

**Contract No:**

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# Characterization of the Environmentally Induced Chemical Transformation of UF<sub>4</sub>

Matthew Wellons, Michael DeVore II, Eliel Villa-Aleman, Michael Summer, Ross Smith, Christopher Klug (NRL), L.A. Giannuzzi (EXLO), Justin Felder (USC), Hanno zur Loye (USC)

Project ID # LDRD-2016-00031

## Overview & Relevance

### Timeline:

Project start date: October 1, 2015  
Project end date: September 30, 2017 (continuation funding)  
Percent complete: 95%

### Barriers Addressed:

Efforts resulted in advancements on the understanding of UF<sub>4</sub> fate within the environment and potential progeny due to environmental exposure. This has strengthened SRNL's capability to meet USG nonproliferation R&D and customer microanalysis needs.

### Budget:

Total project funding: \$345K  
Funding received in FY16: \$220K  
Total funding planned for FY17: \$125K

### Partners:

- Naval Research Laboratory
- University of South Carolina
- L.A. Giannuzzi & Associates LLC

### Overall Objective:

Develop an initial chemical and structural basis for understanding UF<sub>4</sub> hydrolysis in the environment.

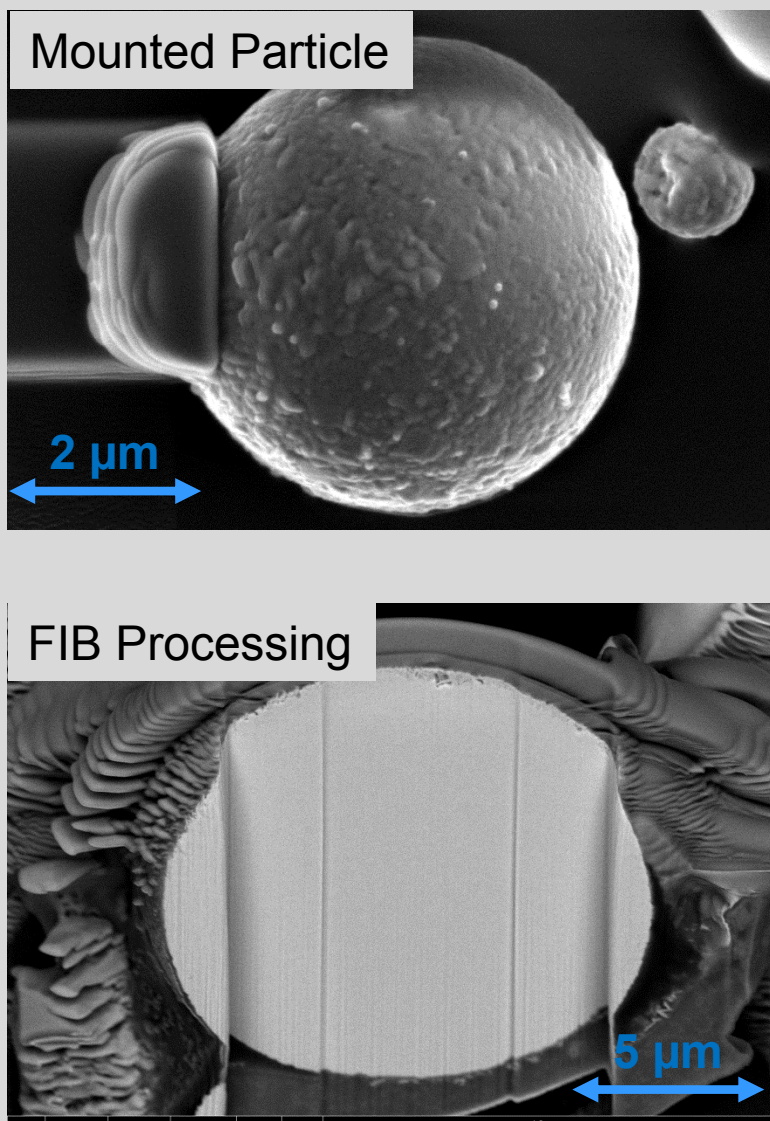
### Objectives in this reporting period:

- <sup>19</sup>F NMR, Raman, and IR spectroscopic characterization various UF<sub>4</sub> hydrates
- TEM/EELS microanalysis of UF<sub>4</sub> hydrate solids
- Reporting/publications of technical results

## Approach

A key challenge with nuclear safeguards environmental sampling is identification of the materials post release due to subsequent chemical reactions with ambient water and oxygen. Uranium Tetrafluoride (UF<sub>4</sub>) is of interest as it is an intermediate in both the upstream and downstream portions of uranium feedstock and metal production processes used in nuclear fuel production. Minimal published research exists relating to hydrolysis of UF<sub>4</sub>, with previous efforts focused on characterization of bulk quantities, laboratory syntheses, and industrially driven pyro hydrolysis processes. The FY16 efforts were dedicated to in-situ Raman spectroscopy and X-ray diffraction characterization of UF<sub>4</sub> during exposure to various relative humidity conditions. The effort mapped several hydrolysis reaction pathways and identified both intermediate, and terminal progeny species.

