SLATT UNDERGRADUATE RESEARCH FELLOWSHIP
FINAL REPORT

SCHOLAR NAME:	Erin Ludwig
FACULTY ADVISOR:	Dr. Melissa Berke
PROJECT PERIOD:	12/2/20 - 1/29/21
PROJECT TITLE:	Using Chemical Lichenometry to Understand Coastal Storm Deposits
CONNECTION TO ONE OR MORE ENERGY-RELATED RESEARCH AREAS (CHECK ALL THAT APPLY):	**( ) Energy Conversion and Efficiency** **(x) Sustainable and Secure Nuclear** **( ) Smart Storage and Distribution** **( ) Transformation Solar** **( ) Sustainable Bio/Fossil Fuels** **(x) Transformative Wind**

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
-learn organic biogeochemical techniques in the laboratory	-trained to use the freeze-dryer, sonicator, and ASE extraction instrument (including sample prep) -trained to perform organic solvent-based lipid fraction separations, including column chromatography	100%
-physically characterize the coastal boulder samples and lichens growing on them	-photographed and measured the size of all aspects of the rock and lichens in order to help identify the rock type and lichen species. Was not able to use XRF at CEST as it was unexpectedly broken during winter term.	90%
-chemically characterize the coastal boulder samples and lichens growing on them	-performed a series of organic solvent-based lipid extractions and purifications on the lichens -through a series of chromatographic columns, I isolated all of the organic compounds present -identified and quantified the various organic compounds on a gas chromatograph (attached to a mass spectrometer)	60%
-assess the likelihood of using these growths for compound-specific radiocarbon dating (chemical lichenometry) to determine how long these boulders have been at the coastline	- basic research was conducted in order to learn more about chemical lichenometry. Abundances were determined, but due to time constraints this goal will be on-going.	25%

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)
EXTERNAL COLLABORATIONS FOSTERED	(Name, Organization, Purpose of Affiliation, and Frequency of Interactions)
WEBSITE(S) FEATURING RESEARCH PROJECT	(URL)
OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)	(Please describe each item in detail)

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 and was overall a positive one. I learned a lot in terms of lab protocols and processes, but I would have like to have more significant results at the conclusion of my research experience. The professor and graduate students who I was working with were helpful and responsive to my needs. I think that having a significant longer period of time in the lab could have helped me to achieve additional results.

FINAL WRITTEN REPORT

Using Chemical Lichenometry to Understand Coastal Storm Deposits

For my research project, I worked on lichen growths on rock samples gathered from western Ireland in the laboratory of Dr. Melissa Berke (Department of CEEES) over the winter session. This research formed the beginning of new research between Dr. Berke, Dr. Andrew Kennedy (CEEES), and Dr. Rónadh Cox (Williams College) aimed at studying the emplacement of coastal boulders. Under the supervision of Dr. Berke and her graduate students, Patrick Cho and Audrey Taylor, I learned organic biogeochemical techniques in the laboratory. The objective of my research was to physically and chemically characterize the coastal boulder samples and lichens growing on them. In the future, this data will be used to assess the likelihood of using these growths for compound-specific radiocarbon dating (chemical lichenometry) to determine how long these boulders have been at the coastline. Large boulders on coastal rock platforms such as those in western Ireland are covered in similar lichen growths and were moved by waves from storm events. However, the size and frequency of the storms that move these boulders, and how long they have been resting there, is still unknown. Studying these boulders and determining the power of the storm necessary to move them will help us learn about extreme coastal events. Understanding coastal storm frequency and power is critical for developing resilient coastal energy infrastructure such as wind turbines and power plants, already under threat from sea level rise.

Before I began the actual research process in the lab, it was critical that I became more comfortable in the lab setting and learned how to operate the equipment and the lab protocols, especially how to keep samples contaminant free. I was trained to use the freeze-dryer, sonicator, and ASE extraction instrument (including sample prep) in the lab. I was also trained to perform organic solvent-based lipid chemical separations; including column chromatography. I learned the basic principle that keeping samples and equipment contaminant free is critical in the lab environment, especially when doing these types of extractions in a lab that studies hydrocarbons that are present in many common substances. In order to keep contaminants out of unwanted areas, clean foil, that has been heated in the oven, is often used to cover jars, beakers, pipets, etc. Additionally, in order to clean lab equipment, I learned that a typical approach is to solvent rinse first with Methanol and then with DCM. Overall, I learned that lab work is very meticulous, and I gained a lot of lab experience and techniques over the winter session.

