Characterization of the Uranium-Bearing Products of Novel Remediation Technologies

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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 is a potential future source of groundwater contamination to the Columbia River
- Remediation efforts include employing novel technologies to sequester the flow of radiological contaminants such as *in situ* subsurface pH manipulation using NH_3 gas
    - Injection of ammonia gas causes an increase pore water pH inducing the dissolution of soil minerals into the aqueous system. The subsequent return to natural pH conditions is believed to result in the recrystallization of soil minerals and the co-precipitation of uranium

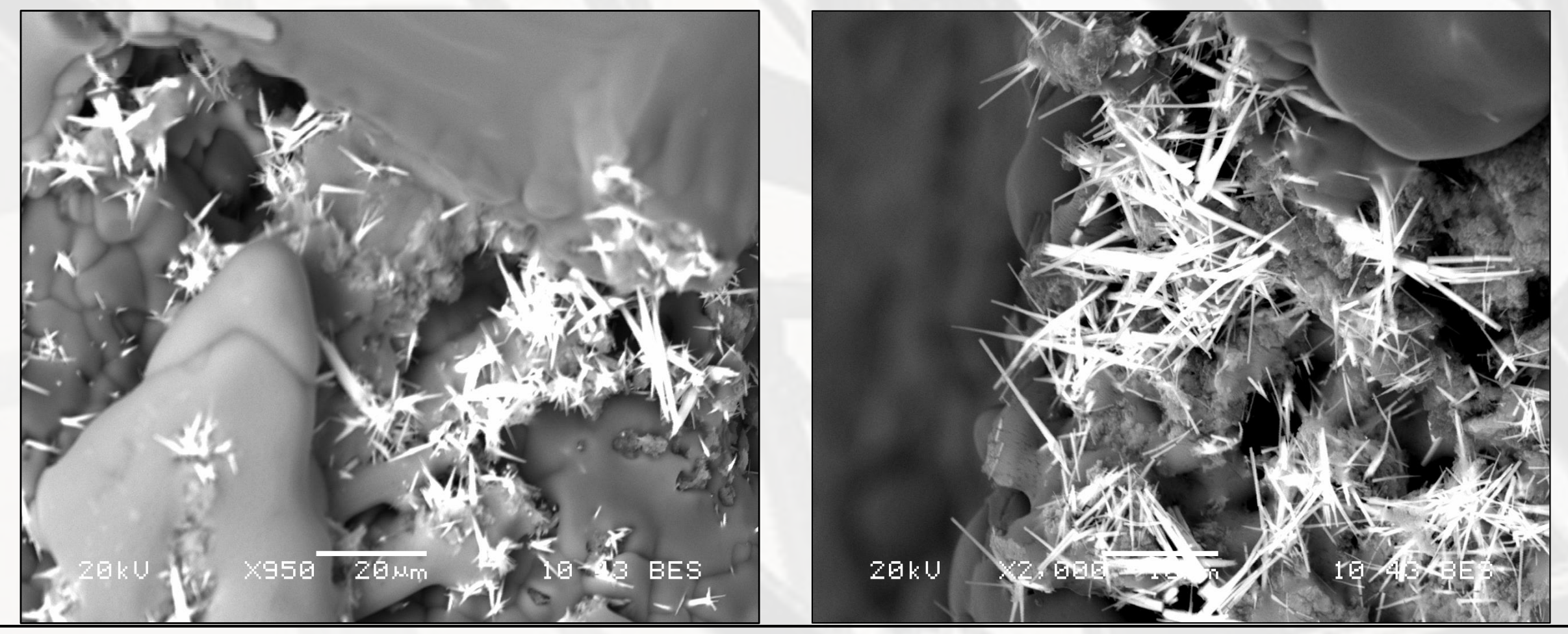
Objectives

- Characterization of uranium bearing precipitates produced by the NH_3 injection method
    - Deduce how uranium is incorporated into the product
    - Discern the chemical formula for the uranium-based phases

