

# SLATT UNDERGRADUATE RESEARCH FELLOWSHIP FINAL REPORT

SCHOLAR NAME:	Madison Brooks
FACULTY ADVISOR:	Peter Burns
PROJECT PERIOD:	Summer 2021
PROJECT TITLE:	Alteration Products of Synthetic Paulsherrerite: Effects of Radiation and High Relative Humidity

CONNECTION TO ONE OR MORE ENERGY-RELATED RESEARCH AREAS (CHECK ALL THAT APPLY):	<input checked="" type="checkbox"/> Energy Conversion and Efficiency <input checked="" type="checkbox"/> Sustainable and Secure Nuclear <input checked="" type="checkbox"/> Smart Storage and Distribution <input type="checkbox"/> Transformation Solar <input type="checkbox"/> Sustainable Bio/Fossil Fuels <input type="checkbox"/> Transformative Wind
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### MAJOR GOALS AND ACCOMPLISHMENTS

Summarize your research goals and provide a brief statement of your accomplishments (no more than 1-2 sentences). Indicate whether you were able to accomplish your goals by estimating the percentage completed for each one. Use the next page for your written report.

RESEARCH GOALS	ACTUAL PERFORMANCE AND ACCOMPLISHMENTS	% OF GOAL COMPLETED
<b>He ion Paulsherrerite experiment</b>	Successful	100%
<b>Raman exposure experiment</b>	Successful	100%
<b>Start cation-exchange soaking experiments</b>	Started	100%
<b>Create an understanding of how frequently used laboratory analytical instruments operate</b>	Successful	100%
<b>Obtain transferable lab, writing, and critical skills</b>	Successful	100%
<b>Build a professional network in college</b>	Successful	100%

### RESEARCH OUTPUT

Please provide any output that may have resulted from your research project. You may leave any and all categories blank or check with your faculty advisor if you are unsure how to respond.

CATEGORY	INFORMATION
EXTERNAL PROPOSALS SUBMITTED	(Sponsor, Project Title, PIs, Submission Date, Proposal Amount)
EXTERNAL AWARDS RECEIVED	(Sponsor, Project Title, PIs, Award Date, Award Amount)
JOURNAL ARTICLES IN PROCESS OR PUBLISHED	(Journal Name, Title, Authors, Submission Date, Publication Date, Volume #, Page #s)
BOOKS AND CHAPTERS RELATED TO YOUR RESEARCH	(Book Title, Chapter Title, Authors, Submission Date, Publication Date, Volume #, Page #s)
PUBLIC PRESENTATIONS YOU MADE ABOUT YOUR RESEARCH	(Event, Presentation Title, Presentation Date, Location)
AWARDS OR RECOGNITIONS YOU RECEIVED FOR YOUR RESEARCH PROJECT	(Purpose, Title, Date Received)
INTERNAL COLLABORATIONS FOSTERED	(Name, Organization, Purpose of Affiliation, and Frequency of Interactions )

<b>EXTERNAL COLLABORATIONS FOSTERED</b>	(Name, Organization, Purpose of Affiliation, and Frequency of Interactions)
<b>WEBSITE(S) FEATURING RESEARCH PROJECT</b>	(URL)
<b>OTHER PRODUCTS AND SERVICES</b> (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)	<p>(Please describe each item in detail)</p> <p><b>Raman spectroscopy</b> is a spectroscopic technique that gives information about the material's local molecular coordination. Raman is used to identify molecular vibrational and rotational modes that are Raman active within the sample.</p> <p><b>Powder X-ray diffraction</b> is used to determine the diffraction pattern of a powder crystalline material. In this technique, the sample is impinged by a beam of X-rays. The detector moves in synchronization with the X-ray source. The angle between the incident beam and collected beam as it diffracts throughout a crystalline sample results in a signal that corresponds to the d-spacing between Miller planes in the crystal. The resulting diffraction patterns are used in a fingerprinting manner to characterize polycrystalline samples.</p> <p><b>Fourier transform infrared spectroscopy</b> is used here to investigate the molecular properties for a given sample. Complimentary to Raman spectroscopy, FTIR detects vibrations between molecules to produce a chemical fingerprint of a compound. FTIR spectroscopy uses infrared radiation to perturb a bond with a permanent dipole moment, which carries a specific vibrational frequency. Vibrational energies are unique to functional groups that are composed of different atoms and bond strengths.</p>

### **RESEARCH EXPERIENCE**

Please let us know what you thought of your research experience: Did this experience meet your expectations? Were lab personnel helpful and responsive to your needs? What else could have been done to improve your experience or achieve additional results?

