Geochemical and Mineralogical Analyses of Cold Spring Deposits from Borup Fiord Pass, a Sulfur-Dominated Arctic Analog for Planetary Environments on Mars and Europa

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GEOCHEMICAL AND MINERALOGICAL ANALYSES OF COLD SPRING DEPOSITS
AT BORUP FIORD PASS, A SULFUR-DOMINATED ARCTIC ANALOG FOR
PLANETARY ENVIRONMENTS ON MARS AND EUROPA

by

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The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above-mentioned discipline.
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Geochemical and Mineralogical Analyses of Cold Spring Deposits from Borup Fiord Pass, a Sulfur-Dominated Arctic Analog for Planetary Environments on Mars and Europa

Thesis directed by Associate Professor Alexis S. Templeton

Sulfur is one of the most ubiquitous elements in the universe and one of those that is crucial for life, as we know it. This graduate dissertation presents the culmination of work conducted to better understand biological and geochemical processes related to sulfur cycling at a sulfur-dominated field site in the Canadian High Arctic. This site, situated in a valley called Borup Fiord Pass, provides a unique environment where sulfide-rich fluids emerge from a glacier and form large deposits of ice that become covered in elemental sulfur. The role of biology is compelling and yet challenging to define in each step of sulfur cycling at Borup Fiord pass, whether one considers the origin of the sulfide (presumed biological sulfate reduction in the subsurface) or one focuses on the processes driving sulfur oxidation and stabilization at the glacier’s surface. This dissertation presents results from a field expedition in 2014 as well as detailed mineralogical and spectroscopic analyses of sulfur-rich materials returned from the field. The importance of sulfur and carbonate minerals at this site is considered. Also, analyses of materials within pyrite alteration features in the valley are explored. These features appear to represent emplaced subsurface sulfide ores, which have been subsequently leached near the surface, forming gossanous structures. The geochemistry and mineralogy of these features is explored, as well as is their potential to serve as analogs for the exploration of Mars. The dissertation then concludes with some consideration of potential future work to be considered as well as a recapitulation of the current state of knowledge of processes at Borup Fiord Pass.
ACKNOWLEDGMENTS

“Do the difficult things while they are easy and do the great things while they are small. A journey of a thousand miles must begin with a single step.”
- Lao Tzu

Sometimes I stare off into the heavens at night and wonder about our universe and what may yet be out there to discover. Could there be other forms of life and intelligence in the cosmos? Will our species ever travel to those other stars, and, if that happens, will we discover something greater about ourselves? I’ve asked myself such questions through all of my life, and the thrill of that wonder has continued to excite me. It’s from such curiosity that I was driven toward a pursuit of scientific understanding. From my earliest collegiate pursuits in biology and chemistry through my learning of astrophysics and geology, I’ve found that I’m intrigued by broad and far-reaching questions about the nature of life in the universe. It was such intrigue that led me to astrobiology and the research that led to this dissertation. When I first learned about the yellow deposits of sulfur on glacial ice at Borup Fiord Pass, I knew that I would love to be involved in the research to better understand that system and its relevancy to the geobiology of Earth and possible life elsewhere.

The deposits of sulfur mentioned above occur at the toe of a glacier in a valley in the Canadian High Arctic. Where they occur, they cover a large area and are visibly yellow in appearance, standing out from the ice and the rock nearby. I recall looking at pictures taken by previous grad students and researchers who’d visited the site and wondering if there was a greater story to be told about the role that microorganisms may play in forming these deposits. As I continued in my research, I started wondering more about the geochemistry and mineralogy of the sulfur deposits. Now, as I look back over my work, I realize that a large portion of my time has focused on the exotic minerals that I found in samples from Borup Fiord Pass. This dissertation seeks to develop an understanding of the mineral occurrences at Borup and focuses on the research I’ve conducted during the past several years of my life.
I was fortunate to be granted the opportunity to travel to this remote field site in the summer of 2014, along with my collaborators, in order to study the sulfur deposits and to collect a variety of samples to complete my work. Though this dissertation cannot cover the full breadth of findings and may only serve as one stepping stone along the path of fully understanding the Borup Fiord Pass sulfur system, I hope that the reader will learn in these pages of the truly strange mineral occurrences and possible biological connections that have been considered during the course of my work. If nothing else, I hope you see the pictures and videos of the Borup Fiord Pass site and perhaps feel a sense of awe and wonder at the beauty of this remarkable location.

Of course, no great journey can be fully accomplished in solitude. My work follows on from the previous research of several other people. My involvement in this research would not have been possible without the support of my graduate adviser, Alexis Templeton. In the fall of 2009, while studying undergraduate astrophysics at the University of Colorado Boulder (CU), Alexis suggested I interview for a research assistant position in her lab with then graduate student Lisa Mayhew. This work was my introduction to the lab and laid the grounds for my application to the graduate program in geology at CU. During the last several years, I have traveled to California, Switzerland, and Canada (including Borup Fiord Pass) with Alexis. She has been a helpful guide and a great friend during my growth as a graduate student. I have a good feeling that I’ve never been the easiest person to advise, which makes me appreciate Alexis’ support, mentorship, and friendship all the more.

Steve Grasby, my collaborator and our field guide while we were in the Arctic, was the first person to publish on research to understand how the sulfur deposits had formed at Borup Fiord Pass. His article from the journal Astrobiology, which was published in 2003, has been a mainstay of my reading through much of the past decade of my life. My copy of that paper is now withered and crinkled and marked up and fading, and it has certainly served me well. Also, former graduate students in the Templeton Lab, Damnhait Gleeson and Katherine Wright, laid the groundwork for
the research that would eventually become my graduate career. In the first years of my work, the only materials I had to work with were the samples that Damnhait and Katherine had returned from their own trips to Borup Fiord Pass. Much as with Steve's writing, I have read and re-read Damnhait and Katherine's writings so often that I can recite a multitude of passages from their contributions.

During our journey to Borup Fiord Pass in 2014, which covered two weeks during that summer, Alexis, Steve, and myself were joined by renowned microbial ecologist John Spear and his graduate student Chris Trivedi, both of the Colorado School of Mines. Much as myself, John has a broad interest in a variety of topics and his insight and support along the way have been extremely beneficial in my graduate career. Chris Trivedi has become a good friend, as he's also experiencing the trials and tribulations of graduate student life, and I treasure the conversations he and I have had in considering our two graduate projects and our own contributions to the work. While I have focused primarily on the geochemistry and mineralogy of materials from Borup, Chris has been focusing much of his work on considering the microbial communities that are present, including extraction of DNA from a large reservoir of samples. It's quite likely that the culmination of Chris' work and mine will build up a reasonable story as to what role the biology may play in relation to the exotic minerals found at Borup.

Brian Hynek and Boswell Wing join Alexis, Steve, and John in composing my graduate committee. I am quite thankful to have their expertise in reviewing this work of writing and their help in taking these final steps in my graduate career. Their support and advice are only made even more unrepayable from the fact that they are the primary audience for this graduate dissertation (and I thank them for reading).

Beyond my fellows and friends in the study of Borup Fiord Pass, I am quite thankful for all of the support of my fellow lab mates in the Templeton Lab. Also, I cannot overlook my friends and family, who have supported me through thick and thin over the years. My journey has been a long
and arduous one, and I couldn’t have become the person I am today without their love and support. Furthermore, this journey I’ve been on would have been far lonelier and far less spectacular without the love and support of my wife, Amanda Lau. We built our relationship from a sense of adventure, and over the past decade have experienced more of the world than some folk will ever know throughout their entire lives. Often, we graduate students talk about seeing a “light at the end of the tunnel” with our graduate work; for me, Amanda has been my light at the end of that tunnel. Looking forward to the next step in our lives together has given me my reason.

Those who know me know that I find science to not just be a journey of discovery but also a journey for sharing. My graduate career has taught me that I have in me a communicator, a storyteller, who can find the means to share what we learn about our place in the universe with people from a variety of backgrounds. Although this graduate dissertation focuses primarily on my research work, I am also thankful that Alexis Templeton and my graduate committee and collaborators have allowed me some space in the pages that follow to consider science communication and how to better share our findings from Borup Fiord Pass than just in research publications. As this part of my life comes to a close, I’m happy to have discovered a bit more about who I am and what I can do in my life to give something back. I hope you enjoy reading this graduate dissertation and find some intrigue in the pages that follow. The ups and downs, the little wins and harsh failures, that came along with the work and the writing of this document may not be apparent to the reader, but, I assure you, what you are about to read is one great accomplishment of my life. I hope you enjoy it!
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CHAPTER 1:

MICROBIAL SULFUR CYCLING IN COLD ENVIRONMENTS AND THE SEARCH FOR EXTRATERRESTRIAL LIFE: AN INTRODUCTION TO BORUP FIORD PASS AS A DYNAMIC, SULFUR-DOMINATED PLANETARY ANALOG SITE

1.1. Overview

Sulfur is one of the most important elements for life as we know it. It's one of the most abundant elements in the universe and occurs in a wide range of chemical forms, which in turn provide for a large range of chemical reactions involving sulfur. The availability and chemical nature of sulfur have led to a great many biological processes that utilize sulfur for energy transduction as well as for the production of biological molecules. For instance, sulfur is utilized in protein folding, can be found in vitamins and enzyme cofactors, and is involved in a variety of sulfur-based metabolisms such as dissimilatory sulfate reduction and anoxygenic photosynthesis. Also, following from its importance to life as we know it, sulfur was likely important for the origin and evolution of the earliest life on Earth. The importance of sulfur for biology cannot be argued, and yet many questions remain with regard to how organisms utilize sulfur for energy transduction and what roles the interaction of living processes with sulfur may play in preserving biosignatures over various timescales and in various environments.

This graduate dissertation addresses open questions about the chemistry and mineralogy of sulfur within low-temperature sulfur-dominated spring systems, through a study of the (bio)geochemical cycling of sulfur at a glacial site in the Canadian High Arctic. This site, situated within a valley called Borup Fiord Pass, provides a unique system for studying processes involving sulfur. In this valley, artesian springs deliver sulfide-rich fluids from the subsurface to the surface of the valley via permafrost-free soil at the base of a large coalescence glacier (informally called “Borup Fiord Pass Glacier”). In previous work, the sulfide within these springs was linked to microbial sulfate reduction within the subsurface. The oxidation of sulfide from the springs is observed to produce deposits of elemental sulfur and gypsum on the glacial ice as well as on icings
produced from the spring fluids. Given the surficial distribution of these mineral deposits, elemental sulfur is not thermodynamically predicted to be stable and should oxidize to form sulfates. Thus, the formation and stabilization of these elemental sulfur deposits has been of interest for what it can teach us about sulfur chemistry in cold, natural systems on Earth and elsewhere. Also, it remains to be addressed to what extent the biology of the Borup Fiord Pass system is involved in the formation and stabilization of the elemental sulfur in the deposits. In addition to the deposition of materials from the spring system, Borup Fiord Pass also presents conspicuous sulfur-rich mineralized features set within the carbonate rock of the proglacial region of the valley. These alteration structures, informally called “paleopipes”, have been inferred to represent a past expression of the modern spring system, thereby providing possible remnant mineralization that provides windows into the subsurface hydrological system. However, much remains to be assessed with regard to their formation and the information about past hydrological processes in the valley that is locked away in the solid materials remaining in these structures.

The spring system and paleopipe features at Borup Fiord Pass are ideal for studying sulfur geobiological processes since the chemistry of sulfur appears to dominate the overall chemistry of the site. Although past research has shown that microorganisms capable of metabolizing sulfur are dominant in the sulfur deposits, and that these organisms possess key genes involved in sulfur oxidation processes, it is still not known to what extent, if any, biological processes drive the production and stabilization of the elemental sulfur at this site. For instance, it is not known if kinetic factors alone can explain the presence of the elemental sulfur in the deposits over time, or if microbial processes favor the presence of the elemental sulfur against basic thermodynamic predictions. Also, previous research has shown that rare and metastable forms of at least two minerals (rosickyite (a polymorph of mineralized elemental sulfur) and vaterite (a polymorph of calcium carbonate)) appear related to the spring system, warranting a more thorough inventory of the mineralogy and mineralogical transformations occurring in this system.
Furthermore, the paleopipes may serve as a unique focal point for connecting the processes that occurred in the past to those of the modern day in the spring system, and these paleopipes must be further studied to make clear their possible role in delineating sulfur cycling and subsurface processes in the past in this unique Arctic setting. Thus, with my graduate work, I sought to better characterize the geochemistry and mineralogy of the modern sulfur spring system as well as of the paleopipes and to identify which features of the site may be influenced by biological activity. Furthermore, as will be highlighted later, Borup Fiord Pass serves as a unique planetary analog here on Earth and may serve in our future geochemical, mineralogical, and astrobiological explorations of other worlds, such as Mars and Europa. From these astrobiological connections, this research becomes highly engaging for a broader audience within the American public and globally. This dissertation thus includes a consideration of the importance of communicating science and presents products from this graduate work intended to share the research conducted on materials from Borup Fiord Pass with a larger audience. However, before approaching a larger synthesis of this work at Borup Fiord Pass and how it has been and will be shared, a few considerations of the importance of sulfur are offered. I start by taking a brief look at the history of sulfur as known by humans and then discuss the importance of sulfur for life. The dynamics of cold, natural systems are then briefly considered before an introduction to Borup Fiord Pass is developed.

1.2. Sulfur in Human History and in Life

Sulfur, the 10th most abundant element in the universe, can be found in giant molecular clouds, meteorites, and all of the worlds of our solar system (Clark, 1981). A requisite for life as we know it, sulfur can take on a great variety of chemical forms, and a multitude of biological metabolisms have evolved to utilize this element. Sulfur has been known to humanity since antiquity and has been one of the most studied of the geobiologically-important elements. Sulfur
may have been an essential ingredient in the origins of life on Earth and so is integral to an understanding of astrobiology. In the title of a 1981 article reviewing the importance of sulfur in astrobiology, Benton Clark (1981) asked if sulfur is the “fountainhead of life in the Universe”. Although such a question could easily itself become the focus of a multitude of dissertations, that question will be briefly addressed in this section.

Sulfur comes to us etymologically from Sanskrit sulvere and Latin sulphurium (Mandeville, 2010), most likely related to the infinitive verb “to burn” (Online Etymology Dictionary). Sulfur, which can be found naturally in its elemental form (viz. a form composed solely of sulfur atoms), was one of the first dozen or so pure mineral elements known to humanity (and may even have been the first; Stimola 2007; Rapp 2009). Sulfur was mentioned in the Ebers Papyrus, an Egyptian medical text dating from ~1550 BCE (Kutney, 2007), where it was discussed as an ingredient in an ointment used for treating granular eyelids (a symptom of then-unknown Chlamydia sp.; Rapp 2009). The character Odysseus speaks of using sulfur to fumigate his home in Homer’s Odyssey, a practice that has continued, with reports in scientific literature of largescale fumigation using sulfur dioxide in American cities for the treatment of disease as late as the 19th century CE (Edson 1889). Also, perhaps ironically, Pliny the Elder speaks of the importance of sulfur to the ancient Greeks in his Natural History, only later to be killed through suffocation from sulfurous fumes during an attempted rescue from the eruption of Mt. Vesuvius that led to the famed destruction of Herculaneum and Pompeii (Kutney, 2007; Stimola, 2007).

The connection of sulfur with volcanic environments led ancient people to associate sulfur with mythologies of the underworld, hell, and demons. For instance, sulfur (referred to as brimstone) rains down as hellfire in the Book of Genesis (and is mentioned a total of 14 times throughout the Bible). Kroonenberg (2013) further explores the importance of sulfur in the hellish narratives of ancient peoples in his book Why Hell Stinks of Sulfur: Mythology and Geology of the Underworld. In his writing, Kroonenberg uses fictional and historical accounts to trace the
exploration of the world beneath our feet, beginning with the perspective of sulfur-rich volcanic environments serving as the connections to the underworld. It’s perhaps not surprising, given this intrigue with sulfur and mythology, that sulfur has been so well-studied through human history. Apart from western history, the ancient Chinese knew of sulfur as early as the 6th century BCE, when it was referred to as “shiliuhuang”, and, by the 2nd century CE, Taoist alchemists were studying the reactivity of sulfur with other metals as well as sulfur’s use as a medicine (Yunming, 1986). The Chinese are known as the earliest manufacturers of rockets, due to their early discovery of gunpowder (a blend of sulfur, charcoal, and potassium nitrate), likely derived from this Taoist alchemical experimentation (Chase, 2003). From this, we can see that sulfur has had a long history of study and use by humankind. But what led sulfur to be so abundant on Earth and why is sulfur so important to biological processes?

Sulfur is a vital element for life as we know it: sulfur has a high relative abundance on the Earth’s surface (350 mg kg⁻¹ in the mean global crust and 905 mg L⁻¹ in the mean global ocean; Haynes 2013), and sulfur is one of the known requisite elements for life (one of the SPONCH¹ elements). Sulfur can be found in chemical oxidation states from -2 in sulfides and reduced organic sulfur compounds to 6+ in sulfates, but also includes a large number of intermediary oxidation state compounds within this range. Sulfur has 4 stable isotopes, and the elemental form of sulfur has over 180 known allotropes and polymorphs (second in number only to carbon, though sulfur has more characterized solid allotropes than any other element; Steudel et al. 2003). Sulfur is of critical importance for biomolecule production (e.g. cysteine, methionine, biological sulfates) as well as many microbial metabolisms. Sulfur reduction, sulfur oxidation, and sulfur disproportionation are all utilized by various forms of life on this planet, driving transitions in sulfur speciation through metabolic processes.

¹ SPONCH stands for sulfur, phosphorous, oxygen, nitrogen, carbon, and hydrogen. The acronym CHNOPS is also sometimes used, as it places the most abundant elements in known living things first.
Sulfur metabolisms are amongst the oldest biological processes to leave traces in the rock record. For instance, investigations of sulfur isotopic signatures in pyrite granules from 3.47 to 3.49 Ga sedimentary units in North Pole, Australia, have suggested that microbial reduction of aqueous sulfate as well as microbial disproportionation of S\(^0\) may have been responsible for the formation of these metal sulfides (Philippot et al., 2007; Shen et al., 2009; Wacey et al., 2010; Wacey et al., 2011; Javaux, 2011). However, some recent work suggests that the sulfur isotopic signatures may instead signify geochemical transformations due to volcanic gas shielding of ultraviolet radiation (c.f. Wing 2012; Muller et al. 2016). If these Paleoarchean signatures of potential microbial sulfur metabolism are actual signatures of past life, then they would be among the oldest evidences of specific biological metabolisms that have been gleaned from the geologic record. However, determination of the ancestry of sulfur metabolisms and their importance for early life on Earth can also be gleaned from phylogenetic analyses. Sulfur metabolisms are abundant across all three known domains of life; phylogenies for the microbial reduction of sulfate or sulfite through the dissimilatory sulfite reductase (dsr) gene appear to show that this metabolic process pre-dates the evolutionary divergence of Bacteria and Archaea (Loy et al., 2008). Sulfur chemistry may even have been amongst the earliest drivers for the origination of life, as we know it (see, for instance, the iron-sulfur world hypothesis; Wächtershäuser 2000; Wächtershäuser 2010).

The cycling of sulfur through its various chemical forms in the environment is intimately linked with the cycling of carbon, nitrogen, oxygen, and iron (see Canfield & Farquhar 2012). Studies of the geobiological processing of sulfur inform our models of how derivations in sulfur speciation and distribution are related to biological activity in modern as well as ancient settings. For instance, sulfates in evaporitic sedimentary deposits, as well as sulfides in pyrite and metal ore deposits, have been used to assess biological dynamics related to ocean and atmosphere chemistry throughout the evolution of the Earth (Farquhar et al., 2010; Canfield and Farquhar, 2012). Studies of sulfur biogeochemistry have been used to assess microbial metabolism and geochemical cycling.
in unique microbial environments such as hypersaline microbial mats (Fike et al., 2008) and low-temperature hydrothermal fields on the seafloor (Brazelton et al., 2006). Furthermore, although not commonly discussed in geobiological circles, the role of sulfur metabolism in multicellular organisms such as plants and animals has been considered (e.g., Ubuka 2002; Hell 1997) and is also an important aspect of modern sulfur cycling on Earth.