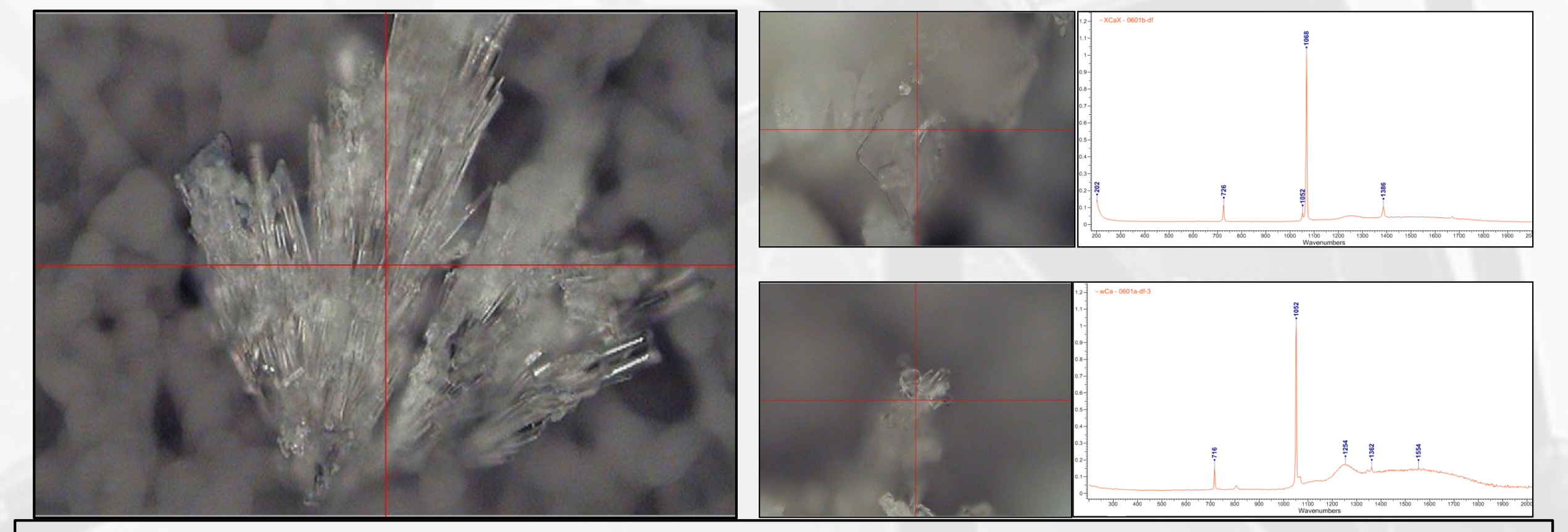
Methodology

- Samples prepared from a solution prepared to mimic conditions observed at the Hanford 200 Area
    - Varying calcium and bicarbonate concentrations
    - Previous studies looked at the effect of time in solution
- Dried samples analyzed by SEM-EDS
    - BEC mode and EDS for uranium identification
- Micro-Raman Spectroscopy performed to attempt to identify the phases of the sample by comparison to reported spectra
- The samples were pulverized and mounted to a custom designed plastic sample holder for XRD analysis
    - Method blanks were prepared for both samples (*sans uranium*)
    - Comparisons were done using *Match!* and references from ICDD powder diffraction files

