

**A NOVEL CONTROLLED ENVIRONMENT STUDY OF
PREBIOTIC ORGANIC MATERIAL IN THE TAGISH LAKE
METEORITE USING RAMAN AND FLUORESCENCE
SPECTROSCOPY: IMPLICATIONS FOR
ASTEROID-RETURN SAMPLE ANALYSIS**

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A THESIS SUBMITTED TO THE FACULTY OF GRADUATE STUDIES IN PARTIAL
FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY

GRADUATE PROGRAM IN EARTH AND SPACE SCIENCE
YORK UNIVERSITY
TORONTO, ONTARIO

July, 2023

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Abstract

Several ambitious missions such as OSIRIS-REx, Hayabusa2 and Mars Sample Return are currently collecting or planning to collect the most pristine planetary samples to analyze on Earth since the Apollo missions. Therefore, it is essential to create instrumentation that will allow preliminary compositional analysis of these materials without the need for sample preparation and in a minimally destructive way, while preventing oxidation, alteration, or contamination from Earth's environment. At York University, a small, transportable environmental chamber with temperature, pressure, and atmosphere control has been integrated on an optical table with a combined UV (266 nm) and Green (532 nm) Raman, laser-induced fluorescence, and time-resolved laser-induced fluorescence instrument. This system can collect high-resolution 2D spectroscopic maps, long accumulation point analysis and time-resolved fluorescence 'fingerprinting' of minerals and organics. The sample chamber is capable of pressures $<10^{-4}$ mbar, temperatures $<-20^{\circ}\text{C}$, and different atmosphere compositions such as nitrogen, argon or carbon dioxide via gas hookup. The intended use of the system is to detect and identify minerals and organics within sensitive or fragile planetary samples using minimally destructive laser-based techniques, while maintaining specific environmental conditions to preserve and maintain the pristineness of the material being analyzed, such as samples returned from planetary missions. To validate the functionality of the system as a laboratory tool for samples returned from space or for planetary science experimentation, several experiments were conducted using different materials to showcase the different modalities of the instrumentation. One such experiment is conducted on a non-pristine piece of the Tagish Lake meteorite, containing some of the most primitive materials in our solar system. The meteorite fragment was kept frozen and in an inert atmosphere during Raman (UV and green) and Fluorescence (UV) analyses. These spectroscopic techniques resulted in high-resolution 2D maps of the surface of the meteorite fragment, showing mineral localities and groupings, as well as organic constituents present. UV-Raman in particular results in spectra containing aromatic and aliphatic hydrocarbon, ketones, and cyano radical peaks, all of which are the basic building blocks of important organic constituents like amino acids which play an integral role in biotic life on Earth. The detection of such compounds in the Tagish Lake meteorite using UV-Raman spectroscopy is novel and provides a unique tool to analyze organic constituents within sensitive materials in a very minimally destructive way with no sample preparation.

Dedication

To my grandfather, Ray Lymer (1936–2022) for teaching me to stay curious, be kind and who had a solution to any problem.



Acknowledgements

I am grateful to my supervisor Dr. Michael Daly, whose support allowed me to grow, learn and become an independent researcher in his lab over the past 10 years. Without his support, I would not have pursued graduate studies and would severely lack confidence in my abilities. I would also like to thank Dr. Kim Tait at the Royal Ontario Museum who has unofficially supervised and supported my research and curiosities throughout my graduate degrees. I am grateful for her generosity with her time and expertise in the area of planetary science. Furthermore, I would like to thank the staff at the ROM for their support and guidance, especially Veronica DiCecco whose friendship and knowledge have aided me throughout my graduate studies. I would like to thank all of the members of the Planetary Instrumentation Laboratory at York University (past and present), especially Dr. Emmanuel Lalla and James Freemantle, who without this project would not have been completed; Dr. Evan Eshleman, who patiently taught me Raman Spectroscopy and optics as an undergraduate student; Dr. Amy Shaw, who's support and encouragement kept me in graduate studies; and Kristen Cote who I cannot thank enough for being a best friend, best pep-talker and one of the smartest people I know. Without the support of my family this project, especially through the pandemic, would not have been completed. Thank you to my family, my husband (and my dog) for uplifting my spirits, letting me vent about my problems, and giving me love and support throughout my graduate studies – I could not have done this without you.

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Preface

Sections of this dissertation have been adapted (to/from) published peer-reviewed articles by the author:

Chapter 2, 3; Instrument Design & Laboratory Results

Lymer, Elizabeth A., et al. “The ESCAPE System: A Combined Raman and Time-Resolved Laser-Induced Fluorescence Instrument to Analyze Planetary Material in a Controlled Environment.” *Advances in Space Research*, accepted June 2023.

Chapter 3; time-resolved fluorescence

Lymer, Elizabeth A., et al. “UV Time-Resolved Laser-Induced Fluorescence Spectroscopy of Amino Acids Found in Meteorites: Implications for Space Science and Exploration.” *Astrobiology* 21.11 (2021): 1350-1362.

Chapter 6; The Tagish Lake Meteorite Spectral Experiment

In Preparation

Lymer, Elizabeth A., Sapers, H., Razzell-Hollis, J., Lalla, E.A., Daly, M.G., Tait, K.T. “Detecting HCN in the Tagish Lake Meteorite Using UV-Raman Spectroscopy”

The ESCAPE system has been used outside of the experiments outlined in this study for the following projects:

- Ankita Das’s Master’s Thesis Data Collection, UV Fluorescence
- NASA JPL & LANL Shocked Feldspar Project, UV Raman

1 Introduction

1.1 Motivation

Several sample-return missions such as OSIRIS-REx, Hayabusa2, and Mars sample return missions recently have or are currently proposing, to collect the most pristine planetary samples we can analyze on Earth since the Apollo missions. Therefore, it is essential to create instrumentation that will allow a preliminary compositional analysis of these materials while preventing oxidation, alteration, or contamination from Earth's environment. JAXA's Hayabusa2 mission (ichiro Watanabe et al., 2017) and most recently, NASA's OSIRIS-REx (Lauretta et al., 2017) mission have collected chemically primitive regolith samples from carbon-rich asteroids, which may contain some of the first water and organic material formed in our solar system (Lauretta et al., 2022; Morota et al., 2020). Samples from primitive asteroids can provide insights into how life evolved on Earth, one of the most pressing questions in the field of astrobiology today (Burton et al., 2012). OSIRIS-REx is expected to meet its sampling target of collecting more than 60g of regolith from asteroid Bennu and is en route back to Earth to deliver the samples in 2023. Typically, sensitive planetary materials like meteorites that contain organics (such as amino acids) and water, are stored frozen and/or in an inert gas environment (nitrogen, argon, helium) to ensure these compounds are not lost or altered through reactions in the Earth's environment. It has been shown in the literature that important organic volatiles such as aldehydes, carboxylic acids, etc. can be lost when the sample temperature rises above freezing and therefore, optimal storage temperatures for these carbon-rich materials returned from space should be below -10°C to minimize contamination (Herd et al., 2016). Similarly, astrobiologically relevant materials are being sampled and cached on Mars from the Perseverance rover which upon collection via secondary mission will also require innovative storage and analysis protocols to avoid terrestrial contamination of the samples (Farley et al., 2020). As samples are returned to Earth from missions to our solar systems planets, moons, and small bodies, it is essential that

we continue to innovate ways to perform preliminary compositional analysis on these sensitive materials while preserving them to the greatest extent possible. This study aims to address this problem with the ESCAPE (Environment Spectrum Chamber for Analysis in Planetary Exploration) system. A controlled environment in which sensitive planetary materials can be analyzed for their mineral and organic components using (266 nm, and 532 nm) Raman and LIF (Laser-Induced Fluorescence) spectroscopy with no sample preparation and minimal destruction to the sample. This chamber environment can sustain low temperatures ($< -20^{\circ}\text{C}$) in an inert atmosphere for the preservation of organic and volatile materials. Therefore, it is an excellent instrument to collect preliminary compositional data for samples returned from space.

Raman, and even more recently, fluorescence spectroscopy are somewhat newly developed planetary science and exploration instruments capable of stand-off, minimally destructive, laser-based spectroscopic analysis of geologic and astrobiological materials. Techniques are still being developed for these instruments using different excitation wavelengths and varying modes of operation from time-gating cameras to using microscope objectives to obtain smaller spot sizes for different planetary applications. Recently, fluorescence and Raman instruments have been flown on missions as payload instruments to search for signs of life on Mars (SuperCam, SHERLOC) (Wiens et al., 2021b; Beegle et al., 2015). Understanding the capabilities and limitations of using Raman and fluorescence instruments with multiple wavelengths of excitation is integral to inform the study and interpretation of complex spectral results of SuperCam and SHERLOC data from Mars upon the possible detection and identification of minerals and organics. This study will continue to fill the knowledge gap surrounding the capabilities of telescopic, stand-off Raman and laser-induced fluorescence spectroscopy for planetary science and exploration through the validation of the ESCAPE system by collecting Raman and fluorescence spectra using a variety of modes, on an array of samples relevant to planetary science and astrobiology.

Furthermore, the studies of primitive, carbonaceous meteorites and interplanetary dust

particles that have already arrived on Earth via impact, provide insights into the formation and evolution of our solar system. In addition to providing clues for potential chemical pathways capable of synthesizing important organics for biotic life such as amino acids, these analyses also offer information on the implications of their presence within the first materials of our solar system and their potential to seed life on Earth. During the past several decades, technologies and techniques have advanced, as have the analyses of carbonaceous materials. For decades, carbonaceous chondrites have been analyzed, including the Murchison, Allende, and Tagish Lake meteorites, which have provided important scientific findings regarding prebiotic organic evolution. Using the mineralogy of the sample as context to determine the plausibility of formation processes, these analyses continue to provide novel insights into the formation and complexity of their organic constituents. In terms of analyzing carbonaceous chondrites, UV Raman spectroscopy has rarely been applied, which makes it an exciting tool that may yield novel results. Because the excitation wavelength of UV-Raman is ideal for carbon-based materials with minimal fluorescence emission, UV-Raman is uniquely capable of detecting organic materials in a minimally destructive manner. It is therefore a novel approach to detect organic constituents within a carbonaceous chondrite like that of the Tagish Lake meteorite by using UV-Raman in a way that is minimally destructive, providing insight into a complex prebiotic formation history. In this study, the ESCAPE system is utilized to collect Raman and fluorescence spectra from the Tagish Lake meteorite while under a controlled environment to not only validate the system for asteroid-sample return preliminary compositional analyses but to also collect some of the most in-depth UV-Raman and fluorescence data of the Tagish Lake meteorite thus far to better understand its complex aqueous and organic history.

1.2 Summary of Major Findings

Chapter 1 presents an overview of the use of Raman and Fluorescence spectroscopy in planetary science and space exploration for detecting mineral and organic constituents in

rock samples; describes what the *search for life* means in planetary exploration; and outlines relevant organic materials to astrobiology and exploration.

Chapter 2 provides a comprehensive overview of the ESCAPE system design, build and integration with a Raman and Fluorescence instrument at York University for the preliminary analysis of sensitive materials.

Chapter 3 Presents spectral results demonstrating the main modes of the ESCAPE system: UV- and Green-Raman, UV LIF, and TR-LIF on laboratory standards and doped-analogue samples. These data verify the functionality of the laser-based interrogation instrumentation of the ESCAPE system and provide examples of the high spectral resolution of the optical instrumentation.

Chapters 4 and 5 build on Chapter 3 to verify different modes of the ESCAPE system using more complex samples. Chapter 4 demonstrates using UV transmission Raman and Fluorescence on water and snowmelt samples; Chapter 5 demonstrates using green-Raman and UV fluorescence with REE-doped Lunar simulant samples. The results in Chapter 4 suggest how useful UV fluorescence spectra are at differentiating water-based samples with contamination and organics compared to UV Raman and FTIR spectroscopy. The results in Chapter 5 illustrate the viability of UV fluorescence in detecting small amounts of REEs (Ce, Y) in lunar simulant samples compared to that of Green-Raman and fluorescence which has been proposed as a potential instrument for REE detection in the literature.

Chapter 6 validates the ESCAPE system as a practical tool for detecting and identifying minerals and organics using minimally destructive laser-based techniques (Raman and fluorescence) in sensitive materials while sustaining conditions desirable for maintaining such materials' pristineness. Chapter 6 provides an in-depth spectroscopic study of the Tagish Lake meteorite, where 2D spectral maps of the meteorite are acquired while keeping the sample at temperatures $< -10^{\circ}\text{C}$ in an inert gas atmosphere (nitrogen, argon). Minerals and organic materials are detected and identified using Raman and Fluorescence spectroscopy, exemplifying the functionality of such instrumentation on fine-grained, fissile, fragile, car-

bonaceous material; and furthermore validating the ESCAPE system as a practical system for triage or preliminary analysis of samples returned from space. Moreover, this chapter provides a novel UV-Raman analysis of the Tagish Lake meteorite, through which, identifies important organic components within the meteorite sample such as aliphatic and aromatic hydrocarbons, ketones, and cyano radicals — the essential building blocks for the synthesis of amino acids on asteroid parent bodies.

1.3 Raman and Fluorescence Spectroscopy for Planetary Science and Exploration

A better understanding of the usefulness of Raman and LIF instruments for planetary science and exploration is currently being developed through laboratory and flight experimentation. Raman and Laser-induced fluorescence (LIF) spectroscopy instruments onboard both NASA’s perseverance (SHERLOC, SuperCam) and ESA’s ExoMars (RLS) rovers are minimally destructive, stand-off, laser-based, spectroscopic instruments to search for signs of life (Beegle et al., 2015; Wiens et al., 2021b). Raman uses the inelastic scattering of light from matter to produce a spectrum unique to each molecular structure. Each molecular bond or crystal lattice structure has characteristic vibrational modes due to different masses of atoms and bond strengths resulting in a characteristic spectrum from interrogated samples. Raman scattering refers to the change in the wavelength of scattered light from the incident wavelength, which depends on whether it’s ‘Stokes’ or ‘anti-Stokes’ scattering. In Stokes scattering, the photon causes an electron to transition to a virtual state and the electron then relaxes into the initial electronic state but a higher vibrational energy state with a corresponding loss of energy in the emitted photon. If the electron returns from the virtual state to a lower vibrational state than it started in, a photon is emitted with a higher energy than that of the incident light and is referred to as anti-Stokes scattering. In this study, we view Stokes scattering, where the resulting photons have a lower energy (longer wavelength) than the incident photon.(Long and Long, 2002). These unique vibrational modes produce sharp peaks at specific locations, producing information which can be used to identify and

quantify unknown substances and to study the structural and chemical changes of molecules under different conditions being of special interest in mineralogy and astrobiology (Edwards et al., 2021). For example, compared to other techniques such as mass spectrometry, Raman spectroscopy has the advantage of not requiring ionization of the sample, which can be useful for analyzing delicate or thermally labile samples (Meher and Chen, 2016). Moreover, in modern Raman systems, multiple spectra can be taken of a sample in a raster method to create 2-dimensional compositional maps of a region of interest. Commonly, Raman spectra can become overwhelmed with fluorescence emission recognized as imposing broad peaks within a spectrum, especially while analyzing materials with organic constituents when using visible and near-infrared wavelengths (e.g., 532, 632, 785 nm). However, using a lower excitation wavelength (e.g., 266 nm) allows the energetic separation of Raman spectra and Fluorescence emission (Eshelman et al., 2014). When using 266 nm excitation, we can also induce fluorescence emission that can be imaged separately from Raman spectra and provide its own useful fingerprints for the detection of minerals and organics within a sample (Eshelman et al., 2014). Fluorescence emission is produced when a photon excites an electron within a molecule to some vibrational level in a higher electronic state. When the electron settles back towards ground state, a photon will be emitted at specific wavelengths, different from the excitation wavelength (Eshelman et al., 2015). UV excitation is particularly good for obtaining organic fluorescence because UV energies are between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for many organic compounds, which is required to create fluorescence spectra (Sauer et al., 2010).

Moreover, because fluorescence emission is produced over several nanoseconds to microseconds, fluorescence emission can be time-resolved (TR) by using a pulsed laser and a time-gated camera. Time-resolved (TR) fluorescence spectroscopy is a unique laser-based non-destructive detection and identification technique for organic material in a substrate. Thus, fluorescence growth and decay are observed over time in a unique way that depends on its composition. By measuring the decay rates of the fluorescence, TR-LIF can identify

the decay rate that is specific to each sample as most amino acids and organic materials have strong fluorescence emission (Eshelman et al., 2015). Therefore, TR-LIF is a valuable tool in the field of Astrobiology gathering information to accurately identify and characterize organic compounds (Lymer et al., 2020, 2021). This technique can provide unique biosignatures for a wide range of organic materials, particularly for amino acids, which makes it extremely useful as a non-destructive technique for organic detection and identification in sample return materials such as asteroids, moon, and other planetary bodies. Laser-induced fluorescence (LIF) spectroscopy has been selected as a suitable technique for planetary in-situ exploration, especially focused on Mars exploration. The main advantage remains that when using $UV - \lambda_{Ex}$, LIF is spatially resolved from Raman spectroscopy, sensitive to potential organic signatures at low concentrations, and requires minimal or no sample preparation. Furthermore, UV-LIF, combined with Raman spectroscopy, emerged as an ideal method for the detection of organic fingerprints on different surfaces given the capabilities to separate the Raman effect from LIF. Among the most relevant instruments that became payload systems on the Perseverance Rover (Mars 2020), SHERLOC (Scanning Habitable Environments with Raman & Luminescence for Organics & Chemicals) and SuperCam (Super Camera) apply LIF as the primary technique for detection of possible life in Mars (Beegle et al., 2015; Wiens et al., 2017). Furthermore, LIF has proven to be a useful mapping technique of small features within CV, CK and CM-type carbonaceous chondrites (Lymer, 2017), in addition to organic identification in planetary analogue samples (Cote et al., 2019). In order to have proper identification, quantitative analyses of such organics are required, and can be achieved using decay rate calculation of fluorescence lifetimes for suspected organic constituents, which is particularly useful in asteroid materials as they are suspected to contain insoluble and soluble organic material similar to that of carbonaceous chondrite meteorites (Burton et al., 2012).

1.3.1 Planetary Sample Analogues

Without access to samples collected *in-situ* from a planetary body, planetary scientists rely on analogues; material with a similar composition or characterization to that of what they want to study in the solar system. Analogues can be laboratory-manufactured regolith or soil simulants of a body from known *in-situ* or inferred, compositional analysis. Even better analogues are natural samples from space such as meteorites, as they are materials that match the known compositions of specific planetary bodies in our solar system and are remnants of the building blocks for other planetary bodies. Carbonaceous chondrites are a group of meteorites that are chemically primitive and are considered to be the leftover building blocks from the first phases of our solar system’s formation (McSween and McSween, 1999). Carbonaceous chondrites have a pre-solar composition and contain relatively high carbon content in the form of inorganic carbon structures (e.g. graphite) and non-terrestrial organic aliphatic and aromatic carbon and molecules such as amino acids, amines, and carboxylic acids (Pizzarello et al., 2001; Pizzarello, 2001; Nakamura-Messenger et al., 2006; Yabuta et al., 2010). In order to develop methods required for the analysis of asteroid samples returned from space, it is important to validate the proposed methodology using samples that are similar to that of carbonaceous asteroids. For example, an ideal analogue for the carbonaceous asteroid material, Bennu, is The Tagish Lake meteorite as it is an ungrouped carbonaceous chondrite with a similar composition to Bennu and has been studied extensively shortly after its fall and collected from a frozen lake in British Columbia, Canada in 2000 (Hildebrand et al., 2006). After the observed fall, samples of the meteorite were collected and immediately transported to institutions with deep freezers. Some of these samples, including ‘pristine’ samples, have been preserved at the Royal Ontario Museum (ROM), frozen and relatively undisturbed since 2000. Samples such as the Tagish Lake meteorite provide useful analogue material to study primitive asteroids similar in composition to that of Bennu or Ryugu, in which samples were collected from the OSIRIS-REX and Hayabusa2 missions respectively (Lauretta et al., 2017; ichiro Watanabe et al., 2017).

1.4 Sample Return Missions

As technology advances, uncrewed space exploration missions now have the capabilities to collect, cache, and/or transport, samples collected from other solar system bodies back to Earth. These samples are incredibly important for furthering planetary science as they contain pristine geologic samples with *in-situ* context from the collection site. Apart from the Apollo Lunar samples, planetary science has been conducted *in-situ* using robotic instruments or remote sensing tools on another body controlled from Earth, or through Earth-bound laboratory analysis using samples that have naturally fallen to Earth in the form of meteorites and dust particles. Returned samples from other bodies would allow for more in-depth laboratory analysis to be conducted on pristine samples with context from the collection site, which in-situ instruments cannot perform yet.

As the search for 'life' continues, questions of the formation and evolution of organic material in our early solar system motivates several space missions this decade. NASA's OSIRIS-REx (Lauretta et al., 2017) and JAXA's Hayabusa2 (ichiro Watanabe et al., 2017) missions have collected chemically primitive regolith samples from the carbon-rich asteroids, possibly containing some of the first water and organic material found in our solar system (Lauretta et al., 2022; Morota et al., 2020), which may provide clues to the evolution of biotic life on Earth (Burton et al., 2012). Furthermore, NASA's Mars 2020 mission has begun collecting multiple samples from the Martian surface with features indicative of water flow or of environments that would most likely preserve organic material. Tens of samples are being collected and cached, waiting on the surface for retrieval from a secondary craft in the future and will hopefully return safely to Earth with the first samples collected *in situ* from Mars (Abilleira et al., 2019). Most scientific techniques for studying concentrations of organic and mineral constituents within planetary materials on Earth are destructive in nature. When small amounts of sample return from asteroids (on the order of 60g in the case of NASA's OSIRIS-REx for example (Lauretta et al., 2017)), questions surrounding the destructive

nature and capabilities of an instrument are extremely important in determining which chemical analysis techniques will take priority over others based on preservation potential. Therefore, it is imperative that we create non-destructive spectral analysis techniques to assess the organic and mineral constituents within these rare and sensitive materials returned to Earth.

1.5 The Complexities of Defining and Discovering ‘Life’ in Planetary Exploration

Defining the term *life* or determining if something is *alive* are often conflated, and are partially philosophical questions. However, as the study of life in our universe (astrobiology) progresses, there are general definitions (theories) for what we are actually searching for in our universe when we say the term life. NASA defines life as: “Life is a self-sustaining chemical system capable of Darwinian evolution and considered the specific features of the one life we know — Terran life.” Alternative definitions exist however, Koshland (2002), for example, set out to answer the question *what is life? is a virus alive?* and through these questions defined seven pillars of life: program, improvisation, compartmentalization, energy, regeneration, adaptability and seclusion. However, these pillars create stringency, as a cell may be alive but a single, lone, rabbit may be dead if all pillars must be met according to Benner (2010) as it cannot reproduce. Some definitions of life have suggested that life must be carbon-based, however, if all biomarkers present on a planetary body were say a single type of compound, alkanes (carbon and hydrogen), such compounds would not support life as we know it on Earth (Benner, 2010).

Planetary science and astrobiology are intrinsically linked as planetary science is the interdisciplinary study of the evolution and formation of our solar system which includes planetary evolution and inevitably the processes that led to conditions suitable for life. The basic elements for life are now being found throughout our solar system - simply as: water, carbon, nitrogen, hydrogen, sulphur, phosphorous; and more complexly as chemical compounds essential to life (amino acids, carboxylic acids, etc.) (Dirk and Irwin, 2004).

The National Academies for Science, Engineering and Medicine published “Origins, Worlds and Life: A Decadal Strategy for Planetary Science and Astrobiology 2023-2032” (National Academies of Science Engineering and Medicine, 2022), a document outlining key science questions, presents priority missions, and research strategy for planetary science and astrobiology exploration in the next decade. In this document, three of the 12 priority science question topics are focused on astrobiology and the search for habitability and life; Topic 9: Insights from terrestrial life; Topic 10: Dynamic habitability; and Topic 11: Search for life elsewhere. Some examples of key scientific research goals relating to these overarching questions are: “Q9.1 What Were the Conditions and Processes Conducive to the Origin and Early Evolution of Life on Earth, and What Do They Teach Us About the Possible Emergence and Evolution of Life on Other Worlds?” (National Academies of Science Engineering and Medicine, 2022), “Q10.4 Organic Synthesis and Cycling: Where and How Are Organic Building Blocks of Life Synthesized in the Solar System?” (National Academies of Science Engineering and Medicine, 2022), and “Q11.2 Biosignature Potential: What Is the Biosignature Potential in Habitable Environments Beyond Earth? What Are the Possible Sources of False Positives and False Negatives?” (National Academies of Science Engineering and Medicine, 2022). In the decadal strategy, the mission portfolio assessment matrix outlines the traceability of the priority science questions (topics) addressed in currently funded missions, with topics 10 (dynamic habitability) and topic 11 (search for life elsewhere) being some of the highest-ranking topics for priority sub-questions being addressed through the aforementioned missions in the Mission Portfolio Assessment Matrix (National Academies of Science Engineering and Medicine, 2022). Furthermore, tools such as the ‘Ladder of Life Detection’ have been created to help guide the design of investigations to detect microbial life or biosignatures while considering the constraints of a robotic space mission (Neveu et al., 2018). The ladder of life detection method from Neveu et al. (2018) outlines criteria for a claim of life detection to be credible, considering the current understanding of life on Earth, a convincing life-detection measurement must be sufficiently: 1) sensitive, 2) contamination-

free, 3) Repeatable and, one or more features must be sufficiently: 1) detectable, 2) preserved (survivable), 3) reliable (measurably different from abiotic signals), 4) compatible with life as we know it.

The ladder of life tool is a binary system to help guide the investigations of potential life-detection methods and to justify convincing claims of biosignature or biotic-life detection in planetary exploration (Neveu et al., 2018). For a life-detection claim to be convincing in astrobiology, all other explanations for that biosignature detection must be put to rest and the biological interpretation must be a last-resort hypothesis. To this end, the ladder of life suggests that there be rules for rejecting abiotic hypotheses for how an organic signature came to be (Figure 1). These rules are highly debatable and ideally, a hypothesis for formation should satisfy more than one rule (Neveu et al., 2018), however, these examples of decision frameworks could be used to discuss combinations of evidence that might preclude abiotic interpretations of an investigation’s findings, and could become a community standard for life detection.

1.5.1 Organic Material in Carbonaceous Meteorites

Carbonaceous chondrites are relatively unchanged since their formation and contain the oldest and most primitive material in our solar system (Scott and Krot, 2003). Several carbonaceous chondrites such as the Murchison and Allende meteorites have been found to contain amino acids and other soluble and insoluble organic matter (Campins et al., 2010; Oró et al., 1971; Becker and Bunch, 1997; Wing and Bada, 1991). Amino acids found in meteorites are known to not be terrestrial contamination as they are chiral, meaning they have both right-handed (D) and left-handed (L) versions of the same amino acid, which can be produced abiotically but not biotically (as such, on Earth) (Burton et al., 2012). Amino acids are of particular interest to scientists as their formation and evolution from chirality to homogeneity in biotic life on Earth are yet to be understood, and amino acids are an important component in proteins, RNA, and DNA (Burton et al., 2012). Biologic

Table 1: The ladder of life decision rules for rejection abiotic hypothesis of organic formation modified from Neveu et al. (2018).

<i>Rule</i>	<i>Description</i>
A	Evidence for Darwinian evolution precludes an abiotic origin even in the absence of any other feature.
B	Evidence for a spectral signature of pigments precludes an abiotic origin even in the absence of any other feature.
C	Evidence for DNA or RNA precludes an abiotic origin even in the absence of any other feature.
D	Evidence for both cell-like features and structural preferences in organics (nonrandom and enhancing function, such as a repeating charge or chirality) precludes an abiotic origin.
E	Evidence for both cell-like features and patterns of complexity in organics precludes an abiotic origin.
F	Evidence for both a response to stimulation and structural preferences in organics precludes an abiotic origin.
G	Evidence for both a response to stimulation and patterns of complexity in organics precludes an abiotic origin.
H	Evidence for both a structural preferences and patterns of complexity in organics precludes an abiotic origin.
I	Without evidence for structural preferences in organics , and unless one of the above rules applies, and abiotic origin cannot be precluded.
J	Without evidence for patterns of complexity in organics , and unless one of the above rules applies, and abiotic origin cannot be precluded.
K	Without evidence for either structural preferences or patterns of complexity in organics, an abiotic origin cannot be precluded, regardless of whether there is evidence for cell-like morphologies or a response to stimulation.

homochirality is thought to be a prerequisite for or early product of life and as such, most life on Earth uses L-amino acids and D-sugars with some rare exceptions that are the opposite (Glavin et al., 2020). This preference for handedness by life on Earth may be a complete coincidence and it is believed that life on other planetary bodies could be the opposite handedness as long as both the amino acids and sugars are opposite from each other (Glavin et al., 2020). However, so far there have been no abiotic sources found for D-amino acids, or an L enantiomeric excess of sugars so any detection of these would be a very strong indication for extraterrestrial life (Glavin et al., 2020).

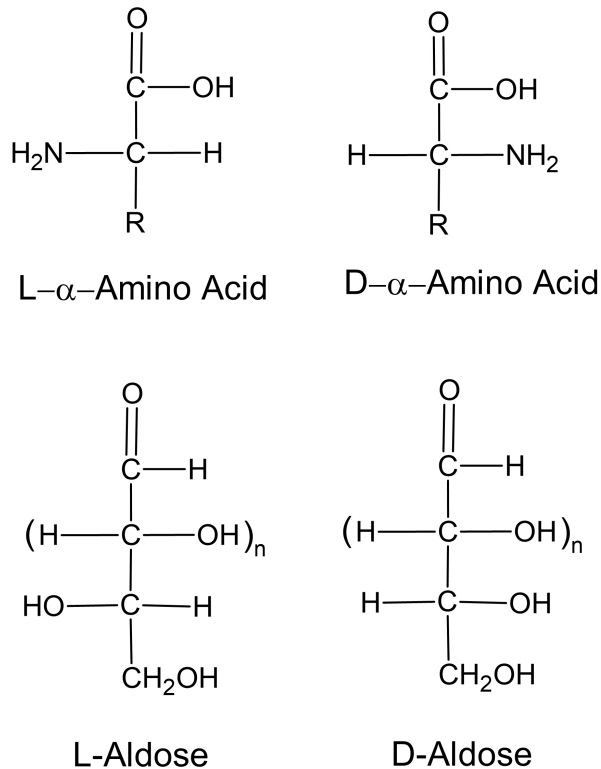


Figure 1.1: Chirality of amino acids and sugars, where (D) denotes right, and (L) denotes left-handedness. Most life on Earth uses L-Amino acids and D-sugars; modified from Glavin et al. (2020).

Laboratory experiments, such as the Miller spark experiment—conducted under a range of plausible prebiotic conditions have shown that amino acids can form by abiotic processes in equal (racemic) mixtures of D–L enantiomers (Glavin et al., 2020). To simulate a primordial Earth, the Miller spark experiment combines simple ingredients for life such as H_2O , CH_4 , NH_3 and H_2S , and with the addition of energy, creates 34 different protein and non-proteinogenic amino acids with similar relative abundances to that found in carbonaceous meteorite samples (Glavin et al., 2020). Furthermore, laboratory experiments have demonstrated that amino acids such as serine, glycine and alanine can be synthesized from analogues of icy interstellar grains (H_2O ices containing, CH_3OH , HCN and NH_3) while exposed to UV light, creating a photochemical reaction (Bernstein et al., 2002).

The formation of amino acids on the asteroid parent bodies from which these meteorites originated is still debated, as there may be several methods for abiotic synthesis,

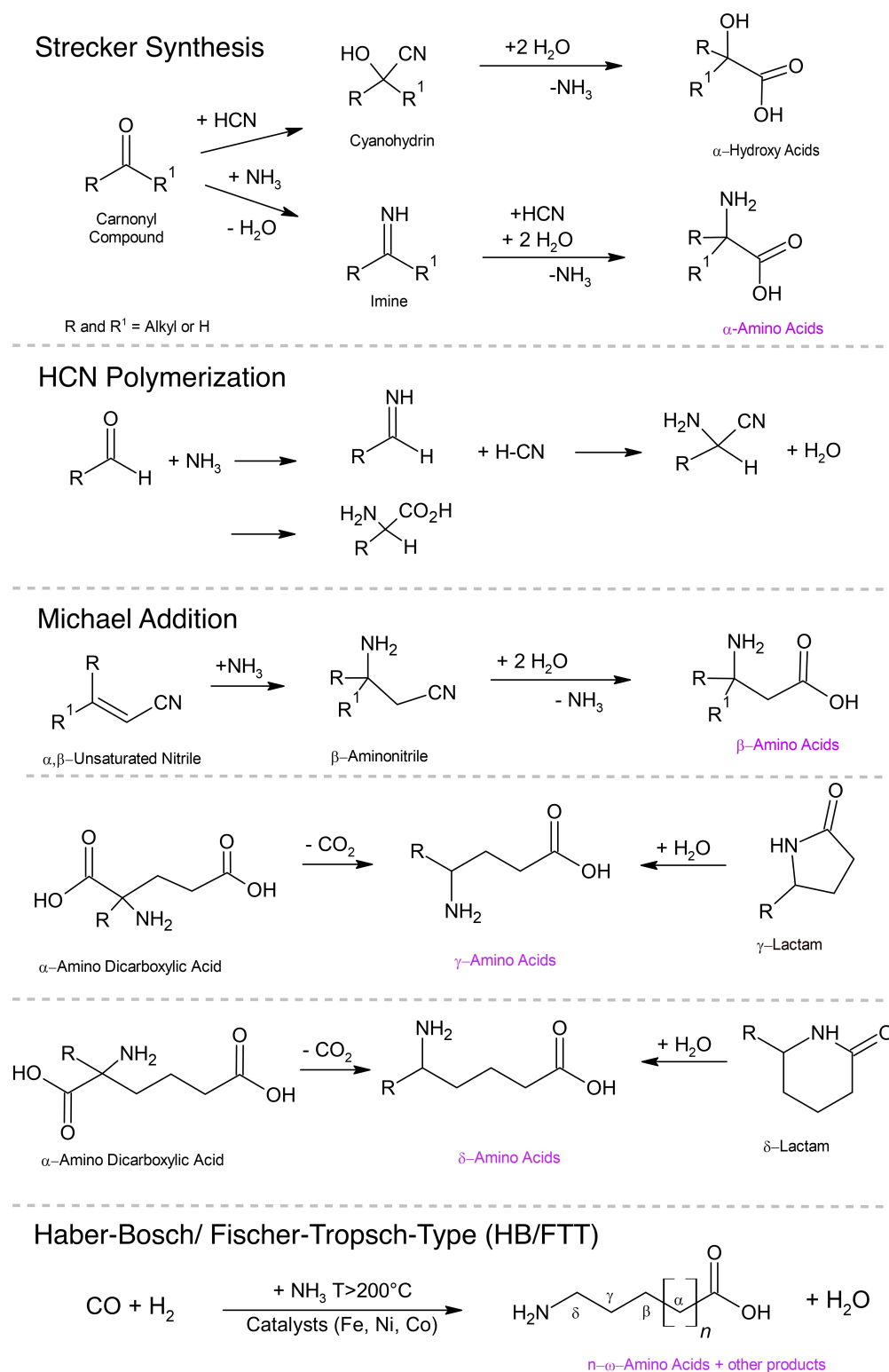


Figure 1.2: Potential chemical pathways for the abiotic synthesis of amino acids on carbonaceous chondrite parent bodies, modified from Glavin et al. (2020); Pizzarello (2012).

with a diverse history (Pizzarello, 2006). Methods for synthesizing α -Amino acids abiotically on a parent body include HCN polymerization or through the Strecker-cyanohydrin pathway when in the presence of water and ammonia (Figure 1.2)(Glavin et al., 2020). Plausible formations for β -, γ -, or δ -Amino acids include different versions of Michael Addition, and furthermore, n - ω -Amino acids and other straight chain hydrocarbons can be formed through Haber-Bosch /Fischer-Tropsch-Type (HB/FTT) reactions (mineral surface-catalyzed reactions of H_2 , CO, and NH_3 at elevated temperatures)(Figure 1.2) (Glavin et al., 2020). Notably, carbonaceous chondrites (such as Murchison and Tagish Lake) have been found to contain L- enantiomeric excesses (L_{ee}) of up to 60%, evidence that abiotic processes can produce large enantiomeric enrichments for some chiral compounds (Table 2) (Glavin et al., 2020). The establishment that enantiomeric excesses in amino acids and sugars can be formed abiotically, suggests that changes must be made to the ladder of life decision-making protocols where $>20\%$ L_{ee} of an amino acid suggests a biosignature detection (Glavin et al., 2020). It still remains unknown whether or not extraterrestrial life in our solar system would be similar to that on Earth, however, the building blocks for life on Earth such as amino acids and sugars are abundant in meteorites/asteroids that could exogenously deliver these important materials to other planets and potentially spark the emergence of biochemistry. Therefore, it is essential to have a deep understanding of the chemical components and raw materials of prebiotic life that are found in meteorites and IDPs (interplanetary dust particles), as well as an understanding of their non-biological chemical background ‘noise’ that could obscure chemical signatures of extinct or extant biological signatures (Glavin et al., 2020). A select few organic molecules, and more specifically, amino acids, relevant to astrobiology are illustrated in Table 2. These amino acids have either been found in meteorites; have been synthesized in a laboratory spark (e.g. Miller spark) or ice photolysis experiment; or have been found in terrestrial biology. Most of the amino acids listed are non-aromatic with the exception of tryptophan, phenylalanine and tyrosine, which are aromatic amino acids (AAA’s). Furthermore, tryptophan is the only amino acid listed that has not been found in

meteorites, yet is used frequently in astrobiology as it, like the other aromatic amino acids, has extremely intense fluorescence/phosphorescence. Tryptophan is ubiquitous in terrestrial biology and plays an important role in synthesizing proteins, however, there has yet to be a reported plausible abiotic synthesis method to form tryptophan under prebiotic conditions (Glavin et al., 2020).

Typically, organic constituents in meteorites are analyzed using crushing, chemical separation and gas chromatography; destructive techniques that provide accurate concentrations and identification of amino acids and other constituents such as in (Pizzarello et al., 2012). These methods were (and remain) a necessity to identify novel extraterrestrial amino acids within the host material in an accurate way. However, these amino acids now known to be present in carbonaceous chondrites can be procured in ‘pure’ form through Sigma Aldrich and can be analyzed in greater concentration than that of the actual amino acids within the carbonaceous chondrites. Because we now know which amino acids have been found using destructive techniques, we can better develop non-destructive techniques for the identification and detection of these constituents. The ability thereof may facilitate the preliminary analysis of sensitive materials such as asteroid sample return material, in addition to instruments searching for biosignatures *in-situ* on other planets such as SuperCam (Wiens et al., 2021b).

Table 2: Examples of relevant amino acids to planetary exploration and prebiotic life, and their occurrences in Biology, ‘Spark’ (Miller spark) and ‘Ice’ abiotic synthesis laboratory experiments and in meteorites; modified from Glavin et al. (2020).

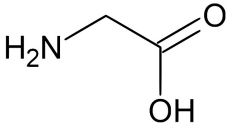
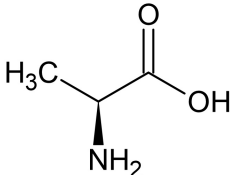
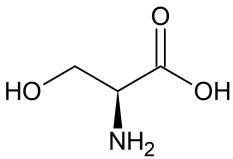
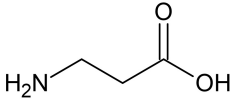
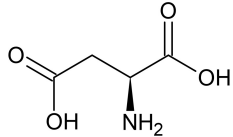
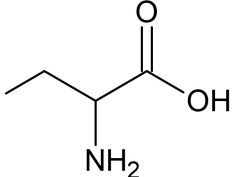
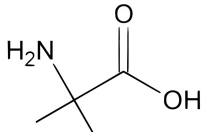
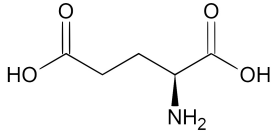
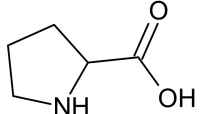
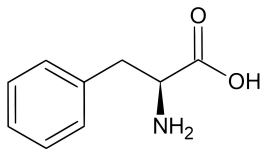
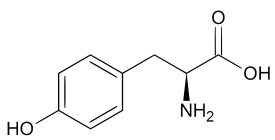
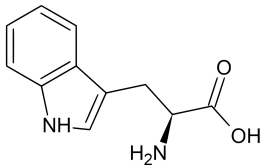
Name	Type	Structure	Meteorite (% L_{ee})	Occurance
Glycine $C_2H_5NO_2$	Proteinogenic Amino Acid		Achiral	Biology, Spark, Meteorites, Ice
Alanine $C_3H_7NO_2$	Proteinogenic α Amino Acid		0.33 (Murchison), 3–7 (Tagish Lake)	Biology (L)(D), Spark, Meteorites, Ice
Serine $C_3H_7NO_3$	Proteinogenic Amino Acid		43 (Murchison), 56–81 (Tagish Lake)	Biology (L), Spark, Meteorites, Ice
β -Alanine $C_3H_7NO_2$	Non-Proteinogenic β Amino Acid		Achiral	Biology, Spark, Meteorites, Ice
Aspartic Acid CH_2COOH	Proteinogenic Amino Acid		14–42 (Murchison) 43–59 (Tagish Lake)	Biology (L), Spark, Meteorites, Ice
α -Aminobutyric Acid $C_4H_9NO_2$	Non-proteinogenic α Amino Acid		1 (Murchison) 4–5 (Tagish Lake)	Spark, Meteorites, Ice

Table 2 continued from previous page

Name	Type	Structure	Meteorite (%L _{ee})	Occurance
2-Aminoisobutyric Acid H ₂ N-C(CH ₃) ₂ -COOH	Non-Proteinogenic Amino Acid		Achiral	Spark, Meteorites, Ice
Glutamic Acid C ₅ H ₉ NO ₄	Proteinogenic Amino Acid		38–42 (Murchison) 51–55 (Tagish Lake)	Biology (L), Spark, Meteorites
Proline C ₅ H ₉ NO ₂	Proteinogenic Amino Acid		49–81 (Murchison)	Biology (L)(D), Spark, Meteorites, Ice
Phenylalanine C ₉ H ₁₁ NO ₂	Proteinogenic Aromatic- Amino Acid		ee n.r.	Biology (L), Meteorites
Tyrosine C ₉ H ₁₁ NO ₃	Proteinogenic Aromatic- Amino Acid		ee n.r.	Biology (L), Meteorites
Tryptophan C ₁₁ H ₁₂ N ₂ O ₂	Proteinogenic Aromatic- Amino Acid		n.d.	Biology (L)

1.6 Contamination Prevention and Storage of Planetary Materials

Astromaterials returned from space are not only scientifically important because they have not been affected by terrestrial weathering like meteorites have; but also have contextual information about the body on which they were collected down to the exact location. This important geologic and geographic context makes samples collected and returned from space all the more precious, and therefore storage and contamination protocols need to be designed and implemented to keep the samples as pristine as possible (Herd et al., 2016). Specific cold curation and clean room facilities have been designed and built to store and prepare sensitive planetary materials such as primitive meteorites and Hayabusa2 returned materials by Herd et al. (2016) and Yada et al. (2014) respectively. Astromaterials pose unique challenges for storage, as materials like carbonaceous chondrites contain important volatiles such as mono- and dicarboxylic acids, aldehydes and amines that would be completely lost if the samples are not handled properly. It has been reported by Herd et al. (2016) that carbonaceous samples may completely lose their volatiles if at temperatures above 0°C, and recommend operating at temperatures from -35°C to -10°C. Furthermore, to prevent reactions and oxidation, operating in an inert gas environment (e.g. nitrogen, argon, helium) in addition to having temperature control is optimal (Herd et al., 2016). Moreover, the samples should not be exposed to water as soluble organics can be lost.

When looking at samples returned from space, it is paramount to limit the ability for terrestrial contamination in the form of inorganic or organic contaminants. To this end, samples returned from the Hayabusa and Hayabusa2 missions are to be sealed in a container that will not be opened until it is in a specially designed clean room facility — The Planetary Material Sample Curation Facility of JAXA (PMSCF/JAXA) (Yada et al., 2014). There, the samples are not exposed to the terrestrial atmosphere, they are only ever in low vacuum or nitrogen environments to prevent reactions and contamination. Furthermore, special consideration is taken to ensure that the rooms and instruments are cleaned by complex

exhaust systems, acid/alcohol distillers, and chambers equipped with mass spectrometers to check for contamination (Yada et al., 2014). Additionally, to sterilize the surface of materials, CO₂ and atmospheric-pressure plasma cleaners are used if there is bacterial or organic contamination (Yada et al., 2014).

These contamination protocols are important to preserve the materials, but also to ensure that if a biosignature is detected in a sample it is unlikely to be terrestrial contamination. Moreover, these protocols are complex and require specific facilities to be comprehensive.

1.7 Contribution to the Field of Study

As we prepare for sample-return missions such as OSIRIS-REx and Hayabusa2, to deliver pristine and scientifically priceless materials from our solar system’s bodies, it is essential to create instrumentation that will allow preliminary compositional analysis of these materials while preventing oxidation, alteration, or contamination from Earth’s environment. Thus, we have built a small, transportable environmental chamber with temperature, pressure, and atmosphere control that has been integrated on an optical table with a combined UV (266 nm) and Green (532 nm) Raman, laser-induced fluorescence, and time-resolved laser-induced fluorescence instrumentation. This system can collect high-resolution 2D spectroscopic maps, long accumulation point analysis and time-resolved fluorescence ‘fingerprinting’ of sensitive samples. These spectral data will provide mineral and organic detection and identification. The sample chamber is capable of pressures $<10^{-4}$ mbar, temperatures $<-20^{\circ}\text{C}$, and different atmospheric compositions such nitrogen, argon, or carbon dioxide via gas hookup to sustain conditions that are conducive to the preservation of space materials. Not only does this system allow for high-resolution spectral imaging, identification and detection of organics, but also does so using standoff, minimally destructive laser-based techniques while the sample remains in its pristine form in an ideal environment during analysis. This system is an optimal tool for triage or preliminary analysis of small samples that have been returned to space to find areas of geologic and astrobiologic interest to inform potential further, more

destructive studies and gain a better, initial, understanding of the samples. Furthermore, this system is a versatile, modular, laboratory tool to mimic different environments and therefore has numerous applications for laboratory experiments for planetary science.

Moreover, through the validation of the ESCAPE system in this work, the most comprehensive spectral mapping of the Tagish Lake meteorite is taking place. Multiple wavelengths (UV, green) of Raman spectroscopy produce in-depth, high-resolution spectral maps of a large portion of the Tagish Lake fragments provided by the Royal Ontario Museum for this study. These spectral data provide useful organic and mineral signatures, similar to that found in the meteorite using more destructive methods, which provide important context for the formation and evolution of the early materials in our solar system. The results of this study provide sufficient data to show how useful UV-Raman spectroscopy is at detecting and identifying minerals, but especially complex organics within carbon-rich planetary materials. These data will inform future experiments using UV-Raman on sensitive materials such as other meteorites and samples returned from space.

2 Instrument Design

The ESCAPE system is a combined Raman and laser-induced fluorescence (LIF) instrument integrated with an environmental sample chamber for the analysis of minerals and organic constituents in sensitive planetary or terrestrial materials. The system is designed to allow for the analysis of samples in different atmospheric conditions (composition, temperature, pressure) that could either mimic a specific planetary environment (Mars, the Moon, an icy body or an asteroid) or keep a sample in conditions that are conducive to preserving sensitive planetary materials. An example of such a sample would be a ‘pristine’ meteorite in a nitrogen or helium atmosphere to prevent oxidation while maintaining frozen temperatures to prevent volatile loss (Herd et al., 2016; McCubbin et al., 2019). Raman and laser-induced fluorescence spectroscopy provide minimally destructive compositional analysis of the samples within the chamber without any sample preparation or destruction.

2.1 Building the ESCAPE Chamber

A 30 x 30 cm environmental chamber was built in the Planetary Exploration Instrumentation Laboratory (PIL) at York University. This chamber went through several months of design and prototyping of internal equipment, cables, and temperature controls before being assembled. The chamber was assembled on an optical breadboard table to allow integration with other instrumentation such as optical instruments and mass spectrometer in a modular fashion. The sample loading door, sapphire window, and fittings were added, followed by the hand-made electrical components, copper cooling plumbing, and thermocouples for temperature control and monitoring. The chamber has been equipped with a high-powered, oil-free vacuum pump and reached a pressure of 1×10^{-5} mbar. To cool the sample stage in the chamber, a heat sink connected to a chiller was installed within the chamber with a thermoelectric cooler on top, together capable of reaching temperatures of -30°C at atmospheric pressure. The sample stage components are mounted on vacuum-compatible 2-axis

Newport motors to facilitate the 2D mapping of samples. The sample stage is able to be chilled to below -20°C at atmospheric pressure. A gas fitting was installed for a nitrogen gas tank hookup, allowing a purge of the chamber from the back out the front door during sample placement to limit humidity. This nitrogen gas is then removed from the chamber using the vacuum pump before analyses.

2.2 Optical Design

Excitation for Raman and Fluorescence analysis in the chamber is provided by both 266 nm and 532 nm TEEM Photonics Nd:YAG lasers. The excitation light is first collimated using short focal distance convex lenses. The two beams are then overlapped using a 1-inch beam variable expander, which focuses the light at the corresponding distance inside the chamber (to focus the spot size at the sample). Additionally, the two beams are directed toward three mirrors, one of which is used for tip/tilt control to ensure proper alignment. The beams are then focused using an off-axis parabolic mirror with a focal distance of 15 cm onto the target through the sapphire window of the chamber and subsequently onto the sample stage. All optical lenses and the off-axis parabolic mirror are designed to enhance UV transmission and reflection for both wavelengths to achieve maximum performance. For 266 nm excitation, a bandpass filter is used to transmit any extraneous light from the laser and reflect only 266 nm. In addition to the bandpass filter just after the laser output, the optical setup includes a SemRock 45-degree dichroic mirror to focus 266 nm light on the parabolic mirror just before the sample. This dichroic mirror is replaced by a SemRock 532 nm dichroic mirror and the bandpass filter is replaced with a MaxLine 532 nm filter when exciting with 532 nm. A 150 mm (diameter) telescope has been customized with a UV-coated secondary mirror and was installed as the collection optics in order to capture as much light as possible emitted from the sample. The telescope consists of a 150 mm primary mirror that focuses light onto a 75 mm secondary mirror. The telescope has been modified to have an $F/\#$ of 13.33. However, the secondary mirror is adjustable and can be used to focus the

collection optics at distances ranging from 2 to 2.25 meters. The total loss of emission optics for both lasers was measured using a Thorlabs Power Meter with an S120UV Photodiode before and after each optical component. The initial laser power at 1000 Hz for the 266 nm laser was 10.5 mW, and the final obtained laser power at the sample was 4.89 mW. Similarly, the initial and final laser power for the 532 nm laser was 32.5 mW and 10.5 mW, respectively. The spot size at the target sample area was 0.5 mm estimated with a razor's edge power measurement. The collection optics focus scattered light from the sample through the collection optics into a 15-meter fibre bundle mounted into the telescope hole. Before reaching the collection optics, either a 266 nm or 532 nm Semrock RazorsEdge long pass Raman filter is installed depending on the excitation wavelength. The collection optics focus scattered light from the sample through the collection optics into a 15-meter fibre bundle mounted into the telescope hole. The fibre-optic cable is manufactured by CeramOptec, capable of transmitting 260 nm–750 nm and has a 50 μm fused silica core and an NA of 0.22 ± 0.2 . To verify the efficiency of the collection optics of the customized telescope coupled with the optical fibre, we connected the system to a 635 nm Andor laser (ME-OPT-0007). The total power of the laser before the fibre was 4 mW, and the power of the laser through the fibre was 3.63 mW and focused at a 30 cm distance through the telescope optics was 0.36 mW, indicating a loss of 90%. The spot size generated by the laser was 2 mm in diameter, which is larger than the laser spot size of 0.5 mm on the target. This ensures that we collect as much light as possible. The fibre is connected via SMA to a mechanical slit in an Andor Solis Shamrock spectrometer (SR-303i) coupled to an iSTAR iCCD (intensified charge-coupled device) camera with ultra-fast gating capabilities. This pairing allows high spectral resolution for UV and green Raman spectroscopy using a 2400 x 2400 line/mm or 1200 x 1200 line/mm diffraction grating, as well as high-resolution UV time-resolved fluorescence spectroscopy using a 600x600 line/mm diffraction grating. These gratings can be simultaneously mounted within the 303i spectrometer and automatically rotated using Andor Solis software. Using an Ocean Optics Mercury-Argon lamp, we calibrate the Shamrock 303i

spectrometer grating offset and mirror focus settings, in addition to calibrating the x-axis for sample collection. After calibrating the spectrometer with the mercury-argon lamp, we can also manually calibrate the x-axis for Raman analysis using pure samples of materials with well-documented, known peak positions (e.g., gypsum or L-Alanine). The resolution of the spectrometer, when used with the iStar iCCD, varied between gratings as follows: 1) between 0.04 and 0.05 nm when using the 2400 x 2400 line/mm grating; 2) between 0.9 and 1.2 nm when using the 1200 x 1200 line/mm grating; and 3) between 0.18 and 0.21 nm when using the 600 x 600 line/mm grating. Several lines from the mercury-argon lamp covered the Raman region when using both the 266 nm and 532 nm lasers. In the case of generating Raman Spectroscopy under 266 nm excitation wavelengths, we used the lines at 296.73 and 302 nm. For the Raman effect under 532 nm, we used the lines located at 546.07 nm and the doublet at 576.96 and 579.07 nm. The resolution of the system also varies with slit opening and therefore was also verified by calculating the FWHM of Ocean Insights Hg-Ar lamp peak centred at 546.074 nm. The FWHM of a Gaussian peak fit to the 546.074 nm peak using the 1200 line/mm grating and a slit size of 30 μm was 0.14 nm (5 cm^{-1}), supporting the factory calculations of resolution of the system (see section 2.6 for more information on calibrating the instrument).

The ESCAPE system has 3 modes of operation:

1. Raman spectroscopy mode (266 or 532 nm excitation)
2. Laser-induced fluorescence mode (266 or 532 nm excitation)
3. Time-resolved laser-induced fluorescence mode (266 or 532 nm excitation)

The system is easily switched between modes by either changing out a few optical pieces (i.e., wavelength-specific Raman filters and dichroic mirrors) or changing iCCD camera settings in Andor Solis acquisition software such as gate delay and ‘accumulate’ mode for Raman and fluorescence spectroscopy vs. ‘kinetic mode’ for time-resolved fluorescence.

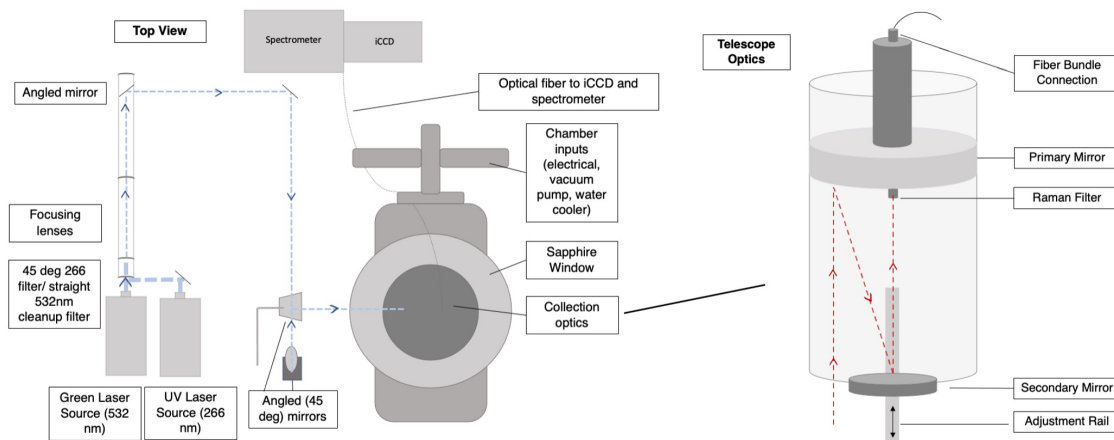


Figure 2.1: Schematics of ESCAPE system breadboard setup (left) and collection optics mounted above chamber window (right).

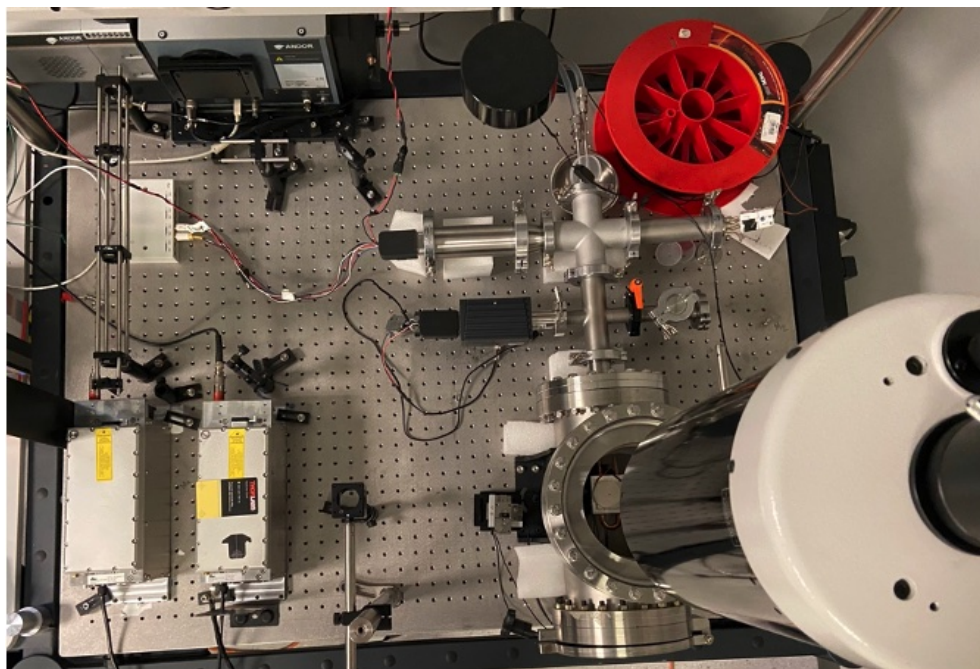


Figure 2.2: Image of ESCAPE system breadboard setup at York University. For scale, the system is on top of a 122 x 91.5 cm optical table.