Investigations of sulfur geobiological processes and the cycling of sulfur on Earth are necessary for assessing the role of sulfur biology for potential living systems on other worlds in our Solar System and elsewhere. For instance, Domagal-Goldman et al. (2011) have proposed that biogenic sulfur gases acting on planetary atmospheres may be capable of providing spectroscopic evidence of active biospheres on extrasolar planets. Similarly, Kaltenegger & Sasselov (2010) have suggested that geologically-active, terrestrial exoplanets with dominant sulfur cycles (i.e. large-scale outgassing of $SO_2$ and $H_2S$ through volcanism) could be spectroscopically discriminated against exoplanets where other geochemical cycles are most abundant. Exoplanet atmosphere investigations may thus reveal the first indications of large-scale, extraterrestrial biospheres through detections of sulfur species and their distribution and relationships to other gases.

Sulfur biology may also have had a role to play if life ever originated and evolved in other regions of our Solar System, including Venus, Mars, and outer solar system moons, such as Europa and Enceladus. Specifically, Mars and Europa, two current targets for astrobiological investigations, may have had past or even present sulfur metabolisms and/or interactions of living processes with sulfur chemistry. Sulfates of calcium and magnesium have been identified globally on Mars through remote sensing, and ferric iron sulfates (e.g. jarosite) have also been detected in certain Martian localities through robotic exploration (see King & McLennan 2010). Schopf et al. (2012) have considered the potential for sulfate deposits on Mars to contain morphological signs of past life, and Norlund et al. (2010) have suggested that jarosite minerals on Mars may be relicts from biological sulfur oxidation processes similar to those seen in some acid mine drainage (AMD) systems on
Earth. The oxidation of sulfide and other forms of sulfur in the Martian past to form the sulfates detected in modern times may have been driven by Martian biological systems. If this has been the case, then sulfate deposits on Mars may hold biosignatures of such past activities. The future exploration of Mars will most certainly include work to determine whether biological mechanisms have been involved in processing sulfur on that planet.

It is now widely accepted that Europa, one of the Galilean Moons of Jupiter, likely has a subsurface ocean under its thick, icy crust. Galileo spacecraft investigations revealed the presence of sulfur-bearing compounds on the surface of Europa, including sulfuric acid, well over a decade ago. These sulfur-bearing compounds may have been delivered exogenously to the Europan surface from Jupiter’s active magnetosphere (Dalton et al., 2013). However, it is also possible that some or all of the sulfur on Europa is endogenous to processes occurring in the subsurface ocean (Chela-Flores, 2006; Carlson et al., 2009). The upcoming Europa Multiple-Flyby Mission (set for launch, and a better name, sometime around the year 2022) should provide much-needed spectroscopic analyses to further explore sulfur-bearing species on the surface and near surface of Europa as well as their distribution at scales that may allow us to better understand their likely source(s). The potential for (bio)geochemical sulfur cycling within Europa and the likelihood of future astrobiological investigations on that moon demand that processes affecting the production and preservation of biosignatures in geochemically-unique, cold subsurface environments on Earth be better characterized. Borup Fiord Pass, the target field site from this graduate dissertation, presents a unique environmental system where discharges of sulfide-rich fluids onto glacial ice drive the deposition of sulfur-rich materials, including gypsum and elemental sulfur (S⁰). The processes involving the geological and biological cycling of sulfur at Borup Fiord Pass present an opportunity to highlight the importance of sulfur as a chemical element. However, before bringing to light an understanding of the sulfur spring system at Borup Fiord Pass, we should consider the importance of icy and glacial systems on Earth.
1.3. The Dynamics of Cold, Natural Systems

Roughly 10% of Earth’s land area is covered by glaciers, ice shelves, and ice sheets, and these biomes are home to distinct microbial ecosystems (Stibal et al., 2015). Although most biology textbooks and courses tend to neglect glaciers, ice shelves, and ice sheets as unique ecosystems, these icy environments are home to a diverse array of life, especially microbial life, and should be considered one of our planet’s general biomes (Anesio and Laybourn-Parry, 2012). For instance, the organic carbon content on the surfaces of glaciers and ice sheets can range from tens to tens of thousands of kilograms per square kilometer (see Hood et al. 2015; Stibal et al. 2012; and references therein). Also, a wide variety of microorganisms have been phylogenetically identified in cold-hosted and glacial environments (e.g., Wadham et al. 2004; Grasby et al. 2003; Mikucki et al. 2004; Anesio & Laybourn-Parry 2012; Mindl et al. 2007; Wright et al. 2013; Stibal et al. 2015).

Glaciated regions are an integral part of the global hydrological system. Multiple biomes and ecosystems are delivered their water through the accumulation and melting of glaciers. These glacially-derived waters serve ecosystems from the tundra to the temperate forest and are crucial to plant, animal, and human populations globally. The dynamic intertwining of glaciology with global climate makes glaciers highly susceptible to global climate change as well as highly important for controlling future climatic conditions. For instance, several times in Earth’s history, much of the globe has been dominated by ice sheets and glaciers, perhaps even through Snowball Earth periods in the Proterozoic, suggesting that the global importance of glacial habitats has shifted with the shifting climate (e.g., Hoffman and Schrag, 2002; Hoffman, 2016). Also, it is currently observed that the Arctic region is responding to the current trend of climate change, through greater amounts of glacier and ice sheet melt, thawing of permafrost, decreased coverage by ice sheets, and summertime melt-out of the Arctic Ocean (e.g., Hinzman et al., 2005; Whiteman et al., 2013; Hood et al., 2015; Sand et al., 2015; Schuur et al., 2015).
Although glacial habitats are relatively understudied compared to other terrestrial biomes, research on microbial interactions with glaciers has detailed how microbes survive and thrive in various glacial habitats (e.g., Wadham et al. 2004; Wright et al. 2013; Hodson et al. 2008; Mindl et al. 2007; Telling et al. 2015; Stibal et al. 2012; Anesio & Laybourn-Parry 2012; Doyle et al. 2013). For instance, supraglacial ecosystems can include wet snow, cryoconite and the holes filled by cryoconite, moraines, and supraglacial streams and ponds. The microorganisms thriving in these systems can gain nutrients from materials released by melting snow and ice as well as exogenous debris blown in by winds or moved through meltwater (Hodson et al., 2008; Stibal et al., 2015). Primary production in supraglacial ecosystems is often driven by photosynthesis (e.g., Hodson et al. 2008), however there are glacial systems where chemolithotrophy is the dominant pathway for primary production (e.g., Wright et al. 2013). A better understanding of these glacial ecosystems is necessary to interpret changes these ecosystems may experience due to the current trend of warming climate and to determine their overall relationships to the global biogeochemical cycling of elements.

Diverse microbial ecosystems have also been found to exist in subglacial settings, where microbiological activity can greatly effect weathering and the overall carbon budget of the subglacial environment (Sharp et al., 1999; Hodson et al., 2008; Hamilton et al., 2013). For instance, microbial cell counts from subglacial systems have been shown to be comparable to those in the active layers over permafrost in tundra systems (Sharp et al., 1999). While the subglacial habitat is oligotrophic, stores of organic carbon from glacial till, sulfides and other minerals present in the soil, as well as rock weathering from glacial and even biological processes provide nutrient and energy sources for microbial populations (e.g., Sharp et al., 1999; Montross et al., 2012; Hamilton et al., 2013; Montross et al., 2014). A recent small subunit (SSU) rRNA sequence analysis for subglacial samples collected from Robertson Glacier (in Alberta, Canada) showed a prevalence of lithotrophic bacteria, autotrophic methanogenic archaea, and heterotrophic eukarya, reflecting a diverse
subglacial community which has become optimized to exploit the limited nutrient and chemical energy stores of this environment (Hamilton et al., 2013). Telling et al. (2015) have also recently shown that subglacial rock comminution (the crushing and grinding of rock by glacial movement) may derive abiogenic H₂, which could have supported subglacial ecosystems that are believed to have existed under glaciers over millions of years, at time scales where subglacial energy sources may have become otherwise depleted. Abiogenic H₂ may then have supported microbial ecosystems in such long-term subglacial systems, through metabolisms such as methanogenesis (Telling et al., 2015).

Subglacial habitats can also include the large number subglacial lakes that have until recently remained unexplored. Subglacial lakes in Antarctica, of which there are at least 145, are estimated to contain a volume of 10,000 km³ of fluid, a large potential repository for subglacial life (Hodson et al., 2008; Tulaczyk and Hossainzadeh, 2011; and references therein). One of these lakes in particular, Lake Vostok, has gained a significant prominence in the scientifically literate public (e.g., Diep, 2013; Oskin, 2015). Lake Vostok is an Antarctic subglacial lake lying beneath 3500-4000 m of ice. Although the lake was first detected in the late 1970s, it was only recently that drilling efforts managed to pierce through the ice to access the lake below. Two holes have successfully drilled into the ice, one in 2012 and another in 2015. In both cases, lake water rose up through the holes and froze. Cores of this frozen ice were later sampled (Bulat, 2016; Leitchenkov et al., 2016). Unfortunately, due to contamination of the samples collected by fluids used to support drilling efforts, most of the information regarding microbial populations is dubious. However, 2 phylotypes detected from 16S rRNA gene sequence analyses have been proposed to have passed certain contamination criteria and may represent the first organisms detected in Lake Vostok fluids (Bulat, 2016). One of the key points of interest for these samples and for further non-contaminated samples that will be collected is that the separation of Lake Vostok from the surface through such
thick ice represents a potential isolated ecosystem and may be one useful analog for future research on the subsurface ocean of Europa.

There are fortunately other ways to study a subglacial lake besides drilling. Blood Falls, located on the Taylor Glacier in the Antarctic Dry Valleys region, presents a system where fluids from a subglacial brine lake discharge through the glacial ice. These spring discharges are enriched in ferrous iron and sulfide, and drive the production of iron oxides and other minerals at the surface (the iron oxides thus formed produce a visibly blood red color on the ice; Mikucki 2005; Mikucki et al. 2004; Mikucki et al. 2009). The brine below Taylor Glacier represents a unique microbial habitat and the discharge at Blood Falls allows easy access for studying the microbial community. For instance, Mikucki and Priscu (2007) have shown through 16S rRNA gene sequence analyses that the dominant organisms sampled from Blood Falls are closely related to known organisms that metabolize sulfur and iron. The most dominant phylotype in their analyses, specifically, shared 99% sequence identity with *Thiomicropsira arctica*, a cultured psychrophilic sulfur oxidizer. Blood Falls thus represents one unique cold environment hosting a spring that allows for geochemical communication from the subsurface to the surface, and an opportunity to study biological activity in the subsurface from the expression of surface materials. Another such system, Borup Fiord Pass, in the Canadian High Arctic, provides another glacial environment with a unique spring system (Grasby et al., 2003; Gleeson et al., 2011; Wright et al., 2013; Lau et al., 2017). However, Borup Fiord Pass does not bear a subglacial lake; instead, a system of artesian springs at the toe of a glacier deliver subsurface fluids through or to the edge of the ice. Unlike Blood Falls, Borup Fiord Pass lacks high levels of dissolved aqueous iron. Instead, high dissolved sulfide in the spring fluids at this site causes spring derived deposits to take on a visually striking yellow color, as is presented in the next section, along with an overview of the previous research conducted at Borup Fiord Pass.
1.4. An Introduction to Borup Fiord Pass

A really extensive deposits of visibly yellow materials form annually on ice surfaces at Borup Fiord Pass on Ellesmere Island in the Canadian High Arctic (Figure 1.1). The visibly yellow deposits at Borup form from saline, sulfide-rich supraglacial springs that discharge from the surface of a coalescence glacier in the valley. This yellow staining, which is due to elemental sulfur ($S_0$), occurs on glacial ice as well as ice formed from the springs and has been seen to cover tens to thousands of square meters of area (Grasby et al. 2003; Gleeson et al. 2011), with the extent of sulfur deposition and location of springs (when they are present) varying from year-to-year.

Located at 81°01’N, 81°35’W, Borup Fiord Pass is a north-south trending valley set within the Krieger Mountains, in the deformed eastern portion of the Sverdrup Sedimentary Basin, a Carboniferous to Eocene depocenter (Embry and Beauchamp, 2008). The geology of this region was first described by Thorsteinsson and Tozer (1957). The underlying rock to the valley is composed of Carboniferous to Permian units, primarily of carbonates. The Sverdrup Basin is an extensive depositional basin spanning much of the Canadian High Arctic (areal extent of $\sim 350,000$ km$^2$) and bearing up to 13 km of sediments spanning back to the Carboniferous (Embry and Beauchamp, 2008). Much of what is known about the subsurface structure of the Sverdrup Basin has been derived from oil exploration wells, which have been drilled in the area since the late 1960s (Embry and Beauchamp, 2008).

Ellesmere Island is the 10th largest island on Earth. This island contains a large portion of the eastern Sverdrup Basin. In this section of the basin, deformation drove a large number of thrust faults and folds to form (Embry and Beauchamp, 2008). Of specific interest to this work are the Carboniferous to Permian deposits within the Sverdrup Basin, as these deposits are the primary rocks underlying the valley at Borup Fiord Pass. For instance, the conglomerate Borup Fiord Formation, the limestone of the Nansen Formation, the shale of the Hare Fiord Formation, and
Figure 1.1. The location of Borup Fiord Pass and sulfur staining near the glacier
Borup Fiord Pass is located in the Canadian High Arctic (a), on Ellesmere Island (red in a; image credit: Connormah, Wikimedia Commons). Panel b shows an image of the valley of Borup Fiord Pass as collected with the Advanced Land Imager (ALI) of the EO-1 satellite in 2006 (credit: NASA/GSFC). The location of the sulfur springs at the toe of the Borup Fiord Pass Glacier is highlighted with a blue arrow. Yellow-stained ice at the toe of the glacier in the summer of 2014 is presented in c. The ice in the foreground is estimated to cover an area of $10^4$ m$^2$. 
especially the evaporite of the Otto Fiord and Mount Bayley Formations, are important local units that are exposed at or near Borup Fiord Pass (or which may play an important role in the formation of the sulfur spring system).

The Otto Fiord and Mount Bayley Formations, as noted above, may be critical in understanding the sulfur spring system at Borup Fiord Pass. The Otto Fiord formation is of Late Mississippian to Middle Pennsylvanian age and bears thick layers of evaporite (anhydrite and halite), limestone, and sandstone as well as subsurface diapiric facies of halite (Davies and Nassichuk, 1975). The Otto Fiord Formation is observed to outcrop 20 km to the north of Borup (Grasby et al. 2003). The Mount Bayley Formation is a Lower Permian evaporite unit, outcropping 19 km to the east of Borup Fiord Pass, which bears anhydrite, carbonates, and shales (Wallace et al., 1994). Both the Otto Fiord and Mount Bayley anhydrite sequences were developed through subaqueous deposition. As will be discussed later, these anhydrite layers are the primary geological sources of sulfur in the region of Borup Fiord Pass. It has been suggested that the Mount Bayley Formation appears to stratigraphically “pinch out” beyond the valley floor of Borup Fiord Pass (Gleeson et al. 2011), so the Otto Fiord Formation is often considered to be the original source of sulfur for the sulfur spring system at the Borup Fiord Pass Glacier (although the Mount Bayley Formation has not been entirely ruled out as a possible source).

Borup Fiord Pass is a valley pass between the Krieger Mountains connecting Borup Fiord to the south to Hare Fiord in the north. The glacier where the sulfur spring system occurs is a coalescence glacier, forming from the mixing of alpine glacial ice from the mountains to the east and west. The northwestern section of the glacier dams a large glacial lake to the north. Also, north of this lake is a region described as Borup Falls, so-called due to the presence of a large waterfall and canyon cut which then leads to Hare Fiord (detailed mapping of these regions was provided by Hill (2014)). Sulfur-rich springs, ices, and associated mineral deposits occur on the southern edge of Borup Fiord Pass Glacier, within the north-central region of the valley (Figure 1.1). The mineral
deposits have previously been shown to contain varying amounts of $S^0$, calcite and vaterite (both CaCO$_3$), gypsum (CaSO$_4$·2H$_2$O), and bassanite (CaSO$_4$·0.5H$_2$O; Grasby et al. 2003; Gleeson et al. 2011; Grasby 2003; Wright et al. 2013).

The fluids in the springs from which these materials derive are near-neutral to alkaline (pH = 7.3-9.5), are low-temperature (-0.3-2.3°C), and have previously been shown to have elevated levels of dissolved H$_2$S (up to 4.2 mM) and SO$_4^{2-}$ (up to 18.6 mM; Gleeson et al. 2011; Grasby et al. 2003; Wright et al. 2013). Grasby et al. (2003) used geochemical analyses and oxygen and deuterium stable-isotope systematics to determine that the springs are likely sourced from glacial meltwater that has been subsided and reacted with local geological units in the subsurface before returning to the surface and emerging onto the glacier. The high levels of sulfide in the springs have been attributed to microbial sulfate reduction in the subsurface (Grasby et al. 2003). Sulfate in the subsurface at Borup may be sourced from the extensive Otto Fiord Formation (though, as previously mentioned, the Mount Bayley Formation is also a potential source of sulfur in the system), while potential inputs of organic carbon to the subsurface may include local intervening shale units, which Grasby et al. (2003) reported have up to 4% organic carbon. Once these sulfidic fluids emerge into the surface environment, biological oxidation of the sulfide from the springs has been hypothesized to be the key process that gives rise to the deposition and stabilization of $S^0$ at this site (Grasby et al., 2003; Gleeson et al., 2011; Wright et al., 2013). However, that has not been shown conclusively. It is also possible that the oxidation of the sulfide and processes allowing for the seasonal stabilization of sulfur on the glacier are entirely abiotic. Thus the processes controlling $S^0$ formation will be further considered later in this dissertation.

Investigations at Borup have identified diverse microbial populations within the spring fluids and sulfur-rich deposits. For instance, dominance by *Marinobacter sp.*, *Polarimonas sp.*, *Pseudomonas sp.*, and *Burkholderia sp.* was observed in samples collected from springs and deposits in 1999, 2000, and 2001 (Grasby et al. 2003), and samples collected in 2006 were shown to be
dominated by members of the class β-Proteobacteria, with *Ralstonia* sp. being the primary member represented (Gleeson et al., 2011). These 2006 samples were also hosted abundant *Thiomicrospira* sp. and *Flavobacterium* sp. as well as members grouping with Sulfuricurvales, Sulfurovumales, and Chlorofelxi classes. The emerging spring fluids during 2009 were dominated by *Ralstonia* sp. and *Burkholderia* sp. while *Flavobacteria* appeared to be the dominant organisms in most surface deposits. A metagenomic study of one of the thicker deposits downstream from the spring source in 2009 showed that *Flavobacteria* sp. only dominated the surface (~1cm) of the deposit while *Sulfurovum* sp. and *Sulfuricurvum* sp. dominated the greater deposit to a depth of ~15 cm. This led Wright et al. (2013) to propose that surface heterotrophy by *Flavobacteria* may provide a microaerophilic micro-environment where organisms like *Sulfuricurvum* and *Sulfurovum* conduct sulfur chemolithotrophy at low pO$_2$. Furthermore, metagenome analysis showed that genes for sulfur oxidation dominated the primary functional genes in the spring deposit. These findings, taken together, suggest that organisms like *Ralstonia* sp., *Marinobacter* sp., and *Burkholderia* sp. are quite capable of thriving within the spring waters at Borup, while organisms such as *Flavobacteria* sp., *Sulfurovum* sp., and *Sulfuricurvum* sp. have been implicated for their potential role in the metabolism and stabilization of sulfur at the surface.

Another interesting research target at Borup Fiord Pass is a series of sulfur-rich mineralized features that can be found set within the local carbonate rock in permafrost, just to the south of Borup Fiord Pass Glacier. These conspicuous exposures appear as elliptical features of friable material up to 5 m in diameter with red staining of materials from the presence of iron oxides. Two of the features also show white gypsum-rich material in the central region, with the red staining from iron oxides occurring in an outer ring (Grasby et al., 2012). Grasby et al. (2012) have proposed a mechanism of sulfuric-acid speleogenesis (SAS) for the formation of these alteration features as conduits for carrying sulfide-rich fluids from the subsurface beneath glacial ice and driving the dissolution and replacement of local carbonate with gypsum. In this mechanism, sulfide in the fluids
is re-oxidized in the near surface environment to produce sulfuric acid, which in turn drives calcite dissolution in the sub-glacial rock. This process acts in time to replace carbonate in the conduit with gypsum. The model proposes that glacial retreat and then permafrost advance causes the sulfide conduits to become “trapped”, leaving the alteration features behind. Grasby et al. (2012) have shown from x-ray diffraction (XRD) of surface materials that these features are primarily composed of gypsum with rims of calcite and interiors that contain up to 15% elemental sulfur ($S^{0}$). Visibly red staining occurs due to minor concentrations of goethite and jarosite. Stable isotope analyses conducted by Grasby et al. (2012) showed that $\delta^{34}S$ and $\delta^{18}O$ values for the gypsum were significantly lower than the values previously seen for sulfates at the spring discharge sites on the glacier, which suggests a different process for their formation.