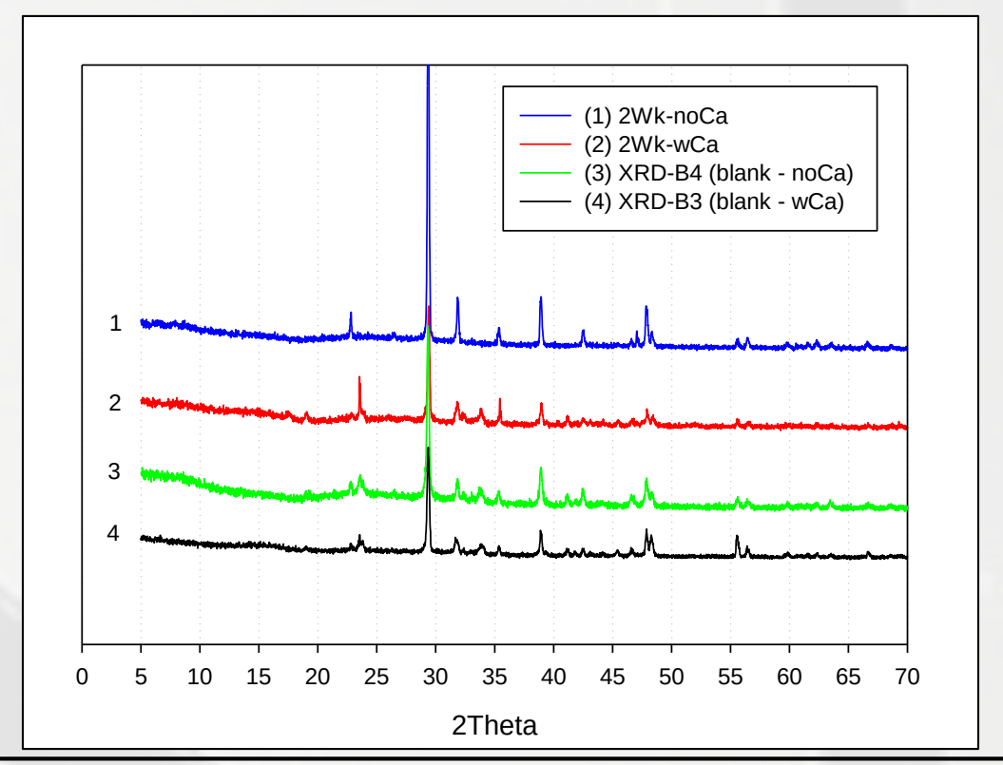
Results



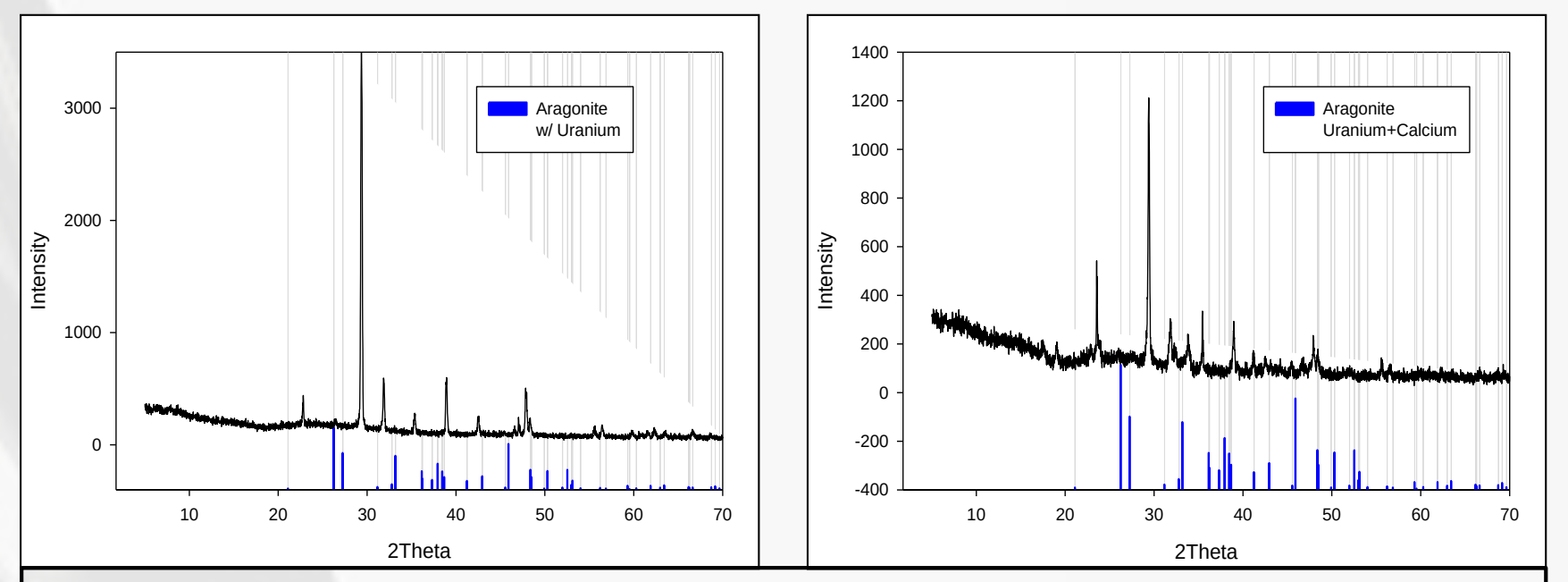
Backscatter SEM images of samples prepared with (L) and without (R) calcium showing the U-rich crystal-like forms