To better probe the chemical and structural transformations, FY17 efforts utilized advanced characterization techniques such as Electron Energy Loss Spectroscopy (EELS) coupled to Transmission Electron Microscopy (TEM) to probe the elemental and chemical speciation of partially hydrolyzed UF<sub>4</sub> at the nanoscale. Additionally solid state <sup>19</sup>F NMR was initiated to characterize the macroscale hydrolysis induced chemical changes. For both characterization methods, collaborators outside of SRNL were engaged for their respective expertise and capability. These measurements were supplemented with techniques such as Raman and FT-IR spectroscopy to structurally characterize a series of UF<sub>4</sub> hydrates with differing water content.



## Spectroscopy of UF<sub>4</sub> Hydrates

A series of UF<sub>4</sub> hydrate polymorphs were characterized to elucidate potential structural and spectral relationships. During the course of the investigation UF<sub>4</sub>·2.5H<sub>2</sub>O was synthesized and characterized by XRD at SRNL. USC collaborators provided two UF<sub>4</sub> hydrates synthesized by mild hydrothermal reduction which were UF<sub>4</sub>·0.33(H<sub>2</sub>O) and U<sub>3</sub>F<sub>12</sub>(H<sub>2</sub>O). All three materials were characterized via Raman and FT-IR spectroscopy, and compared with anhydrous UF<sub>4</sub>.

The O-H stretching region (3200-3600 cm<sup>-1</sup>) within the IR spectra is representative of the local chemical environment around the H<sub>2</sub>O moieties present. Each peak represents a different coordination environment such as a F...H-O hydrogen bond or multiple hydrogen bonds. The UF<sub>4</sub>·2.5H<sub>2</sub>O system also demonstrates O...H-O hydrogen bonds where multiple water molecules are within close proximity. The H-O-H bending mode (~1600 cm<sup>-1</sup>) is a function of the number of nonequivalent crystallographic sites water molecules occupy within the crystal structure. Correspondingly UF<sub>4</sub>·2.5H<sub>2</sub>O demonstrates two peaks within this region compared to a single peak for the other hydrates.

The Raman spectra of all three hydrates and the anhydrous UF<sub>4</sub> are dominated by phonon and acoustic bands where for all four species the bands below ~450 cm<sup>-1</sup> likely represent a combination of F-F, U-F, and U-O vibration modes. Based on the U-F polyhedra within their respective crystal structures; structural and spectral similarities are demonstrated between UF<sub>4</sub>·2.5H<sub>2</sub>O and U<sub>3</sub>F<sub>12</sub>(H<sub>2</sub>O), and UF<sub>4</sub>·0.33(H<sub>2</sub>O) and UF<sub>4</sub> respectively.