2.3 Raman Spectroscopy Mode

Raman spectroscopy takes advantage of the physical characteristics of molecular bonds to create a unique spectral signature for each compound. Raman scattering occurs when a molecule is excited by a laser source, causing vibration within the molecule. This vibra-

tion leads to the inelastic scattering of a photon, which has a shift in frequency away from the excitation wavelength due to the change in energy in the molecule (Long and Long, 2002). This Raman shift is measured as scattered light intensity (in counts) vs. Raman shift from the excitation wavelength (inverse centimetres). Because Raman bands or peaks relate to a vibrational mode from molecular bonds, a spectrum is essentially a fingerprint used to identify organics or minerals in the target sample (Eshelman et al., 2014). Raman identification becomes complex when there are fine-grained, mixed materials often found in natural samples as the fingerprints are now a convolution of multiple constituents. Spectral unmixing models are also challenging to use in this scenario, especially when working remotely when the material compositions and proportions are not known prior to interrogation (Razzell Hollis et al., 2020). For Raman spectroscopy, the ESCAPE system provides 266 or 532 nm laser excitation. UV Raman spectroscopy is ideal for mineral and organic detection and identification as the Raman spectra are energetically separated from fluorescence emission, which typically overwhelms Raman spectra in longer excitation wavelengths (Eshelman et al., 2014; Asher and Johnson, 1984; Tarcea et al., 2008; Abbey et al., 2017). A challenge for UV Raman Arises, however, when analyzing iron-rich materials, as iron absorbs both incident and scattered UV light in the 255-275 nm range (Razzell Hollis et al., 2021). As there are many minerals rich in iron, Raman spectroscopy using 532 nm is often used for mineral identification. There are also many spectra to compare with for easier identification (i.e., RRUFF mineral database (Lafuente et al., 2016)).

The ESCAPE system has a Raman spectral range with 266 and 532 nm laser excitation of 280 to $>4000\text{ cm}^{-1}$ at a spectral resolution of 5 cm^{-1} (Table 1), however, higher resolutions can be achieved using a finer grating (2400 lines/mm). Each laser in the ESCAPE system has a spot size at the sample of $<0.5\text{ mm}$, or just under $500\text{ }\mu\text{m}$ (see Table 3). To acquire Raman spectra an optical delay (47 ns for 266 nm, and 40 ns for 532 nm) is input into the Andor Solis software. These delay values sync the iCCD camera opening during the peak intensity of the laser pulse hitting the sample and being collected by the iCCD. A gate width

of <10 ns is used when acquiring Raman spectroscopy, and in the ESCAPE system, a gate width of 4–6 ns is used to capture the optimal Raman signal. The number of accumulations and exposure time varies depending on the sample being analyzed and how Raman-active it is. Typically, in the ESCAPE system an exposure time of 0.1s is used, and accumulations usually vary between 40–200 to give an acquisition time of 4–20s on average. Using this system, longer acquisition times up to several minutes per sample are not typically needed but are possible for minerals with weak Raman signals.

2.4 Laser-Induced Fluorescence (LIF) Mode

Fluorescence is produced by exciting an electron to a higher vibrational state, upon relaxation a photon is emitted at a longer wavelength (measured in nanometers) than excitation. When using UV light, we can energetically separate Raman scattering from fluorescence. In the ESCAPE system, we use 266 nm excitation to induce fluorescence emission from a sample, which appears as a broadband spectrum. Fluorescence is particularly useful for detecting organic material such as amino acids, carboxylic acids, amines etc., as they have very strong fluorescence emission (Lymer et al., 2021). The ESCAPE system has a fluorescence spectral resolution of 0.07 nm (Table 1) while using a 1200 lines/mm grating in the Shamrock Spectrometer. The same delay is used for taking single broad-band spectra of fluorescence emission as for Raman scattering and is based on the 266 nm delay time (47 ns) and 532 nm delay time (40 ns). The iCCD gate width is also opened more than Raman scattering and is usually >10 ns–100 ns. The imaging window is changed from Raman shift (Table 1) to wavelength in the range of 266–850 nm. Acquisition times are typically short using this system with accumulation values around 10–100 and an exposure time of 0.1s, resulting in a total data collection time of 1–10 seconds.

2.5 Time-Resolved Laser-Induced Fluorescence (TR-LIF) Mode

Time-resolved fluorescence spectroscopy is a technique for imaging fluorescence growth and decay overtime on the order of nanoseconds to–microseconds depending on the chemical structure of the sample. From TR-LIF we can calculate the unique decay rates for each material analyzed, allowing for better identification (Eshelman et al., 2015; Lymer et al., 2021).

Using the ESCAPE system, TR-LIF spectroscopy is performed using ‘kinetic mode’ in the iSTAR iCCD camera, usually with a 0.1 ns continuous step, over 200 spectra series: thus, creating a 20 ns long data set of intensity vs. wavelength. Generally, a 20 ns window is used for data collection as organic material has a decay rate of <5 ns and minerals have a decay rate that is typically >10 ns (Lymer et al., 2021). An excitation wavelength of 266 nm is used for TR-LIF, and the fluorescence window typically used is 270–550 nm but can be extended up to 850 nm using the 303i Shamrock spectrometer. When TR-LIF data is acquired using the ESCAPE system, different settings for the delay, gate width, and exposure can be used to best image the sample; however, the standard acquisition settings used are a delay just below that of peak laser intensity, with a similar gate width than used for Raman, of 3–10 ns.

Table 3: ESCAPE Raman and LIF Instrument Parameters Compared to That of SHERLOC (Wiens et al., 2021a; Bhartia, R. et al., 2021) and LiRS Instruments modified from (Shkolyar et al., 2021) and SuperCam from (Wiens et al., 2021b). Both LIRS and SuperCam are combined Raman, LIF and LIBS instruments, however, LIBS parameters were left out of the table as we focus on Raman and LIF parameters only here.

Parameter	SHERLOC (Raman/LIF)	LIRS (Raman/LIF/LIBS)	SuperCam (Raman/LIF/LIBS)	ESCAPE System (Raman/LIF)	
Laser Source	NeCu Transverse Excited Hollow Cathode Glow Discharge	Diode-Pumped Solid- State Nd:YAG	Pulse, ND:YAG	Passive Q-switch Solid State Nd:YAG Lasers	
Laser Repetition Rate	10–160 Hz	5–50 kHz	10 Hz	500 Hz – 2 kHz	
Laser Excitation (nm)	248.6	266	532	266	532
Energy per unit area on sample surface (J/cm^2)	5.6	5–28 (Varies with working distance)	> 1 ($>10 \text{ mW}/\text{mm}^2$)	3.54 (Varies with working distance)	6.78 (Varies with working distance)
Spectral Resolution (Raman; cm^{-1})	40	16	12	5 (at 1200 l/mm)	5 (at 1200 l/mm)
Spectral Resolution (Fluorescence; nm)	0.269	0.1	0.3–0.4	0.07 (with 1200 l/mm grating)	
Raman Spectral Range cm^{-1}	810 to >3400	280 to >4000	105 to 4000	280 to >4000	550 to >4000
Fluorescence Range (nm)	275–350	270–850	535–855	270–850	260 to 532, 536–800
Spot Size (μm)	100–120	~ 10	1300–5000 (Varies with working distance)	480	460
Working Distance (mm)	~ 48	200–500	~ 2000 –2500 to 7000	370–2000	370–2000
Time-Resolved Measurements	Not Possible	Possible (1 ns temporal resolution)	Possible (10 ns temporal resolution)	Possible (0.1 ns temporal resolution)	

2.6 ESCAPE System Calibration Methods

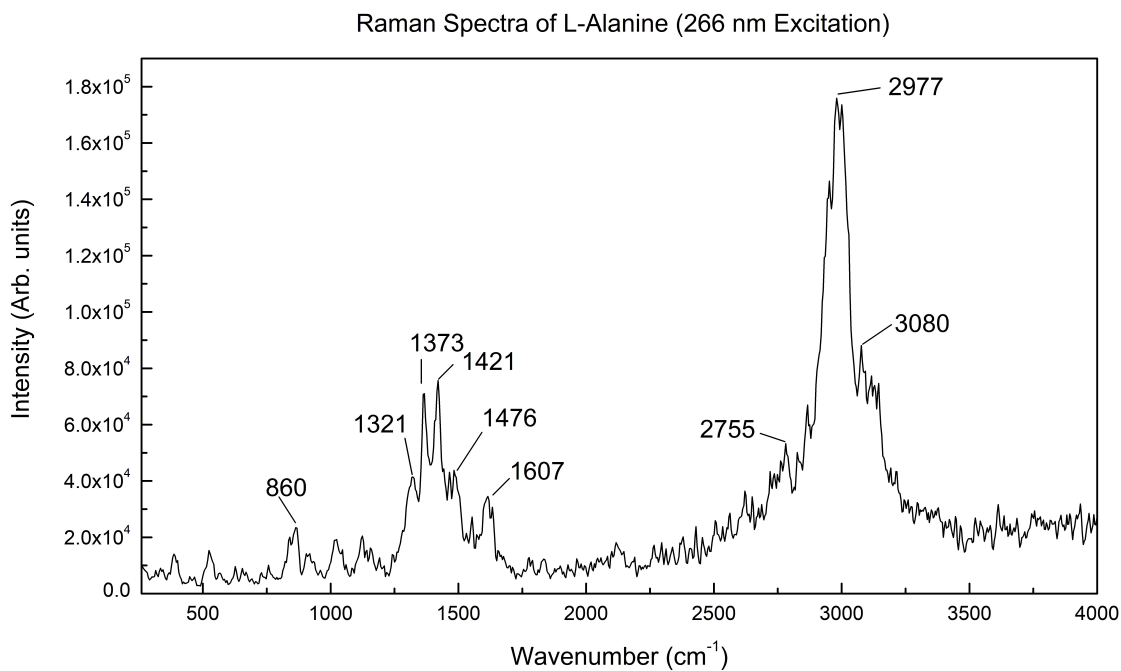
Calibration is extremely important for Raman spectroscopy especially because precise peak positions are crucial for the accurate identification of organics and minerals as each spectrum is a unique spectral fingerprint for the compounds present. Systematic calibration is also important for comparing Raman and fluorescence data collected on different instruments. There are several standard methods for calibrating the x-axis, intensity, and bandwidth for Raman instruments that use standardized calibration sources with known or specific peak positions or intensity such as mercury-argon and deuterium-halogen lamps (Jakubek and Fries, 2022). The ESCAPE instrument is calibrated in the following conditions: each day before a set of data collection, when switching between different resolution gratings in the spectrometer (600 vs. 1200 vs. 2400 lines/mm resolution), or when switching between wavelengths. Additionally, the x-axis may need to be re-calibrated more often than a full spectrometer re-calibration as changing between Raman shift and wavelength on the x-axis requires different inputs for manual x-calibration.

For a full spectrograph calibration, settings in Andor Solis are adjusted depending on excitation wavelength and a calibration light source is used with known peak positions. Spectrometer ‘offset’ calibrations should be completed when changing between diffraction gratings. The offset calibration ensures that the centre of the observation window selected and the actual centre of the spectrograph are in good alignment. To accomplish this, we use a known peak to centre on from a standard light source, in this case, an Ocean Optics mercury-argon (Hg-Ar) lamp. This lamp has a very bright peak at 546.074 nm, which is perfect to use for offset calibrations. The centre wavelength is set to this value and a single acquisition of the lamp is taken. Because the lamp is so bright, typical acquisition settings to collect spectra from a light source differ from that of regular acquisition settings (i.e. Acquisition mode: single shot, trigger: internal, DDG: Fire Only, Exposure time: 0.01 seconds, Gain: 10). The centre of the spectrograph is ‘offset’ until the peak from the Hg-Ar lamp and the the

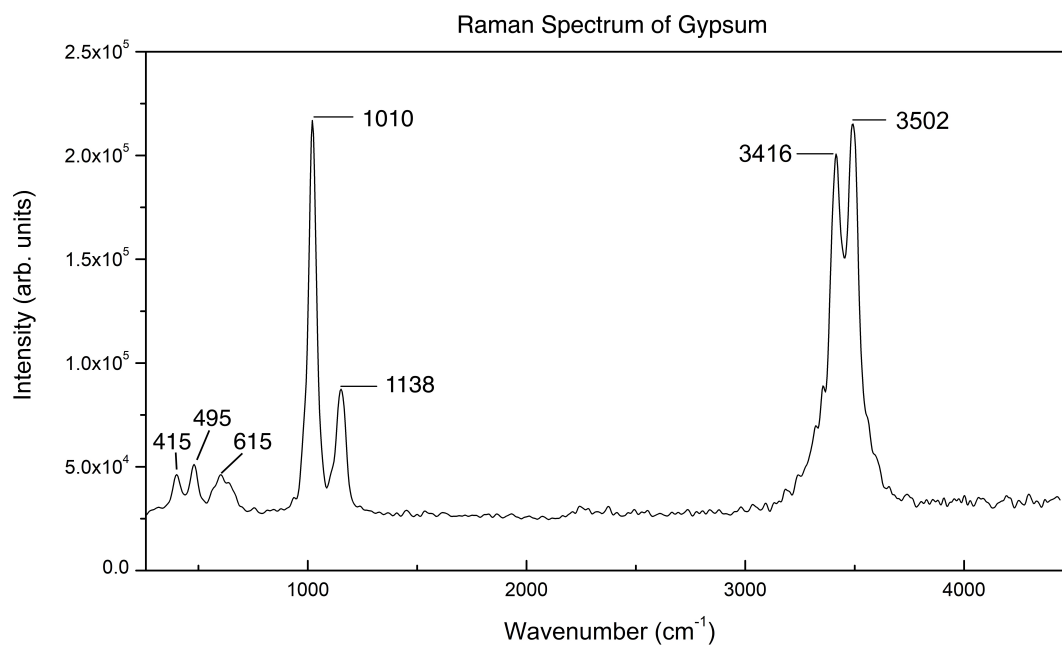
centre line aligned. Subsequently, the x-axis should be calibrated using sources with known peak positions once the spectrograph is centred. For a desired wavelength (nm) x-axis, the Hg-Ar lamp is used as the known peaks are in nanometers, whereas if the desired x-axis is Raman shift (cm^{-1}) then a laboratory standard is used such as gypsum or L-alanine where Raman vibrational peaks are known in (cm^{-1}). Examples of manual x-calibration reference images can be seen in Figure 2.3. When setting the x-axis for mapping, the calibration spectra are flipped to align correctly with the x-axis in the LabView mapping software.

Further instrument calibrations include intensity calibration and bandwidth calibration. Both of these calibrations are time sensitive according to Jakubek and Fries (2022) and are dependent on instrument settings (i.e. slit opening, gain, intensifier settings). Bandwidth calibration is the measure of the FWHM (full-width half maximum) value for samples with known Raman bandwidth peaks. A bandwidth calibration is only really necessary if the spectra from a remote instrument are to be replicated (i.e. SHERLOC breadboard calibration). However, a bandwidth resolution calculation in this fashion was conducted for the ESCAPE system at varying slit openings and diffraction gratings used in the studies presented here. For bandwidth resolution, the FWHM of the 546.074 nm spectral line generated by the Ocean Insights HG-1 mercury-argon light source was calculated with a slit opening of 30, 50, 150, and 250 μm using the 600 lines/mm and 1200 lines/mm gratings respectively. The average spectral resolution (FWHM of line 546.074) is 0.14 nm, or 5 cm^{-1} when using 30 μm slit opening and 1200 lines/mm diffraction grating. Opening the slit to 250 μm and using the 600 lines/mm grating decreases the spectral resolution to 0.99 nm or 35 cm^{-1} . These measurements are presented in Table 4. These measurements are in good agreement with resolution calculations for the system based on Andor specifications.

An instrument response function (IRF) can be calculated for a system using an Ocean Optics deuterium-hydrogen lamp where the intensity at specific wavelengths is well characterized. The instrument response curve provided by Ocean Optics is then divided by the intensity curve collected by the instrument to obtain the IRF (Jakubek and Fries, 2022). The



(a) 266 nm Raman Spectrum of L-Alanine



(b) 266 nm Raman Spectrum of Gypsum

Figure 2.3: Raman spectra of laboratory standards with known peak positions for calibration of Raman x-axis.

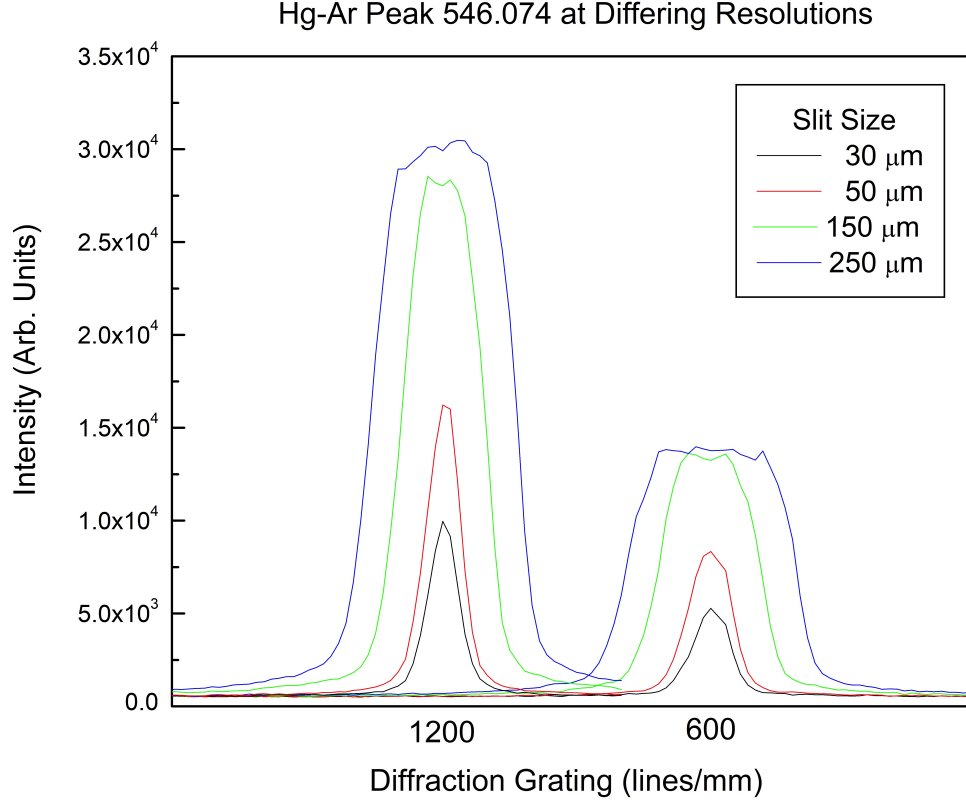


Figure 2.4: Visual representation of FWHM of Hg-Ar lamp peak 546.074 nm changing with grating and slit opening.

Table 4: Spectral resolution variation of the ESCAPE system with slit size and diffraction grating measured by FWHM calculations of spectral peak 546.074 nm generated by Ocean Insights HG-1 mercury-argon light source.

Diffraction Grating	Slit Opening	FWHM (nm)	Resolution cm^{-1}
1200 lines/mm	30 μm	0.1513	5.4
	50 μm	0.1733	6.1
	150 μm	0.3515	12.4
	250 μm	0.5274	18.4
600 lines/mm	30 μm	0.2813	9.9
	50 μm	0.3078	10.8
	150 μm	0.6023	21.3
	250 μm	0.9990	35.3

IRF can be used as a correction factor to be applied to spectra taken by the instrument on different days to compare intensities accurately. Relative intensity—or one peak compared to another in a single spectra do not require this calibration, and is mostly used in this study.

The ESCAPE system’s motorized sample stage is also calibrated before collecting 2-dimensional raster maps. Each motor is meticulously calibrated using a 2-dimensional scale placed in the centre of the motorized stages and moving them at specific millimetre increments until the number of steps per millimetre is calibrated to be correct. To check the accuracy, the ‘relative move’ function is used in the LabView Raman Mapping software. When the relative move matches the millimetres moved on the sample stage scale (using a trace of the laser spot) at different scales (e.g. 0.1 mm vs. 5 mm relative move increments) then the motors are calibrated.

3 Results I: Raman and Fluorescence of Laboratory Standards

3.1 Preparation of Laboratory Standard Samples

For calibration and preliminary analysis using the ESCAPE system, ‘pure’ (>95%) synthesized amino acids from Sigma-Aldrich were crushed with a mortar and pestle (cleaned and sterilized with isopropyl alcohol), and 0.5 - 1g of crushed sample is pelletized. Synthesized minerals such as gypsum (CaSO_4) were also supplied by Sigma-Aldrich and pelletized in the same way as the organic samples. Several small hand samples of geologic standards are also available in the laboratory for analysis such as quartz, calcite, anorthite, and olivine (dunite). These hand samples were not prepared in any way for Raman and fluorescence analysis. These laboratory samples are analogues for minerals and organics commonly found in meteorites and other planetary materials (Becker and Bunch, 1997; Pizzarello et al., 2008; Parker et al., 2022). Laboratory analogues such as these are also essential for proper calibration and preliminary testing of the ESCAPE system as they have unique peaks over a large spectral window and at varying intensities. Ensuring that the ESCAPE system obtains good spectra for these laboratory standards promotes confidence in subsequently obtaining accurate data while analyzing unknown or samples that have not yet been analyzed.

3.2 Spectral Analysis of Laboratory Standards

A few examples of each type of data product from the ESCAPE system are shown in Figure 3.1 and 3.2, mostly of geologic and astrobiological standards of common planetary minerals and organics that have been found in carbonaceous meteorites (Becker and Bunch, 1997; Pizzarello et al., 2008) and most recently in, Hayabusa sample return material (Parker et al., 2022).

Examples of UV Raman spectra are shown in Figure 3.1 and 3.2. With the spectral resolution of the ESCAPE system, we can resolve the O-H doublet of gypsum in a UV

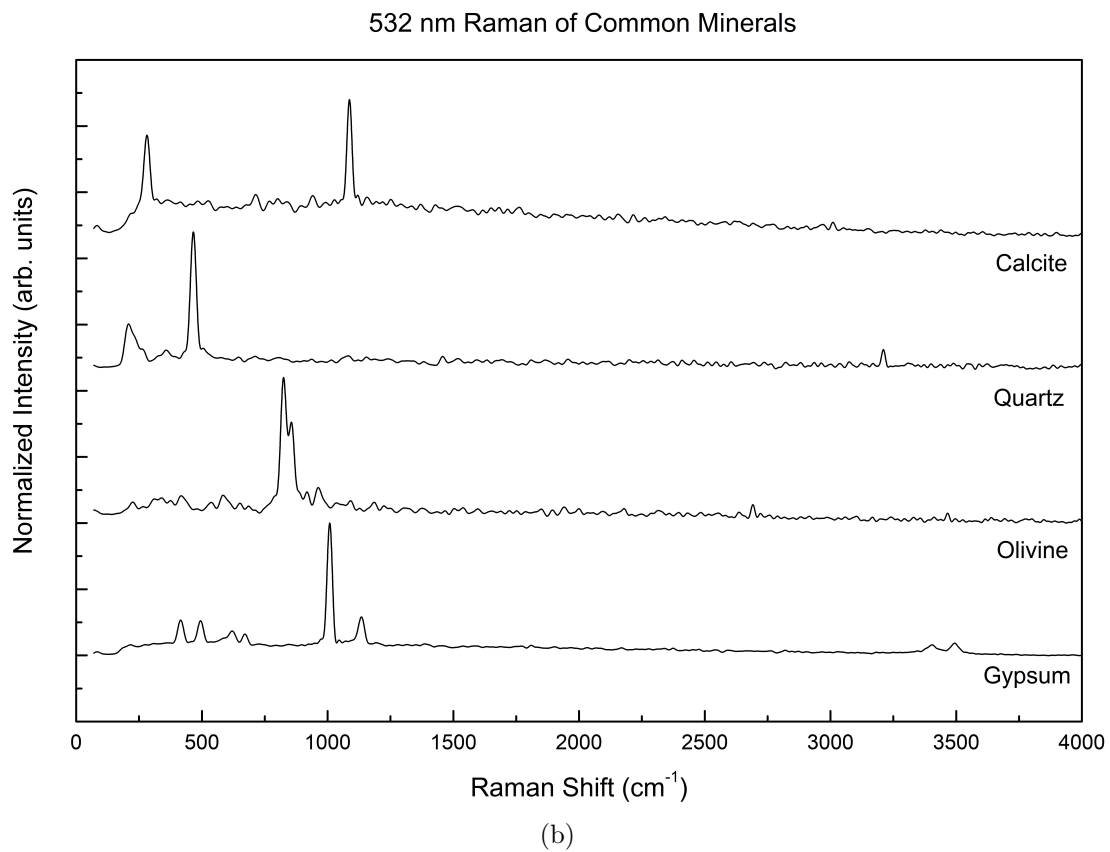
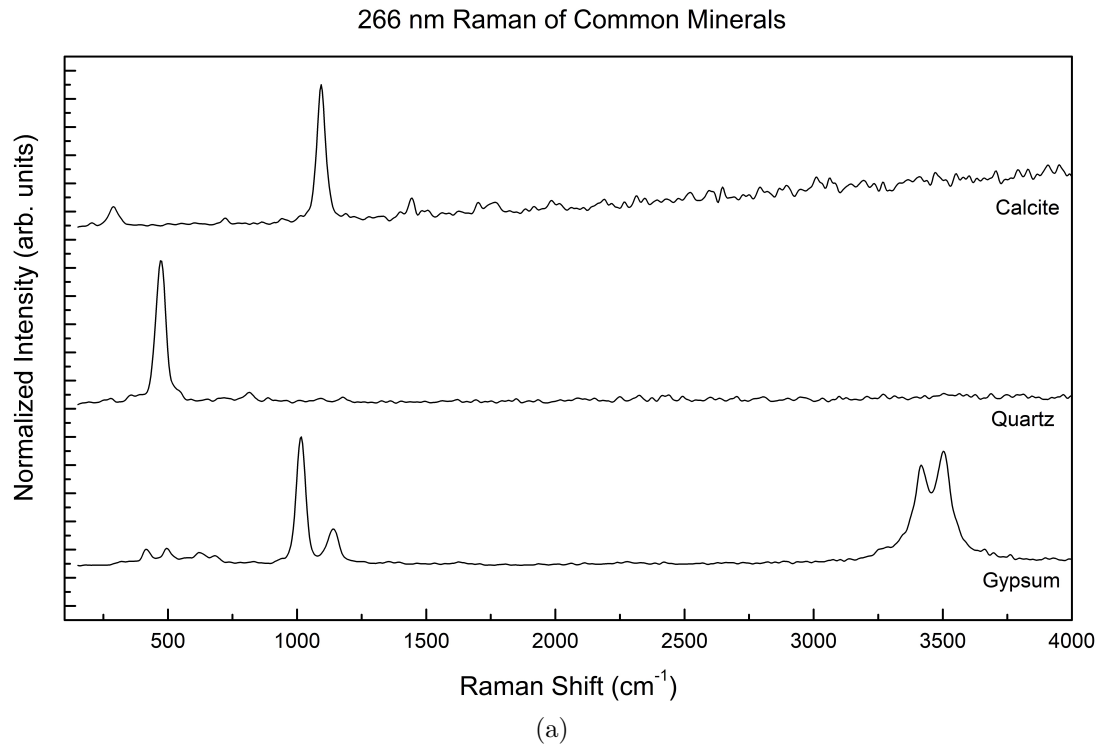


Figure 3.1: (a) 266 nm and (b) 532 nm excitation of common mineral standards gypsum, calcite, quartz, and olivine (fayalite, 532 nm only) These spectra are background subtracted.

Raman spectrum at $\sim 3500\text{ cm}^{-1}$. Using the UV Raman mode of the ESCAPE system, we can see minerals that have peaks ranging from $280\text{--}4000\text{ cm}^{-1}$. The UV Raman spectrum for several common minerals in Planetary and Earth sciences such as gypsum, calcite and quartz are shown in Figure 3.1. Their spectra show good Raman resolution (clear, identifiable peaks) and have peaks both at lower and higher wavenumbers. Each of these mineral spectra are collected with a fast acquisition time of just 10 seconds.

UV Raman spectra from standard samples of pure organic material found within carbonaceous planetary materials are also shown in Figure 3.2. These spectra are very similar to each other with overlapping peaks just below $\sim 3000\text{ cm}^{-1}$, representing the C-H bond. The lower wavenumber peaks are unique to each amino acid and are therefore more useful for the identification of the amino acid. Each UV Raman spectrum for the amino acids is collected with a 10-second acquisition time. Examples of 266nm fluorescence spectra taken of organics found in carbonaceous planetary materials are shown in Figure 3.2. These spectra show the region for Raman excitation when using UV Raman from 270–300 nm and the fluorescence region 270–550 nm where typical fluorescence broadband peaks are present for organic material (Figure 3.2). As seen with glycine, 2-aminoisobutyric acid, β -alanine, and L-glutamic acid, single-spectrum fluorescence can look very similar between samples. Fluorescence peaks for non-Raman active materials such as tryptophan and phenylalanine are also shown in Figure 3.2. LIF from the non-aromatic compounds have spectra which is a combination of weak intrinsic organic fluorescence and fluorescence from contaminants remaining from the organic synthesis or extraction process. For instance, the organic standard utilized in our study had a purity of 99%, leaving the possibility that trace amounts of aromatic or unsaturated contaminants introduced during manufacturing could be responsible for the observed bands (32). As a result, the upward shift of peak features from amino acid to saturated aliphatic acids and hydrocarbons could be attributed to differences in organic structure, such as the presence of aromatic moieties, unsaturated chains, ring structures, molecular size, and residual traces during manufacturing. Due to the complexity of

PAH and AAA molecular structures, further research is necessary to accurately identify the fluorescence emissions.

Examples of Raman spectra using 532 nm excitation are shown in Figure 3.1. The same minerals as used in 266 nm excitation Raman results are shown with the addition of fayalite (iron-rich olivine). Using 532 nm with the ESCAPE system, we can resolve the olivine doublet, attributed to the symmetric and asymmetric stretching vibrational modes of the SiO_4 tetrahedron. The olivine standard presented here is fayalitic, which we can see reflected in the Raman spectrum as the lower wavenumber peak ($\sim 817 \text{ cm}^{-1}$) in the olivine doublet has a relatively higher intensity than the higher wavenumber peak at ($\sim 840 \text{ cm}^{-1}$) as described in (Kuebler et al., 2006) Using 532 nm excitation, we are able to observe both the lower wavenumber peaks of gypsum between $400\text{--}1100 \text{ cm}^{-1}$, but also the O-H doublet faintly just before 3500 cm^{-1} .

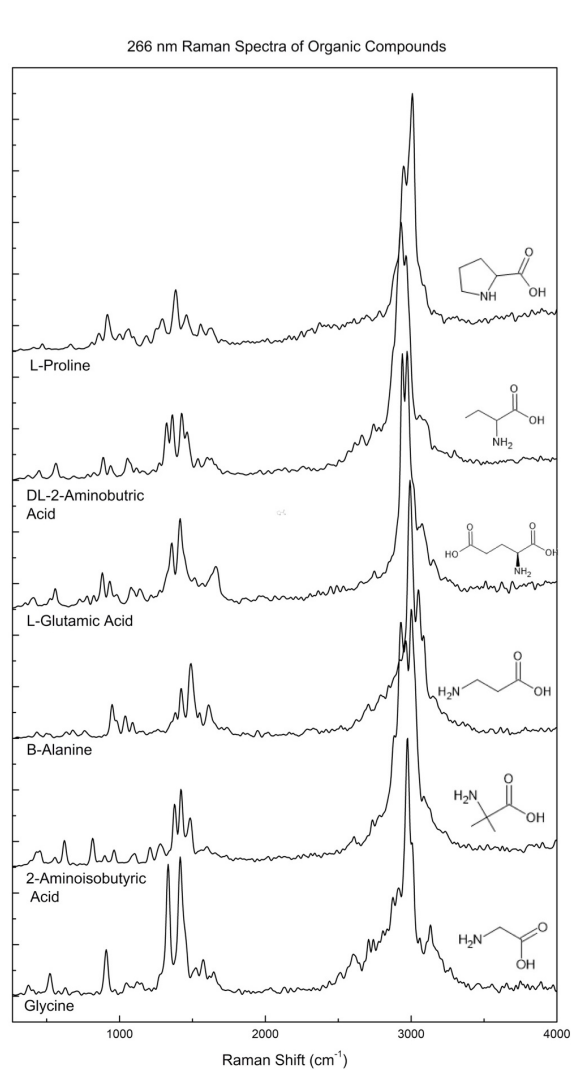
532 nm Raman and Fluorescence spectra of the same organics as described above are also shown in Figure 3.3. These spectra are 15-second acquisitions over the 534–700 nm spectral window ($200\text{--}4000 \text{ cm}^{-1}$). Raman of pure organics is more difficult on the older pressed pellets used for UV analysis, so fresh powders decanted from the bottle are used for these acquisitions. Broadband fluorescence is somewhat evident from $200\text{--}2000 \text{ cm}^{-1}$, and the peaks around 3000 cm^{-1} are less prominent than in that of the UV Raman spectra. However, with 532 nm excitation, we are able to obtain Raman spectra of Tryptophan (weak peaks around $1000\text{--}1500 \text{ cm}^{-1}$) and Phenylalanine, which, when using UV only produce fluorescence.

Table 5: Raman peak positions using $\lambda_{Ex} = 266, 532$ nm with the ESCAPE system, compared to that of literature computed or measured values and their associated vibrational/stretching modes. (***) value does not exist or could not be found in the literature. α , scissoring; β , bending; δ , deformation; ν , stretching (s, symmetric; as, asymmetric).

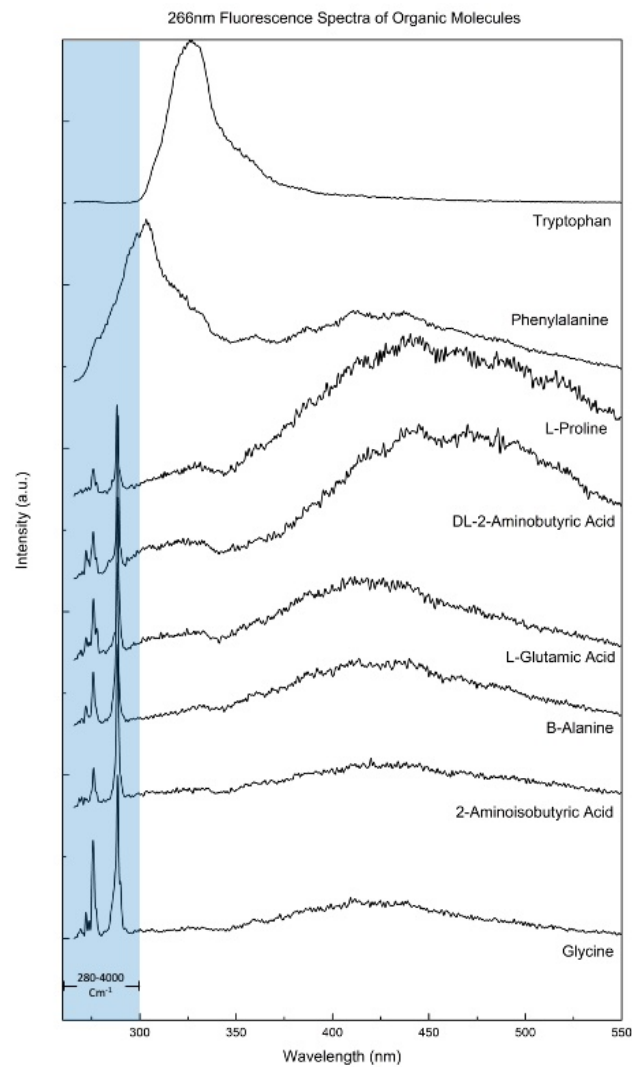
Mineral/ Organic	266 nm Peak Positions (cm^{-1})	532 nm Peak Positions (cm^{-1})	Literature Peak Positions (cm^{-1})	Vibrational Mode	Stretching Mode	Citation
Gypsum CaSO_4	415	415	415	ν_2 (SO_4)		Krishnamurthy and Soots (1971)
	495	495	495	ν_2 (SO_4)		
	624	623	621	ν_4 (SO_4)		
	675	672	671	ν_4 (SO_4)		
	1016	1010	1006	ν_1 (SO_4)		
	1138	1135	1140	ν_3 (SO_4)		
	3416	3406	3405	ν_1 (H_2O)		
	3502	3497	3500	ν_3 (H_2O)		
Quartz SiO_4	***	207	206		A_1	Krishnamuti (1958)
	471	466	466		A_1	
Calcite CaCO_3	288	281	281		E_g	Rutt and Nicola (1974)
	1098	1086	1085		A_{1g}	
	1444	***	1435		E_g	
Olivine (Mg,Fe) $_2$ SiO_4	***	585	588	SiO_4 Bending		Kuebler et al. (2006)
	***	824	815–825	SiO_4 Stretching		
	***	856	838–857	SiO_4 Stretching		
	***	920	921	SiO_4 Stretching		
	***	966	967	SiO_4 Stretching		

Table 5 continued from previous page

Mineral/ Organic	266 nm Peak Positions (cm ⁻¹)	532 nm Peak Positions (cm ⁻¹)	Literature Peak Positions (cm ⁻¹)	Vibrational Mode	Stretching Mode	Citation
D-L Aminoiso- butyric Acid	1382	1393	1383	$\Omega(\text{CH}_2)$		Yalagi et al. (2019)
	1428	1437	1441	$\delta(\text{CH}_2)$		
	1488	1492	1482	$\delta(\text{NH}_3^+)$		
	***	1522	1568	$\delta(\text{NH}_3^+)$		
	2932	2945	2936	$\nu_s(\text{CH}_3)$		
	2969	2988	2969	$\nu_{as}(\text{CH}_2)$		
	3002	3022	3012	$\nu_{as}(\text{CH}_2)$		
	***	3042	3044	$\nu_{as}(\text{NH}_3^+)$		
β -Alanine	1362	1335	1395	$\nu(\text{CO}_2^-)$		Yalagi et al. (2019)
	1428	1408	1434	$\Omega(\text{CH}_2)$		
	1549	***	1556	$\delta_{as}(\text{NH}_3^+)$		
	2931	2916	2936	$\nu_{as}(\text{CH}_2)$		
	2992	2974	2936	$\nu_{as}(\text{CH}_2)$		
	3024	3018	3016	$\nu_{as}(\text{CH}_2)$		
Glycine	1340	1326	1350	$\nu_s(\text{CH}_2)$		Ahmed et al. (2012)
	1414	1413	1445	$\nu_s(\text{CH}_2)$		
	2978	2974	2963	$\nu_{as}(\text{NH}_3^+)$		
	3011	3008	3028	$\nu_{as}(\text{NH}_3^+)$		
Glutamic Acid	1363	***	1356	ωCH_2		Sumayya et al. (2008)
	1419	1413	1411	ν C-N amide		
	1651	***	1645	$\delta(\text{NH}_2)$ amide		
	2941	2940	2933	$\nu_{as}(\text{CH}_2)$		
	2974	2969	2967	$\nu_{as}(\text{CH}_2)$		
Proline	1298	1267	1290		Stretching C-C	Zhu et al. (2011); Freire et al. (2017)
	***	1374	1376		Stretching C-C	
	1465	1466	1453		***	
	2955	2945	2984		C-H Stretching	
	3011	3008	3006		C-H Stretching	

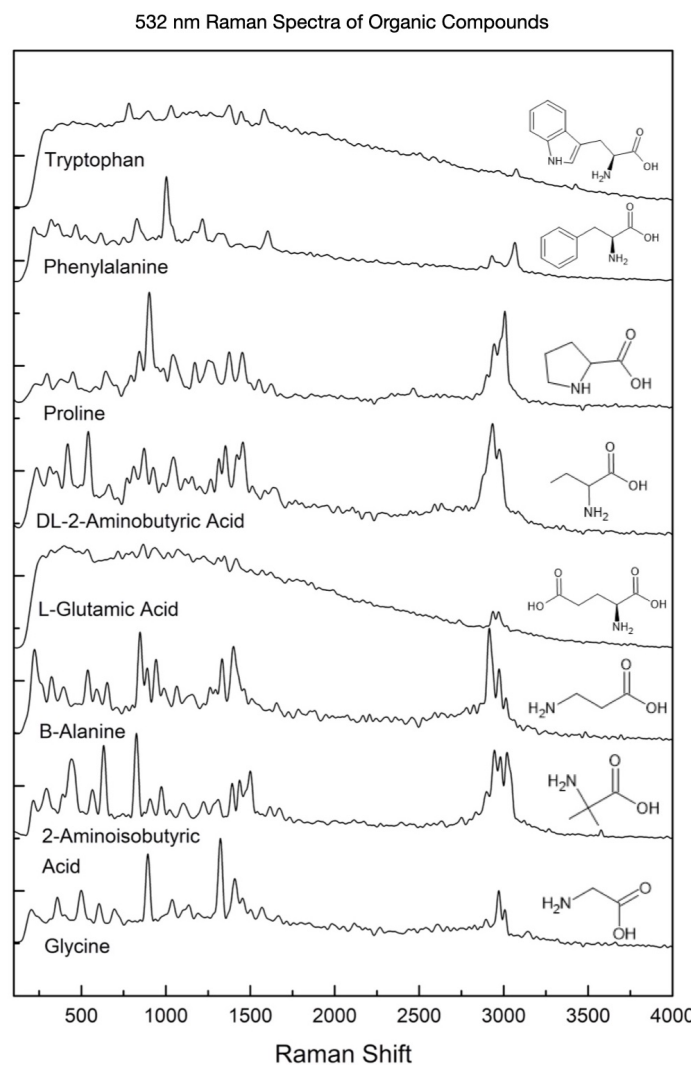


(a) 266nm Raman Spectra of Amino acids

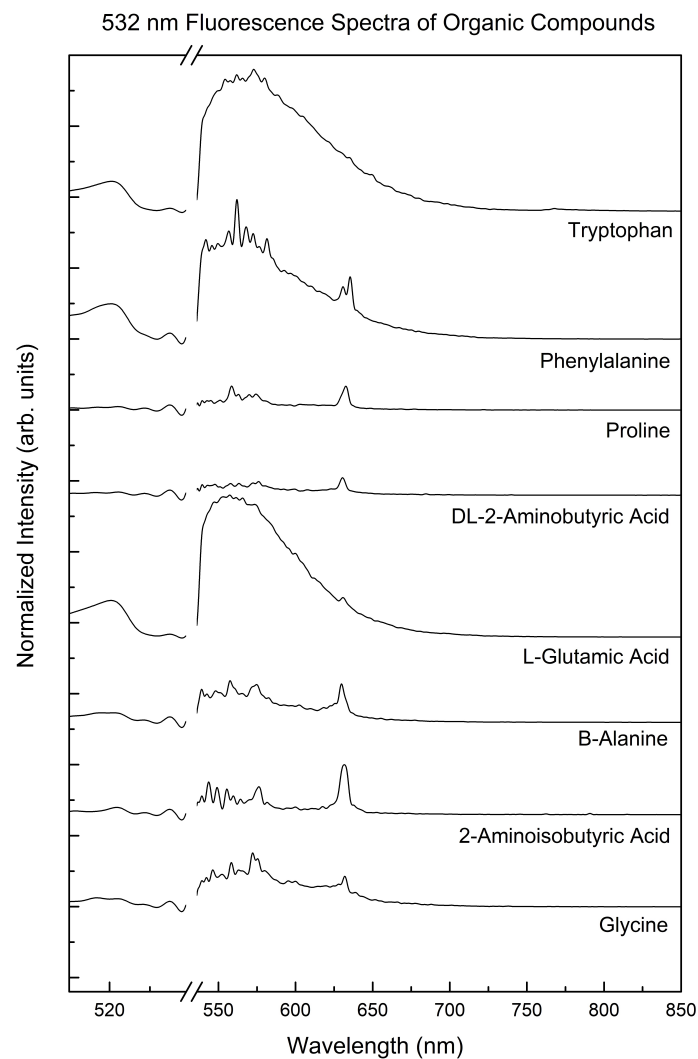


(b) 266nm Fluorescence Spectra of Amino Acids

Figure 3.2: 266nm Raman and fluorescence spectra of common amino acids found within carbonaceous chondrite meteorites and Hayabusa2 samples.



(a) 532 nm Raman spectra of amino acids



(b) 532 nm Fluorescence spectra of amino acids.

Figure 3.3: 532 nm Raman and fluorescence spectra of common amino acids found within carbonaceous chondrite meteorites and Hayabusa2 samples. The laser line is removed at 532 nm in fluorescence spectra.

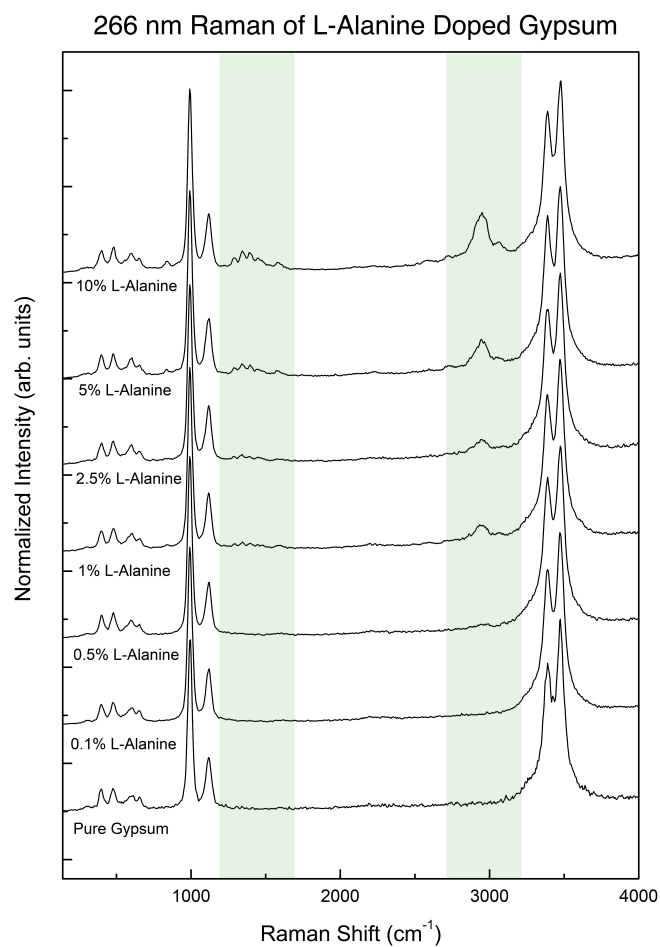
3.3 Spectroscopy of Doped Laboratory Samples

3.3.1 Preparation of Amino Acid-Doped Simulant Pellets

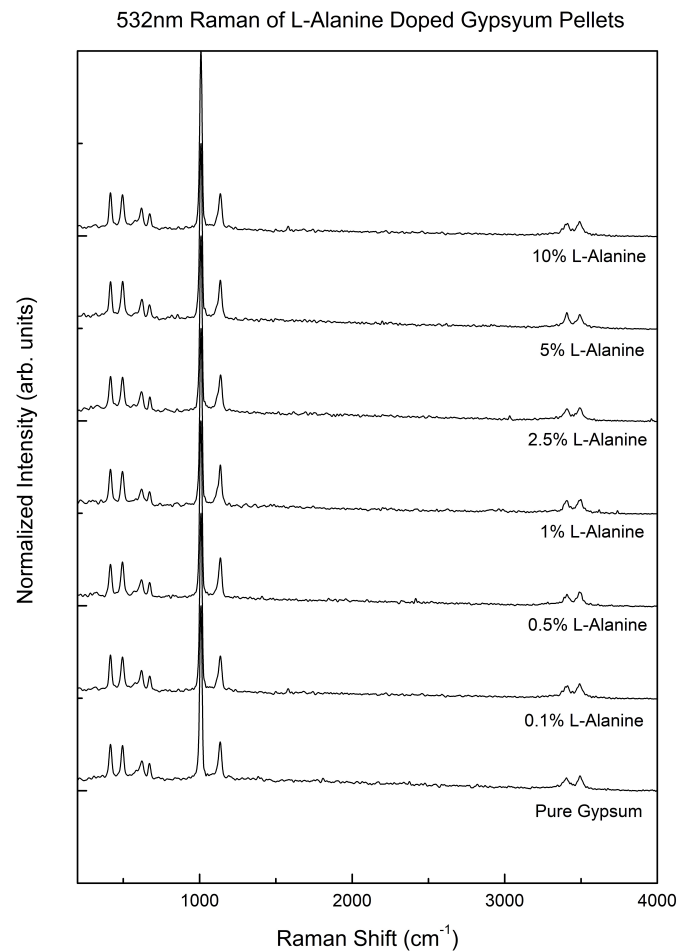
Amino acids and standard substrates (either simulant material or pure synthesized mineral) were powdered using a mortar and pestle, weighed carefully, and mixed using ethanol and magnetic stirrers while heated to 35°C while under a slight vacuum. The mixed samples were then baked for another 24 hours in a 35°C oven. Once fully dry, the mixtures were pelletized using about 1g of each mixture. The pellets were then placed in the chamber on a piece of microscope paper to avoid contamination. Further contamination protocols include using gloves and handling samples very minimally, storing them in individual small plastic zip bags, and changing the paper or cleaning the sample stage with ethanol between each sample analyzed.

3.3.2 Raman Analysis of Alanine-Doped Gypsum

266 nm Raman Spectra of L-alanine-doped gypsum pellets at varying concentrations from 1–10 wt% are shown in Figure 3.4. The gypsum control pellet serves as a guide to the Raman spectra of pure gypsum for reference and moving upward in the image, the concentration of L-alanine increases. In the UV range, Raman bands for L-alanine are visible in 1200–1600 cm^{-1} and 2700–3100 cm^{-1} ranges starting at around 0.5 wt% alanine to gypsum. At this concentration, a very small peak is seen around 3000 cm^{-1} , but it is difficult to resolve anything in the weaker 1200–1600 cm^{-1} range. Once the concentration reaches 1 wt%, the lower wavenumber region of L-alanine Raman peaks appears. As the concentration of L-alanine increases to 5% we can clearly see Raman peaks in both of the defining regions for organics. Raman of organic compounds using 532 nm excitation is often weaker than when using 266 nm excitation, and an example of this phenomenon can be seen in Figure 3.4 b. In the same gypsum series with varying concentrations of L-alanine, we do not see any Raman of organics even at 10 wt% L-alanine to gypsum using 532 nm excitation.



(a) 266 nm Raman Spectra of L-Alanine Doped Gypsum Pellets



(b) 532 nm Raman Spectra of L-Alanine Doped Gypsum Pellets

Figure 3.4: Raman spectra of varying concentrations of L-alanine-doped gypsum pellets, ranging in concentration from pure gypsum to 0.1–10 wt% L-alanine to gypsum. Highlighted in green are the primary regions of L-Alanine ($\sim 1200\text{--}1600\text{ cm}^{-1}$; $\sim 2700\text{--}3100\text{ cm}^{-1}$) visible when excited by 266 nm (a), but not by 532 nm at the same concentrations (b).

Using $\lambda=532$ nm excitation the gypsum Raman peaks are very intense and therefore obfuscate any Raman signal that may be produced from organic material at low concentrations.

3.3.3 Fluorescence Analysis of Cerium-Doped Mars Analogue Samples

Fluorescence spectra acquired of Ce^+ doped Mars analogue samples (MGS-1) using 266 nm excitation with the ESCAPE system are shown in Figure 3.5, previously prepared for and acquired by the LiRS instrument (described in Table 3) and published in (Shkolyar et al., 2021). Cerium is a potential biomimicer with very similar fluorescence pattern and intensity to that of the amino acid tryptophan (see Figure 3.2). Most of the samples used in Shkolyar et al. (2021) have not survived through the couple of years since the original data acquisition and subsequent publishing, however, the remaining intact samples are analyzed using the ESCAPE system here. These samples of varying cerium concentrations (50-8000 ppm cerium to MGS-1) follow the same trend as in (Shkolyar et al., 2021) where increasing Ce^+ concentration results in an increase in fluorescence intensity (Figure 3.5). These preliminary data indicate the ESCAPE system is working well and is able to reproduce published data from other instruments with as good resolution and at a faster acquisition time.

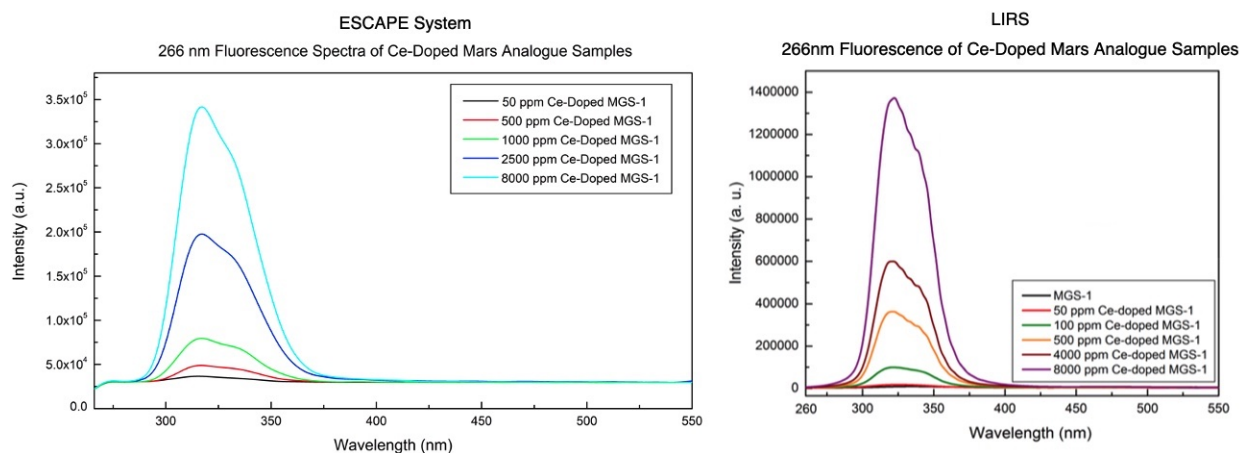


Figure 3.5: Fluorescence spectra (left) of varying concentrations of cerium-doped Mars analogue pellets, ranging in concentration from pure MGS-1 to 50-8000 ppm cerium compared to that of the same samples from Shkolyar et al. (2021) (right).

3.3.4 266 nm Limit of Detection using Tryptophan-Doped Gypsum

The limit of detection for the fluorescence instrument has been tested by creating pelletized samples of tryptophan-doped gypsum. Pure (>95%) samples of CaSO_4 (gypsum) and Tryptophan were obtained through Sigma Aldrich. These materials were carefully weighed using a Sartorius Cubis scale with an error of 0.0001 g. The pure gypsum powder was crushed with a mortar and pestle and sieved to <355 μm (smaller than laser spot size at 500 μm). For the study, 10g of gypsum were mixed with incremental concentrations of tryptophan from 50–1000 ppm (0.0005–0.01 g). The measured amount of tryptophan was then mixed into methanol and subsequently mixed with gypsum fully saturated with methanol. Magnetic stirrers were used in each mixing beaker to ensure an even mixing over a 35°C hot plate for 3 hours until partially dry. The samples are left in a fume hood for 24 hours to ensure drying was complete. The doped-gypsum powders were crushed again using a clean mortar and pestle and hand mixed once more by hand. The powders are then pelletized using $\sim 1\text{g}$ of sample. The pellets were placed on the sample stage in the ESCAPE chamber and UV fluorescence and Raman spectra are acquired. Using 266 nm excitation, we can see the broad fluorescence peak of the tryptophan at a concentration of 50 ppm within pure gypsum as a pelletized sample taking the average of 5 spots 3.6. Each spot is one acquisition with an exposure time of 0.1 s, 100 accumulations (10-second acquisition time), and a gate width of 100 ns. The wavelength range collected was 268–550 using a 600 L/mm grating and 266 nm excitations. When repeating the experiment using 532 nm excitation (534–850 nm window), we can see the fluorescence intensity increase when tryptophan is present at 50 ppm.

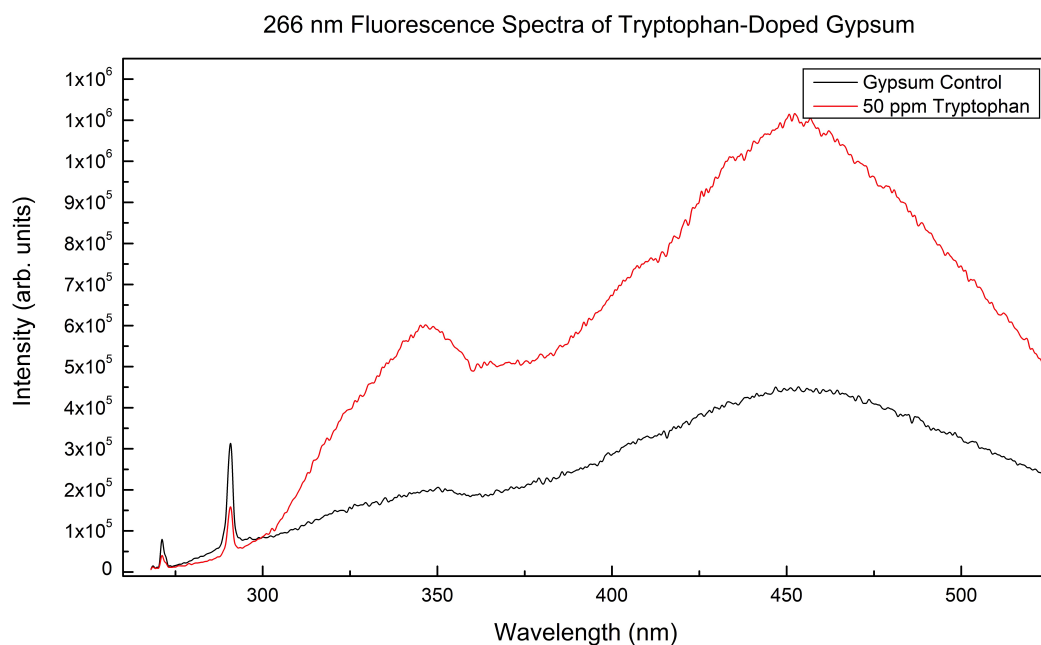
In Figure 3.6, we see the sample labelled ‘Gypsum Control’ has Raman peaks at 274 nm (1150 cm^{-1}) and 289 nm (3050 cm^{-1}) and some broadband fluorescence peaking at 450 nm, most likely from gypsum itself and some leftover methanol from mixing. We also see the sample labelled ‘50 ppm Tryptophan’ representing the tryptophan-doped gypsum sample with a concentration of 50 ppm, which has relatively smaller gypsum peaks compared to the control, and a larger fluorescence peak at $\sim 340\text{ nm}$, corresponding to tryptophan. Similarly,

in Figure 3.6, the Raman gypsum peaks within the 50 ppm tryptophan sample are relatively less intense than in the gypsum control sample and have higher fluorescence intensity in the 534–700 nm region.