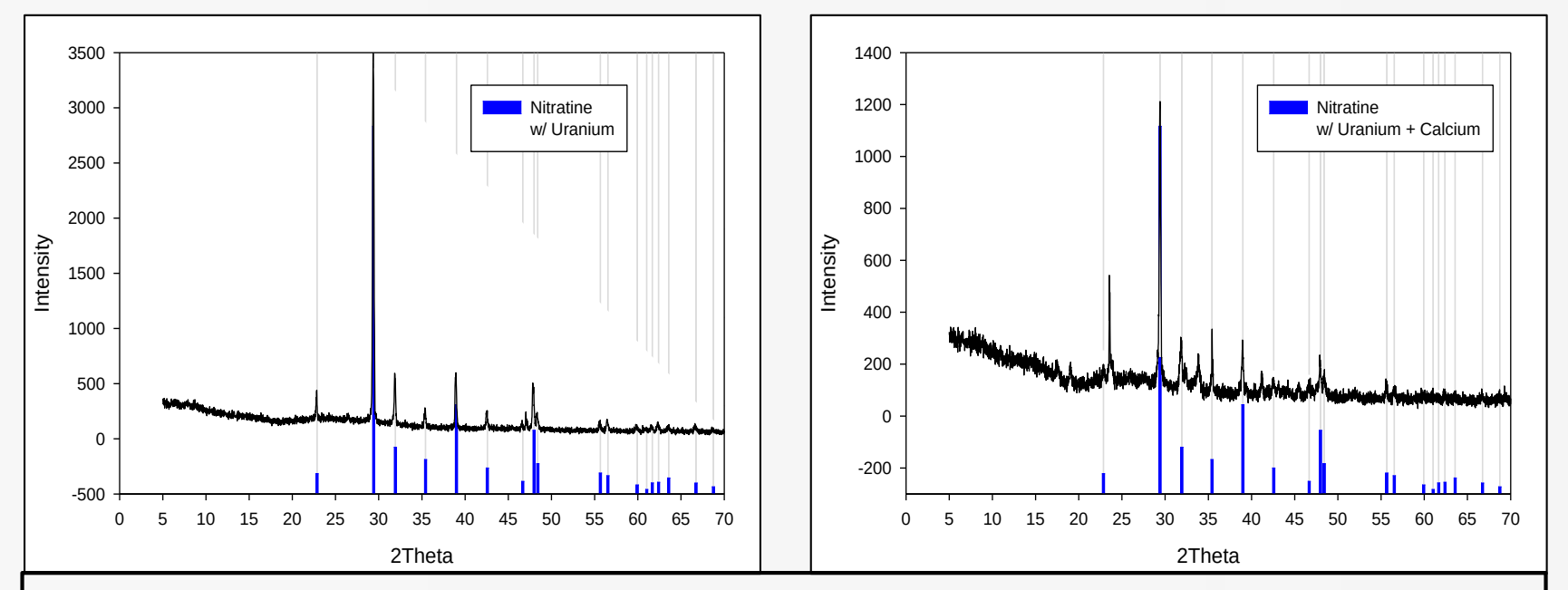
Micro-Raman image and spectra for samples prepared with (top) and without (bottom) calcium



