, all samples were gold coated using an SPI-Module Control and Sputter unit. EDS analysis was accomplished using an EDAX Sapphire detector with UTW Window paired with Genesis software. Micrographs were prepared in both secondary electron and backscatter modes with the objective lens aperture 2 at 30 μm diameter and the spot sizes (condenser lens) ranging from 35-40".

3.0 RESULTS AND DISCUSSION

Analysis using SEM/EDS allowed investigation of the effects of variables such as length of time in the "mother solution" and the presence of Ca in the artificial solution mixture on the morphology of the experimentally prepared uranium-bearing precipitates. The analytical techniques permitted a comparison of the qualitative and quantitative changes resultant from altering preparation methods, component concentrations, and time.

3.1 Analysis of Supernatant Solutions

Several precipitate preparation methods were evaluated, particularly the effect of the centrifugation on the concentration of uranium in the supernatant solution, for the purpose of determining the methods that would be used in the subsequent experiments.

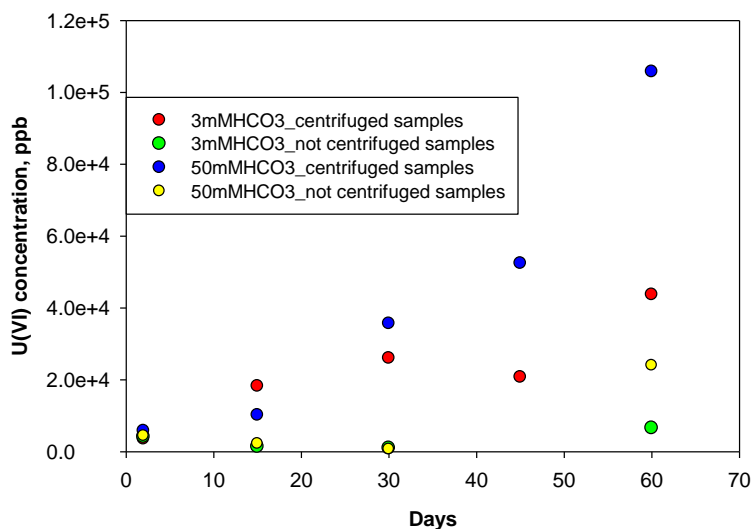


Figure 1. Effect of sample centrifugation on the concentration of U(VI) in the supernatant solution

Batches 1 and 2, prepared with 3 mM HCO₃ and 50 mM HCO₃, respectively, have similar sample composition; however, the precipitate preparation procedures for batch 1 included centrifugation and batch 2 samples were not centrifuged to prepare the gel precipitates for drying. Data from Figure 1 illustrate that the supernatant solutions from the centrifuged samples prepared with 50 mM HCO₃ and kept in the “mother solution” for 60 days were 2.4 times higher in uranium content compared to samples prepared with 3 mM HCO₃. The concentration of U(VI) in the supernatant solution from samples not centrifuged and kept in the “mother solution” for the same period of time was found to be lower by 6.7 times for the samples prepared with 3 mM HCO₃ and by 4.4 times for samples prepared with 50 mM HCO₃. One possible explanation is that the high separation forces of the centrifuge drive dissolved uranium from the amorphous gel precipitates to the supernatant solution, resulting in lowering the uranium concentration in the precipitates.

Similar assessments of supernatant solution were conducted for batch 2 samples amended with and without 5 mM of Ca. Non-centrifuged samples were decanted and the gel precipitates were placed in the incubator for drying.

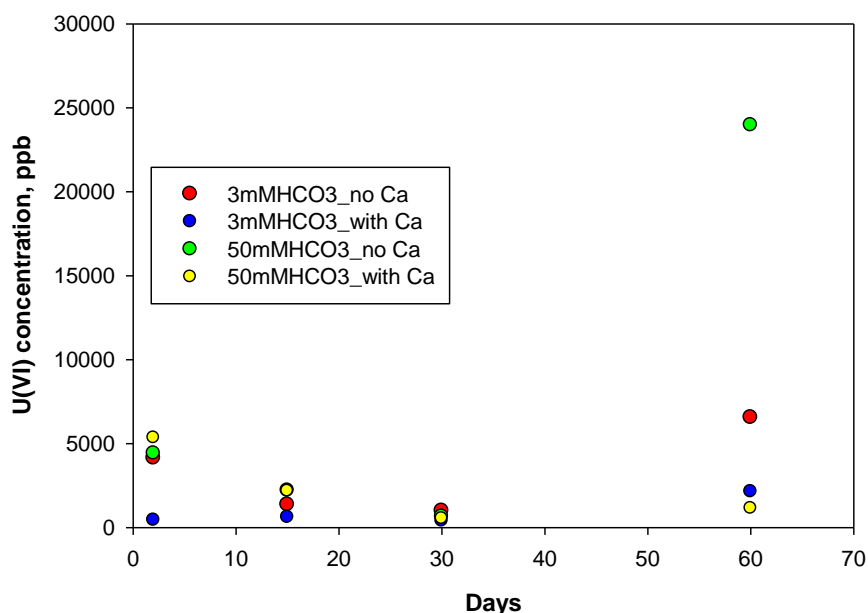


Figure 2. Effect of 5mM Ca on the concentration of U(VI) in the supernatant solution

The presence of Ca in the samples composition mixture caused a reduction of U(VI) in the supernatant solution; U(VI) concentration in supernatant solutions decanted from samples amended with 3 mM HCO_3^- and 5 mM Ca were noted to decrease by 3 times as compared to analogous samples without Ca. This decrease was much more pronounced (21 times) for consequent samples with and without Ca amended with 50 mM HCO_3^- (Figure 2). Based on the results of these experiments, sample preparation procedures of precipitates for the following solubility experiments will not include a centrifugation step.

3.2 SEM-EDS Results of Centrifuged Samples of Batch 1

Figure 3 through Figure 9 present data on the sets of sample precipitates prepared out of the solution mixture composed of 100 mM Si, 5 mM Al, 3 mM HCO_3^- , and 200 ppm U(VI). All samples were centrifuged and then decanted before placing the precipitates to dry. The SEM images pertaining to these samples show that precipitates are typically amorphous silica globules (Iler, 1979). After 2 weeks of being kept in the “mother solution,” the sample surface morphology of set # 2 (Figure 4) showed evidence of elongated forms, contrasted to the more spherical silica colloidal particles found in set #1 (Figure 3). Quantitative measurements of the composition in these elongations revealed little to no uranium and a considerably higher atomic percentage of sodium. EDS indicated that samples were not homogeneous and featured a non-uniform distribution of uranium throughout the sample. The highest atomic percentage of U, ranging between 0.8% and 1.1%, was found in set #1 and set #4 (1 month); the atomic percentage of U

in the following samples were much less, in the range of 0.02 to 0.56%. No crystalline forms were found in these sets. The decline in U was attributed to the sample preparation procedures, particularly centrifugation (Figure 1).