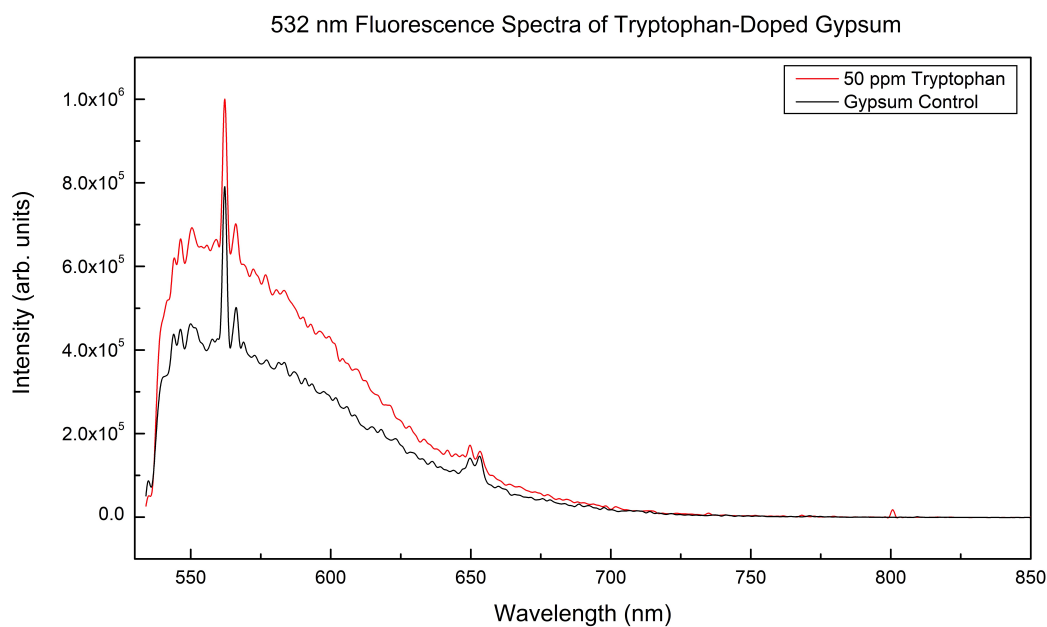
3.3.5 Fluorescence Analysis of Low Concentration Organic-Doped Analogue Samples

The relationship between intensity and concentration of organic in analogue doped samples seems to become less correlated as concentrations get into the hundreds of ppm range instead of thousands. Examples of this phenomenon occurring in different substrates are presented in Figure 3.7 and Figure 3.8. Interestingly, for each of these plots, 500 ppm tryptophan is the only concentration out of correlation with increasing intensity with increasing concentration. In two instances, 500 ppm tryptophan is lower in intensity than expected and in one instance it is much higher than expected. Alternatively, 1000 ppm of tryptophan in figure 3.8 is much lower in intensity than expected. It is unclear from these data why this phenomenon is occurring, however, it is only visible when the step size between concentrations is small and the concentrations are lower than 1000 ppm.

In Figure 3.8, ‘Gypsum Control’ and 50 – 100 ppm Tryptophan-Gypsum mixes have been plotted against each other. In the control gypsum, we can observe Raman peaks at 274 nm (1150 cm^{-1}) and 289 nm (3050 cm^{-1}) and some broadband fluorescence peaking at 450, most likely from gypsum itself and some leftover methanol from mixing. Several minerals such as gypsum absorb UV radiation and emit visible light because of certain mineral impurities such as activators (i.e., Mn, Cr, Fe, and Dy). These activators are incorporated in structures as possible dopants and do not form part of the crystal lattice. As such, they become optically active ions presenting luminescence between quantized electronic energy states of the electrons. However, other factors such as lattice defect centers, which can involve trapped electrons, ‘holes’ or missing electrons, ion vacancies, and the substitution of ions with different charges than those normally found at a given lattice site can also contribute to fluorescence (Lalla et al., 2021). The samples with increasing tryptophan in



(a) 266 nm Fluorescence Spectra of 50 ppm Tryptophan-Doped Gypsum vs. Gypsum Control Sample



(b) 532 nm Fluorescence Spectra of 50 ppm Tryptophan-Doped Gypsum vs. Gypsum Control Sample

Figure 3.6: (a) 266 nm and (b) 532 nm excitation of 50 ppm Tryptophan-Doped Gypsum pellets. Raman and Fluorescence spectra of Gypsum Control (gypsum mixed with methanol, and subsequently drying) and the average of 5 random points taken of the pellet of gypsum doped with 50 ppm tryptophan, mixed with methanol and dried.

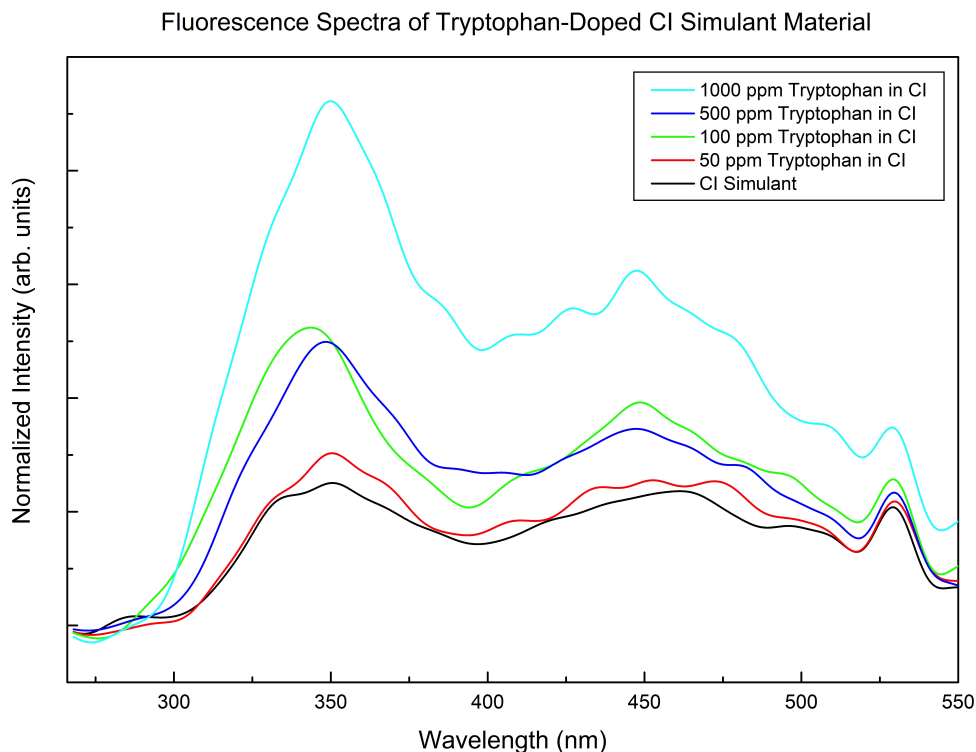
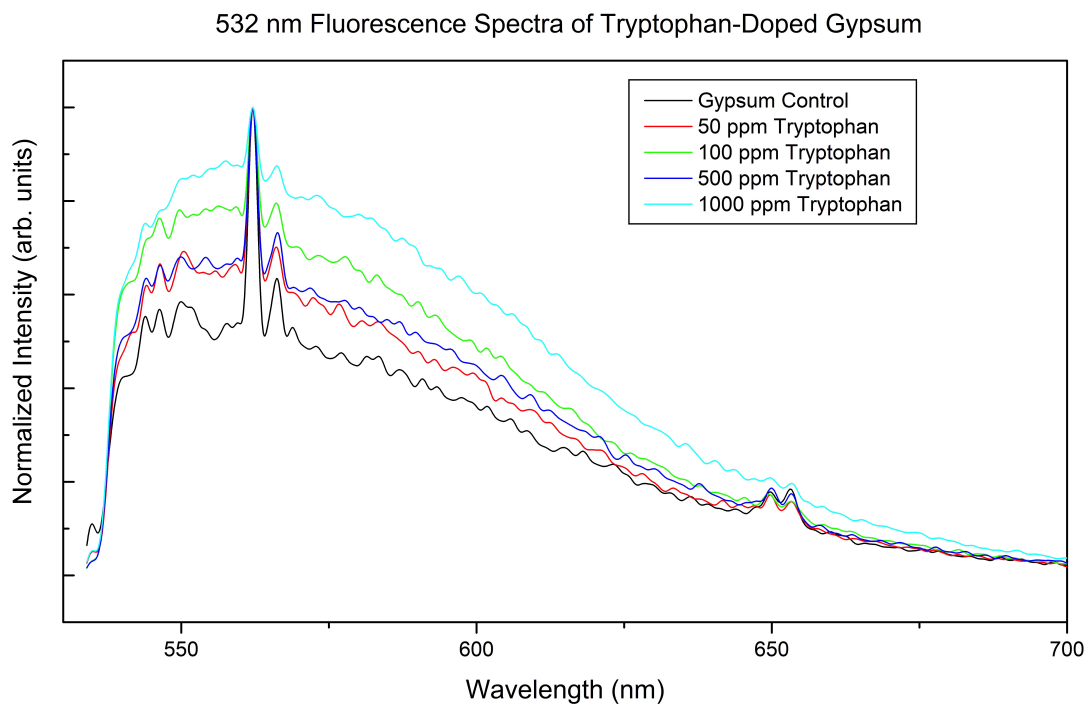


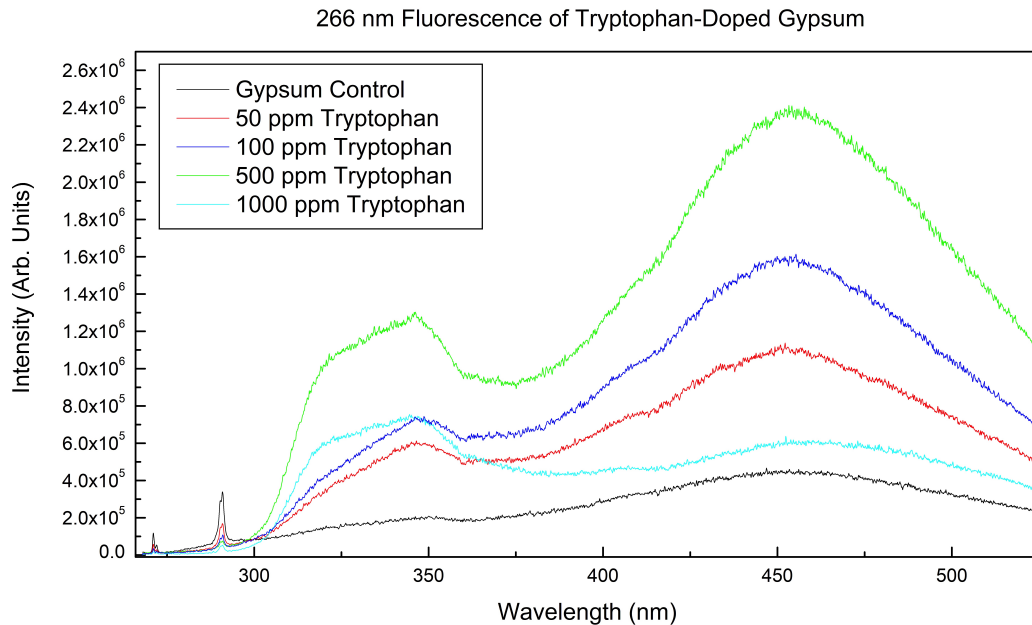
Figure 3.7: 266 nm spectra of Tryptophan-Doped CI pellets at concentrations ranging from 50–1000 ppm.

gypsum (50–500 ppm) are shown in Figure 5 with a correlative increase of intensity in fluorescence with increasing tryptophan concentration in the region of 300–350 nm. We can see in the sample 50-ppm tryptophan relatively smaller gypsum peaks compared to the control, and a larger fluorescence broad peak at ~ 325 –350 nm, corresponding to tryptophan.

From analyzing the low-concentration amino acid-doped samples, we can however, observe that the sensitivity of the instrument is at least 50 ppm tryptophan in gypsum. The confidence in this statement is based on the fact that the samples were meticulously made so that the grain sizes were smaller than the spot size of the instrument, and to ensure that the sample was mixed as well as possible in the PIL laboratory and we can observe the fluorescence intensity above the baseline control samples in the 325–350 nm range corresponding to tryptophan. Furthermore, to ensure that the analysis is more statistically accurate, a 49-point (7x7) raster map was taken of the 1 cm diameter 50 ppm tryptophan-gypsum pellet at a step size of 0.5 mm. Each of these points has increased fluorescence from the baseline



(a) 532 nm Fluorescence Spectra of Tryptophan-Doped Gypsum Series



(b) 266 nm Fluorescence Spectra of Tryptophan-Doped Gypsum Analogue Series

Figure 3.8: (a) 532 nm and (b) 266 nm spectra of Tryptophan-Doped Gypsum pellets at varying concentrations from 50–1000 ppm.

control sample in the region of 325–350 correlating to tryptophan fluorescence (Figure 3.9).

266 nm Fluorescence Spectra of 50-ppm Tryptophan-Gypsum Sample 49-point Raster Map

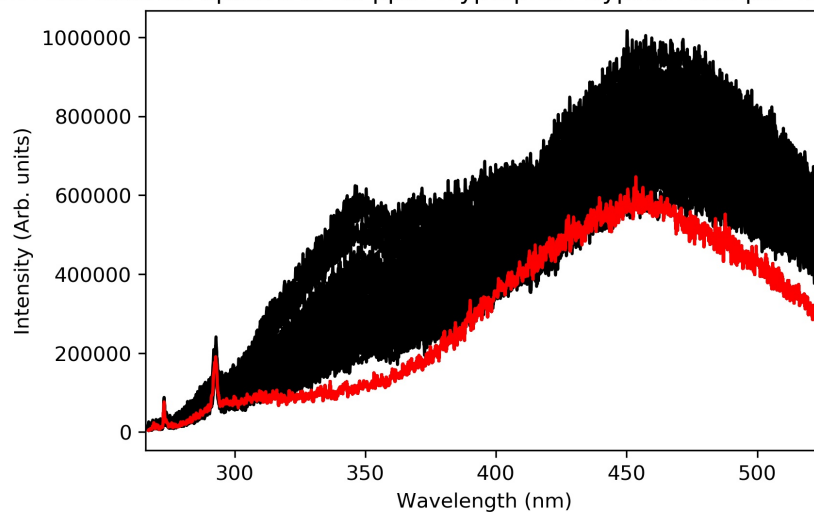


Figure 3.9: 266 nm raster map spectra stacked of each point ($n=49$) on 50 ppm tryptophan-Doped gypsum pellet shown in black, compared to gypsum control pellet with no tryptophan (red). All of the spectra from the 50 ppm tryptophan pellet (black) show higher fluorescence intensity than the control (red) in the region of tryptophan fluorescence (325–350 nm).

3.4 Time-Resolved Fluorescence of Laboratory Standards

An example of a time-resolved fluorescence spectroscopy ‘fingerprint’ (2D contour map) is shown with intensity increasing from blue to yellow at a certain wavelength over a 20 ns period for the sample β -alanine (Figure 3.10).

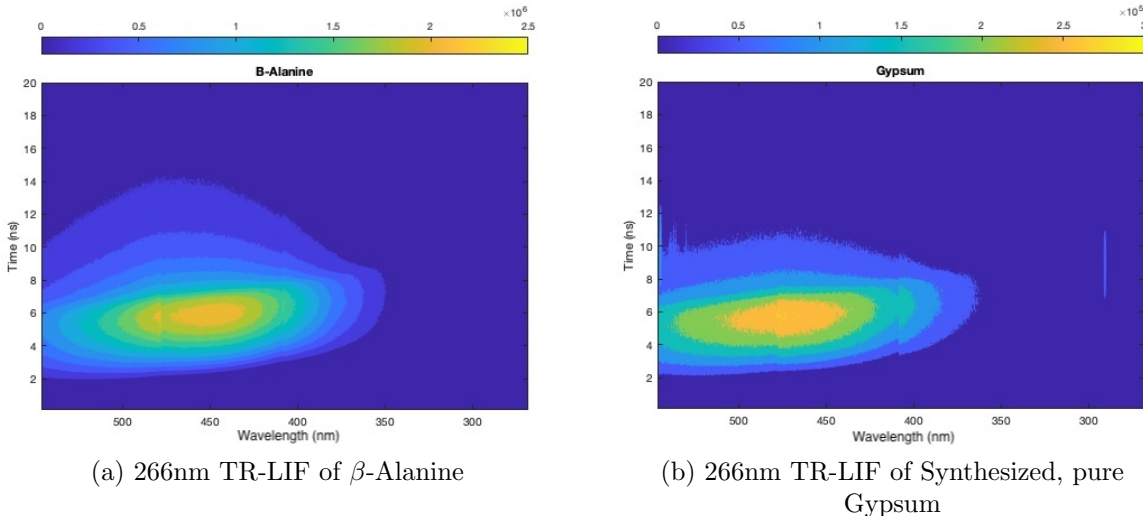


Figure 3.10: Examples of 266 nm time-resolved laser-induced fluorescence (TR-LIF) of laboratory samples (a) β -Alanine and (b) Gypsum.

The broadband peak intensity of β -Alanine is around 425–450 nm, and the growth and decay of the sample are seen within the 20 ns period. The gypsum standard (pure $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ from Sigma-Aldrich) has a relatively less intense TR-LIF fingerprint and most likely has a shorter lifetime than that of natural gypsum because it contains fewer impurities. However, we cannot really assess the true decay rate without calculating the lifetime (τ).

The true decay rate (τ) can be calculated from TR-LIF data such as these through methods outlined in (Lymer et al., 2021) and compared to each other. It was found from previous works on similar systems (Lymer et al., 2021) that mineral decay rate τ values were often > 15 ns and decay rates of organics $\ll 15$ ns. Decay rates were calculated for the same common amino acids presented in this work, with a previous UV-Fluorescence instrument compared to minerals quartz and calcite (Figure 3.11) (Lymer, 2017; Lymer et al., 2021).

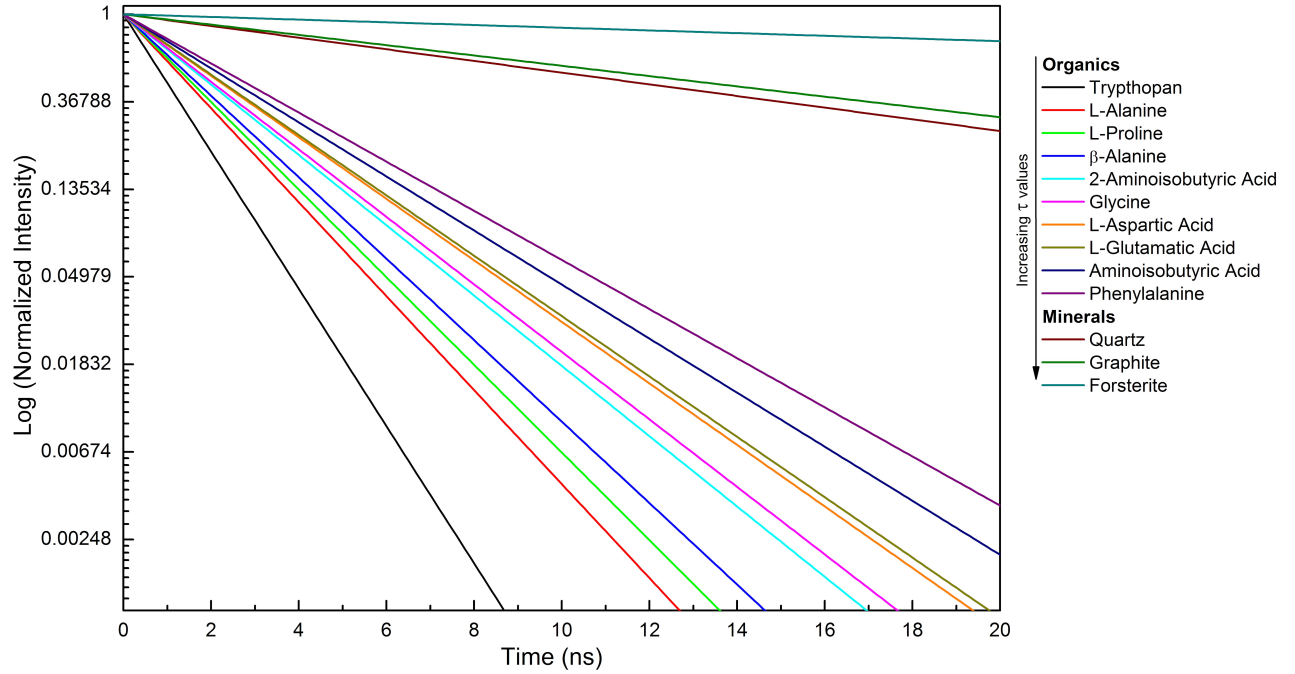


Figure 3.11: Calculated decay rates (plot here in natural logarithm) of common organics and minerals over 20 ns measured with a previous LIF instrument published in (Lymer et al., 2021). Organics tend to have shorter decays than mineral fluorescence.

Table 6: Calculated decay rates (τ) of common organics and minerals presented in this work (published in Lymer et al. (2021)), measured with a previous iteration of a LIF instrument in the PIL laboratory, compared to literature values reported in Chen et al. (1978); Pan et al. (1993); Cote et al. (2019); Garcia et al. (2009).

<i>Amino acid</i>	λ_{max} , <i>this study (nm)</i>	τ , <i>calculated (ns)</i>	λ_{max} , <i>reference (nm)</i>	τ , <i>reference (ns)</i>	<i>Refs.</i>
Phenylalanine	~295	3.56	384	2.8	Chen <i>et al.</i> (1978)
Aminoisobutyric acid	~410	3.23	355	3.6**	Pan <i>et al.</i> (1993)
L-Glutamic acid	~445	2.89	382	3.3	Chen <i>et al.</i> (1978)
L-Aspartic acid	~315	2.84	376	3.1	Chen <i>et al.</i> (1978)
Glycine	~410	2.59	381	2.9	Chen <i>et al.</i> (1978)
2-Aminoisobutyric acid	~410	2.48	355	3.6**	Pan <i>et al.</i> (1993)
β-alanine	~315	2.14	380	3.0	Chen <i>et al.</i> (1978)
L-Proline	~415	1.99	***	***	***
L-Alanine	~420	1.86	382	3.1	Chen <i>et al.</i> (1978)
Tryptophan	~325	1.55	385	1.8	Chen <i>et al.</i> (1978)
Minerals					
Forsterite	~460	65	***	***	Current work
Quartz	***	***	~450	15	Cote <i>et al.</i> (2019)
Graphite	~440	17	***	***	Current work
Calcite	***	***	***	90	Garcia <i>et al.</i> (2009)

Fluorescence decay rates of 10 amino acids found in carbonaceous chondrites at the specified λ_{max} , and corresponding decay rate values published in the literature. λ_{max} is shown in Fig. 1 as asterisk (*).

**Organics present in dilution at a high concentration with other solvents.

***Not available in the references or current studies).

Calculating the lifetime typically consists of selecting a fluorescence band or band region corresponding to the organic in question. The intensity of the band (or maximum intensity of the band region) is taken over incremental gate delays. Doing so generates an empirical decay curve (Eshelman et al., 2015). Given the need to correct for laser signal and detected gate, it is insufficient to merely take the empirical decay. In order to account for these corrections, we implemented a series of steps to model the relationship between the observed decay, laser pulse, and detection gate given as defined in eq. 1,

$$f_{observed} = f_{laser} \otimes f_{decay} \otimes f_{gate} \quad (1)$$

where $f_{observed}$ is the observed decay, f_{laser} is the profile of the laser pulse, f_{gate} is the profile of the detector, f_{decay} is the true lifetime, and $\otimes$ is the convolution operator. Correspondingly, what we would like to obtain is eq. 2,

$$f_{decay} = [[f_{observed} \otimes f_{gate}]^{-1} \otimes f_{laser}]^{-1} \quad (2)$$

where $[\otimes]^{-1}$ denotes the deconvolution or inverse convolution operator.

The process consists of firstly fitting a first-order exponent to the observed decay, in addition to modelling a Gaussian profile for f_{laser} and a rectangular function profile for f_{gate} . The observed decay, laser profile, and gate profile were then transformed from the time domain to the frequency domain using a Fast Fourier Transform (FFT). Once transformed, a deconvolution between the observed decay and the gate profile is performed, the result of which is deconvolved with the laser profile. The deconvolutions were performed using a least-square approximation method. The resultant of the two deconvolutions is then transformed back into a time-domain. Finally, a first-order exponential function is fit to the result of the aforementioned steps in order to obtain the effective decay rate f_{decay} (see appendix A for

Table 7: Decay Rate Calculations (τ) in Nanoseconds of Laboratory Standards at λ_{max} . Data measured using the ESCAPE system and is compared to that of the LIF system used in (Lymer et al., 2021).

<i>Sample</i>	λ_{max} <i>ESCAPE (nm)</i>	τ <i>calculated (ns)</i>	λ_{max} <i>reference (nm)</i>	τ <i>reference (ns)</i>	<i>Reference</i>
Tryptophan	~ 355	1.88	~ 325	1.55	(Lymer et al., 2021)
β -Alanine	~ 455	2.08	~ 315	2.14	(Lymer et al., 2021)
Gypsum	~ 475	4.19	—	—	—

TR-decay rate deconvolution code and examples of data produced to obtain τ values).

In this study, the τ (decay rate) is calculated using the deconvolution methods described above. Ideally, the λ_{max} should be chosen at the maximum intensity across the whole fluorescence spectrum of a sample, however many sample maximums from (Lymer et al., 2021) were chosen to best match the λ_{max} of that from the literature to better compare the accuracy of the τ calculation methods. In the ESCAPE system, laboratory standards Tryptophan, β -Alanine, and synthesized gypsum (Sigma Aldrich $\text{CaSO}_4 \cdot \text{H}_2\text{O}$) are measured using TR-LIF (Figure 3.10) and decay rates (τ) are calculated and displayed in Table 7. Calculated decay rates from TR-LIF measurements acquired using the ESCAPE system are comparable to that of Lymer et al. (2021) and Chen et al. (1978) (Tables 6, 7).

3.5 Discussion of Laboratory Standard Results

Typically, when designing an instrument for space flight, tradeoffs are made to ensure that scientific and engineering goals are met while maintaining weight and size constraints for the mission. For an instrument designed specifically for use in a laboratory setting, such as the ESCAPE system, fewer tradeoffs have to be made as there are fewer constraints surrounding weight and size and therefore a typical tradeoff between wavelengths (532 nm (green) and 266 nm (UV)) does not need to be made. Excitation in the green wavelengths has typically been chosen for space flight Raman instruments with the scientific goal of determining the mineralogy of geologic areas of interest. More recently, such as with the SHERLOC instrument, UV-excitation modes have been chosen for Raman instruments as

there is more interest in looking for organic material as well as minerals (Beegle et al., 2015). Based on our laboratory results, we can observe (Figure 3.1) that Raman spectra using green excitation have very good mineral peak resolution from 100–1500 cm^{-1} , and $\lambda=532$ nm is especially good at looking at iron-rich minerals in comparison to $\lambda=266$ nm. UV-Raman has a shortfall when it comes to analyzing iron-rich minerals due to the known iron quenching of UV incident and reflected light in the wavelength range of 255–275 nm (Razzell Hollis et al., 2021). However the laboratory results show, UV-Raman has good non-iron-rich mineral resolution from 200–4000 cm^{-1} . This region is of particular interest because organics are typically present in the regions of 600–1600 cm^{-1} and organic CH bonds around 2400–2600 cm^{-1} (Cote et al., 2019). Furthermore, water and OH peaks are present in the region of 3400–3500 cm^{-1} , which is much less intense using a green excitation wavelength. Green-Raman excitation is often plagued by fluorescence emission, which can overwhelm the Raman spectrum. An example of fluorescence in green-Raman spectra is in Figure 3.3 and Figure 3.6. When looking at pure organic materials, the Raman spectra are ‘propped’ on a broad-band spectrum of fluorescence. Because of this, green-Raman can become difficult to use when there is a low Raman signal and when looking at material with organic constituents. Conversely, UV Raman can be energetically separated from fluorescence emission and the spectra can be imaged separately (e.g. figures 3.2, 3.6). Because there is no need to tradeoff between wavelengths when designing the ESCAPE system, both wavelengths are available for use in their best use-case scenarios such as green-Raman for iron-rich minerals (often found in planetary materials), and UV-Raman and fluorescence for sulphates and organic materials.

The spectral resolution of the ESCAPE system has been found to be comparable to that of LIRS and SUPERCAM and much improved from the SHERLOC instrument (Table 3). Spectral resolution is another common science/engineering tradeoff as high-resolution spectrometers often have moving parts, and can be larger, more expensive and more difficult to use for flight instrumentation. Spectral resolution is also traded for signal intensity - as

the more light that is let into the system by increasing slit sizes, reduces spectral resolution. Science goals often drive spectral resolution, as specific target materials have a known spectral fingerprint and that fingerprint needs to be resolved for proper identification. For example, the mineral olivine has two geochemical end-members: fayalite (Fe-rich), and forsterite (Mg-rich), represented in a Raman spectrum as a doublet peak around 825–858 cm^{-1} . When the spectral resolution is good enough to see the doublet as two peaks, the end-member can be identified (Kuebler et al., 2006). To resolve this doublet, the spectral resolution needed must be better than 20 cm^{-1} , and according to (Kuebler et al., 2006) ideally, 5–7 cm^{-1} to do quantitative analysis. Other organic materials, such as amino acids, are only really differentiated from each other by small Raman peaks in 1200–1600 cm^{-1} range, which also requires a spectral resolution that is adequate to resolve those peaks. The ESCAPE system is able to resolve the olivine doublet using 532 nm, as well as the OH doublet in gypsum, and small Raman peaks in amino acids using 266 nm and therefore is adequate for planetary material analysis.

Fluorescence emission can obscure Raman spectra, obfuscating important peaks, especially when analyzing organic material. However, laser-induced fluorescence emission of non-aromatic organics using UV excitation can be energetically separated from that of UV Raman spectra and the fluorescence emission has been shown to be useful on its own for detecting organic constituents in a substrate. Aromatic compounds such as tryptophan and phenylalanine have intense UV fluorescence making their detection and identification relatively easy with this system, however, their fluorescence is in the same region as UV Raman, making separation of these organics from minerals difficult without using lower excitation wavelengths like deep-UV excitation. New analysis methods are being worked to quantitatively identify constituents using time-resolved fluorescence spectroscopy alone (Eshelman et al., 2014, 2015; Lymer et al., 2021, 2020). The fluorescence results from the ESCAPE system are similar, or better, in terms of the resolution to that of previously published results looking at the fluorescence of amino acids found in meteorites (Lymer et al., 2020, 2021). UV

laser-induced fluorescence continues to be a sensitive and fast technique for detecting organic constituents, however, Raman or semi-quantitative TR fluorescence is needed to differentiate between organic materials. Because the ESCAPE system utilizes an ultra-fast gated camera, high-resolution time-resolved fluorescence spectroscopy ‘fingerprints’ can be taken such as Figure 3.10.

The fluorescence sensitivity on the ESCAPE instrument is efficient, as, within 5 points of acquisitions, the system was able to detect 50 ppm of tryptophan in a pure gypsum substrate. This is useful as many organics within carbonaceous meteorites have been present in concentrations like this detection limit based on chromatography (Pizzarello et al., 2001). Furthermore, calculated TR-LIF decay rates from laboratory standards using the ESCAPE system are comparable to that of values published in Lymer et al. (2021), and Chen et al. (1978) using different LIF systems and potential calculation methods. It was found in Lymer et al. (2021) and others that organics typically have a τ of 1.55–3.55 ns, whereas minerals have τ values of 15–70 ns. The calculated τ of gypsum for this study, however, does not fall into this trend with a lifetime of 4.19 ns. This result nevertheless makes sense as the gypsum used is a synthesized ‘pure’ sample from Sigma-Aldrich and most likely does not contain the same trace elements that are present within natural minerals which give them their long fluorescence lifetimes (Lymer et al., 2021). The ESCAPE system is yielding spectra that allow the resolution of important peaks that are used for the identification of minerals using 532 nm excitation such as the olivine SiO_4 doublet, which has been used to identify whether olivine is iron or magnesium-rich based on the relative peak heights and wavenumber offset (Kuebler et al., 2006). Using 266 nm excitation, the ESCAPE system also provides high-resolution mineral spectra, when the minerals are not rich in iron due to the known iron quenching of UV incident and reflected light in the wavelength range of 255–275 nm (Razzell Hollis et al., 2021). Utilization of both 266 and 532 nm excitation in combination allows the ESCAPE system to have both mineral and organic detection and identification capabilities in complex natural samples with varying mineralogy and organic

content. Raman and LIF spectroscopy are recently being considered and chosen as flight instruments for space exploration and astrobiology (Wiens et al., 2021b; Abbey et al., 2017; Beegle et al., 2015). However, combining such instruments with an environmental chamber in the laboratory would allow for minimally destructive spectroscopic analysis of very sensitive samples that require specific environments for long-term preservation, to gain compositional information without altering or contaminating the sample. This type of analysis could be used as a ‘triage’ or preliminary analysis to look for areas of mineral or organic interest in samples returned from space missions such as NASA’s OSIRIS-REx while keeping the sample at specific environmental conditions.

4 Results II: UV TR-LIF for the Detection of Snowmelt and Water Contamination

This experiment is designed to use transmission UV-Raman and Fluorescence to observe differences in snowmelt and water samples ranging from sterile water to field samples and laboratory-made doped samples. Transmission Raman is usually conducted in a linear plane where the sample is placed in the optical path of the laser, passing through the sample and collected in the collection optics. In the ESCAPE system, we can utilize transmission-Raman and fluorescence by placing a UV-coated mirror on the sample stage, on which the transparent sample will rest. In this setup, the light enters the sample holder — a quartz cuvette filled with liquid passes to the UV-coated mirror where it is reflected back through the sample and the light is collected into the telescope. This alignment allows for the light collected to contain information all the way through the water column in the sample cuvette instead of reflecting off the surface, in a typical Raman/fluorescence setup. Analyzing different snow and water samples in this manor will demonstrate both the types of UV fluorescence (time-resolved and laser-induced spectra) and Raman data that can be collected using the ESCAPE system, as well as show the usefulness of UV fluorescence in icy body astrobiology and exploration.

4.1 Sample Collection and Preparation

For this experiment, eight samples were analyzed all in liquid form. Three samples were collected from around Toronto — two fresh snowmelt samples collected from the surface of ground snow within 24 hours after falling, and one sample of Lake Ontario water from Balmy Beach around the same time as snowfall. One sample was collected from a tall snowbank in Ottawa, created by plowing a hospital parking lot and was visibly contaminated with brown silt or sand. One sample was collected of Toronto tap water from the PIL sink after running it for several minutes. Two samples were made in the laboratory of sterile water doped

with small amounts of the amino acids tryptophan and tyrosine. To make samples doped with < 1 mM (millimole = 10^{-3} mol/L), 18 mg of tryptophan and tyrosine were added to 100 mL of sterile water and mixed with magnetic stirrers at 35°C until dissolved. This mixture results in a concentration of 0.88 mM DL-Tryptophan and 0.99 mM DL-Tyrosine, making the samples extremely comparable to that of (Eshelman et al., 2019) where similar concentrations of tryptophan and tyrosine were studied in ice by fluorescence spectroscopy (see Appendix C for detailed calculations). For control, a sample of sterile water was also tested in this experiment. Each of the samples are stored in sterile sample vials and was decanted into 3.5 mL quartz cuvettes cleaned with isopropyl alcohol and dried (Figure 4.1).

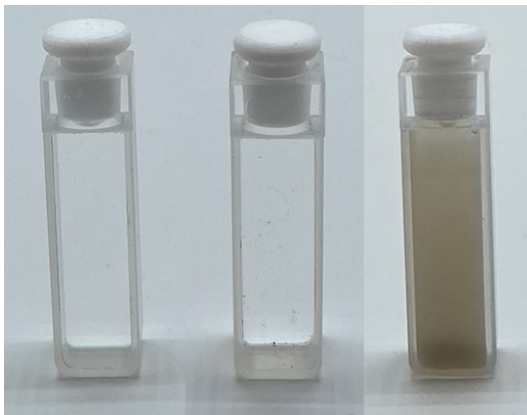


Figure 4.1: Examples of Quartz cuvettes holding 3.5 mL liquid samples from left to right: ‘Sterile water’, ‘Backyard snowmelt’, ‘Ottawa snowbank’.

4.2 Experimental Setup

To conduct UV-Raman and UV-Fluorescence, the quartz cuvettes are placed one at a time on top of a UV-coated mirror on the sample stage in the ESCAPE system chamber. The acquisition setting specifications for UV-Raman, UV-LIF and UV TR-LIF are shown in Table 8. The UV-Raman analysis is conducted using a TTL width of 5ns, whereas the LIF spectra are collected with a TTL width of 100 ns to capture all the fluorescence light. TR-LIF 3D ‘fingerprints’ are collected using ‘kinetic’ mode, where every 0.1 ns the gate is stepped in time with a consistent gate width of 5 ns for 200 steps. A 200-length series with a step size of

0.1 ns results in a fluorescence fingerprint of the sample over 20 ns in time. The delay when collecting TR-LIF is reduced by 5-10 ns from the ideal delay time to capture the growth and decay of the fluorescence over the 20 ns window.

Table 8: 532 nm Raman mapping acquisition settings for the Tagish Lake Meteorite

Parameter	Raman Values	LIF Values	TR-LIF Values
Acquisition Mode	Accumulate	Accumulate	Kinetic
Trigger	External	External	External
Exposure time	0.1 s	0.1 s	0.1s
Gain	4000	3000-4000	3000-4000
Number of Accumulations	600	100	4
TTL Width	5 ns	100 ns	100 ns
DDG Delay	47.5 ns	47.5 ns	40 ns
Gate Step	—	—	0.1 ns
Kinetic Series Length	—	—	200
Camera Temperature	-35°C	-35°C	-35°C
Slit Opening	30 μm	30 μm	30 μm
Laser Rep. Rate	2 kHz	2 kHz	2 kHz

When utilizing FTIR (Fourier transform infrared spectroscopy), each quartz cuvette was placed independently between the laser utilizing the bench setup of an Agilent Cary 660 FTIR with 2 cm^{-1} resolution and a spectral viewing window of $400\text{-}6000\text{ cm}^{-1}$. The instrument is aligned before data acquisition and background spectra are collected to subtract from each sample acquisition.

4.3 Spectral Analysis of Water and Snowmelt Samples

4.3.1 FTIR Results

FTIR analysis (Figure 4.2) shows slight changes in the water absorption band around cm^{-1} when comparing the sterile water to that of samples with doped or natural contamination such as $< 1 \text{ mM}$ tryptophan doped sterile water. The sterile water and two fresh snowmelt samples ('Backyard' and 'Fresh') FTIR spectra show very little variation from each other. Samples labelled 'Ottawa snowbank', 'Lake Ontario' and 'Toronto Tap Water' also show some resemblance to each other in the $3800\text{--}4000 \text{ cm}^{-1}$ region, where there is a sharper, thin absorption band compared to the snowmelt and sterile samples. ' $< 1 \text{ mM}$ Tryptophan' and ' $< 1 \text{ mM}$ Tyrosine' have very similar FTIR spectra to each other, as expected because of their similar compositions. These

samples have a very weak water absorption band between $3500\text{--}4000 \text{ cm}^{-1}$, as the amino acid spectra are overwhelmingly strong and dominate the spectral window. Even with the amino acid contamination, however, we can see the resemblance of the spectra to that of the Lake Ontario sample which would naturally contain organics and dissolved minerals.

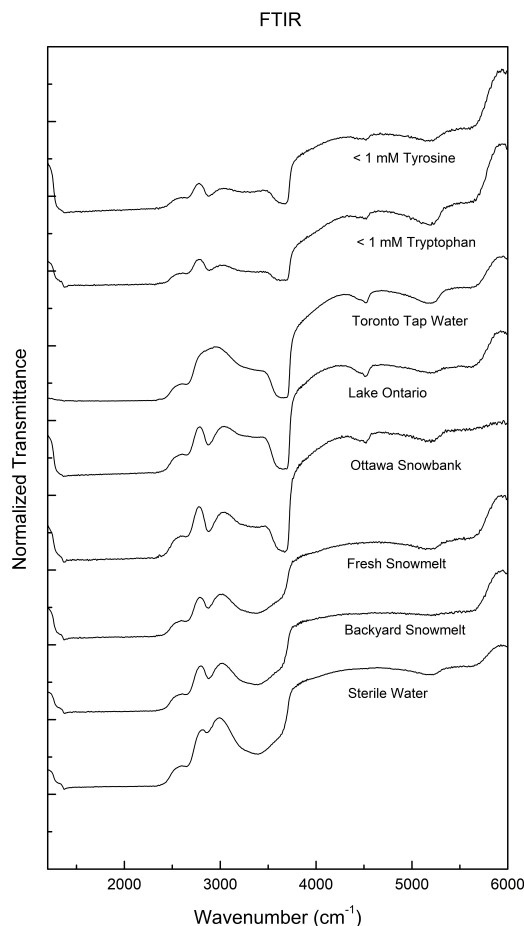


Figure 4.2: FTIR spectra of eight water and snowmelt samples.

4.3.2 UV Raman Spectroscopy Results

Six of the eight samples in the study are presented here with Raman spectra (Figure 4.3), as aromatic amino acids such as tryptophan and tyrosine do not have Raman vibrational peaks with UV excitation. The primary Raman peak in these spectra is the vibrational stretching peak of O-H is a doublet of asymmetric and symmetric stretching modes at $3200\text{--}3400\text{ cm}^{-1}$. In the UV-Raman spectra from the samples in this study, we see small peaks at $\sim 1600\text{ cm}^{-1}$ most likely correlating to the H-O-H bending mode of water. The primary peak in these spectra is at 3378 cm^{-1} relating to the O-H Raman band. A Gaussian peak was fit to each of the sample spectra to obtain the precise peak positions of the O-H mode (example: Figure 4.4). Samples: Sterile water, Fresh Snowmelt, Backyard Snowmelt, Ottawa Snowbank and Lake Ontario all have an O-H peak position of $3378 \pm 1\text{ cm}^{-1}$. The sample ‘Toronto Tap Water’ has a slightly shifted O-H peak at 3385 cm^{-1} . The shift in the O-H Raman peak in tap water may be due to different trace elements within the water, chlorine or other added components, mostly showing as an increase in fluorescence in the higher wavelength region (Figure 4.3).

Beyond this shift in the O-H peak of water in the sample of tap water, there is very little variation in peak position - however, the relative intensity of this peak does change - or rather decrease with an increase in contamination potential within the sample. For example, the water Raman peak intensity in descending order of samples is Sterile water, Fresh snowmelt, Backyard snowmelt, Lake Ontario, Tap water, and Ottawa snowbank. As observed in Figure 4.1, the sample ‘Ottawa Snowbank’ is extremely dirty and a lot less transparent than that of the other samples with less contamination. This opaqueness results in less intensity in the Raman signal, especially of water which we are trying to observe in Figure 4.3.

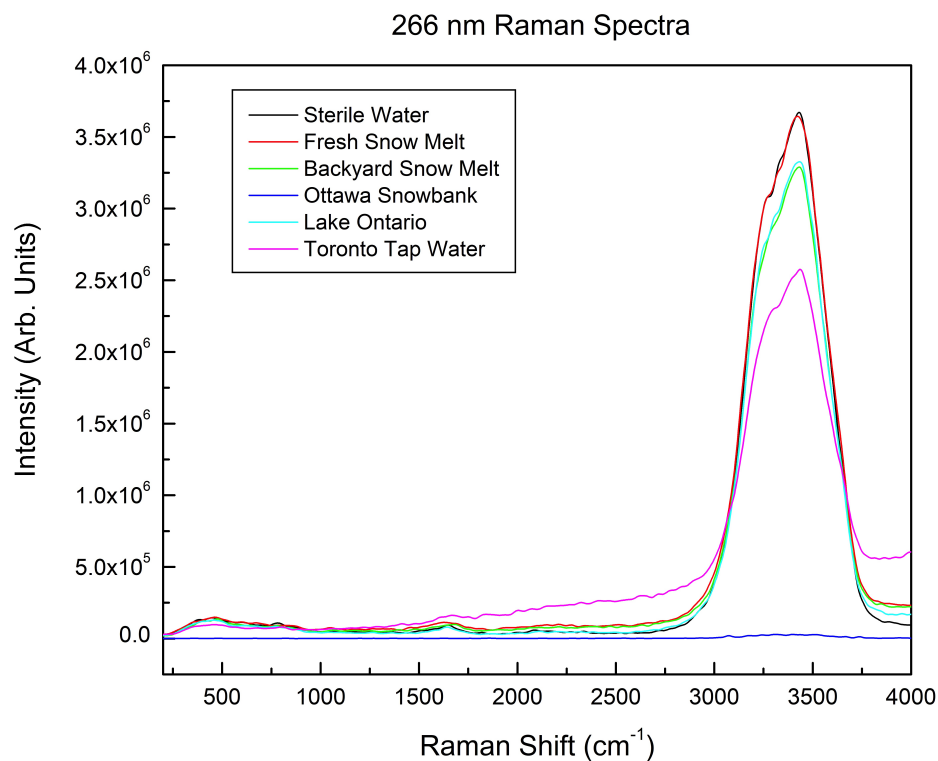


Figure 4.3: 266 nm Raman spectra showing H_2O peak at 3577 cm^{-1} in 6 water and snowmelt samples.

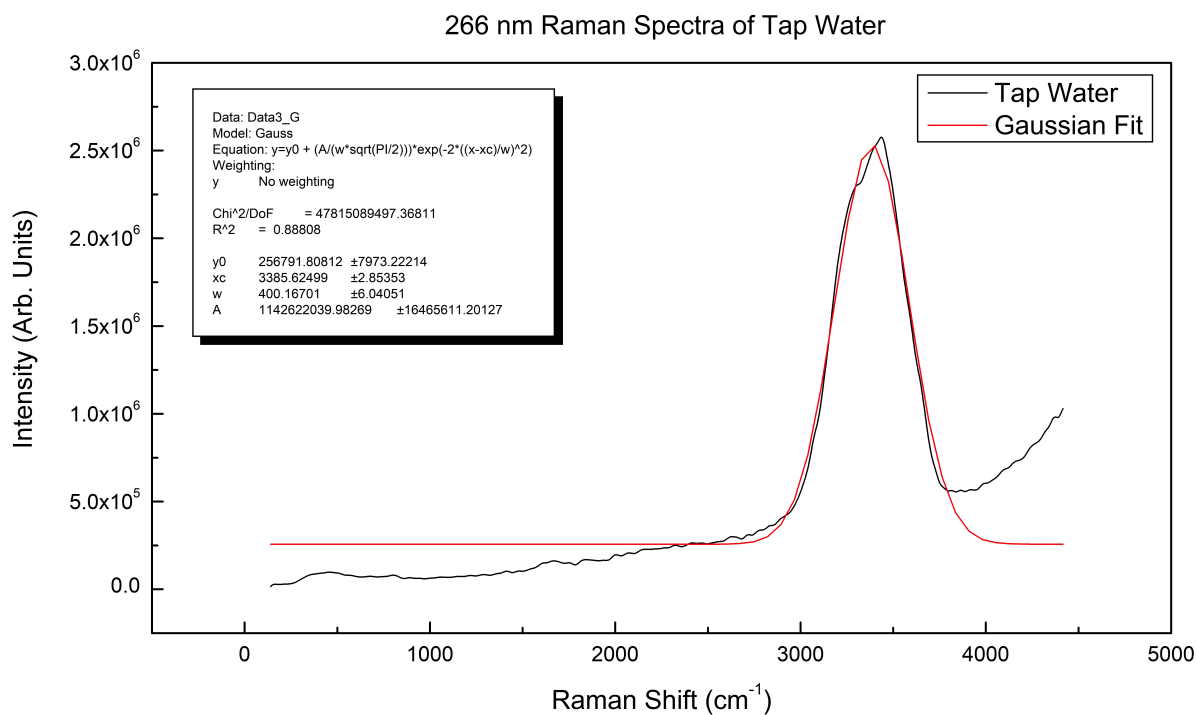


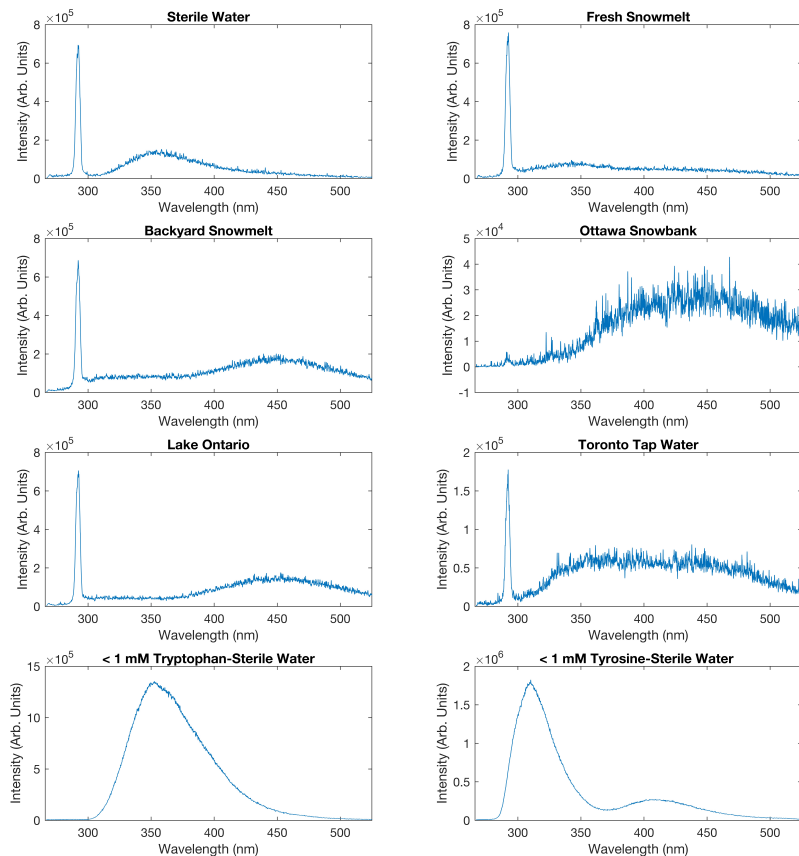
Figure 4.4: Gaussian Peak Fit to 266 nm Raman Water Peak of Toronto Tap Water.

4.3.3 UV LIF and Time-Resolved Fluorescence (TR-LIF) Spectroscopy Results

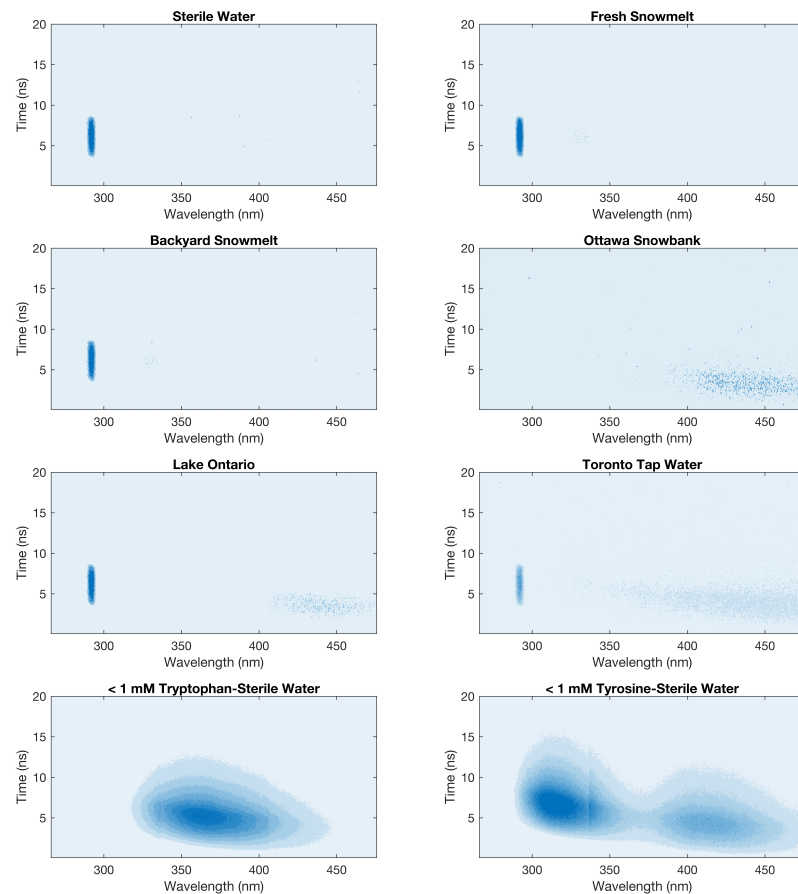
Single-spectra fluorescence (LIF) and time-resolved LIF (Figure 4.5) are collected using the ESCAPE system on all eight of the samples in this study. The LIF spectra show both the Raman region (266-350 nm) and the fluorescence region (300-525 nm). The Raman O-H peak is visible in all of the spectra at 292 nm except for the two amino acid-doped samples (< 1 mM tryptophan and tyrosine), the same result as when looking at the UV-Raman spectra in the previous section of results. The LIF spectra of ‘Sterile water’ shows a sharp O-H Raman peak and a small broad-band peak of fluorescence at just over 350 nm. Similarly, the LIF spectra of ‘Fresh Snowmelt’ also have a sharp O-H Raman peak and a very weak broad-band fluorescence peak at 350 nm. Sample ‘Backyard Snowmelt’ differs slightly from the first two with a sharp O-H Raman peak and a broad-band fluorescence peak at 450 nm. The sample labelled ‘Lake Ontario’ has a remarkably similar LIF spectrum to that of ‘Backyard Snowmelt’. The sample ‘Ottawa Snowbank’ has a very weak Raman O-H peak and intense broad-band fluorescence in the region of 350–550 nm peaking around 425–450 nm. Similarly, ‘Toronto Tap Water’ has broad-band fluorescence over most of the fluorescence region, however, the fluorescence is more intense in the 350 nm region than in higher wavelengths and has a more intense O-H Raman peak than that of ‘Ottawa Snowbank’. Both the samples < 1 mM tryptophan and tyrosine have very different LIF spectra than the other samples, with no sign of water and very intense fluorescence in the 300–400 nm region. < 1 mM tryptophan has very intense, broad fluorescence peaking at 350 nm. < 1 mM tyrosine also has very intense fluorescence peaking around 325 nm, with an additional, much weaker and broad peak around 415 nm.

TR-LIF of all eight samples is presented in Figure 4.5(b) as 2-dimensional contour plots with dark blue representing the intensity (z) in the spectra at specific wavelengths (x) over time (y). We can observe in samples ‘Sterile Water’, ‘Fresh Snowmelt’ and ‘Backyard Snowmelt’ that these samples have an O-H Raman peak (Short-lived) that is more intense than any fluorescence present in the LIF spectra (Figure 4.5 (a)). Conversely, the

sample ‘Ottawa Snowbank’ shows noisy fluorescence in the region of 350–500 nm without an O-H Raman peak really present. Samples ‘Lake Ontario’ and ‘Toronto Tap Water’ show both the O-H Raman peak and slight fluorescence in the region of 400–500 nm for ‘Lake Ontario’ and 300–500 nm for ‘Toronto Tap Water’. These data match and complement the LIF single-spectra well in Figure 4.5 (a). Samples < 1 mM tryptophan and < 1 mM tyrosine have TR-LIF 2D contour plots that show the growth and decay of their fluorescence peaks over time. We can observe in < 1 mM tyrosine the difference in intensity and time between the two main fluorescence peaks at 325 nm and 415 nm.



(a) 266 nm LIF of Snowmelt and Water Samples



(b) 266 nm TR-LIF of Snowmelt and Water Samples

Figure 4.5: UV LIF spectra and TR-LIF contour 'fingerprint' plots of eight snowmelt and water samples.

After reviewing the results of the TR-LIF of the initial 8 samples, four more samples were made by diluting the original < 1 mM Tryptophan and Tyrosine samples to make < 0.5 and < 0.25 mM tryptophan and tyrosine in water samples. The TR-LIF (Figure 4.6) of all the doped water samples have similar ‘fingerprints’, with lessening intensity as concentration decreases in each sample respectively. The decay rates (τ) are calculated in nanoseconds for each of the concentrations of tryptophan and tyrosine in water in Table 9, showing an increase in decay rate (1.88–2.55 ns and 1.24–1.86 ns) with decreasing concentration for both tryptophan and tyrosine respectively. Furthermore, when we plot the exponential decrease in concentration against the calculated decay rates for each sample, we can see that there is a similar trend in the rate of decay depending on the concentration of tryptophan and tyrosine in water. The only other water sample that had a strong enough fluorescence signal to calculate a decay rate fluorescence lifetime is ‘Toronto Tap Water’. This sample has a much longer life than that of the organics tryptophan and tyrosine at 3.01 ns (Table 9).

Table 9: Calculated Decay Rates of < 1 mM, < 0.5 and < 0.25 mM Tryptophan and Tyrosine Respectively in Water.

<i>Sample</i>	$\lambda_{max, ESCAPE} (nm)$	$\tau, calculated (ns)$
1 mM Tryptophan	~ 355	1.88
0.5 mM Tryptophan	~ 355	1.95
0.25 mM Tryptophan	~ 355	2.55
1 mM Tyrosine	~ 325	1.24
0.5 mM Tyrosine	~ 325	1.42
0.25 mM Tyrosine	~ 325	1.86
Toronto Tap Water	~ 325	3.01

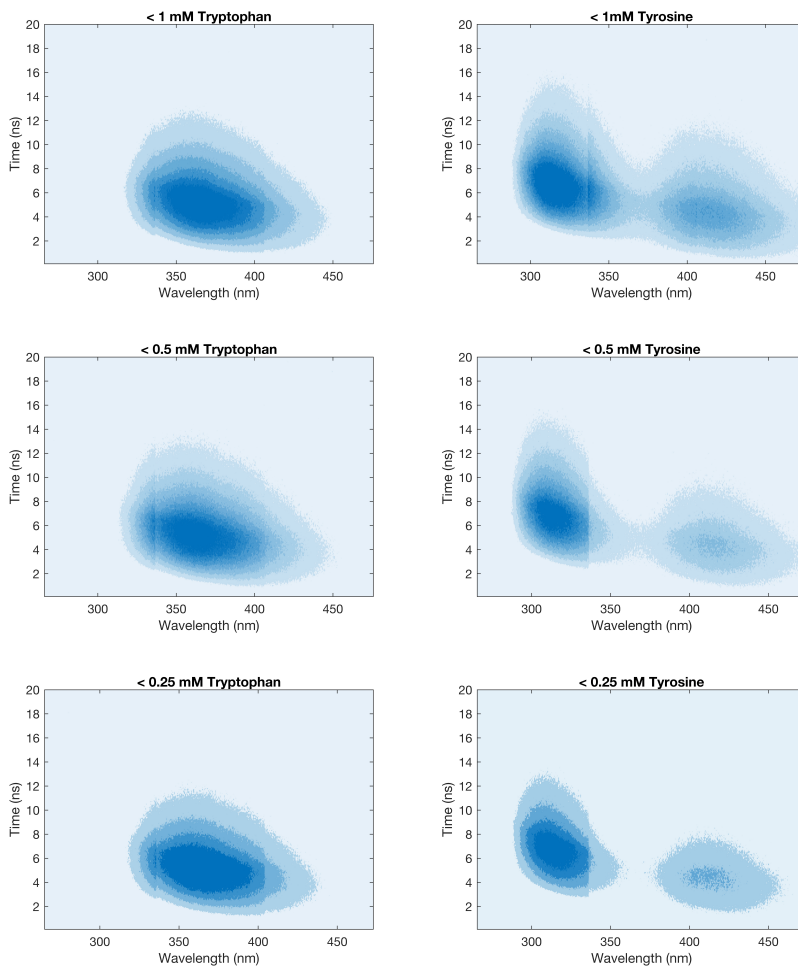


Figure 4.6: Time-resolved fluorescence spectra of <1 , <0.5 and <0.25 mM concentrations of tryptophan-sterile water and tyrosine-sterile water.