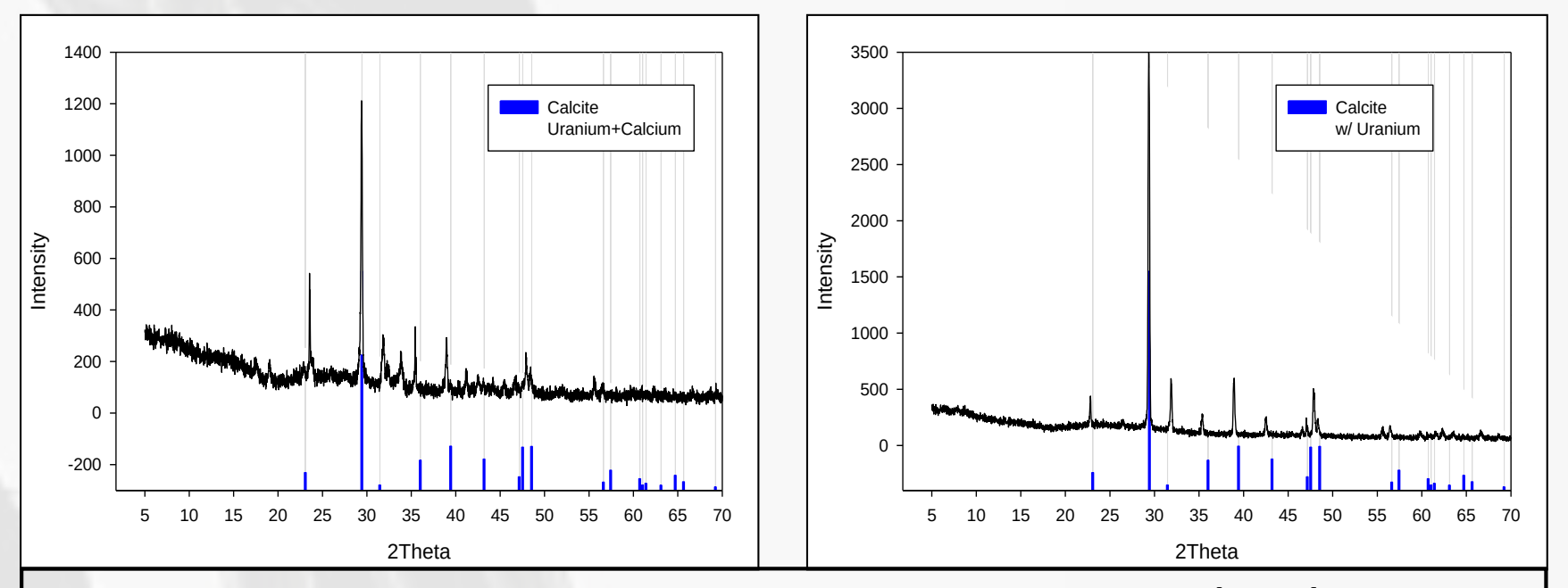
Comparison of XRD patterns for samples prepared with and without calcium & corresponding U-free blanks



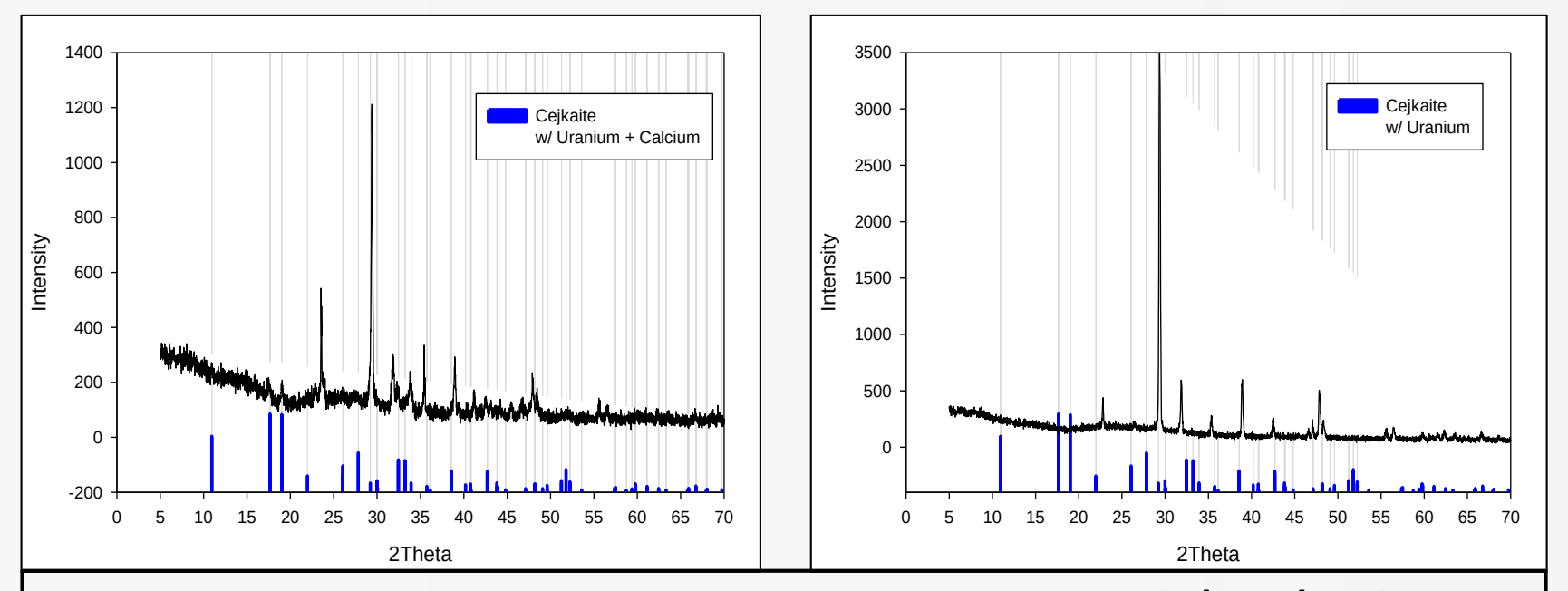
Comparison of XRD patterns for uranium-containing sample ($^{w}/$ & $^{w}/_{o}$ Ca) to the pattern for aragonite ($CaCO_3$)