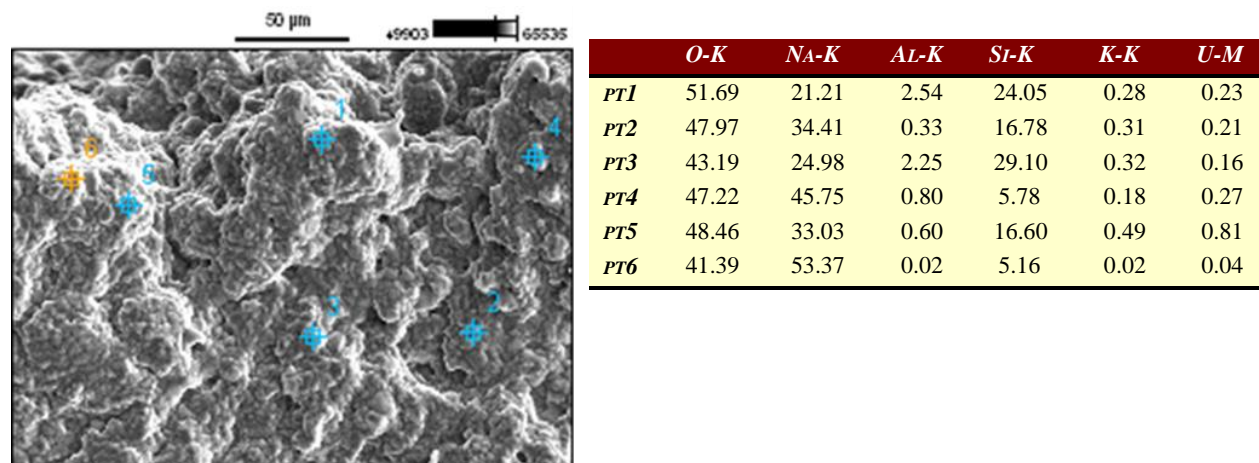


Figure 3. Set # 1 (after 2 days) SEM image (left) and EDS data (right) for centrifuged samples amended with 3 mM HCO₃⁻.

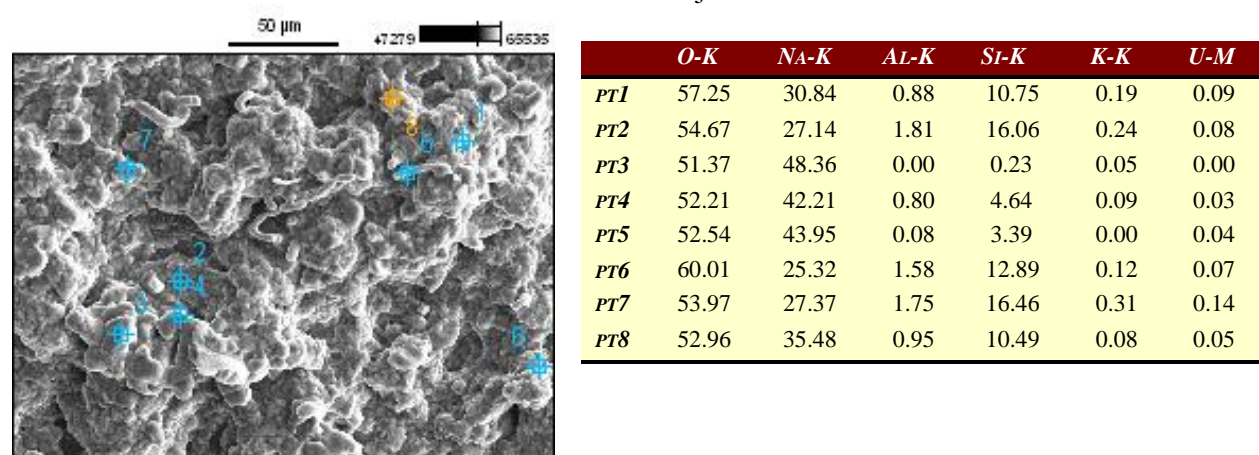
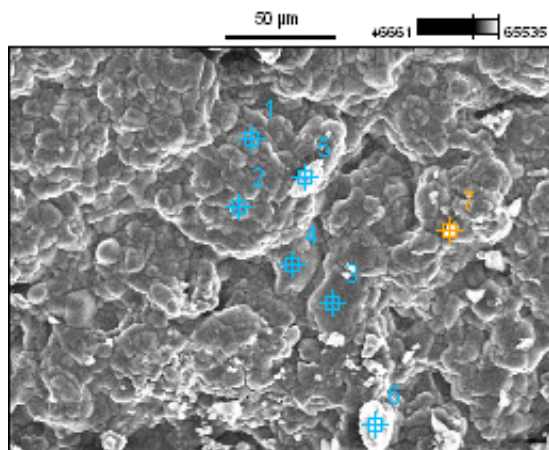
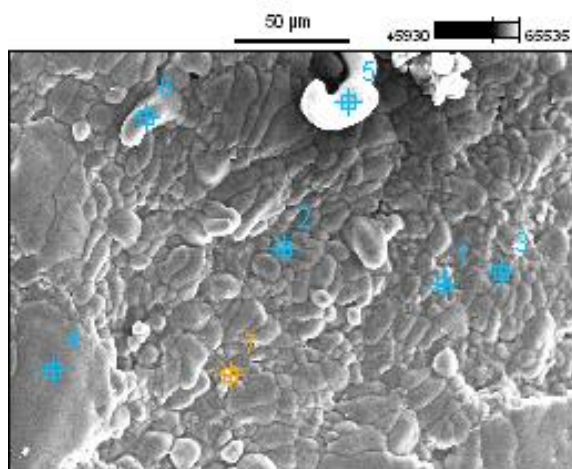


Figure 4. Set # 2 (after 2 weeks) SEM image (left) and EDS data (right) for centrifuged samples amended with 3 mM HCO₃⁻.



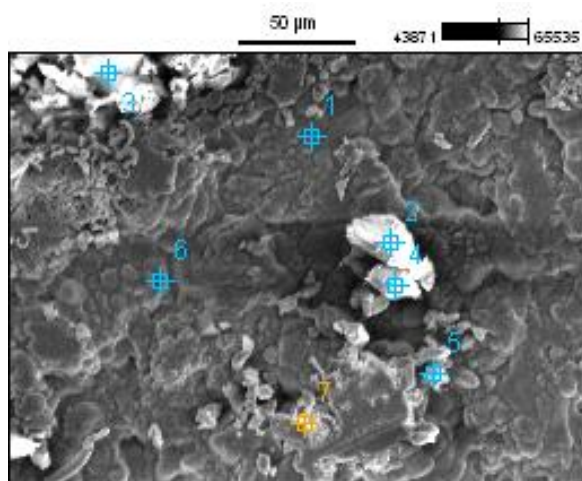
	<i>O-K</i>	<i>Na-K</i>	<i>Al-K</i>	<i>Sr-K</i>	<i>K-K</i>	<i>U-M</i>
<i>PT1</i>	54.14	41.05	0.21	4.43	0.08	0.04
<i>PT2</i>	45.27	51.95	0.35	2.26	0.01	0.16
<i>PT3</i>	51.02	48.50	0.00	0.19	0.09	0.20
<i>PT4</i>	50.06	49.67	0.00	0.21	0.06	0.00
<i>PT5</i>	45.20	22.51	0.97	28.87	1.34	1.11
<i>PT6</i>	64.35	8.25	2.74	24.15	0.31	0.19
<i>PT7</i>	57.81	22.82	0.43	18.45	0.23	0.26

Figure 5. Set # 3 (after 1 month) SEM image (left) and EDS data (right) for centrifuged samples amended with 3 mM HCO₃.