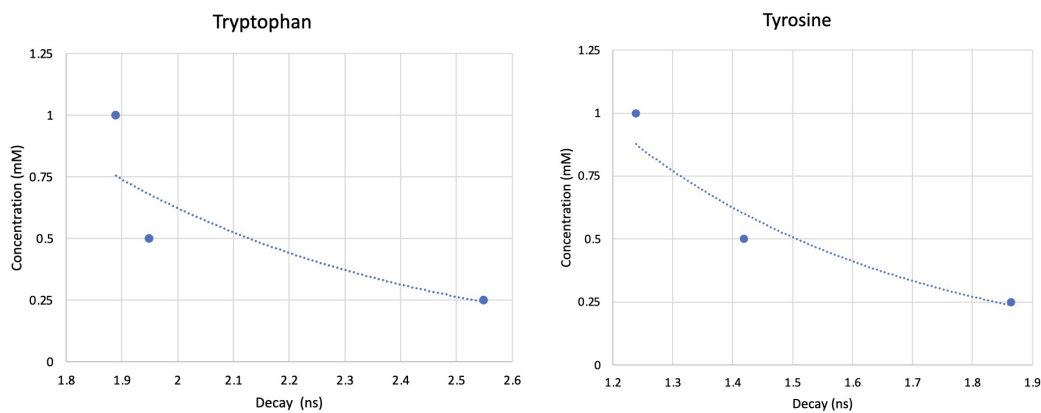


Figure 4.7: Time-resolved fluorescence decay rates of <1 , <0.5 and <0.25 mM concentrations of tryptophan-sterile water and tyrosine-sterile water. $\lambda_{max} = 355$ nm for tryptophan, 325 nm for Tyrosine.

4.4 Discussion of UV Spectral Analysis of Snowmelt and Water Contamination

The purpose of the *UV Spectral Analysis of Snowmelt and Water Contamination* experiment is two-fold:

1. To demonstrate the transmission Raman functionality of the ESCAPE system
2. To demonstrate the viability of UV Fluorescence as a tool for detecting organics relevant to astrobiology and planetary icy body exploration in liquid.

The results of this study suggest that transmission UV fluorescence can be utilized to produce spectral data products of organics and contaminants in liquid samples that are distinguishable and unique compared to that of UV Raman and FTIR analyses. Furthermore, the results of the TR fluorescence of varying concentrations of tryptophan in sterile water indicate that UV fluorescence is very good at detecting organics in liquid water at low concentrations ($<0.25 - <1$ mM). TR-LIF decay rate calculations (τ) of the varying concentrations of tryptophan and tyrosine in sterile water yielded results similar to that of varying organic and REE concentrations in substrates from Shkolyar et al. (2021), where higher concentrations of the fluorescent dopant results in shorter τ than that of lower concentrations (which have a larger τ values). This result is somewhat counter-intuitive, but has a simple explanation as described in Shkolyar et al. (2021), where higher concentrations of tryptophan also resulted in smaller τ than their lower concentration counterparts due to a ‘self-reabsorption’ phenomenon, a type of fluorescence quenching occurring which allows radiation-less transition of energy decay back to the ground state (Lakowicz, 2006; Eshelman et al., 2018). The trend of exponential decrease of concentration with exponential τ suggests that fluorescence lifetimes are somewhat predictable depending on the concentration within a sample. The concentration of tryptophan and tyrosine in these samples was based on a previous study by Eshelman et al. (2019), where 1 mM of tryptophan and tyrosine were used

to dope ice core samples. The results of this study are in agreement with Eshelman et al. (2019), where UV Fluorescence was extremely useful for detecting both organics in their substrates (water vs. ice). Moreover, the higher calculated τ of Toronto Tap Water compared to that of the organic samples tyrosine and tryptophan suggest that the fluorescence emission from the sample may be due to a complex mix of organic and chemical components (like chlorine, fluoride etc.) that may contribute to a slightly higher τ than organics (1.5–3.5 ns), but not as high of an average τ as minerals (15–70 ns) as found in Lymer et al. (2021). Further study into if longer acquisitions of TR-LIF measurements result in data useful for decay rate calculations should be accomplished, as it is a useful tool for differentiating between samples, and potentially quantifying the amount of an identified material within water.

Furthermore, this study provides insights into the usefulness of UV fluorescence in detecting organics at very low concentrations, down to < 0.25 mM. The results of this experiment show the usefulness of a UV instrument for not only water contamination studies on Earth but icy-body astrobiology exploration in space as well. Future studies could include comparing the UV fluorescence results to that of a standardized physical chemistry instrument such as GC-MS (gas-chromatography mass spectrometry). The sample size of this experiment was small, however, the qualitative and quantitative results will help build the foundational knowledge of how to use such instrumentation for organic detection and identification in the planetary exploration of icy bodies like Europa or Enceladus.

Practical future uses for transmission Raman are boundless, from analyzing human tissues to pharmaceutical quality control and rapid water contamination detection. However, this study also points to the usefulness of transmission fluorescence, applied in the same way as Raman but possibly obtaining more unique results depending on the samples being analyzed - especially if they are organic in nature. This research could be applied to future studies of organic distribution in ice, the detection of microbes in groundwater at small concentrations or even the viability of a UV Raman/fluorescence instrument for the detection of organics on icy bodies.

This study: *UV Spectral Analysis of Snowmelt and Water Contamination* shows both the 1) functionality of the transmission UV Raman/Fluorescence modes and the UV TR-LIF modes of the ESCAPE system and 2) the viability of a UV transmission Fluorescence instrument for the detection of organics and contamination in water and snowmelt samples compared to that of Raman or FTIR analyses alone.

5 Results III: Detecting REEs in Lunar Analogue Samples using LIF Analysis

This experiment is designed to demonstrate the viability of using UV or green laser-induced fluorescence to detect rare earth elements (REEs) in lunar material. The lunar surface has been considered a potential location for the development of a space-base to act as a potential fuelling and manufacturing gateway for deep space exploration. In this effort, several missions to the Lunar surface are being planned over the next decade, including proposed exploration and resource utilization rovers and lander systems such as Lino et al. (2020); Just et al. (2022). Lunar regolith contains important resources for the manufacturing of propellants in the form of volatiles. Lunar regolith also contains concentrations of trace elements that are hard to extract, finite resources on Earth and are important for the manufacturing of electronics and therefore referred to as rare Earth elements (REE). REEs such as cerium and yttrium can be found in lunar impact breccia material and KREEP basalts (material rich in potassium (K), REEs, and phosphorus (P)) (National Academies of Science Engineering and Medicine, 2022; McLeod and Krekeler, 2017). The first step in determining if there are enough resources on the moon to be utilized in an efficient way for space manufacturing and resource utilization is reasonable detection of such materials in a systematic way through instrumentation that is flight-ready. Detection and identification of REEs in the lunar regolith will require instrumentation as a rover or lander payload capable of fast and reliable results, such as that from laser-induced fluorescence spectroscopy. LIF instrumentation now has flight heritage through the SHERLOC and Supercam instruments onboard the Perseverance rover (NASA Mars 2020) (Wiens et al., 2021b; Beegle et al., 2015). To further understand the spectral signatures and detectability of REEs in the lunar regolith, this chapter will analyze the limitations and capabilities of detecting Y and Ce in Lunar regolith analogue samples using UV and green laser-induced fluorescence (LIF).

5.1 Sample Synthesis and Preparation

Following the procedural method of CePO_4 synthesis based on Lalla et al. (2021); Verma and Bamzai (2014), to synthesize YPO_4 at a molar ration of 1:1, 10 g yttrium (III) nitrate hexahydrate $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.8% pure) and 3.5 g di-ammonium hydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$), are measured and mixed with ultra-pure water (50 mL) for 2 hours using magnetic stirrers at 80°C . Ammonium hydroxide (NH_4OH) is added, drop-wise to this solution, raising the pH from ~ 1 – 12 and increasing the volume of the solution to >120 mL. The thick, milky precipitate from this reaction is then twice-filtered with ultra-pure water and dried at room temperature for 24 hours under a fume hood. The precipitates are then crushed using a mortar and pestle and transferred to a oven-safe crucible and baked at 800°C for another 24 hours. The powder is again crushed and mixed with mortar and pestle and then dry-mixed with lunar mare simulant (LMS-1, Exolith lab) with a mortar and pestle at concentrations of 1000, 2000, 5000, and 10000 ppm YPO_4 in LMS-1 (see Appendix C for detailed measurements and calculations).

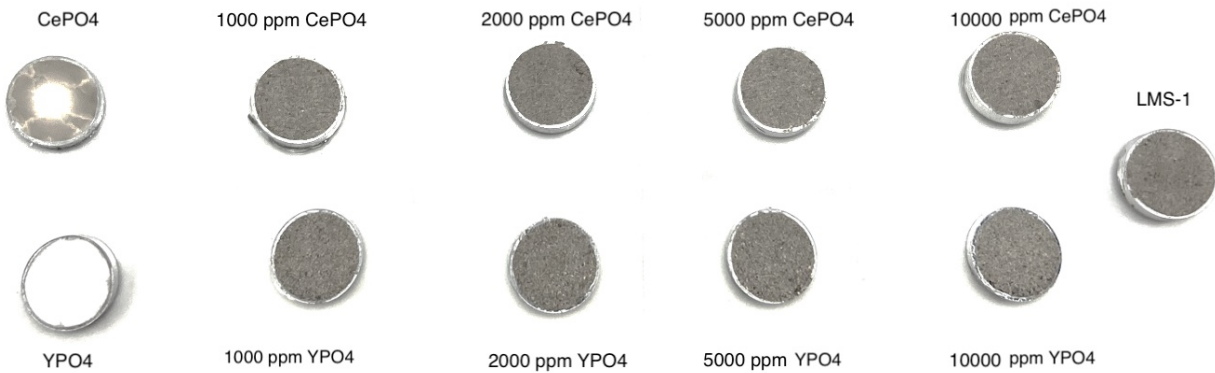


Figure 5.1: Lunar Regolith (LMS-1), CePO_4 , YPO_4 , and doped-lunar analogue samples at 1000, 2000, 5000, and 10000 ppm of CePO_4 and YPO_4 in LMS-1 pellets in aluminum collapsible cups.

Samples of pure YPO_4 , CePO_4 (from (Lalla et al., 2021)) and LMS-1, along with mixtures of 1000, 2000, 5000, and 10000 ppm CePO_4 and YPO_4 respectively in LMS-1 are pelletized in compressible tapered aluminum briquetting cups using ~ 0.5 g of mixture. The

Lunar mare regolith simulant, LMS-1 (Exolith Lab) is manufactured to replicate lunar regolith/soil texture (mean particle size 91 μm , range: 0.04–1000 μm) and mineralogy by combining terrestrial rock and mineral samples (pyroxene (32.8 wt%), glass-rich basalt (30 wt%), anorthosite (19.8 wt%), olivine (11.1 wt%) and ilmenite (4.3 wt%)). LMS-1 also contains ~ 12 ppm Y and 30 ppm Ce, measured by XRF analysis. Because the synthesis of CePO_4 and YPO_4 are molar ratios 1:1, the weight % concentration ratios are $\sim 75\%$ (Ce, Y) to 30% (PO_4) according to reaction calculations and chemical analysis by (Verma and Bamzai, 2014). Because of this ratio, the actual concentration of Ce and Y in the doped lunar samples are $\sim 75\%$ of the reported REE–Phosphate concentration. Further chemical and structural analysis of the newly synthesized YPO_4 for this study should be conducted in the future before publication to better understand the crystal habit, size, composition and purity.

5.2 Experimental Setup

For this lunar analogue experiment, both UV and green LIF setups are used to collect spectra from each sample in the ESCAPE system. To produce Laser-induced fluorescence 2D spectra, we use the same delay times as Raman (40.5 ns for green, 47.5 ns for UV), but a longer gate width is used at 100 ns. Each sample is placed within the ESCAPE system on the sample stage, and point analyses are taken at random positions on the 1 cm diameter pellets. For UV and green analysis, 10 random point spectra are taken of the LMS-1 sample to obtain an average spectrum for the heterogeneous material.

All Green analyses are completed with 10-point averages of each sample due to very low SNR. UV LIF analysis is completed with 5-point averages of each sample because of a higher SNR (with the exception of the LMS-1 sample).

Table 10: UV and Green LIF Acquisition Settings for REE-Doped Lunar Analogue Samples

Parameter	UV LIF Values	Green LIF Values
Acquisition Mode	Accumulate	Accumulate
Trigger	External	External
Exposure time	0.1 s	0.1 s
Gain	1000–4000	4000
Number of Accumulations	100	200
TTL Width	100 ns	100 ns
DDG Delay	47.5 ns	40.5 ns
Camera Temperature	-35°C	-35°C
Slit Opening	30 μm	30 μm
Laser Rep. Rate	2 kHz	2 kHz
Diffraction Grating	600 l/mm	600 l/mm

5.3 Green LIF/Raman Analysis of REE-Doped Lunar Analogue Samples

When interrogating the synthesized YPO_4 and CePO_4 samples with $\lambda_{Ex}=532$ nm, there is little to no broad-band fluorescence present (Figure 5.2), even when opening up the gate width from 5 ns (Raman average) to 100 ns (LIF average). There are, however, strong Raman peaks in the region of 145–2500 cm^{-1} for both YPO_4 and CePO_4 , mostly relating to the symmetrical and asymmetrical bending and stretching vibrational modes of (PO_4). Phosphate (PO_4) peaks at ~ 1000 and 1140 cm^{-1} are strong in both samples and look similar to that of SO_4 peaks such as in the mineral gypsum seen in section 3. The Raman peaks for YPO_4 and CePO_4 in the region of <750 cm^{-1} differ from each other (Table 11), allowing for identification of the samples using Raman peak analysis. Conversely, the LMS-1 Lunar Mare simulant sample does not have any discernible Raman peaks, (most likely due to its fine-grained nature and heterogeneity) but does have broad-band fluorescence when using $\lambda_{Ex} = 532$ nm (Figure 5.2).

When we analyze with $\lambda_{Ex}=532$ nm with Raman/LIF, the REE-doped LMS-1 samples with 1000, 2000, 5000, and 10000 ppm concentrations of YPO_4 and CePO_4 respectively,

Table 11: 532 nm Raman Peak Positions of YPO_4 and CePO_4 synthesized samples compared to that of literature values in Frost et al. (2010); Errandonea et al. (2018).

YPO_4 Raman Peak Positions (cm^{-1})	CePO_4 Raman Peak Positions (cm^{-1})	Literature Peak Positions (cm^{-1})	Literature Peak Assignments	Citations
298	284	282	$B_g(T)$	(Frost et al., 2010) (Errandonea et al., 2018)
—	407	407	$A_g(\nu_2)$	
484	470	497	$\nu_2(\text{PO}_4^{3-})$	
578	578	563	$\nu_4(\text{PO}_4^{3-})$	
658	625	620	$B_g(\nu_4)$	
—	733	—	—	
1000	972	975	$\nu_{1s}(\text{PO}_4^{3-})$	
1060	1062	1065	$\nu_{3as}(\text{PO}_4^{3-})$	

there is very little variation in the spectra, and the concentration levels are indiscernible from each other (Figure 5.3). Fairly weak, broad-band fluorescence dominates the spectra with no intensity variation associated with increasing REE concentration either with YPO_4 or CePO_4 .

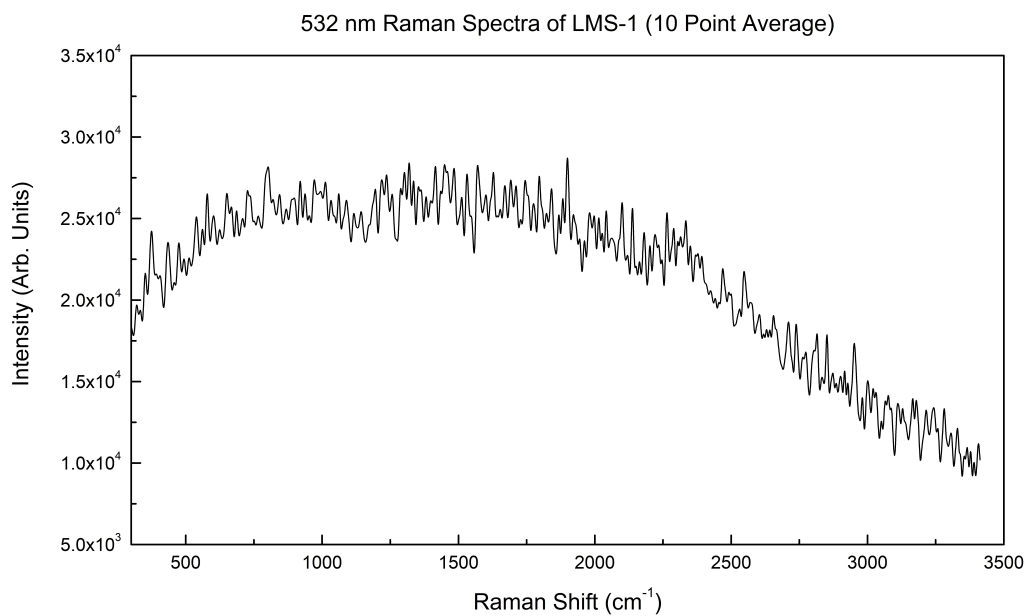
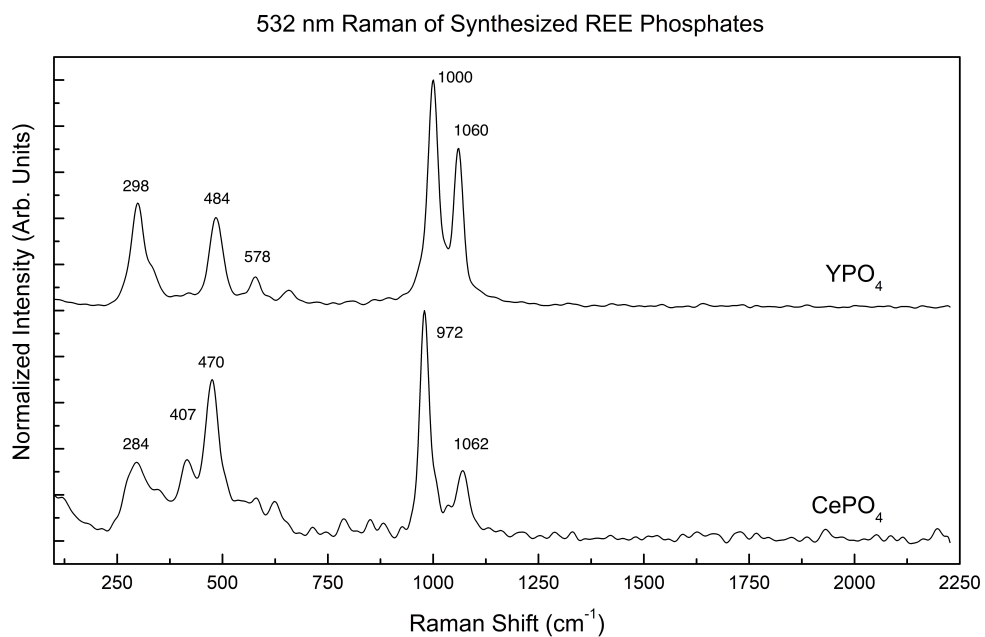
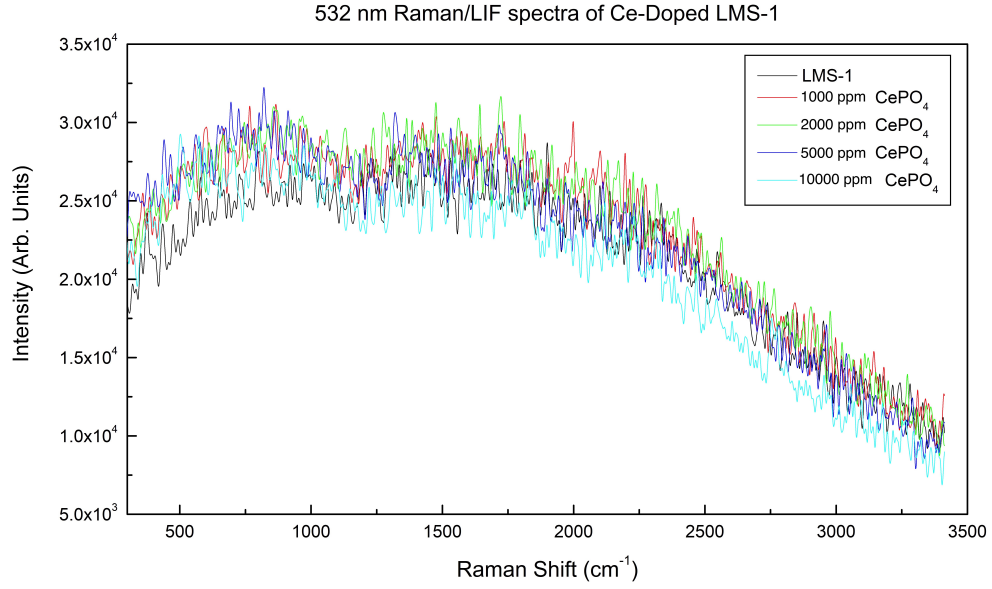
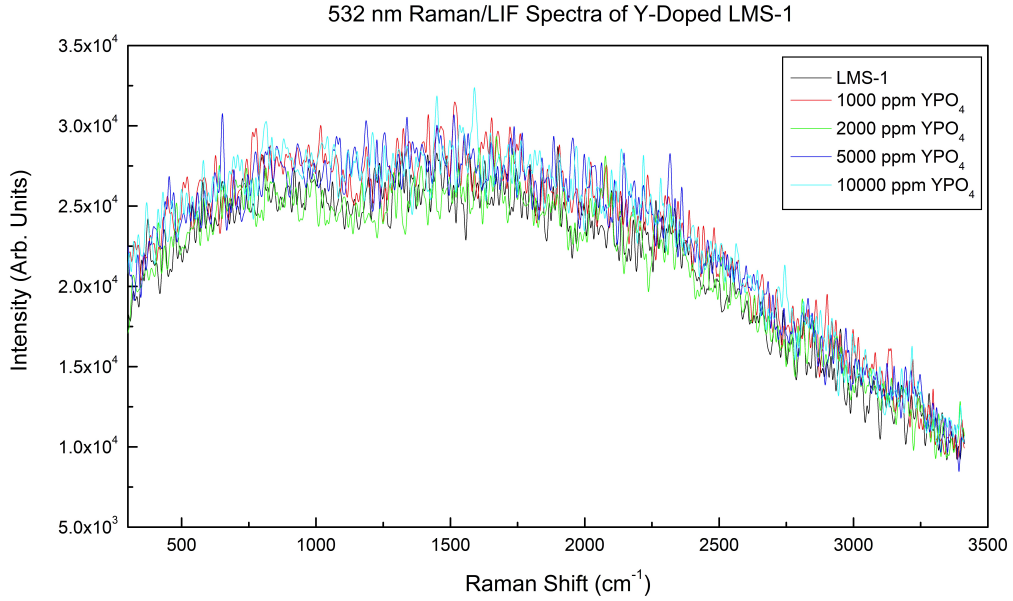


Figure 5.2: 532 nm Raman/LIF of (a) synthesized YPO_4 and CePO_4 ; and (b) LMS-1 ($n=10$) Lunar Mare Simulant from Exolith Lab; all samples pelletized.



(a) 532 nm Raman/LIF of 1000, 2000, 5000 and 10000 ppm CePO_4 in LMS-1 ($n=10$ for each sample)



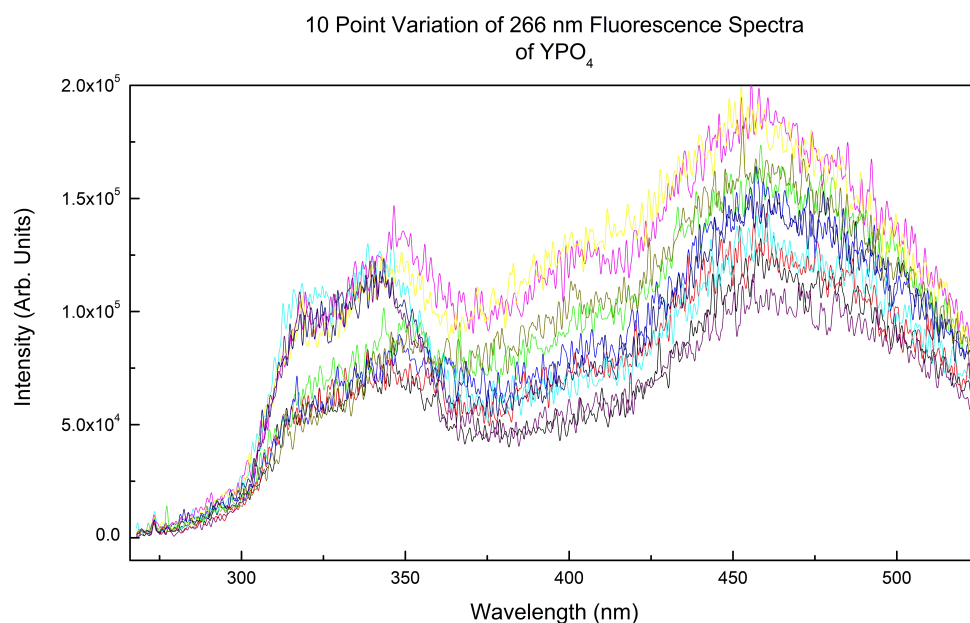
(b) 532 nm Raman/LIF of 1000, 2000, 5000 and 10000 ppm YPO_4 in LMS-1 ($n=10$ for each sample)

Figure 5.3: 532 nm Raman/LIF of varying concentrations of synthesized YPO_4 and CePO_4 in LMS-1; $n=10$ for each sample, all samples pelletized.

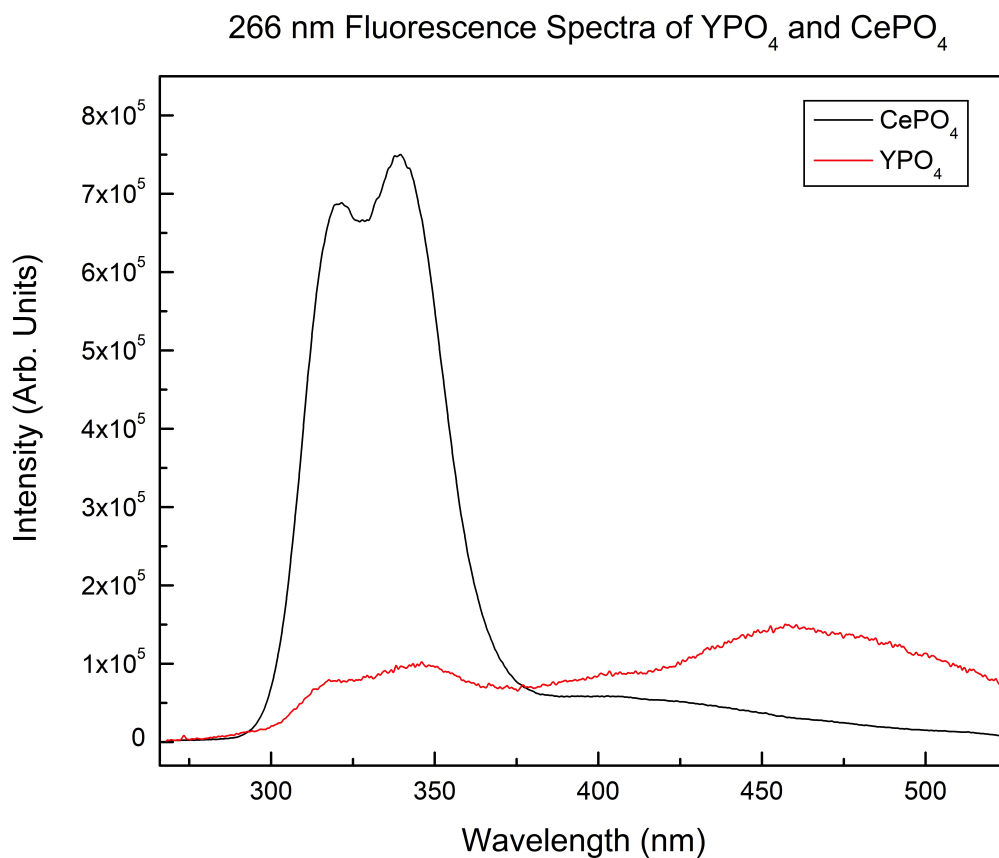
5.4 UV LIF Analysis of REE-Doped Lunar Analogue Samples

When interrogating the lunar REE samples with $\lambda_{Ex}=266$ nm, there is strong LIF emission, especially with $CePO_4$ (Figure 5.4). YPO_4 also has fluorescence, but is much less intense than $CePO_4$ and has a lot of point variation even within the pure synthesized sample (Figure 5.5). Point variation may be due to the size of the crystals formed during the chemical reaction. The pure YPO_4 samples appear to have fluorescence in the same region as $CePO_4$ (300–350 nm) appearing as a doublet peak at 320 and 338 nm, as well as a broadband fluorescence at 450 nm that may be due to impurities in the sample. Because $CePO_4$ has such intense fluorescence, the gain on the iCCD camera is turned down to 1000 from 4000 to protect it from over-saturation.

Figure 5.5 shows the fluorescence spectral series of 1000, 2000, 5000 and 10000 ppm $CePO_4$ and YPO_4 in LMS-1 Lunar Mare simulant respectively. Similarly to the Ce-doped MGS-1 samples in section 3, the fluorescence intensity in the range of 325–350 nm increases with increasing concentration fairly linearly. YPO_4 , also shows fluorescence in the same region as $CePO_4$, but at a lesser intensity. The YPO_4 intensity does not increase linearly with increasing concentration unlike $CePO_4$. The concentration of 1000 ppm YPO_4 in Figure 5.5 emphasizes this non-linear pattern of fluorescence intensity with concentration. Interestingly, the fluorescence spectra of the YPO_4 -Doped LMS-1 look more intense in the region of 300–350 nm than the pure YPO_4 fluorescence 10-point average spectra. Variations in intensity could occur based on crystal structure, packing, orientation when mixed etc. The fluorescence signature of YPO_4 and $CePO_4$ in the LMS-1 look very similar to each other with only a subtle difference in relative peak intensity between the 325 and 338 nm peaks (325<338 in $CePO_4$, 325>338 in YPO_4).

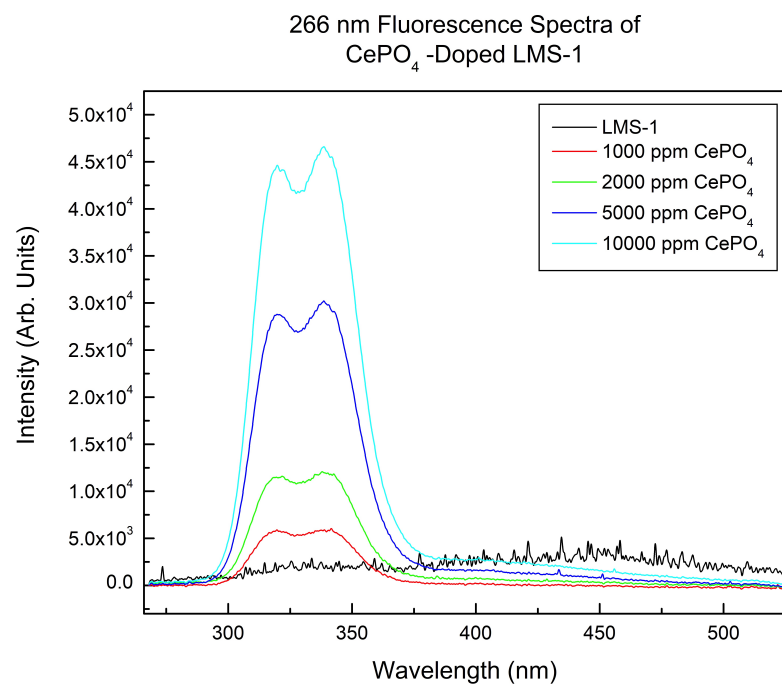


(a) Point variation in 266 nm LIF of YPO_4 , $n=10$.

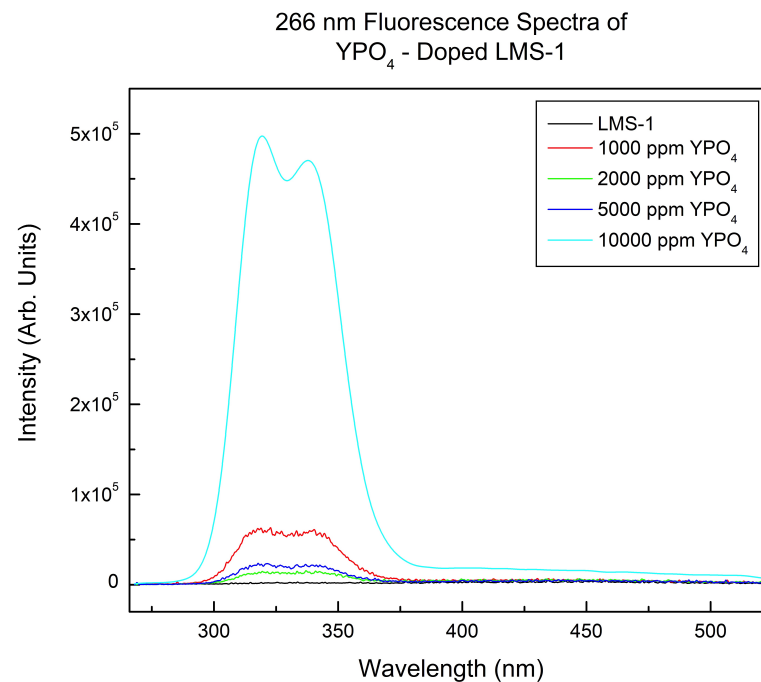


(b) 266 nm Fluorescence of CePO_4 and average of YPO_4 ($n=10$).

Figure 5.4: 266 nm Fluorescence of YPO_4 and CePO_4 synthesized samples.



(a) 266 nm Fluorescence of 1000, 2000, 5000 and 10000 ppm concentrations of CePO₄ in LMS-1 (gain = 1000)



(b) 266 nm Fluorescence of 1000, 2000, 5000 and 10000 ppm concentrations of YPO₄ in LMS-1 (gain = 4000)

Figure 5.5: 266 nm Fluorescence spectra of 1000, 2000, 5000, 10000 ppm concentrations of (a) CePO₄ and (b) YPO₄ in LMS-1 Lunar Mare simulant.

5.5 Discussion of UV and Green LIF Analysis of REE-Doped Lunar Analogues

The purpose of this study: *UV and Green LIF Analysis of REE-Doped Lunar Analogues* is to determine if rare Earth elements found in abundance on the moon could be detected by UV or Green laser-induced fluorescence analysis at varying concentrations in Lunar Mare regolith simulant. Some studies have suggested that $\lambda_{Ex} = 532$ nm may produce fluorescence of REEs such as in Ollila et al. (2014) and Fuchs et al. (2021), however, this study is to determine if $\lambda_{Ex} = 532$ nm or $\lambda_{Ex} = 266$ nm LIF would be better for detecting and identifying REEs (Ce, Y) in Lunar regolith. The results of this study show that Green-LIF is not suitable for detecting YPO_4 or CePO_4 , as there is no LIF emission generated at this wavelength. Green-Raman does produce good spectra of pure YPO_4 and CePO_4 but is not sensitive enough to differentiate YPO_4 and CePO_4 from the noisy signal of Lunar Mare at varying concentrations. The results of this study suggest that UV-LIF is a viable option for the detection of REEs YPO_4 and CePO_4 in Lunar Mare, as it is detectable in (phosphate) concentrations of 1000, 2000, 5000 and 10000 ppm in LMS-1 simulant. When the fluorescence emission is very intense, such as with CePO_4 , there is a linear trend between increasing concentration and increasing intensity within the samples—however, this trend was not linear within the weaker emission of YPO_4 LIF in LMS-1.

This data supports the results found in Fuchs et al. (2021), showing that $\lambda_{Ex} = 532$ nm LIF is not suitable to induce YPO_4 or CePO_4 fluorescence emission, but $\lambda_{Ex} = 266$ nm is. This study, however, provides further information about the detectability of varying concentrations of these phosphates in lunar regolith simulant using $\lambda_{Ex} = 266$ nm LIF. Interestingly, the data show very similar LIF spectra for both YPO_4 and CePO_4 , which is seemingly in line with the findings in Fuchs et al. (2021), where they state that the YPO_4 standard samples do not have their own luminescence, and the only luminescence from the sample comes from trace contaminants of Ce^+ , and thus both CePO_4 and YPO_4 have the same fluorescence spectra. Furthermore, if Y does not have its own luminescence and only

emits luminescence from that of Ce contamination, then the fluorescence spectra obtained in this study may also be Ce contamination, as the Y (III) Nitrate hexahydrate is reportedly 99.8% pure according to Sigma Aldrich. This effectively means that the cerium concentrations analyzed in the YPO_4 -doped LMS-1 samples are 0.2% of the reported concentrations (i.e. LMS-1 with 1000 ppm YPO_4 could possibly contain only 2 ppm Ce). This would account for the low intensity of YPO_4 fluorescence even in the pure sample and could account for the very low intensity of the YPO_4 in varying concentrations in LMS-1 analogue samples. The concentrations of Y and Ce in Lunar primitive-KREEP basalts have been found to be around 300 ppm each, and these results imply that at such concentrations, the Ce would be detectable with a UV-LIF like the ESCAPE system, however analysis should be completed at 300 ppm to verify these results, and further analysis to determine the exact amount of Ce present within these analogue samples should be conducted (Crawford, 2015).

Based on the results of this experiment, UV LIF would be the preferred method for detecting small concentrations of Lunar REEs YPO_4 (Ce) and CePO_4 in lunar simulant regolith over Raman spectroscopy. Future work of this study includes supplementing this data with that of TR-LIF and LIBS to better understand the use of these types of instrumentation for lunar resource exploration. Future studies could look at other REEs important to space exploration using the ESCAPE system as it can operate both $\lambda_{Ex} = 266$ and 532 nm, to determine which wavelength is suitable for the most amount of targeted Lunar REEs. The practical applications of this research are to inform future flight Raman/LIF/LIBS instruments that will be sent to the moon over the next decade during the Artemis-era of resource exploration to support investigations into the feasibility of creating a lunar manufacturing base for deep space exploration. Further analysis of the structure and composition of the synthesized YPO_4 will provide more context for the results of this study and confirm if contamination is present. Furthermore, TR-LIF analyses can be accomplished on these samples, which may further the results of Shkolyar et al. (2021) where higher concentrations of REEs in a substrate resulted in lower τ values compared to their lower concentration counterparts.

The results of this study: *UV and Green LIF Analysis of REE-Doped Lunar Analogues*, demonstrate the use of UV and Green-LIF, and Green-Raman modes of the ESCAPE system with chemically complex materials — YPO_4 and CePO_4 doped lunar simulant samples. These experimental results illustrate how versatile the ESCAPE system is and how easily transferring and correlating data between $\lambda_{Ex} = 266$ and 532 nm is.

6 Results IV: The Tagish Lake Meteorite Spectral Experiment

The Tagish Lake Meteorite experiment was designed to utilize all of the functionality of the ESCAPE system for validation as a potential tool for preliminary compositional analysis of highly sensitive sample return material. In this experiment, a non-pristine piece of the Tagish Lake meteorite is placed in the ESCAPE system with a nitrogen atmosphere and a $<-10^{\circ}\text{C}$ sample stage to mimic the conditions in which to maintain a pristine sample of the same composition. Under these conditions, spectral maps are acquired and further, more high-resolution point of interest analysis is undertaken, to analyze the mineral and organic content of the sample.

6.1 Tagish Lake Meteorite Description

The Tagish Lake meteorite's name is attributed to the lake on which it fell in Northern British Columbia on January 18, 2000. The fireball was witnessed from several locations and was detected by the US Department of Defence IR sensors, allowing for an easy find and recovery of material in a matter of days. On January 25, 2000, Jim Brook started recovering material, gathering several dozens of pieces in total weighing about 0.85 kg (Brown et al., 2000). Due to the location and time of year in which the meteorite fell, the ambient temperatures remained below zero the days prior to collection. The temperature, in combination with a rapid response from Jim Brook, minimized the terrestrial alteration and contamination of the samples.



Figure 6.1: A non-pristine fragment of the Tagish Lake Meteorite (C2 Ungrouped). 0.55 mm in length, 168 mg in weight. Small, visible chondrules are lighter in colour than the dark, fissile, phyllosilicate-rich matrix. Sample provided by the Royal Ontario Museum (ROM).

These samples collected into plastic bags on the frozen lake by Mr. Brook are considered to be ‘pristine’. Several months later in April and May of 2000, a field expedition recovered over 400 more fragments from above and below the icy surface of the lake. These samples are considered to be non-pristine and are partially degraded due to immersion in meltwater on the lake as it thawed in the spring (Brown et al., 2000).

Shortly after the observation of the fall, the preatmospheric mass, orbit, and semi-major axis were calculated by Brown et al. (2000). The preatmospheric mass was calculated to be around 200,000 kg, with an orbit indicating Tagish had an affinity to the Apollo group of asteroids (a group of Near Earth Asteroids (NEAs)), a semi-major axis in the middle of the asteroid belt, with the bodies radius thought to be around 2-4m (Brown et al., 2000). These characteristics are consistent with a perceived linkage to C, D and P-type asteroids, and the initial spectra showed similarities with CM and CI meteorites (Brown et al., 2000). The bulk density of the recovered pristine material was determined to be 1.67 gcm^{-3} soon after collection, a value much lower than any other meteorite yet seen (Zolensky et al., 2002). The porosity of the meteorite is reported to be 35 – 43% with a weighted average of $40\% \pm 1\%$, and the estimated parent body porosity is 37 – 58% (Hildebrand et al., 2006). Such low bulk density and high porosity are more extreme than any other meteorite analyzed and only have similarities to IPD (interplanetary dust) particles (Hildebrand et al., 2006).

When looking at a fragment of the Tagish Lake meteorite, it is apparent that the material is extremely dark, mostly black in colour with small chondrules or aggregates visible to the naked eye and is noticeably porous and fissile. Detailed petrographic descriptions of different pristine and non-pristine fragments have been reported by Brown et al. (2000); Izawa et al. (2010); Blinova et al. (2014) and Zolensky et al. (2002) and are summarized here. The Tagish meteorite is a brecciated, ungrouped, type 2 chondrite, with a low shock value of S1- typical to carbonaceous chondrites (Zolensky et al., 2002; Brown et al., 2000). Defining characteristics of the Tagish Lake meteorite include: a phyllosilicate-rich matrix with sparse chondrules, olivine aggregates, sparse CAIs, and a variety of loose grains such

as olivine, magnetite, Fe-Ni sulphides, Cr-Ni Phosphides, and carbonates (Zolensky et al., 2002). The fragments are porous and most pore walls are filled with Ca-carbonates. It is originally reported in Zolensky et al. (2002) that there are two main lithologies in the Tagish Lake meteorite: carbonate-rich and carbonate-poor. However, in Izawa et al. (2010) it is proposed that the mineralogy of the meteorite is more varied than previously reported. Izawa et al. (2010) proposes two distinct lithologies in addition to Zolensky et al. (2002) carbonate-poor and carbonate-rich lithologies as (1) inclusion-poor magnetite and Sulfide-rich lithology, and (2) a carbonate-rich, siderite-dominated lithology. The carbonate-rich and carbonate-poor lithologies described by Zolensky et al. (2002) are very similar in that they have a phyllosilicate-supported matrix, and in the carbonate-poor lithology, this matrix mostly consists of saponite, serpentine and Fe-Ni sulphides, whereas in the carbonate-rich lithology, the matrix is primarily saponite. The carbonate-poor lithology contains rare chondrules (in both lithologies at $1/\text{cm}^2$; average diameter 0.25-1 mm similar to CM) or rounded, chondrule-like objects that have been aqueously altered to phyllosilicates. Magnetite is described to be common in most lithologies except for the carbonate-rich lithology as framboids and plaquettes. Magnetite and sulphides are common in both chondrules and rims within the carbonate-poor lithology. Most chondrules have altered, $200\mu\text{m}$ thick phyllosilicate-rich rims (Zolensky et al., 2002) that most likely formed by multiple precipitation events during low-temperature alteration on the parent body (Blinova et al., 2014). Olivine aggregates outnumber chondrules 5:10 in Tagish Lake, and the aggregates ($100\text{-}500\mu\text{m}$ in size) are comprised of mostly olivine with or without pyroxene, if not replaced by phyllosilicates. In the carbonate-poor lithology, there are also several altered CAIs ($200\text{-}300\mu\text{m}$ size) with a sinuous texture and phyllosilicate-rich rims, variable Al_2O_3 content, sparse magnetite, pyroxene, olivine and siderite grains (Zolensky et al., 2002). The interior of the CAIs is dominated by carbonates (mostly dolomite and minor calcium-carbonate), spinel, and phyllosilicates (saponite and serpentine). Along with a sinuous texture, the CAIs contain rare perovskite in dolomite which indicated alteration (Zolensky et al., 2002). Sulphides are abundant in

the matrix and are found as pyrrhotite and pentlandite in this sample. The carbonate-rich lithology is very similar to the carbonate-poor lithology in mineralogy and abundance of chondrules, however, there is an absence of fine-grained clasts and CAIs. The carbonate-rich lithology is notably more fine-grained according to Zolensky et al. (2002) and the matrix mostly consists of saponite. Fe-Mg-Ca-Mn carbonates are more abundant and visible in the hand sample. The majority of carbonates are of breunnerite composition but are complex intergrowths of different generations of carbonates, varying wildly in composition (Zolensky et al., 2002). These unique intergrowth carbonate structures are rimmed and have irregular fractures filled with siderites, thought to be formed by a fracture event on the parent body followed by replacement of cooling of siderite. Carbonates are also found to be complexly intergrown with magnetite and phyllosilicates in aggregate structures - most likely previously olivine aggregates (Zolensky et al., 2002). These lithologies show a complex aqueous alteration history on the Tagish Lake parent body. Izawa et al. (2010) also found gypsum and talc within the meteorite, however, there was no evidence of a terrestrial or extraterrestrial origin for these minerals as of yet.

Table 12: Mineralogy of the Tagish Lake Meteorite, reported in Izawa et al. (2010). Total weight percent reported by Bland et al. (2004).

Mineral	Composition	Weight% (Bland et al.)
Saponite-Serpentine	$\text{Mg}_2\text{Fe}_{0.75}\text{Si}_3\text{AlO}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$	60.3
Olivine	MgFeSiO_4	7.9
Magnetite	Fe_3O_4	8.9
Siderite	FeMgCaCO_3	14.4
Calcite	CaCO_3	n.d.
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	n.d.
Pyrrhotite	FeS	8.5
Pentlandite	FeNiS	0.6
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	n.d.
Talc	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	n.d.

Shortly after the fall and collection of the Tagish Lake meteorite, studies began to determine the organic contents of the meteorite and compare it to that of other carbonaceous

meteorites, such as Murchison (CM2). Preliminary studies of small fragments resulted in a determination that the Tagish Lake meteorite contained minimal amino acids and those that were present may be terrestrial contamination (Kminek et al., 2002). However, similar to the geologic heterogeneity findings in Tagish Lake, organic heterogeneity was found through further study of different fragments collected from the impact site (Simkus et al., 2019). The Tagish Lake meteorite has been found to contain both soluble, and insoluble organic matter. Much like the mineralogy of the Tagish Lake meteorite, the organic content of this sample is unique and presents a new example of chemical evolution not seen before in meteorites. The soluble organics present include mono and dicarboxylic acids, dicarboximides, pyridine carboxylic acid, sulfonic acid, and both aliphatic and aromatic hydrocarbons, amides and small amounts of amino acids (Pizzarello et al., 2001). Insoluble carbon in the Tagish Lake meteorite exhibits aromatic characteristics, deuterium enrichment and fullerenes that contain both helium and argon of ‘planetary’ nature as opposed to solar values (Pizzarello et al., 2001). A large L-enantiomeric excess ($L_{ee} \sim 43\text{-}59\%$) of α -hydrogen aspartic and glutamic acids from liquid chromatography was found in the Tagish Lake meteorite, whereas alanine was found to be nearly racemic ($D \approx L$) (Glavin et al., 2012). Because the isotopes of the amino acids found in the samples fall well outside the normal terrestrial range, they are considered to be indigenous to the sample. An abundance of aspartic acid is found within the aqueously altered fragments of Tagish Lake, suggesting the formation of these building blocks for life on the parent body. Furthermore, a small initial L_{ee} could be extremely amplified during aqueous alteration on the parent body because as large enantiomeric excess of conglomerate forming α -H amino acids are more easily formed in the crystallization process compared to racemic, leading to the large L_{ee} of L-aspartic and L-glutamic acid we see today in Tagish Lake (Glavin et al., 2012). This non-terrestrial amino acid excess provides supporting evidence for the hypothesis that significant enantiomeric enrichment of some amino acids could form by abiotic processes on primitive bodies before the emergence of life (Glavin et al., 2012). The main, unique, organic characteristics/features of the Tagish Lake mete-

orite are the dominance of water-soluble carboxyl and di-carboxyl components, the scarcity of amino compounds, the aromatic character of the insoluble carbon, and features suggestive of interstellar origin (i.e. aromaticity, elevated δD and the pyrolytic release of mostly PAHs) (Pizzarello et al., 2001).

Table 13: List of soluble organics and their concentrations found in the Tagish Lake meteorite modified from Pizzarello et al. (2001).

Class	Tagish Concentration (ppm)	Murchison Concentration (ppm)
Aliphatic hydrocarbons	5	> 35
Aromatic hydrocarbons	1	15–28
Dicarboxylic acids	17.5	> 30
Carboxylic acids	40	> 300
Pyridine carboxylic acids	7.5	> 7
Dicarboximides	5.5	> 50
Sulfonic acids	20	67
Amines	< 0.1	8
Amides	< 0.1	n.d.
Hydroxyl acids	b.d.	15
Amino acids	< 0.1	60

For this spectral experiment, a non-pristine fragment of the Tagish Lake meteorite is on loan from the Royal Ontario Museum. This fragment (Figure 6.1), once whole, has split into two daughter fragments from the original parent. The fissile nature of the sample makes it extremely fragile, and thus it was decided that a non-pristine fragment would be used for this experiment as there is no way to prove that the pristine sample has remained pristine by conducting any measurements after the experiment. Thus, a non-pristine fragment is used here under conditions in which a pristine sample would theoretically have the best chances of remaining pristine through atmosphere and temperature regulation.

6.2 Experimental Setup

For this experiment, the ESCAPE system is set up to analyze mineral and organic constituents while maintaining a consistent temperature and atmospheric conditions to preserve the integrity of the fragile Tagish Lake sample. The system will mimic specific con-

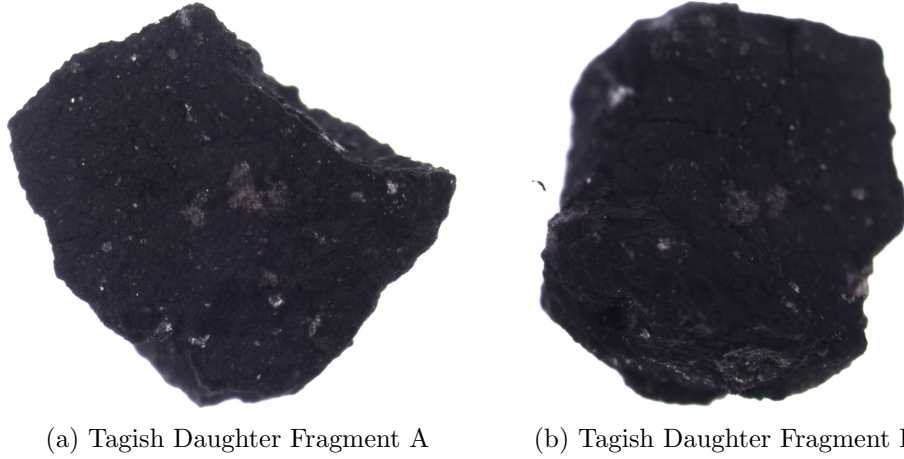


Figure 6.2: Two non-pristine fragments–(a) and (b) from a parent fragment on loan from the Royal Ontario Museum (ROM) for spectral analysis. Samples 0.4mm at longest point.

ditions (nitrogen-rich atmosphere, freezing temperatures) that are optimal for maintaining the pristineness of a pristine version of this sample (Herd et al., 2016; McCubbin et al., 2019). To begin the experimental setup, the iCCD camera is chilled to -35°C in Andor Solis and the spectrometer for the system is calibrated as mentioned in 2.6 for either Raman or LIF mode depending on which spectral technique is used that day for mapping. Following the spectrometer and manual x-axis calibrations, the chamber is pumped with an oil-free vacuum pump to 4 mbar. Once the chamber reaches 4 mbar, the air is sufficiently extruded to begin chilling the sample stage heat sink to -10°C without condensation. As the heat sink is cooling, the LabView Mapping software is engaged to connect to the iCCD camera and motors for the sample stage. The sample stage motors are calibrated as described in section 2.6 and are turned on via the LabView mapping software. When the heat sink chiller temperature reaches -10°C , the Peltier thermoelectric cooler on top of the heat sink is set to -28°C to maintain a sample stage temperature of -14°C (Figure 6.3). Once the sample stage is cool, the chamber door is loosened and the chamber is positively pressurized with nitrogen gas until the door opens. The sample, having been retrieved briskly from the -45°C freezer, is removed from its sample container in the chamber, and placed on the sample stage while nitrogen gas is flowing.

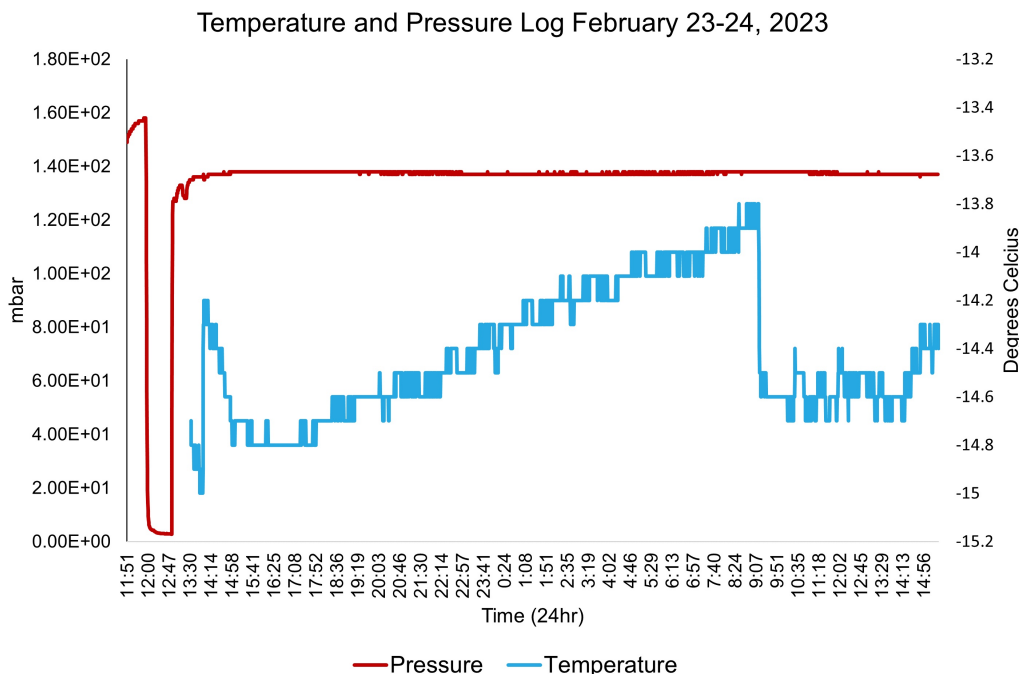


Figure 6.3: Pressure and temperature log for 532 nm Raman map of the Tagish Lake meteorite. The pressure (red) is reduced to 4 mbar before the cooling if the heat sink begins. The chamber is then re-pressurized with pure nitrogen gas before the sample stage is cooled to -14°C and the temperature recording begins (blue).

The Tagish Lake fragment is placed on the sample stage and aligned under the laser spot. A mapping area is traced out on the surface of the sample by moving the laser spot around the perimeter of the intended mapping area. The laser spot is finally aligned before the map begins in the top right corner of the intended mapping area. The map is executed by moving from the top right corner, down each column starting at the top. When the last spot in a column is taken, the motors move the stage to the top row and over a single column and continue in this manner until the final spot in the map is reached—after which the stage returns to the starting position.

The acquisition settings for collecting maps of different λ_{Ex} for Raman and fluorescence are presented in Table 14. Because of additional (unintentional) electronic delays incited by the mapping software to the iCCD camera, a longer (~ 3.5 ns) on top of the regular delay for each wavelength is used while mapping. Mapping acquisitions tend to be a lower resolution

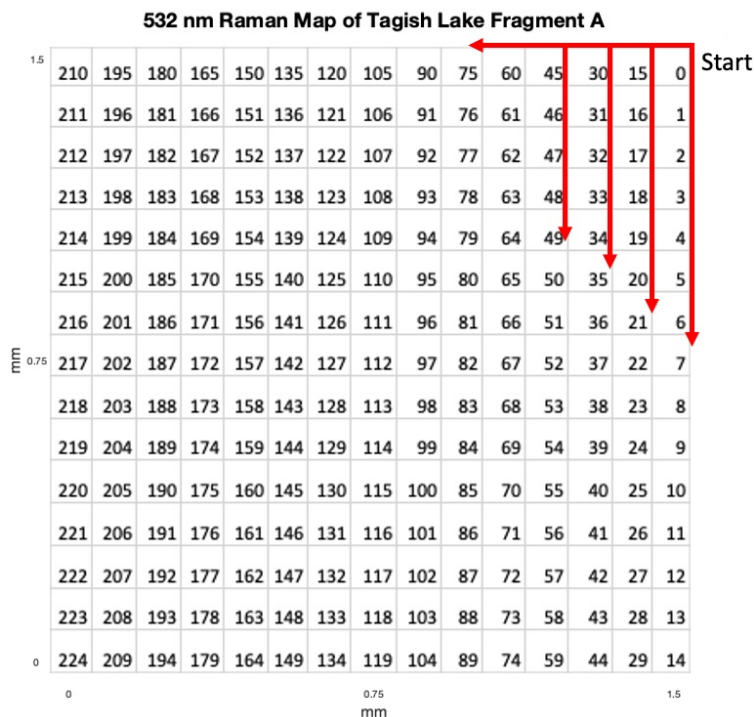


Figure 6.4: Example of how the raster maps are acquired with points labelled starting at position 0, ending at position 224, with a total of 225 points acquired. The maps are collected down each column starting in the top right corner of the intended mapping area.