Research on the sulfur deposits at Borup Fiord Pass has included several short-duration visits with field sampling over multiple summer seasons, beginning in the 1990s. The scientific exploration of Borup has suggested the involvement of likely BSR in the subsurface, the production and stabilization of the sulfur deposits (which also contain gypsum and calcite), microbial communities capable of metabolizing sulfur, unique mineral occurrences potentially related to biological sulfur cycling (including vaterite ($CaCO_{3}$) and rosickyite ($\gamma-S_{8}$), metastable phases of calcium carbonate and mineralized elemental sulfur, respectively), and the red-stained mineralized features as potential relicts of ancient sulfide springs. In order to further explore the sulfide springs, sulfur deposits, mineral features, and associated processes occurring at Borup Fiord Pass, a long duration field excursion to Borup Fiord Pass occurred in the summer of 2014. That field excursion and the research on the materials then collected are the basis for much of this graduate dissertation. The research team in 2014 included myself, Alexis Templeton (CU Boulder), John Spear and Chris Trivedi (Colorado School of Mines), and Steve Grasby (Canadian Geological Survey). Our field campaign and associated research were funded by an Exobiology grant from NASA. The major objectives of this work were to more thoroughly interrogate the aqueous geochemistry and
sulfur mineralogy of the Borup deposits; to explore the microbial community composition and function across various spatial and geochemical scales at this site; to assess whether the red-stained features and surrounding materials represent potential remnants of past springs; and to explore the formation and stabilization of biosignatures at this field site and to assess their potential use in future geobiology and astrobiological investigations.

1.5. Questions Concerning Borup Fiord Pass

As mentioned in the overview, I conducted the research for this dissertation to better characterize the geochemistry and mineralogy of the modern sulfur spring system as well as of the paleopipes and to identify which features of the site may be influenced by biological activity. However, this impetus fits within the scope of a few larger, driving questions that have sculpted not only my research but also all of the work conducted to better understand the spring system at Borup Fiord Pass. These questions include:

- What low-temperature processes occur in the subsurface to produce such high levels of sulfide as have been measured in the springs and aufeis? What are the subsurface hydrological dynamics within the valley?

- What (bio)geochemical processes are involved in the formation and stabilization of elemental sulfur and other forms of sulfur in the modern spring and aufeis deposits?

- Do the alteration features in the valley represent past sulfur springs? If so, or even if not, then how are these features related to the modern processes in the sulfur springs?

- What roles do microbial communities play in the cycling of sulfur at various scales within the Borup Fiord Pass spring system? What is the biosignature inventory at the field site, are
these biosignatures preserved in time and space? At what levels of observation and analysis do robust biosignatures present themselves?

• How can we use the findings from the sulfur-dominated, icy environment of Borup Fiord Pass to inform our explorations of other environments on Earth as well as on other worlds?

Some answers have already been provided for these questions, while some key points remain to be explored. For instance, while Grasby et al. (2003) demonstrated that subsurface fluids at Borup Fiord Pass are likely not subjected to the necessary temperatures for thermochemical sulfate reduction (>140°C), suggesting that biological sulfate reduction (BSR) is the only probable pathway for the regional sulfur-bearing geological units to source the sulfide in the spring fluids, it is still uncertain as to whether the true source of the sulfur is the Otto Fiord Formation or the Mount Bayley Formation (or even both). In much of our previous work, it has been assumed that the Otto Fiord anhydrite is the source of the sulfur, as the Mount Bayley appears to “pinch out” stratigraphically (Gleeson et al., 2011), however the sulfur isotope data reported for both formations are very similar and would both fit the model of BSR as currently conceived at Borup Fiord Pass (Otto Fiord’s average δ34S=14.6‰ while Mount Bayley’s average δ34S=13.1‰; Grasby et al. 2003; Wallace et al. 1994). Beyond the source of sulfur for the sulfur springs, there also remains much to be determined as to the hydrological structure of the subsurface at Borup Fiord Pass. Another point where previous research is suggestive but not complete is in the determination of whether microbial communities within the mineral deposits in the modern spring system are driving the oxidation of the sulfide and producing elemental sulfur in these materials. Elemental sulfur is thermodynamically stable under a limited range of Eh and pH conditions (Figure 1.2), and should only be slightly stable at the conditions present in the surface deposits at Borup (T=0-5°C;
Figure 1.2. Pourbaix diagram for sulfur
Reducing potential (Eh; relative to the standard hydrogen electrode (SHE)) is plotted against pH for the stability of major sulfur species at standard atmospheric pressure and 0°C. Tan colored fields represent mineral phases while blue fields represent aqueous species. The diagram was plotted assuming values for sulfate and calcium ion activities that are within order-of-magnitude of values from fluids collected from Borup melt pools in 2014. Plot was created using Act2 of Geochemist’s Workbench (Aqueous Solutions, LLC).
pH=5.5-7.5; exposed to atmospheric oxygen; Gleeson et al., 2011; Grasby et al., 2003; Wright et al., 2013). $S^0$ is even less stable at the conditions present in the spring fluids, which are even more basic (pH=7.3-9.5). These physical parameters suggest that sulfide oxidation should favor the production of sulfates over $S^0$, and yet $S^0$ is abundant throughout the summer (no in-field observations exist outside of summer months and snow precludes satellite identification; Gleeson et al. 2010). It is possible that the continued oxidation of $S^0$ to sulfate is kinetically hindered. This leads to the question: does the stabilization of the elemental sulfur on glacial and spring-derived ice suggest biological production and stabilization of the sulfur? For instance, over multiple field seasons, microorganisms have been identified through 16S rRNA gene sequence analyses which are genetically similar to cultured organisms which have been identified as sulfur oxidizers (Gleeson et al. 2011; Grasby et al. 2003; Wright et al. 2013), and several genes involved in microbial sulfur oxidation have been found to be abundant in a metagenome from one of the spring deposits (Wright et al., 2013). While biological processes involved in forming $S^0$ and other sulfur intermediates as well as sulfates appear quite likely in the field, it is equally possible that these microbial communities are instead established once $S^0$ is formed and they then drive the further oxidation of sulfur to sulfate. To first assess the biogenicity of the materials in the spring deposits, it is critical to inventory the geochemistry and mineralogy of the materials and their pathways of formation. Such an inventory is part of the overall goal of this dissertation, seeking to further our understanding of the dynamics that give rise to S mineralization within the spring deposits.

Finally, although the paleopipe features have been implicated as remnant springs (Grasby et al., 2012), much remains to be determined as to the types of biosignatures are generated and retained in the features, and over what scales these biosignatures can be detected. A large portion of the graduate work leading into this dissertation was focused on assessing the geochemistry and mineralogy of materials within the paleopipes and to better understand their geological origin in relation to the surrounding region. Although determining the subsurface structure of the valley is
difficult without implementing geophysical methods (such as ground penetrating radar), connecting the hydrological processes leading to the modern spring system with the known fault structures of the valley and the paleopipe features may lead to a better understanding of the mysteries that lie beneath the surface at Borup Fiord Pass. This consideration and the others derived from the questions above will be considered throughout this dissertation and then will be revisited in Chapter 6.

1.6. Overview of Following Chapters

Chapter 2: “An Excursion into the Field: Borup Fiord Pass, 2014”

This chapter provides an overview of the 2014 field excursion, including findings from the field and work that has been conducted on materials that were returned to the lab. Several key activities and results that will be considered in more depth in the manuscripts developed in Chapters 3 and 4 are also first presented here.

Chapter 3: “Low-temperature formation and stabilization of rare allotropes of cyclooctasulfur (β-S₈ and γ-S₈) in the presence of organic carbon at a sulfur-rich glacial site in the Canadian High Arctic”

The intriguing discovery of the three primary polymorphs of mineralized elemental sulfur (which are also allotropes of sulfur) within “sulfur bubbles” forming on an aufeis melt pool at Borup Fiord Pass is presented. This work reveals the association of organic carbon with the sulfur during the formation of beta-sulfur, leading to the hypothesis that sulfide oxidation in the presence of organic carbon allows for the formation of rare monoclinic forms on sulfur in cold systems.

Chapter 4: “Sulfur- and Iron-Rich Mineralogical Features Preserved in Permafrost in the Canadian High Arctic: Analogs for the Exploration of Habitable Environments on Mars”

This chapter presents a comprehensive analysis of the mineralogy, sulfur oxidation state, and sulfur isotopic composition of materials collected from the red-stained mineralized
features and surrounding region at Borup Fiord Pass. This work highlights the discovery of pyrite as a primary component of the materials that were collected in the shallow subsurface. It is hypothesized that pyrite was emplaced in the near-surface and was then later oxidatively weathered, forming a physical structure and surface alteration mineralogy similar to known terrestrial gossans. Although the mechanism of pyrite emplacement is unknown, some potential processes are presented. The chapter also considers the search for potential habitable systems on Mars and the pyrite alteration features as analogs for some such systems.

**Chapter 5: “Future Work: Unraveling the Mysteries of Borup Fiord Pass”**

Potential missing pieces of information about the field site that would further out knowledge of the sulfur springs are considered in this chapter, thus framing this dissertation within the work that has come before and the work that still needs to be done.

**Chapter 6: “Recapitulation and Concluding Remarks”**

In this chapter, the data, interpretations, and future considerations from Chapters 2-5 are reviewed, and a presentation of the current conceptual model of processes occurring at Borup Fiord Pass is presented. The importance of the findings from this dissertation is again considered before the final concluding remarks are given.

**Appendices:**

Chapters 2 through 4 all have supplemental information that is provided in the appendices. These sections include extra data and figures that may aid the reader in visualizing the considerations and interpretations of each chapter. Where relevant, the appendices are cited in Chapters 2-4.
2.1. Overview

Areally extensive deposits rich in elemental sulfur ($S^0$) form annually on ice surfaces at Borup Fiord Pass on Ellesmere Island in the Canadian High Arctic. These visibly yellow deposits form from saline, sulfide-rich supraglacial springs that discharge near the terminus of a coalescence glacier in the valley. Elemental sulfur, gypsum, and carbonates are found within the surficial deposits, and the springs from which these materials derive are alkaline and have elevated levels of dissolved $H_2S$ and $SO_4^{2-}$ (Gleeson et al., 2011; Grasby et al., 2003; Wright et al., 2013). Stable isotope and geochemical analyses have been interpreted as showing that the springs are sourced from glacial meltwater in the subsurface that has reacted with local geological units before returning to the surface. The high levels of sulfide in the springs have been attributed to microbial sulfate reduction in the subsurface (Grasby et al., 2003). Also, biological oxidation of the sulfide at the surface has been hypothesized to then play a key role in the deposition and stabilization of $S^0$ at this site (Wright et al., 2013). The continued oxidation of $S^0$ eventually leads to the formation of sulfates, such as gypsum (though gypsum also forms from the sulfate in the spring waters; Grasby et al., 2003); however, the $S^0$ appears to be stable on glacial and spring-derived ices throughout summer months (the site has not been visited in the winter). Thiosulfate has been measured in the field and, along with other intermediate sulfur species that may exist (but have not been measured), may be a product of biological sulfur oxidation (Wright et al., 2013).

Another key point of interest at this site is the presence of elliptical features of sulfur-rich material that can be found set within the local carbonate rock of the valley to the south of the current site of spring emergence. These conspicuous exposures appear as red-stained, friable material up to 5 m in diameter (the red coloration is due to the presence of iron oxides in these materials; Grasby et al., 2012). The two largest of these exposures have central regions marked by
white, gypsum-rich material. Grasby et al. (2012) have proposed a mechanism of sulfuric-acid speleogenesis (SAS) for the formation of these alteration features as past conduits for carrying sulfide-rich fluids from the subsurface beneath glacial ice and driving the dissolution and replacement of local carbonate with gypsum in the near-surface. However, much remains to be assessed with regard to these features and their potential connection to the modern-day supraglacial springs.

The surface expression of the sulfur spring system, the aufeis, and red-stained, gypsum-rich features at Borup Fiord Pass provide an opportunity for better understanding biological and geochemical sulfur cycling in the subsurface. The sulfide in the springs carries a diagnostic signature of life, in the form of sulfur isotopes, where the sulfide is depleted in $^{34}\text{S}$ relative to the geological source of sulfate from which the sulfur is hypothesized to have been derived. Also, the potential role for microorganisms in driving or mediating the formation and stabilization of elemental sulfur and intermediate sulfur species (i.e. those having oxidation states between sulfide and sulfate) in the modern springs and spring-derived ices justifies efforts to characterize the sulfur-rich materials and microbial communities at Borup Fiord Pass. Thus, in order to further explore the sulfide springs, sulfur deposits, the gypsum-rich mineral features, and associated (bio)geochemical processes, a field excursion to Borup Fiord Pass occurred in the summer of 2014. The major objectives of this field excursion included the following:

- Thoroughly interrogate the aqueous geochemistry and mineralogy of the Borup springs, ices, melt waters, and mineral deposits; sampling of some sites over time was intended to provide a better understanding of temporal as well as spatial variability in sulfur mineralization.
• Explore microbial community composition and function across various spatial and geochemical scales at this site (this part of the research is conducted by Chris Trivedi at the Colorado School of Mines, partnering with the work presented in this dissertation).

• Probe the gypsum-rich mineral features and surrounding materials to better assess the connection of these features to the modern spring system; sampling was to be conducted at the surface as well as at depth using a shovel and a coring drill.

• Explore the formation and stabilization of chemical, mineralogical, and morphological biosignatures at this field site and assess their potential use in future geobiological and astrobiological investigations.

This chapter reviews the state of the Borup Fiord Pass site during the 2014 field excursion, including key observations and data collected in-field. Findings from geochemical and mineralogical analyses of samples upon return from the field are also presented.

2.2. Observations in the Field

The 2014 field excursion to Borup Fiord Pass took place over two weeks, from 19 June to 2 July. Field researchers include the author (Graham Lau) and Alexis Templeton of the University of Colorado Boulder, John Spear and Chris Trivedi of the Colorado School of Mines, and Stephen Grasby of the Geological Survey of Canada. Upon reaching the field site via helicopter, it was immediately observed that a large icing covered in yellow sulfur existed at the toe of the Borup Fiord Pass Glacier (Figure 2.1). During investigation of the field site in the following two weeks, no sulfide spring was observed, but the sulfur-covered ice at the toe of the glacier became a primary focus of the work during that period.
Figure 2.1. Sulfidic aufeis at Borup Fiord Pass in 2014
The yellow-stained aufeis and ice blister region in (a) are viewed from the northwest. A wider view of the valley in (b) gives a view from the east. The image in (b) has been manipulated to highlight the yellow staining of the aufeis, which runs from the toe of the glacier and down the valley.
2.2.1. Sulfur and Aufeis

The large sulfur-covered ice has been determined to be an aufeis. Aufeis (German for “ice on top”; pronounced /auf.aɪs/) are a common feature of High Arctic perennial springs and rivers and are formed by freezing of fluids released during winter months (Clark & Lauriol, 1997; Yoshikawa, Hinzman, & Kane, 2007). In aufeis, surface layers of ice are overridden by more fluid that then also freezes, forming successive layers of ice. The aufeis observed in 2014 stood out as yellow/green ice emitting a recognizable odor of sulfide. This aufeis has been estimated to be ~5x10^4 m^2 in areal extent (Lau et al., 2017), appearing thickest and most extensive at the toe of the glacier. As shown in Figure 2.1, this section of the aufeis stands atop glacial till, while the ice itself then drops into a small canyon (forming recognizable ice waterfalls). The aufeis fills the canyon floor and follows the topographic drop to the east; leaving this small canyon, the aufeis the stretches out from the canyon into the valley. The aufeis continues for ~1 km down the valley (see Fig. 2.1b). Near to the glacier, a large ice blister had formed on the aufeis and was suspected as the site of spring emergence that formed the aufeis itself (Fig. 2.1a and Appendix Fig. A1.1).

Over the course of field work, sulfur was seen to be freshly forming on the aufeis as well as on freshly fallen snow and ice from the glacier which had erupted from a glacial crevasse during the first day of field work and fell onto the surface of the aufeis. Sulfur formed at the surface of this new-fallen snow and ice (later work showed that the material was sulfur, though its bright yellow appearance and knowledge of the field suggested this to be the case; see Appendix §A1.1 and Fig. A1.2). Digging into sections of the ice revealed no observable yellow material below the surface layers.

A target for exploration emerged during the 2014 campaign in the form of melt pools that formed on the surface of the aufeis (Fig. 2.2). These melt pools formed from the melting of the aufeis, but then bubbles of gases were observed to be coming up through the melt pools from the ice below.
Figure 2.2. Melt pools and sulfur bubbles
A selection of images show some of the melt pools on the aufeis (a-d) as well as the collection of sulfur bubbles (e). The melt pool in c is ~2 m in length.
Along with these bubbles was an apparent increase in the odor of hydrogen sulfide. Although a detailed analysis of the gas composition was not completed in this work (see §A1.5), deployment of a silver foil in one of the melt pools showed immediate formation of silver sulfide, suggesting high levels of dissolved sulfide in the melt pool fluids (see Fig. A1.3). In some places, goopy yellow agglomerations presumed to be primarily sulfur (due to apparent hydrophobic interaction with the fluid) appeared to form on and around the bubbles where they met the water-air interface at the surface of a melt pool. These materials have been termed “sulfur bubbles” (Fig. 2.2e). A large amount of yellow precipitates formed around the edges of the melt pools as well (Fig. 2.2c). The melt pools were observed to freeze and re-melt over daily cycles and to change in the activity of bubble release and appearance over the course of multiple days. Where measured in-field, fluids in the melt pools were 0-0.2°C with pH values of 5.5 to 6.0. Previous measurements of temperature and pH in flowing springs ranged from -0.3-2.3°C and 7.3-9.5, respectively, while spring-derived ice (aufeis) and sulfur deposits were 0-5°C and 5.5-7.5, respectively (Gleeson et al., 2011; Grasby et al., 2003; Wright et al., 2013). The in-field measurements from 2014 agree with these previous measurements for aufeis and sulfur deposits (while pH values are slightly acidic compared to the circumneutral to basic values previously measured for the sulfide springs).

Another intriguing discovery with the aufeis melt pools was the formation of subaqueous cryoconite holes at the bottom of the pools. Cryoconite holes, which are also sometimes called "sun cups", are a common formation in glacial environments, where they form from dust grains and other debris which absorb greater solar radiation and drive increased melting in the nearby ice, creating conic holes that melt into the ice and allow for even further accumulation of materials (Cook et al., 2015; Hoffman, 2016; Stibal et al., 2015; Wharton et al., 1985). The cryoconite holes in aufeis melt pools grew in their extent during the field campaign, and they slowly filled with whitish/yellowish precipitates from the melt pool fluid. The cryoconite appeared to grow more extensive in volume during the course of field work, suggesting continual precipitation of material
from the melt pool fluids. The cryoconite in the melt pools and on the aufeis was notably far lighter in color and finer in textural appearance than cryoconite forming high on the glacier or far down-valley.

While sampling from some ice materials of the aufeis in the canyon, one observation revealed that layers of the aufeis below the surface had visible cryoconite holes. This suggests that the formation of the aufeis at this location was not continuous, with some ice melting at a surface layer that was then itself overridden by more ice at a later point.

2.2.2. Alteration features

The valley to the south of the glacier was also explored during the 2014 field season. Interpretations from field observations and analyses of samples are reported further in Chapter 4. In general, six of the alteration features have now been discovered (two more than were previously documented); mineralogical analyses of the material in the alteration features revealed abundant pyrite as well as a mineralogical suite reminiscent of pyrite alteration in an acidic, oxidative system (similar to other terrestrial gossans); and organic carbon was detected in association with pyrite, elemental sulfur, and iron oxides throughout these materials. As presented in Chapter 4, these features serve as appropriate analogs for pyrite alteration systems that may exist (or have existed) on Mars.

2.3. Findings and Interpretations

Note: Details of analytical methods are reported in Section 2.6.