In order to characterize the physical and chemical components of the rock samples and lichens, I learned and performed a series of lab analyses at Dr. Berke's lab. I photographed and measured the size of the rock and lichens in order to help identify the rock type and potential lichen species as shown in Figures 1-4 below.

Figure 1. 191019 BUR1: Sandstone rock with *Rhizocarpon geographicum* lichen (map lichen).

Figure 2. 191019 BUR2: Limestone rock with *Xanthoria parietina* lichen (common orange lichen)

Figure 3. 191019 BUR3: Limestone rock with *Caloplaca thallincola* lichen (orange-yellow crustose lichen)

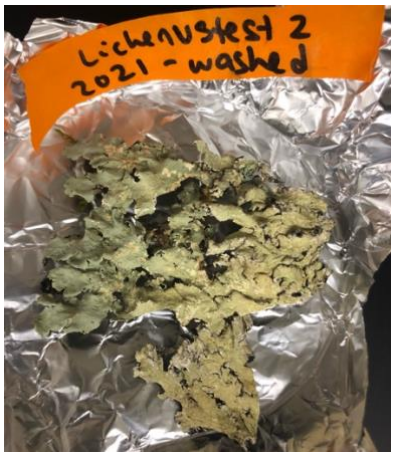

Figure 4. LichenUStest2 2021.

I performed a series of organic solvent-based lipid extractions and purifications of lichens from the United States, as an initial test, as well as the lichens from Ireland. I performed a series of organic solvent-based lipid extractions and purifications through a series of chromatographic columns that served to separate compounds by polarity. I prepped the ground sample by grinding it up using a mortar and pestle. Prior to running the columns, I rinsed the lichens with DI water the night before, rinsed with 3 aliquots of 9:1 DCM:Methanol, sonicated, and pipetted liquid out from each vial in between runs. These various organic compounds were quantified, and later to be identified, on a gas chromatograph (attached to a mass spectrometer) in Dr. Berke's lab. Identifying the compounds and their abundances in the future will be important to determine if these are possible candidates for compound-specific radiocarbon dating.

Shown below are some of the gas chromatograph traces that I generated. Since this work was exploratory, I found many unusual results that I will discuss below. I produced six chromatograph traces including ground and whole lichen for *n*-alkanes, PLFA (phospholipid-derived fatty acids), and TLE (total lipid extract). In the traces, the largest peak around 18.75 minutes is the standard. Based on these results, we know that we can use far less standard in future injections. For alkanes, the time (minutes) is dependent on the number of carbons in the alkane chain. Peaks to the right of the standard in the *n*-alkane traces show the presence of mid-chain alkanes which is surprising because these are expected to be found in higher plants and it was expected that most peaks would be to the left of the standard. The PLFA extracts represent almost all of the polar compounds because all remaining substances came off the column with the methanol rinse.