(lower signal-to-noise ratio and wider slit opening to allow more light in) compared to that of point of interest acquisitions to ensure that the maps are collected in a timely matter while being able to resolve peaks of interest within the sample.

When the map is started, the temperature of the sample stage is monitored via thermocouple by a Data logger program every 30 seconds. The atmospheric pressure can also be monitored, however, once the Tagish sample is aligned, the chamber door is closed and the nitrogen gas flow is turned off. The combination of cooling the heat sink while under 4 mbar pressure, and only having a nitrogen environment after the sample is placed, allows for no ice condensation on the internal chamber equipment and on the sample itself.

While spectral maps are being acquired, the experiment can be monitored remotely using TeamViewer. On the monitor, the sample stage temperature logger, pressure readout and LabView Mapping Software can be monitored and adjusted as needed. Additionally, a webcam can be used to view the electronics and breadboard setup. To ensure safe remote

Table 14: 532 nm Raman mapping acquisition settings for the Tagish Lake Meteorite

Parameter Settings	Raman Map (532 nm)	Raman Map (266 nm)	Fluorescence Map (266 nm)
Acquisition Mode	Accumulate	Accumulate	Accumulate
Trigger	External	External	External
Exposure time	0.1 s	0.1 s	0.1 s
Gain	4000	4000	4000
Number of Accum.	1560	1560	200
Accum. Cycle Time	0.12 s	0.12 s	0.12 s
Read Frequency	5	5	5
Camera Temp.	-35°C	-35°C	-35°C
DDG Delay	44 ns	50.5 ns	50.5 ns
DDG Width	5 ns	5 ns	100 ns
Integrate on Chip	On	On	On
IOC Frequency	5000 Hz	5000 Hz	5000 Hz
Fast Insertion Delay	ON	ON	ON
Laser Rep. Rate	2 kHz	2 kHz	2 kHz
Slit Opening	250 μm	250 μm	250 μm
Diffraction Grating	600	1200	600
Spectral Window	128–2230 cm^{-1}	145–4300 cm^{-1}	340–410 nm

use, several precautions have been taken to monitor and emergency stop the experiment if needed. The laser power source and DC power supply for the Peltier thermoelectric cooler are connected to smart plugs. The smart plugs allow for remote power control of these two pieces of equipment, turning off the laser in case of emergency or at the end of data collection. The ability to turn off the power supply remotely is a precaution in the rare chance that the Peltier cooler fails and enters a heating and cooling cycle—putting a fragile sample in jeopardy of disaggregation. Several different signs are used to prevent a person from entering the room while the laser is on overnight while unsupervised. In addition to signage, a door alarm is set overnight that when triggered turns off the smart plug connected to the laser power supply, thus turning off the laser upon entering the room.

As soon as the map is finished, all of the spectra are saved as individual text files in a directory specified in the LabView mapping software. These spectra are opened in a LabView-based, map viewing software that creates an image from specified peaks of interest. Each spectrum represents one point in the map and when there is a specific point containing

a good Raman peak, we move to this point from the starting location using the same step size in the Mapping software to conduct points of interest high-resolution analysis. Raman peaks are differentiated from noise if they are 2-3x more intense than that of the noise based off of Vandenabeele et al. (2012). The noise in the spectra are also smoothed when plot in Origin Labs using a FFT filter, and any peaks that are still present after smoothing, even if at lower intensity than 2x greater than the noise, are considered for Raman peak analysis in this study but are not positively identified, rather considered as a possible identification or suspected identification. Higher resolution and background subtracted point analyses are achieved by using the smallest slit opening possible ($\sim 30 \mu\text{m}$), a 1200 or 2400 lines/mm grating, and a long acquisition time (more accumulations). The high-resolution point analysis acquisition parameters will vary based on the composition of the material being analyzed and the type of data being collected. Because of this, point analysis acquisition settings will be described with the results to provide more context of how challenging the material was to image.

Once the map and point analyses are completed, the sample is removed from the sample stage and placed in it's container while the nitrogen gas is flowing through the chamber. The sample container is then returned to the deep freezer where it is stored at -45°C .

6.3 Spectral Analysis Results of the Tagish Lake Meteorite

6.3.1 532 nm Raman of Tagish Lake

A 532 nm Raman map was acquired of the Tagish Lake meteorite Fragment A. The mapping area is centred on the fragment, with some visible brownish-coloured features in the top-center of a mostly very dark, black, extremely fine-grained matrix (Figure 6.5). The map size is 1.5mm^2 with a step size of 0.1 mm, resulting in 225 spectral points in total (Figure 6.4). Each point has a corresponding spectrum which is plotted in Figure 6.6. A baseline fluorescence correction was applied to each spectra using the spectral software: Opus. All of the spectra contain two peaks related to carbon D and G bands at 1383 , and 1592 cm^{-1} respectively. Some of the spectra appear to be more intense due to fluorescence (most likely from minerals) augmenting the baseline spectra to be at a higher intensity. When the spectra are baseline corrected, it is easier to visualize smaller Raman peaks present and convoluted with the intense carbon.

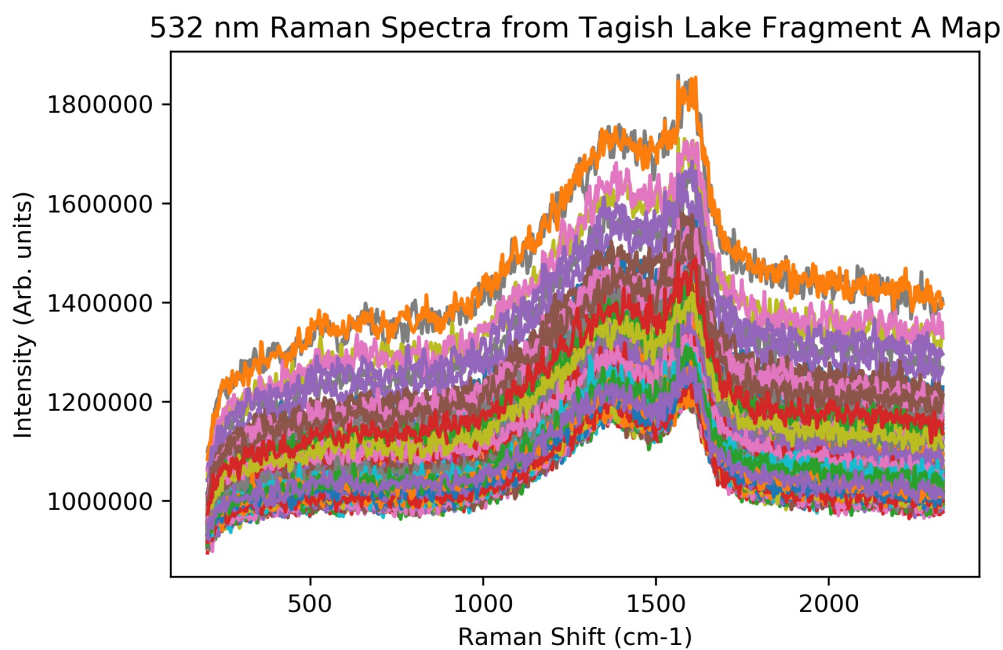


Figure 6.5: Tagish Lake fragment A spectral mapping area.

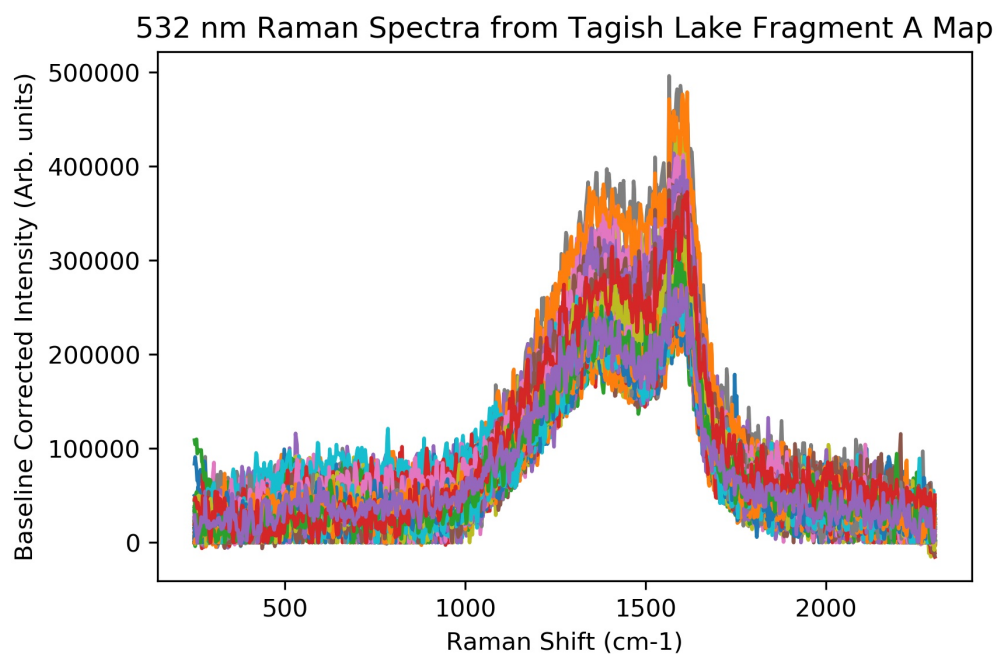
2D plots of the uncorrected spectra show the peak intensity for carbon (expected to be

mostly in the dark, matrix material) is at its highest in areas of mineral interest based on visible features in the sample and not as intense in the surrounding matrix (Figure 6.5 and Figure 6.7).

When using the uncorrected spectra to create the 2D maps of different peak areas of interest (e.g. 1380 cm^{-1} for carbon D band, and 850 cm^{-1} for olivine) the maps had very little variation from each other. To understand if this was due to an increase in fluorescence emission raising the overall intensity of the spectra in mineral areas of interest, a baseline correction is applied and the maps are re-plotted using the corrected spectra (Figure 6.7). Using the baseline corrected spectra, mineral peaks now become more obvious and in reasonable locations when plotting 2D maps. One Raman peak that was somewhat prevalent in the mapping spectra was 1092 cm^{-1} , corresponding to the main Raman peak of calcite (Figure 6.8). The calcite is most intense in the top centre of the mapping area in a fine-grained, brownish spot visible in the microscope picture (Figure 6.5). Furthermore, sulphate Raman peaks corresponding to gypsum were mapped centred on 1010 and 1140 cm^{-1} (Figure 6.9). The gypsum peak intensity is also brightest in the same area as calcite in the top centre mineral area of interest. Fine-grained minerals in the matrix are also mapped with peak positions around $540\text{--}550$, $640\text{--}650\text{ cm}^{-1}$, and 680 cm^{-1} (Figure 6.10), possibly corresponding to phyllosilicate-like minerals or magnetite. The location of these peaks is varied and dispersed throughout the image, not correlating well with any features, but does correlate with matrix-rich areas. The common mineral olivine, often found as large single grains or aggregates in the Tagish Lake matrix is mapped with peak positions around 825 and 858 cm^{-1} depending on composition. The olivine in Figure 6.11 is most intense on the bottom edge of the mapping area where there are several visible to the eye, small, white features on the meteorite. The correlating spectra to bright points on the map show a small, broader (because the slit is open to $250\text{ }\mu\text{m}$) peak for olivine around 820 cm^{-1} with other phyllosilicate-like mineral peaks in the spectrum as well.

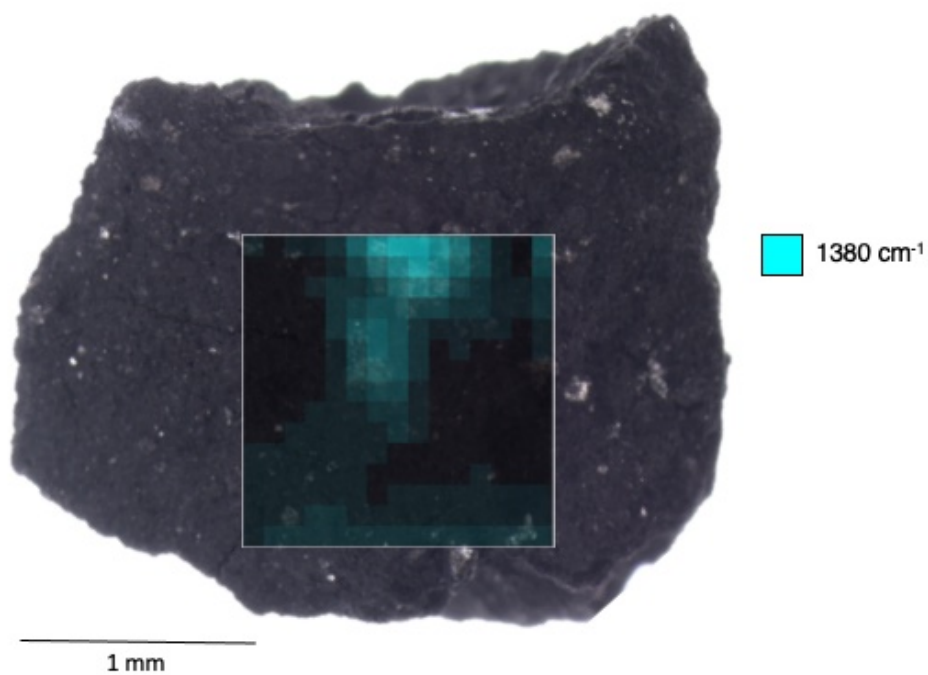


(a) 532 nm Raman mapping spectra with no baseline corrections

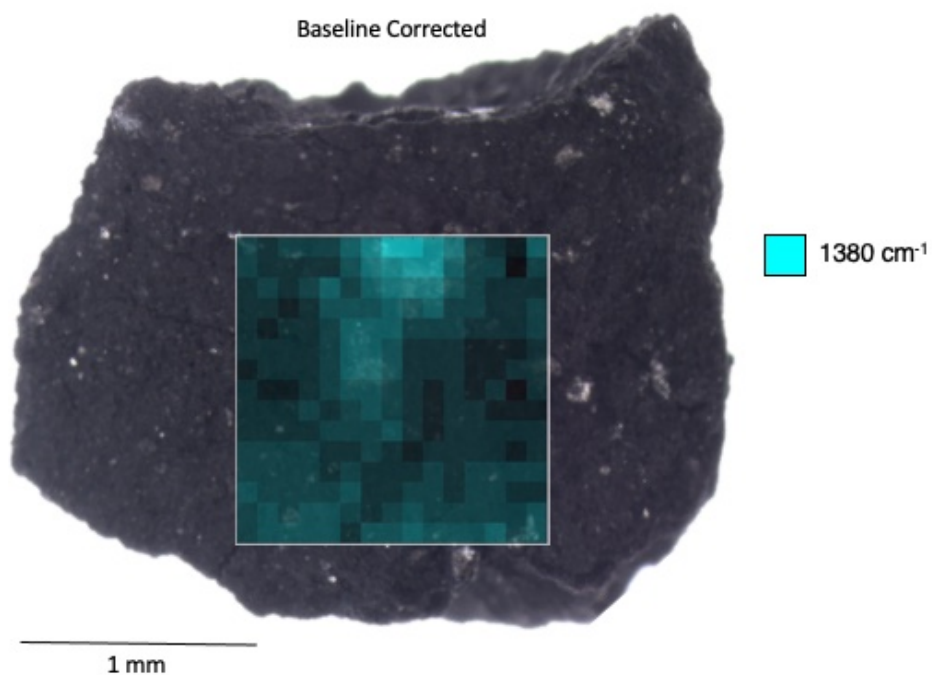


(b) 532 nm Raman mapping spectra with baseline correction

Figure 6.6: 532 nm Raman mapping spectra without corrections (a), versus with baseline correction and snipping (b). These figures are a representation of each point spectrum plot on top of each other to distinguish points of interest that have intense peaks common to all points, or unique to few spectra - which are then analyzed further.

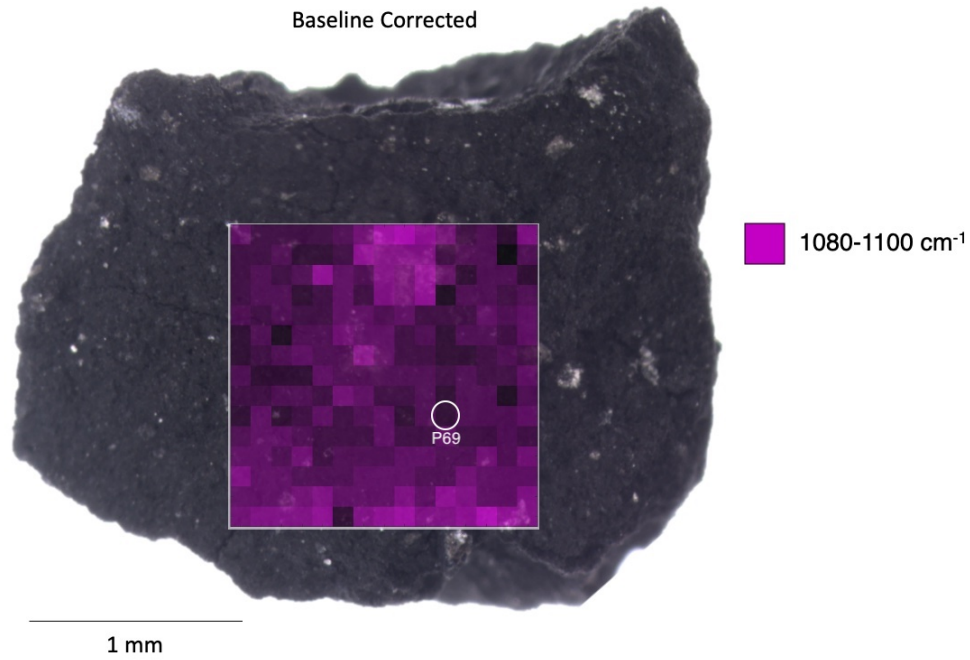


(a) 532 nm Raman map of carbon in Tagish Lake (uncorrected).

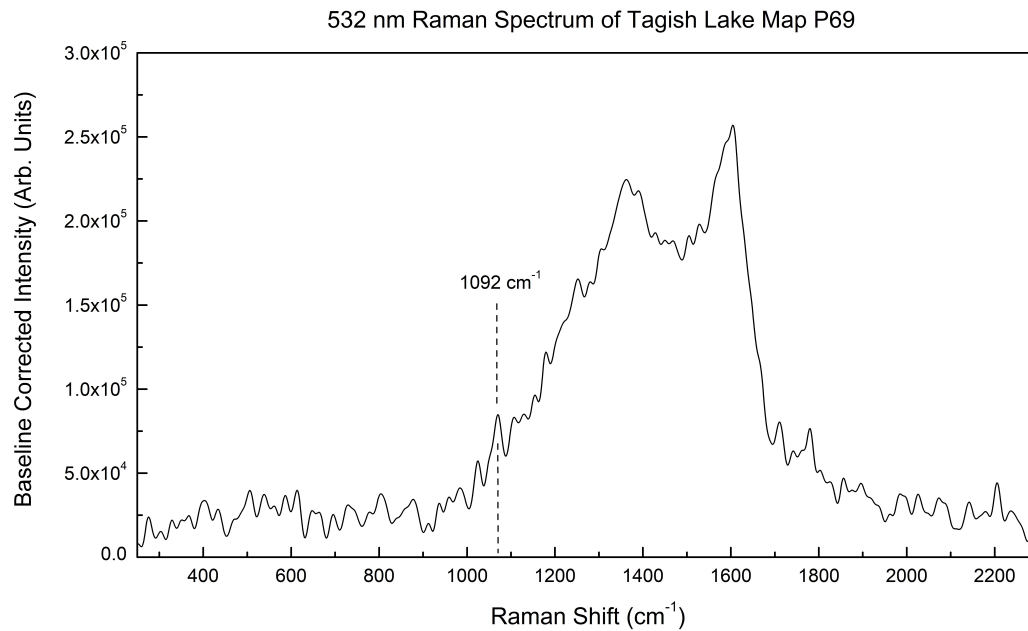


(b) 532 nm Raman map of carbon in Tagish Lake with baseline-corrected spectra.

Figure 6.7: 532 nm Raman map of carbon (a) uncorrected, versus with baseline correction and snipping (b).

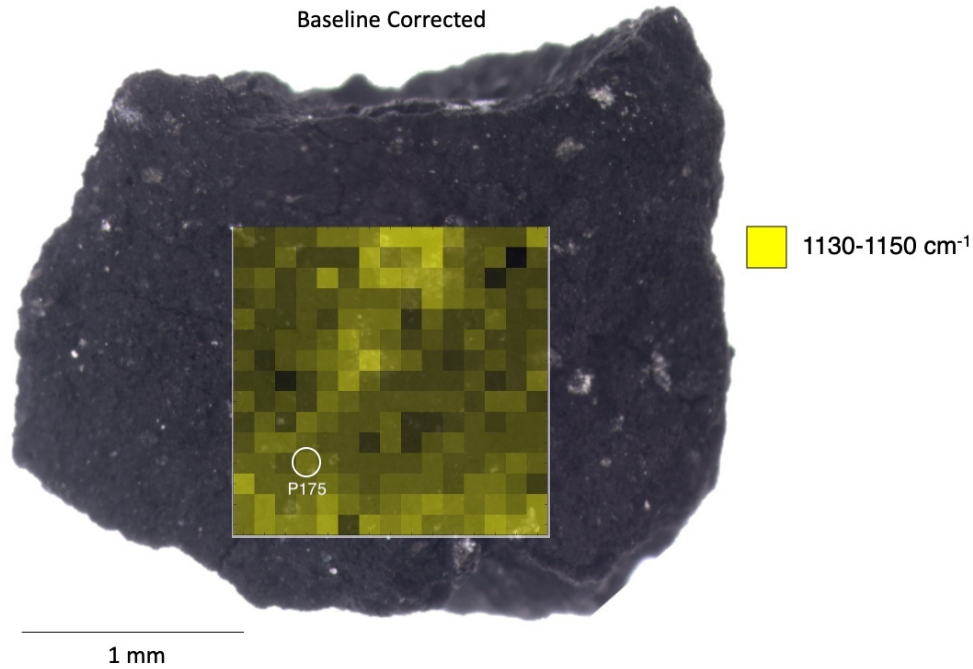


(a) 532 nm Raman map of calcite in Tagish Lake (baseline corrected).

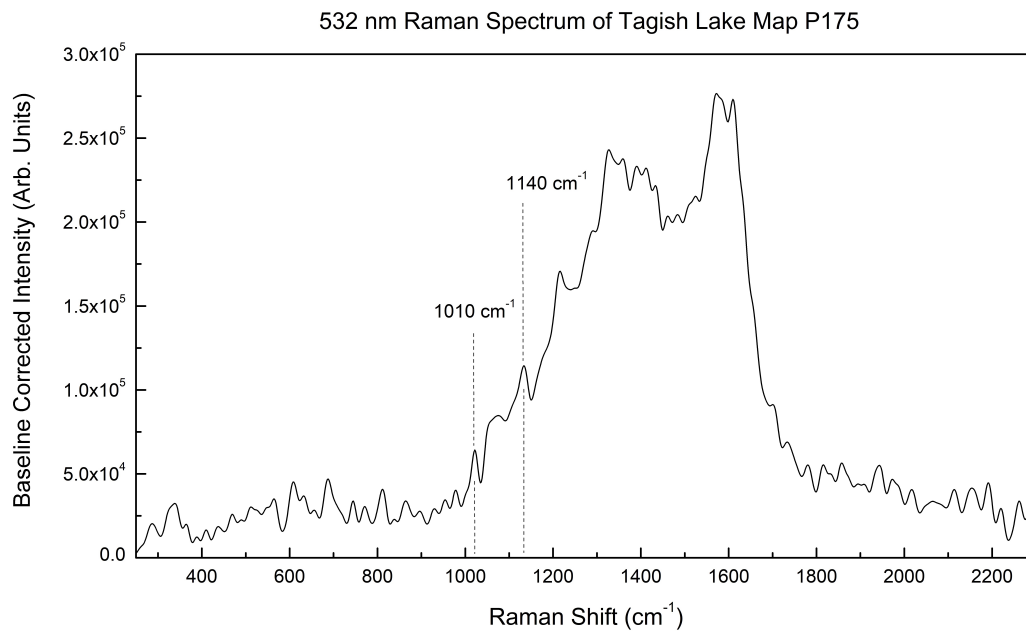


(b) 532 nm Raman Map of Tagish Lake point 69 with baseline correction and labelled calcite peak at 1092 cm^{-1} .

Figure 6.8: (a) 532 nm Raman baseline corrected map of calcite peak centred around 1092 (1080–1100 mapping range) cm^{-1} . Peak intensity shown as a function of brightness; and (b) 532 nm Raman mapping point spectra P69, showing calcite peak at 1092 cm^{-1} .

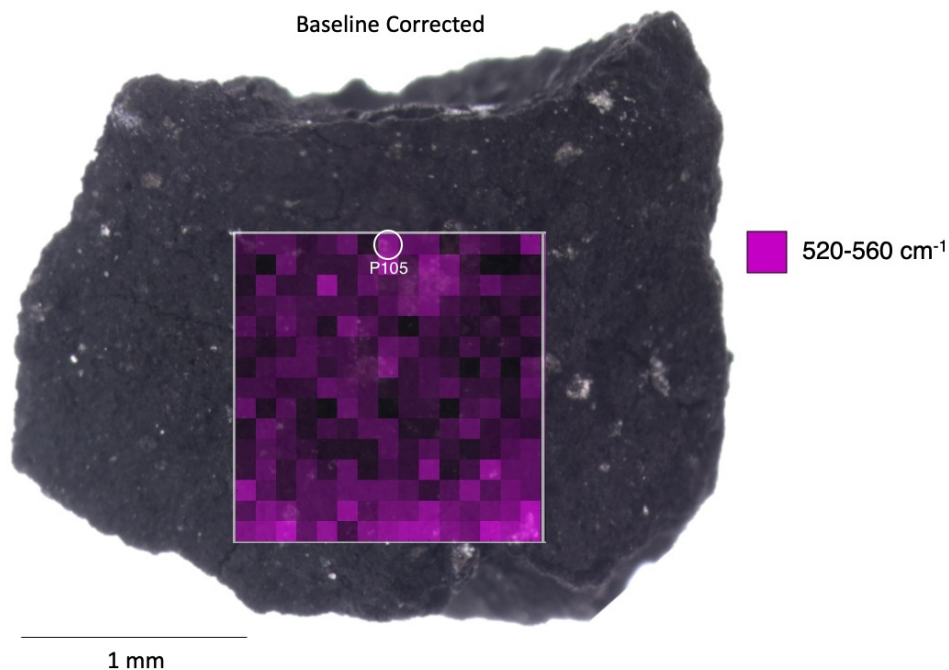


(a) 532 nm Raman map of gypsum in Tagish Lake (baseline corrected).

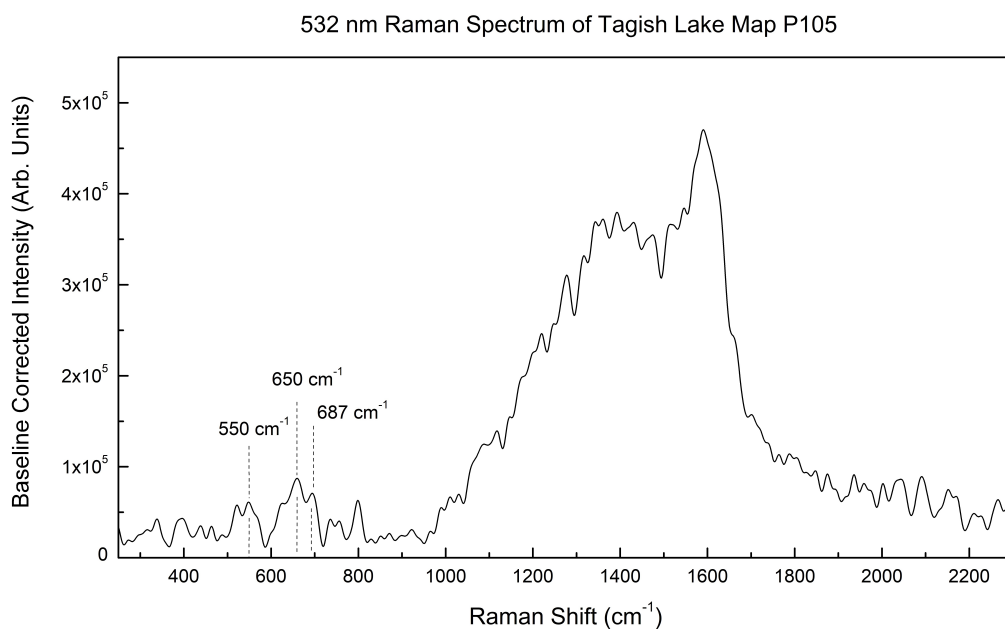


(b) 532 nm Raman Map of Tagish Lake point 175 with baseline correction and labelled gypsum peaks at 1010 and 1140 cm^{-1} .

Figure 6.9: (a) 532 nm Raman baseline corrected map of gypsum peak centred around 1140 ($1130\text{--}1150$) cm^{-1} . Peak intensity shown as a function of brightness; and (b) 532 nm Raman mapping point spectra P175, showing gypsum peaks at 1010 and 1140 cm^{-1} .

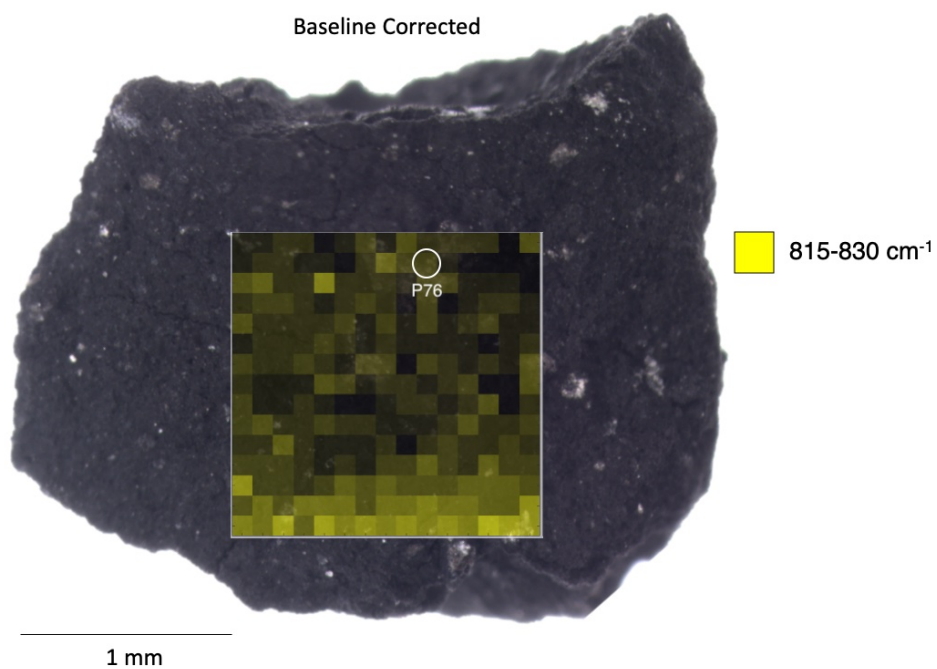


(a) 532 nm Raman map of phyllosilicate-like minerals in Tagish Lake (baseline corrected).

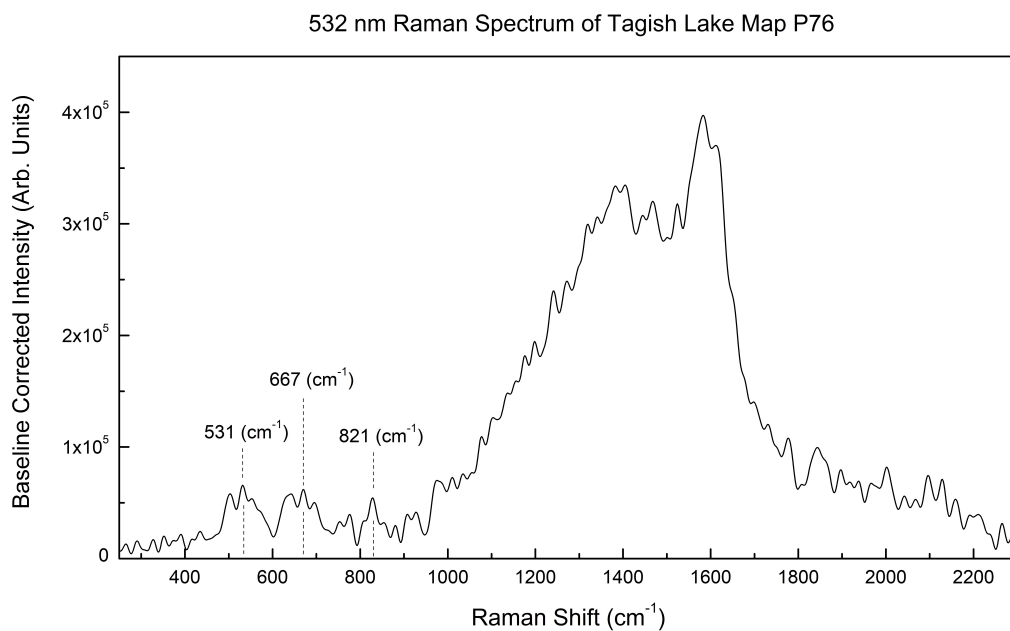


(b) 532 nm Raman Map of Tagish Lake point 105 with baseline correction and labelled phyllosilicate peaks at 550, 650, and 680 cm^{-1} .

Figure 6.10: (a) 532 nm Raman baseline corrected map of phyllosilicate-like mineral peaks mapped in the range of 520–560 cm^{-1} . Peak intensity shown as a function of brightness; and (b) 532 nm Raman mapping point spectra P105, showing phyllosilicate peaks at 550, 650 and 680 cm^{-1} .



(a) 532 nm Raman map of phyllosilicate-like minerals and possibly olivine in Tagish Lake (baseline corrected).



(b) 532 nm Raman Map of Tagish Lake point 76 with baseline correction and labelled phyllosilicate-like peaks at 531 and 667, and possibly olivine at 821 cm^{-1} .

Figure 6.11: (a) 532 nm Raman baseline corrected map of olivine Raman peak centred around 820 (815–830 range) cm^{-1} . Peak intensity is shown as a function of brightness; and (b) 532 nm Raman mapping point spectra P76, showing phyllosilicate-like peaks at 531, 667 and olivine at 821 cm^{-1} .

High-resolution single spectra are taken of points of interest generated from the uncorrected 2D maps of the Tagish Lake meteorite mapping area. Unfortunately, these points of interest (POIs) look no better than the original mapping spectra, most likely because the use of the 1200 lines/mm grating did not let in enough Raman light from the 532 nm Raman excitation and only carbon peaks were resolved.

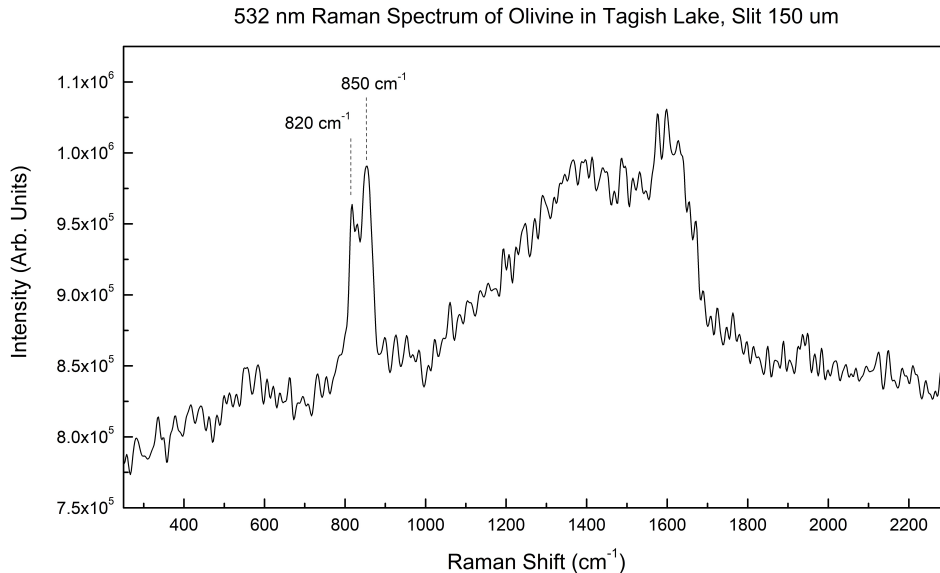


Figure 6.12: Tagish Lake fragment B spectral point of interest - olivine, from visible olivine aggregate. Slit size: 150 μm to resolve the olivine doublet with peaks at 820 and 850 cm^{-1} in this sample. Doublet relative peak intensities suggest that the olivine composition in forsterite (Mg-rich). Spectra is not baseline corrected, but is background subtracted.

Other single spectra points were also taken of areas of interest visibly noticeable on the surface of the meteorite fragments, not in the designated mapping area. An example of a point of interest was a visible olivine aggregate on a rounded edge of fragment B (feature in the top left corner of Figure 6.1). This feature of fragment B is extremely hard to map as it is on such a rounded edge and the sample would need to be supported while mapping, decreasing the contact with the sample stage, and thus not remaining frozen. These spectral points of interest do, however, show that an olivine-rich area in this type of material could be analyzed using this system. The uncorrected spectra in Figure 6.12 show olivine peaks at 820 and 850 cm^{-1} from the Tagish Lake fragment B olivine aggregate. The mechanical

slit opening in the spectrometer was reduced to 150 μm for this acquisition to gain better spectral resolution in order to resolve the olivine Raman doublet. The relative peak (850 greater than 820 cm^{-1}) intensities from the resolved doublet suggest that the composition is magnesium-rich, and thus the olivine end member present is most likely forsterite.

6.3.2 266 nm Raman of Tagish Lake

A 266 nm Raman map was acquired of the Tagish Lake meteorite Fragment A. The map is centred on the fragment, targeting the same area as the 532 nm Raman map, with some visible brownish-coloured features in the top-center of a mostly very dark, black, extremely fine-grained matrix-rich mapping area (Figure 6.5). The map size is 1.5mm² with a step size of 0.1 mm, resulting in 225 spectral points in total (Figure 6.4). Each point has a corresponding spectrum, plotted in Figure 6.14. Because the mapping areas were aligned by eye, they may differ in location slightly from each other. 266 nm Raman mapping took the same amount of time (20 hours) as the 532 nm mapping as they have very similar acquisition settings. Based on the stacked spectra from the map in Figure 6.14, there are two distinct and prevalent peaks of interest in most of the points from the map at 1600 cm^{-1} and 2300 cm^{-1} .

The 266 nm Raman maps of the Tagish Lake meteorite mapping area on fragment A, like the 532 nm Raman data show prominent carbon D&G peaks at 1380 and 1590 cm^{-1} visible in all of the mapping spectra. These peaks are mapped in Figure 6.19. Raman peaks in the region of 500–550 cm^{-1} are mapping in Figure 6.15, with the corresponding labelled spectra from an intense peak in the map. Peaks in the 500–550 cm^{-1} are correlated to that of the Si-O-Si bond Raman band, and can be indicative of phyllosilicates or potentially pyroxene group minerals when the band is weaker and accompanied by higher wavenumber peaks around 1010 cm^{-1} . The map showing peak intensity at 550 cm^{-1} has strong intensity on the left side of the map, correlating well with the brown-coloured features in the top-left-of-centre and bottom-left corner of the 266 Raman mapping area (Figure 6.13). The Raman peak at



Figure 6.13: Tagish Lake fragment A spectral mapping area for 266 nm Raman.

650 cm^{-1} is mapped in Figure 6.16 with the corresponding map spectra at the most intense point, P200. This Raman peak most likely correlates to the mineral magnetite, often found in the phyllosilicate-rich matrix of the Tagish Lake meteorite. The common Si-O-Si Raman band is mapped at 1010 cm^{-1} in Figure 6.17 with the corresponding most intense point from the map, P196. This peak is indicative of silicates like phyllosilicates or chain-like pyroxene group minerals. Again, these minerals are most intense on the left side of the mapping area where we can see visible features in the matrix. A Raman peak at 850 cm^{-1} is mapped in Figure 6.18 with the corresponding spectra at point P190, showing the true peak location at 840 cm^{-1} . This peak is strong and indicative of the Si-O_4 vibrational mode seen in olivine. As previously mentioned, 266 nm Raman is not particularly good at imaging Fe-rich minerals such as olivine, however, olivine in carbonaceous meteorites is typically extremely Mg-rich which 266 nm Raman could resolve. 266 nm Raman seems to also be resolving secondary carbon Raman peaks (beyond primary D&G bands) in the $2800\text{--}3100\text{ cm}^{-1}$ range, which can provide insights into the type of carbon present in the sample. A secondary aliphatic carbon peak at 2900 cm^{-1} is mapped in Figure 6.20, with the corresponding intense point spectra

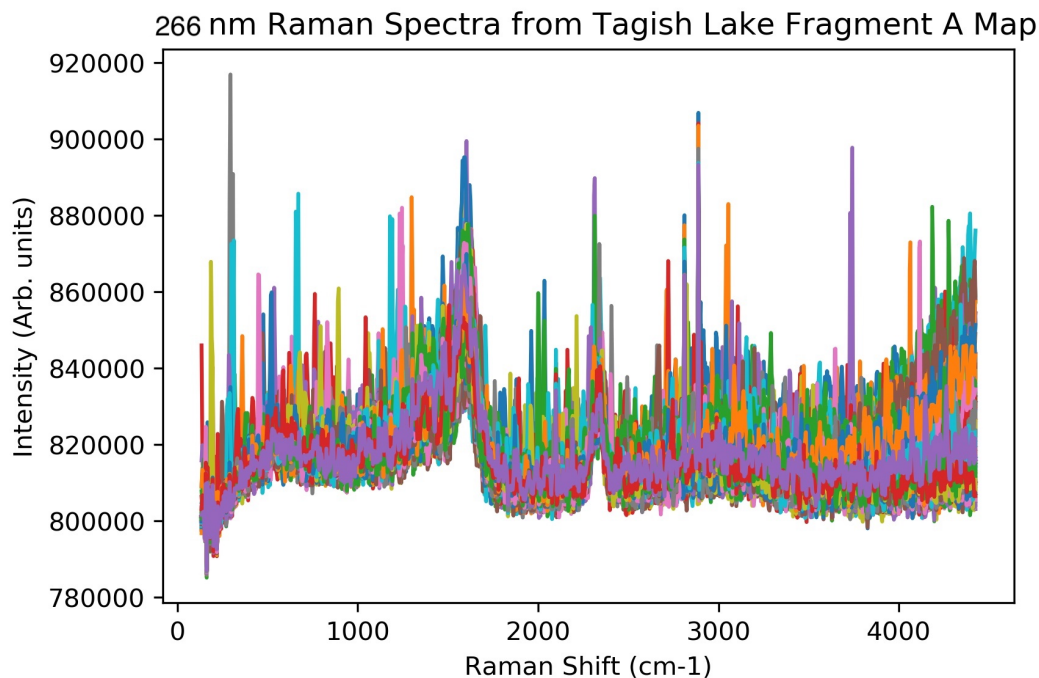
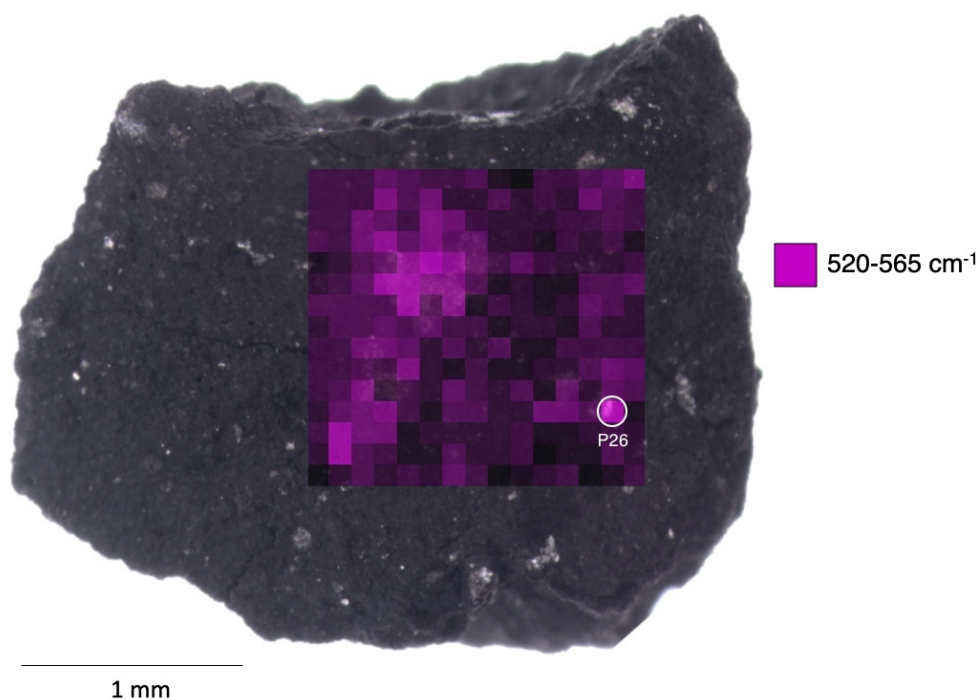


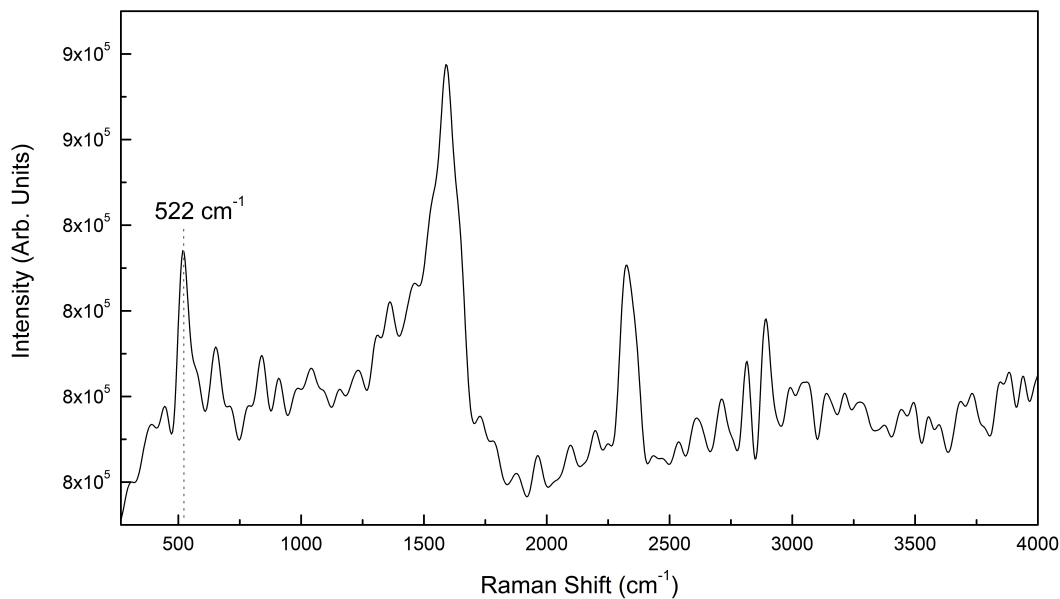
Figure 6.14: 266 nm Raman spectra from map of Tagish Lake fragment A without background subtraction or baseline correction. There are two distinct regions of interest from the spectra: 1600 cm^{-1} and 2300 cm^{-1} . This figure represents each point spectrum plot on top of each other to distinguish points of interest that have intense peaks common to all points, or unique to few spectra - which are then analyzed further.

from the map at point 0, showing the true peak position to be 2888 cm^{-1} . Additionally in the spectra of P0, we can observe two Raman peaks at 2800 and 2888 cm^{-1} both correlating to C-CH₃ Raman band and a peak at 3042 cm^{-1} corresponding to aromatic C-H Raman band.



(a) 266 nm Raman map of phyllosilicate-like minerals in Tagish Lake at 520–565 cm^{-1} (spectra not baseline corrected).

266 nm Raman Spectrum of Tagish Lake Map P26

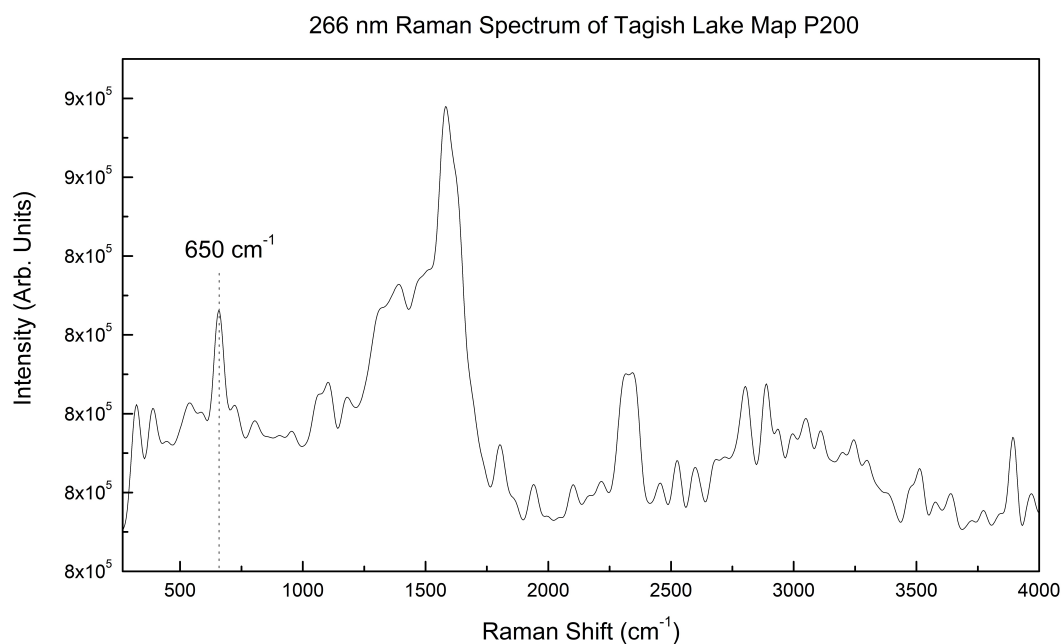


(b) 266 nm Raman spectrum from Tagish Lake Map point 26, labelled with phyllosilicate-like peaks at 520–565 cm^{-1} .

Figure 6.15: (a) 266 nm Raman map of phyllosilicate-like peak at 520–565 cm^{-1} . Peak intensity shown as a function of brightness; and (b) 266 nm Raman mapping point spectra P26, showing a phyllosilicate-like peak at 522 cm^{-1} .

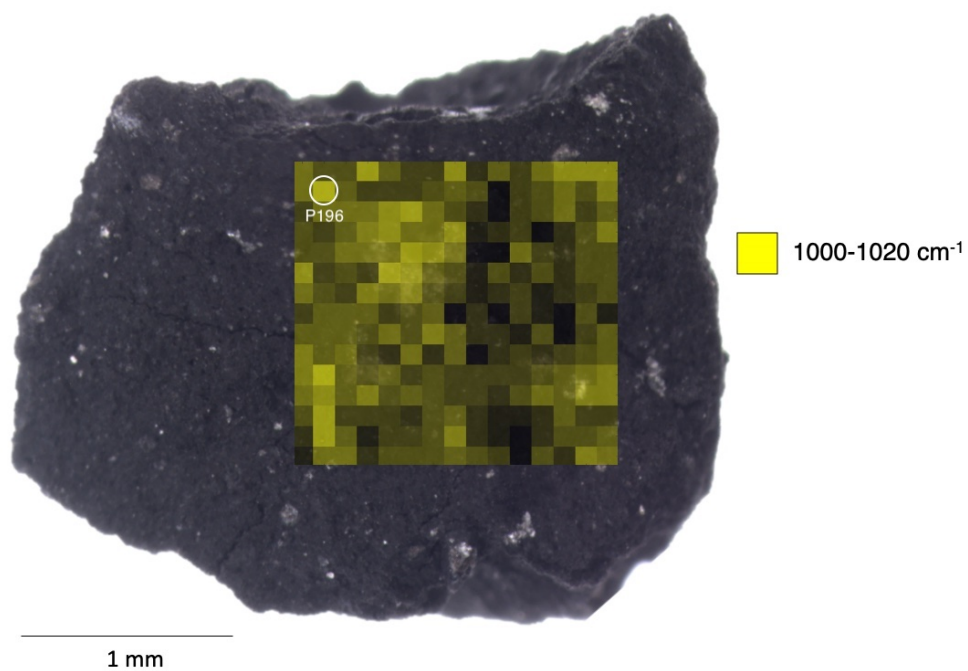


(a) 266 nm Raman map of magnetite-like mineral in Tagish Lake at 650 cm^{-1} (spectra not baseline corrected).

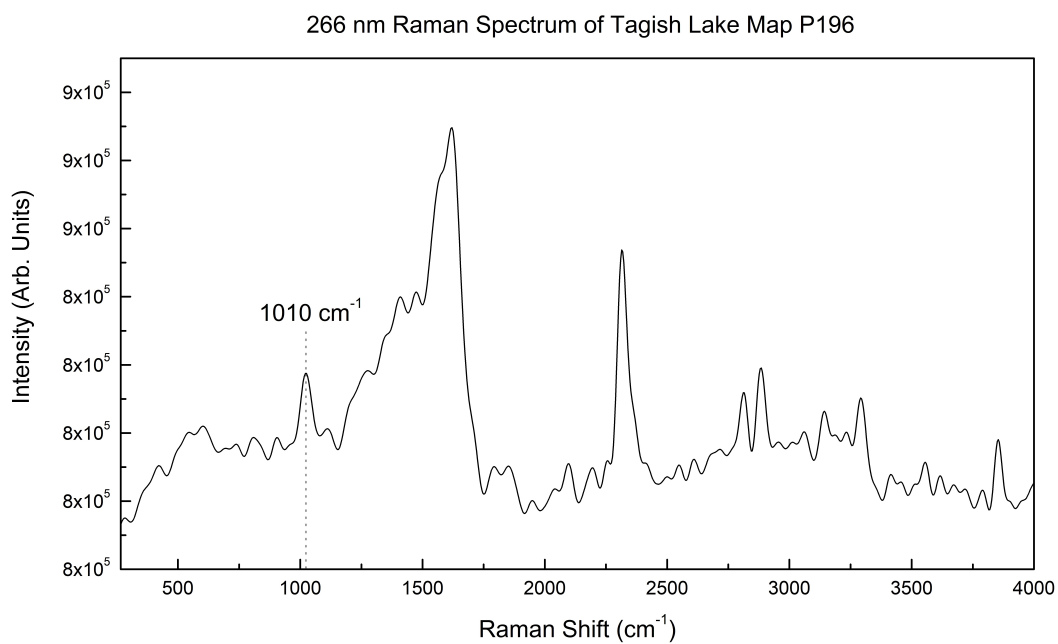


(b) 266 nm Raman spectrum from Tagish Lake Map point 200, labelled with magnetite mineral-like peak at 650 cm^{-1} .

Figure 6.16: (a) 266 nm Raman map of the magnetite-like peak at 650 cm^{-1} (640–660 range) cm^{-1} . Peak intensity shown as a function of brightness; and (b) 266 nm Raman mapping point spectra P200, showing a magnetite-like peak at 650 cm^{-1} .

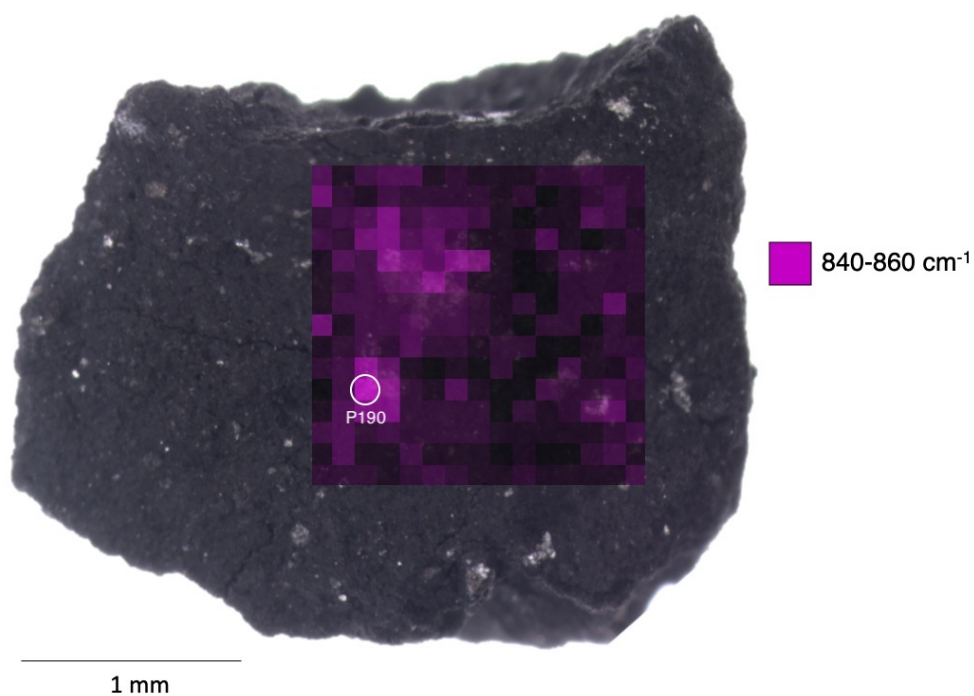


(a) 266 nm Raman map of SiO peak in Tagish Lake at 1010 cm^{-1} (not baseline corrected spectra).