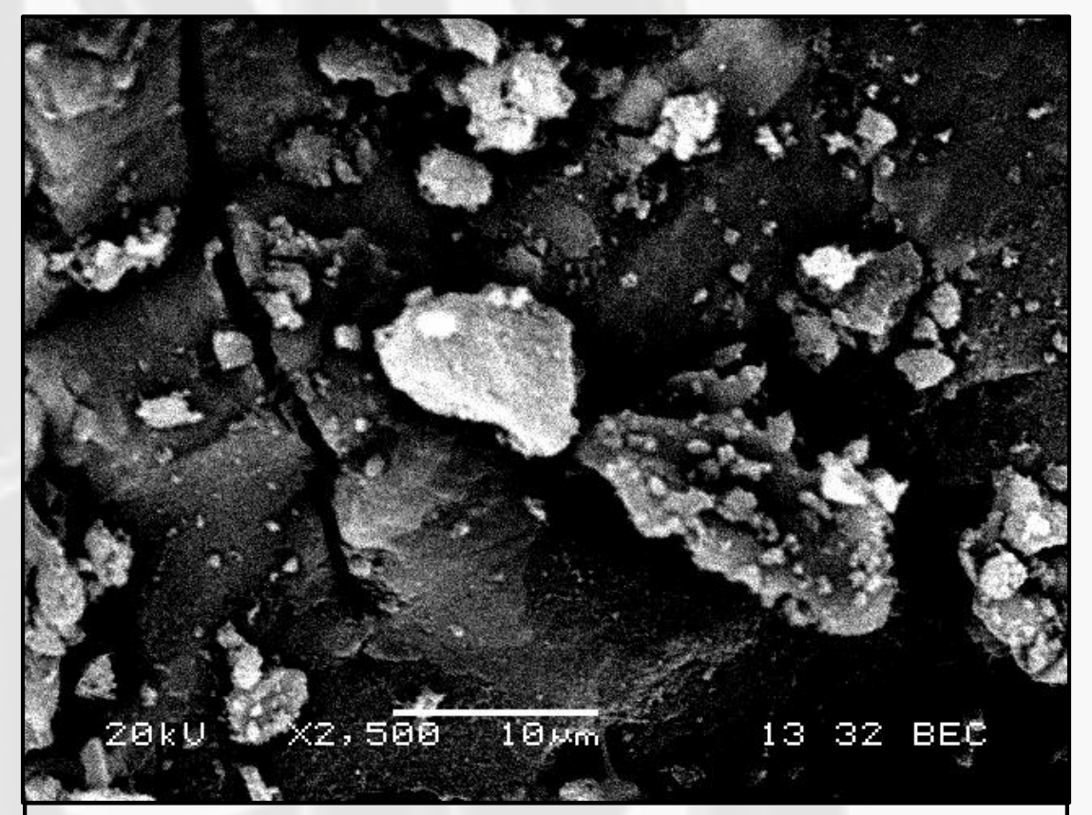
Comparison of XRD patterns for uranium-containing sample ($^{w}/$ & $^{w}/_{o}$ Ca) to the pattern for nitratine ($NaNO_3$)