2.3.1. Aqueous Chemistry of the Aufeis Materials

One hypothesis that emerged from field observations was that the aufeis was formed from spring fluids and that the ice blister marked the original site of emergence of a spring (or springs) that formed this aufeis. Ice blisters are common occurrences in cold regions, where spring, river, or
melt water flow has been confined and forced overlying ice to raise and crack, thus forming the appearance of a blistered mound of ice (Gosnell, 2007; Kovacs, 1992). It then seems apparent that some fluid flow at or below the aufeis must have driven the formation of the ice blister (other ice blisters were also observed on the aufeis further down the valley and likely formed from fluid movement during the formation of the aufeis; see §A1.1). At Borup, the yellow coloration of the aufeis, odor of hydrogen sulfide, and the textural appearance of the aufeis at its contacts with the glacial ice were immediate signifiers of the likely derivation from sulfide springs in the system. Materials from the aufeis, including melt pool fluids and the ice itself as well as ice and melt water from the glacier, were sampled for sulfide and aqueous chemical species. Sampling locations for aqueous geochemistry are shown in Figure 2.3, which highlights “Glacial Melt Water” (GMW), “Melt Pool” (MP) fluid, and melted “Ice” (I) samples (see Table A1.1 for images and information for each of these sampling locations).

A select number of these sites were sampled for sulfide through precipitation with excess zinc acetate (forming ZnS). Sulfide was then measured using an elemental analyzer paired with isotope ratio mass spectrometry (EA-IRMS), performed in the Isotope Science Laboratory at the University of Calgary. Sulfide ranged from 0.22 to 2.25 mM in these materials (Table 2.1), with the highest values reported for the samples closest to the ice blister. These sulfide concentrations agree with previously published values for sulfide concentrations in active spring fluids (ranging from 6 \( \mu \)M to 4.2 mM; Gleeson et al., 2011; Grasby et al., 2003; Wright et al., 2013). The highest sulfide concentration in 2014 (2.25 mM) derives from ice collected on top of the ice blister (MP1; see Fig. 2.3).

Analysis of major cations and anions was conducted using inductively-coupled plasma optical emission spectroscopy (ICP-OES) and ion chromatography (IC), respectively (Tables 2.2 and
Figure 2.3. Sample locations for aqueous geochemistry samples
Arrows are used to identify locations on the glacier and aufeis where samples were collected for aqueous geochemical analysis (as reported in Table 1). Blue arrows indicate Glacial Melt Water; red arrows for Melt Pool fluid; and green arrows for ice samples. The views in these images are from the southeast (a) and east (b).
Table 2.1. Measurements of dissolved sulfide in fluid and ice samples
Concentrations of sulfide are listed for select samples (see Fig. 2.3), with an error estimate of ± 0.01 mM. Melt pool samples taken from melted ice are identified (where ice was collected beside the melt pool); other melt pool samples were precipitated directly from fluid.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Date Collected</th>
<th>Sulfide (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP1 (Ice)</td>
<td>30 June</td>
<td>2.25</td>
</tr>
<tr>
<td>MP2</td>
<td>23 June</td>
<td>1.62</td>
</tr>
<tr>
<td>MP2</td>
<td>28 June</td>
<td>0.22</td>
</tr>
<tr>
<td>MP2 (Ice)</td>
<td>28 June</td>
<td>0.35</td>
</tr>
<tr>
<td>MP4 (Ice)</td>
<td>28 June</td>
<td>1.00</td>
</tr>
<tr>
<td>I3</td>
<td>28 June</td>
<td>0.55</td>
</tr>
<tr>
<td>I4</td>
<td>28 June</td>
<td>0.32</td>
</tr>
<tr>
<td>I5</td>
<td>28 June</td>
<td>0.52</td>
</tr>
<tr>
<td>I6</td>
<td>28 June</td>
<td>0.32</td>
</tr>
</tbody>
</table>
Table 2.2. Major anions for selected aqueous samples from 2014
Sample locations are described in the text and shown in Figure 3. Dates of collection listed give only the day, as all samples were collected in June of 2014. CBE is the charge balance error (in %), discussed in the text. All data are presented in mM. DL is “detection limit” for the instrument. Where below DL, cells are left blank. NM shows where “no measurement” was taken.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Date</th>
<th>F⁻</th>
<th>Cl⁻</th>
<th>Br⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>S₂O₃²⁻</th>
<th>CBE (%)</th>
</tr>
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<tbody>
<tr>
<td>GMW1</td>
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<td></td>
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<td></td>
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<td>NM</td>
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<td></td>
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<td>NM</td>
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<td></td>
<td></td>
</tr>
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<td>MP1</td>
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<td></td>
<td>3.963</td>
<td></td>
<td>3.806</td>
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<td></td>
<td>30</td>
<td></td>
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<td></td>
<td>2.146</td>
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<tr>
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<td></td>
<td>23</td>
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<td>85.939</td>
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<td>9.145</td>
<td>0.032</td>
<td>5.282</td>
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<tr>
<td></td>
<td>30 (ice)</td>
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<td>58</td>
<td>0.014</td>
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<td>0.009</td>
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</table>
Table 2.3. Major cations for selected aqueous samples from 2014
Samples are presented as described in the text and shown in Figure 3. Dates of collection listed give only the day, as all samples were collected in June of 2014. Charges have been assumed, as chemical species were measured as total atomic concentrations. Where multiple charged species are possible, a “T” subscript implies total concentration. SiO$_2$ is the assumed state of Si in the samples. CBE is the charge balance error (in %), discussed in the text. All data are presented in mM. DL is “detection limit” for the instrument. Where below DL, cells are left blank.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Date</th>
<th>SiO$_2$</th>
<th>Mn$_T$</th>
<th>Fe$_T$</th>
<th>Mg$^{2+}$</th>
<th>Ca$^{2+}$</th>
<th>Na$^+$</th>
<th>K$^+$</th>
<th>CBE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GMW1</td>
<td>23</td>
<td>0.00018</td>
<td>0.0014</td>
<td>0.120</td>
<td>0.150</td>
<td>0.469</td>
<td></td>
<td></td>
<td>93</td>
</tr>
<tr>
<td>GMW2</td>
<td>28</td>
<td>0.48672</td>
<td>0.00018</td>
<td>0.00018</td>
<td>0.00036</td>
<td>0.01603</td>
<td>0.53575</td>
<td></td>
<td>14</td>
</tr>
<tr>
<td>MP1</td>
<td>27</td>
<td>0.010</td>
<td>0.00018</td>
<td>0.743</td>
<td>3.504</td>
<td>2.846</td>
<td></td>
<td></td>
<td>-7</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.001</td>
<td>0.00018</td>
<td>0.379</td>
<td>1.974</td>
<td>1.525</td>
<td></td>
<td></td>
<td>-7</td>
</tr>
<tr>
<td>MP2</td>
<td>21</td>
<td>0.094</td>
<td>0.00036</td>
<td>6.966</td>
<td>11.305</td>
<td>27.068</td>
<td>0.199</td>
<td></td>
<td>-8</td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>0.116</td>
<td>0.00055</td>
<td>0.0007</td>
<td>9.165</td>
<td>12.638</td>
<td>38.250</td>
<td>0.210</td>
<td>-25</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.042</td>
<td>0.00018</td>
<td>3.930</td>
<td>6.712</td>
<td>14.072</td>
<td>0.073</td>
<td>25</td>
<td></td>
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<tr>
<td></td>
<td>30 (ice)</td>
<td>0.13</td>
<td>0.00064</td>
<td>5.6</td>
<td>14</td>
<td>35</td>
<td>0.23</td>
<td>-11</td>
<td></td>
</tr>
<tr>
<td>MP3</td>
<td></td>
<td>0.035</td>
<td>0.00018</td>
<td>0.0002</td>
<td>2.382</td>
<td>7.406</td>
<td>8.682</td>
<td>0.065</td>
<td>-2</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.031</td>
<td></td>
<td></td>
<td>2.578</td>
<td>5.161</td>
<td>9.553</td>
<td>0.053</td>
<td>-31</td>
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<tr>
<td>MP4</td>
<td>26</td>
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<td>0.00036</td>
<td>3.919</td>
<td>9.379</td>
<td>15.982</td>
<td>0.099</td>
<td></td>
<td>-12</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.019</td>
<td>0.00018</td>
<td>2.138</td>
<td>5.109</td>
<td>7.965</td>
<td>0.036</td>
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</tr>
<tr>
<td>MP5</td>
<td>22</td>
<td>0.165</td>
<td>0.00091</td>
<td>11.775</td>
<td>18.608</td>
<td>47.545</td>
<td>0.302</td>
<td>-3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.024</td>
<td>0.00018</td>
<td>2.196</td>
<td>4.989</td>
<td>8.840</td>
<td>0.052</td>
<td>-36</td>
<td></td>
</tr>
<tr>
<td>I1</td>
<td>28</td>
<td>0.046</td>
<td></td>
<td></td>
<td>2.166</td>
<td>8.978</td>
<td>8.661</td>
<td>0.023</td>
<td></td>
</tr>
<tr>
<td>I2</td>
<td>22 (crust)</td>
<td>0.022</td>
<td>0.0002</td>
<td>0.301</td>
<td>0.975</td>
<td>1.259</td>
<td></td>
<td>4</td>
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</tr>
<tr>
<td></td>
<td>22</td>
<td>0.047</td>
<td>0.00018</td>
<td>5.598</td>
<td>12.302</td>
<td>21.434</td>
<td>0.130</td>
<td>-5</td>
<td></td>
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<tr>
<td>I3</td>
<td>28</td>
<td>0.046</td>
<td>0.0004</td>
<td>3.321</td>
<td>8.201</td>
<td>13.615</td>
<td>0.089</td>
<td>-10</td>
<td></td>
</tr>
<tr>
<td>I4</td>
<td>25</td>
<td>0.007</td>
<td></td>
<td>1.346</td>
<td>1.722</td>
<td>5.252</td>
<td>0.024</td>
<td>9</td>
<td></td>
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<tr>
<td>I5</td>
<td>25</td>
<td>0.007</td>
<td>0.00018</td>
<td>1.178</td>
<td>1.777</td>
<td>4.330</td>
<td>0.041</td>
<td>-3</td>
<td></td>
</tr>
<tr>
<td>I6</td>
<td>28</td>
<td>0.005</td>
<td>0.0002</td>
<td>0.826</td>
<td>2.749</td>
<td>3.233</td>
<td>0.013</td>
<td>-2</td>
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<tr>
<td>DL</td>
<td></td>
<td>0.001</td>
<td>0.00002</td>
<td>0.0001</td>
<td>0.001</td>
<td>0.002</td>
<td>0.004</td>
<td></td>
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</tr>
</tbody>
</table>
2.3). Some samples were collected from the same site over multiple days. The normalized major cation chemistry of 2014 samples compared to previous measurements for springs, glacial melt water, and sulfur deposits from 2000, 2006, and 2009 reveals that 2014 measurements plot along with previous measured samples from Borup Fiord Pass (Fig. 2.4). The cation distributions in melt pool fluid and melted ice samples from 2014 are similar to those reported for sulfide springs bearing the highest measured levels of sulfide from 2006 and 2009 (the springs sampled in 2000 have a closer cation distribution to the melt waters from that year as well as to the sulfur deposit from 2009; as reported by Gleeson et al. (2011), the springs in 2000 were sampled later in the summer, during a period of greater dilution from glacial melt). The major cation distributions reveal a consistent trend for samples collected at Borup Fiord Pass from multiple field seasons spanning 15 years, supporting the hypothesis that the aufeis was sourced from a sulfide spring.

Anion chemistry appears to show similar trends to cation chemistry. For instance, samples of glacial melt water have the lowest Cl⁻ concentrations, while the highest are found in melt pools and on the aufeis near the blister. The highest chloride concentrations were measured in melt pool fluids collected at site MP2 (85.9 mM; sampled 23 June) and site MP5 (75.6 mM; sampled 22 June; see Fig. 2.3). Melt pool sites MP2 and MP5 also have the highest sulfate concentrations, at 18.6 mM and 16.0 mM, respectively. 18.6 mM SO₄²⁻ was also reported for the sulfide spring sampled in 2006 (Gleeson et al., 2011). That sulfide spring and the melt pool bearing the same sulfate concentration in 2014 have the highest reported sulfate concentrations from Borup Fiord Pass to date.

Charge balance for aqueous geochemical data was performed by converting concentrations of aqueous anions and cations to molar equivalents of charge per kilogram of sample. The charge balance error (CBE) is a conventional measure of the variation in charge balance from the expected equivalence.
Figure 2.4. Major cation chemistry of aqueous samples
This ternary diagram reports the normalized proportions of the major cations: Ca$^{2+}$, Mg$^{2+}$, and Na$^{+}$+K$^{+}$. 2014 samples include those for Melt Pools and Ice, as reported in Table 1. Data for a sulfide spring and sulfur-rich deposit from 2009 were reported by Wright et al. (2013), while data for a sulfide spring in 2006 were reported by Gleeson et al. (2011). Data for springs and melt waters in 2000 are here reported as average values of the data reported for these fluids by Grasby et al. (2003).
between positive and negative charges and is reported here in Tables 2.2 and 2.3 (see §A1.3 for explanation of the calculation). Generally, a $|\text{CBE}| < 5\%$ is considered acceptable for most analytical laboratories (Freeze & Cherry, 1979; Zhu & Anderson, 2002), though much larger errors have been found to be common in published reports (see Fritz, 1994). CBE is fairly poor for glacial melt water samples (GMW1,2; which have CBEs of 93% and 14%, respectively). Solutions of low ionic strength (and thus low ion content) are prone to greater errors in charge balance (Fritz, 1994), and so the larger error may be expected for those samples. However, most of the melt pool and ice samples also have $|\text{CBE}| > 5\%$, suggesting errors in measurements or a number of potentially missing anions and cations in this system.

Sample MP2 (collected on June 30th) is one that has a high, positive CBE (25%). This usually indicates data for which either cationic measurements are biased toward greater values or some anionic species are missing from the charge balance consideration. Two of the most likely anions that may cause positive inclinations of the CBE for these data are dissolved carbonate and sulfide. For most systems, dissolved carbonate is a major contributor to alkalinity. Although we had initially intended to measure alkalinity in the field, this measurement was not possible. However, bicarbonate concentrations have been previously measured at Borup Fiord Pass. In spring fluids from 2000, 2006, and 2009, bicarbonate ranged from 0.2 to 1.1 mM (Gleeson et al., 2011; Grasby et al., 2003; Wright et al., 2013). Adding even the highest value for bicarbonate previously measured to the geochemical data for site MP2 only improves the charge balance by 3%. However, if data for the highest measured sulfide from 2014 (2.25 mM) are added, then the CBE drops to 13% (a more acceptable value for qualitative analysis, though still greater than 5%).

Samples which had a CBE $<< -5\%$ include MP2 (data from June 23rd and 30th (ice)), MP3 (June 30th), and MP5 (June 30th). A bias towards anions or missing cation data can explain such low values. Missing cations species that have previously been measured which may be missing from our overall understanding of the fluid chemistry from Borup Fiord Pass in 2014 includes ammonium
(NH$_4^+$), a potentially important missing species. Wright et al. (2013) reported ammonium within spring fluids as well as within a sulfur-rich deposit downstream from the spring in 2009. They reported 254 µM NH$_4^+$ in spring fluids and 15 µM NH$_4^+$ in the sulfur deposit. Extrapolating from the highest levels of ammonium shifts data with low CBE to greatly positive CBE values. Assuming even the lowest level of ammonium previously reported still shifts the data for these samples to greatly positive values of CBE. This suggests that ammonium is a major missing cation from the chemical data collected in 2014 (though other unmeasured, dissolved metals may also be important).

2.3.2. Minerals in the Melt Pools and Cryoconite Holes

Various solid materials were collected during the 2014 field excursion. These included precipitates from the aufeis and melt pool edges, the sulfur bubbles, cryoconite, and dried sulfur and glacial till. X-ray diffraction (XRD) and Raman microspectroscopy were used to probe many of these samples. As Table 2.4 shows, primary mineral components of the samples analyzed included S$^0$, gypsum, calcite, halite, and quartz. While it’s hypothesized that S$^0$ is formed through biological oxidation of the sulfide in the aufeis materials, the gypsum, calcite, and halite may all be forming through precipitation of supersaturated dissolved species in the fluids (although some gypsum may also form from continued biological and/or abiotic oxidation of the S$^0$). Quartz in these materials, meanwhile, may be derived from aeolian sources. Perhaps some of the most intriguing findings come from the discovery of exotic sulfur and carbonate minerals within the Borup 2014 samples; namely, the identification of three allotropic forms of elemental sulfur in melt pool sulfur bubbles as well as the detection of the sulfate carbonate mineral rapidcreekite in melt pool cryoconite (Table 2.4). The detection of rapidcreekite is discussed below, while a consideration of the detection of three allotropes of elemental sulfur is presented in Chapter 3.
Table 2.4. General mineralogical findings for select samples

A brief description of each sample is provided. Fits are listed as best-matched x-ray diffraction patterns, ordered by intensity of the dominant diffraction line in the pattern. Questionable pattern fits are shown in parentheses. Where $S^0$ is listed as a fit, it is implied that the fit is for alpha-cyclooctasulfur (see text). Intriguing discoveries of rare mineral forms are underlined in the table and further discussed in the text.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Description</th>
<th>XRD Pattern Fits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glacial Cryoconite</td>
<td>Brown, grainy cryoconite from the glacier above the aufeis (near site GMW1)</td>
<td>Quartz, (phylosilicate minerals)</td>
</tr>
<tr>
<td>Melt Pool Cryoconite (MP2)</td>
<td>Cryoconite which had formed at the bottom of the melt pool</td>
<td>Gypsum, halite, calcite, rapidcreekite</td>
</tr>
<tr>
<td>Melt Pool Sulfur Bubbles (MP2)</td>
<td>Sulfur-rich material forming on gas bubbles at the air-fluid interface at the surface of the melt pool</td>
<td>Three allotropes of elemental sulfur</td>
</tr>
<tr>
<td>Melt Pool Cryoconite (MP5)</td>
<td>Cryoconite from a melt pool in the canyon aufeis region</td>
<td>Gypsum, calcite</td>
</tr>
<tr>
<td>Fresh Sulfur on Snow</td>
<td>Yellow precipitates forming on snow after 2 days beside the ice blister region</td>
<td>Calcite, $S^0$, $SiO_2$</td>
</tr>
<tr>
<td>Sulfur Falls Ice (I2)</td>
<td>Scrapings of yellow precipitate and ice from the side of lower sulfur falls (same site as I2)</td>
<td>Calcite, $S^0$</td>
</tr>
<tr>
<td>Snow Cone Sulfur</td>
<td>Yellow precipitates forming on top of a “snow cone” near MP5 on the aufeis in the canyon.</td>
<td>Gypsum, calcite, $S^0$</td>
</tr>
<tr>
<td>Melt Pool Rim</td>
<td>Yellow precipitates that formed at the rim of a melt pool in the aufeis in the valley (near site I6)</td>
<td>$S^0$, (halite)</td>
</tr>
<tr>
<td>Green/Yellow Goop at the Ice Blister</td>
<td>Green/yellow material forming on top of the blister, assumed to be elemental sulfur</td>
<td>Calcite, $S^0$, quartz, gypsum</td>
</tr>
<tr>
<td>White Goop at the Ice Blister</td>
<td>White material that formed on top of the green/yellow goop and only appeared to form several days after the green/yellow materials</td>
<td>Gypsum, calcite</td>
</tr>
</tbody>
</table>
Most of the cryoconite material that was collected in 2014 was composed of gypsum, calcite, and elemental sulfur, as identified through XRD (e.g., Table 2.3). Scanning electron microscopy and energy dispersive spectroscopy (SEM/EDS) of cryoconite samples revealed well-formed, tabular mineral grains composed of Ca, S, and O; likely gypsum. In some regions, globular elemental sulfur (identified with EDS) was adhered to the surfaces of the tabular grains (Fig. 2.5a,b). Cubic mineral grains (likely calcium carbonate; Ca, C, and O identified with EDS) are also abundant in this material (Fig. 2.5c), and globules of elemental sulfur were also identified associated with these cubic grains (Fig. 2.5d). With the high concentrations of calcium and sulfate, the fluids measured are near saturation with respect to gypsum (see §A1.4; note: mineral saturation calculations are questionable due to the poor CBE for aqueous data). Although dissolved bicarbonate (HCO$_3^-$) was not measured in the fluid samples from the aufeis in 2014, assuming a level of bicarbonate approaching the highest measured value for spring fluids in the past shows that the fluids are undersaturated with respect to calcite (§A1.4). However, the presence of carbonate mineral precipitates indicates that dissolved carbonate species must exist in the fluids. One intriguing constraint on dissolved carbonate concentrations within melt pool MP2 (Fig. 2.3) is the detection of a rare mineral of hydrated calcium sulfate carbonate called rapidcreekite.