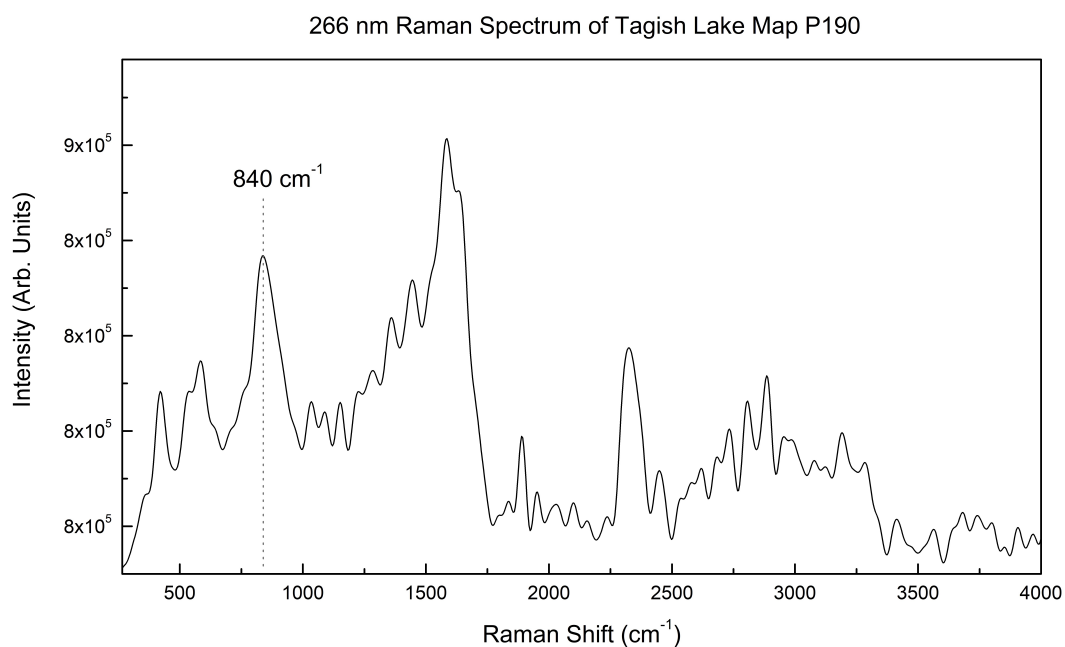


(b) 266 nm Raman spectrum from Tagish Lake Map point 196, labelled SiO peaks at 1010 cm^{-1} .

Figure 6.17: (a) 266 nm Raman map of SiO peak at 1010 (1000 – 1012 range) cm^{-1} . Peak intensity shown as a function of brightness; and (b) 266 nm Raman mapping point spectra P196, showing a SiO Raman peak at 1010 cm^{-1} .

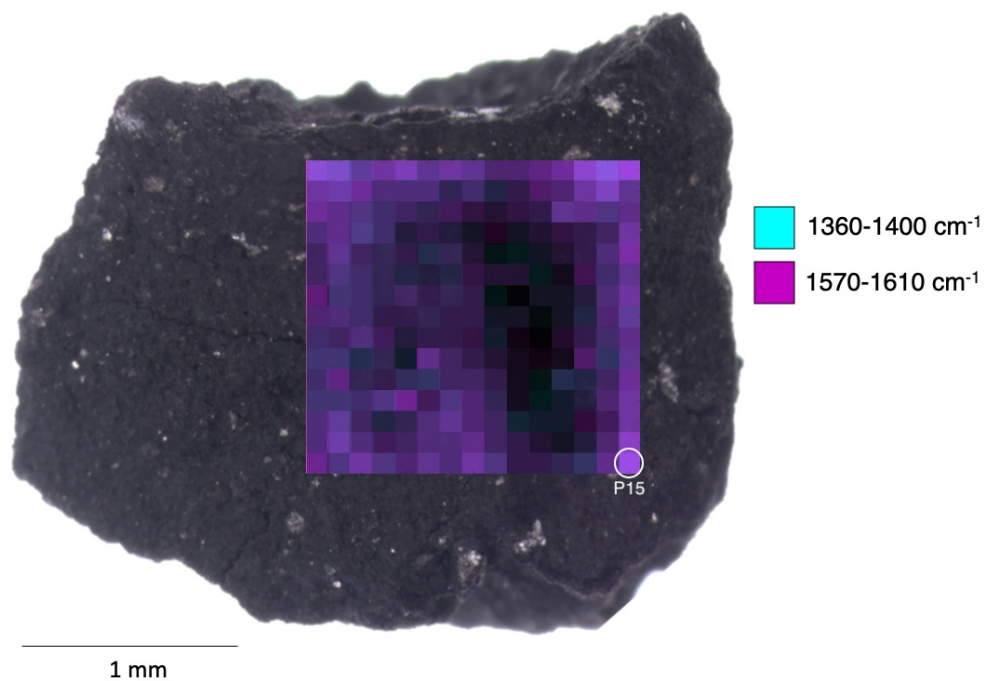


(a) 266 nm Raman map of olivine-like mineral in Tagish Lake at 850 cm^{-1} (not baseline corrected spectra).

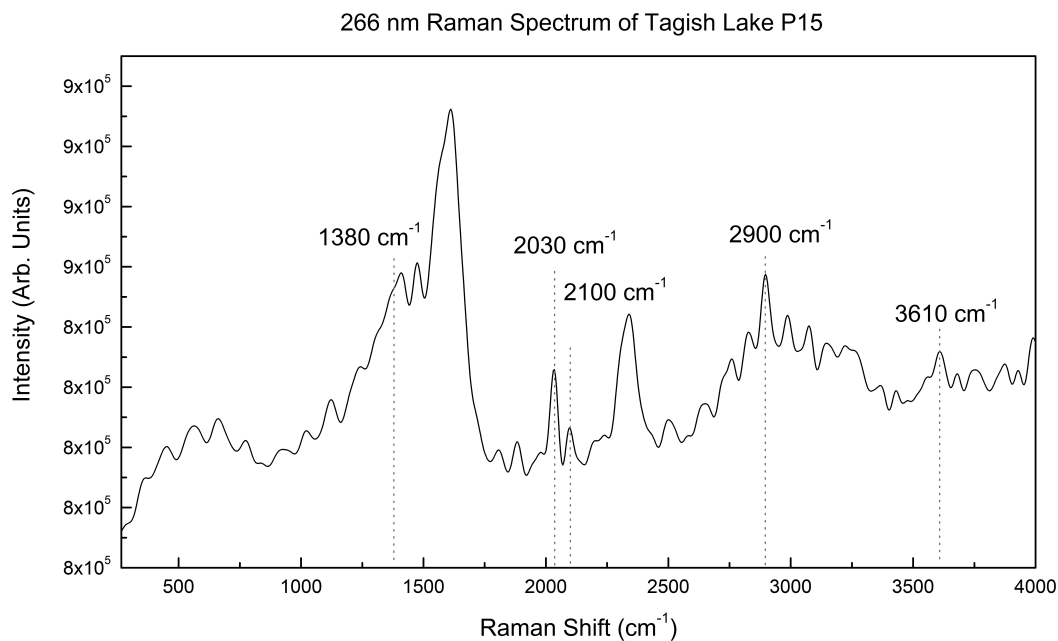


(b) 266 nm Raman spectrum from Tagish Lake Map point 190, labelled with olivine-like peak at 840 cm^{-1} .

Figure 6.18: (a) 266 nm Raman map of the olivine-like peak at 850 ($840\text{--}860$ range) cm^{-1} . Peak intensity shown as a function of brightness; and (b) 266 nm Raman mapping point spectra P190, showing a olivine-like peak at 840 cm^{-1} .

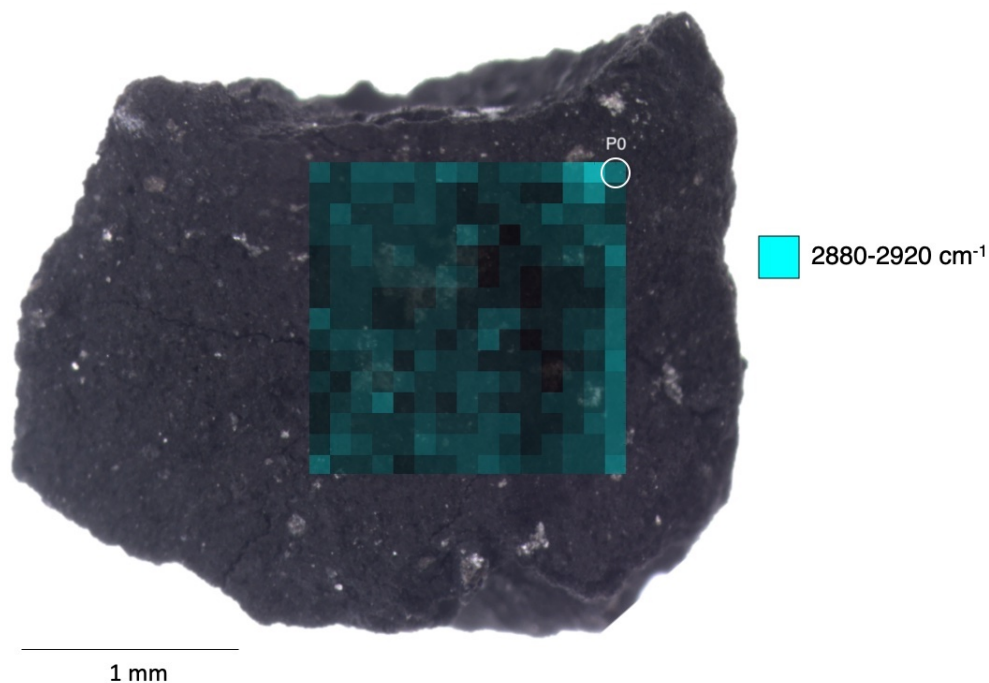


(a) 266 nm Raman map of carbon D&G bands in Tagish Lake at 1380 and 1590 cm^{-1} (not baseline corrected spectra).

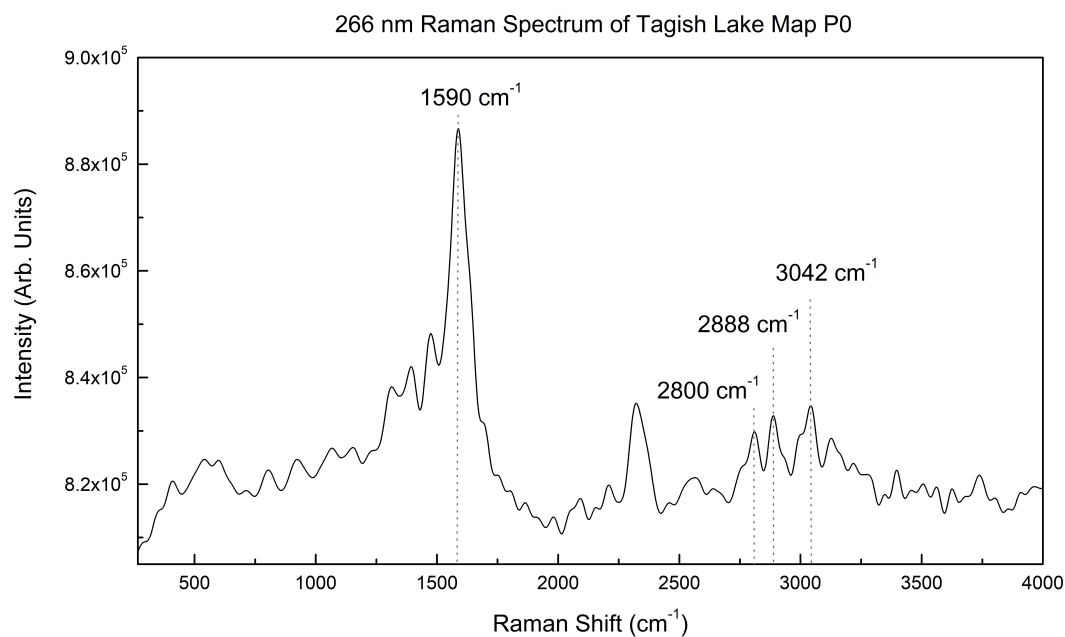


(b) 266 nm Raman spectrum from Tagish Lake Map point 15, labelled with carbon Raman peaks at 1380, 1590 and in this spectra 2900 cm^{-1} .

Figure 6.19: (a) 266 nm Raman map of carbon Raman peaks at 1380 and 1590 cm^{-1} . Peak intensity shown as a function of brightness; and (b) 266 nm Raman mapping point spectra P15, showing carbon D&G peaks at 1380 and 1590 cm^{-1} and secondary carbon at 2880 cm^{-1} .



(a) 266 nm Raman map of aliphatic carbon in Tagish Lake at 2900 cm^{-1} (not baseline corrected spectra).



(b) 266 nm Raman spectrum from Tagish Lake Map point 15, labelled with carbon Raman peaks at 1380 , 1590 and in this spectra 2888 cm^{-1} .

Figure 6.20: (a) 266 nm Raman map of secondary carbon Raman peak 2900 (2880 – 2920 range) cm^{-1} . Peak intensity shown as a function of brightness; and (b) 266 nm Raman mapping point spectra P0, showing secondary aliphatic carbon at 2800 and 2888 cm^{-1} and aromatic carbon at 3042 cm^{-1} .

Points of mineral and organic interest were identified from the LabView Viewer program's initial plots of the 266 nm Raman map acquired from the Tagish Lake mapping area. Points of interest were collected using longer acquisition times than that of the maps with a total acquisition time of 4 minutes per point in Andor Solis. In the POI 29 spectrum (Figure 6.21) we can see peaks like 555 and 1617 cm^{-1} correlating to known peaks like phyllosilicates and carbon G band respectively (see peak position table 15). The carbon G band is slightly shifted in this case from 1590, which shows the variation in the carbon peak positions between individual spectra depending on the other components convoluting the spectra. Peak 2875

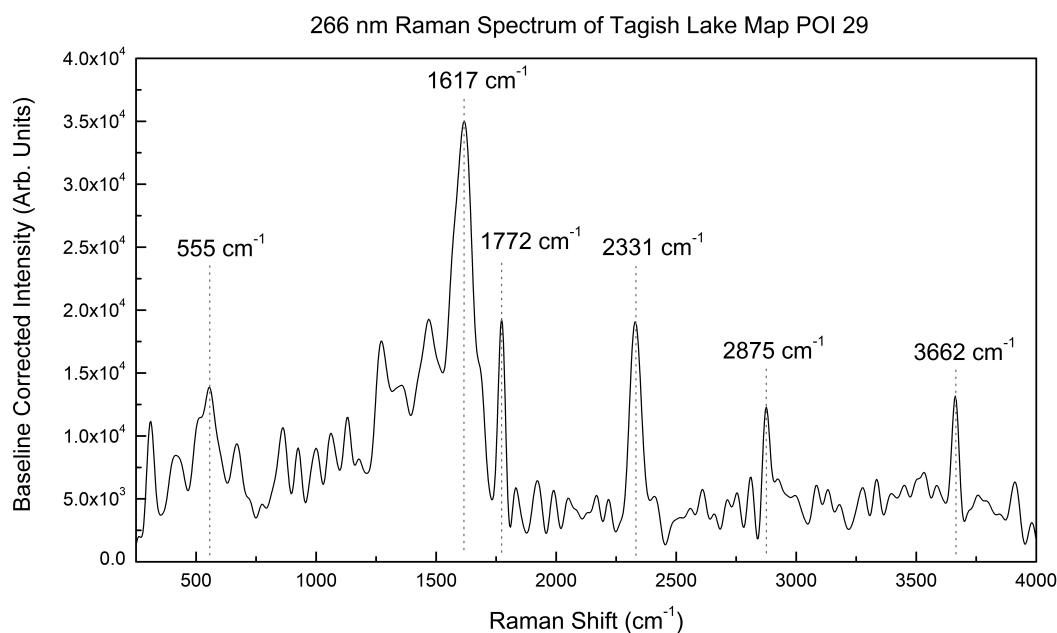


Figure 6.21: 266 nm Raman spectra POI 29 from map of Tagish Lake fragment A with background subtraction and baseline correction with labelled peaks at 555, 1617, 1772, 2331, 2875 and 3662 cm^{-1} .

cm^{-1} is moderately strong in the higher-accumulation time, point of interest (POI)s spectrum labelled POI 29, correlating to secondary aliphatic C-CH₃ or aromatic C-H bonding. Finally, the last peak labelled in POI 29 is 3662 cm^{-1} , an O-H stretching frequency most likely attributed to hydrous phyllosilicates and less likely to alcohol (Wang et al., 2015). There is also a labelled peak at 1772 cm^{-1} with an unknown Raman band correlation but is in similar regions to that of lactones (cyclic carboxylic esters) or anhydride where there is a C=O bond.

A Raman peak at 2331 cm^{-1} has been very prevalent in a lot of the acquisitions and that is because it is the Raman peak of the N_2 bond, resolved from the atmosphere in the chamber when the sample has very low signal to noise. Peak 2875 cm^{-1} is moderately strong in POI 29, correlating to secondary aliphatic C-CH₃ or aromatic C-H bonding (Lin-Vien et al., 1991).

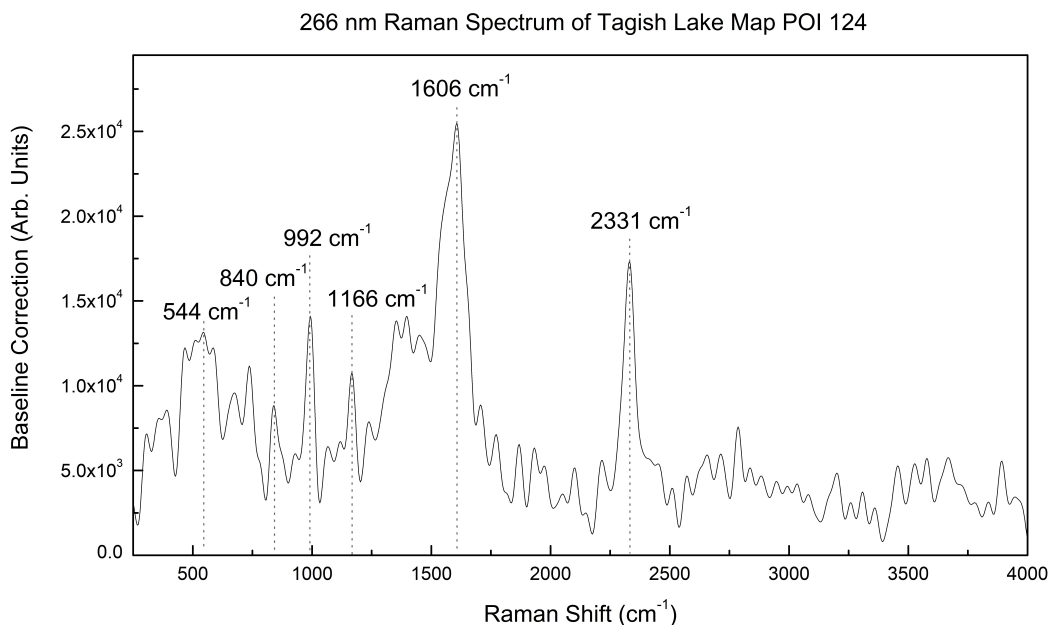


Figure 6.22: 266 nm Raman spectra POI 124 from map of Tagish Lake fragment A with background subtraction and baseline correction and labelled peaks at 544, 840, 992, 1166, 1606 and 2331 cm^{-1} .

POI 124 has labelled Raman peaks at 544, 840, 992, 1166, 1606 and 2331 cm^{-1} displayed in Figure 6.22. As established, peaks 544 and 840 cm^{-1} most likely correlate to phyllosilicates and olivine respectively (Wang and Jolliff, 2015; Wang et al., 2015). The Raman peak at 992 cm^{-1} is most likely Si-O-Si bonding similar to that of the peak at 1010 cm^{-1} . However, $990\text{--}1100\text{ cm}^{-1}$ region can also be assigned to aromatic rings (Lin-Vien et al., 1991). The 1166 cm^{-1} Raman peak is intriguing because it could correspond to the C-N stretching in Amines. The 1606 and 2331 cm^{-1} peaks in POI 124 correlate to the G band of carbon and N_2 from the atmosphere respectively.

High-accumulation and high-resolution POI spectra can be very complicated to analyze

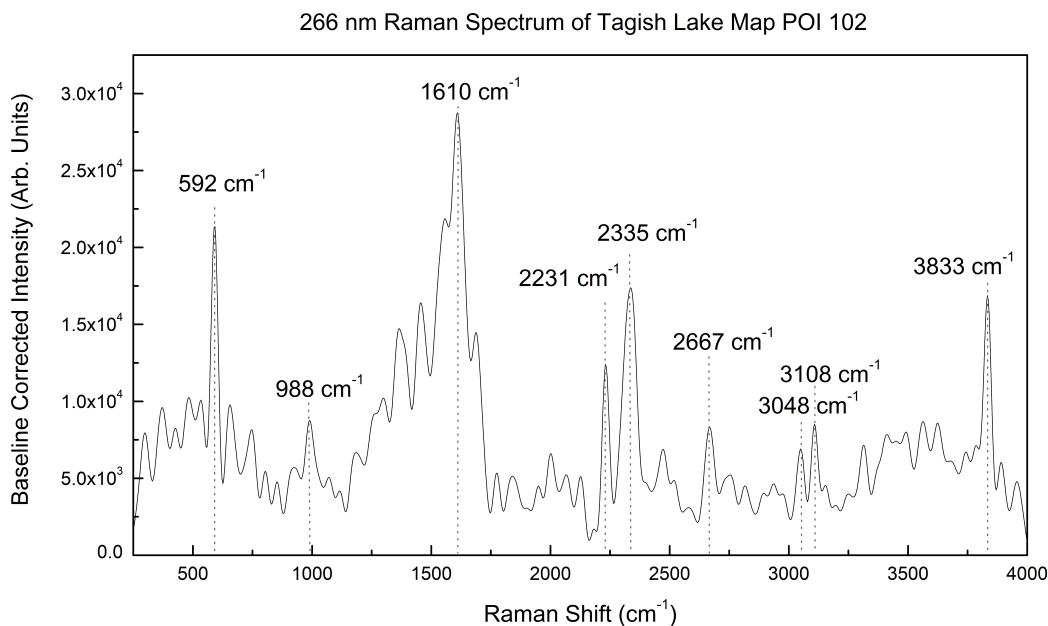


Figure 6.23: 266 nm Raman spectra POI 102 from map of Tagish Lake fragment A with background subtraction and baseline correction and labelled peaks at 592, 988, 1610, 2231, 2335, 2667, 3048, 3108, and 3833 cm^{-1} .

as they have many peaks due to the heterogeneous and fine-grained nature of the Tagish Lake sample. An example of this complicated convolution is in POI 102 (Figure 6.23). Similar to the other spectra, the peak at 592 cm^{-1} is most likely related to phyllosilicates such as saponite that are common in Tagish Lake (Wang and Jolliff, 2015). The peak at 988 cm^{-1} similar to the peak in POI 124 could be correlating to Si-O-Si bonding or aromatic rings (Lin-Vien et al., 1991). The carbon G band in this spectrum is strong at 1610 cm^{-1} . Interestingly, the peak at 2231 cm^{-1} correlates well to that of -CN (isocyanate) which has been detected in carbonaceous antarctic meteorites in previous work (Dobrică et al., 2011) using 244 nm excitation but not yet in the Tagish Lake meteorite. Furthermore, the distribution of the peak 2230 cm^{-1} is mapped in Figure 6.24 shows similarity to that of the carbon distribution and does not resemble noise. Similarly to other points of interest, the Raman peak at 2335 cm^{-1} is an N_2 peak from the atmosphere. Raman peak 2667 cm^{-1} is harder to identify, however, it could be a 2D carbon peak. Furthermore, peaks 3048 and 3108 cm^{-1} are both related to the asymmetrical stretching of $=\text{CH}_2$ for cycloalkanes (Lin-Vien et al., 1991). The

Raman peak at 3833 cm^{-1} remains unidentified. Further analysis on the carbon and nitrogen regions of the Raman window will be reported in section 6.4.

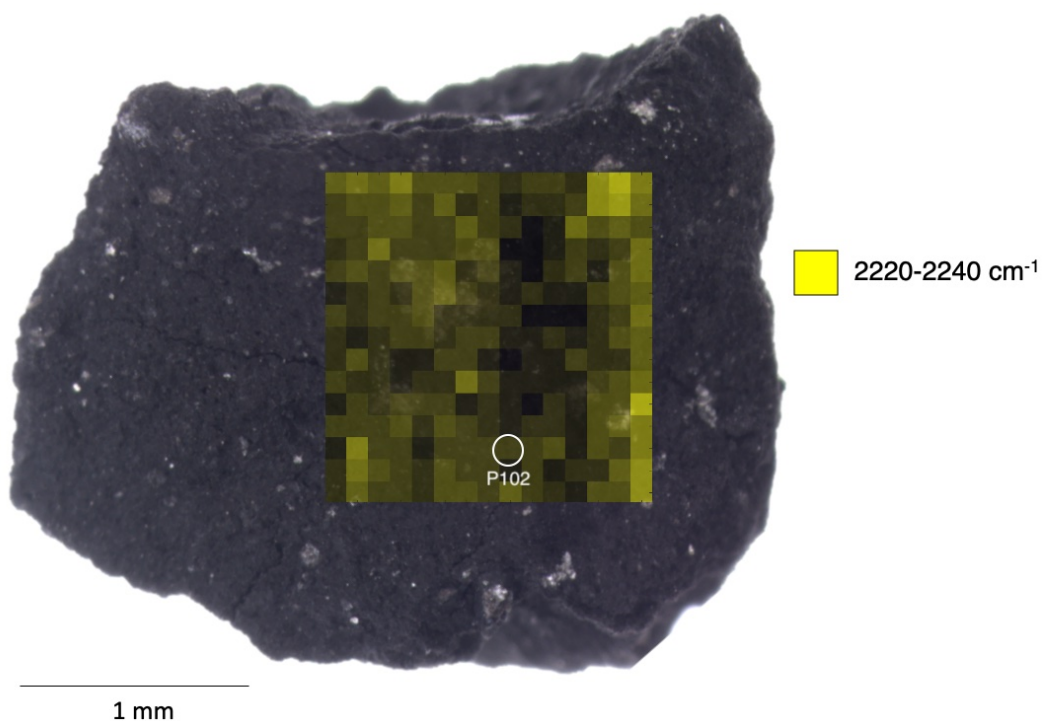


Figure 6.24: 266 nm Raman Map of Peak 2230 cm^{-1} in Tagish Lake Fragment A in nitrogen atmosphere.

Table 15: Raman peak position assignments for features in Tagish Lake with $\lambda_{Ex} = 532$ nm and $\lambda_{Ex} = 266$ nm based on literature findings. (***) Represents a undefined value with the ESCAPE system.

Raman Peak Positions (cm ⁻¹) $\lambda_{Ex} = 532$ nm	Raman Peak Positions (cm ⁻¹) $\lambda_{Ex} = 266$ nm	Peak Assignment	Possible Identification	Citation
520–550	500–550	Cr ₂ O ₃	Spinel,	(Wang et al., 2015)
640–650	592	FeO	Phyllosilicate	(Wang and Jolliff, 2015)
680	***	Si-O-Si	(Saponite)	
***	650	FeO	Magnetite, Phyllosilicate	(De Faria et al., 1997)
820	840	SiO ₄ Stretching	Olivine	(Wang et al., 2015)
850		SiO ₄ Stretching		(Wang and Jolliff, 2015)
1010	990–1010	Si-O-Si, or ν_1 (SO ₄	Silicates,	(Wang et al., 2015)
1140	***	ν_3 (SO ₄)	Gypsum	(Krishnamurthy and Soots, 1971)
1092	***	CaCO ₃ A _{1g}	Calcite	(Rutt and Nicola, 1974)
***	1166	ν C-C		(Zhu et al., 2011)
1380	1380	D	Carbon	(Matrajt et al., 2004)
1590	1592	G		(Dobrică et al., 2011)
				(Nakamura et al., 2002)
***	1606	Ring Stretching	Aromatic Ring	(Ferrari and Robertson, 2000)
***	1772	C=O	Ketone	(Lin-Vien et al., 1991)
***	2030	-N=C=S	Isothiocyanate	(Lin-Vien et al., 1991)
***	2096–2130	HCN	Hydrogen Cyanide	(Brewer and Aikens, 2010) and;
***	2103–2224	-CN	Isocyanate	(Ferrari et al., 2003)
***	2331	N ₂	Nitrogen	(Lin-Vien et al., 1991)
***	2667	2D	Carbon	(Frank et al., 2011)
***	2800–2900	C-CH ₃ , Aromatic C-H	Aliphatic Carbon,	(Lin-Vien et al., 1991)
	2900–2940	ν_{as} (CH ₂)	Aromatic Carbon	(Sumayya et al., 2008)
***	3000–3100	C-H Stretching	Aromatic Carbon	(Freire et al., 2017)
***	3610	O-H	Phyllosilicates	(Wang et al., 2015)

6.3.3 266 nm Fluorescence of Tagish Lake

A 266 nm fluorescence map was acquired of the Tagish Lake meteorite Fragment A. The map is centred on the fragment, targeting the same area as the 532 and 266 nm Raman map, with some visible brownish-coloured features in the top-center of a mostly very dark, black, extremely fine-grained matrix-filled mapping area (Figure 6.5). The map size is 1.5mm^2 with a step size of 0.1 mm, resulting in 225 spectral points in total (Figure 6.4). Each point has a corresponding spectrum, which is plotted in Figure 6.26. Because the mapping areas were aligned by eye, they may differ in location slightly from each other. Fluorescence mapping was a lot quicker than Raman mapping due to less need for long accumulation times because fluorescence emission is stronger than Raman scattering. Some of the spectra appear to be more intense in the 350–400nm fluorescence region. There is a variation in types of fluorescence spectra from this map, sharper fluorescence peaks such as that at 380 nm, very broad fluorescence at > 400 nm and convoluted fluorescence from potentially multiple sources in the 350–380 nm region.



Figure 6.25: Tagish Lake fragment A spectral mapping area for 266 nm Fluorescence.

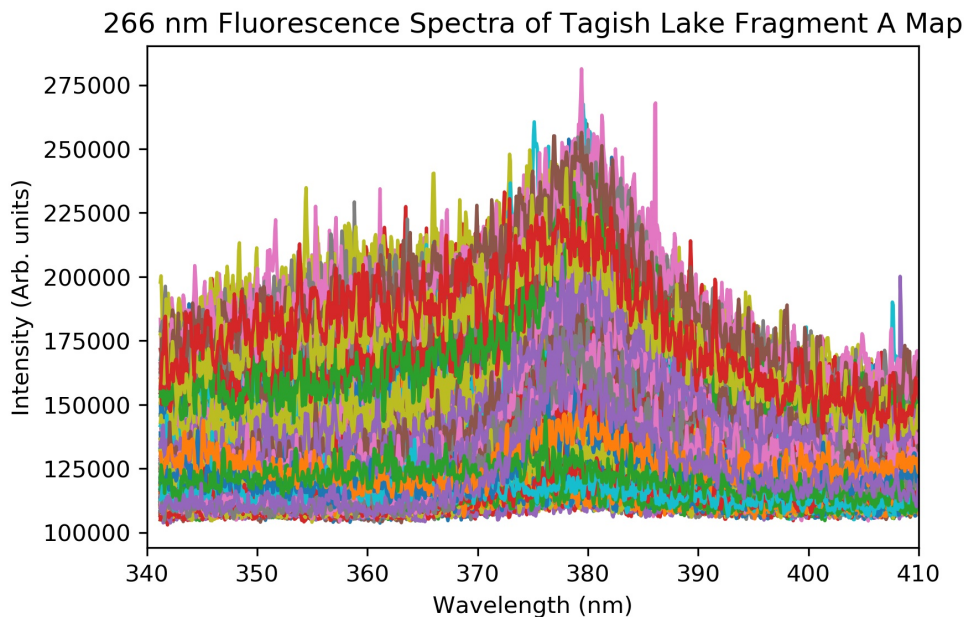
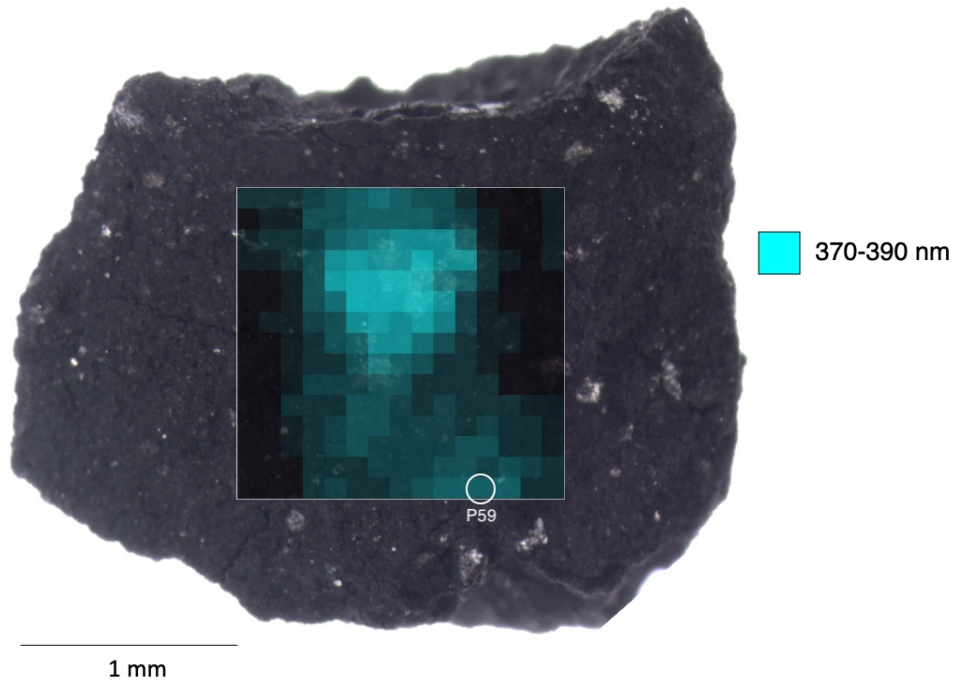


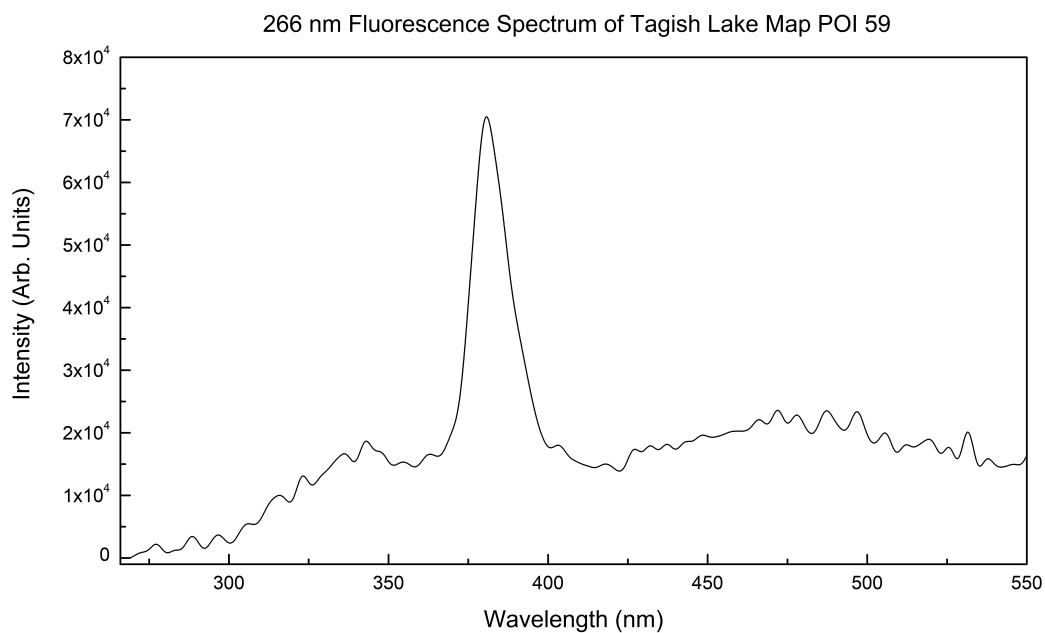
Figure 6.26: 266 nm fluorescence spectra from the 225-point raster map of Tagish Lake fragment A. These spectra have no baseline correction or background subtraction. This figure represents each point spectrum plot on top of each other to distinguish points of interest that have intense peaks common to all points, or unique to few spectra - which are then analyzed further.

In Figure 6.27 we can observe the fluorescence map of 380 nm peak intensity in the Tagish Lake fragment A sample. The peak intensity correlating to the spectral peaks seems to appear in the same region as peak Raman intensity, as well as some fluorescence at 380 nm appearing in the bottom left corner of the spectral mapping region. Points of interest that were high in fluorescence in the 380 nm region from the raster maps were then re-acquired with a longer acquisition time and larger spectral window than that of the maps (266–550 nm). Point of interest 59 is plotted in Figure 6.27. Figure 6.28 shows the fluorescence map of peak 350 nm, seemingly situated primarily in the top-center feature of the sample mapping area. Points of interest with intensity at 350 nm show a strong association with peak 380 nm, which also is intense in the same top-centre region of the mapping area (Figure 6.28). Other Points of interest with similar 350 and 380 nm peak convolution are exemplified in Figure 6.29. From the raster points of the fluorescence map, it was evident that there was some fluorescence at higher wavelengths than the mapping spectral window could image. These

points were then re-acquired as points of interest (POI) using a larger spectral window and a longer acquisition time to show broad-band fluorescence around 450 nm such as in Figure 6.30.

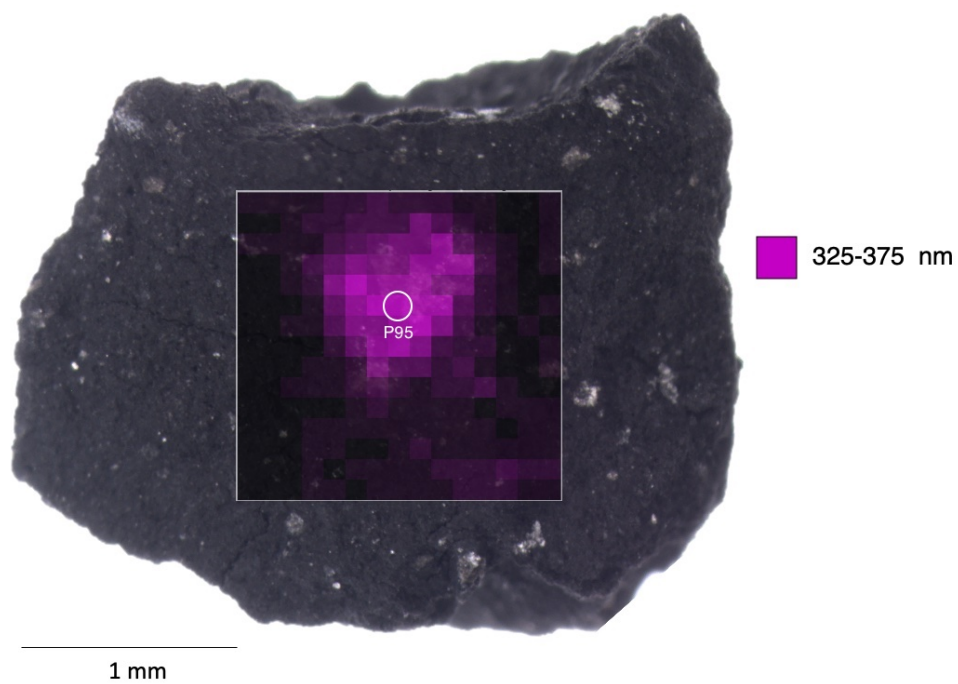


(a) 266 nm fluorescence map of 380 nm peak.

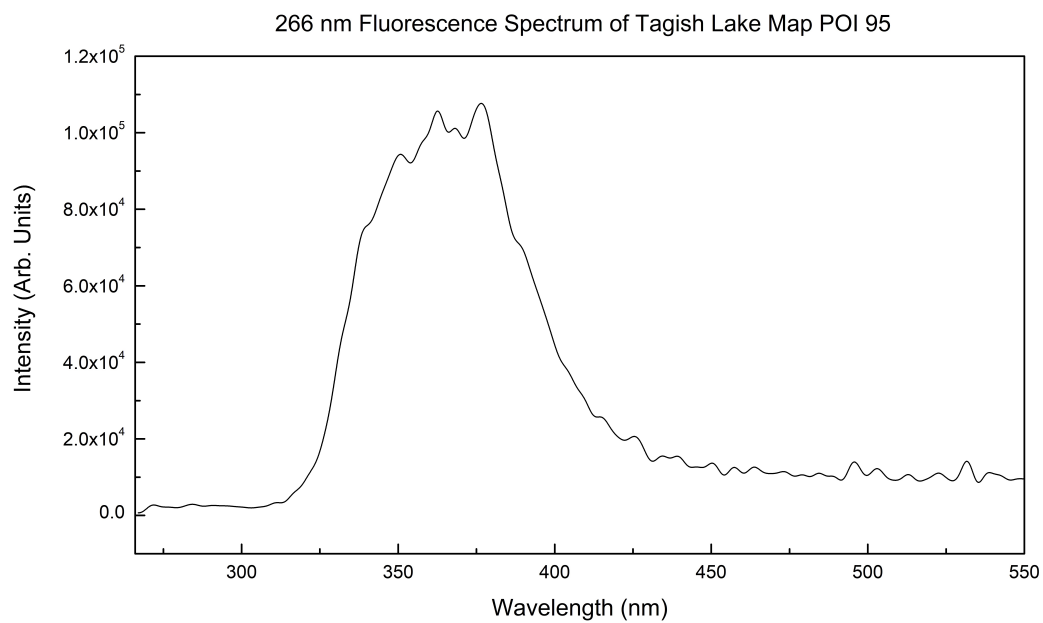


(b) 266 nm fluorescence spectra of point of interest (POI) 59

Figure 6.27: (a) 266 nm fluorescence map of 380 nm peak displayed in cyan with Peak intensity shown as a function of brightness; and (b) 266 nm fluorescence mapping point of interest (POI) spectra, POI 59.



(a) 266 nm fluorescence map of 350 nm peak.



(b) 266 nm fluorescence spectra of point of interest (POI) 95

Figure 6.28: (a) 266 nm fluorescence map of 350 nm peak displayed in magenta with Peak intensity shown as a function of brightness; and (b) 266 nm fluorescence mapping point of interest (POI) spectra, POI 95.

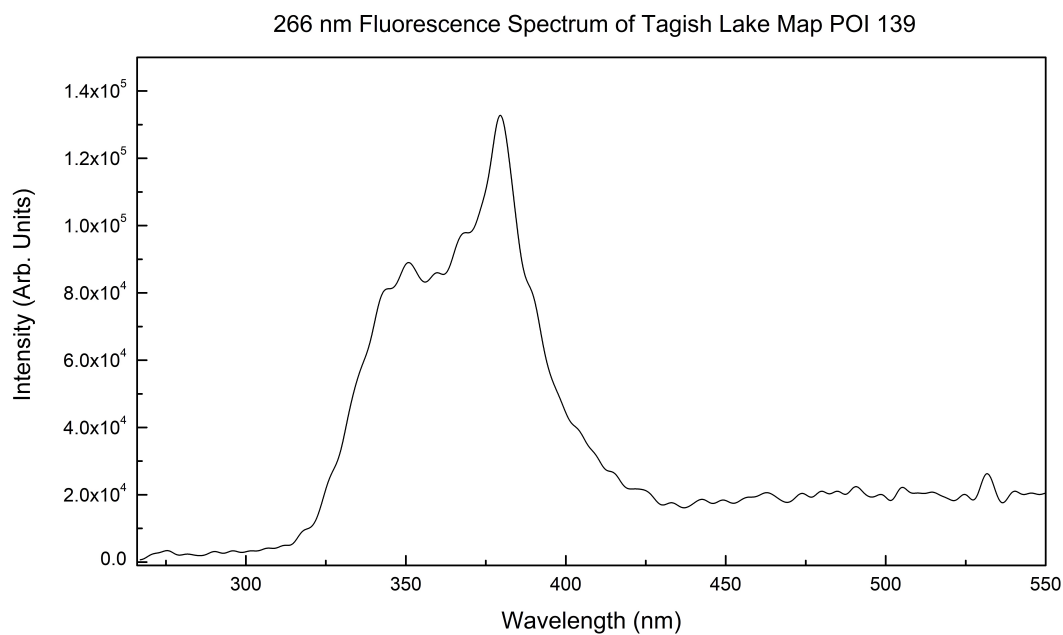


Figure 6.29: 266 nm Fluorescence spectra POI 139, long acquisition of peaks 350 and 380 nm appearing together.

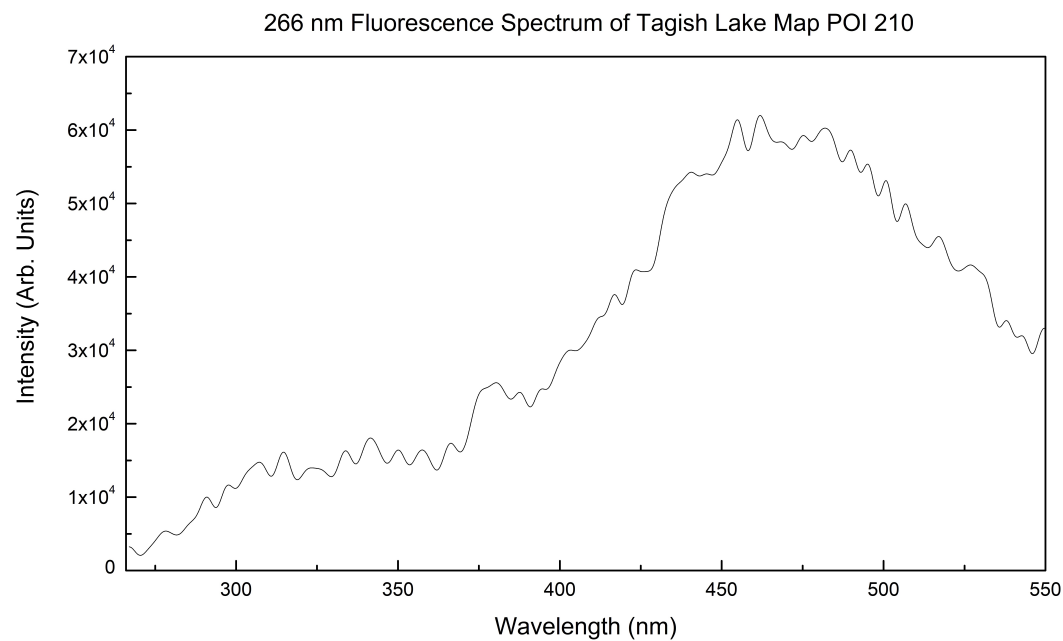
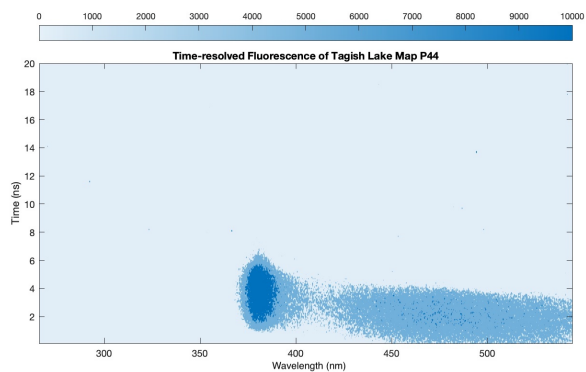
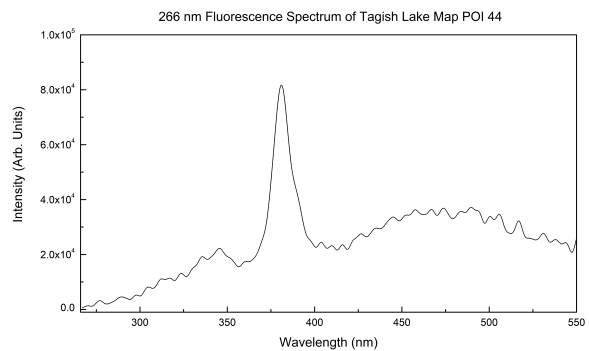


Figure 6.30: 266 nm Fluorescence spectra POI 210, long acquisition of peak 475 nm.



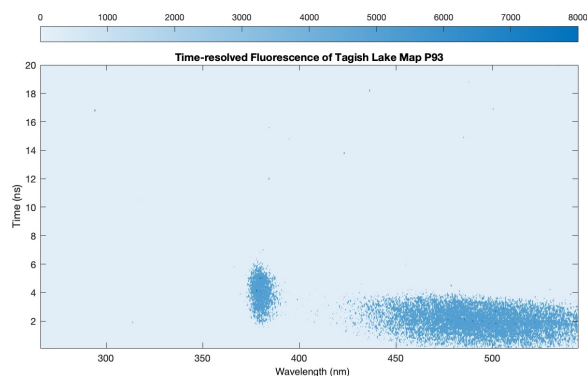
(a) 266 nm TR-LIF contour plot of POI 44.



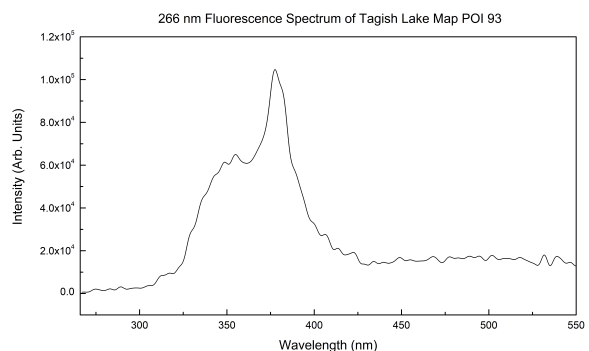
(b) 266 nm fluorescence spectra of point of interest (POI) 44

Figure 6.31: (a) 266 nm time-resolved contour plot of Tagish Lake fluorescence map point of interest 44; and (b) 266 nm fluorescence spectra of Tagish Lake fluorescence map point of interest 44.

Time-resolved fluorescence spectra were also taken at POIs from the original fluorescence map over 20 ns. POI 44 has a strong fluorescence peak at 380 nm, similar to that of POI 50, and mapped in Figure 6.27. The TR-LIF of this point shows that the fluorescence is most intense in the 350–380 nm range with some minor fluorescence from 400–550 nm. POI 93 has a very similar TR-LIF to that of POI 44, with less intensity at 380 nm and slightly shifted higher wavelength fluorescence from 450–550 nm. POI 210 has very weak TR-LIF in the same region we see fluorescence accumulating in the single shot spectra from 400–550 nm. Most of the fluorescence results are qualitative due to the fact that there is very little data available to identify spectra with as of yet, however, the fluorescence in the region of 380 nm (both time-resolved and spectra) bear a resemblance to that of the TR-LIF of the pyroxene mineral, augite, demonstrated in Lymer et al. (2021). Unfortunately, no TR-LIF decay rates were calculable from the TR-LIF measurements as the fluorescence signal was not strong enough.

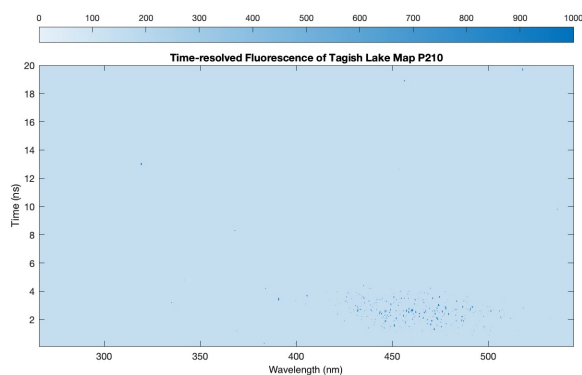


(a) 266 nm TR-LIF contour plot of POI 93.

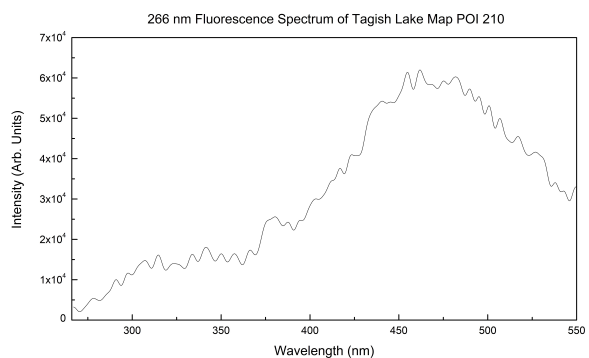


(b) 266 nm fluorescence spectra of point of interest (POI) 93

Figure 6.32: (a) 266 nm time-resolved contour plot of Tagish Lake fluorescence map point of interest 93; and (b) 266 nm fluorescence spectra of Tagish Lake fluorescence map point of interest 93.



(a) 266 nm TR-LIF contour plot of POI 210.



(b) 266 nm fluorescence spectra of point of interest (POI) 95

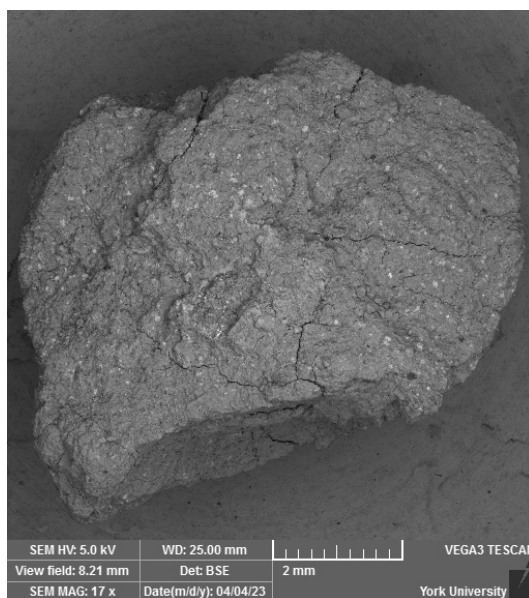
Figure 6.33: (a) 266 nm time-resolved contour plot of Tagish Lake fluorescence map point of interest 210; and (b) 266 nm fluorescence spectra of Tagish Lake fluorescence map point of interest 210.

6.3.4 FTIR and SEM of Tagish Lake Meteorite

For further context, spectral data are taken of the Tagish Lake meteorites using Scanning Electron Microscopy (SEM) and Fourier-transform Infrared (FTIR) spectroscopy. SEM images were collected in a TESCAN VEGA environmental SEM instrument that allows imaging without any sample coating or preparation. Tagish Lake fragment A was placed on a clean (using isopropyl alcohol) stub in the sample stage and loaded into the chamber. Images were taken under a high vacuum and 5 kV beam to collect both scattered electron (SE) and backscattered electron (BSE) images (Figure 6.34). These images show the uneven surface of the sample fragment and its fissile/fragile nature of it with visible cracks. An overlay of a 25x magnifications BSE image over the Tagish Lake fragment A mapping area is displayed in Figure 6.35.



(a) Secondary Electron Image of Tagish Lake Fragment A .



(b) Backscattered Electron Image of Tagish Lake Fragment A

Figure 6.34: Scattered and backscattered electron images of Tagish Lake Fragment A, at 5 kV and no coating.