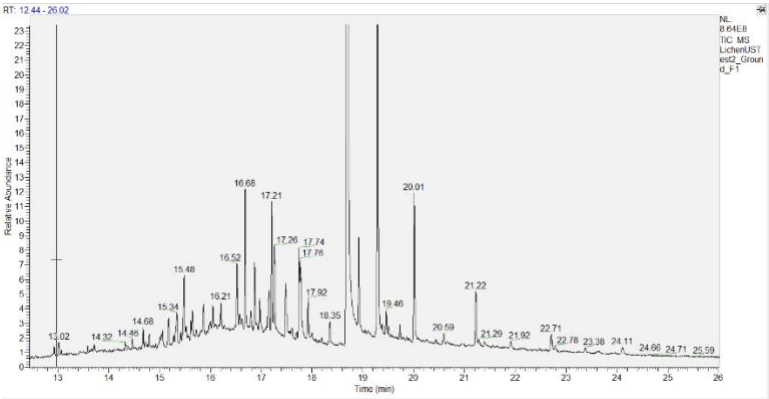

Figure 5. Lichen Ground Alkane

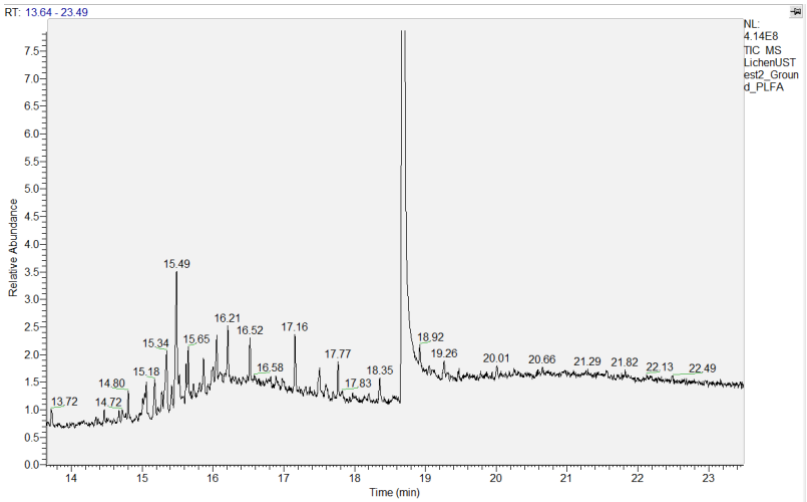

Figure 6. Lichen Ground PLFA

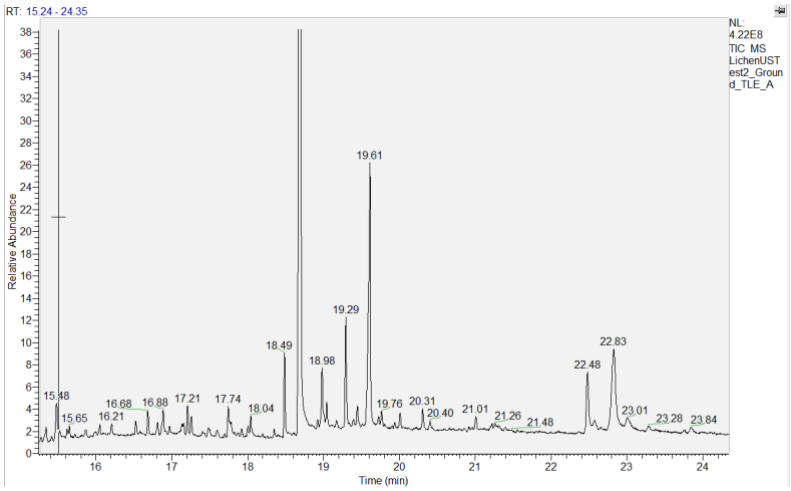

Figure 7. Lichen Ground TLE

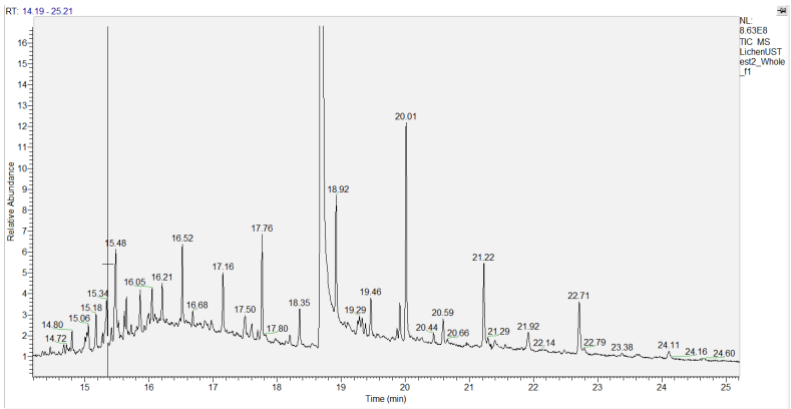

Figure 8. Lichen Whole Alkane

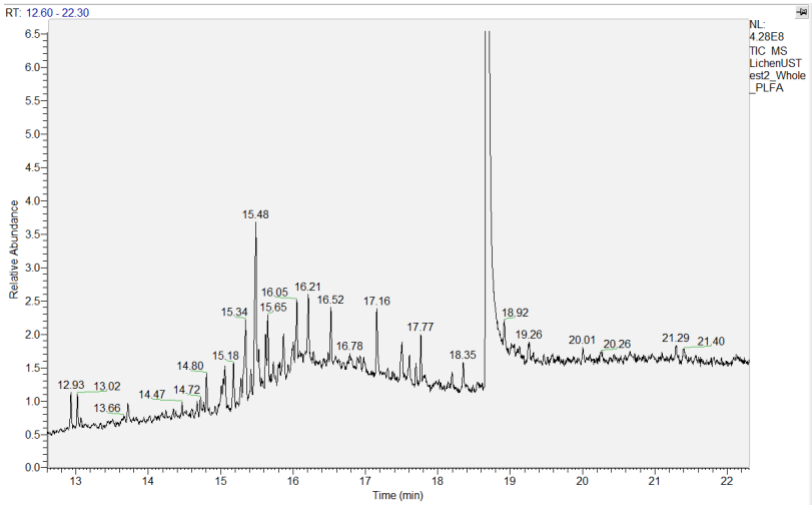

Figure 9. Lichen Whole PLFA

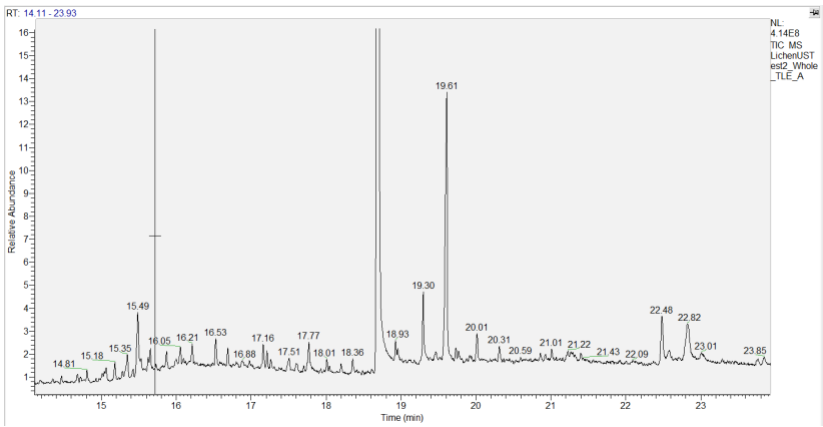

Figure 10. Lichen Whole TLE

Lichen Ground Alkane:

- Relatively large peaks at times (minutes) at 15.48, 16.52, 16.68, 17.21, 17.26, 17,74, 17.76, 20.01, 21.22, 22.71 many of which are found in the lichen whole *n*-alkane

Lichen Ground PLFA:

- Hump with indistinguishable peaks, called an unresolved complex mixture (UCM), to the left of the standard shows that there are many compounds there and an additional technique and instrumentation will be needed to resolve the peak and the (likely) thousands of individual compounds there
- Relatively large peaks at times (minutes) at 15.49, 16.21, 16.58, 17.16, 17.77 some of which are also found in the whole PLFA and *n*-alkane

Lichen Ground TLE:

- Relatively large peaks at times (minutes) at 18.49, 18.98, 19.29, 19.61, 22.48, 22.83 that are not found in the ground *n*-alkane and ground TLE which tells us there are some other compounds other than *n*-alkanes and PLFA which represents an area for further exploration
- Some similar peaks found in the whole TLE, but peak at 19.61 has greater abundance in the ground sample than the whole sample

Lichen Whole Alkane:

- Relatively large peaks at times (minutes) at 15.48, 16.52, 17.16, 18.92, 20.01, 21.22, 22.71 many of which are found in the lichen ground *n*-alkane

