

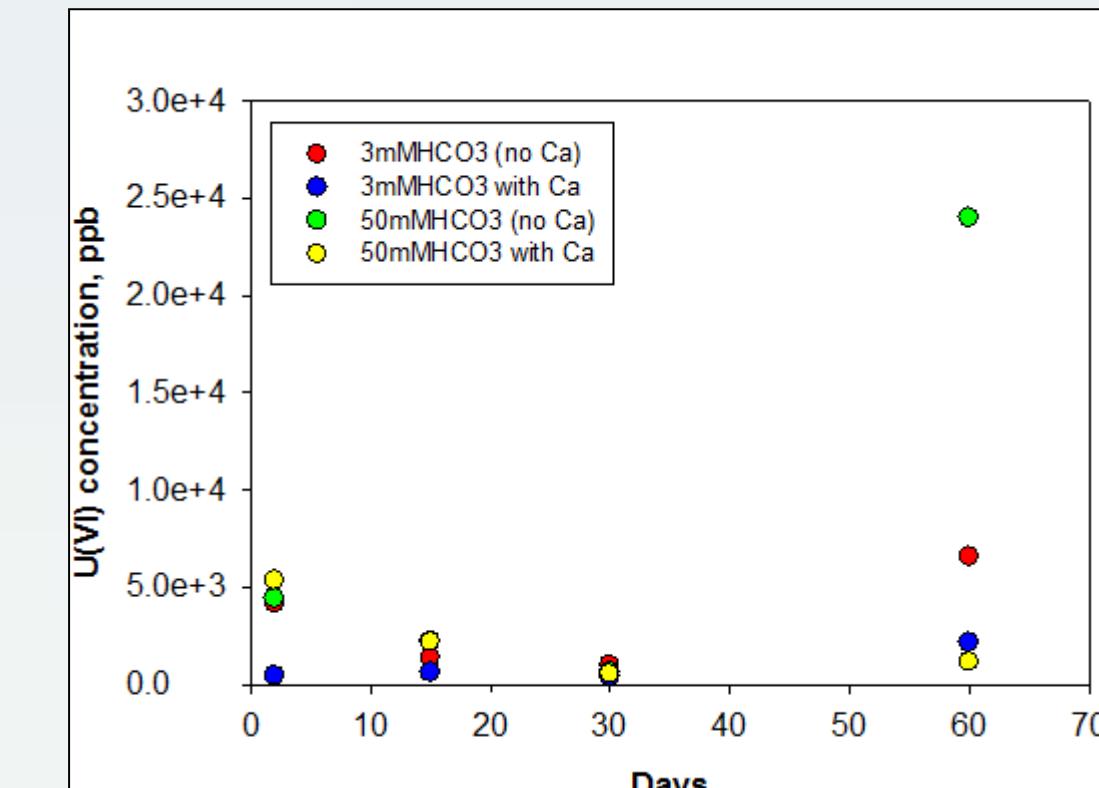
# Analysis of Morphological Changes of Uranium-Bearing Precipitates Over Time by SEM/EDS