FTIR spectra are also acquired from a small piece of the fragment that had become detached when it was transported from the Royal Ontario Museum to York University. This

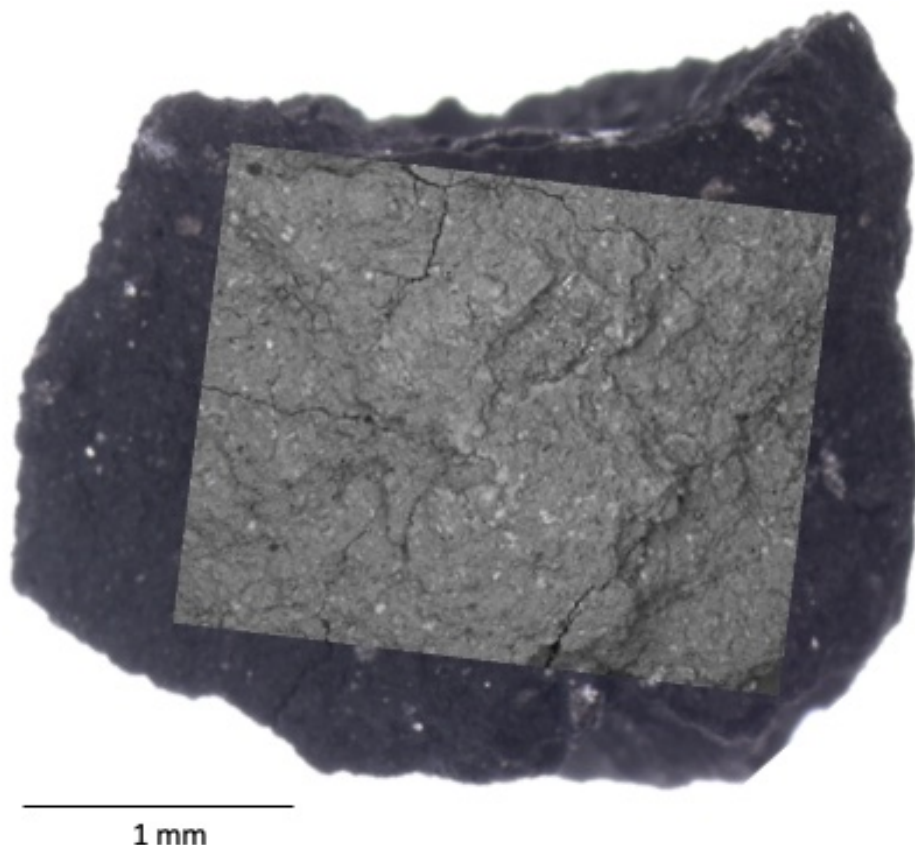
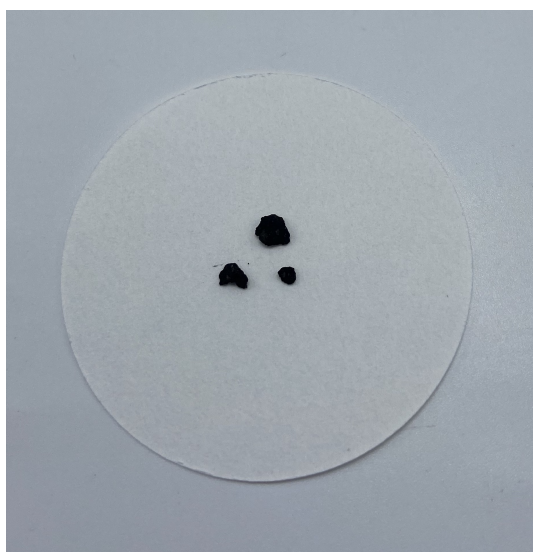
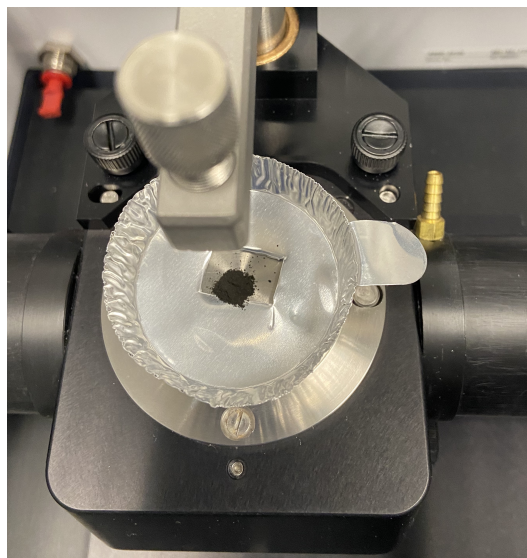


Figure 6.35: Backscattered electron image at 25x magnification overlay with the Tagish Lake fragment A image in the spectral mapping area.

small, thin, fragment was crushed using a clean mortar and pestle to a very fine powder. All of the powdered sample (weighing 31.3 mg total) was transferred to the Agilent Cary 660 FTIR bench. In the bench, an attenuated total reflectance (ATR) accessory is placed and a background spectrum is taken. On top of the ATR crystal, the powdered sample is placed and reflectance spectra are taken (Figure 6.36). Multiple spectra were taken of the powder at 4 cm^{-1} resolution, and for each acquisition, the powder was rearranged over the ATR crystal to ensure that a representative average spectra is acquired. An aluminum cup with a hole cut out is placed around the powder to scoop and transfer the sample back to a container once the acquisitions are finished. The average FTIR spectra from the non-pristine piece of Tagish Lake meteorite that was used for this study is displayed in Figure 6.36. A comparison spectra of Tagish Lake using microscopic FTIR from Matrajt et al. (2004) is also



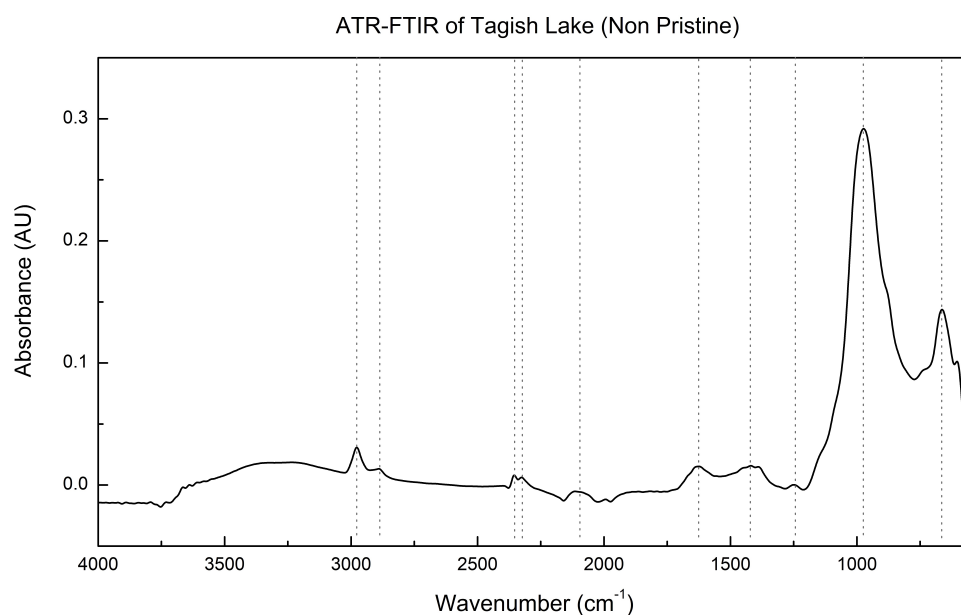
(a) Tagish Lake Fragments Powderized for FTIR Analysis



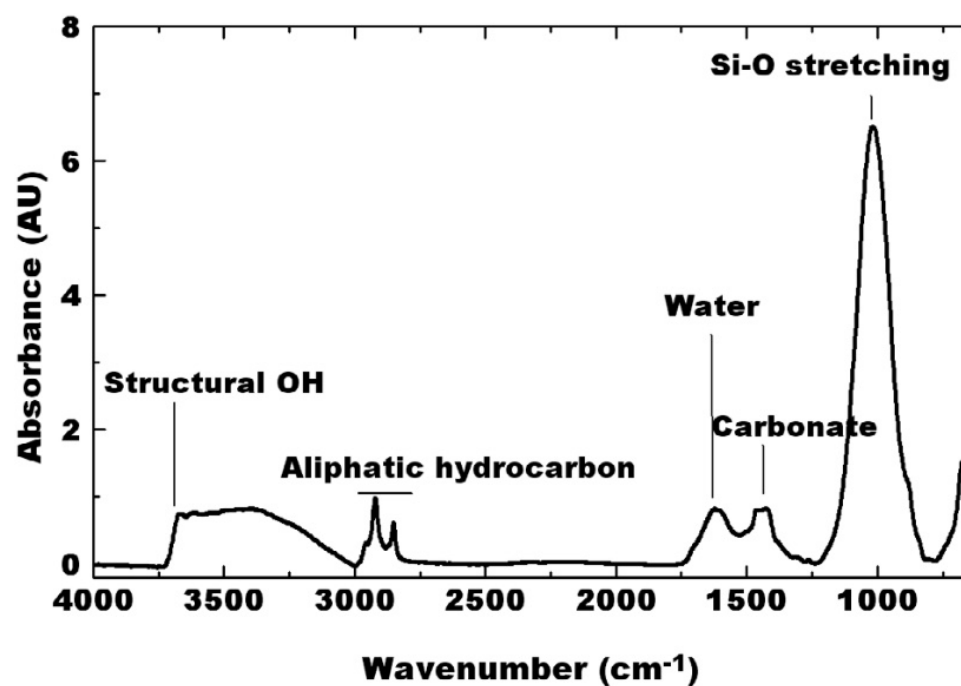
(b) ATR-FTIR accessory with Tagish Lake Powder

Figure 6.36: Tagish Lake fragments to be powderized for FTIR analysis, weighing 31.3 mg total, and subsequent powder placed on the ATR accessory in the FTIR bench.

displayed in Figure 6.37. Labelled lines 975 , 1400 , 1625 , 2977 and 2883 cm^{-1} along with the structural OH hump above 3600 cm^{-1} match the band assignments in Matrajt et al. (2004) as Si-O stretching, carbonate, water, aliphatic hydrocarbon respectively. Additional peaks are observed in the ATR-FTIR spectra from York at 663 , 2100 , 2325 , and 2354 cm^{-1} . Most of these bands are very weak and therefore a proper identification would be difficult, however the stronger peak at 663 cm^{-1} correlates to that of olivine (Gilmour et al., 2019).



(a) Average ATR-FTIR Spectra of Tagish Lake Non-pristine Sample



(b) Average micro-FTIR Spectra of Tagish Lake Meteorite from the Literature

Figure 6.37: (a) ATR-FTIR average spectra of the Tagish Lake non-pristine fragment at York University. Peak lines positioned at 663, 975, 1250, 1400, 1625, 2100, 2325, 2354, 2977 and 2883 cm^{-1} . (b) Average microscope FTIR spectra of the Tagish Lake meteorite from Matrajt et al. (2004)

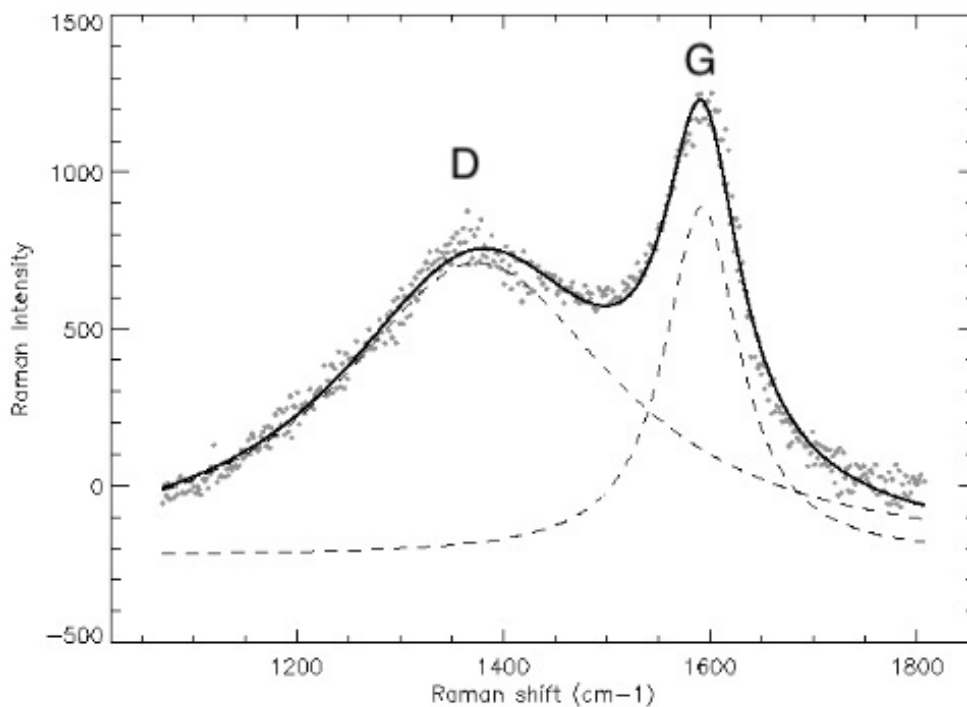
6.4 Analysis of Carbon and Nitrogen Bonds in the Tagish Lake Meteorite Spectra

6.4.1 Analysis of Carbon D&G Bands Using Green-Raman Interrogation

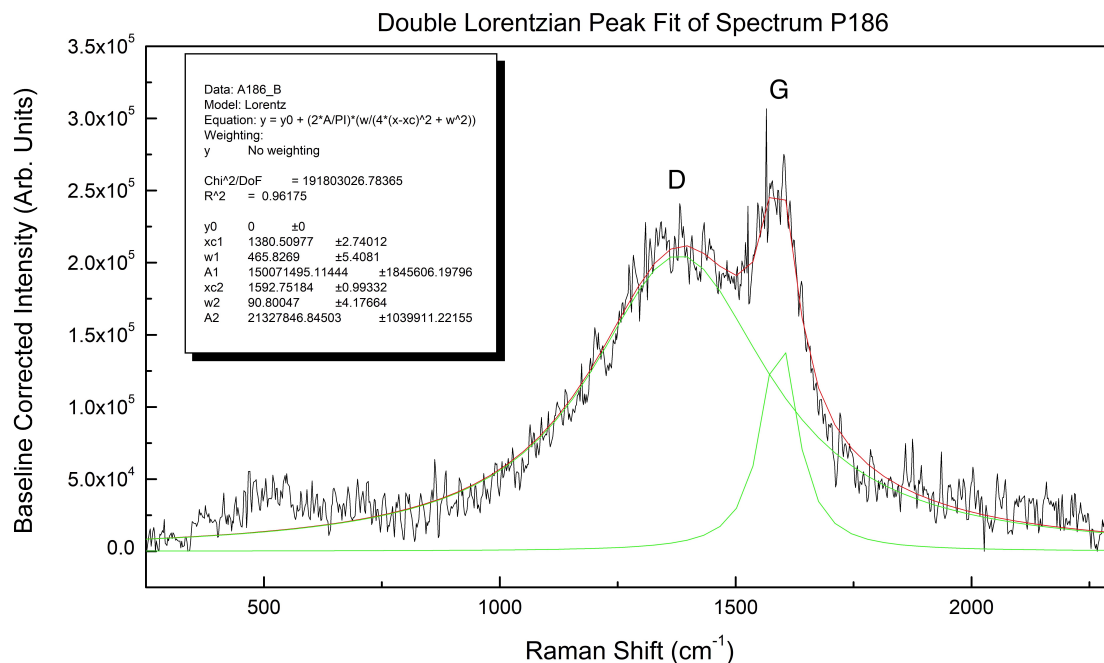
The D (disordered) and G (graphitic) bands of carbon are ever-present (at ~ 1380 and 1592 cm^{-1} in the 532 nm Raman spectra collected of the Tagish Lake meteorite fragment A in this study. Similarly, in Matrajt et al. (2004); Nakamura et al. (2002); Dobrică et al. (2011), this carbon spectral pattern was also prevalent in Tagish Lake when using 514 nm excitation. Carbon Raman band change peak position, relative intensity and FWHM depending on the composition and structure of the carbon present within the sample. We can further analyze the carbon within the Tagish Lake meteorite by fitting an ideal Lorentzian model to our spectra to determine the actual peak positions of the carbon D&G bands and compare them to that of the literature. Once the V_{max} and FWHM for the D&G bands are found we can also record the intensity and calculate the I_D/I_G relative peak intensity ratio and the ratio of area (D) under the peak compared to the total area of the D&G bands ($A_D/(A_D+A_G)$) (Table 16). Compared to that of Matrajt et al. (2004), the V_{max} values, I_D/I_G , and ($A_D/(A_D+A_G)$) calculated from this work are extremely similar. The FWHM (G) is also very similar to that of Matrajt et al. (2004), however, the FWHM (D) is significantly larger in this work, most likely due to the slit opening of these measurements being 250 μm (see section 2.6 for more information on resolution changes with slit opening).

Table 16: Analysis of carbon D&G bands in the Tagish Lake meteorite from 5 points of 532 nm Raman analysis using Lorentzian model peak fit compared to 6 points from Matrajt et al. (2004).

	2-Lorentzian Model Matrajt et al., 2004	2- Lorentzian Model This Work
V_{max} (D)	1378.80 ± 7.27	1378.58 ± 8.42
V_{max} (G)	1593.89 ± 1.47	1593.45 ± 1.14
FWHM (D)	328.11 ± 19.23	452.67 ± 34.51
FWHM (G)	88.56 ± 7.54	90.98 ± 7.90
I_D/I_G	0.85 ± 0.06	0.84 ± 0.03
$A_D/(A_D + A_G)$	71.51 ± 1.60	86.53 ± 2.31



(a) D&G carbon Raman band fit with Lorentzian model, modified from Matrajt et al. (2004) using 514 nm excitation.



(b) D&G carbon Raman band fit with Lorentzian model from 532 nm excitation interrogation in this work.

Figure 6.38: Carbon peak fitting analysis using Lorentzian model peak fitting in this work compared to that in Matrajt et al. (2004)

6.4.2 Analysis of Carbon and Nitrogen bonds from UV-Raman Spectral Interrogation

Using 266 nm Raman excitation, interesting primary and secondary carbon peaks are visible within the Tagish Lake mapping data. Primary carbon D&G bands located at ~ 1380 and 1590 cm^{-1} look slightly different to that of the 532 nm excitation Raman due to carbon Raman bands being resonant, meaning they change location and shape slightly based on the excitation wavelength. The UV carbon D&G bands from the Tagish Lake meteorite mapping data match well to that of UV carbon bands from carbonaceous Antarctic meteorites from Dobrică et al. (2011). In Figure 6.39 we can see that the carbon G band is a prominent, sharp peak; whereas the D band using UV excitation is more of a shoulder than a peak of its own off of the G band. In Figure 6.39 we can also see aliphatic C-H stretching at $\sim 2900\text{ cm}^{-1}$, and aromatic C-H stretching at $\sim 3100\text{ cm}^{-1}$ (Lin-Vien et al., 1991).

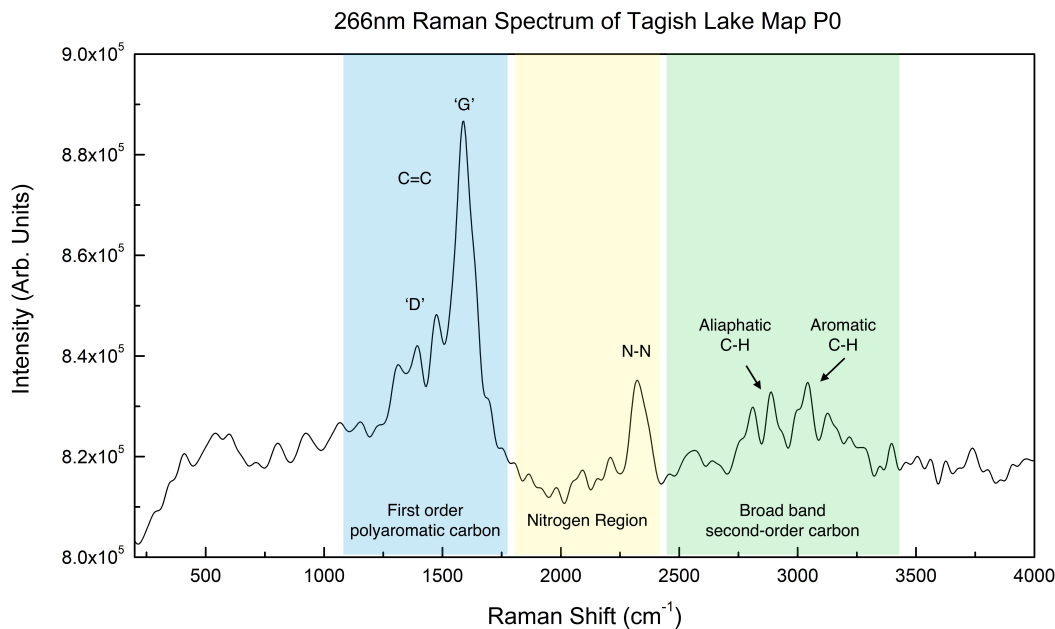


Figure 6.39: Primary (D&G bands) and secondary (aliphatic and aromatic) carbon present in the 266 nm Raman map of Tagish Lake.

Looking further at the UV Raman data, we also see peaks in the nitrogen region ($1600 - 2500\text{ cm}^{-1}$) of the Raman window. This region is particularly interesting because there are

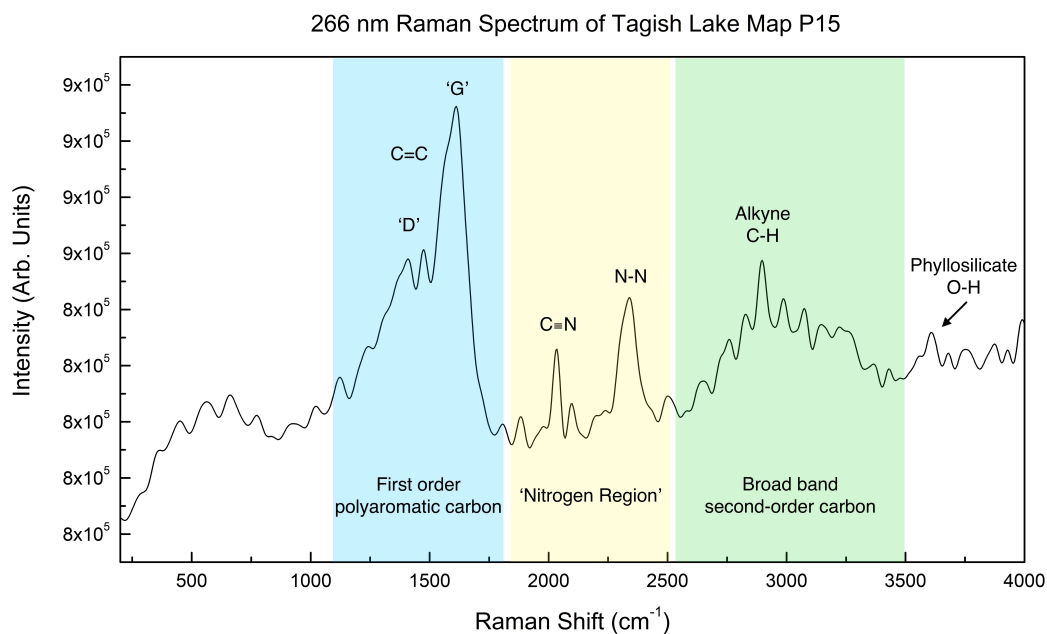


Figure 6.40: Primary (D&G bands) and secondary (alkyne) carbon peaks along with isocyanate (-CN) present in the 266 nm Raman map of Tagish Lake.

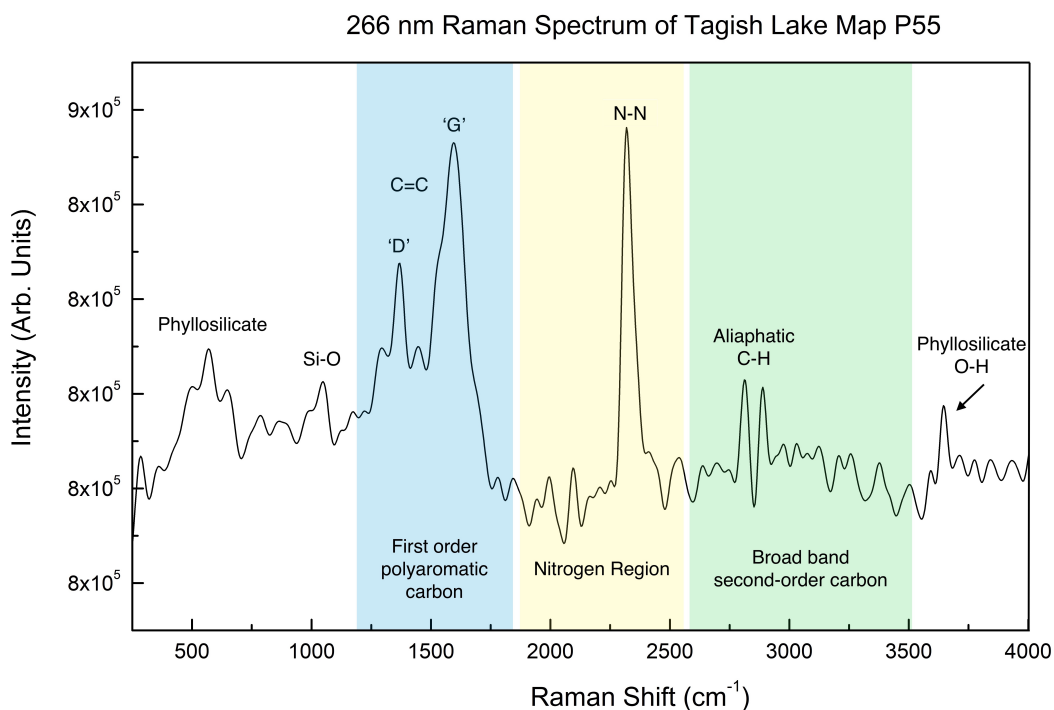


Figure 6.41: Primary (D&G bands) and secondary (aliphatic CH) carbon peaks along with nitrogen (N_2) peak present in the 266 nm Raman map of Tagish Lake.

rarely Raman peaks appearing in this region unless they are a nitrogen species; and thus a region of interest for possible astrobiological implications. In Figure 6.40 there are two clear Raman peaks in the nitrogen region — one at $\sim 2100\text{ cm}^{-1}$ and one at 2333 cm^{-1} . The peak at 2100 cm^{-1} is most likely -CN (isocyanate), or HCN (hydrogen cyanide), similar to that in which we saw at 2224 cm^{-1} in Figure 6.23 from the points of interest of the mapping data in section 6.3.2 (see also peak identifications from the Tagish Lake maps in Table 15). Interestingly, we see the nitrogen peaks for -CN appearing with the carbon secondary peaks, suggesting that there could be a relationship between them, potentially components of an organic molecule. The peak at 2333 cm^{-1} is an N_2 nitrogen peak. This N_2 nitrogen peak is very prevalent in the data, as we see in Figure 6.41, it can even be sometimes more intense than the rest of the spectra. This peak is most likely resolved from the nitrogen environment in which the sample is contained while the mapping data is collected.

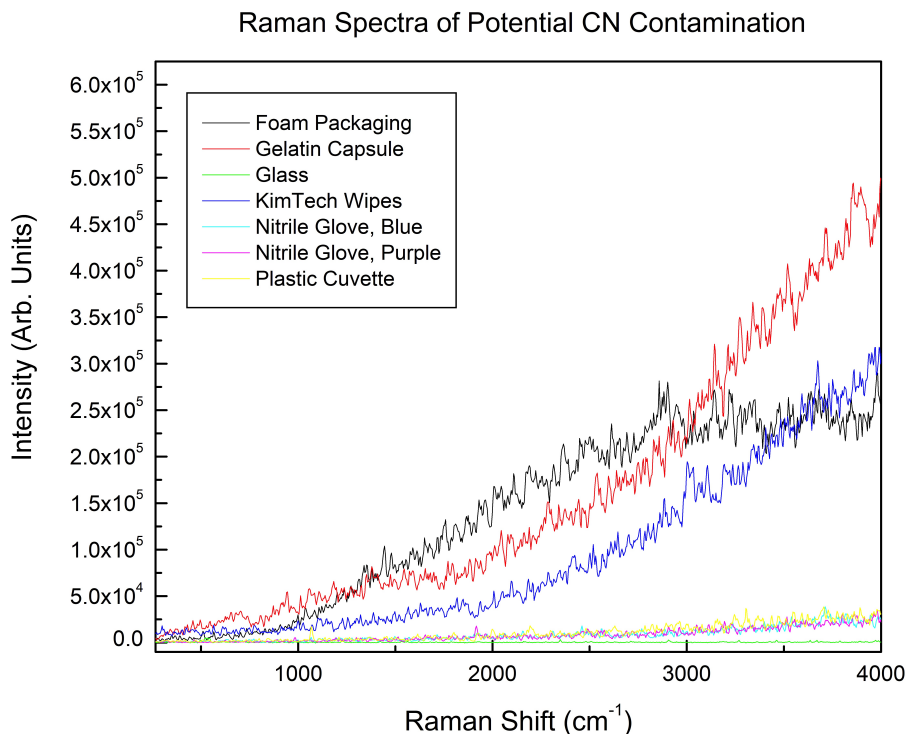


Figure 6.42: 266 nm Raman analysis of possible packaging and handling contaminants of nitrogen using the same acquisition settings used to collect mapping data.

To ensure that the N_2 nitrogen peak is from the atmosphere and not from potential con-

tamination, 266 nm Raman data was collected of possible contaminants that had touched the sample before data collection such as packaging materials, nitrile gloves, the sample holders from the museum, etc. None of these materials showed any significant Raman peaks (Figure 6.42), and therefore are very unlikely to have contaminated the sample.

Furthermore, the surface that the UV maps were collected on was only very recently exposed to the environment, as the sample broke in half from its transportation from The ROM to York University. Therefore, it would be very unlikely that storage contaminants would reach this surface in the middle of the sample as typically contaminants can be removed using instruments such as plasma cleaners which take μm -scale material off the surface of samples. To further study the nitrogen peak located at $\sim 2333\text{ cm}^{-1}$, an experiment was conducted where an N_2 nitrogen peak was located on a spot on the Tagish Lake sample in a terrestrial atmosphere (air). When the peak

was found, the air was then removed to 4 mbar pressure from the chamber, and another acquisition was taken. The chamber was then filled with an argon-only atmosphere and a third acquisition was taken.

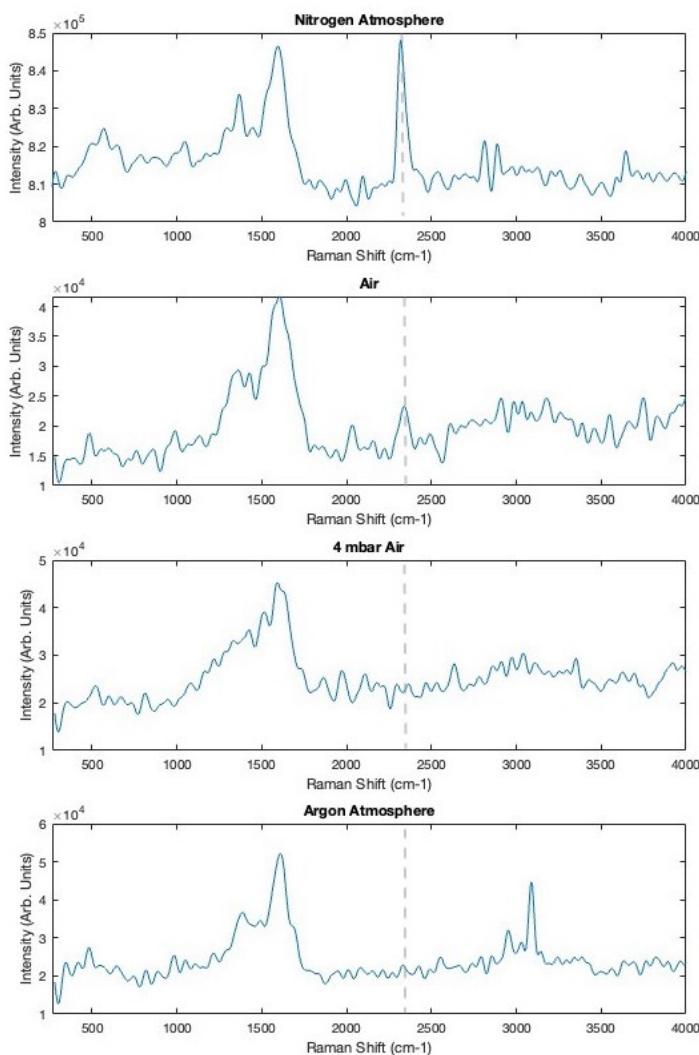


Figure 6.43: 266 nm Raman analysis of N_2 Peak in Nitrogen atmosphere, air, 4 mbar air, and argon atmosphere.

In Figure 6.43, we can observe the strong N_2 peak in the nitrogen environment. In the air environment, we can also see a moderate N_2 peak. However, as the air is removed, at the same point on the sample, the peak disappears. Furthermore, The peak does not reappear in the argon environment. This suggests that the N_2 peak is atmosphere-related and not a feature of the sample itself. The peak is most likely resolved from this material and not other Raman samples because of the incredibly low signal-to-noise ratio of the Tagish Lake material.

6.4.3 Analysis of Carbon and Nitrogen bonds from UV-Raman Spectral Interrogation in an Argon Atmosphere

To better understand if the other peaks (apart from N_2) resolved in the ‘nitrogen Raman region’ were synthesized from the almost pure nitrogen gas atmosphere in which the UV-Raman Tagish Lake Fragment A maps were collected, or a constituent in the sample itself; a second UV-Raman map was collected in an argon atmosphere of Fragment B (fragment B had not previously been studied in the nitrogen environment) (Figure 6.44). In Figure 6.45, Raman peaks at 1620, 2216, 2811, 2888, and 3610 cm^{-1} are observable. Noticeably, there are no peaks in this map’s spectra at 2333

cm^{-1} , which is the Raman peak associated with nitrogen gas (N_2).

There are, however, peaks around 2216 cm^{-1} in multiple spectra relating to aromatic nitrile or isocyanate ($-CN$). This peak is now present in both Tagish Lake fragment A (Figure 6.2) in a nitrogen

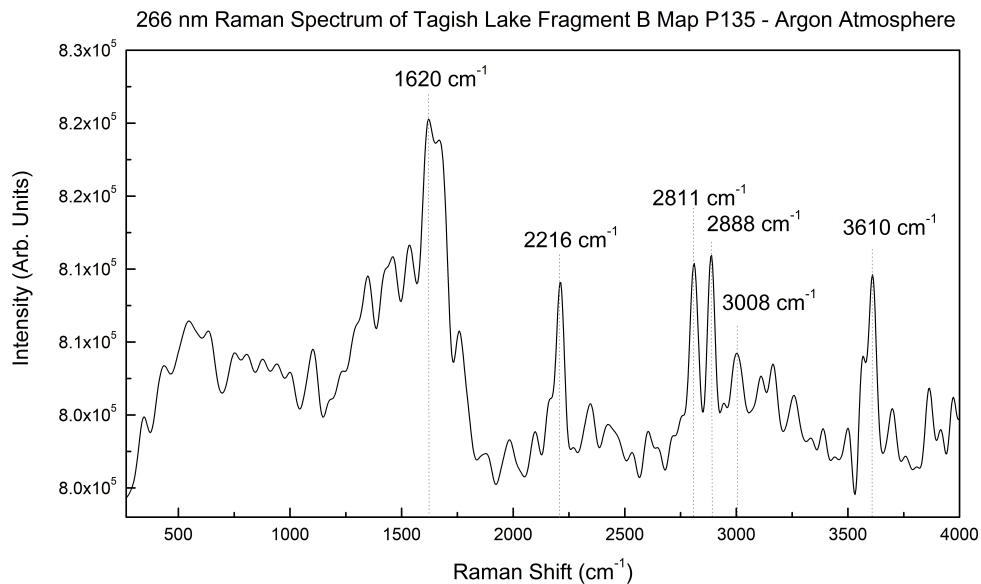
environment and Tagish Lake fragment B (Figure 6.2) in an argon en-



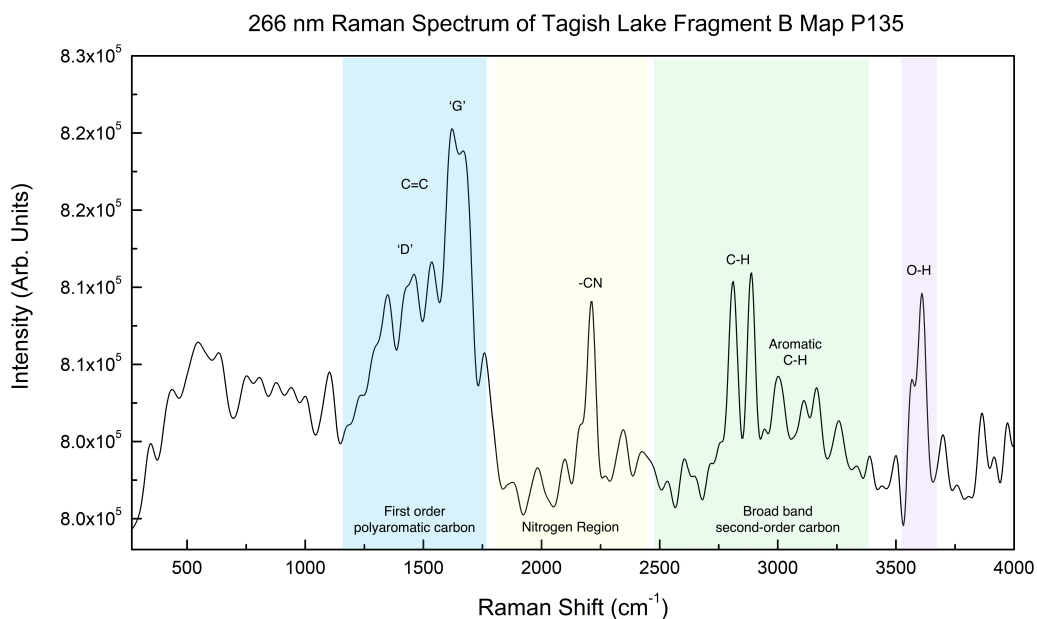
Figure 6.44: Tagish Lake fragment B UV-Raman mapping area under an argon atmosphere.

vironment while interrogating with $\lambda_{Ex} = 266$ nm. Some Raman peaks appear to be slightly

shifted in the pure argon atmosphere from that of nitrogen, such as the carbon G band shifted from 1592 to 1620 cm^{-1} as the average position, and 2230 to 2216 cm^{-1} for the -CN band average position.



(a) Uv-Raman spectra of Point 135 from Map of Tagish Lake Fragment B in an Argon Atmosphere with peak positions labelled at 1620, 2216, 2811, 2888, and 3610 cm^{-1} .

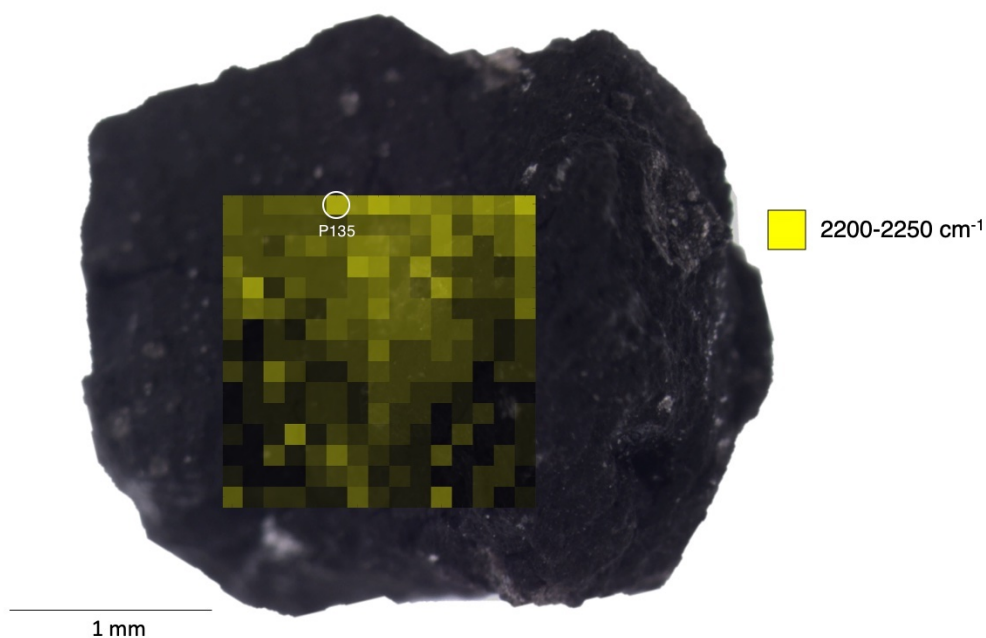


(b) Uv-Raman spectra of Point 135 from Map of Tagish Lake Fragment B in an Argon Atmosphere with Raman vibrational Mode Associations Labelled.

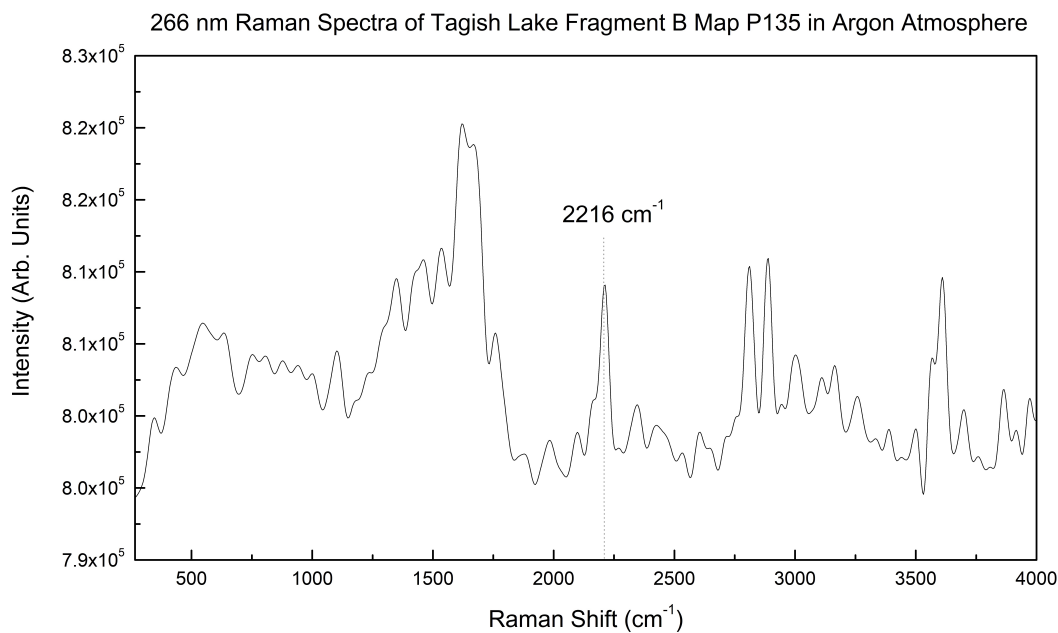
Figure 6.45: UV-Raman Spectra of isocyanate (-CN) peak at 2216 cm^{-1} in Tagish Lake Fragment B while under Argon Atmosphere.

The distribution of peak 2216 cm^{-1} (-CN) within fragment B is mapped in Figure 6.46. The distribution of the peak appears to have its own pattern and is concentrated in the centre of the map. This peak distribution does not appear to be noise because areas of high peak intensity are grouped together in a similar way to other organic or mineral distributions within these samples. Similarly to the Tagish Lake fragment A, the symmetrical face of Tagish Lake fragment B has some mineral peaks present in the regions of magnetite (650 cm^{-1}) and olivine (850 cm^{-1}). When mapping the 650 cm^{-1} peak on fragment B, the magnetite seems to be concentrated more in the central-top and right-top corner of the map (Figure 6.47). Similarly, when mapping the Raman peak 850 cm^{-1} , representing olivine (Figure 6.48), the intensity of the peak is focused in the center of the map, correlating to the light minerals, visible in the mapping area (Figure 6.44). Furthermore, when mapping the primary ($1600\text{--}1650\text{ cm}^{-1}$, Figure 6.49) and secondary carbon (2880 cm^{-1} , Figure 6.50) it is apparent that the carbon is fairly ubiquitous throughout the sample like in fragment A, but is notably absent in the bottom right corner of the fragment B mapping area.

Figure 6.51 shows examples of the Raman peak for -CN appearing within the fragment B mapping spectra at average $\sim 2216\text{ cm}^{-1}$. This peak seems to appear with secondary carbon peaks at $2800\text{--}2900\text{ cm}^{-1}$ in most instances, as well as with the -OH Raman peak at 3610 cm^{-1} occasionally. There are also some weaker peaks within the cyanate region highlighted ($2000\text{--}2300\text{ cm}^{-1}$) in Figure 6.51 at 2030 cm^{-1} , 2098 and 2100 cm^{-1} relating to isothiocyanate (-N=C=S), hydrogen cyanide (HCN) and thiocyanate $[\text{SCN}]^{-}$ respectively.

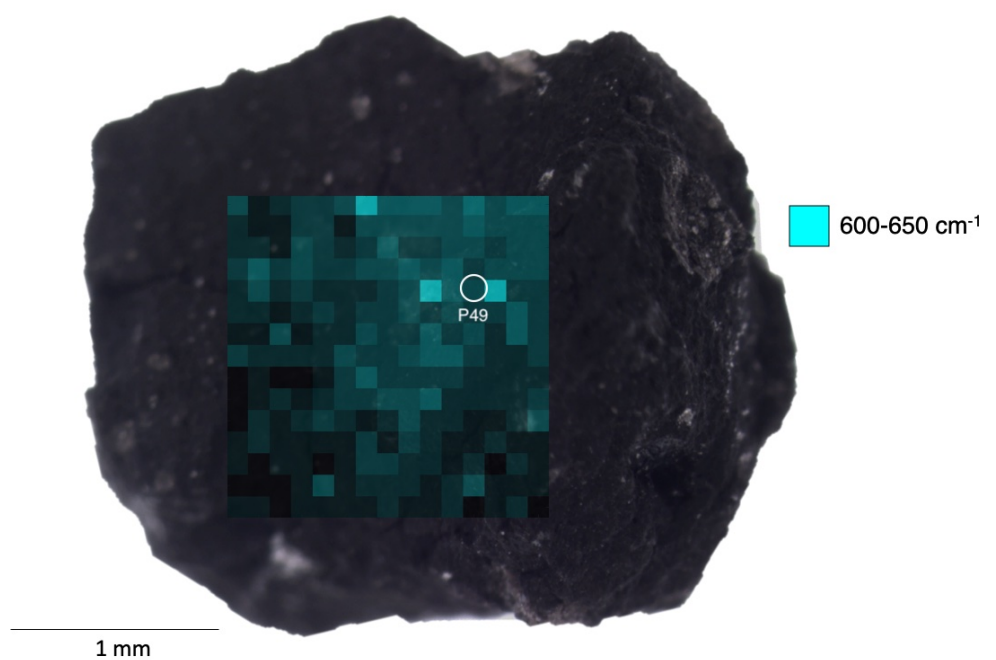


(a) 266 nm Raman map of -CN in Tagish Lake Fragment B at 2216 cm^{-1} in argon atmosphere (spectra not baseline corrected).

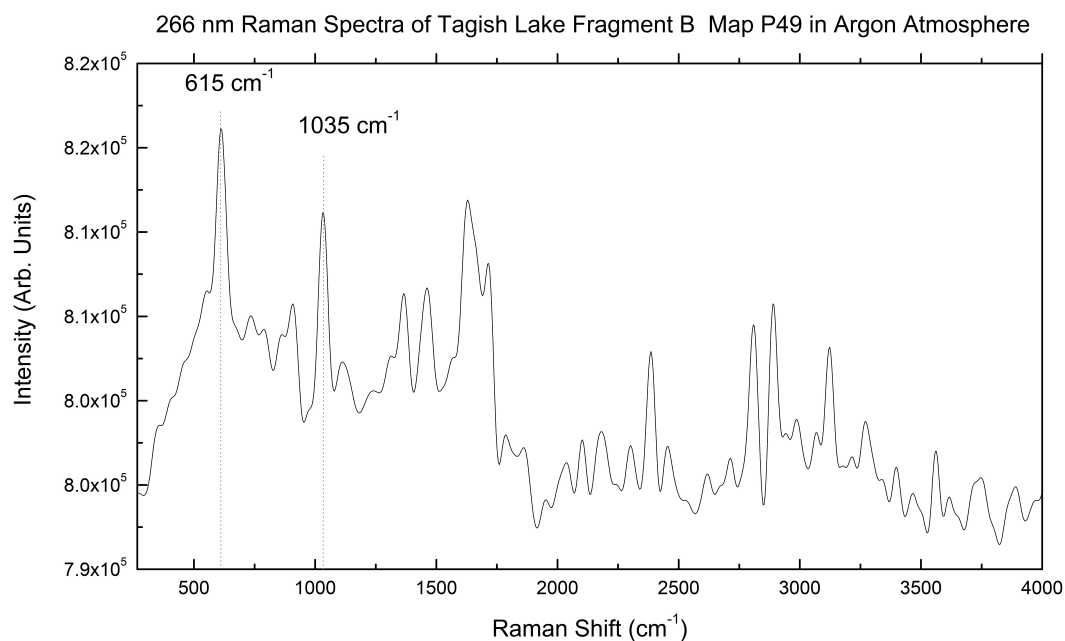


(b) 266 nm Raman spectrum from Tagish Lake Fragment B Map point 135, labelled with -CN peak at 2216 cm^{-1} while in argon atmosphere.

Figure 6.46: (a) 266 nm Raman map of -CN Peak at 2216 cm^{-1} (2200–2250 range) cm^{-1} in Tagish Lake fragment B while in pure argon atmosphere. Peak intensity shown as a function of brightness; and (b) 266 nm Raman mapping point spectra P135, showing a -CN Peak at 2216 cm^{-1}

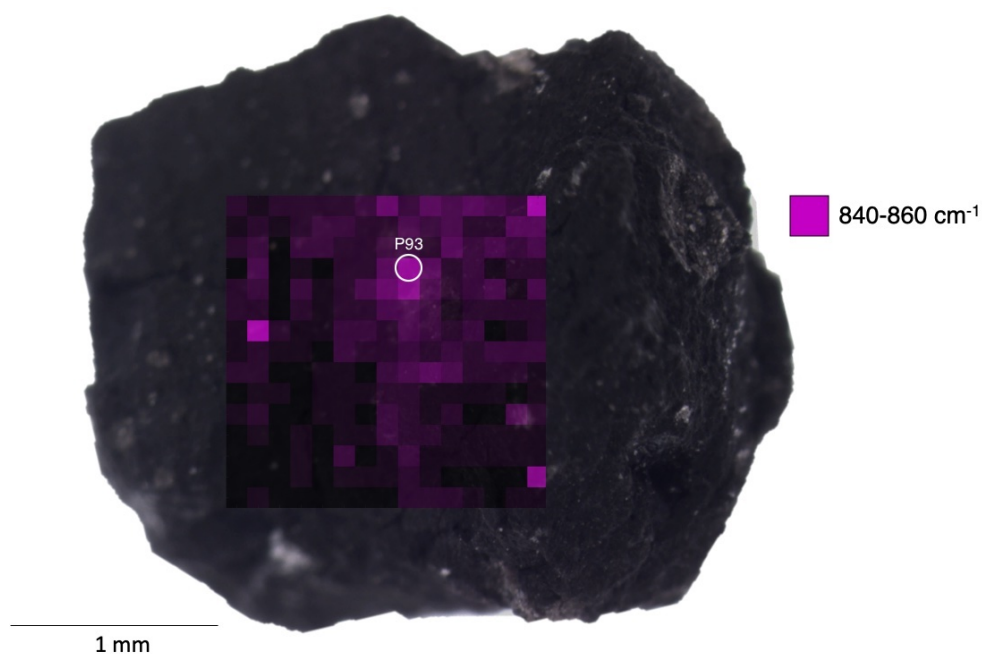


(a) 266 nm Raman map of phyllosilicate-like minerals in Tagish Lake at 615 and 1035 cm^{-1} in argon atmosphere (spectra not baseline corrected).

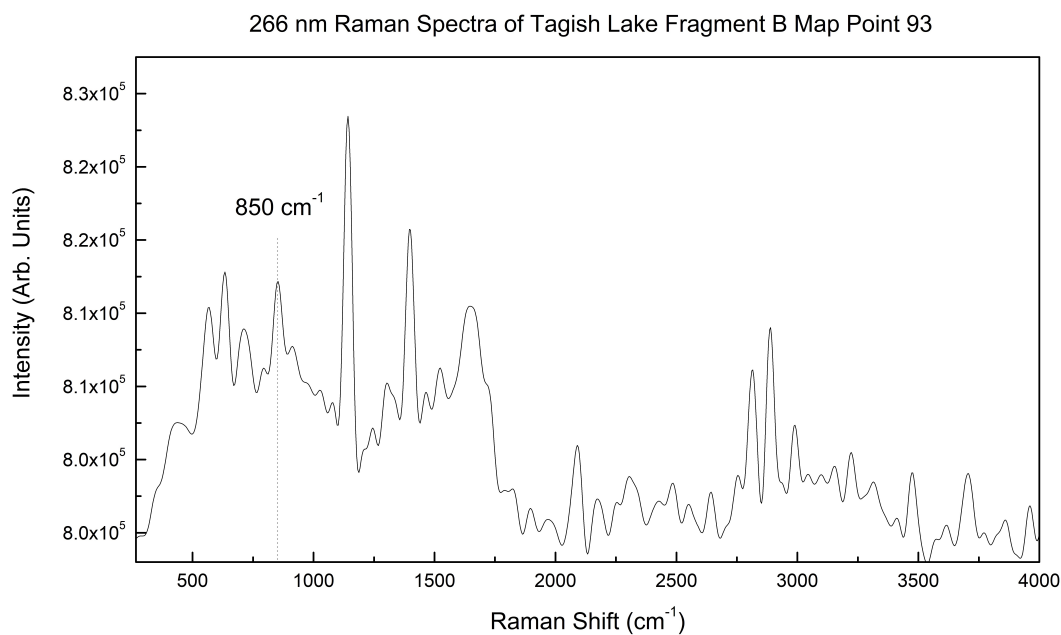


(b) 266 nm Raman spectrum from Tagish Lake Map point 49, labelled with phyllosilicate-like peaks at 615 and 1035 cm^{-1} .

Figure 6.47: (a) 266 nm Raman map of phyllosilicate-like peak centred around 650 (600–650 range) cm^{-1} . Peak intensity shown as a function of brightness; and (b) 266 nm Raman mapping point spectra P49, showing a phyllosilicate-like peak at 615 and 1035 cm^{-1} .

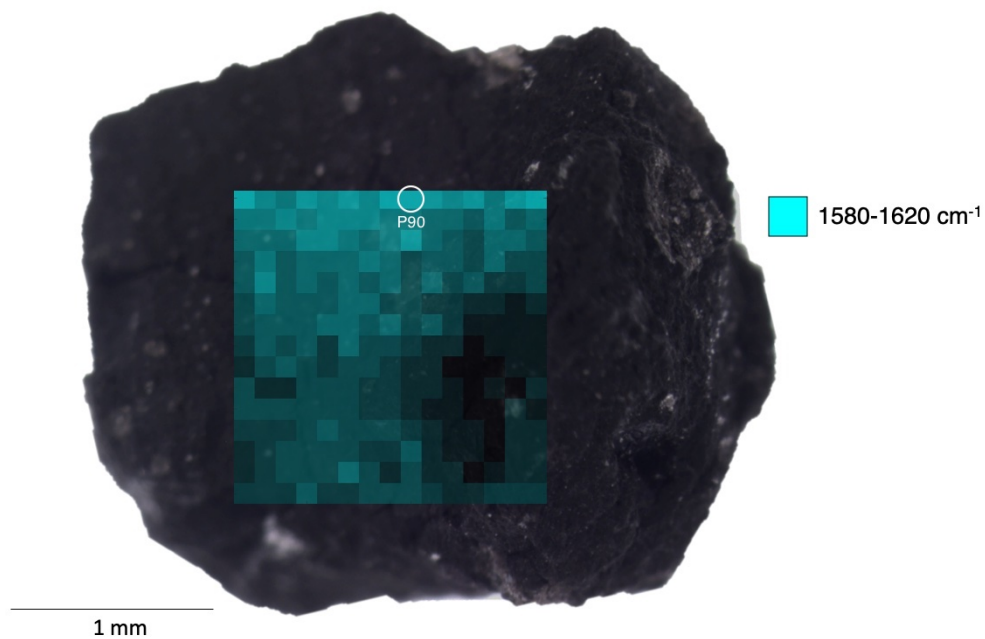


(a) 266 nm Raman map of olivine-like mineral in Tagish Lake Fragment B at 850 cm^{-1} in argon atmosphere (not baseline corrected spectra).

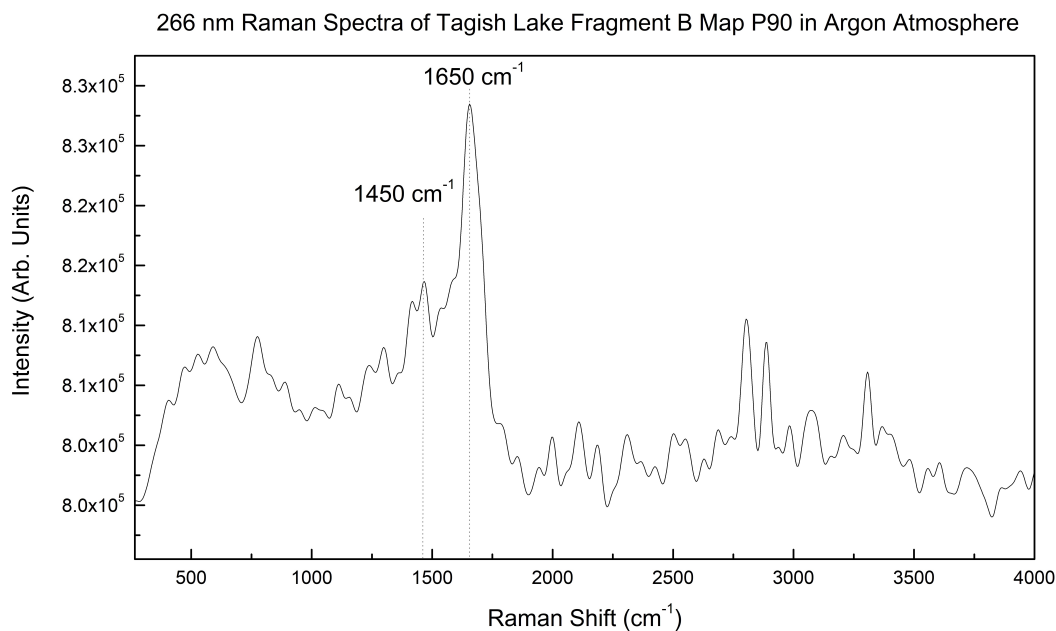


(b) 266 nm Raman spectrum from Tagish Lake Map point 93, labelled with olivine-like peak at 850 cm^{-1} .

Figure 6.48: (a) 266 nm Raman map of Tagish Lake fragment B olivine-like peak centred around 850 (840–860 range) cm^{-1} in an argon atmosphere. Peak intensity shown as a function of brightness; and (b) 266 nm Raman mapping point spectra P93, showing a olivine-like peak at 850 cm^{-1} .

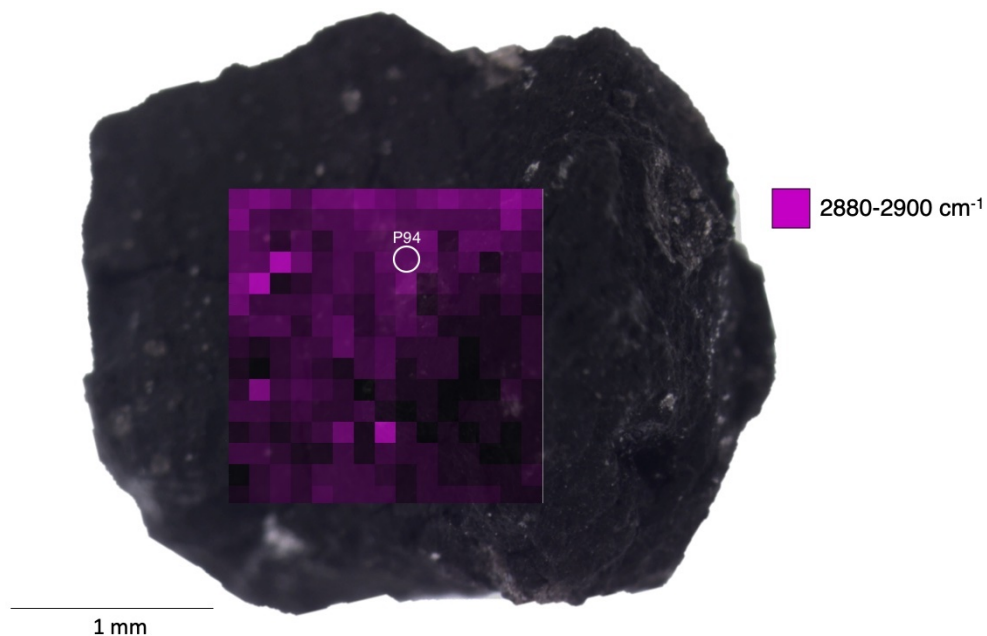


(a) 266 nm Raman map of carbon G band in Tagish Lake fragment B at 1600–1650 cm^{-1} in argon atmosphere (not baseline corrected spectra).

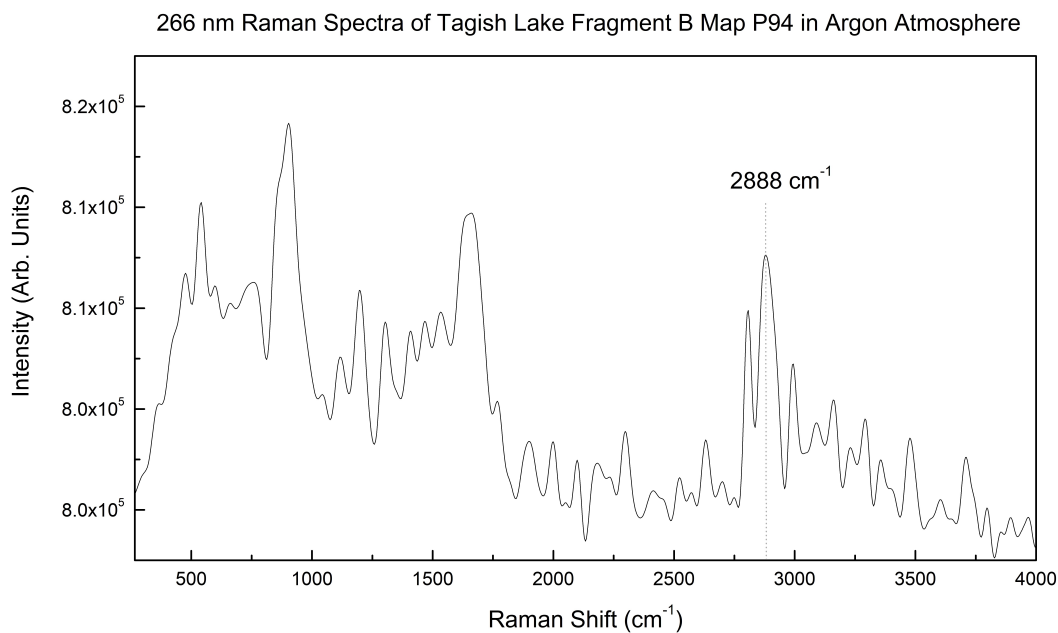


(b) 266 nm Raman spectrum from Tagish Lake fragment B Map point 90, labelled with carbon Raman G band at 1650 cm^{-1} in argon atmosphere.