**My research experience met my expectations. The lab personnel were very helpful and responsive to my needs. The Burns group at Notre Dame is very welcoming and encouraging. They were very happy to have me join their team. I am grateful to be part of an effective and cooperative team. I will be continuing my research with them in the fall. There is nothing I can think of that could have been done to improve my experience. Overall, my research was successful and I achieved my research goals.**

### **FINAL WRITTEN REPORT**

(Please use the space below to describe your research project and objectives, any findings and results you can share, and graphs, charts, and other visuals to help us understand what you achieved as a result of this research experience.)

The University of Notre Dame

**Alteration Products of Synthetic Paulsherrite: Effects  
of  
Radiation and High Relative Humidity**

Madison R. Brooks, Dr. Peter Burns, Savannah E. Benjamin, and Dr. Jay A. LaVerne

Slatt Final Written Report

August 16th, 2021

## Abstract

The production of studtite,  $[(\text{UO}_2)_2\text{O}_2(\text{H}_2\text{O})_2] \cdot 2(\text{H}_2\text{O})$  or  $\text{UO}_4 \cdot 4(\text{H}_2\text{O})$ , resulting from the irradiation of Paulsherrerite (PS),  $\text{UO}_2(\text{OH})_2$ , was examined. For the purpose of this experiment, Paulsherrerite was synthesized from hydrothermally synthesized metaschoepite (MS),  $[(\text{UO}_2)_4\text{O}(\text{OH})_6] \cdot 5\text{H}_2\text{O}$ . The characterization of the material was performed before and after irradiation by powder X-ray diffraction (PXRD), Raman spectroscopy (Raman), and Fourier transform infrared spectroscopy (FTIR). The material was irradiated with a 3 MeV  $\text{He}^{2+}$  ion accelerator beam that delivers 5 MeV  $\text{He}^{2+}$  ions. The irradiated sample received large doses in an effort to simulate long time scale exposure to high radiation field; for reference 1 MGy typically corresponds to 25 years of exposure in a Hanford waste tank. The motive behind this experiment is to gain a better understanding of the alteration behavior of Paulsherrerite under ionization radiation and humid conditions.

## Introduction

Hydrated uranium oxides and hydroxides are of importance to the nuclear community because they are alteration products of spent nuclear fuel. These materials are formed by aqueous corrosion of uranium-based nuclear fuels [1]. Currently, there are about 90,000 metric tons of nuclear waste in the US. As a product of The Manhattan Project, The Hanford Nuclear Site in Washington was created in 1943. The Hanford Site stores “56 million gallons of radioactive waste in 177 underground storage tanks” [2]. The Yucca Mountain Repository is the proposed site to store high level reactive waste and spent nuclear fuel. The top of Yucca Mountain will be used as a tunnel complex to store radioactive waste concealed by barriers [3]. The radioactive waste matrix has many different radionuclides that interact with each other to produce various alteration phases. Studtite is an alteration phase that has been identified on several fuel claddings in storage areas at the Hanford Site [4]. The formation of studtite is of importance because it is formed when radiolytic hydrogen peroxide reacts with a uranyl mineral. Studtite and its dehydrated form, metastudtite,  $\text{UO}_4 \cdot 4(\text{H}_2\text{O})$ , are significant because they are the only known peroxide minerals in existence. Both of these uranyl peroxides form on nuclear fuel in water by water radiolysis through the production of hydrogen peroxide.

Radionuclides have extremely long half lives, meaning they will likely persist beyond human civilization. Thus, it is important to conduct experiments on nuclear materials as if they were under similar conditions as stored used nuclear fuel. Past work has shown that alteration products such as hydrated uranium oxides are formed as corrosion products in spent nuclear waste by nearby alpha and gamma emitters [5]. For this experiment, we will be investigating the transformation products of irradiated Paulsherrerite stored at high relative humidity. The ultimate goal of this experiment is to attempt to model long-term self-irradiation of Paulsherrerite by ionization of 5 MeV  $\text{He}^{2+}$  particles in a He ion source. By irradiating the material via  $\text{He}^{2+}$  ion irradiation we are attempting to imitate the long-term self-irradiation of Paulsherrerite on a short time-scale. A 5 MeV  $\text{He}^{2+}$  ion beam was selected to be comparable to the energy of alpha particles emitted from the uranium phases investigated here. I hypothesize that under ionizing conditions and the introduction of surface water through high relative humidity that the hydrated uranium oxide, Paulsherrerite, will undergo significant alteration, completely changing the mineral structure.