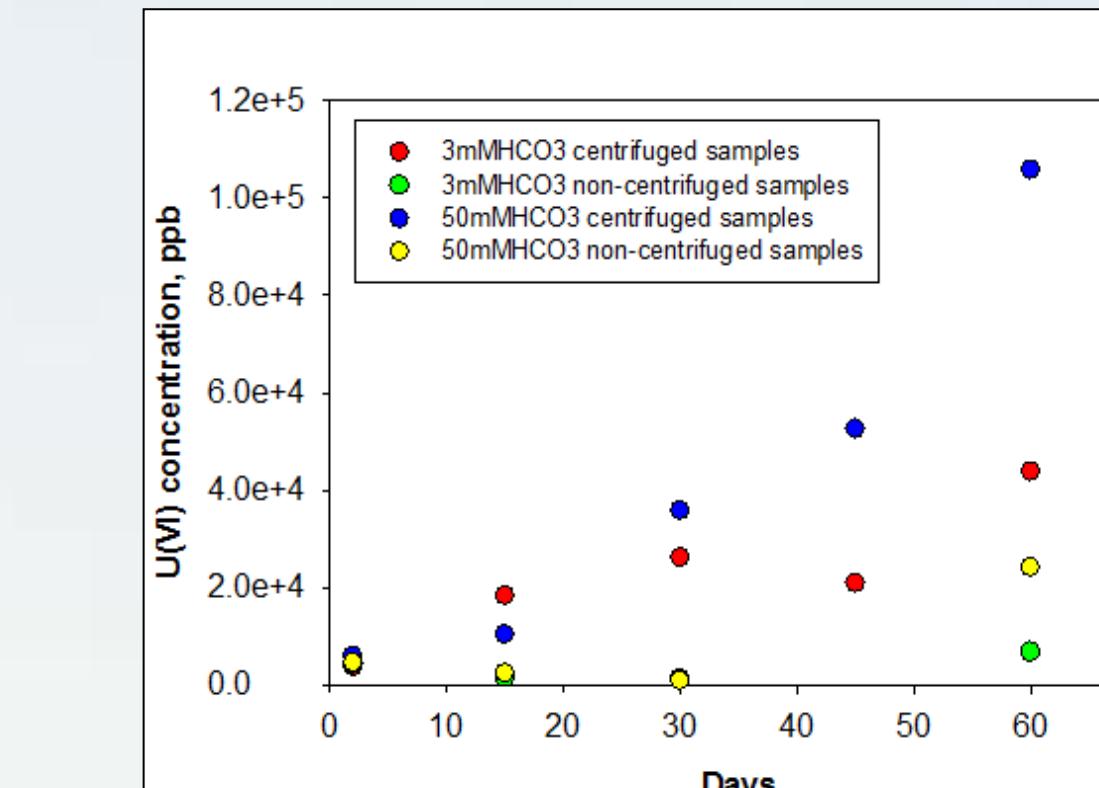
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## Background

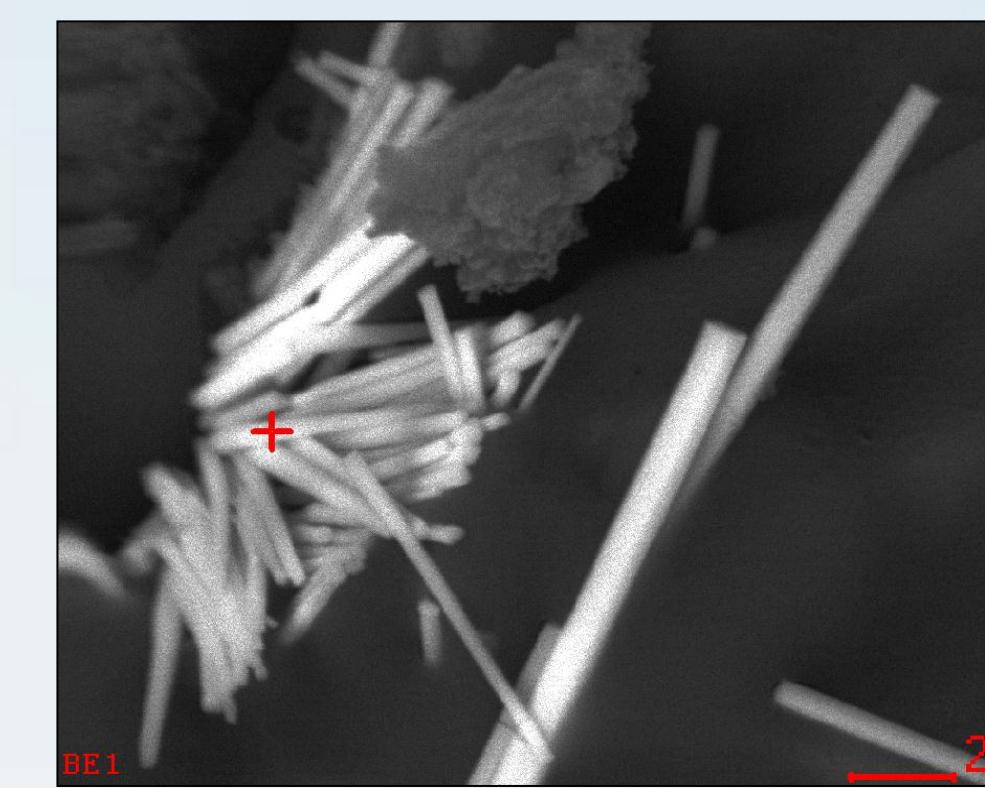
- Hanford, WA has seen copious amounts of contamination from leakage and spillage of radiological waste
- Uranium is a primary vadose zone contaminant in the Hanford 200 area and potential future source of groundwater contamination to the Columbia River
- Remediation efforts include employing novel technologies to sequester the flow of radiological contaminants
  - In Situ* subsurface pH manipulation using NH<sub>3</sub> gas