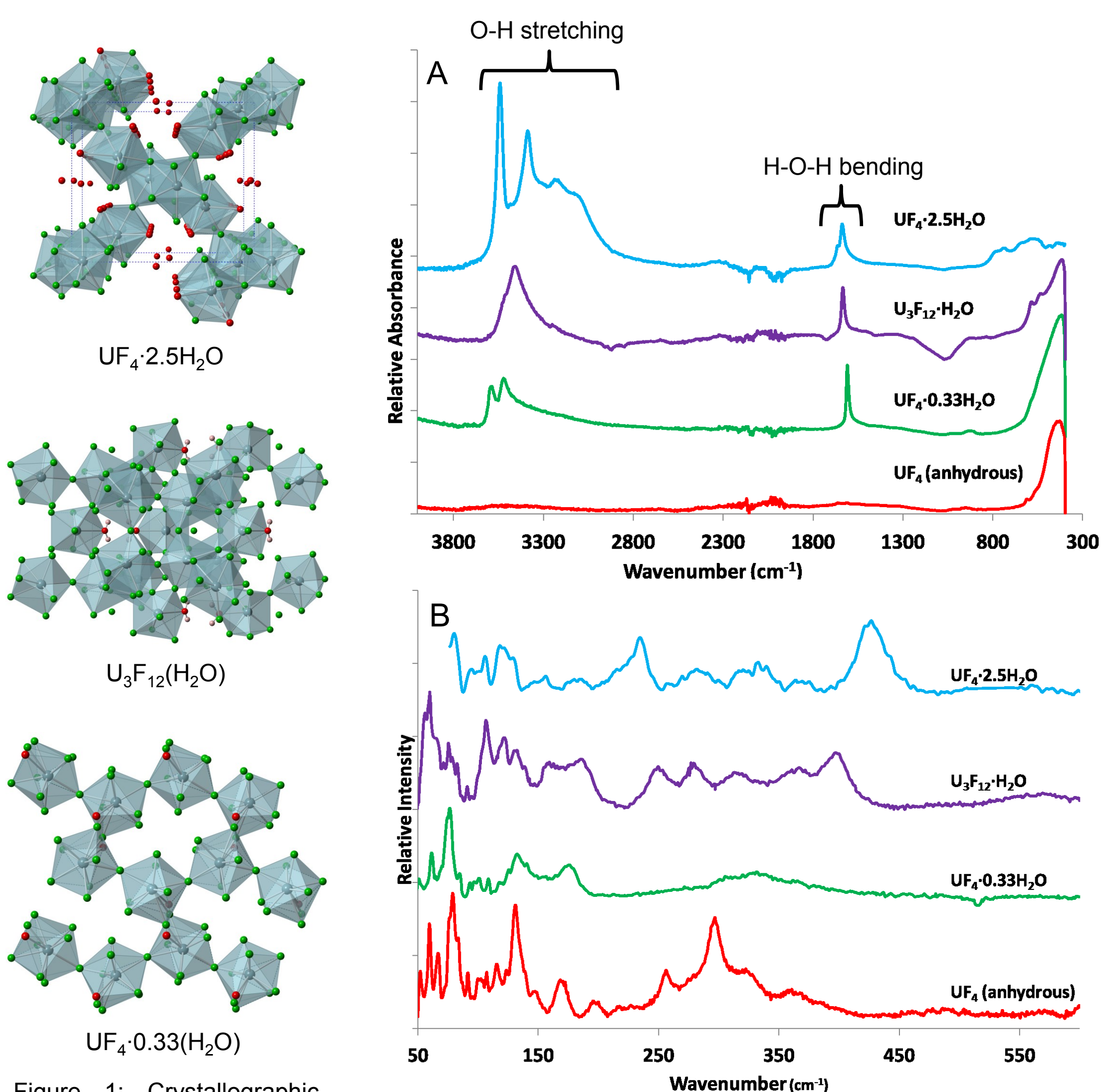


Figure 1: Crystallographic representations of the UF<sub>4</sub> hydrates

Figure 2: A) FT-IR of UF<sub>4</sub>·2.5H<sub>2</sub>O, U<sub>3</sub>F<sub>12</sub>·H<sub>2</sub>O, UF<sub>4</sub>·0.33H<sub>2</sub>O, and UF<sub>4</sub> (anhydrous) showing the different stretches of the OH regions. B) Raman Spectra of the UF<sub>4</sub> hydrates

## TEM/EELS Characterization

Microanalysis characterization of the internal structure was conducted on UF<sub>4</sub> materials post exposure to elevated humidity. Examination via TEM/EELS demonstrated complex internal microtexture and chemistry with measurable variance in the local elemental content and bonding environment. A collaborator used focused ion beam (FIB) methods to process six samples generated at SRNL under differing humidity conditions. Two typical examples of the combined TEM/EELS and energy dispersive spectroscopy (EDS) measurements performed on lamella is shown.

EDS mapping of particle edge and interior demonstrates oxygen rich and fluorine deficient sites. These regions coincide with the exposed material surface or internal vacancies which likely formed during initial synthesis. The fluorine deficiency is consistent with prior FY16 observations where the prolonged hydrolysis of UF<sub>4</sub> resulted in the formation of U<sup>6+</sup> species (i.e. UO<sub>x</sub>F<sub>y</sub>) via oxidation with reduced fluorine content.

TEM/EELS was performed to chemically characterize the uranium, oxygen, and fluorine atoms present within the multiple layers evident near the material surface. An example EELS spectrum demonstrates the five transition states for uranium, where the P1, P2, P3, and O4/5 edges represent energy loss due to electron beam interactions with the 6s, 6p, 6p and 5d core electrons respectively. Oxygen and fluorine K-edge transitions are also present and represent transition states associated with core 1s<sup>2</sup> electrons. Interpretation of the EELS data is ongoing.