Rapidcreekite (Ca$_2$(SO$_4$)(CO$_3$)$\cdot$4H$_2$O) was detected by XRD as well as Raman microspectroscopy within the MP2 cryoconite. Microscope images reveal both tabular and elongated mineral grains within this material (Fig. 2.6). Raman spectra show materials that appear to be associations of gypsum, calcite, and/or elemental sulfur, but also rapidcreekite (Fig. 2.6), apparently in the elongated mineral grains (and not detected thus far in the more tabular grains). Rapidcreekite is a rare mineral and has only been detected in a limited number of natural systems (Onac et al., 2013; Roberts, 1986). Its presence may suggest that [SO$_4^{2-}$]/[CO$_3^{2-}$]>>1 in the melt pool.
Figure 2.5. Electron micrographs of cryoconite materials
Cryoconite within a shallow melt pool near the ice blister (near to site MP3) revealed abundant tabular and well-formed grains (likely calcium sulfate; a) as well as globular sulfur (red box in a; region magnified in b). Multiple cross-shaped twinned minerals identified as likely calcium sulfate from EDS (c) as well as cubic grains (likely calcium carbonate; d) were identified as well. The white arrows in d show the location of globules of elemental sulfur.
Materials in the sample include abundant elongated (a) and tabular (b) crystals. Raman spectra are presented in (c) for the materials from these regions (color coded to match arrows in (a) and (b)), as well as for relevant standards (discussed in text). Region (d) shows more of the elongated crystals, while (e) and (f) show magnified regions from yellow and teal boxes in (d), respectively.

Figure 2.6. Raman microspectroscopy of cryoconite from melt pool MP2
during rapidcreekite formation, as has been determined by other authors (Onac et al., 2013; Roberts, 1986; the solubility constant for rapidcreekite has not been well-constrained). Although this does not set a qualitative upper limit for carbonate concentration, it does conceptually suggest that the dissolved sulfate concentrations must be far greater than those for carbonate in the samples where rapidcreekite had formed.

2.3.3. Organic Carbon in 2014 Samples

A more thorough understanding of the microbial communities at Borup Fiord Pass is necessary for determining the role that life plays in forming and stabilizing the sulfur-rich deposits. Also, determining which signs of life are imprinted into the materials at Borup Fiord Pass, thus forming biosignatures, is necessary for relating our findings from this remote Arctic site to processes occurring in other sulfur-dominated environments on Earth as well as on other worlds. One place to start in such analyses is characterizing the organic carbon content of the various materials of interest in the field. For instance, combustion methods have been used to assess the total organic carbon (TOC) in a number of samples, including cryoconite and sulfur bubbles from melt pools; yellow precipitates on the aufeis; dry, yellow precipitates on glacial till; yellow precipitates that formed within a microlysimeter after 24 hours of deployment in some melt fluid on the surface of the aufeis; and some of the glacial till mud that formed in the middle of the aufeis at the blister region (see dark patch within aufeis in Fig. 2.3). All cryoconite and yellow precipitates on the aufeis have TOC values ranging from 0.07 to 1.30% (by weight). Meanwhile, the lysimeter material and the glacial till have much higher values, at 1.82 and 2.49%, respectively. The lysimeter is specifically designed to filter fluids and thus is likely concentrated in the organic material from the pool of fluid where it was deployed. The 2.49% TOC in the glacial till is intriguing as the glacial till may represent one possible surface input of organic carbon into the spring and aufeis system.
Raman microspectroscopy is one method that can be used to identify the distribution of carbon within the Borup materials. For instance, Raman microspectroscopy allowed for the discovery of several rod-shaped filaments coated in sulfur along with dark carbon-rich grains in the sulfur bubble material from site MP2 (Fig. 2.7). Further characterizations of the sulfur bubbles using Raman microspectroscopy are presented in Chapter 3, and Chapter 4 presents extensive Raman spectral data for the red-stained, gypsum-rich materials from south of the glacier.

Synchrotron-based x-ray absorption methods were also used to analyze the materials from Borup 2014. For instance, synchrotron-based, x-ray absorption spectroscopy (XAS) was used to probe the bulk speciation of sulfur within a variety of the 2014 Borup samples (Fig. 2.8). Most materials were shown to bear pyrite, $S^6$, and/or sulfate. However, sulfur XAS can detect organosulfur compounds. For instance, sulfur XAS of the cryoconite and sulfur bubbles from site MP2 revealed $S^0$ in the sulfur bubbles and a mix of sulfate and a sulfur functional group with a similar oxidation state to S-methylmethionine (Fig. 2.9). It was expected that sulfate would be present in this material, but the detection of a potential sulfonium functional group at the bulk scale is intriguing (though a potential biological role for such a sulfur functional group in bulk cryoconite material is currently unknown).

Another synchrotron-based x-ray method that was applied to samples from Borup 2014 is scanning transmission x-ray microscopy (STXM). STXM allows for element-specific, nanoscale imaging of x-ray transmissive materials paired with nanoscale x-ray absorption spectroscopy. STXM of 2014 Borup samples was conducted at the C K-edge and S L-edge. STXM was used to map the distribution and characterize the speciation of carbon and sulfur in samples at a 35 nm spatial resolution. The STXM data for melt pool sulfur bubbles showed a spatial association between organic carbon and elemental sulfur globules in the materials and is further considered in Chapter 3 (and published in Lau et al., 2017). STXM was also used to assess the carbon speciation within
Figure 2.7. Rods, globules, and grains from the melt pool sulfur bubble material

Images a through d show some of the rod-like material observed in this sample. One rod (e) was mapped and revealed solely elemental sulfur through Raman spectroscopy (see “Sulfur Rod” spectrum in g). Some darker grains were observed, as in f, which appear to be composed of elemental sulfur and organic carbon (see “Dark Grain” spectrum in g). The spectrum for elemental sulfur (S0) is presented in g for comparison. Peaks for organic carbon (the D- and G-bands) in “Dark Grain” are magnified within the inset.
Figure 2.8. X-ray absorption spectra of sulfur model compounds and 2014 Borup samples
Fluorescence intensity is plotted against absorption energy for model compounds (left) and 2014 samples (right). Model sulfur compounds show that increasing oxidation states for sulfur (plotted from bottom to top) causes the main absorption peak to shift to higher energy. For 2014 Borup samples (right), a double vertical line shows the locations of peaks fit with pyrite (glacial till) or $S^0$ (all others). A single vertical line shows the location of peaks that fit with sulfate. Samples are, from top to bottom: Glacial Till (collected from exposed material beside the aufeis), Lysimeter (material precipitated within a microlysimeter deployed near MP5), Dried Sulfur (yellow material collected from the surface of till near the aufeis; potentially from previous years of sulfur formation), Fresh Sulfur (yellow material that formed on fresh snow that had fallen on top of the aufeis), MP3 (melt pool 3, as discussed in the text), Aufeis Crust (yellow crust on top of the aufeis beside a melt pool), Melt Pool (another melt pool not previously listed in the chapter; this melt pool is just to the southeast of MP3), Aufeis (material collected from the aufeis close to stream emergence from a glacial crevasse), and Glacial Cryonite (cryoconite material collected from the glacier: data were very noisy, but still contained sulfur functional groups).
Figure 2.9. X-ray absorption spectra for site MP2 samples
Spectra for cryoconite (blue) and sulfur bubbles (red) from site MP2 are presented with the best fit model compounds. Sulfur bubbles only reveal a fit with elemental sulfur while cryoconite appears to fit with $S^0$, gypsum, and a sulfonium salt. The spectra for $S^0$ and gypsum are part of the Templeton Lab’s model compound library. The spectrum for a sulfonium salt (methionine methylsulfonium chloride) presented in the figure was collected on the ID21 beamline at the European Synchrotron Radiation Facility by user Sylvain Bohic and is available online at http://www.esrf.eu/home/UsersAndScience/Experiments/XNP/ID21/php/Database-SOrganic.html. See Bohic et al. (2008) for further information.
some samples from the red-stained mineral features in the valley (see Chapter 4). STXM was also conducted on four further unique types of sample material from the aufeis in 2014. These are the yellow crust of material deposited over the ice from sample I2 on “sulfur falls”, some yellow goop that formed over one of the melt pools and included sulfur bubbles, the material collected in a microlysimeter after one day of deployment (Figs. 2.10-2.12), and some of the fresh sulfur that had formed on top of glacial ice that fell onto the aufeis after our first day of field work.

The crust of material on Sulfur Falls shows sulfur and carbon in association, with several large grains (>1 µm) that were shown through sulfur L-edge XANES to be composed of gypsum (Fig. 2.10a,b). An analysis of the carbon speciation within one region (roughly 3.5x3.5 µm²) where carbon surrounded one such grain revealed the presences of multiple organic and inorganic carbon functional groups (Fig. 2.10c,d). For instance, the region revealed an abundance of carbonate (fitting with the green spectrum in Fig. 2.10c,d) though most of the material showed the presence of aromatic and aliphatic carbon, carboxyl carbon, and functional groups of carbon and oxygen (such as alcohols, ethers, and/or hydroxylated aliphatic carbon; red and green regions in Fig. 2.10c). The carbon functional groups may represent a variety of biologically-derived organic carbon. Reference spectra for organic carbon materials are shown in Figure 2.10d (adapted from Chan et al., 2010), and include protein, polysaccharides, DNA, and a lipid. The carbon functional groups expressed in this sample can be found in all of these organic carbon compounds and may represent the organic carbon inventory of the microbial community within this sample.

STXM of sulfur bubble material shown in Figure 2.11 is from sulfur bubble material collected from a melt pool roughly located between sites I3 and I4 in Figure 2.3. This sulfur bubble material may indicate the sulfur and carbon expression of sulfur bubble material after multiple days of formation (the sample appeared to be a large cover of material and had been observed to have begun forming two days previously). One immediately striking observation from STXM of this
Figure 2.10. STXM images and x-ray absorption spectra for sulfur crust on sulfur falls

An image at 320.0 eV (a) shows a carbon rich region of the yellow crust over the aufeis of sulfur falls (same region as sample I2). The blue box in a shows the location of the difference map of optical densities in b, which shows carbon in blue (288.2 vs. 280.0 eV) and sulfur in yellow (163.0 vs. 160.0 eV). This same region is then shown in c, where the region is colorized to match fits for two carbon x-ray absorption spectra as reported in d (viz. greens and reds in c match the colorized spectra at the top of the plot in d; the blue regions in c are those which had organic carbon in insufficient concentrations for data collection). Reference spectra for multiple organic carbon compounds are also shown in d. These reference data are reported by Chan et al. (2010) and are as follows: a protein (bovine serum albumin; BSA), alginate (an acidic polysaccharide), agarose (a neutral polysaccharide), a sample of DNA, and a lipid (1,2-dipalmitoyl-sn-glycero-3-phosphoethanolamine). Vertical lines, included to highlight the carbon functional groups in the two sample spectra, represent the following carbon functional groups (transitions, line styles, and energies are in parentheses): unsaturated or aromatic carbon (1s→π* C=C; solid grey line; 285.2 eV); aliphatic carbon, aromatic carbonyl, ketones, and/or phenols (1s→σ; dotted black line; 287.6 eV); carboxyl (1s→π* C=O; solid black line; 285.2 eV); alcohols, ethers, and/or hydroxylated aliphatic carbon (1s→σ* C=O; dashed black line; 289.3 eV); and carbonate (1s→π* C=O; double grey line; 285.2 eV; e.g., Chan et al., 2010; Liu et al., 2013; and references therein). Scale bars in a and b are 1 µm.
Figure 2.11. STXM maps and spectra for melt pool sulfur bubble material

Sulfur and carbon maps are shown for two different regions in a and b. Sulfur data are the difference in optical densities (OD) from 163.0 to 160.0 eV (yellow in a; red in b). Carbon data are the differences in OD from 288.6 to 280.0 eV (blue in a; green in b; highlighting organic carbon) as well as 290.2 to 288.6 eV (blue in b; highlighting carbonate). Sulfur and carbon XANES spectra are shown in (c) and (d), respectively. The orange spectrum in c comes from the rod-shaped sulfur-rich structure in a, while the red spectrum comes from the sulfur-rich spot toward the bottom center of b. Vertical lines in c highlight the well-known peak locations for elemental sulfur (163.3 eV and 164.6, shown as solid and dotted lines, respectively). The spectra in d are colorized to match fits within the map data in d (white circles in the inset show where the representative spectra for map fitting were collected). Vertical lines represent the following carbon functional groups (transitions, line styles, and energies are in parentheses): quinone/benzoquinone (1s→π* C=C; solid grey line; 284.4 eV); aliphatic carbon, aromatic carbonyl, ketones, and/or phenols (1s→σ; solid black line; 286 eV); aliphatic carbon (1s→3p/σ* C-C; dashed black line; 287.8 eV); carboxylics (1s→π* C=O; double dotted black line; 288.6 eV); carbonate (solid grey lines; 290.2, 295.5, 298.1, and 301.7 eV); and potassium (L-edge peaks; dotted black lines; 297 and 300 eV; e.g., Brandes et al., 2004; Brandes, et al., 2010; Chan et al., 2010; Cosmidis & Benzerara, 2014; Lau et al., 2017; Liu et al., 2013; and references therein).
Material from the lysimeter appears to be primarily gypsum with associations of organic carbon (a-d). A STXM image presented in a was collected at 170.0 eV (above the sulfur L-edge). A map of optical densities for sulfur from the same region (b) shows differences in 163.0 vs. 160.0 eV (reds) and 173.0 vs. 170.0 eV (greens). The plot in c shows a representative spectrum for the green colored regions within the yellow box in b (a reference spectrum for gypsum is also shown; spectrum modified from Jalilehvand, 2006). Another optical density map, shown in d, contrasts data for carbon from 288.2 to 280.0 eV (shown in blue); yellows are regions of no difference, but are presented to show associations with organic carbon. The scale bar in a is 5 µm (and applies to images in b and d as well).
material was a long grain that appeared to be composed solely of elemental sulfur (and was thus called the "sulfur rod") which also showed two lima bean-shaped regions attached to the rod which appeared rich in organic carbon (Fig. 2.11a,c). The spectrum for the sulfur in the rod shown in Figure 2.11c confirmed the structure was composed of elemental sulfur. Unfortunately, although the lima bean-shaped structures reveal the presence of organic carbon, the spectra that were collected from these regions suffered from instrumental errors (optical glitches). However, it is possible that given the shape and size of these regions (lima bean-shaped and 1-4 µm) that they were microbial cells within the material. Future work will be necessary to determine if STXM of these materials can return organic carbon spectra of such potential microbial cells.

Another region of the sulfur bubble material revealed an abundance of globs of elemental sulfur (red regions in Fig. 2.11b and red spectrum in Fig. 2.11c) associated with carbon-rich regions (including another lima-bean shaped structure of about 1-4 µm in size; top of the image in Fig. 2.11b). As the spectra in Figure 2.11d reveal, multiple potential organic carbon functional groups were also detected in this region. Though much of the carbon-rich material in Figure 2.11b appear to be carbonate (blue regions; blue spectrum in Fig. 2.11d), the green regions in Figure 2.11b and associated spectra reveal the presence of aliphatic and aromatic carbon, carboxylic groups, and potentially quinone/benzoquinones (in the shoulder ~284.4 eV in the light green spectrum in Fig. 2.11d). These peak identifications are derived from previous studies by Brandes et al., 2004; Brandes et al., 2010; Chan et al., 2010; Lau et al., 2017; Liu et al., 2013 (and multiple references therein). These findings from sulfur bubbles, taken with the findings presented in Chapter 3, suggest that the sulfur bubbles are a key target in understanding the biological processes occurring in aufeis melt pools at Borup Fiord Pass.

Material that collected within the microlysimeter revealed the presence of sulfate (likely in a grain of gypsum), with associated organic carbon-rich regions through sulfur and carbon STXM (Fig. 2.12). The microlysimeter was used to collect pore fluids for geochemical analyses, but was
later found to have collected a high concentration of organic carbon (likely as the lysimeter concentrated organic carbon from the aufeis melt; data were collected as total organic carbon (TOC) and showed 1.82% TOC in the lysimeter). The sulfate that formed within the lysimeter appeared to form large grains (Fig. 2.12), though these must have precipitated within the lysimeter as it only collected pore fluids and would not allow for the collection of larger grains of material directly.

The sulfur and carbon STXM data reveal organic carbon functional group potentially indicative of biological activity within aufeis materials. Also, the lima bean-shaped regions detected through STXM imaging of the sulfur bubbles may be microbial cells. A more thorough interrogation of these results as well as further submicron-scale sulfur and carbon spectroscopy are warranted to better understand the imprint of biological function within aufeis materials. Unfortunately, much of the carbon XANES spectra that were collected for this work suffer from optical glitches that occurred on the beamline, precluding a thorough consideration of the data at the current time.

2.4. Conclusion

The field excursion to Borup Fiord Pass in 2014 has revealed new observations and findings related to the modern-day sulfur spring system and the region of red-stained mineral features in the valley. Although the yellow coloration of the ice from elemental sulfur was first observed in 1988 by helicopter and field excursions have occurred since 1999 (e.g., Gleeson et al., 2011; Gleeson et al., 2012; Grasby et al., 2003; Grasby et al., 2003; Grasby et al., 2012; Wright et al., 2013), there were many new discoveries that occurred in 2014. For instance, this is the first time that an ice blister presented itself through a thick aufeis at the toe of the glacier, suggesting a site of spring emergence that led to the formation of the aufeis as well as of the ice blister. Also, although yellow sulfur-rich deposits and sulfur-rich aufeis had been detected previously, this is the first time that it was determined that the formation of the elemental sulfur from sulfide in the aufeis was a dynamic
process that was actively occurring over days and weeks (and potentially even hours). Also, this is the first time that melt pools forming on the surface of a sulfur-rich aufeis were presented as a key target in understanding the sulfur spring system. These melt pools allow for a characterization of “sulfur bubbles” forming at the air-water interface as well as of the cryoconite that forms from active mineral precipitation at the bottoms of the melt pools. While mineralogical analyses mostly showed that calcite, gypsum, and elemental sulfur are the primary components of materials collected from the aufeis, the finding of monoclinic allotropes of sulfur ($\beta$-S$_8$ and $\gamma$-S$_8$) in the sulfur bubbles and rapidcreekite in the cryoconite are intriguing as these minerals forms are rare and little explored in their role in cold, sulfur-dominated systems like Borup Fiord Pass. Rapidcreekite, a rare calcium sulfate carbonate mineral, in the cryoconite may reveal controls on the fluid chemistry through a variety of processes, potentially including the microbial processes occurring in the melt pools.

2.5. Overview of Methods

Sample Collection. Ice, mineral, and fluid samples were collected at Borup Fiord Pass ($81^\circ$ 01’N, $81^\circ$ 35’W; Figure 1) in June 2014. Fluid pH was measured in the field with test strips (Carolina Biological Supply Co.; Burlington, North Carolina, USA). Temperatures were measured with a Hach HQ40d portable field meter (Hach Company; Loveland, Colorado, USA). Cryovials of material were stored in a liquid nitrogen (LN) dewar upon collection and until return to the University of Colorado Boulder. Other samples were stored on ice for transport. All samples were then placed in a -70°C freezer until needed for analyses.

Aqueous Geochemistry. A large number of aqueous samples (fluid as well as melted ice) were collected during the 2014 field campaign for analysis of major cations and anions using inductively-coupled plasma optical emission spectroscopy (ICP-OES; for cations) and ion chromatography (IC; for anions). Samples were filtered (0.22 µm membrane), and samples for ICP-OES were acidified
using concentrated nitric acid to preclude the precipitation of analytes. Samples were collected in 15 mL and 50 mL polypropylene tubes. ICP-OES and IC measurements were performed on an ARL 3410+ ICP-OES and a Dionix 4500I IC, respectively, at the Laboratory for Environmental and Geological Studies (LEGS) at the University of Colorado Boulder. ICP-OES was used to measure S, Si, Mn, Fe, Mg, Ca, Na, and K, while IC was used to measure F, Cl, NO₂⁻, Br⁻, NO₃⁻, PO₄³⁻, SO₄²⁻, and S₂O₃²⁻.

**X-ray diffraction (XRD).** XRD data were collected on either a D2 PHASER desktop diffractometer (Bruker Corporation; Billerica, Massachusetts, USA) or a D500 diffractometer (Siemens AG; Berlin, Germany). X-rays were generated as Cu Kα radiation and data were collected from 10° to 65° coupled-2θ/θ with 2-second dwell times per step and steps of 0.02° 2θ. Prior to data collection, samples were dried and then ground to a fine powder. Samples were packed on Si-wafers for reduced background and rotated during data collection to reduce common orientation effects. XRD patterns were analyzed using DIFFRAC.EVA (Bruker) or Jade (v.9; MDI; Livermore, California, USA). Search/Match and line fitting features were used in various configurations to find reproducible fits. Patterns were matched using the Crystallography Open Database (COD; Downs and Hall-Wallace, 2003; Gražulis et al., 2009; Gražulis et al., 2012) for DIFFRAC.EVA and the JCPDS PDF-2 database (2001 release; ICDD: Newtown Square, PA, USA, 2001) for Jade.