## Major Modes of Analysis

### *Raman Spectroscopy*

Raman spectroscopy is a spectroscopic technique that gives information about the material's local molecular coordination. Raman is used to identify molecular vibrational and rotational modes that are Raman active within the sample. The Raman effect occurs when the sample is exposed to monochromatic light. The change in wavelength of light when monochromatic light is directed at matter is known as the Raman effect [7]. Rayleigh scattering occurs when the photon has the same energy after interacting with a molecule. Stokes and Anti-Stokes Raman scattering occurs where there is a change in energy of the emitted photon. The change in wavelength of the incident light corresponds to the vibrational frequency of the molecule [8]. Raman spectroscopy is specifically leveraged for uranium mineral characterization as the uranyl bond is a particularly strong Raman scatterer.

Using a Renishaw inVia instrument Raman spectroscopy measurements were performed with a 785 nm excitation laser, a 20x objective, and a spot size of 10  $\mu\text{m}$ . The laser was set to 0.5% laser power with 10 second exposure time and 3 accumulations per scan. Cosmic ray removal was applied to all scans. Several spots were scanned on each sample to ensure consistency of spectra.

### ***Fourier transform infrared spectroscopy***

Fourier transform infrared spectroscopy is used here to investigate the molecular properties for a given sample. Complimentary to Raman spectroscopy, FTIR detects vibrations between molecules to produce a chemical fingerprint of a compound. FTIR spectroscopy uses infrared radiation to perturb a bond with a permanent dipole moment, which carries a specific vibrational frequency. Vibrational energies are unique to functional groups that are composed of different atoms and bond strengths [11]. FTIR probes vibrational modes of uranyl ions, hydroxide ligands, and interlayer water molecules. While molecules with permanent dipole moments like water are not Raman active, they can be detected using FTIR making it advantageous for describing the water content for the samples investigated here.

FTIR spectra for this experiment were obtained using a Bruker LUMOS FT-IR in attenuated total reflectance (ATR) mode. Full range scans were collected from 600-3998  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ .

### ***X-ray powder diffraction***

Bulk purity of the samples were confirmed by X-ray powder diffraction. PXRD is used to determine the diffraction pattern of a powder crystalline material [9]. In this technique, the sample is impinged by a beam of X-rays. The detector moves in synchronization with the X-ray source. The angle between the incident beam and collected beam as it diffracts throughout a crystalline sample results in a signal that corresponds to the d-spacing between Miller planes in the crystal. Miller planes are a construction of space reciprocal to the real space within the crystal lattice. Using Bragg's law,

$$n\lambda = 2d \sin\theta, \quad (1)$$

the spacing between each Miller plane can be solved for. Here  $n$  is an integer,  $\lambda$  is the wavelength of light,  $\theta$  is the incident angle and the  $d$  is the distance between each lattice plane used to obtain information about the crystalline structure [10]. While single crystal X-ray diffraction leverages Bragg's law for resolving exact atomic positions, powder

X-ray diffraction only provides information on the spacing between Miller planes. The resulting diffraction patterns are used in a fingerprinting manner to characterize polycrystalline samples.

PXRD measurements were obtained using a Bruker D8 Advance Davinci powder X-ray diffractometer with a Cu K $\alpha$  X-ray source. Material was dry mounted onto zero-background silicon holders. Each scan was collected from 5-45° 2 $\theta$  while the sample was rotated at 15 rpm with anti-scatter and receiving slits removed.

## Experimental Section

### *Synthesis of Metaschoepite*

A bulk sample of hydrothermally synthesized metaschoepite was used in a heating experiment. The method for synthesis of pristine metaschoepite was adapted from a source that provided a detailed synthesis and well-defined characterization of the material [12]. Uranyl nitrate hexahydrate was ground into a powder and heated on a hot plate to dryness until amorphous UO<sub>3</sub> formed. Upon dryness, the powder was placed in a Teflon lined Parr vessel with water. A Parr bomb is a sealed vessel used to prepare samples for instrumental analysis. The mixture was heated at 75°C for 24 hours.