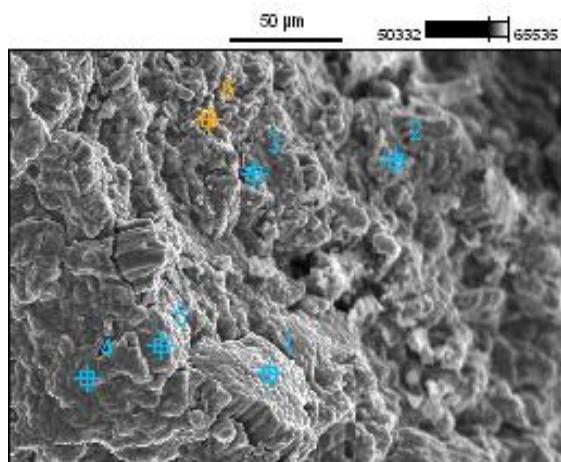
	<i>O-K</i>	<i>Na-K</i>	<i>Al-K</i>	<i>Si-K</i>	<i>K-K</i>	<i>U-M</i>
<i>pt1</i>	39.85	34.71	1.17	17.53	0.70	0.22
<i>pt2</i>	55.82	42.73	0.08	1.29	0.02	0.06
<i>pt3</i>	53.66	46.24	0.00	0.10	0.00	0.00
<i>pt4</i>	50.96	48.55	0.00	0.28	0.15	0.07
<i>pt5</i>	47.09	52.87	0.00	0.00	0.00	0.03
<i>pt6</i>	50.19	49.34	0.00	0.30	0.18	0.00
<i>pt7</i>	57.00	41.21	0.11	1.60	0.04	0.03

Figure 6. Set # 4 (after 1.5 month) SEM image (left) and EDS data (right) for centrifuged samples amended with 3 mM HCO₃.



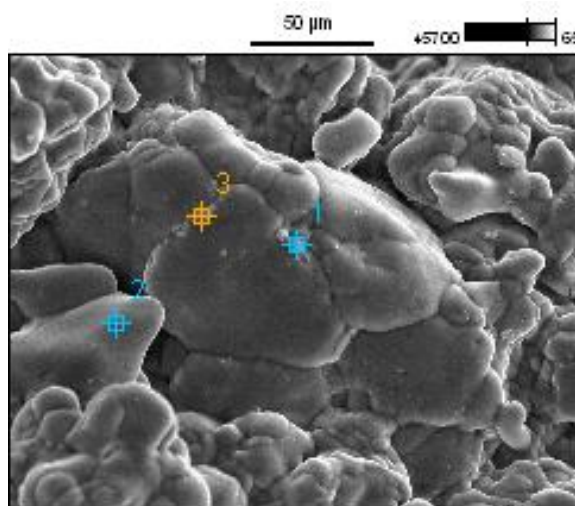
	<i>C-K</i>	<i>O-K</i>	<i>Na-K</i>	<i>Al-K</i>	<i>Si-K</i>	<i>K-K</i>	<i>U-M</i>
<i>pt1</i>	0.00	51.78	47.98	0.00	0.21	0.00	0.02
<i>pt2</i>	6.71	42.57	10.00	1.30	37.87	0.98	0.56
<i>pt3</i>	7.19	50.32	26.44	0.55	15.02	0.32	0.16
<i>pt4</i>	0.00	49.27	46.13	0.00	4.32	0.29	0.00
<i>pt5</i>	0.00	56.96	37.23	0.24	5.48	0.07	0.02
<i>pt6</i>	0.00	56.18	43.71	0.00	0.11	0.00	0.00
<i>pt7</i>	9.36	54.31	33.57	0.15	2.52	0.08	0.02

Figure 7. Set # 5 (after 2 month) SEM image (left) and EDS data (right) for centrifuged samples amended with 3 mM HCO₃.



	<i>C-K</i>	<i>O-K</i>	<i>Na-K</i>	<i>Al-K</i>	<i>Si-K</i>	<i>K-K</i>	<i>U-M</i>
<i>pt1</i>	12.29	52.10	35.19	0.06	0.34	0.02	0.00
<i>pt2</i>	10.38	54.90	34.24	0.00	0.43	0.00	0.04
<i>pt3</i>	7.74	55.48	34.35	0.11	2.26	0.01	0.04
<i>pt4</i>	49.25	27.05	21.79	0.93	0.41	0.00	0.56
<i>pt5</i>	0.00	48.60	51.25	0.00	0.11	0.00	0.03

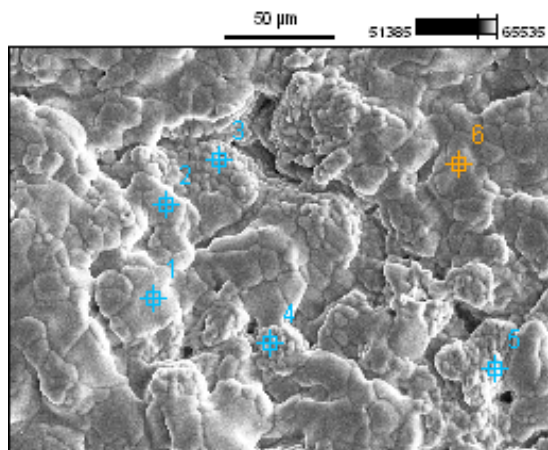
Figure 8. Set # 6 (after 3 month) SEM image (left) and EDS data (right) for centrifuged samples amended with 3 mM HCO₃.



	<i>C-K</i>	<i>N-K</i>	<i>O-K</i>	<i>Na-K</i>	<i>Al-K</i>	<i>Si-K</i>	<i>K-K</i>	<i>U-M</i>
<i>pt 1</i>	12.52	12.10	51.54	19.68	0.56	3.47	0.05	0.04
<i>pt 2</i>	2.85	16.39	50.52	30.08	0.00	0.04	0.00	0.04
<i>pt 3</i>	7.49	10.88	51.80	22.67	0.34	6.64	0.01	0.07

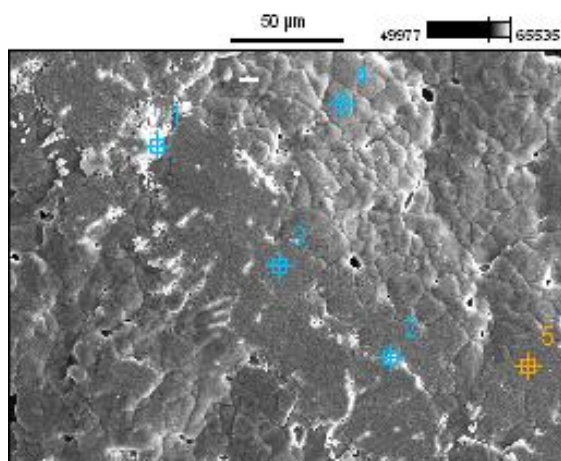
Figure 9. Set # 7 (after 4 month) SEM image (left) and EDS data (right) for centrifuged samples amended with 3 mM HCO₃

The most interesting results in these experiments were observed in the samples that combined 100 mM Si, 5 mM Al, 50 mM HCO₃⁻, and 200 ppm U (Figure 10-Figure 16). The development of crystalline structures was observed after keeping the precipitates for 1.5 months in the “mother solution” (Figure 13). Several EDS points taken on the crystals and around the sample surface showed that the distribution of uranium was not uniform, with the atomic percentage ranging between 0.01-2.57%. The higher U atomic percentage correlated with higher C atomic percentages; however, we were not able to confirm this correlation with other samples.