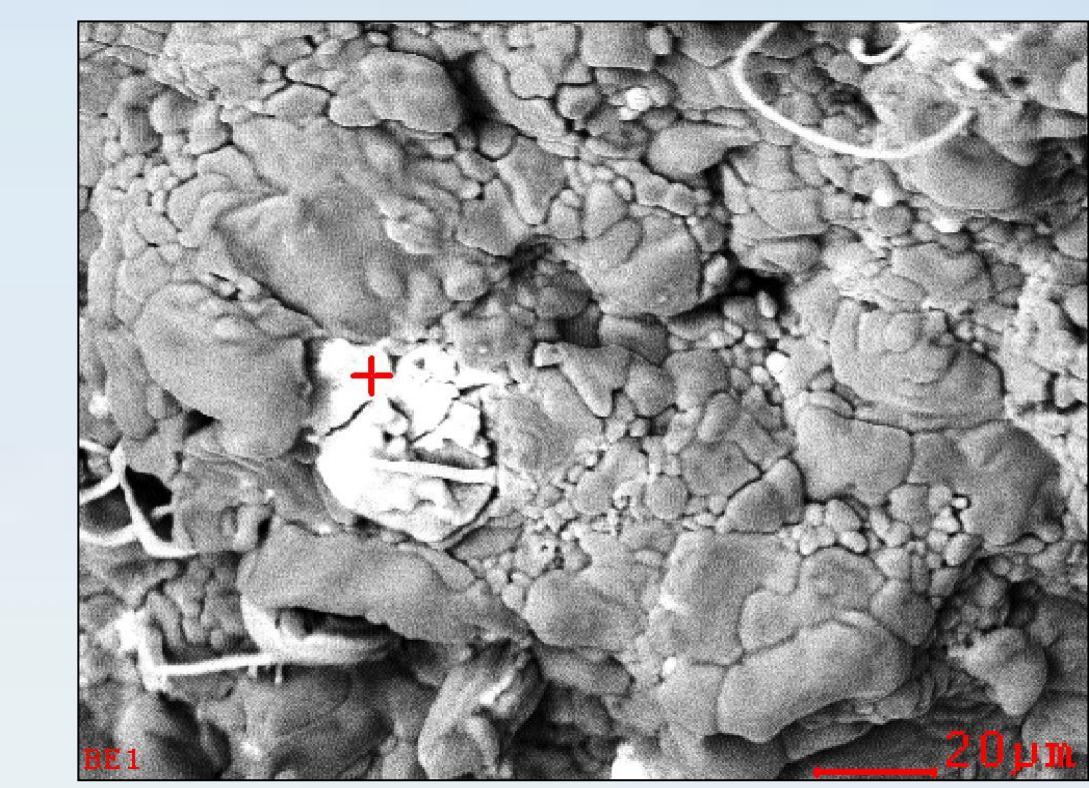
Effect of sample centrifugation on the concentration of U(VI) in the supernatant solution



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



SEM & EDS of precipitate from 50 mM bicarbonate (no calcium) after 1 month in solution



SEM & EDS of precipitate from 50 mM bicarbonate + 5 mM calcium after 3 months in solution