### *Synthesis and Characterization of Paulscherrerite from Metaschoepite*

The metaschoepite was placed into an oven at 100 °C for 24 hours. After heating, the material was characterized by Raman spectroscopy and X-ray powder diffraction. As shown in Figure 1 below, the characterization revealed that the resulting material was consistent with Paulscherrerite. Although the obtained PXRD data of the MS heated at 100 °C for 24 hours had reasonable agreement with the reference data (right), the obtained Raman data in comparison to Raman data reported in the Brugger et al, 2011 publication describing Paulscherrerite was less conclusive (Figure 2). This is likely owing to the fact that Raman is more of a surface technique, which may account for slight differences in the uranyl peaks. The peak at ~750 cm<sup>-1</sup> is not reported in the paper and did not show up on every spot collected on Raman of the heated material. Despite the Raman data not completely consistent with the published spectrum, we are still confident that the material we obtained is Paulscherrerite.

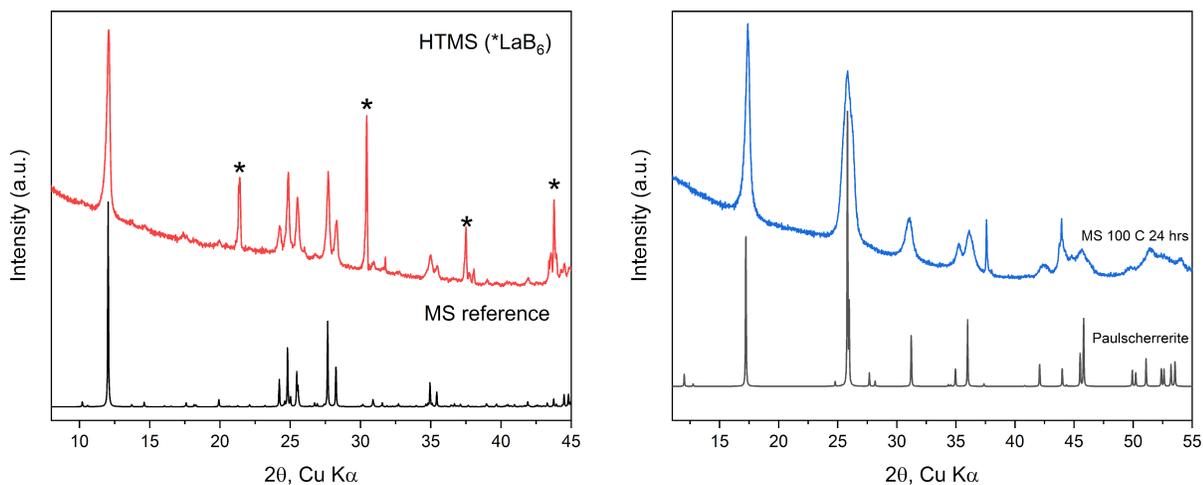


Figure 1. (Left) PXRD of the Metaschoepite Used to Obtain Paulscherrerite (Right).

Data Set:[Book1]Sheet11B Date:8/4/2021  
 BaseLine:Constant Adj. R-Square=9.97985E-01 # of Data Points=406  
 Ch#2=1.78688E+04 Degrees of Freedom=396  
 SS=7.07605E+06