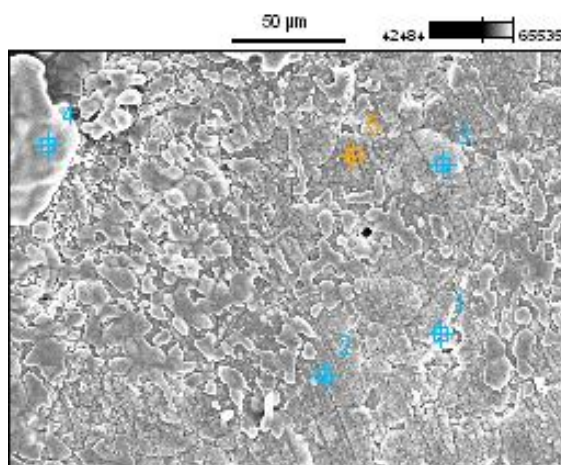
	<i>O-K</i>	<i>Na-K</i>	<i>Al-K</i>	<i>Si-K</i>	<i>K-K</i>	<i>U-M</i>
<i>pt1</i>	45.35	24.53	0.99	22.34	6.45	0.33
<i>pt2</i>	47.71	31.68	0.44	15.76	4.19	0.21
<i>pt3</i>	54.17	24.70	1.10	18.35	1.59	0.09
<i>pt4</i>	49.18	31.12	0.83	16.95	1.79	0.14
<i>pt5</i>	58.38	27.08	0.80	12.80	0.86	0.09
<i>pt6</i>	45.60	32.97	0.11	16.13	4.82	0.37

Figure 10. Set # 1 SEM image (after 2 days) and EDS data (right) for centrifuged samples amended with 50 mM HCO₃.



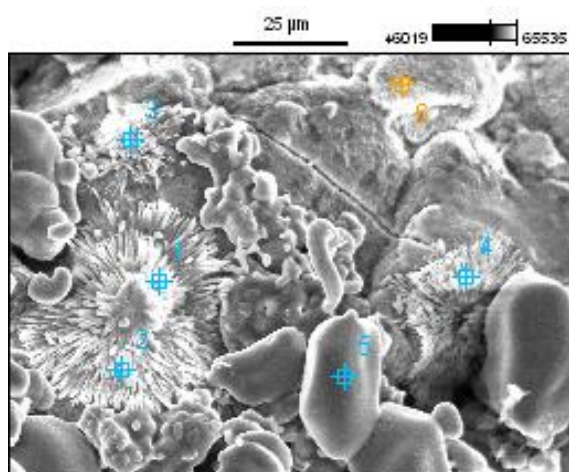
	<i>O-K</i>	<i>Na-K</i>	<i>Al-K</i>	<i>Si-K</i>	<i>K-K</i>	<i>U-M</i>
<i>pt1</i>	52.31	47.16	0.12	0.00	0.28	0.14
<i>pt2</i>	53.10	46.62	0.00	0.10	0.17	0.01
<i>pt3</i>	49.28	45.92	0.10	0.00	4.68	0.01
<i>pt4</i>	49.79	48.79	0.18	0.28	0.95	0.00
<i>pt5</i>	50.05	46.00	0.09	0.00	3.85	0.00

Figure 11. Set # 2 SEM image (after 2 weeks) and EDS data (right) for centrifuged samples amended with 50 mM HCO₃.



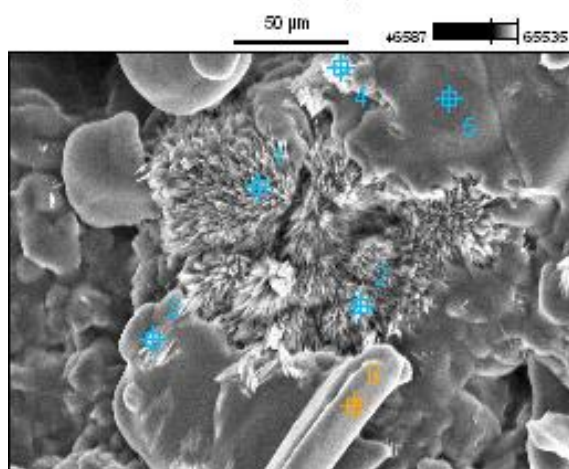
	<i>O-K</i>	<i>Na-K</i>	<i>Al-K</i>	<i>Si-K</i>	<i>K-K</i>	<i>U-M</i>
<i>pt1</i>	57.70	18.46	1.09	19.76	2.84	0.16
<i>pt2</i>	53.83	19.56	1.34	21.47	3.57	0.23
<i>pt3</i>	49.65	24.27	1.02	18.78	6.02	0.26
<i>pt4</i>	52.42	47.06	0.00	0.26	0.24	0.02
<i>pt5</i>	58.31	16.31	1.07	20.82	3.43	0.06

Figure 12. Set # 3 SEM image (after 1 month) and EDS data (right) for centrifuged samples amended with 50 mM HCO₃.



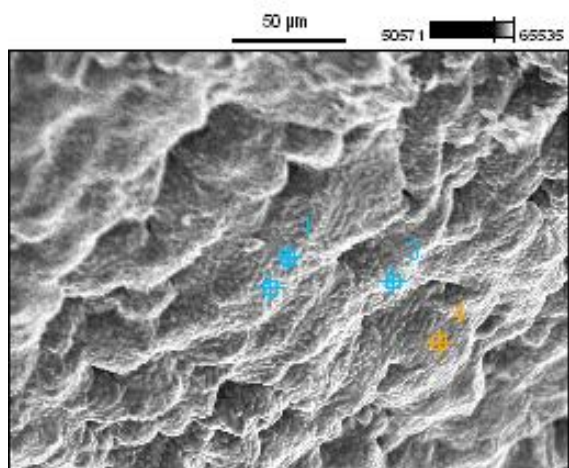
	<i>C-K</i>	<i>O-K</i>	<i>Na-K</i>	<i>Al-K</i>	<i>Si-K</i>	<i>K-K</i>	<i>U-M</i>
<i>pt1</i>	46.37	38.46	5.83	0.00	1.16	5.97	2.22
<i>pt2</i>	42.15	36.91	6.22	0.23	4.92	7.31	2.26
<i>pt3</i>	31.35	45.59	19.61	0.04	2.22	1.01	0.18
<i>pt4</i>	44.98	37.63	6.38	0.11	1.80	6.81	2.31
<i>pt5</i>	26.01	50.49	0.26	0.00	0.00	23.24	0.00
<i>pt6</i>	13.45	54.42	10.79	0.80	15.28	5.16	0.10

Figure 13. Set # 4 SEM image (after 1.5 month) and EDS data (right) for centrifuged samples amended with 50 mM HCO₃.