## Results

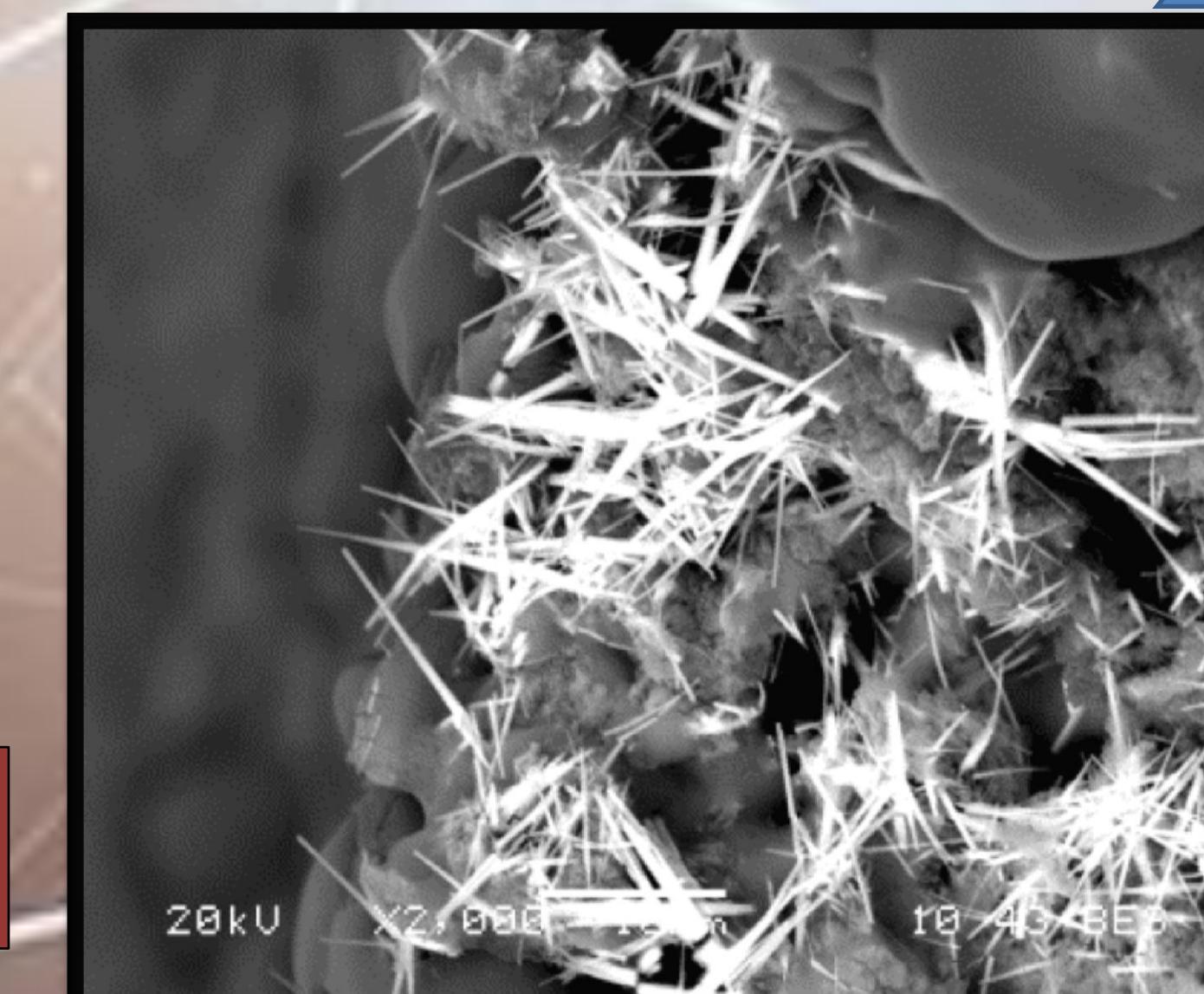
Element	Wt%	At%
CK	10.54	17.23
NK	07.70	10.79
OK	42.80	52.56
NaK	18.50	15.81
AlK	00.28	00.20
SiK	02.24	01.57
ClK	00.02	00.01
UM	17.12	01.41
KK	00.68	00.34
CaK	00.13	00.06
Matrix	Correction	ZAF

Element	Wt%	At%
CK	01.85	06.62
NK	03.44	10.55
OK	14.47	38.83
NaK	01.49	02.78
AlK	00.53	00.85
SiK	06.69	10.23
SK	00.33	00.44
ClK	00.95	01.15
UM	52.93	09.55
KK	17.13	18.81
CaK	00.19	00.20
Matrix	Correction	ZAF