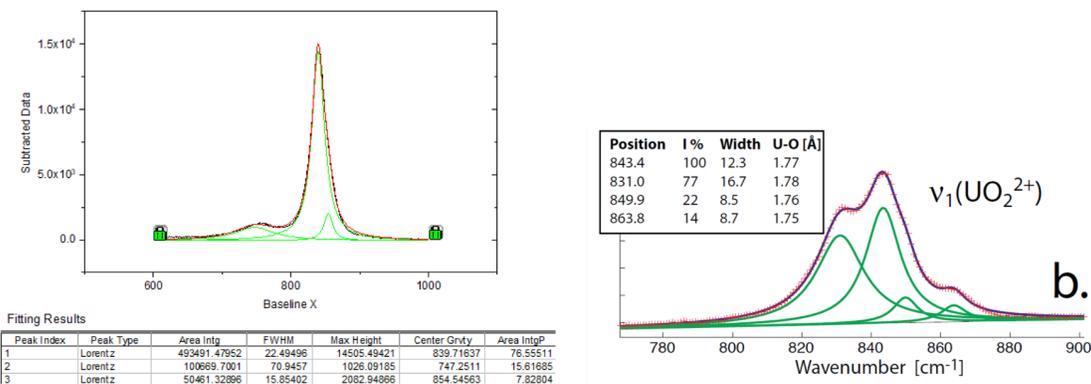


Figure 2. Raman Fitting of the Uranyl Peaks in Paulscherrerite Compared to that Published by Brugger et al., 2011[6].

After characterization of Paulscherrerite was carried out, humidity and irradiation experiments were performed on the material. A humidity chamber was constructed from a sealed vessel with the sample placed on an elevated surface above a saturated salt solution to suppress the relative humidity to ~85%. Particles of PS were placed onto carbon stubs for He ion irradiation. One part of the sample was in-line with the ion beam and subjected to high relative humidity (irradiated), while the other isolated part of the sample was subjected to only flowing hydrated Argon gas (no irradiation). In this report, I will refer to the isolated part as the hydrated Argon blank. A third PS sample was subjected to high relative humidity only. The irradiated sample received a dose of about 100 MGy.

## Results and Discussion

After the irradiation was performed, Raman was collected on the three samples on the same day (Figure 3) and 3 days post-irradiation (Figure 5). Interestingly, the Raman spectra for the hydrated Argon blank showed clear signals that are consistent with studtite, at 820 and 864  $\text{cm}^{-1}$  (Figure 4, left). However, the Raman spectra for the irradiated sample, named PS 100 MGy, had poor signal to noise ratios, making them difficult to deconvolute using peak fitting software (Figure 4, right). Nonetheless, we are confident that studtite formed on the irradiated sample as well. The peak positions are within the expected range for the symmetric uranyl and peroxy stretches at approximately 820 and 864  $\text{cm}^{-1}$ , respectively.

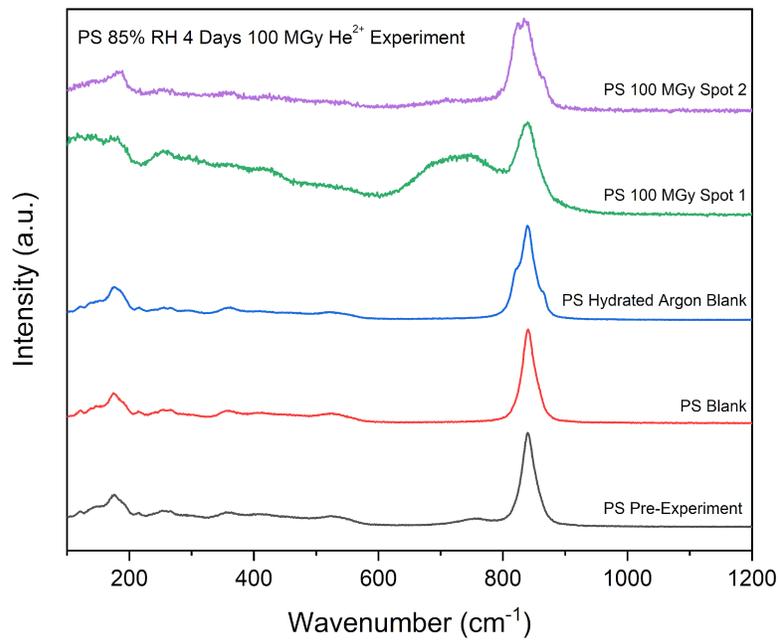


Figure 3. Raman Collected on Paulscherrerite on the Same Day Irradiation was Performed.