	<i>C-K</i>	<i>O-K</i>	<i>Na-K</i>	<i>Al-K</i>	<i>Si-K</i>	<i>K-K</i>	<i>U-M</i>
<i>pt1</i>	34.37	44.55	20.24	0.00	0.64	0.18	0.03
<i>pt2</i>	32.15	46.83	20.90	0.00	0.00	0.12	0.00
<i>pt3</i>	24.34	48.73	22.55	0.01	0.12	4.25	0.00
<i>pt4</i>	33.30	45.73	20.16	0.00	0.43	0.35	0.04
<i>pt5</i>	17.63	38.08	43.88	0.00	0.27	0.14	0.00
<i>pt6</i>	24.51	52.31	0.60	0.00	0.03	22.54	0.02

Figure 14. Set # 5 SEM image (after 2 month) and EDS data (right) for centrifuged samples amended with 50 mM HCO₃.



	<i>C-K</i>	<i>O-K</i>	<i>Na-K</i>	<i>Al-K</i>	<i>Si-K</i>	<i>K-K</i>	<i>U-M</i>
<i>pt1</i>	50.20	30.72	10.53	0.14	6.02	1.25	1.14
<i>pt2</i>	42.40	36.17	11.77	0.19	7.29	1.21	0.97
<i>pt3</i>	63.31	19.97	6.28	0.19	7.83	1.39	1.03
<i>pt4</i>	21.38	50.42	12.26	0.76	13.32	1.40	0.46

Figure 15. Set # 6 SEM image (after 3 month) and EDS data (right) for centrifuged samples amended with 50 mM HCO₃.

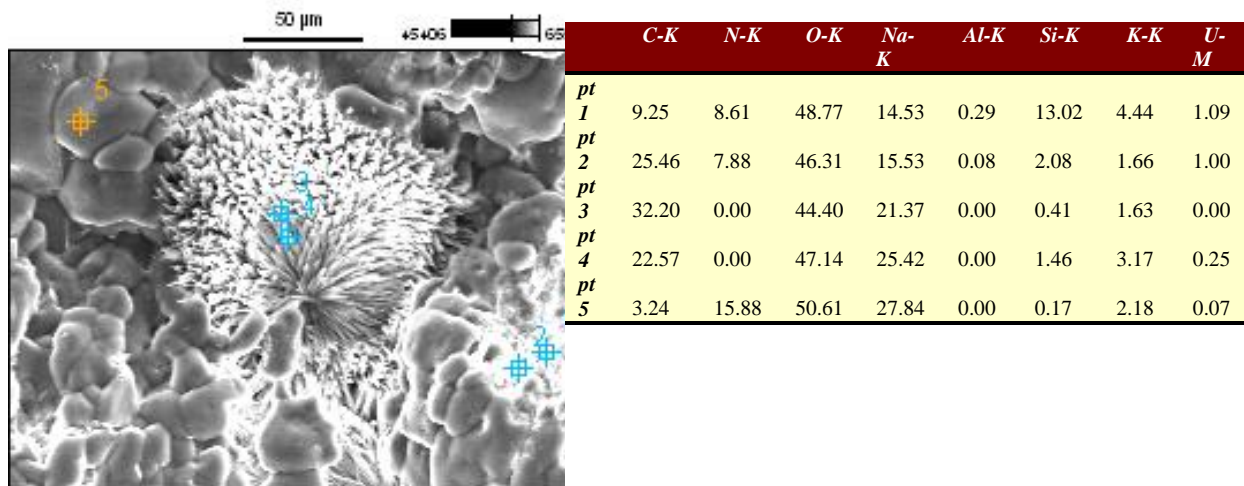


Figure 16. Set # 7 SEM image (after 4 month) and EDS data (right) for centrifuged samples amended with 50 mM HCO₃.

3.3 SEM/EDS Observations of Batches 2 and 3

3.3.1 The effect of bicarbonate (HCO₃) concentrations and addition of calcium (Ca)

During the SEM-EDS analysis, samples prepared using high (50 mM) and low (3 mM) concentrations of bicarbonate were used to evaluate the effect on precipitate morphology with varying times. At low magnification, the samples often showed bright “hot spots” which were treated as points of interest because of potential for relatively high uranium content. Semi-quantitative EDS analysis was used to confirm the increased atomic percentage of uranium. Upon further observation, at increased magnification, several of the uranium-rich areas showed crystal-like structures somewhat consistent with some prior analyses (Figure 17A). Others showed what appeared to be amorphous uranium-bearing areas which were often highly-incorporated deep into the sample, unlike the needle-shaped uranium crystals which appear to be growing on, within, and/or through the rest of the precipitate (Figure 17B).

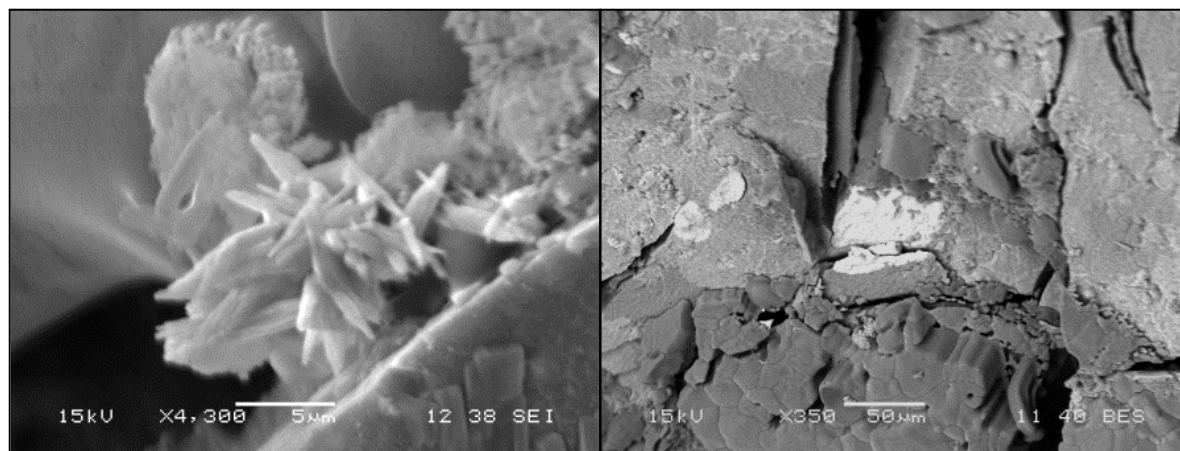
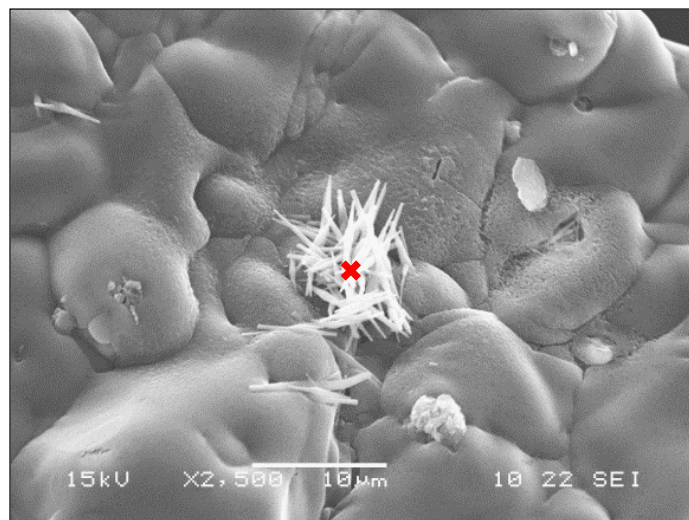


Figure 17. (Batch 2) Uranium-rich regions of the A) 50 mM HCO₃⁻ - 2 day sample and B) 50 mM HCO₃⁻ + 5 mM Ca - 3 month sample.