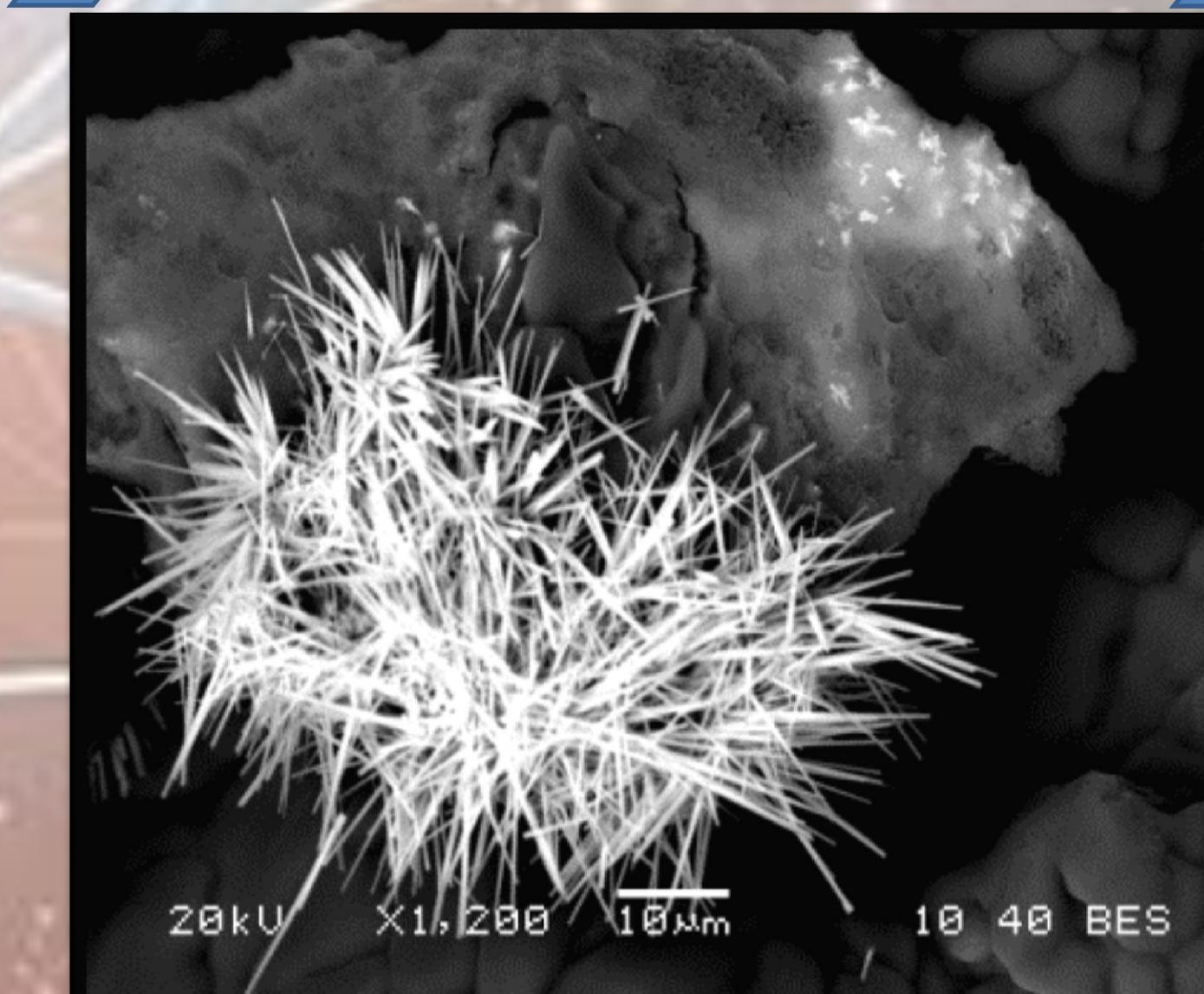
## Objectives

- Characterization of uranium bearing precipitates produced by the NH<sub>3</sub> injection method
  - Optimize the sample preparation procedures for future studies
  - Evaluation of the effect time in solution has on precipitate morphology