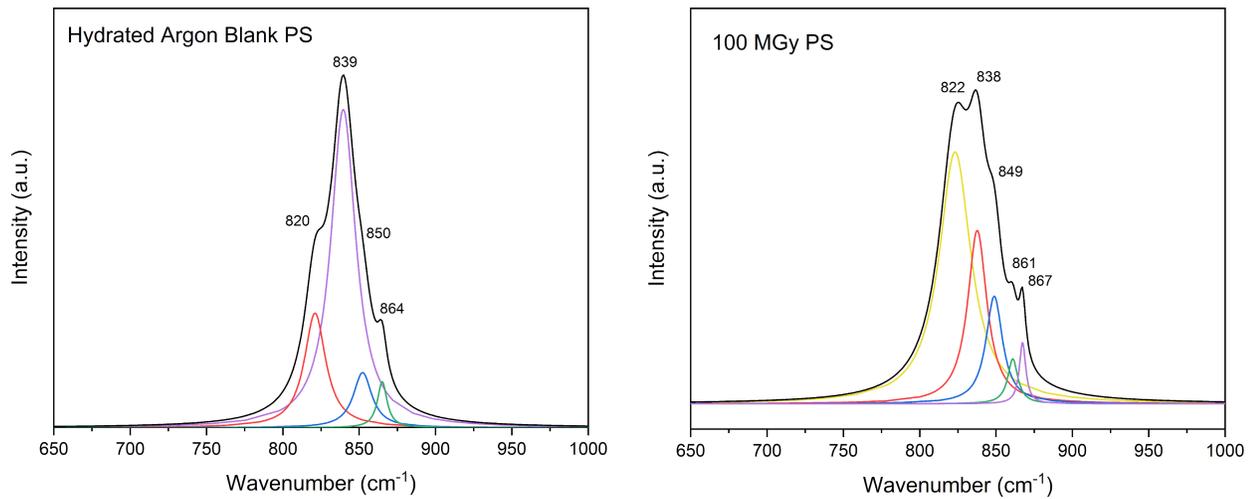


Figure 4. Raman Peak Fitting for the Uranyl Region of the PS Hydrated Argon Blank (left) and PS 100 MGy (right) Samples.

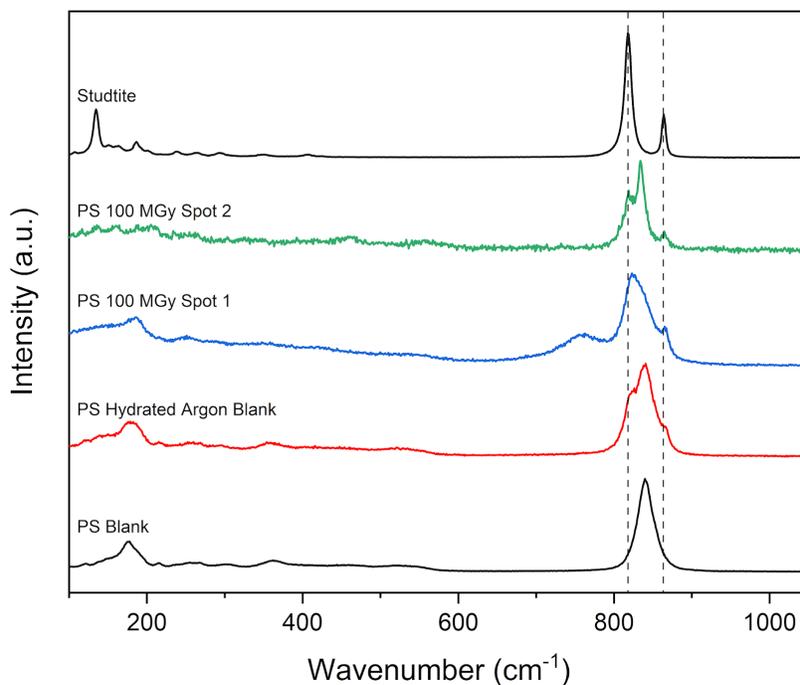


Figure 5. Raman Collected on Paulscherrerite Samples 3 Days Post Irradiation was Performed.

FTIR was collected on the samples 4 days after irradiation was performed (Figure 6). The spectra of the PS 100 MGy and the PS hydrated Argon blank are almost identical to the spectra of studtite. The region ranging from 1600-700  $\text{cm}^{-1}$  for the irradiated sample and hydrated Argon blank are consistent with each other, however the O-H stretching region from 3600-3000  $\text{cm}^{-1}$  is slightly different between the two samples. The hydrated Argon blank has a slightly broader peak at 3400  $\text{cm}^{-1}$ , most likely because the sample was more hydrated. Nevertheless, we can definitively conclude that Paulsherrite synthesized from metaschoepite is able to form studtite in irradiated and humid conditions. Because no studtite was detected on the unirradiated 85% RH blank, we can attribute its formation to the  $\text{He}^{2+}$  ion beam interaction with the sample. This implies that self-irradiation of uranyl materials such as Paulscherrerite through alpha particle emission may produce radiolytic products on nearby water that influence its alteration behavior.