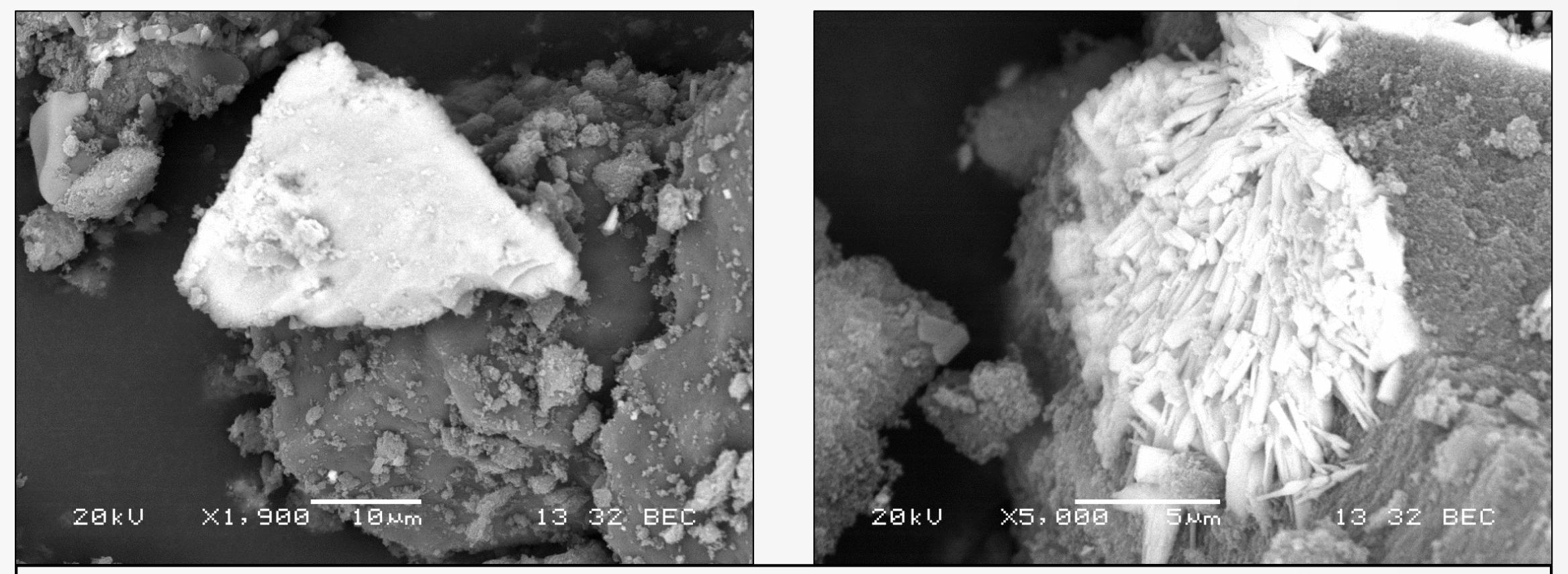
Comparison of XRD patterns for uranium-containing sample ($^{w}/$ & $^{w}/_{o}$ Ca) to the pattern for calcite ($CaCO_3$)



Comparison of XRD patterns of uranium-containing sample ($^{w}/$ & $^{w}/_{o}$ Ca) to the pattern for cejkaite ($Na_4(UO_2)(CO_3)_3$)



SEM image of the pulverized $^{w}/$ Ca sample after XRD analysis (*no uranium identified*)



SEM image of the uranium-rich areas of the pulverized $^{w}/$ Ca sample after XRD analysis *(identified via EDS)*

Discussion/Conclusions

- SEM, in backscatter electron capture mode, of dried samples allowed areas of higher average atomic number to be identified. EDS analysis supported the prediction that these areas would have an elevated concentration of uranium.
- Micro-Raman Spectroscopy of the samples revealed bands, at 800 cm^{-1} & 1000 cm^{-1}, which are consistent with reported values/ranges for the stretches of $(UO_2)^{2+}$ and $(CO_3)_2^{-}$, respectively.
- Powder XRD analysis confirmed the presence of crystalline material in the precipitate.
    - *Match!* software and PDF comparisons suggest that nitratine ($NaNO_3$), the most prominent peak of which occurs at $2\Theta = 29$, overwhelmingly dominated all samples.
    - Speciation predictions in similar studies suggested that calcium carbonate forms (i.e.: calcite, vaterite, & aragonite) would be produced but comparisons of their most prominent peaks showed little to no match.
    - Though it was not included in predictions, cejkaite ($Na_4(UO_2)(CO_3)_3$) has emerged as a potential identity of the uranium-bearing phase that was visualized by SEM/EDS.
        - Significant matches for the 2 most prominent peaks ($2\Theta \approx 17.5$ & 19) and a potential match for the 3rd ($2\Theta \approx 11$) obscured in elevated noise early in the pattern.
- SEM-EDS analysis (post-XRD) confirmed presence of uranium-rich phases in the sample with calcium. *None detected in the sample without calcium*.

Future

- The characterization of the major U-phases was hindered by the contribution of unexpected amounts of nitratine formed.
    - The sample preparation will be modified to minimize sodium content and increase uranium concentrations

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