**Raman microspectroscopy.** Raman microspectroscopy of samples was performed using a LabRAM HR Evolution Raman spectrometer (Horiba, Ltd.; Kyota, Japan) with reflected light microscopy for imaging and a 532 nm green laser for Raman spectroscopy. Data collection and analysis was conducted using Horiba’s LabSpec 6 (v6.4.1.63) spectroscopy suite. Raman spectra were processed using LabSpec and peaks were fit with reference compounds from the RRUFF database (Lafuente, Downs, Yang, & Stone, 2015), either manually or by using the program Know-It-All (Bio-Rad Laboratories, Hercules, California, USA). Spectral maps, where collected, were processed using LabSpec. Map data were corrected using the Instrument Correction System (ICS) process and then were subtracted to baselines using 3rd degree polynomial functions applied over
100+ data points. Noise points were added into baselines for low signal data. Map data were analyzed using the classical least squares (CLS) and multivariate curve resolution (MCR) applications within LabSpec to spatially resolve components within map regions and to detect the range of components within map data.

*Scanning electron microscopy and energy dispersive spectroscopy (SEM/EDS).* Materials for electron microscopy were thawed and dried and then placed on carbon tape on an aluminum stub. Samples were sputter coated with Au to decrease charging artifacts. Electron microscopy was conducted at the Nanomaterials Characterization Facility (NCF) at the University of Colorado Boulder using either a JEOL JSM-7401F field-emission scanning electron microscope (FE-SEM) paired with a NORAN energy dispersive spectroscopy (EDS) x-ray detector (Thermo Fisher Scientific; Waltham, Massachusetts, USA) or a JEOL JSM-6480LV SEM outfitted with a NORAN EDS detector. For both instruments, SEM was conducted in secondary electron mode with accelerating voltages from 2-5 kV for imaging and 15 kV for EDS.

*Total organic carbon (TOC).* Measurements of TOC were made in the Aridlands Ecology Laboratory at the University of Colorado Boulder using an ECS 4010 CHN Elemental Combustion System (Costech Analytical Technologies; Valencia, California, USA) as well as in the Arikaree Environmental Laboratory at the Institute for Arctic and Alpine Research (INSTAAR) using a FlashEA 1112 Series CHN Analyzer (Thermo Fisher Scientific; Waltham, Massachusetts, USA). Samples for measurement of TOC were thawed and dried at room temperature before repeat washings with concentrated HCl to remove carbonates. Analyses were calibrated with atropine standards.

*X-ray absorption spectroscopy (XAS).* Bulk sulfur K-edge XAS was conducted using beamline 4-3 at the Stanford Synchrotron Radiation Lightsource (SSRL). Beamline 4-3 provides x-ray spot sizes of 2 x 12 mm² for bulk XAS in the S K-edge x-ray absorption range (~2400 to 2600 eV). The beamline is fitted with a Ni-coated Si mirror and an LN-cooled Si(111) double-crystal
A Lytle detector was used to collect x-ray fluorescence from samples that were cooled under a liquid helium cryostream. Materials were thawed and then immediately dispersed as thin films on sulfur-free tape before being placed in the cryostream for data collection. The beamline was calibrated by setting the first major absorption peak of thiosulfate at 2472.02 eV. XAS data were processed using SIXPack (Webb, 2005) and results were compared to the previous literature (e.g., Pickering et al., 2001; Jalilehvand, 2006; George et al., 2008; Almkvist et al., 2010; and Manceau and Nagy, 2012) as well as to model sulfur compounds which had been prepared in the same manner as above and analyzed under the same instrumental parameters.

**Scanning transmission x-ray microscopy (STXM).** STXM was conducted at the S L-edge and C K-edge using the soft x-ray spectromicroscopy (SM) beamline, 10ID-1, at the Canadian Lightsource (CLS) in Saskatoon, Saskatchewan, Canada. The monochromator was calibrated using the standard 3p Rydberg transition of gaseous CO$_2$ at 294.96 eV, and the beamline provided a 35 nm spatial resolution for measurements. Samples were prepared through repeated washings with ultrapure water to remove salts. Samples were then mixed with ultrapure water and allowed to settle. Supernatants were sampled with micropipettes (to subsample only x-ray transmissive material) and material was deposited on gold TEM grids. Material was then thoroughly dried before analysis. Sample were placed in a vacuum chamber for STXM collection; the chamber was evacuated to ~13 Pa and then back-filled with He to standard atmospheric pressure before data acquisition. Scanning transmission x-ray images were collected for sulfur at four energies (160, 163, 170, and 173 eV). These energies were selected to target variations in x-ray transmission intensities for reduced and oxidized sulfur compounds (160 vs. 163 eV and 170 vs. 173 eV, respectively; e.g., Jalilehvand, 2006). For carbon, images were collected at 280.0 eV (below the C K-edge) and 288.2 eV (the absorption energy of 1s→π* electronic transitions of carbon in amide groups; Benzerara et al., 2004). STXM data were processed using the aXis2000 software package (Hitchcock, 2015). Transmission intensity data for images were converted to optical densities (OD). The differences in
OD between images was used to generate maps of sulfur and organic carbon distribution within sample materials. These maps were then used to select regions for collections of stacks of images, using small steps in incident energy over a region of energies through either the sulfur L-edge or the carbon K-edge. These image stacks were used to generate x-ray absorption near edge structure (XANES) spectra, which were then analyzed with aXis2000 and compared to the literature for functional group interpretations.
CHAPTER 3:
LOW-TEMPERATURE FORMATION AND STABILIZATION OF RARE ALLOTROPS OF CYCLOOCTASULFUR (β-S₈ AND γ-S₈) IN THE PRESENCE OF ORGANIC CARBON AT A SULFUR-RICH GLACIAL SITE IN THE CANADIAN HIGH ARCTIC

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3.1 Abstract

Large-scale deposits of elemental sulfur form annually on a glacier’s surface at Borup Fiord Pass in the Canadian High Arctic. However, the mechanisms of mineralization and stabilization of elemental sulfur at this site are currently unknown. Here we show that x-ray diffraction (XRD) data for fresh sulfur precipitates collected from the surface of a melt pool over sulfide-rich ice reveal the presence of three sulfur allotropes, α-S₈, β-S₈, and γ-S₈ (the three solid forms of cyclooctasulfur (S₈)). The detection of the β-S₈ allotrope of elemental sulfur is notable, since β-S₈ typically only forms in high temperature environments (>96°C). The γ-S₈ allotrope is also rare in natural settings and has previously been implicated as a signature of microbial sulfur cycling. Using combustion and infrared spectroscopy approaches, organic carbon is also detected within the sample bearing the three allotropes of elemental sulfur. Electron microscopy and scanning transmission x-ray microscopy (STXM) at the C K-edge show that the sulfur precipitates are intimately associated with the organic carbon at the submicron scale. The occurrence of β-S₈ and γ-S₈ in this low-temperature setting indicates that there are unknown pathways for the formation and stabilization of these rare allotropes of elemental sulfur. In particular, we infer that the occurrence of these allotropes is related to their association with organic carbon. The formation of carbon-associated sulfur globules may not be a direct by-product of microbial activity; however, a potential role of direct or indirect microbial mediation in the formation and stabilization of β-S₈ and γ-S₈ remains to be assessed.
3.2. Introduction

Sulfur is one of the most abundant elements in the universe and is the 6th most abundant element on Earth by weight (Mandeville, 2010). Sulfur also has a high relative abundance at the Earth's surface (350 mg kg⁻¹ in the mean global crust and 905 mg L⁻¹ in the mean global ocean; Haynes, 2013). The chemical oxidation states of sulfur range from 2- in sulfides to 6+ in sulfates. These sulfides and sulfates are commonly transformed through a wide range of less-abundant sulfur intermediates in a dynamic global biogeochemical sulfur cycle (Sievert, Kiene, & Schulz-Vogt, 2007). Tracing the intermediates in the sulfur cycle may reveal much about biogeochemical processes involving sulfur in a variety of environments (e.g. Zopfi et al., 2004). For instance, elemental sulfur (S⁰) is a primary intermediary in the biotic and abiotic oxidation of sulfide (e.g. Helz, 2014; Pjevac et al., 2014) and can also serve as a reactant for microbially mediated sulfur reduction, oxidation, and disproportionation reactions (e.g. Zopfi et al., 2004; Boyd and Druschel, 2013; Pjevac et al., 2014). Even though S⁰ has a low solubility in water (Kamyshny, 2009) and is far less reactive than sulfides, polysulfides, and other sulfur intermediates, the range of environments in which S⁰ is stable are limited (e.g. anoxic marine settings, volcanic and fumarolic systems, and in caprock deposits overlying salt domes; Davis and Kirkland, 1979; Zopfi et al., 2004; Sievert et al., 2007; and Mandeville, 2010).

One unique natural environment bearing deposits of elemental sulfur occurs at Borup Fiord Pass, a valley located on northern Ellesmere Island in the Canadian High Arctic (Figure 3.1a). At this site, extensive deposits of S⁰ derived from sulfide-rich supraglacial springs form on ice surfaces and have been observed during summer field campaigns over many years (Gleeson et al., 2011; Damhnait F. Gleeson et al., 2010; S.E. Grasby et al., 2003; Wright et al., 2013). Borup Fiord Pass has been of interest due to the extensive formation and stabilization of the elemental sulfur in a glacial environment where it is not geochemically predicted to persist (Grasby et al., 2003). Also, microbial sulfur cycling at this site may provide unique biosignatures, possibly aiding geobiological and
astrobiological investigations in other Earth and planetary systems (Gleeson et al., 2010; Wright et al., 2013). Thus, during the summer of 2014, we revisited the Borup Fiord Pass glacier and collected samples of sulfur, ice, and fluids to interrogate their chemistry and mineralogy. In particular, we focused on fresh films of $S^0$-rich material that were forming on the surfaces of gas bubbles at the fluid-air interface on top of melting ice rich in dissolved sulfide. We show herein that this “sulfur bubble” material contains three allotropes of solid $S^0$, two of which are not expected to form in a relatively cold setting, and that the sulfur globules appear to have formed in association with organic carbon.

3.3. The Borup Fiord Pass Spring System

Borup Fiord Pass occurs within the Krieger Mountains, in the deformed eastern portion of the Sverdrup Sedimentary Basin, a Carboniferous to Eocene depocenter (Embry & Beauchamp, 2008). The sulfur deposits at this location appear as visibly yellow accumulations of material overlying glacial ice in areas ranging from tens to thousands of square meters (Figure 3.1b; Grasby et al., 2003; Gleeson et al., 2012). This site in the Canadian High Arctic is thought to be one of the best Earth-based analogs for the potentially sulfurous material concentrated within the lineae on Europa (see Chela-Flores, 2006, Hand et al., 2007, and references therein). Continued research at Borup could play an important role in the development of instrumentation to explore the materials that develop at the dynamic boundaries between surface ices and subsurface anoxic fluids, as well as for the detection of biosignatures in sulfur-rich systems. The biological oxidation of sulfide at Borup Fiord Pass has been hypothesized to play a key role in the deposition and stabilization of elemental sulfur at this site (Grasby et al., 2003; Gleeson et al., 2011; Wright et al., 2013), though that has not been shown conclusively. The sulfur deposits appear to form from saline, sulfide-rich
Figure 3.1. Borup Fiord Pass: Site location and sulfur bubble collection

A line drawing and map (a) show the location of Ellesmere Island in the Canadian High Arctic. The inset shows the locations of Borup Fiord Pass and nearby Eureka (meteorological station). The sulfidic aufeis with yellow $S^0$ deposits at the toe of Borup Fiord Pass Glacier is shown in b. A dashed red line has been added to show where glacial ice and aufeis interface. The blue star shows the location of the melt pool where sulfur bubbles were sampled for this study. Collection of sulfur bubbles on top of melt pool is shown in c with a human hand for relative scale. The melt pool designated by the blue star in b and the site of sulfur bubble collection in c is shown in full in d. The ice blister on the aufeis can be seen in the background. Co-authors Trivedi and Templeton give relative scale.
supraglacial springs that form at Borup Fiord Pass and discharge from the glacier’s surface. Elemental sulfur, gypsum (\(\text{CaSO}_4\cdot2\text{H}_2\text{O}\)), and carbonates (including vaterite (\(\mu\text{-CaCO}_3\)), a rare, metastable form of calcium carbonate) are found on the glacial surface and surrounding areas (Grasby et al., 2003; Grasby, 2003). High levels of sulfide in the springs have been attributed to microbial sulfate reduction in the subsurface before the fluids are released into the surface environment (Grasby et al., 2003). Sulfate in the subsurface at Borup Fiord Pass may be sourced from the extensive Otto Fiord Formation (an anhydrite (\(\text{CaSO}_4\)) and halite (\(\text{NaCl}\)) rich evaporite deposit), while potential inputs of organic carbon to the subsurface may include local intervening shale units which contain up to 4% organic carbon (Grasby et al., 2003).

3.4. Sulfur Allotropes

Elemental sulfur has more well-characterized solid allotropes than any other element (Steudel & Eckert, 2003). Allotropes of \(S^0\) exist as short and long chains as well as rings of sulfur atoms, with the most stable and most common atomic arrangement of sulfur bearing an 8-membered ring of sulfur atoms (cyclooctasulfur; \(S_8\)). Cyclooctasulfur in solid form can take on three polymorphic arrangements known as \(\alpha-S_8\), \(\beta-S_8\), and \(\gamma-S_8\) (alpha-, beta-, and gamma-cyclooctasulfur, respectively); each of these allotropes vary in how the \(S_8\) rings are packed together in their crystal structure (Meyer, 1976; Steudel & Eckert, 2003). Alpha-cyclooctasulfur is the most common allotrope found in natural systems, while beta-cyclooctasulfur has been found in high-temperature fumarolic settings (\(\beta-S_8\) is only predicted to form above \(\sim96^\circ\text{C}\); Steudel and Eckert, 2003) and gamma-cyclooctasulfur has been found in both fumarolic environments as well as in systems where sulfide oxidation occurs in the presence of organic matter (Meisser et al., 2000; Douglas and Yang, 2002).

Here, we report finding all three allotropes of mineralized cyclooctasulfur (\(\alpha-S_8\), \(\beta-S_8\), and \(\gamma-S_8\)) within a layer of sulfur-rich precipitates that were collected from the “sulfur bubbles” at Borup
Fiord Pass. These allotropes were identified through x-ray diffraction (XRD) data. As \( \beta-S_8 \) and \( \gamma-S_8 \) are usually found in high-temperature systems, they are not expected to be found at this cold, glacial site. In particular, our finding of \( \beta-S_8 \) in the sulfur bubble sample described above is, to our knowledge, the first detection of \( \beta-S_8 \) in any cold, natural system. Although it is unknown how these rare forms of sulfur are produced and stabilized in this cold environment, we detect the presence of organic matter within the sulfur bubble material and hypothesize that the organic matter has a role in the formation of \( \beta-S_8 \) and \( \gamma-S_8 \). Thus, to probe the potential relationship of organic matter with these rare allotropes of sulfur, we used electron microscopy, Fourier transform infrared spectroscopy (FTIR), scanning transmission x-ray microscopy (STXM) at the carbon K-edge, and sulfur K-edge x-ray absorption near-edge structure (XANES) spectroscopy to further interrogate the sulfur bubble material. This provides information on the submicron-scale morphology of the material as well as on the organic carbon functional groups within the sample, and supports a hypothesis that \( \beta-S_8 \) and \( \gamma-S_8 \) can be mineralized at low temperatures through direct interactions between sulfide and organic matter.

3.5. Materials and Methods

Ice, mineral, and fluid samples were collected at Borup Fiord Pass (81° 01’N, 81° 35’W; Figure 3.1) in June 2014. Fluid pH was measured in the field with test strips (Carolina Biological Supply Co.; Burlington, North Carolina, USA). Temperatures were measured with a Hach HQ40d portable field meter (Hach Company; Loveland, Colorado, USA). Bubbles of sulfur that had formed on top of one of the melt pools (Figure 3.1c, d) were collected in 2 mL polypropylene cryovials on 21 June 2014. Material that had accumulated within cryoconite holes (i.e. conic holes formed when dust grains lower the albedo of ice and cause differential melting of the ice) at the bottom of this melt pool after several days were sampled into cryovials on 24 June 2014 (referred to herein as "cryoconite material"; Figures 3.2 and A2.1). Cryovials of sulfur bubbles and cryoconite material
were stored in a liquid nitrogen (LN) vacuum flask upon collection and until return to the University of Colorado Boulder, where the cryovials were then placed in a -70°C ultralow temperature (ULT) freezer until needed for analysis. Fluids from the melt pool were filtered into 15 mL polypropylene tubes for ion chromatography (IC) and inductively coupled plasma optical emission spectroscopy (ICP-OES) for measuring major anions and cations, respectively. Samples for ICP-OES were acidified upon collection using concentrated nitric acid. Fluids from melted ice as well as multiple melt pools were sampled for sulfide concentrations from 23 June to 1 July 2014 (including the melt pool where sulfur bubbles were collected). These fluids were filtered into high-density polyethylene (HDPE) bottles and mixed with abundant powdered zinc acetate to precipitate zinc sulfide for later gravimetric determination of sulfide.

ICP-OES and IC measurements were performed on an ARL 3410+ ICP-OES and a Dionix 4500I IC, respectively, at the Laboratory for Environmental and Geological Studies (LEGS) at the University of Colorado Boulder. Total organic carbon (TOC) measurements for cryoconite material were made in the Aridlands Ecology Laboratory at the University of Colorado Boulder using an ECS 4010 CHN Elemental Combustion System (Costech Analytical Technologies; Valencia, California, USA). Measurements of TOC within the sulfur bubbles sample were made in the Arikaree Environmental Laboratory at the Institute for Arctic and Alpine Research (INSTAAR) at the University of Colorado Boulder using a FlashEA 1112 Series CHN Analyzer (Thermo Fisher Scientific; Waltham, Massachusetts, USA). The samples for TOC were thawed and dried at room temperature before repeat washings with concentrated HCl to remove carbonates. All carbon analyses were calibrated with atropine standards.

XRD data were collected on a D2 PHASER desktop diffractometer with a Lynxeye detector in 1D mode (Bruker Corporation; Billerica, Massachusetts, USA). X-rays were generated at 30.0 kV and
Figure 3.2. Formation of sulfur bubbles over the melt pool
This conceptual diagram shows the solid sulfidic aufeis (grey) with trapped H₂S. The H₂S entering the melt pool is then delivered to the air/fluid interface, where S⁰ is produced and “sulfur bubbles” form. Material precipitating from the melt pool preferentially settles into the cryoconite holes and may to continue to undergo S-oxidation and mineral transformation.
10.0 mA as Cu Ka radiation. Data were collected from 10° to 80° coupled 2θ/θ with steps of 0.02° and 1 second dwell times per step. Samples were thawed and then dried on a zero-background Si wafer for XRD data collection. Samples were run within 12 hours of thawing. The sample was spun at 20 rpm during data collection to ensure random orientation. XRD patterns were analyzed using DIFFRAC.EVA (Bruker) or Jade (v.9; MDI; Livermore, California, USA). The Search/Match and line fitting features were used in various configurations to find reproducible fits. Patterns were matched using the Crystallography Open Database (COD; Downs and Hall-Wallace, 2003; Gražulis et al., 2009; Gražulis et al., 2012) for DIFFRAC.EVA and the JCPDS PDF-2 database (2001 release; ICDD: Newtown Square, PA, USA, 2001) for Jade.

Fourier transform infrared spectroscopy (FTIR) was carried out on bulk sample material that had been thoroughly dried (>24 hours) over anhydrous calcium sulfate and then ground to a fine powder with an agate mortar and pestle and diluted with dried KBr before being pressed into a pellet for transmission measurement. FTIR data were collected under a CO₂/H₂O-purged atmosphere on a Nicolet Nexus 670 FTIR spectroscope and analyzed using OMNIC software (Thermo Fisher Scientific; Waltham, Massachusetts, USA). Data were collected from 4000 to 400 cm⁻¹ with a step size of 1.928 cm⁻¹. Data are the average of 32 scans with suppression of residual CO₂ and H₂O peaks. Automatic baseline correction was applied to the final spectrum.