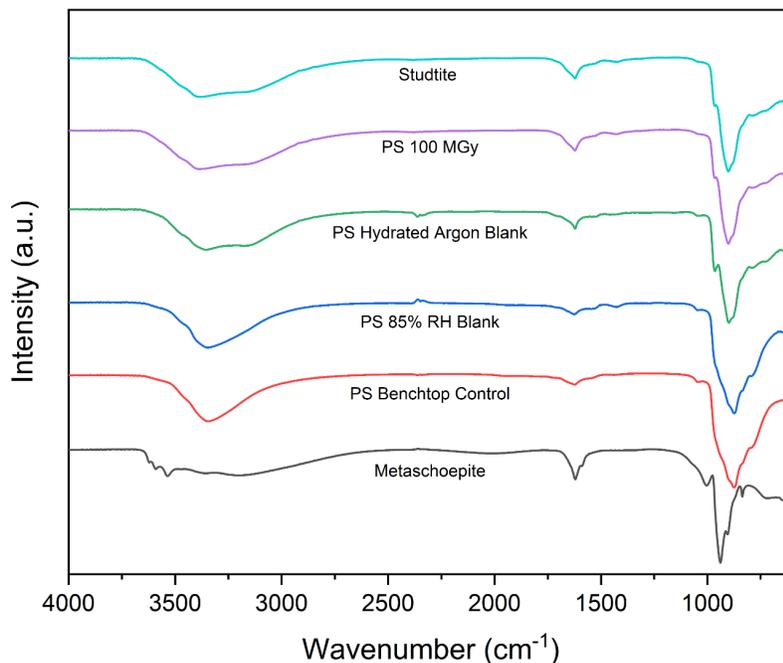


Figure 6. FTIR Collected on Paulscherrerite Samples 4 Days Post Irradiation was Performed.

## Future Research

The next step for future work concerning this experiment would be to apply the previously described methodology to other uranyl hydroxides that have cations incorporated into their structure. Different cation-bearing uranyl hydroxide hydrates are of importance because different cation-containing uranyl hydroxide hydrates can sequester important radionuclides like Np and Sr which impact their environmental mobility. For instance, instead of using metaschoepite as the starting material, we would use other uranyl hydroxides such as becquerelite,  $\text{Ca}(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot 8(\text{H}_2\text{O})$ , and compreignacite,  $\text{K}_2(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot 7\text{H}_2\text{O}$ . These cation-bearing uranyl hydroxides will be synthesized from metaschoepite in a soaking experiment in addition to their direct synthesis. Previous work has shown that schoepite spontaneously transforms into compreignacite and becquerelite in the presence of  $\text{K}^-$  and  $\text{Ca}^{2+}$ , respectively [13]. The solution data analysis indicates that at pH values higher than 4.5 hydrolysis action occurs at room temperature after a relatively short contact time. Once the cation-bearing uranyl hydroxides are synthesized and characterized, they will be exposed to the same irradiation conditions as in the previous experiment to see if studtite will form. Additionally, thermogravimetric analysis will be conducted on each of the synthesized materials to determine the material's thermal stability and moisture/solvent content. We will also be setting up Raman exposure experiments. It has been brought to our attention that the Raman laser could be inducing alteration during characterization of the material. For this reason, Raman exposure experiments will be set up by varying laser power and exposure time.

Overall, my fellowship experience has allowed me to develop valuable lab skills that I will continue to carry into the rest of my undergraduate research. My research has also greatly improved my critical thinking and analytical skills. This opportunity has not only influenced my decision to apply to graduate school, but also my career interest in nuclear physics and actinide chemistry. Specifically, my research experience has spiked my interest in nuclear remediation and recycling of used nuclear fuel. My participation in undergraduate research has provided me with several opportunities, such as one-on-one work with graduate students, post-doctoral researchers, and faculty. I'm grateful for an enriching experience that strongly influenced my career trajectory.

## References

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