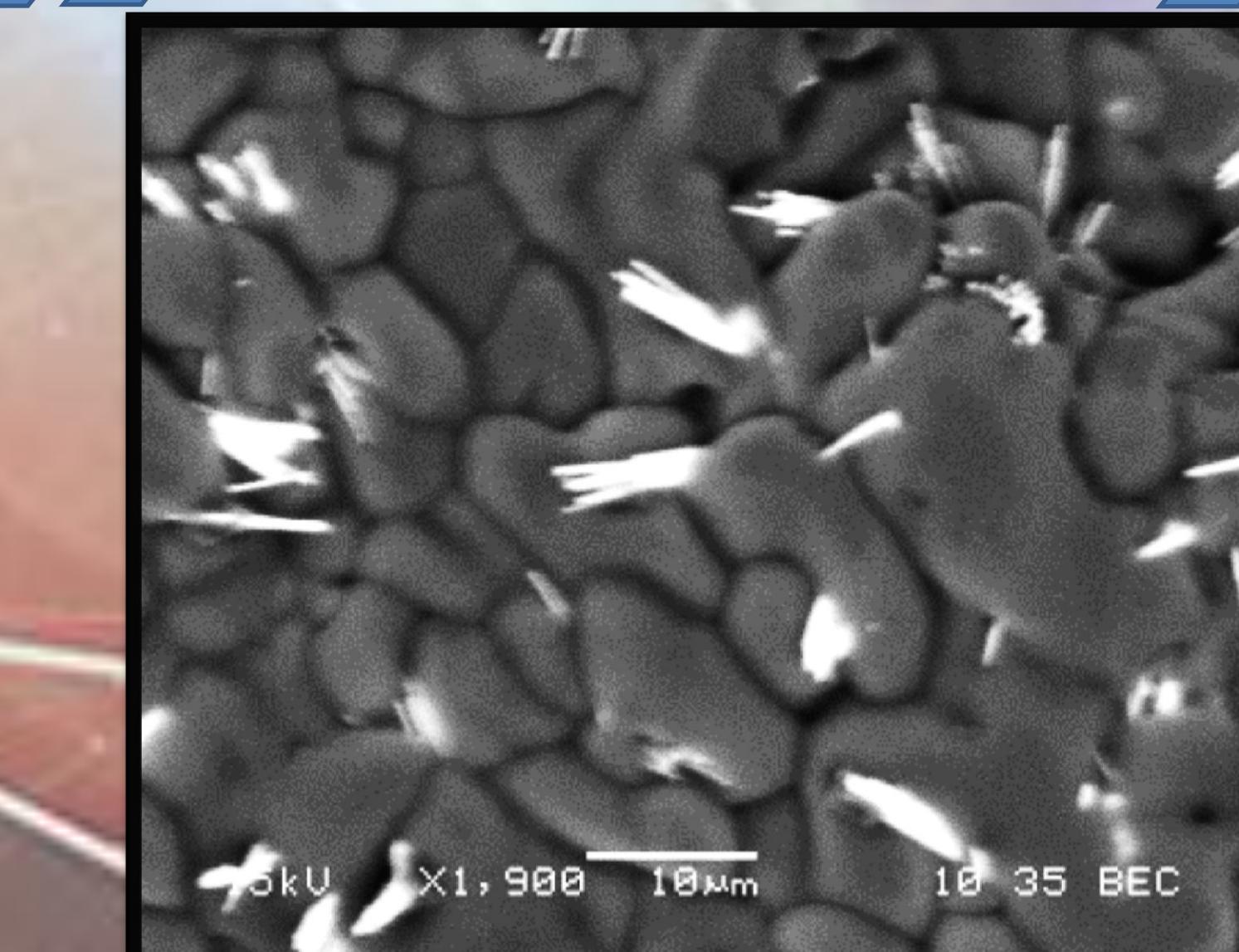
2 weeks



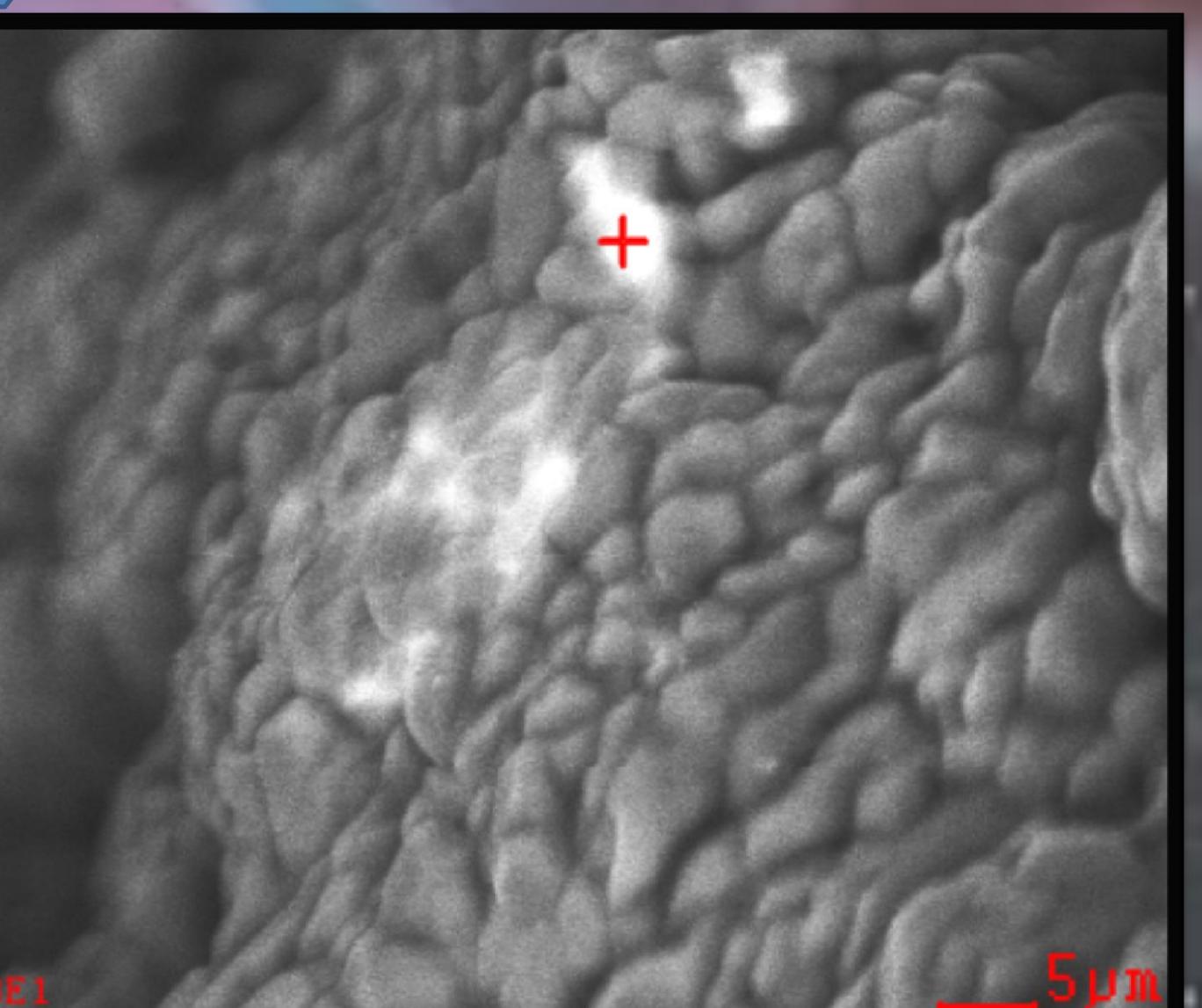
1 month



2 months



3 months



## Methodology

- Synthetic pore water prepared to mimic the Hanford Site's 200 Area vadose zone conditions
  - Solutions are amended with 200ppm of commercially available uranyl nitrate stock solution
- Variables changed to test their impact on precipitate morphology
  - Centrifuging vs. without centrifuging
  - Low (3mM) vs. high (50mM) bicarbonate [HCO<sub>3</sub><sup>-</sup>]
  - With vs. without calcium
- Remediation method is applied and precipitate dried
- Supernatants were analyzed by kinetic phosphorescence analyzer (KPA) for uranium (VI) content
- Dried samples mounted and analyzed by scanning electron microscopy and energy dispersive spectroscopy (SEM/EDS)

Timelines showing evolution of U-rich areas on precipitates, prepared using with (L) and without (R) calcium, over 3 months

## Discussion

- The comparison of SEM micrographs on centrifuged and non-centrifuged samples showed little differentiation between the two
  - The KPA analysis of the supernatants solutions showed that uranium content increased with centrifugation
- The crystal-like and amorphous uranium-rich phases were exclusive to the samples prepared with high bicarbonate concentrations
  - No appreciable difference between with and without calcium
- Over 3 months, uranium "hot spots" changed from the crystal-like structures present on the 2 day sample to the amorphous uranium-rich areas seen in the 3 month samples

## Conclusions

- Qualitative analysis of uranium-bearing precipitates suggested sample preparation procedures would best be limited to high bicarbonate concentration, with calcium, and without centrifugation
- Further analysis to characterize the U-bearing phases are ongoing
  - Geochemical modeling software for uranium speciation
  - XRD, XPS, FT-IR/RAMAN

## Acknowledgements

DOE Fellow Ashley Wardlow, Dr. Ravi Gudavalli, Thomas Beasley of the Florida Center for Analytical Electron Microscopy, Dr. Leonel Lagos, and the DOE-FIU Science & Technology Workforce Development Program