Sulfur bubble material for electron microscopy was thawed and dried and then placed on carbon tape on an aluminum stub. The sample was sputter coated with Au to decrease charging artifacts. Electron microscopy was conducted at the Nanomaterials Characterization Facility (NCF) at the University of Colorado Boulder using a JEOL JSM-7401F field-emission scanning electron microscope (FE-SEM) paired with a NORAN energy dispersive spectroscopy (EDS) x-ray detector (Thermo Fisher Scientific; Waltham, Massachusetts, USA). FE-SEM was conducted in secondary electron mode with accelerating voltages from 2-3 kV for imaging and 15 kV for EDS.
Scanning transmission x-ray microscopy (STXM) was conducted at the C K-edge at the soft x-ray spectromicroscopy (SM) beamline, 10ID-1, at the Canadian Lightsource (CLS) in Saskatoon, Saskatchewan, Canada. The monochromator was calibrated using the standard 3p Rydberg transition of gaseous CO\textsubscript{2} at 294.96 eV. STXM was used to map the distribution and characterize the speciation of carbon in the sample at a 35 nm spatial resolution. STXM data were collected on a sample which was prepared through repeated washings with ultrapure water to remove salts followed by drying on a Si\textsubscript{3}N\textsubscript{4} window of 50 nm thickness (Norcada Inc., Edmonton, Alberta, Canada). The sample was placed in a vacuum chamber for STXM collection; the chamber was evacuated to ~13 Pa and then back-filled with He to standard atmospheric pressure before data acquisition. Scanning transmission x-ray images were collected at 280.0 eV (below the C K-edge) and 288.2 eV (the absorption energy of 1s→\pi* electronic transitions of carbon in amide groups; Benzerara et al., 2004). Transmission intensity data for these images were converted to optical density (OD). The difference in OD of the two images was used to generate maps of organic carbon distribution in the sample. Stacks of images in regions of interest were then collected at the carbon K-edge from 260 eV (below the edge) to 340 eV (well above the edge) using steps as small as 0.114 eV through the edge region (283-293 eV; larger steps are used outside of this region). These image stacks were used to generate C K-edge x-ray absorption near edge structure (XANES) spectra. Carbon K-edge STXM and XANES spectroscopy data were processed using the aXis2000 software package (Hitchcock, 2015). Carbon XANES spectra were extracted from these image stacks and compared to the literature for peak locations of various carbon functional groups (e.g., Cosmidis and Benzerara, 2014). Reference spectra for organic carbon compounds were provided courtesy of Clara Chan (University of Delaware) and are discussed in Chan et al. (2010). Spectra for carbonates presented in Brandes et al. (2010) were extracted using Web Plot Digitizer (http://arohatgi.info/WebPlotDigitizer) and used as references for our data (see Section 3.6.3). We had initially intended to collect sulfur L-edge data for this sample as well, however absorption by
the Si$_3$N$_4$ window prevented that analysis (the strong absorption of the Si L-edge around 100-120 eV masked any signal from sulfur, which has an L$_{2,3}$-edge around 160 eV).

Bulk sulfur K-edge XANES spectroscopy was also conducted on the sulfur bubble material using beamline 4-3 at the Stanford Synchrotron Radiation Lightsource (SSRL) in August of 2015. Beamline 4-3 provides x-ray spot sizes of 2 x 12 mm$^2$ for bulk x-ray absorption spectroscopy at energy ranges including the S K-edge absorption range (~2400 to 2600 eV). The beamline is fitted with a Ni-coated Si mirror and an LN-cooled Si(111) double-crystal monochromator. A Lytle detector was used to collect x-ray fluorescence from samples that were cooled under a liquid helium cryostream. Sulfur bubble material was thawed and then immediately dispersed as a thin film on sulfur-free tape before being placed in the cryostream for data collection. The beamline was calibrated by setting the first major absorption peak of thiosulfate at 2472.02 eV. Sulfur XANES spectroscopy data were processed using SIXPack (Webb, 2005) and results were compared to the previous literature (e.g., Pickering et al., 2001; Jalilehvand, 2006; George et al., 2008; Almkvist et al., 2010; and Manceau and Nagy, 2012) as well as to model sulfur compounds which had been prepared in the same manner as above and analyzed under the same instrumental parameters.

3.6. Results

3.6.1 Field Observations

During the 2014 field season at Borup Fiord Pass, we observed a large sulfur-covered structure of spring-formed ice (an aufeis) approximately 5x10$^4$ m$^2$ in area and up to ~5 meters thick (Figure 3.1b). Aufeis are a common feature formed by High Arctic perennial springs and are formed by freezing of spring fluids released during winter months (e.g. Grasby et al., 2003; 2014). In 2014, a large amount of this aufeis (~10$^4$ m$^2$ in area) had built up around the glacier’s edge, while the rest followed a local channel east and then southward through the valley (not visible in Figure 3.1b). While exploring the aufeis, we noted the odor of H$_2$S gas apparently emanating from the ice.
We also observed that after being cleared, fresh surfaces of the aufeis were covered by yellow precipitates that formed within one day. This suggests that the formation of elemental sulfur from sulfide oxidation at this site is an active process.

Numerous melt pools had formed across the surface of the aufeis, and conspicuous films of yellow material developed at the fluid/air interface. The melt pools exhibited a strong hydrogen sulfide odor, and when a silver foil was placed in a melt pool where sulfur bubbles were forming, the silver foil instantly reacted, as indicated by the discoloration of the foil (see Figure A2.2). This discoloration is indicative of the reaction of the silver with dissolved sulfides to form AgS (e.g., Gilhooly et al., 2014). Trapped gases within the ice below the melt pools were liberated during melting and formed bubbles that rose to the surface (Figure 3.2). In many cases, films of sulfur formed over these bubbles when they met the surface, hence the name “sulfur bubbles”. The melt pool where the sulfur bubbles for this study were collected was approximately 1 m in width, 2 m in length, and 10 cm in depth and located near the central region of the built up aufeis structure at the toe of the glacier (Figure 3.1c). The studied pool was representative of numerous similar features in the area.

Cryoconite material for this study was collected from the bottom of the melt pool using sterile pipettes. The cryoconite holes grew in size during the two-week duration of our fieldwork, from roughly 2 cm in diameter at first observation to 4 cm when cryoconite material was sampled. The cryoconite material appeared as whitish precipitates that built up at the bottom of the melt pool during the field campaign. The pH of the melt pool fluid measured in the field was 5.5 to 6.0 while the temperature of the fluid was 0-1°C (both measurements were collected at one time-point on 21 June 2014, at the same time that the sulfur bubbles were sampled).
3.6.2 Fluid Chemistry

The concentrations of major dissolved cations and anions in the fluid from the melt pool show that the fluids are relatively salty and thus they are not derived directly from glacial ice (Table 3.1). Comparisons of the aqueous chemistry of the melt pool fluids to the measurements for nearby glacial melt water, as well as to the spring fluid chemistry reported for an actively flowing sulfide-spring in 2009 (Wright et al., 2013), show that the melt pool is a briny solution that more closely resembles the spring waters (Table 3.1). All major cation species except iron and manganese are also more similar between the spring fluid and the melt pool than the glacial melt. Levels of thiosulfate and sulfate are also similar between the previous spring fluid measurement and the melt pool from the aufeis. Notably the sulfate in the melt pool, at 18.6 mM, is the highest ever recorded in a sample from Borup Fiord Pass. Also, while chloride values in the 2009 spring fluid are roughly two orders of magnitude higher than in the glacial melt, there is nearly two-fold more chloride in the melt pool compared to the active spring of 2009. Nitrate is also much higher in the melt pool than in the 2009 spring (90 µM compared to 3 µM).

The sulfide value obtained through gravimetric analysis on 2009 sulfide-spring fluid by Wright et al. (2013) was 3.99 mM (128 mg L⁻¹). Samples for gravimetric determination of sulfide from 2014 yielded sulfide values ranging from 0.22±0.03 to 2.25±0.16 mM (7±1 to 72±5 mg L⁻¹), with the pool that produced the sulfur bubbles in this study giving the lowest recorded sulfide value. However, the sample for sulfide was collected on 28 June 2014, 7 days after the collection of the sulfur bubbles and at a time when the pool appeared to no longer be active in sulfur bubble production and the fluids no longer reacted instantaneously with a silver foil.
Table 3.1. Geochemical data measured for melt pool fluid compared to glacial water and previous sulfide spring data

Alkalinity and pH were not accurately determined and thus are not reported. Concentrations of measured species are reported in mM. Fluid from the melt pool as well as from a melt sample from the nearby glacier, both collected in 2014, are compared to previously published data for the fresh sulfide spring in 2009 (Wright et al., 2013). Glacial Melt data come from a sample collected topographically high on the glacier, above the location of the sulfidic aufeis. NM is “not measured”. Si data are reported here as SiO$_2$. Charges for cations have been assumed or are marked as total values. DL is below “detection limit” (relevant DL values are 4 μM (K$^+$), 0.3 μM (SiO$_2$), 1.1 μM (F$^-$), 0.6 μM (Br$^-$), and 0.8 μM (NO$_3^-$)).

<table>
<thead>
<tr>
<th>Species</th>
<th>2009</th>
<th>2014</th>
<th>Glacial Melt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Spring</td>
<td>Melt Pool</td>
<td>Glacial Melt</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>51.8</td>
<td>38.2</td>
<td>0.470</td>
</tr>
<tr>
<td>K$^+$</td>
<td>0.302</td>
<td>0.210</td>
<td>(DL)</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>12.9</td>
<td>9.17</td>
<td>0.121</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>17.3</td>
<td>12.6</td>
<td>0.150</td>
</tr>
<tr>
<td>Fe$_T$</td>
<td>0.0050</td>
<td>0.0007</td>
<td>0.001</td>
</tr>
<tr>
<td>Mn$_T$</td>
<td>0.0010</td>
<td>0.0005</td>
<td>0.010</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>0.0411</td>
<td>0.0541</td>
<td>(DL)</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>13.0</td>
<td>18.6</td>
<td>0.4</td>
</tr>
<tr>
<td>S$_2$O$_3^{2-}$</td>
<td>0.103</td>
<td>0.172</td>
<td>(NM)</td>
</tr>
<tr>
<td>Cl$^-$</td>
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<td>86.0</td>
<td>0.9</td>
</tr>
<tr>
<td>F$^-$</td>
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<td>0.0621</td>
<td>(DL)</td>
</tr>
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<td>Br$^-$</td>
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<td>0.0212</td>
<td>(DL)</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>0.0030</td>
<td>0.0908</td>
<td>(DL)</td>
</tr>
</tbody>
</table>
3.6.3 Analyses of Sulfur Bubbles and Cryoconite Material

Bulk sulfur K-edge XANES spectroscopy conducted on the sulfur bubble material produced a spectrum that correlates with spectra for elemental sulfur with a potential minor feature derived from sulfate (e.g., Pickering et al., 2001; Jalilehvand, 2006; George et al., 2008; see Figures A2.5 and A2.6). While this shows that sulfur within the sulfur bubble material is primarily elemental sulfur, XRD was required to determine the speciation of crystalline material within the sample.

XRD data for the sulfur bubble material was collected on a sample that had been thawed and dried and then immediately analyzed. These data can be fit well by inclusion of all three allotropes of cyclooctasulfur (Figure 3.3a): α-S₈ (COD 9008577), β-S₈ (COD 9009891), and γ-S₈ (COD 9007886). This same sample of the sulfur bubble material was then purposefully left at room temperature for 2 weeks before XRD was performed again. The new XRD pattern showed only α-S₈ in the diffractogram (Figure 3.3b), suggesting the instability of the rarer forms of S⁰ when dried and left at room temperature. In order to ensure replicability of the detection of three allotropes of sulfur within the sulfur bubble material, more of the material was thawed and analyzed several months later and XRD again showed the presence of α-S₈, β-S₈, and γ-S₈ (Figure A2.3). XRD data were also obtained for the cryoconite material within the melt pool collected on 24 June 2014. These data show peaks for gypsum and halite with a minor peak for calcite, but do not show peaks for any forms of elemental sulfur (Figure A2.4). Interestingly, the diffractogram for this sample also includes a very good fit for rapidcreekite, a rare hydrated sulfate carbonate mineral with formula Ca₂(SO₄)(CO₃)·4H₂O. Rapidcreekite has only been identified in a limited number of localities globally and has been implicated to form under constrained conditions with high levels of dissolved sulfate compared to carbonate (Onac et al., 2013; Roberts, 1986).

Total organic carbon (TOC) was 0.07 wt.% C in the sulfur bubbles and 0.20 wt.% in the cryoconite material. FTIR spectroscopy was used to characterize the bulk sulfur bubble material,
Figure 3.3. X-ray diffractograms for sulfur bubble material
X-ray diffraction (XRD) data collected on a sample that was dried onto a no-background Si wafer. Data are presented here from 2θ of 20° to 40°. Peaks fit with diffraction patterns for α-S₈, β-S₈, and γ-S₈ are pointed out with tan dash-dot-dot, green dashed, and blue solid lines, respectively. a) Diffractogram for the sulfur bubbles immediately after drying on the wafer. b) The same sample after two weeks at room temperature.
including the detected organic carbon (Figure 3.4). The FTIR spectra include several absorptions interpreted to derive from functional groups in hydrated sulfates and thiosulfate as well as carbonate and elemental sulfur (see §A2.5). For instance, the O-H stretch region shows an intense, broad feature centered at 3405 cm\(^{-1}\) interpreted to derive from the O-H bonds in hydrated inorganic salts. Intense absorption bands ranging from 994 to \(~\)1160 cm\(^{-1}\) are interpreted as deriving from S-O stretches within sulfates and thiosulfates (Coates, 2000; Degenhardt & McQuillan, 1999; Lane, 2007). Features at 1427 and 875 cm\(^{-1}\) are diagnostic for carbonates (Coates, 2000), though their low intensity suggests only minor amounts of carbonate in the sample. Furthermore, two intense peaks at 465 and 451 cm\(^{-1}\) may be indicative of S-S stretching within \(S_8\) molecules (Eckert & Steudel, 2003; §A2.5 presents further consideration of peak features associated with inorganic functional groups).

Diagnostic absorption peaks from the C-H stretches of methyl and methylene groups in aliphatic carbon compounds are observed as two sharp features at 2922 and 2851 cm\(^{-1}\) (representing asymmetric and symmetric stretches, respectively) as well as a broad shoulder at 2955 cm\(^{-1}\). A feature at 1384 cm\(^{-1}\) with an associated shoulder at \(~\)1367 cm\(^{-1}\) may be indicative of geminal dimethyl group splitting of the symmetric C-H bend, while a small, broad feature at \(~\)1469 cm\(^{-1}\) is interpreted as the asymmetric bending of aliphatic C-H bonds. A series of absorptions, centered on the strongest band at 1631 cm\(^{-1}\), is interpreted here as deriving from the -C=C-stretches of olefinic carbon groups, though multiple features on the shoulder of that peak are interpreted as deriving from sulfates and/or thiosulfate (§A2.5). Furthermore, a strong absorption band at 1195 cm\(^{-1}\) may be from S-O stretching of organic sulfates, which may then implicate some of the minor features around 1384 cm\(^{-1}\) to arise from such materials as well (Coates, 2000).

Scanning electron micrographs show globular sulfur in particle sizes ranging from the nm to 10s of \(\mu m\) in scale within the sulfur bubble material. We also observe a component of the sulfur
**Figure 3.4. FTIR transmission spectrum for sulfur bubble material**

Infrared transmission is reported as the normalized, baseline-corrected % transmission vs. wavenumber (cm$^{-1}$). Functional group assignments are shown. Aliphatic C-H and olefinic C=C are shown as blue long-dash and green solid lines, respectively. Organic sulfate, inorganic sulfate, and thiosulfate are shown as grey small-dashed lines. Carbonate peaks are highlighted with purple dotted double lines. Elemental sulfur is shown with red solid double lines. The peak absorbances are further discussed in the text and supplementary information section A2.5.
material that appears smooth and, in some cases, euhedral (Figure 3.5). However, no specific
domain size or structure can be determined for these apparently euhedral sections. FE-SEM images
show that nanospherical sulfur particles commonly aggregate together into larger, submicron
globs. These submicron particles appear to aggregate together in many places to form larger,
icron-sized globules, often with hollow regions within them. These globules appear in many
places to take on the form of a spherical “cage” of sulfur (Figure 3.5a). EDS data revealed that sulfur
and carbon are present in all globular materials from this sample (Figure A2.4). The unidentified,
smooth phase is observed within the sulfur bubble materials in Figure 3.5b,c. When analyzed with
EDS, even at lower accelerating voltages, the electron beam destroys this smooth material (see
Figures A2.7 and A2.8), though it can still be identified as containing sulfur and carbon.

STXM mapping of the sulfur bubble material at the C K-edge reveals submicron scale
associations between dense globules and carbon-rich material within the sample. The dense
globules are so optically thick that transmission data could not be obtained for them (Figure 3.6a).
The difference in optical densities collected for a region at 280.0 eV and 288.2 eV can be used to
generate a map of carbon (Figure 3.6b). A smaller region of one such carbon map was then selected
for stack collection and C XANES analyses (Figure 3.6d). Two representative C K-edge XANES
spectra from the carbon-rich material are shown in Figure 3.6c; XANES spectra have been
normalized below and above the carbon edge for visual comparison. The top spectrum in Figure
3.6c (Spectrum 1; solid red line) represents the majority of the carbon-rich material in this region
while the bottom spectrum in Figure 3.6c (Spectrum 2; dashed green line) represents the carbon-
rich material surrounding the opaque globules. Figure 3.6d shows how the carbon-rich material in
the map has been fitted using Spectra 1 and 2 from Figure 3.6c.

Peaks in the two C XANES spectra shown in Figure 3.6c have been assigned to carbon
functional groups by comparisons to peak energy positions of carbon standards reported in the
Figure 3.5. Electron micrographs of sulfur bubble material
Secondary electron images collected at 2-3 kV showing globular sulfur. Sulfur globules appear to form from nanospherules of sulfur that aggregate into larger particles (a). Smoother phases within the sample appear associated with globular sulfur (b,c).
Figure 3.6. Carbon STXM map and XANES spectra of sulfur bubbles

a) STXM image collected at 288.2 eV. b) STXM map of organic carbon, showing the difference in optical density data for images at 280.0 and 288.2 eV. Opaque globules appear outlined by carbon-rich material. The yellow box shows where a stack of images was collected for C XANES spectroscopy. c) XANES spectra for carbon-rich material in two distinct regions of the stack (Spectrum 1 (red) and Spectrum 2 (green)). Calibrated standards plotted for comparison include a lipid (1,2-dipalmitoyl-sn-glycero-3-phosphoethanolamine; from Chan et al., 2010) and aragonite with organic carbon (from Brandes et al., 2010). Vertical lines show known peak locations for calcium carbonate (dotted lines at 290.22, 295.35, 298.23, and 301.25 eV), potassium L-edge features (dashed lines at 297.03 and 299.74 eV), and relevant organic groups (solid lines at 287.17 and 288.41 eV; see text). The inset (d) shows the same region as that shown in the yellow box in (b). The map area can be fit by the spectra in (c), showing the distribution of carbonate-rich areas (red, Spectrum 1) and organic carbon (green, Spectrum 2). There is no spectroscopic information for the opaque globule (blue). The scale bars in (a) and (b) are 2 μm.
literature (e.g., Brandes et al., 2004; Brandes et al., 2010; Chan et al., 2010; Cosmidis and Benzerara, 2014). Spectrum 1 shows absorption peaks typical of calcium carbonates, including the strong $\pi^*$ resonance at 290.2 eV as well as three $\sigma^*$ resonances at 295.2, 298.2, and 301.3 eV (Brandes et al., 2010). Brandes et al. (2010) analyzed the C K-edge spectra of several carbonate minerals and pointed out that calcite and aragonite (both calcium carbonates) are indistinguishable using C K-edge XANES peaks for carbonate; all four peaks are at the same energy positions. However, Spectrum 1 in this study appears far more similar to the aragonite spectrum of Brandes et al. (2010), with a strong shoulder around 287.2 eV and a peak around 288.4 eV (288.5 eV in their spectrum; see Figure 3.6c). Brandes et al. (2010) reported that their aragonite spectrum came from a sample of coral skeletal material containing up to 5% organic carbon, explaining the shoulder and the peak at 288.5 eV. The similarities between their organic carbon-rich aragonite spectrum and our spectrum suggest that Spectrum 1 is that of a carbonate (likely a calcium carbonate) enriched in organic matter. Specifically, the broad absorption shoulder centered around 287.0 eV in this spectrum is inferred to be caused by absorption by aliphatic groups (Brandes et al., 2004, 2010; Chan et al., 2010). Absorptions at 288.4 eV in both of the spectra in Figure 3.6c are inferred here as carboxylic/ester carbon groups (commonly at 288.4/288.5 eV; Benzerara et al., 2004; Chan et al., 2010). Spectrum 2 in Figure 3.6c does not have the characteristic carbonate peaks except for a small peak at 290.2 eV that might be from the typically strong $\pi^*$ resonance peak of carbonates. This spectrum has two strong peaks at 297.0 and 299.7 eV, which appear to be diagnostic peaks for the potassium L$_{2,3}$-edge (Karim Benzerara et al., 2007), suggesting the presence of potassium salts within the sample. A strong absorption peak at 288.4 eV in this spectrum, which we interpret as carboxylic carbon groups, suggests that the material surrounding the opaque globules is rich in organic carbon. A C XANES spectrum for the phospholipid 1,2-dipalmitoyl-sn-glycero-3-phosphoethanolamine was provided courtesy of Clara Chan (Chan et al., 2010), and is shown in Figure 3.6c for comparison of organic functional group peaks. Peaks inferred to be from organic
functional groups in our spectra align well with peaks from the phospholipid at 287.3 and 288.4 eV (inferred in Chan et al. (2010) to derive from aliphatic/aromatic and carboxyl/ester groups, respectively).