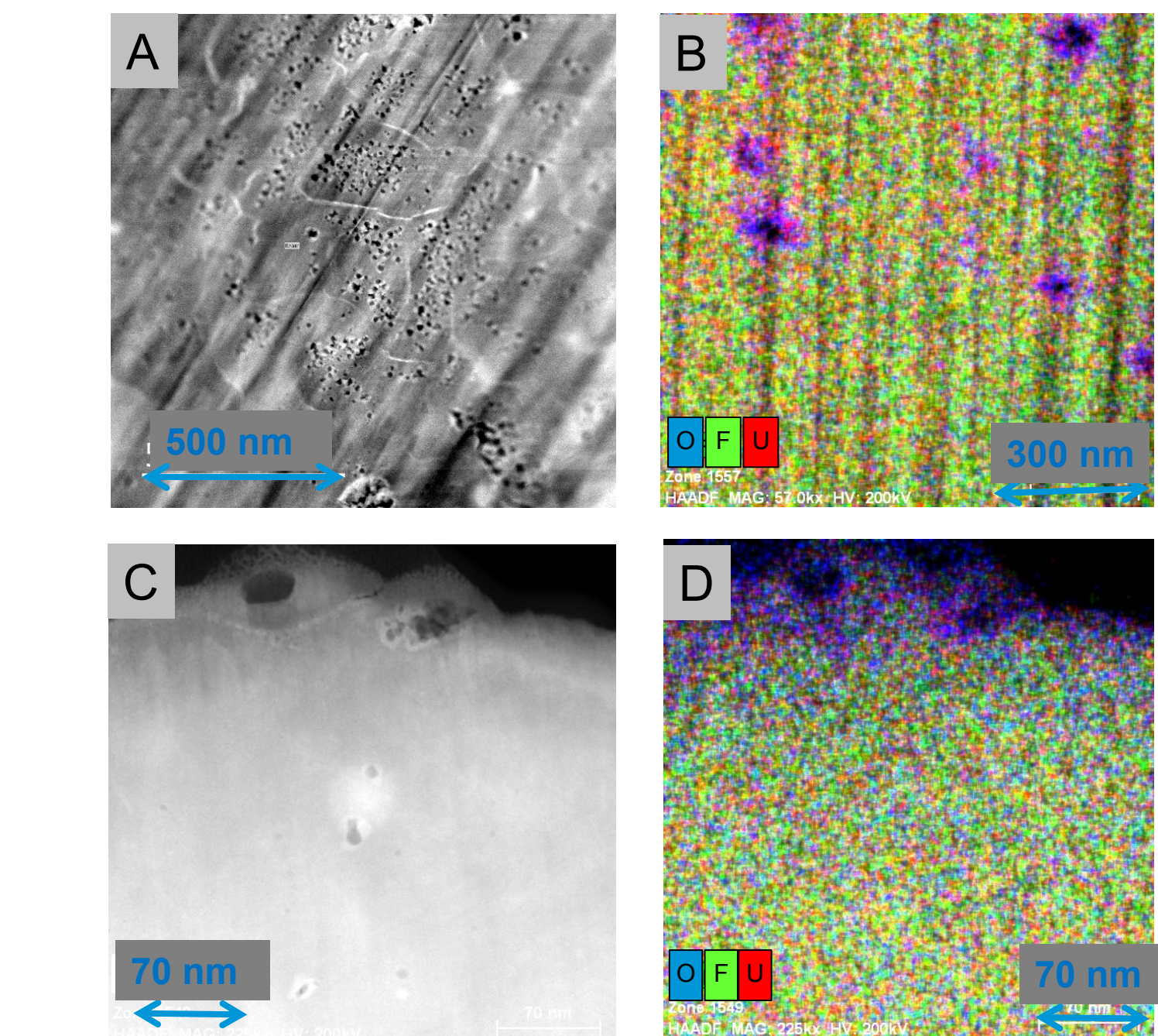


Figure 3: Combination of TEM images and EDS mapping where; A) TEM micrograph showing pores within the interior of particle exposed after FIB processing. B) EDS mapping where pores show reduced fluorine content relative to the bulk material. C) TEM micrograph of the original particle surface and D) corresponding EDS mapping where the surface shows reduced fluorine content relative to the bulk internal material.