The samples prepared with high bicarbonate concentrations (50 mM) showed the uranium-dense regions as crystal-like structures or as an amorphous collection. While either or both forms could be present, the majority of 50 mM HCO₃⁻ samples that exhibited hot spots showed them in this crystal-like form. EDS analysis of these areas resulted in uranium atomic percentages that regularly exceeded 1% and often reached up to 10% (Figure 18). Studies on uranium-heavy regions on prior samples (Year-End Technical Report for Project 2, May 2012) rarely reached 1%. The change can most likely be attributed to the increase in uranium to 200 ppm added in more recent precipitate preparation methods.



<i>Element</i>	<i>Wt%</i>	<i>At%</i>
<i>CK</i>	12.11	20.26
<i>NK</i>	08.25	11.83
<i>OK</i>	39.22	49.27
<i>NaK</i>	18.18	15.89
<i>AlK</i>	00.16	00.12
<i>SiK</i>	00.46	00.33
<i>SK</i>	00.14	00.09
<i>ClK</i>	00.17	00.10
<i>UM</i>	20.60	01.74
<i>KK</i>	00.61	00.31
<i>CaK</i>	00.11	00.05
<i>Matrix</i>	Correction	ZAF

Figure 18. SEM image of (Batch 2) 50 mM HCO₃⁻ + 5 mM Ca - 2 month sample

Unlike the high bicarbonate samples, the low bicarbonate (3 mM HCO₃⁻) samples showed no crystal-like uranium-bearing formations. In the few instances where an amorphous uranium-dense area was identified,

the atomic percentage did not exceed 1%. The reduced uranium content is consistent with previous studies (Year-End Technical Report for Project 2, May 2012) that showed an increase in uranium removal from the solution, and therefore into the precipitate, when bicarbonate concentration increased from 3 mM to 50 mM.

Though prior studies showed that the addition of 5 mM of calcium resulted in increased uranium removal from the supernatant, there was no appreciable qualitative difference between samples prepared with and without calcium. A comparison of the EDS analysis performed on equivalent samples saw no correlation between the calcium addition and changes in the spectroscopic data. The backscatter electron capture micrographs of the low bicarbonate, calcium-containing samples did reveal bright high average atomic number “hot spots”, which were thought to be a uranium-rich component of the precipitate. EDS analysis revealed the hot spots to actually be rich in calcium, carbon, and oxygen.

The uranium-bearing needle-like structures formed are of special interest for additional experiments aimed at the characterization of the solid phases.

3.3.2 The effect of sample centrifugation

Batch 3 was prepared with the intention of comparing centrifuged and non-centrifuged samples side-by-side, to study the impact of the preparation process on precipitate morphology. In order to efficiently represent the range of the study, imaging and spectroscopy were limited to the 2 day, 1 month, and 3 month versions of the calcium-containing samples. The lack of uranium-rich sites on the 3 mM bicarbonate samples required analysis to be limited to the high bicarbonate samples.

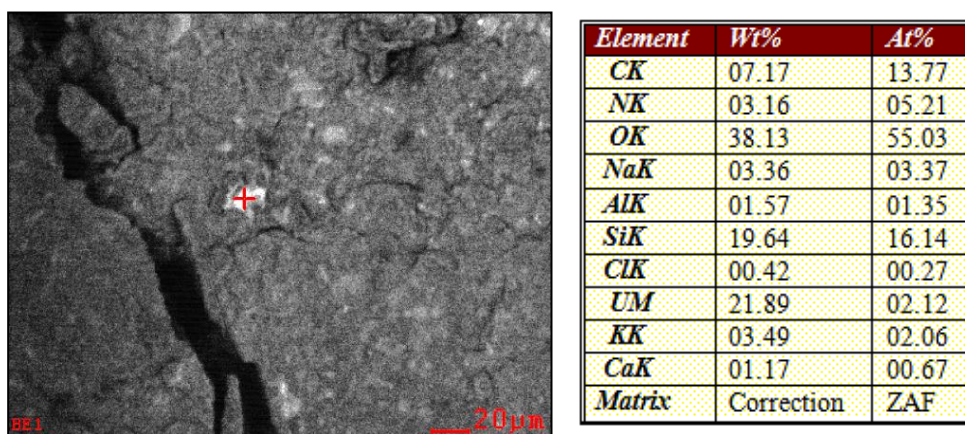


Figure 19. (Batch 3) BEC image and EDS data for 50mM HCO₃⁻+5 mM Ca - 3 month sample (centrifuged) sample

The backscatter electron capture images of the centrifuged samples revealed areas of varying average atomic number as light and dark patches throughout the rough sample surface. The pattern was fairly consistent across the time study. With one exception, EDS revealed no hot spots signaling areas of concentrated uranium (Figure 19). BEC imaging and EDS analysis of the 3 month sample revealed at least one area of increased uranium content, relative to the rest of the sample. In this opportunity, the uranium-bearing precipitates did not show any discernible systematic structure. Increased magnification did not appear to reveal any of the crystal-like structures observed in samples analyzed previously.

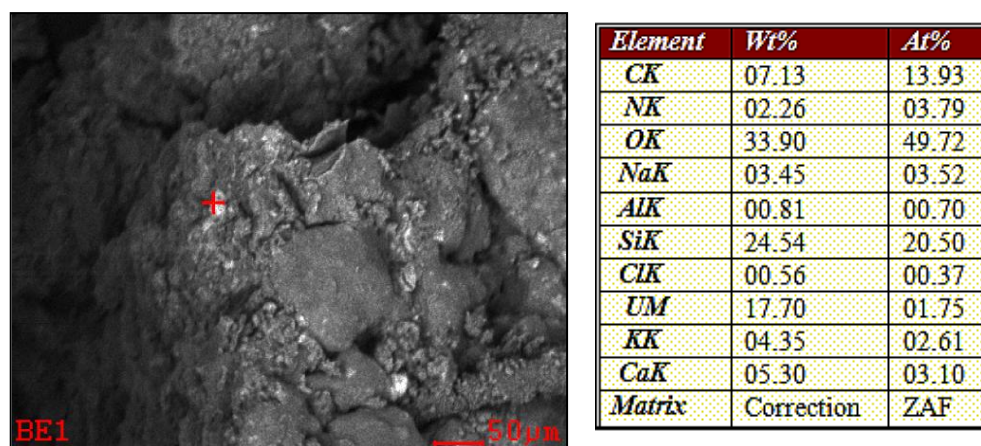


Figure 20. (Batch 3) 50 mM HCO₃+5mM Ca - 3 month (non-centrifuged) sample

The non-centrifuged samples produced images revealing a rough, uneven textured surface. On the two shorter duration samples, backscatter detection revealed some light and dark areas but none with a significant uranium increase. Similar to centrifuged samples, only the 3 month, non-centrifuged precipitate showed “hot spots” with localized uranium atoms (Figure 20). Further magnification of these uranium-rich sites showed no sign of crystal formation.