Lichen Whole PLFA:

- Hump with indistinguishable peaks, called an unresolved complex mixture (UCM), to the left of the standard shows that there are many compounds there and an additional technique and machinery are needed to resolve the peak
- Relatively large peaks at times (minutes) at 15.48, 16.05, 16.21, 16.52, 17.16, 17.77 some of which are also found in the ground PLFA and *n*-alkanes

Lichen Whole TLE:

- Relatively large peaks at times (minutes) at 15.49, 19.30, 19.61, 22.48, 22.82 some of which are found in the ground TLE
- Some similar peaks found in the ground TLE

Generally, when looking at ground versus whole samples, similar peaks and abundances present themselves in the GC traces. The clean peaks in the traces, the ones that go straight up and right back down, are good candidates for future dating. If future studies show that these peaks are in most lichens, they would be the best candidates for dating lichens.

Future work will include using the X-ray Fluorescence (XRF) instrument to examine the elemental composition around the lichen and below the lichen, to examine whether elemental removal by lichen growth might be occurring. Additional future work will include examining whether the rock matrix contained any organic acids (from lichen growth) by grinding the rock surface and performing a similar extraction as described above. This will let us know whether there are lichen compounds shielded from the weather and trapped in rock pores (developed from lichen growth). Results from these analyses will address the feasibility of this technique for lichen dating to aid in studying extreme coastal storm deposits in western Ireland and elsewhere globally.