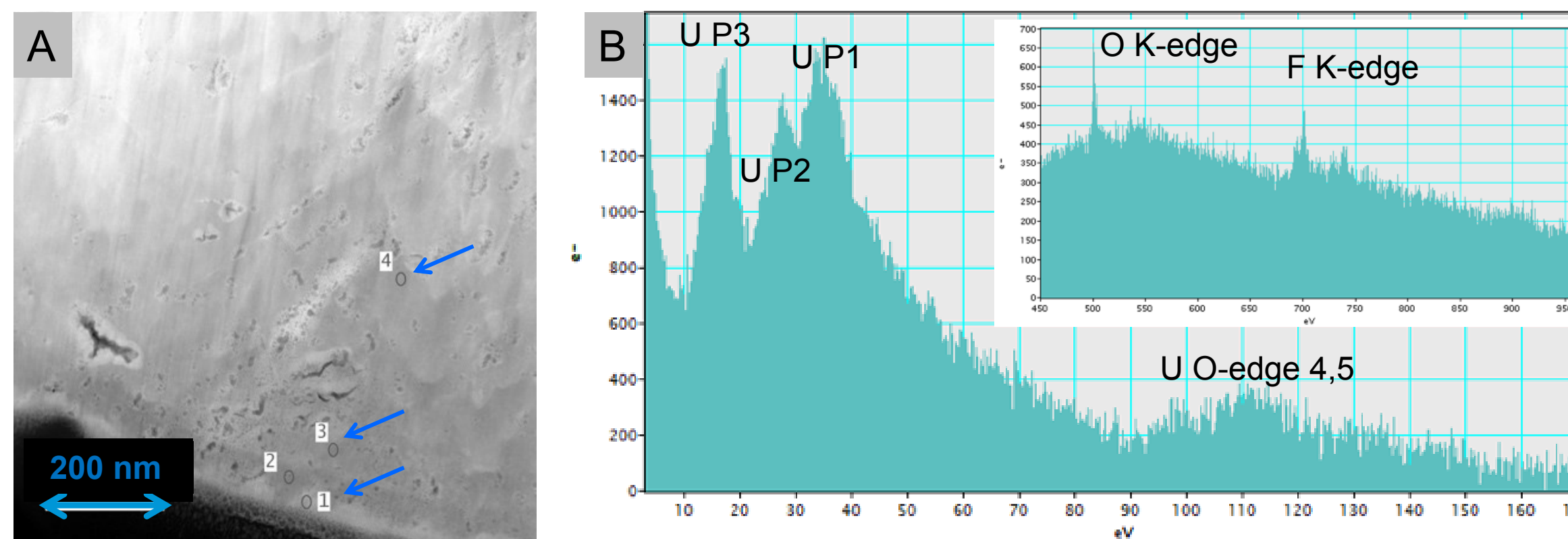


Figure 4: A) TEM image of a lamella specimen with EELS measurement locations noted. B) Spectra collected from the specimen nearest the material surface where peak consistent with U, O, and F are present.

## Collaborations and Contracts

Naval Research Laboratory - Dr. Chris Klug

- NMR spectroscopy characterization

L.A. Giannuzzi and Associates - Dr. Lucille Giannuzzi

- Electron microscopy methods and related sample preparation

University of South Carolina - Dr. Hanno zur Loye

- Provided additional UF<sub>4</sub> hydrate specimens and crystallographic input/discussion

## Remaining Challenges and Barriers

- Although measurement of UF<sub>4</sub> hydrolysis kinetics via <sup>19</sup>F NMR has begun – analysis is ongoing.
- TEM/EELS has been successfully utilized to characterize UF<sub>4</sub> hydrolyzed materials – however data analysis is ongoing.
- Two publications are currently in progress for the spectroscopy of UF<sub>4</sub> hydrates and the microanalysis of UF<sub>4</sub> hydrate solids.

## Proposed Future Work

- SRNL/ORNL/LLNL FY18-19 proposal to National Nuclear Security Administration – Defense Nuclear Nonproliferation R&D is pending for the “Advanced Materials Characterization” project.
- SRNL FY18 proposal to the Office of International Nuclear Safeguards – Safeguards Technology Development Program is funded for the “Generation and Characterization of U Solid Solution Particulate Reference Materials” project.

## Project Summary

- This effort has successfully developed an initial chemical and structural basis for understanding UF<sub>4</sub> hydrolysis in the environment.
- Multiple UF<sub>4</sub> hydrate polymorphs have been characterized via Raman and IR spectroscopy; complex UF<sub>4</sub> hydrate solids have been characterized by TEM/EELS.
- Technical results have been reported in one external peer-reviewed publication; with two additional publications in progress.

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