The SEM and EDS data provided little reason to warrant selecting whether or not to centrifuge samples in future experiments. The decision not to centrifuge future samples is supported by related experiments outlined in the 3.1 section of this report showing that centrifugation during preparation of precipitates results in an increased uranium concentration in the supernatant solution (Figure 1).

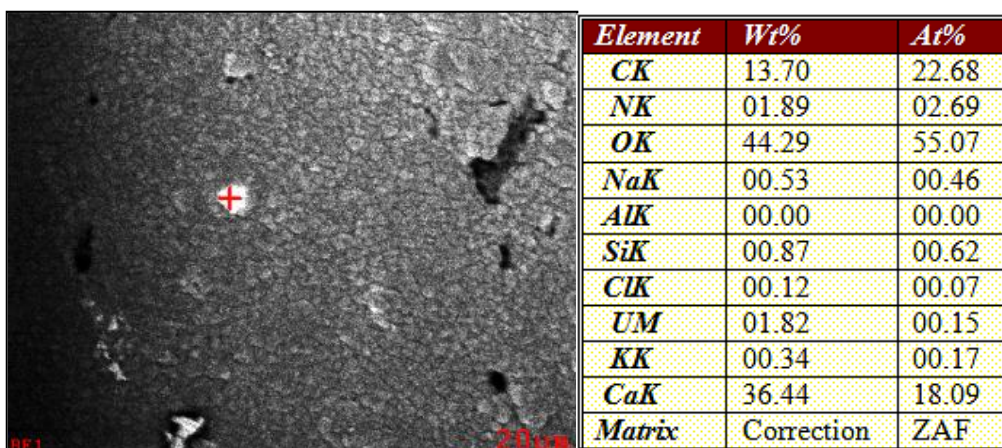


Figure 21. (Batch 3) 50 mM HCO₃+5 mM Ca - 1 month (non-centrifuged) sample BEC image and EDS data

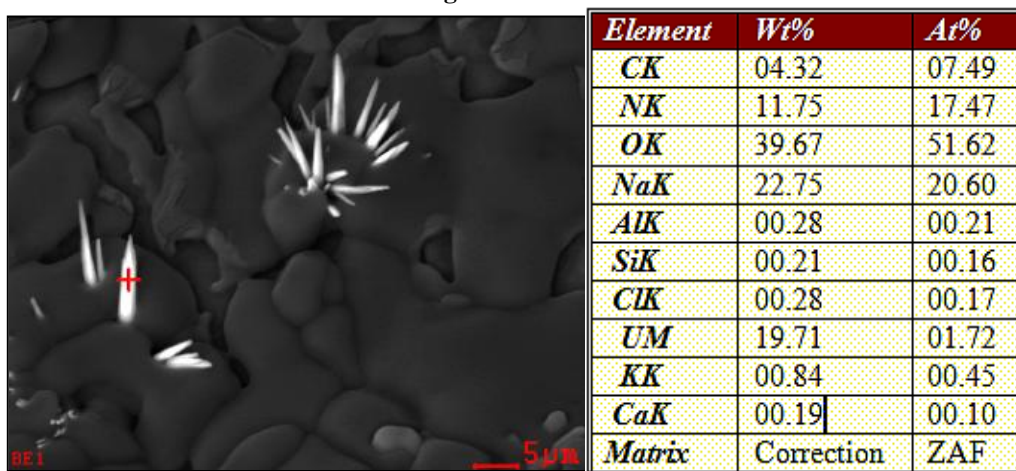


Figure 22. (Batch 2) 5 0mM HCO₃+5 mM Ca - 1 month sample BEC image and EDS

Equally as important as the effect of centrifugation, the consequence of changing the preparation method for batch 3 can be evaluated by comparison with equivalent samples from batch 2. There is a stark contrast regarding the surfaces of samples from the two different batches. The smooth Si-rich areas present in batch 2 samples are nowhere to be found in batch 3 (**Error! Reference source not found. & REF_Ref345688510 \h * MERGEFORMAT Error! Reference source not found.**). This difference is presumably due to the frequent vortexing of the primary solution before taking homogeneous samples to prepare dried precipitates. Most obvious in this comparison is that very few points of high uranium content were found in batch 3’s non-centrifuged samples. The precipitates produced in batch 3 presented no signs of crystalline uranium where their batch 2 counterparts showed both crystal-like and amorphous uranium-rich components. This result merits the decision to forgo use of the batch 3 preparation methodology.

3.3.3 Morphological changes with time

The evolution of sample morphology with increased time in solution for the high bicarbonate precipitates is similar for samples prepared with and without calcium. Early-on in the experiment, the uranium-rich, needle-like forms appear to grow on, in, and through the precipitate (Figure 23 & Figure 24 A-C). As the amount of time in solution increases, it appears as though the smooth Si-rich component that coats the precipitate increasingly overtakes the uranium-bearing solids. After 3 months, rather than the crystal-like structures found previously, uranium-rich areas appear as amorphous areas with no discernible structure (Figure 23D & Figure 24D). The backscatter imaging of Figure 25 shows the high level of incorporation into the precipitate after 3 months in solution. Based on the crack in the material, it is clear that the uranium-dense region of this sample extends into the sample.

Further analysis is required to gauge structural and mineralogical characteristics of the precipitates, which is planned to be evaluated by means of X-ray diffraction.

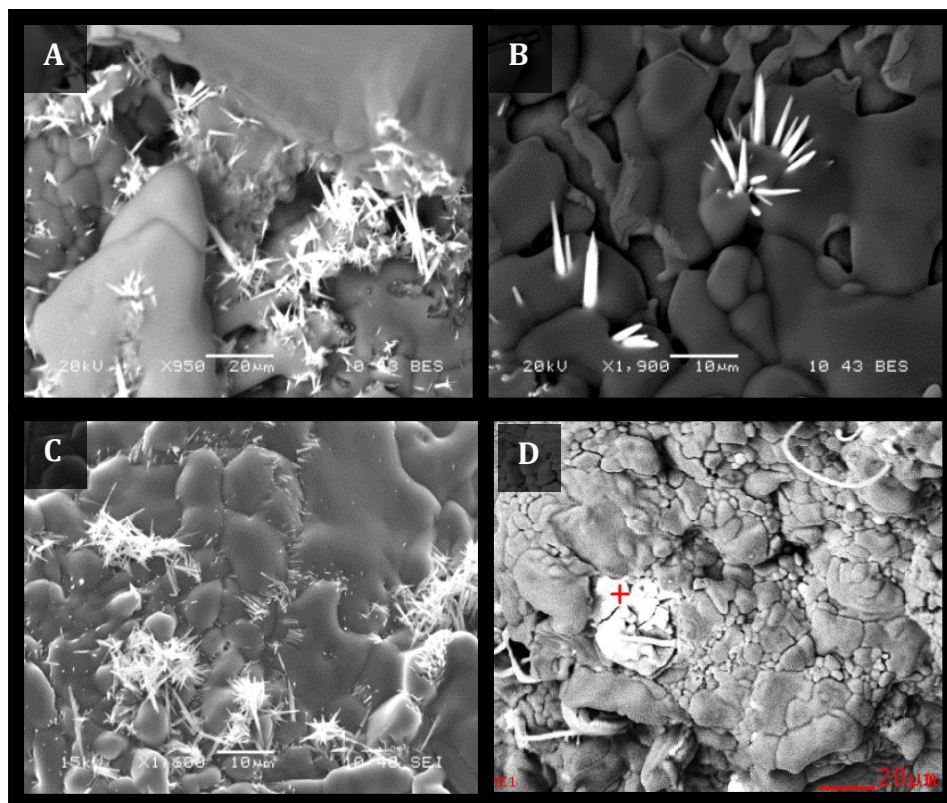


Figure 23. Precipitates formed from batch 2 solutions containing calcium (5 mM) and high bicarbonate (50 mM) concentration after 2 weeks (A), 1 month (B), 2 months (C), and 3 months (D).