Figure 6.49: (a) 266 nm Raman map of carbon Raman peak at 1650 cm^{-1} . Peak intensity shown as a function of brightness; and (b) 266 nm Raman mapping point spectra P15, showing carbon G band at 1650 cm^{-1} in argon atmosphere.



(a) 266 nm Raman map of aliphatic C-H stretching of secondary carbon in Tagish Lake Fragment B at 2880 cm^{-1} (not baseline corrected spectra).



(b) 266 nm Raman spectrum from Tagish Lake Fragment B Map point 94, labelled with secondary aliphatic carbon Raman peak 2888 cm^{-1} .

Figure 6.50: (a) 266 nm Raman map of secondary carbon Raman peak centred around 2880 cm^{-1} (2880–2900 range) cm^{-1} in Tagish Lake fragment B while under argon atmosphere. Peak intensity is shown as a function of brightness; and (b) 266 nm Raman mapping point spectra P94, showing secondary aliphatic carbon at 2888 cm^{-1} in Tagish Lake Fragment B while in an argon atmosphere.

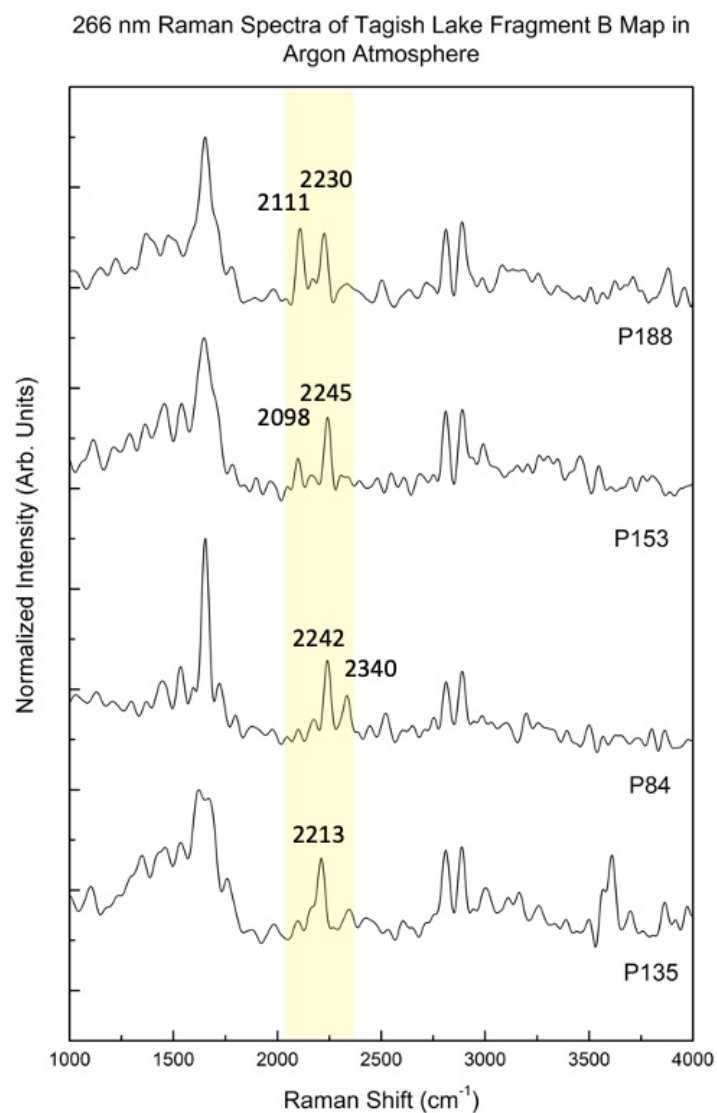


Figure 6.51: Examples of -CN Raman Peak $\sim 2216\text{ cm}^{-1}$ in Tagish Lake fragment B mapping area under argon atmosphere.

6.5 Discussion of the Tagish Lake Spectral Experiment Results

The study: *The Tagish Lake Meteorite Spectroscopic Experiment* is designed to use the ESCAPE system to collect Raman (266 and 532 nm) and Fluorescence (UV, LIF and TR-LIF) spectroscopy data products from a non-pristine piece of the Tagish Lake meteorite. A meteorite which is high in carbon content contains organic molecules such as amino acids and carboxylic acids – the primitive building blocks of life, and whose fall was observed and thus the samples collected relatively quickly from the surface of a frozen lake in Canada. The purposes of this study are multifaceted, to:

1. Validate the ESCAPE system as a useful tool for the analysis of minerals and organics of sensitive planetary materials while under specific environmental conditions.
2. Demonstrate the utility of UV Raman spectroscopy for detecting and identifying complex organic materials in carbonaceous chondrites.

Telescopic-Raman of the Tagish Lake meteorite is a daunting challenge as the fragments are very small (4 mm at their longest point) with even smaller (1 mm) features that are visible under a microscope and a large number of visible features appear to be olivine aggregates. The material is extremely fine-grained, dark, and fissile – posing issues for handling, analyzing and obtaining good spectral data from. However, all of these features also make the sample a close analogue to asteroid regolith from Bennu, set to return to Earth in late 2023 (Lauretta et al., 2022).

Green-Raman mapping of the Tagish Lake meteorite in a nitrogen atmosphere, while maintaining a temperature of $<-10^{\circ}\text{C}$; interestingly resulted in much of the spectra being overwhelmed by carbon D and G (disordered and graphitic) peaks. This result is interesting as the Tagish Lake meteorite may have up to 5 wt% carbon, however, most of the matrix material is extremely fine-grained phyllosilicates, which usually are not very Raman active and have very low signal-to-noise, even when analyzing phyllosilicates alone. The D& G band positions are in good agreement with results shown in Dobrică et al. (2011); Ferrari

and Robertson (2000); Matrajt et al. (2004); Nakamura et al. (2002). The FWHM of the D band within this study’s results, however, does appear to be larger than that in Dobrică et al. (2011); Matrajt et al. (2004). This is most likely due to either 1) how the spectra are cut and baseline corrected before a Lorentzian peak fit or 2) the FWHM is wider due to the slit opening being large at $250\text{ }\mu\text{m}$ in this study, reducing the spectra resolution to 35.3 cm^{-1} with the 600 lines/mm diffraction grating. The green-Raman spectral analysis also resulted in the detection of mineral peaks, suggested to be phyllosilicate-like (potentially saponite (Wang et al., 2015; Wang and Jolliff, 2015)), magnetite, olivine, calcite and potentially gypsum. These mineral identifications based on Raman spectra agree with the petrographic description of Tagish Lake by Zolensky et al. (2002); Izawa et al. (2010). This study also produced 2D maps of each mineral (and inorganic carbon) peaks, which appear to be correlated to visible features within the microscopic images of the mapping face of the Tagish Lake meteorite, further suggesting that 2D Raman maps can visualize the distribution of these minerals within very fine-grained, carbon-rich materials.

UV-mapping of the Tagish Lake meteorite in a nitrogen atmosphere, while maintaining a temperature of $<-10^{\circ}\text{C}$, also resulted in much of the spectra being overwhelmed by carbon and in this case, mostly a carbon G band. The results of UV mapping also suggest that the carbon G band is slightly higher in Raman shift from that of Green-Raman, which agree with results such as Dobrică et al. (2011). This shift can also be attributed to the carbon 2D band located just above 1600 cm^{-1} , which is activated more intensely using UV Raman compared to green, which can convolve with the carbon G band and therefore make it seem as if the Raman shift of the peak is slightly higher. Ferrari and Robertson (2000) also suggests that the carbon D & G bands are resonant, and therefore Raman shift slightly changes depending on Raman excitation wavelength (increases cm^{-1} with decreasing excitation wavelength). The UV Raman spectral results of this study suggest similar mineral identifications to that of green-Raman mapping, with the detection of spinel, phyllosilicate-like minerals and olivine. The UV spectral data also suggests that there is significant aliphatic and aromatic carbon

within the sample which is in agreement with Matrajt et al. (2004); Pizzarello et al. (2001); Nakamura-Messenger et al. (2006). The UV Raman spectra from this study also imply that there may be ketones and cyano radicals (-CN, SCN, HCN) within the sample. These results are often seen in the same point spectra as aliphatic or aromatic carbon peaks and sometimes O-H Raman peaks, suggesting there is a complex organic nature to the sample, detectable by UV Raman. The detection of -CN within the UV Raman spectra in a nitrogen environment prompted a secondary, repeated experiment of similar nature, wherein the sister fragment (fragment B) to the original study was analyzed in a pure argon atmosphere with UV Raman. Within these secondary UV Raman data, we repeatably identify -CN within the spectra, suggesting that it is within the sample and not be synthesized by the nitrogen atmosphere and UV laser. When we map the distribution of this -CN peak, the peak intensity map does not appear to be noise as it seems to have a pattern, somewhat correlating with the carbon in the fragment. The natural question that arises from this identification is why does there appear to be such an abundance of cyano radicals in the sample, and why are the peaks so intense in relation to the carbon D & G bands, especially compared to the limited studies of -CN Raman spectra in the literature (Ferrari et al., 2003; Dobrică et al., 2011). It has been postulated by (Pizzarello, 2012), after finding ≤ 10 ppm HCN in the Murchison meteorite, that other asteroids that have not gone through such intense cyanohydrin reactions (see section 1) as the Murchison meteorite parent body clearly has by its amount of amino acids present, they would expect to see much more HCN present within a sample. What has been interesting about the Tagish Lake meteorite, is that it has extremely high organic content in the form of aliphatic and aromatic hydrocarbons, but has relatively low abundances of amino acids compared to that of other carbonaceous chondrites like the Murchison meteorite (Pizzarello et al., 2001; Kminek et al., 2002; Glavin et al., 2012, 2020). This low abundance of amino acids may provide an explanation as to why there is such a high abundance and intensity of -CN peaks within the Tagish Lake meteorite. Furthermore, despite low concentrations of amino acids, curiously, an abundance of nitriles and cyano

species were found within the Tagish Lake meteorite by Pizzarello et al. (2001); Gilmour et al. (2001). The spectral results of this study show the first instance (that the author is aware of), of cyano radicals found by Raman analysis within the Tagish Lake meteorite. As established by the literature surrounding abiotic synthesis of amino acids on asteroid parent bodies (Pizzarello, 2012; Glavin et al., 2020, 2012), HCN plays an important role in chemical pathways to produce such amino acids through Strecker-synthesis and HCN polymerization (section 1). Furthermore, finding a low abundance of amino acids and a seemingly high abundance of cyano radicals within a single sample suggest that the hypothesis by Pizzarello (2012) may be correct, in that a parent body that has not gone through intense aqueous alterations with cyanohydrin reactions, then there may be an abundance of HCN leftover from the solar nebulae. The heterogeneous and complex nature of the Tagish Lake meteorite may mean that this discovery would not be in all of the Tagish Lake fragments, and thus more fragments should be analyzed with UV Raman for -CN peaks that have undergone aqueous alteration to better understand this relationship.

UV-Raman spectra also showed a unique feature in this study — the ability to resolve nitrogen gas from the atmosphere. These N_2 peaks were distinct when mapping within a pure nitrogen environment, but also were visible when mapping in air. To confirm that this peak was in fact N_2 from the atmosphere, and not contamination or an artifact produced by the UV laser interrogation further investigation was accomplished. The first study of collecting data from anything the sample came in contact with (nitrile gloves, packaging, paper etc.) indicates that it was most likely not a contamination problem. The results of a small study verified the hypothesis — where an N_2 peak was located on the sample while it was in air, the air was pumped from the chamber and the peak in the same location was gone. The same results were produced in a pure argon atmosphere - no peak of N_2 was formed from the UV analysis. These results suggest that UV-Raman can resolve N_2 gas easily when there is a low signal-to-noise, and this future studies of carbonaceous material in argon gas should be considered.

Although this study shows data preparing to detect amino acid spectral signatures in meteorite and asteroid materials, there were no such signals detected in the Tagish Lake meteorite. This is somewhat of a reasonable result as there are measured amino acid concentrations of only 0.1 ppm in some pieces of the Tagish Lake meteorite (Pizzarello et al., 2001). It was important, however, to have the spectra available as a database from amino acids that have been found in such materials to compare to and ensure that we could have a positive identification with the system if amino acids were present in concentrations high enough to detect with Raman and fluorescence spectroscopy (possibly 50 – 100 ppm).

The results of the UV Raman mapping spectral, similar to that of green-Raman also show a good correlation between mineral peak intensity distributions with features within the samples, indicating that the visible features are most likely larger-grained minerals surrounded by extremely fine-grained carbon and phyllosilicate-rich matrix. Similarly, UV Fluorescence maps have a high correlation between areas of bright peak intensity on the maps and features within the sample - however, the main difference is that the matrix is mostly devoid of fluorescence, and thus the features become very prominent. The lack of ability to identify minerals based on fluorescence is somewhat tied to the limitations in spectral databases like that of the Raman mineral database RRUFF by Lafuente et al. (2016). However, a benefit of fluorescence which may make up for the lack of identification is its unique speed. The average Raman map in this study took 20 hours to collect, whereas the fluorescence map and TR points of interest were all collected within 4 hours. This quick acquisition time should be utilized as a triage technique for larger samples when searching for mineral or organic points of interest – followed by in-depth Raman analysis for better identification. These results are in good agreement with that of Lymer et al. (2020), where LIF was suggested as a triage or preliminary analysis technique for carbonaceous chondrites.

This study was conducted on a small (non-pristine) fragment of the Tagish Lake meteorite, and further studies could include using a pristine piece of meteorite and repeating the experiments in an argon atmosphere to see if the results are in agreement. Furthermore,

chemical analysis beyond FTIR and SEM can be undertaken of fragments A and B to analyze the mineral components present as the samples can be heterogeneous from each other and could provide useful context to the Raman identifications made in this study. Future work could also include a small volatile study on a pristine piece of the Tagish Lake meteorite, as the ESCAPE system was designed to have the potential integration with a mass spectrometer. The sample could be placed in the chamber at a cold temperature and slowly warmed and the volatiles emitted from the sample could be analyzed with mass spectrometry. Moreover, a study into the viability of TR-LIF decay rate calculations on materials that have low signal-to-noise ratio such as the Tagish Lake meteorite should be accomplished to determine if higher TR fluorescence emission is possible with longer acquisition times.

Practically, this study validates the ESCAPE system's use as a tool to detect and identify mineralogical and organic constituents within sensitive planetary materials while maintaining specific environmental conditions; thus can be put to use in a myriad of ways for planetary science and exploration studies mimicking other bodies environments, while interrogating samples in a minimally destructive way with Raman and fluorescence spectroscopy. Since the design and implementation of the system, it has been requested by other researchers to analyze shocked feldspars, mars analogues, and other carbonaceous chondrites. Moreover, the system was designed with the intent to be modular, and therefore can be used as a stand-off telescopic Raman and fluorescence instrument independently from the chamber environment, or conversely, the chamber can be used with other breadboard instrumentation.

7 Conclusions

This dissertation presents the ESCAPE system, a combined Raman and TR-LIF instrument with an environmental chamber built at York University to perform minimally destructive spectroscopic point and mapping analyses on sensitive planetary materials while sustaining conditions conducive to maintaining sample pristineness. The ESCAPE system combines 266 and 532 nm Raman, LIF and TR-LIF spectroscopy into a single instrument, integrated with an environmental chamber capable of temperatures below -20°C , pressure $<10^{-5}$ mbar, and variable atmospheric composition depending on the sample needs. The spectroscopic performance is on par or better than flight and laboratory instruments (such as SHERLOC, SuperCam and LIRS) previously published in Wiens et al. (2021b); Shkolyar et al. (2021). In this manuscript we have outlined the three main ‘modes’ of operation for the ESCAPE system:

1. Raman spectroscopy mode (266 or 532 nm excitation)
2. Laser-Induced Fluorescence Mode (266 or 532 nm excitation)
3. Time-resolved laser-induced fluorescence mode (266 or 532 nm excitation)

These modes allow for time-efficient detection and identification of both minerals and organic constituents within a sample. Point analysis, 2D raster mapping, and time-resolved analysis are possible with the ESCAPE system. Using laboratory standards, it is found that the spectral resolution is great enough to resolve mineral peaks such as the olivine SiO_4 doublet using green-Raman spectroscopy and water O-H doublet using UV-Raman spectroscopy. This finding is important, as most geologic experiments would require such resolution to differentiate between end-members of mineral groups to discern composition (such as fayalite and forsterite in the olivine group of minerals). These particular doublets, serve as an indication of the high spectral resolution of the system in a practical application. Furthermore, to determine the capabilities of the system at detecting low concentrations of organics in a

substrate, laboratory-made doped samples are analyzed. A series of varying concentrations of tryptophan in a substrate indicates that the ESCAPE system can at the very least detect 50 ppm tryptophan in gypsum using UV and Green Fluorescence spectroscopy. This result demonstrates the usefulness of fluorescence instrumentation in detecting small amounts of organic materials in a substrate, similar to what would be investigated during the ‘search for life’ in planetary samples.

To determine if UV Fluorescence spectroscopy and time-resolved laser-induced fluorescence (TR-LIF) are useful for the detection and possible identification of organics and contamination in snow and water samples, eight samples are collected and analyzed in the ESCAPE system. These samples include a collection of fresh snow from around Toronto, Lake Ontario water, Tap water, Sterile water, and laboratory-made doped samples of tryptophan and tyrosine in water at varying concentrations ($<1\text{--}0.25\text{ mM}$). Analysis of the samples utilized a specific technique of spectroscopy where light is passed through the sample using an additional mirror, called transmissive Raman/Fluorescence. This technique allows the constituents within the water column to be analyzed while in a quartz cuvette, rather than just reflecting off the surface. UV-Raman is collected of each sample, showing only slight variation in Raman O-H peak positions, and resulted in no vibrational modes for the aromatic amino acid-doped samples, tryptophan and tyrosine. Furthermore, FTIR analysis is completed on all the samples, also showing very little and barely differentiable variation between spectra. UV-LIF and TR-LIF, however, result in unique spectra and ‘fingerprints’ of each sample. The LIF and TR-LIF results are differentiable enough to identify specific components, such as pure water, mineral contamination and organic constituents based on their shapes and locations in the ‘fingerprint’. Calculated decay rates are in good agreement with that of (Lymer et al., 2021; Shkolyar et al., 2021) for tryptophan and tyrosine and indicate that there is a relationship between the concentration of organic and the fluorescence lifetime that is somewhat predictable, where higher concentrations of organics result in lower τ values compared to their lower concentration counterparts. The fluorescence results of this

study as a whole are in agreement with Eshelman et al. (2019) and imply that UV fluorescence is an exceedingly useful technique for organic and contaminant detection in water samples compared to that of Raman and FTIR analysis. Furthermore, this study indicated the potential usefulness of a UV fluorescence instrument to search for biosignatures in water or ice, such as a flight instrument on an icy body like Enceladus.

While fluorescence emission has often been seen as a hindrance to Raman spectroscopy, a large portion of this work is to demonstrate the viability of UV fluorescence instrumentation in several different applications. To further understand the usefulness of fluorescence spectroscopy for planetary exploration, Lunar analogue samples are made to contain synthesized REE-phosphates that are thought to produce high fluorescence/phosphorescence like organics. These samples are similar to the basaltic materials that would be searched for on the Lunar surface containing important trace elements for manufacturing components needing REEs, as propositions of a ‘Lunar space-base’ continue. Rare Earth elements (REEs) yttrium and cerium have been found in concentrations of around 300 ppm in KREEP basalts on the moon (Crawford, 2015). To understand if fluorescence spectroscopy could detect these elements, varying concentrations (1000, 2000, 5000, 10000 ppm) of synthesized CePO_4 and YPO_4 are added to Lunar mare simulant (LMS-1). Using $\lambda_{Ex} = 532$ nm, Raman vibrational peaks are observed of the CePO_4 and YPO_4 on their own, but no discernible Raman peaks of LMS-1. Furthermore, green fluorescence did not seem to excite the samples in such a way to create discernible fluorescence emission. Conversely, UV interrogation produces strong fluorescence emission of Ce and weaker emission of Y Fluorescence. The intensity of CePO_4 fluorescence increases linearly with an increasing concentration within the LMS-1 substrate, whereas that of YPO_4 does not. The results of this study are in agreement with that of Fuchs et al. (2021), where $\lambda_{Ex} = 532$ nm does not induce fluorescence emission from CePO_4 or YPO_4 , but may with other REEs. Fuchs et al. (2021) also suggests that YPO_4 does not have its own fluorescence emission, but rather only emits fluorescence of Ce contamination within the sample. The implication of this result being true, suggests that the results of

YPO₄ fluorescence spectra in this study may also be Ce contamination, implying that UV fluorescence can detect incredibly small amounts of Ce in lunar mare analogue materials, on the order of 2–10 ppm. This study indicates UV fluorescence as an exceedingly good technique for detecting small amounts of REEs in a Lunar analogue substrate and suggests that if there were lunar exploration instrumentation being produced for the detection of REEs on the surface, UV-LIF should be considered.

Finally, to validate the ESCAPE system as a tool for the spectroscopic analysis of sensitive planetary materials while under controlled conditions to sustain pristineness, the Tagish Lake meteorite is analyzed using Raman, fluorescence and TR-LIF. This study not only verifies the capabilities of the system to sustain temperatures and atmospheres conducive to limiting oxidation reactions and maintaining volatile constituents in a sensitive, carbon-rich material - but also provides some of the most in-depth spectroscopic analyses of a carbonaceous chondrite thus far. Green-Raman, UV-Raman, UV-Fluorescence and UV time-resolved fluorescence are all conducted on the Tagish Lake meteorite in this study, resulting in comprehensive spectral maps of mineral and organic distribution in areas on the sample and show the complexities of such a fine-grained, dark, fissile material. From these spectroscopic results, a comprehensive analysis of the carbon and nitrogen species within the sample take place, showing agreement in the inorganic carbon compositions through peak positions using green-Raman to that of Dobrică et al. (2011); Matrajt et al. (2004), indicating that the most-intense carbon components of the sample are disordered aliphatic and aromatic hydrocarbons. Furthermore, the identification of minerals using green and UV-Raman are in agreement with the comprehensive petrographic descriptions of the sample by Zolensky et al. (2002); Izawa et al. (2010), where calcite, olivine, gypsum, magnetite, and phyllosilicate-like minerals are detected. Unfortunately, there was no positive identification of amino acids within the Tagish Lake meteorite using Raman or fluorescence spectroscopy in this study – however, due to their relative abundance being around ≤ 0.1 ppm within Tagish Lake, it is a reasonable result. Even though there are limited amino acids within Tagish Lake, there

may be abundant amino acids present within future samples returned from missions like OSIRIS-REx, and therefore it is important to analyze these amino acids using Raman and fluorescence spectroscopy to obtain spectral data that would allow for a positive identification of such material in the future.

Moreover, the detection of species within the nitrogen Raman region resulted in the identification of cyano radicals, an extremely important reagent in the cyanohydrin system, from which amino acids can be abiotically synthesized from. This result is the first detection of a -CN species within the Tagish Lake meteorite and has great implications for the understanding of the early parent body formation and prebiotic reactions that took place. The Tagish Lake meteorite has been somewhat of an enigma in the astrobiology circle, as it was expected to contain some of the largest abundances of amino acids yet found in carbonaceous chondrites because of its superb preservation; however, the fragments were found to have relatively low amino acid abundance and were severely heterogeneous in nature compared to that of the Murchison meteorite. The detection of -CN, at a such regular frequency in a fragment and in such intensity using UV-Raman provides an explanation as to why there are so few amino acids present, as the body had not yet gone through enough aqueous alteration with cyanohydrin reactions to use up most of the cyano radicals like HCN present. This study demonstrates the usefulness of UV-Raman in detecting and identifying complex organic materials within severely fine-grained, dark, fissile, planetary materials similar to what may be returned from asteroid Bennu by the OSIRIS-REx mission. Furthermore, this detection and identification were made while there was no sample preparation, coating or destruction and while under environmental conditions that maintain sample pristineness.

With hundreds of millions to billions of dollars currently being proposed to spend on the contamination protocols and non-destructive analyses of samples returned from asteroids and Mars in the near future, the experiments of this study show that non-destructive techniques such as Raman and fluorescence spectroscopy should be considered, as well as small-scale laboratory chamber systems for such analyses to gain foundational chemical in-

formation from samples at an extremely low cost in comparison to what is being proposed. The experiments in this study validate the ESCAPE system as a useful tool for laboratory experimentation for planetary science and exploration, but also a potential technique for the preliminary analysis of sensitive materials returned from space. the ESCAPE system is capable of conducting non-destructive chemical analysis of very small, fragile, rocky materials and should be seriously considered as a technique for the detection of organics within asteroid-sample return material in the future brought back from missions such as OSIRIS-REx and can be used as an experimental system to inform the Earth-based preparations for Mars sample-return materials. The results of such data collected on primitive samples returned from space could provide insights into the formation and evolution of our solar system and help answer questions of how the ingredients for life on Earth formed in the early solar system.

8 Future Work

8.1 Continuation of the Tagish Lake Experiment

In this study, a non-pristine piece of the Tagish Lake meteorite was utilized. I propose, that future studies use a pristine piece of the meteorite to confirm volatile and organic components. A number of future studies could be completed using the system and a pristine piece of the meteorite, including repeating the argon experiment to ensure that -CN is detectable in other fragments and a volatile identification experiment. The volatile experiment would require the connection of a mass spectrometer to the chamber (such as the portable mass spectrometer in the PIL laboratory). When the mass spectrometer is attached, the pristine, frozen sample would undergo slow temperature increases until it is above 0°C, to release volatile components such as aldehydes, carboxylic acids, etc. The potential risks are that the sample would be too small to result in any detectable volatiles by the mass spectrometer, however, trials can be completed using laboratory synthesized samples in similar proportions

before the pristine piece of Tagish Lake is used. Furthermore, for this study, the chamber would have to be decontaminated – meaning a method for cleaning and testing to make sure there are no contaminants within the chamber is also needed.

Furthermore, to better understand the concentration of cyano radicals within different fragments of the Tagish Lake meteorite, a study should be conducted using GC-Mass spectrometry to obtain a quantification of HCN, -CN and other potential species found within the nitrogen region using UV-Raman. These results can be compared to those in Pizzarello (2012), whose results show the abundance of HCN within the Murchison meteorite, which has undergone extensive cyanohydrin reactions to form a large abundance of amino acids.

8.2 Using the ESCAPE System for Planetary Science Laboratory Experimentation

Subsequent to this dissertation, the ESCAPE system should be used as a laboratory tool for different planetary science and exploration projects that are in need of a chamber environment to mimic a planetary body, spectroscopic analyses, or both at the same time, as the ESCAPE system is designed and built to be flexible, interchangeable and accommodate the needs of different experimental setups. For example, the gas hookup allows for inert, or non-inert gases to fill the chamber ranging from nitrogen to argon to carbon dioxide. Temperature can be sustained at $<-30^{\circ}\text{C}$ to potentially warming temperatures, or incrementally increased/decreased to accommodate a freezing or warming experiment via PID control box. The pressure can range from the airless body to Mars atmospheric conditions (or positively pressurized with gas) and can be monitored via a pressure gauge connected to a Python readout. The chamber is modular in nature and can be integrated with other optical instrumentation such as LIBS/LAMIS or mass spectrometry. Furthermore, spectroscopic studies can utilize a singular wavelength (532 nm, 266 nm) or interchange between the two, allowing for analysis of Fe-rich Mars analogue material, to carbon-rich asteroid materials. 2D spectral maps, point analyses, and 3D TR-LIF fingerprints can all be collected using the system on

a myriad of samples such as liquids, other meteorites, laboratory analogues and samples returned from space.

8.3 Modifications to the ESCAPE System

Modifications and improvements should be made to the ESCAPE system over time to fit the needs of the average user or for specific intended uses such as if sample-return mission materials are available for analysis. Such improvements could be integrating a liquid nitrogen cooling system for the entire chamber, instead of just the sample stage being cooled. Future analysis may require modification to the optical system, such as adding a microscope objective before the collection optics to reduce the spot size and potentially increase the spatial resolution and accuracy of 2D mapping.

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Appendices

A TR-LIF Decay Rate Code

Example of the decay rate calculation of tryptophan:

```
% 1. Read the data
filename = 'Tryptophan.txt';
data = importdata(filename);

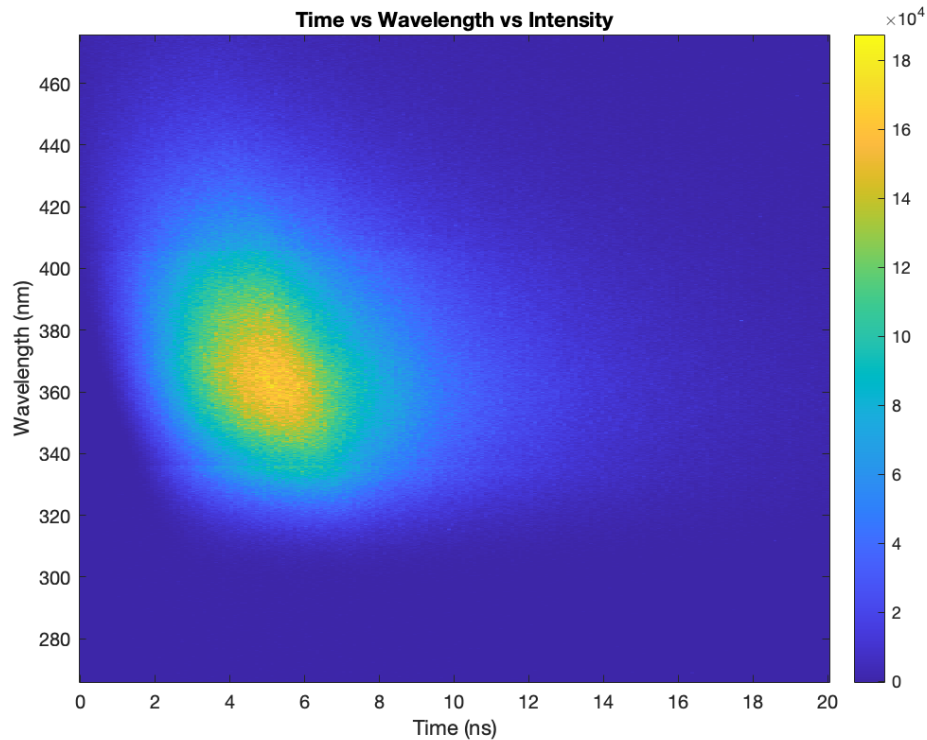
% 2. Determine the wavelength region for each spectrum
wavelength = data(:, 1);
intensity = data(:, 2:end);
times = linspace(0, 20, size(intensity, 2));

% 3. Smooth the data
smooth`intensity = zeros(size(intensity));
for i = 1:size(intensity, 2)
    cfit = fit(wavelength, intensity(:, i), 'smoothingspline');
    smooth`intensity(:, i) = feval(cfit, wavelength);
end

% 4. Plot Time vs Wavelength vs Intensity in 2D color-map
figure;
imagesc(times, wavelength, smooth`intensity);
colorbar;
title('Time vs Wavelength vs Intensity');
xlabel('Time (ns)');
ylabel('Wavelength (nm)');
set(gca, 'YDir', 'normal');

% Plot Wavelength vs Time vs Intensity in 2D color-map
figure;
imagesc(wavelength, times, smooth`intensity);
colorbar;
title('Wavelength vs Time vs Intensity');
xlabel('Wavelength (nm)');
ylabel('Time (ns)');
set(gca, 'YDir', 'normal');

% 5. 2D plot of Time vs Intensity at designated lambda (max intensity
% wavelength
idx`355nm = find(wavelength == 355);
% Find the index of the closest wavelength value to 355 nm
```



```
[ , idx] = min(abs(wavelength - 355));
```

```
% 6.Extract the intensity values at the closest wavelength index
intensity`355nm = intensity(idx, :);
```

```
% Smooth the normalized intensity values (Option 1 - moving average filter)
window`size = 5; % Adjust the window size to change the smoothing level
b = (1/window`size) * ones(1, window`size);
```

```
% Normalize the intensity`355nm values
intensity`355nm`normalized = intensity`355nm / max(intensity`355nm);
```

```
% Smooth the normalized intensity values using a moving average filter
intensity`355nm`smoothed = filter(b, 1, intensity`355nm`normalized);
```

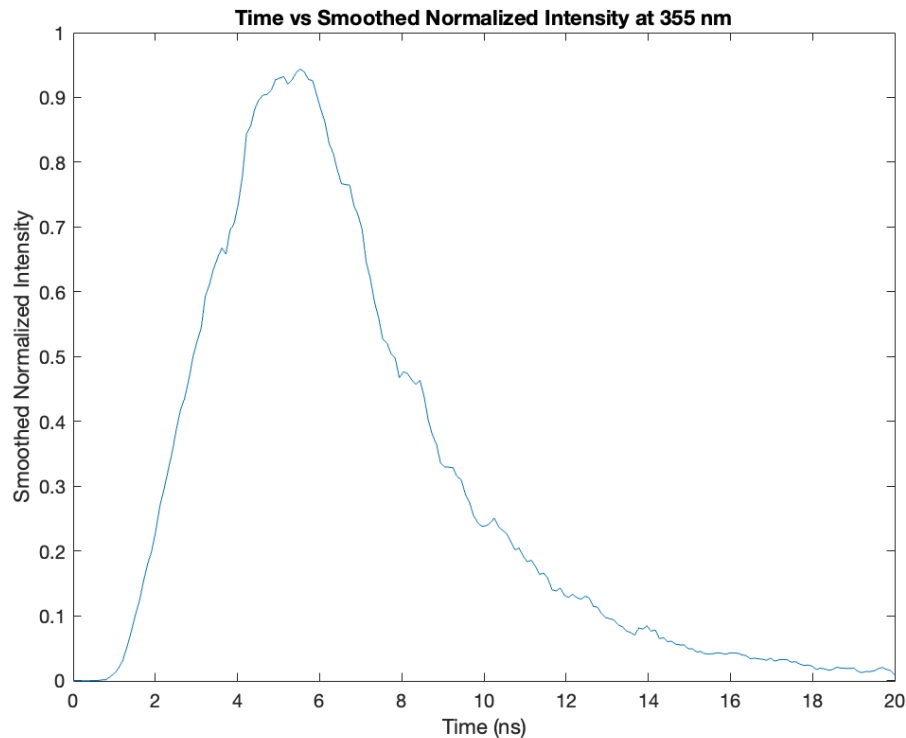
```
% Smooth the normalized intensity values (Option 2 - using smooth function)
intensity`355nm`smoothed = smooth(intensity`355nm`normalized, window`size);
```

```
figure;
plot(times, intensity`355nm`smoothed);
title('Time vs Smoothed Normalized Intensity at 355 nm');
xlabel('Time (ns)');
ylabel('Smoothed Normalized Intensity');
```

```

disp(['Length of times: ', num2str(length(times))]);
disp(['Length of intensity'355nm'smoothed: ',
num2str(length(intensity'355nm'smoothed))]);

```



```

% 7. Find the index of the time step with the highest intensity at 355 nm
[max'intensity'355nm, max'idx] = max(intensity'355nm);
tmax = times(max'idx);
disp(['Highest intensity value at 355 nm: ', num2str(max'intensity'355nm)]);
disp(['Corresponding time: ', num2str(tmax), ' ns']);

% Find the index of the first value greater than or equal to max'intensity'355nm
first'greater'idx = find(intensity'355nm >= max'intensity'355nm, 1);

% Create a new array starting from first'greater'idx
intensity'355nm'trimmed = intensity'355nm'(first'greater'idx:end);
% 9. Update the times array to match the new intensity'355nm'trimmed array
times'trimmed = times(first'greater'idx:end);

% Plot the new Figure for the Decays
figure;
plot(times'trimmed, intensity'355nm'trimmed);
title('Trimmed Time vs Intensity at 355 nm');

```



```

xlabel('Time (ns)');
ylabel('Intensity');

times`trimmed` = times`trimmed` - tmax;

% Plot the updated arrays with Tmax out
figure;
plot(times`trimmed`, intensity`355nm`trimmed);
title('Time (Subtracted by tmax) vs Intensity at 355 nm');
xlabel('Time (ns)');
ylabel('Intensity');

% 10. Normalizing the values for calculations
% Calculate the absolute value of intensity`355nm`trimmed
intensity`355nm`trimmed`abs` = abs(intensity`355nm`trimmed);

% Normalize the intensity values
intensity`355nm`trimmed`abs`normalized` = intensity`355nm`trimmed`abs` /
max(intensity`355nm`trimmed`abs);

% Plot the updated arrays
figure;
plot(times`trimmed`, intensity`355nm`trimmed`abs`normalized);
title('Time (Subtracted by tmax) vs Normalized Absolute Intensity at 355 nm');
xlabel('Time (ns)');
ylabel('Normalized Intensity');

% 11. Life and decays for the Amino-acid the values doesn't work for curvefit.

% Define the mono-exponential decay function
decay`fun` = @(params, t) params(1) * exp(-t ./ params(2)) + params(3);

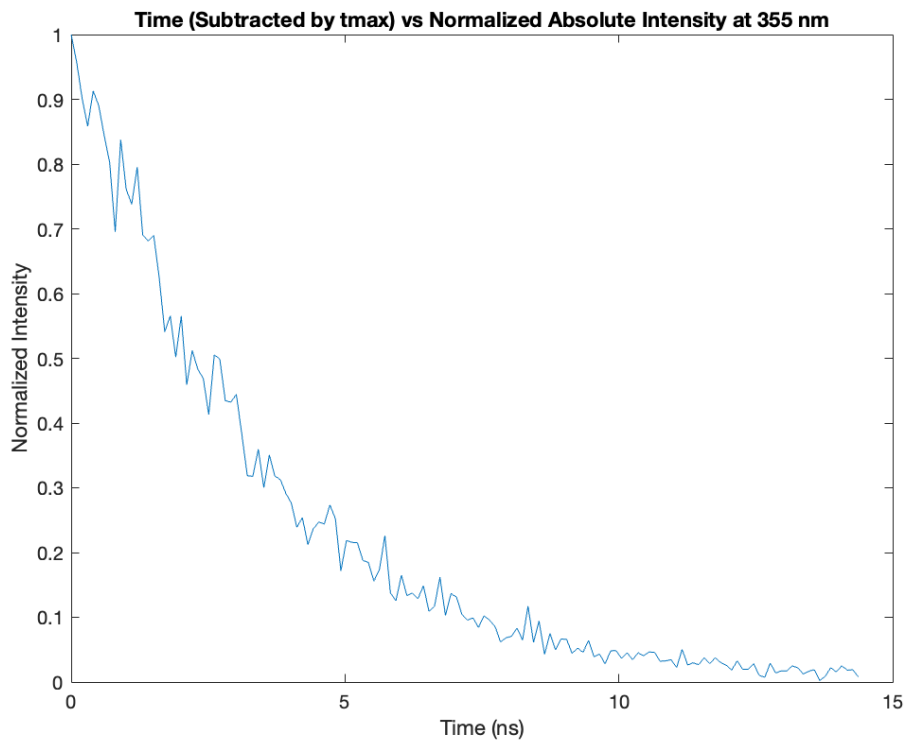
% Set the lower and upper bounds for the parameters
lower`bounds` = [0, 0, 0];
upper`bounds` = [max(intensity`355nm`trimmed`abs`normalized), 10 * tmax, 1];

% Set the initial guess for the parameters
initial`guess` = [1, 1, 0];

% Fit the data using lsqcurvefit
[params`fit`, ] = lsqcurvefit(decay`fun`, initial`guess`, times`trimmed`,
intensity`355nm`trimmed`abs`normalized`, lower`bounds`, upper`bounds`);

% Calculate the fitted curve using the optimized parameters
fitted`curve` = decay`fun`(params`fit`, times`trimmed`);

```



```
% Plot the curve fit along with the data - If you want to see the decay
figure;
plot(times'trimmed, intensity'355nm'trimmed'abs'normalized, 'b.', 'MarkerSize', 10);
hold on;
plot(times'trimmed, fitted'curve, 'r-', 'LineWidth', 2);
hold off;
title('Time (Subtracted by tmax) vs Normalized Intensity at 355 nm (Fitted)');
xlabel('Time (ns)');
ylabel('Normalized Intensity');
legend('Data', 'Fitted curve', 'Location', 'best');
saveas(gcf, 'fitted'curve'plot.png'); If you to save the image
```

```
% Display the lifetime (tau)
disp(['Lifetime (tau) = ', num2str(params'fit(2)), ' ns']);
```

```
% Save the curve fit data to a .mat file
save('fitted'curve'data.mat', 'times'trimmed', 'fitted'curve', 'params'fit');
```

```
% Save data to ASCII file of the 355 Output
output'filename = 'output.txt';
dlmwrite(output'filename, [times' intensity'355nm], 'delimiter', ',', 'precision', '%.6f');
disp(['Data saved to "', output'filename, '".']);
```

```

% Laser Pulse Generation

% Laser pulse parameters
pulse_duration = 10; % Pulse duration (FWHM) in nano seconds
pulse_center = 0; % Pulse center in seconds

% Number of points (odd number)
num_points = 144; % Review the number of points from the times trimmed – Watch here

% Time vector
time = linspace(0, 10, num_points); % Adjust the time range as needed
% Generate laser pulse
sigma = pulse_duration / (2*sqrt(2*log(2))); % Standard deviation of the Gaussian
pulse = exp(-((time - pulse_center).^2) / (2 * sigma^2));

% Normalize the pulse amplitude to peak at 1
pulse = pulse / max(pulse);

% Adjust the pulse center to be centered at the time corresponding to max intensity 355nm
% pulse_center = tmax - 0.9 ; % Start with tmax and repeat until the laser pulse is in the
same position % When you do it at the beginning try to make % the match of bands in the
last plot.
% Time vector (use the full times vector)
time = times;

% Generate laser pulse
sigma = pulse_duration / (2 * sqrt(2 * log(2))); % Standard deviation of the Gaussian
pulse = exp(-((time - pulse_center).^2) / (2 * sigma^2));

% Normalize the pulse amplitude to peak at 1
pulse = pulse / max(pulse);

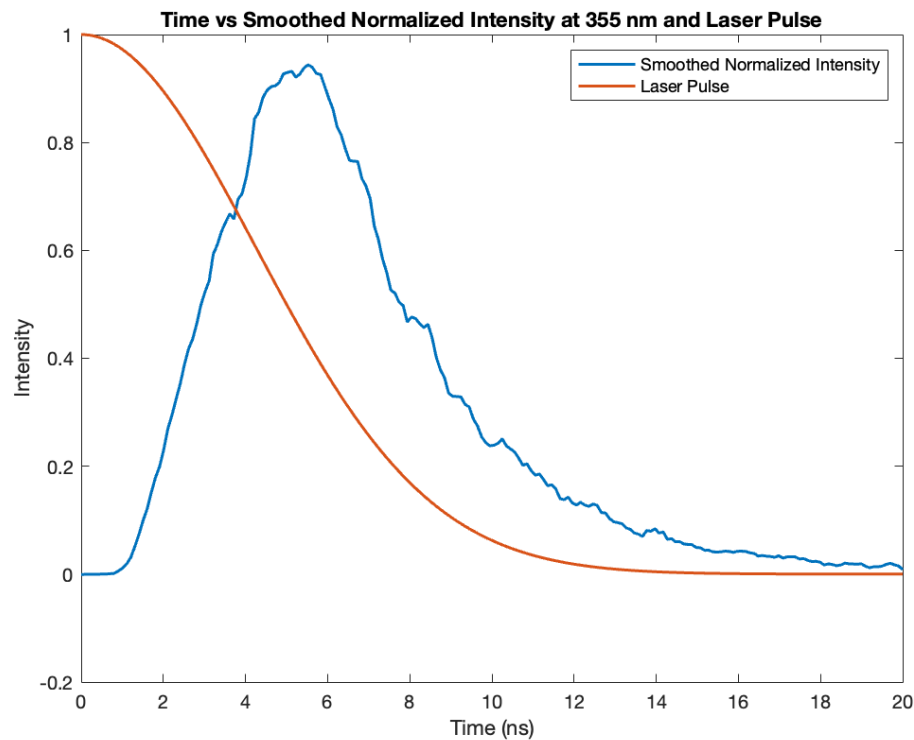
% Create a new time vector with the same length as the pulse
time_pulse = linspace(times(1), times(end), length(pulse));

figure;
plot(times, intensity_355nm_smoothed, 'LineWidth', 1.5);
hold on;

% Plot using the new time vector for the laser pulse
plot(time_pulse, pulse, 'LineWidth', 1.5);

title('Time vs Smoothed Normalized Intensity at 355 nm and Laser Pulse');
xlabel('Time (ns)');

```



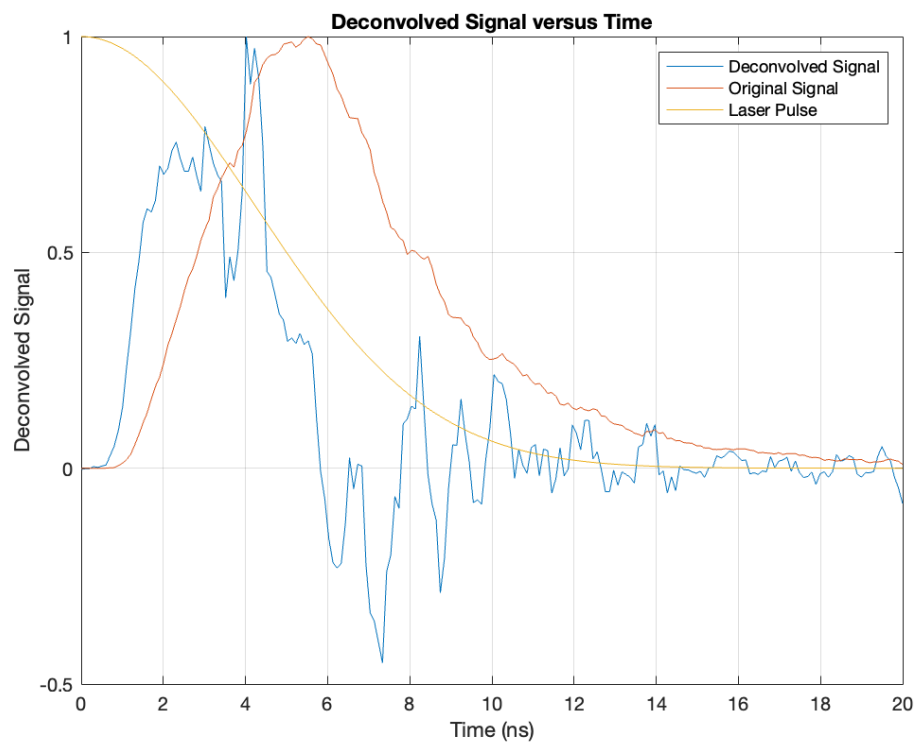
```

ylabel('Intensity');
legend('Smoothed Normalized Intensity', 'Laser Pulse');
hold off;

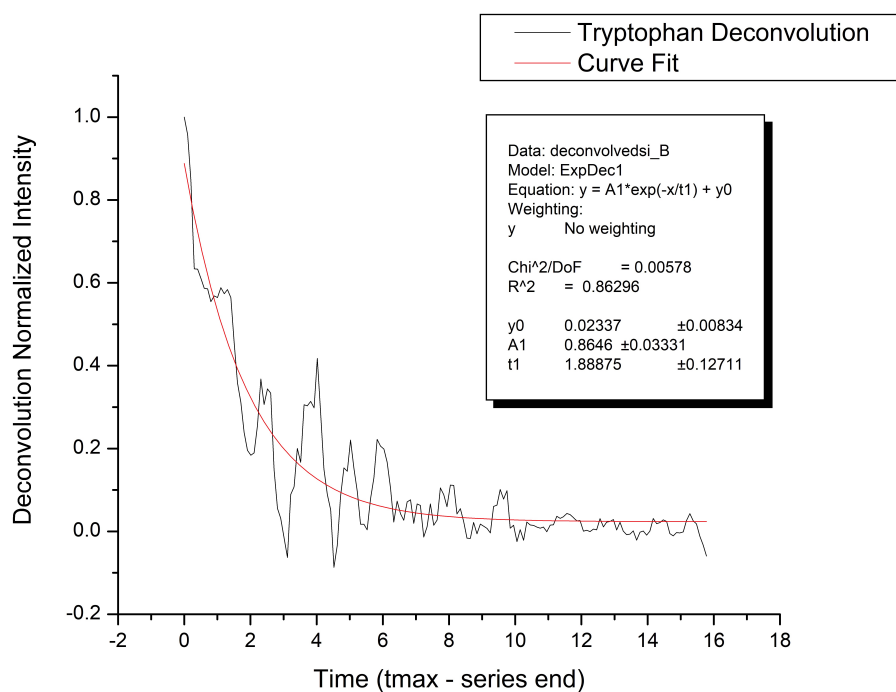
% Signal Deconvolution
intensity'355nm'smoothed = intensity'355nm'smoothed ./ max(intensity'355nm'smoothed);
deconvolved'signal = deconv([intensity'355nm'smoothed'
zeros(1,length(intensity'355nm'smoothed)-1)], pulse');
smoothed'deconvolved = movmean(deconvolved'signal, 5);
norm'smooth'deconvolved = smoothed'deconvolved ./ max(smoothed'deconvolved);

figure;
plot(time, norm'smooth'deconvolved);
hold on;
plot(time, intensity'355nm'smoothed);
hold on;
plot(time, pulse);
grid on;
legend('Deconvolved Signal', 'Original Signal', 'Laser Pulse')
title('Deconvolved Signal versus Time');
xlabel('Time (ns)');
ylabel('Deconvolved Signal');

```



The deconvolution data is then exported to the spectral processing software Origin, where a curve is fit to the the function and the exponential decay is calculated from the t(max intensity) to the end of the series.



B Temperature and Pressure Logs from Tagish Lake Mapping Experiments

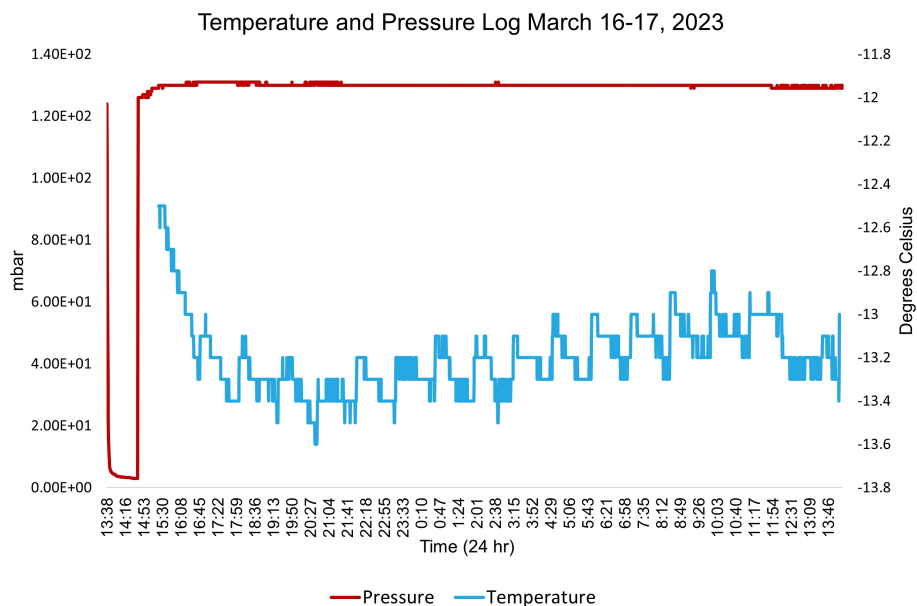


Figure B.1: Temperature-Pressure Log for 266 nm Raman Map of the Tagish Lake meteorite. Mapping time = 20 hours, plus setup and POI interrogation.

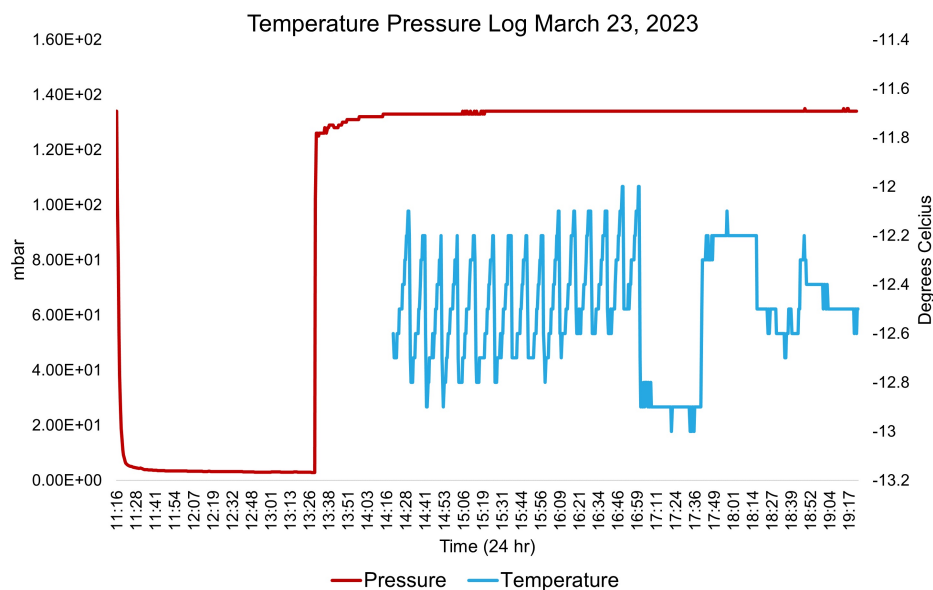


Figure B.2: Temperature-Pressure Log for 266 nm Fluorescence Map of the Tagish Lake meteorite. Mapping time = 4 hours, plus setup and POI interrogation.

C Laboratory Samples and Their Weights for Mixing

Table 17: Laboratory Samples and Their Purity

Laboratory Standard	Purity	Sigma-Aldrich Identification
Tryptophan	98%	T0254 –5G
Phenylalanine	98%	P2126– 100G
L-Proline	—	P5607–25G
L-Glutamic Acid	99%	G1251– 100G
L-Aspartic Acid	98%	A9256– 100G
Glycine	—	G5417– 100G
β - Alanine	99%	146064– 25G
Aminoisobutyric Acid	99%	162663– 25G
Alanine	98%	A7627– 100G
2-Aminoisobutyric Acid	98%	850993– 25G
Calcium Sulfate Dihydrate	99%	C3771-500G
Yttrium (III) Nitrate Hexahydrate	99.8%	237957-25G
Di-Ammonium Hydrogen Phosphate	—	1012070500

CI (carbonaceous chondrite (CI-type)) Analogue materials from the University of Central Florida and is labelled as UCF-DSI-CI-2. The mineralogy is as follows:

Table 18: Composition of CI Simulant

Mineral	Wt%
Mg-Serpentine	51.3
Magnetite	10.0
Vermiculite	9.6
Olivine	7.0
Pyrite	7.0
Attapulgit	5.3
Sub-bituminous coal	5.0
Ferrihydrite	4.8

C.1 Mixing Weights

C.1.1 Tryptophan-Doped Gypsum

Gypsum from Sigma Aldrich (calcium sulphate dihydrate) is sieved to $<355 \mu\text{m}$ and mixed with methanol (enough to cover the sample and make a slurry). Concentrations of 50, 100, 500 and 1000 ppm tryptophan are mixed into 10g of the gypsum substrate. The mixing weights (using the formula $100 \text{ ppm} = 0.001\text{g}/10\text{g}$) are as follows:

Table 19: Tryptophan-Doped Gypsum Weight Measurements

Concentration	Tryptophan (g)	Gypsum (g)	Methanol (mL)
Gypsum Control	0	10	25
50 ppm	0.0005	10	25
100 ppm	0.001	10	25
500 ppm	0.005	10	25
1000 ppm	0.01	10	25

C.1.2 Tryptophan-Doped CI Analogue

Concentrations of 50, 100, 500 and 1000 ppm tryptophan are mixed into 10g of CI analogue as substrate. The mixing weights are as follows:

Table 20: Tryptophan-Doped CI Weight Measurements

Concentration	Tryptophan (g)	CI Analogue (g)	Methanol (mL)
CI Analogue Control	0	10	25
50 ppm	0.0005	10	25
100 ppm	0.001	10	25
500 ppm	0.005	10	25
1000 ppm	0.01	10	25

C.1.3 Organic Concentrations in Sterile Water

Tryptophan and tyrosine are dissolved within sterile water to obtain concentrations of <1 mM, <0.5 mM, and <0.25 mM. The molar mass of tryptophan is 204.23 g/mol, and the molar mass of tyrosine is 181.19 g/mol. The original mixture to dilute to smaller concentrations is as follows:

$$n = \frac{m}{M} \quad (3)$$

$$\text{molar}[] = \frac{\text{mol}}{L} \quad (4)$$

For tryptophan and tyrosine, 0.018 g of each were measured out and dissolved in 100 mL of water, resulting in 0.8 (0.000881 mol/L) and 0.99 mM (0.00099 mol/L) respectively. These solutions are then diluted with more sterile water to create lower concentrations.

C.1.4 Lunar REE Analogue Mixing

Once the synthesized samples of YPO_4 and CePO_4 were prepared, they are mixed with Exolith Lab Lunar Mare simulant LMS-1 at the following weights and concentrations:

Table 21: REE-Doped Lunar Samples Weight Measurements

Concentration	YPO ₄ (g)	CePO ₄ (g)	LMS-1 (g)
LMS-1	0	0	0.6
YPO ₄	0.6	0	0
CePO ₄	0	0.6	0
1000 ppm YPO ₄	0.0625	0	6.25
2000 ppm YPO ₄	0.125	0	6.25
5000 ppm YPO ₄	0.3125	0	6.25
10000 ppm YPO ₄	0.625	0	6.25
1000 ppm CePO ₄	0	0.0625	6.25
2000 CePO ₄	0	0.125	6.25
5000 CePO ₄	0	0.3125	6.25
10000 CePO ₄	0	0.625	6.25