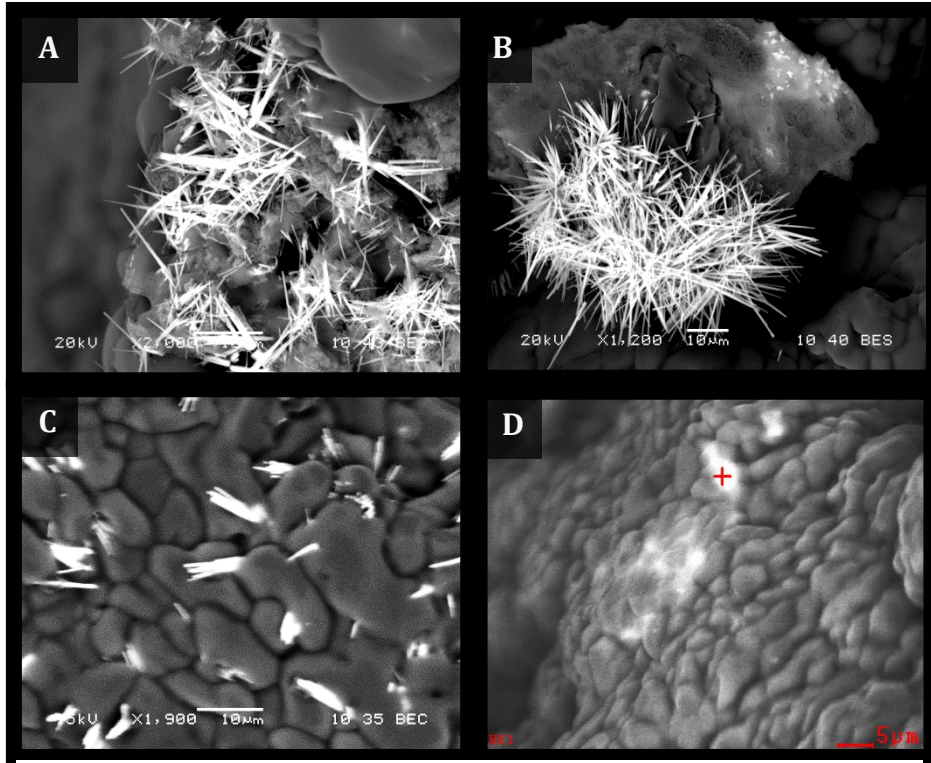


Figure 24. Precipitates formed from batch 2 solutions containing high bicarbonate (50 mM) concentration (no calcium) after 2 weeks (A), 1 month (B), 2 months (C), and 3 months (D)

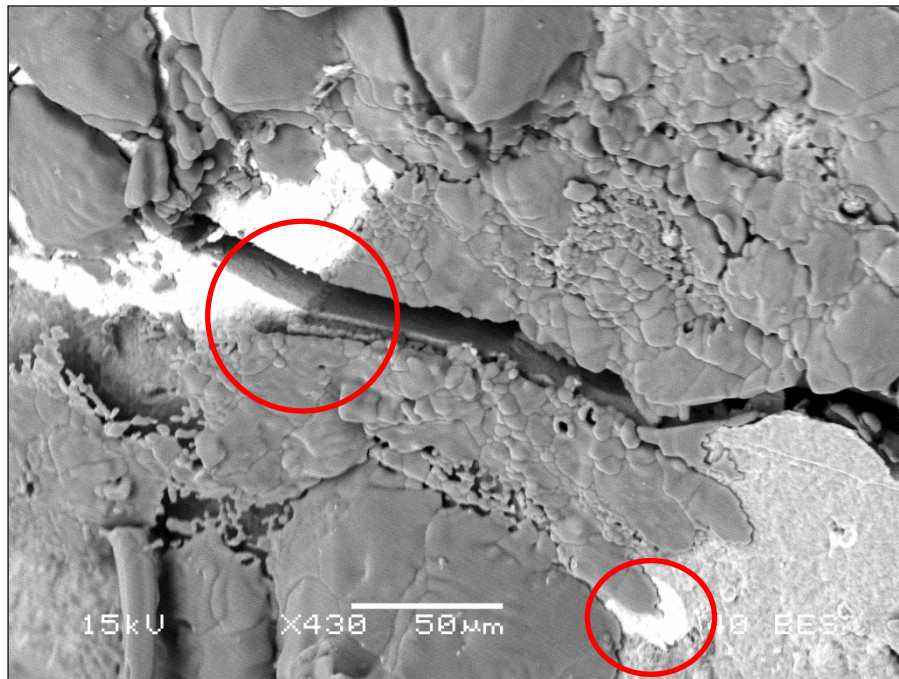


Figure 25. BEC image of a uranium-rich region of a 50 mM HCO₃ + 5 mM Ca - 3 month sample

4.0 CONCLUSION

Uranium-bearing precipitates prepared with and without Ca and with “high”(50 mM) and “low” (3 mM) concentrations of bicarbonate were evaluated by mean of SEM/EDS analysis. The experiments were also designed to test the effect of the centrifugation step during sample preparation procedures on the morphology of the precipitates. A comparison of the 50 mM and 3 mM bicarbonate samples definitively showed that the expected uranium-rich crystal forms were exclusive to samples prepared with a high bicarbonate concentration. Similarly, the amorphous uranium-dense areas were far more prevalent in the high bicarbonate samples.

Though the EDS comparison of the centrifuged and non-centrifuged samples provided little insight into the differences between the two, the evaluation of the supernatant solutions of the two samples showed a distinct increase in uranium content with centrifugation, signifying, *ipso facto*, a decrease of uranium in the precipitate. The loss of uranium from the precipitate not being ideal, it was concluded that the centrifugation step was not suitable for use in future experimentation. The comparison of the individual solution method analyzed in a sacrificial mode applied for batch 2 sample preparation, and the single primary "mother solution" method, used for batch 3, showed a stark contrast. The most noticeable difference included the scarcity of crystalline-like areas with high uranium content in samples prepared by the latter. This unambiguous difference allowed it to be decided that the batch 2 sample preparation procedure was the best process for future use. Together, these experimental results allow for optimization of a sample preparation methodology that can be used as the project continues forward.

The time studies used to study the evolution of the precipitate with increasing aging time in solution saw samples bearing high-uranium crystal-like formations early on and amorphous uranium-rich areas at the later period. Supplementary analyses, by methods such as XRD, are ongoing to further the understanding of the changes occurring with time. Experiments designed to foster development of a clearer understanding of the structure and mineralogy of the precipitate are also ongoing.

5.0 ACKNOWLEDGEMENT

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