3.6.4. Addendum: Raman Microspectroscopy Identification of Beta-Sulfur

After the publication of the original version of this manuscript, it was determined that Raman microspectroscopy may be capable of differentiating α-S₈ and β-S₈. The ν₂ bending Raman mode for α-S₈ occurs at 218-220 cm⁻¹ and has been well-documented in the literature (e.g., Eckert and Steudel, 2003). A region of the sulfur bubble material that was mapped using Raman revealed a variation in this peak (Figure 3.7). It was discovered that, while other elemental sulfur Raman peaks were consistent, this bending mode in Raman spectra for one mapped region shifted from ~219 cm⁻¹ to ~221 cm⁻¹ in measured Raman shift. Only one documented study of Raman spectroscopy exists in the literature (see Gautier and Debeau, 1976); however, this study showed that at 40 K and 373 K the ν₂ bending mode occurs at 221 cm⁻¹. The detection of two Raman shift positions for the ν₂ bending mode in Raman spectral data for the sulfur bubbles may reveal the detection of both α-S₈ and β-S₈ in this material using this spectroscopic method. In support of this, there are several regions in the same mapped area where both of these ν₂ bending modes are detected, supporting the dual identification of α-S₈ and β-S₈ in these mapped spots. This potential detection of β-S₈ using Raman microspectroscopy is very important and should be further explored.

3.7. Discussion

We interpret the aqueous geochemical data reported here (Table 3.1) to show that the sulfidic aufeis observed in 2014 was derived from the sulfide-spring system at Borup Fiord Pass.
Figure 3.7. Sulfur bubble Raman microscopy

The smooth phase was observed in a reflected light microscope image of the sulfur bubble material (top center of a). Raman mapping of this region revealed two apparent phases of elemental sulfur (b). Red colored regions in (b) are mapped to fluorescence intensities from 218.5 to 219.5 cm\(^{-1}\) while blues map to 221 to 222 cm\(^{-1}\). Averaged spectral data from these two regions (yellow ellipses in b) are shown in (c) along with a spectrum where both peaks are apparent (purple in c; pointed out by white arrow in b). The inset in (c) highlights peak variation inferred to derive from allotrophic variations in elemental sulfur. The \(v_2\) bending Raman mode for \(\alpha\)-S\(_8\) occurs at 218.5 cm\(^{-1}\), while this mode for \(\beta\)-S\(_8\) occurs at 221 cm\(^{-1}\) (Eckert & Steudel, 2003; Gautier & Debeau, 1976).
Concentrations of major cations and anions are more similar between the melt pool fluid and the spring water reported from 2009 than they are to glacial melt fluids, suggesting that the aufeis formed from a spring. Also, a region of uplifted ice near the toe of the glacier (see Figure 3.1b) is hypothesized to be the original site of spring emergence forming the aufeis. A return to the site in the summer of 2015 by co-author Grasby revealed that a large depression had formed where this uplifted ice had been in the previous year.

While total organic carbon data from the sulfur bubbles and cryoconite material show that these samples have detectable concentrations of organic carbon compounds, it is unknown to what extent organic carbon is being delivered to the aufeis and associated melt pools through the subsurface springs or if this organic material is being formed in situ through microbial processes. Previous studies have assumed that surface autotrophy, such as lithotrophic S-oxidizing metabolisms, was required for carbon inputs into the system. However, Wright et al. (2013) report 3.9 mg L\(^{-1}\) DOC in the 2009 sulfide spring as the fluids emerge from the subsurface. In addition, numerous heterotrophic bacteria, such as Flavobacteriaceae, are also present and may potentially be sustained by the degradation of complex organic carbon compounds derived from the subsurface fluids.

STXM and XANES spectroscopy were used to further explore the chemical speciation of organic carbon in these materials. STXM maps of carbon (e.g., Figure 3.6b) show large accumulations of carbon-rich materials in association with relatively thick globules that are optically opaque. It is likely that the opaque globules are elemental sulfur; globules of S\(^{0}\) of the same size were observed in FE-SEM images (Figure 3.5) and bulk S XANES showed the sulfur in the sample to be composed of zero-valent elemental sulfur. The C XANES spectra of the carbon-rich material associated with these opaque globules have absorption peaks that have been identified as carboxylic and aromatic functional groups. Although these functional groups were not identified in FTIR data, the infrared spectrum was collected for bulk material while C XANES spectra were
collected for carbon-rich regions at the submicron scale. Most of the carbon-rich material in the sulfur bubbles observed at the nanoscale through STXM appears from XANES spectroscopy to be carbonate associated with organic carbon, appearing similar to a spectrum for organic carbon-rich aragonite reported by Brandes et al. (2010). It should be noted that although we do not have Ca L-edge XANES data showing that our carbonate rich material is calcium carbonate, the C K-edge XANES peaks fit with those of calcium carbonates versus other carbonates (Brandes et al., 2010).

Results from FTIR and carbon XANES spectroscopic analyses confirm the detection of complex organic matter in the sulfur bubbles. FTIR data suggests that the sulfur bubble material contains inorganic functional groups associated with hydrated sulfates and thiosulfate, carbonates, and elemental sulfur, as well as revealing the presence of aliphatic carbon groups and possible alkene C=C bonding. Also, an intense absorption peak at 1195 cm$^{-1}$ may derive from stretching of S-O bonds in organic sulfates. Carbon XANES data provide further direct confirmation of aliphatic/aromatic groups as well as carboxylic/ester groups.

FE-SEM imaging of the material from the sulfur bubbles shows globular sulfur particles within this sample (Figure 3.5). Globule formation of elemental sulfur has been well-documented in a variety of natural settings, especially in the intra- and extra-cellular formation of S$^0$ globules through microbial sulfide oxidation (e.g., Prange et al., 2002; George et al., 2008; He et al., 2010; Eichinger et al., 2014). A smooth phase of material was also observed within the sulfur bubbles (Figure 3.5b,c). This smooth phase was extremely sensitive to beam damage, precluding thorough examination using EDS (see Figure A2.5). In some regions, this material appeared to have a euhedral structure (Figure 5b) while in other places the material appears anhedral or amorphous (Figure 3.5c). Everywhere in the sample that this material was observed it was associated with the globular sulfur. Where globular sulfur and the smooth material are in contact the two phases appear intimately associated. The detection of organic carbon from FTIR and carbon XANES spectroscopies, as well as STXM imaging showing the association of organic material with opaque
globules, may suggest that the smooth material observed in FE-SEM images is an organic-rich phase in association with the $S^0$ in the sulfur bubbles.

The extensive formation of elemental sulfur at Borup Fiord Pass is highly enigmatic, since $S^0$ is not thermodynamically stable under the highly oxidizing, near-neutral pH conditions at the surface of the sulfidic aufeis (Gleeson et al., 2011). Now, on the basis of the x-ray diffraction data for the sulfur bubbles from Borup Fiord Pass, we report what is, as far as we know, the first finding of $\beta$-$S_8$ in a low-temperature environment. We find this $\beta$-$S_8$ co-existing with two other sulfur allotropes, $\alpha$-$S_8$ and $\gamma$-$S_8$. The finding of actively forming $\beta$-$S_8$ is surprising, as the monoclinic $\beta$-$S_8$ form of elemental sulfur is not expected to form below $\sim$96°C (Steudel & Eckert, 2003). The temperatures of the spring fluids, sulfidic ices, and sulfur deposits are around 0-5°C (Grasby et al., 2003; Gleeson et al., 2011; Wright et al., 2013; and this study) indicating that $\beta$-$S_8$ has a much broader environmental stability than previously recognized.

$\beta$-$S_8$ is a monoclinic crystal form of $S_8$. This allotrope is known as a high-temperature polymorph of $S^0$, formed by heating solid $\alpha$-$S_8$ to $>$96°C or by slowly quenching a melt of elemental sulfur (Steudel & Eckert, 2003). Below $\sim$96°C crystals of $\beta$-$S_8$ will revert to the more stable $\alpha$-$S_8$ form. For instance, crystals of $\beta$-$S_8$ formed from cooling of a sulfur melt have been shown to transform to $\alpha$-$S_8$ within as little as 1 hour at room temperature and as long as several weeks when cooled to -20°C (Goldsmith & Strouse, 1977). However, recent endeavors in the laboratory preparation of monoclinic sulfur have revealed the potential ability to stabilize $\beta$-$S_8$ at circa room temperature for longer durations in the presence of organic and inorganic carbon.

For instance, Moon et al. (2013) created $\alpha$-$S_8$ nanowires encapsulated in $\sim$3 nm carbon layers to test their usefulness for Li-S batteries. These encapsulated sulfur nanowires were heat treated at 400 °C, and subsequent analysis through electron diffraction revealed that most of the sulfur in the nanowire had converted to $\beta$-$S_8$. Moon et al. (2013) report that $\beta$-$S_8$ in their nanowires
then appears stable at room temperature through the duration of their experiments and when cycled with a full charge in their battery system, leading these authors to propose that the carbon shell around the sulfur drives the stabilization of β-S₈ in their nanowires. However, other recent endeavors have shown formation and stabilization of β-S₈ without exceeding 96°C. For instance, in experiments with developing sulfur nanoparticles through a water-in-oil microemulsion technique, Guo et al. (2006) showed that for sulfur nanoparticles formed by reacting microemulsions of sodium polysulfide and hydrochloric acid (both prepared in theolin, Span80, Tween80, butanol, and water) the resultant S⁰ was of the β-S₈ form. Their β-S₈ finding came through XRD analysis after a vacuum drying step at 80°C, although they do not report further on the duration of stability of their β-S₈ nanoparticles.

More recently, Choudhury et al. (2013) used a modification of this water-in-oil microemulsion technique to prepare β-S₈ nanoparticles (identified with XRD) using only a rotary vacuum evaporation step for drying. These authors report formation and stabilization of β-S₈ at room temperature for at least the 3-month duration of their experiments. Although the authors did not identify their β-S₈ again using XRD, the size of their monoclinic sulfur nanoparticles (characterized through TEM), when stored at 4°C, remained almost unaltered. The results of Guo et al. (2006), Choudhury et al. (2013), and Moon et al. (2013) show the formation and room-temperature stabilization of β-S₈ (at least temporarily) through an as-of-yet unknown interaction of sulfur with inorganic and organic forms of carbon.

The γ-S₈ allotrope of elemental sulfur also forms monoclinic crystals. Though also a rare allotrope of sulfur, γ-S₈ has been identified as a unique mineral named rosickyite. This study presents the second time that diffraction data for sulfur-rich material collected from supraglacial icings at Borup Fiord Pass have shown the presence of rosickyite at this site. The previous detection of rosickyite was obtained from a sample of sulfur-rich sediment downstream from an active spring (Damhnait F Gleeson et al., 2012). To date, several studies have implicated microbial sulfide oxidation as a driver for the formation of rosickyite in natural samples (Douglas & Yang, 2002;
Meisser et al., 2000). For example, Meisser et al. (2000) detected rosickyite growing as an alteration product from the oxidation of pyrite associated with asphalt in a Swiss mine. Depletion of the $^{34}$S isotope in rosickyite compared to the parent pyrite in these samples led Meisser et al. (2000) to conclude that the rosickyite had formed from microbial sulfur oxidation. Similarly, Douglas and Yang (2002) detected rosickyite in conjunction with an endoevaporitic microbial community in Death Valley, California. A dearth of exogenous organic material, as well as the association of rosickyite with microbial cells and extracellular components, led these authors to hypothesize that microbial sulfate reduction and subsequent microbial sulfide oxidation was responsible for the formation of rosickyite in their samples. These findings led Gleeson et al. (2012) to hypothesize that the rosickyite in their sulfur sediment from Borup Fiord Pass may be the product of biological S-oxidation in these materials.

We hypothesize that the presence of organic matter in the melt pool fluids during the oxidation of sulfide and formation of $S_0$ at Borup Fiord Pass gives rise to the formation of both $\beta$-$S_8$ as well as $\gamma$-$S_8$. There is a clear co-association of organic carbon with the sulfur in the sulfur bubbles. This hypothesis for the formation of monoclinic sulfur ($\beta$-$S_8$ and $\gamma$-$S_8$) under environmental conditions is also supported by the experimental studies that have shown that $\beta$-$S_8$ can be formed and temporarily stabilized at temperatures below 96°C in the presence of carbon (Choudhury et al., 2013; Guo et al., 2006; Moon et al., 2013). Our present data do not inherently suggest that $\beta$-$S_8$ and $\gamma$-$S_8$ are formed by the action of microorganisms, since the organic carbon in the melt pool may be from exogenous sources (i.e. organic rich shales in the subsurface), and we cannot at this time constrain the mechanism through which the association of organic carbon and sulfur drives the formation of the monoclinic allotropes of elemental sulfur. Although previous research has hypothesized rosickyite ($\gamma$-$S_8$) to be a possible biosignature of microbial sulfide oxidation (Douglas & Yang, 2002; Damhnait F Gleeson et al., 2012; Meisser et al., 2000), it may simply be that microbial activity commonly generates appropriate dissolved organic carbon that participates in the
precipitation and the stabilization of $\gamma$-$S_8$. Thus, microbial processes may be only indirectly involved and not inherently necessary for organic carbon and sulfur to interact and form monoclinic sulfur allotropes in cold natural systems. For instance, recent laboratory work by Cosmidis and Templeton (2016) has shown that reactions of sulfide and organic carbon in opposing gradients of sulfide and oxygen can drive the formation of $S^0$ encapsulated in unique carbonaceous, biomorphic structures in the absence of any microbial activity. Although they do not report the mineralogy of $S^0$ formed in these reactions, they do show that organic carbon in their experiments controls the morphology of $S^0$ formed.

A consideration of our results that must be mentioned is the storage of samples in LN and at -70°C before XRD detection of sulfur allotropes. Although there is a possibility that the ultralow temperature freezing and subsequent thawing of samples causes some changes to the materials within those samples, we do not suspect that the metastable phases of sulfur detected in our sulfur bubble sample are artifacts of the freezing process. A multitude of sulfur-rich materials have been collected from Borup Fiord Pass through the years and subsequently frozen at -70 or -80°C for time periods ranging from weeks to years before being thawed for analysis. We have previously detected $\alpha$-$S_8$ in many of these samples, but this is the first time that $\beta$-$S_8$ has been detected. However, the $\gamma$-$S_8$ allotrope has previously been detected in a Borup sample which had been stored on ice in transit from the field to the laboratory before being frozen to -80°C (see Gleeson et al., 2012). This suggests that the metastable phases of sulfur detected in Borup samples are truly phases of sulfur formed in the field. However, the implementation of a field-portable XRD at Borup Fiord Pass in future research endeavors will be necessary evaluate any potential artifacts from the freezing process.

Further research into the possible mechanism(s) through which organic carbon and sulfur interact during the oxidation of H$_2$S in the laboratory and in the field will be necessary to determine the physicochemical constraints on the formation of $\beta$-$S_8$ and $\gamma$-$S_8$ in natural systems. Furthermore, although our current research suggests that the formation and stabilization of $\beta$-$S_8$ and $\gamma$-$S_8$ in cold,
natural settings may not be an inherent biosignature, future research into the role of in situ microbial activity in the given detections of $\beta$-$S_8$ and $\gamma$-$S_8$ in unexpected localities is needed.

3.8. Conclusion

Two rare monoclinic allotropes of $S^0$ have been shown to form in sulfur bubbles forming on a melt pool at a cold glacial site in the Canadian High Arctic. The stabilization of $\beta$-$S_8$ and $\gamma$-$S_8$ is inferred to occur through interaction of organic carbon and sulfur. This is the first detection of the $\beta$-$S_8$ form of $S^0$ in a cold, natural setting and suggests that the formation and stabilization of $\beta$-$S_8$ may be more commonplace and over a much wider range of environmental conditions than previously thought. Intriguingly, $\beta$-$S_8$ and $\gamma$-$S_8$ in our sample of sulfur bubble material appeared metastable, reverting to $\alpha$-$S_8$ in less than two weeks at room temperature. This may suggest that $\beta$-$S_8$ and $\gamma$-$S_8$ have been sampled in previous works without being detected due to their metastable nature.

Future research on sulfide-oxidation in the presence of dissolved organic compounds is required to propose a mechanism for the formation of $\beta$-$S_8$ and $\gamma$-$S_8$, and to determine whether microbial activity is necessary to stimulate the process. It is not currently known if the organic carbon within the melt pool on the sulfidic icing at Borup Fiord Pass is derived in situ through microbial processes or is delivered to the surface through the sulfide-spring system. However, the interaction of organic matter with sulfur in natural settings may form monoclinic sulfur allotropes more widely than is currently recognized. Furthermore, this work does not preclude the possibility that microbial processes of sulfur oxidation are involved in the proposed organic carbon-sulfur interactions. Further work will be necessary to determine the role that various forms of organic matter may play in unique sulfur distributions in natural systems.
3.9. Acknowledgements

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CHAPTER 4:

SULFUR- AND IRON-RICH MINERALOGICAL FEATURES PRESERVED IN PERMAFROST IN THE CANADIAN HIGH ARCTIC: ANALOGS FOR THE EXPLORATION OF HABITABLE ENVIRONMENTS ON MARS


Abstract

Elliptical sulfate-rich features, stained red by the presence of iron oxides, are set within permafrost and carbonate rock at Borup Fiord Pass in the Canadian High Arctic. These mineralized features exhibit co-localization of sulfur minerals in multiple oxidation states (including pyrite, elemental sulfur ($S_0$), and gypsum) while iron mineralogy includes jarosite, goethite, and hematite. Through application of x-ray diffraction (XRD) and Raman microspectroscopy, we demonstrate that these features encapsulate central cores with abundant pyrite; while $S_0$, sulfate, and iron-bearing secondary minerals appear to have formed from oxidative weathering of the pyrite. These features appear similar to terrestrial gossans and represent a habitable system relevant to Mars exploration.

We use Raman microspectroscopy and scanning transmission x-ray microscopy (STXM) to show that organic carbon is associated with the minerals within these features. The origin of this carbon remains enigmatic; however, we consider the possibility that this carbon, along with etching of the pyrite grains and encrusted filaments detected in the features, may be indicative of biological activity during alteration of the pyrite. Here we also consider how geological sulfide emplacements and their weathered surface expressions may provide a target for future surface and remote sensing studies of habitable environments on Mars.
4.1. Introduction

Sulfate-rich mineralized features at Borup Fiord Pass, in the Canadian High Arctic, may represent key analogs for the exploration of habitable, low-temperature, iron- and sulfur-rich mineralized systems on Earth and on Mars. These features stand out as elliptical concentrations of red-stained, friable material up to 5 m in diameter (Grasby et al., 2012). They may represent a near-surface biologically-active system, where the large-scale emplacement of pyrite has occurred and subsequent alteration of that pyrite has formed diagnostic mineral assemblages including oxidized iron and sulfur minerals. Such pyrite oxidation systems provide necessary redox gradients and electron donors/acceptors for life as we know it, and such habitable near-surface systems may exist on Mars (e.g., Burns and Fisher, 1990; Burns and Fisher, 1990; Zolotov and Shock, 2005; Amils et al., 2007; Norlund et al., 2010).

Pyrite is the most common metal sulfide mineral at the Earth’s surface and has been used throughout recorded human history as an indicator of valuable ore deposits (e.g., Rickard and Luther, 2007). Pyrite can form through multiple pathways, including through magmatic and volcanic/hydrothermal sources as well as through low-temperature, biologically-driven processes. Sulfide ore deposits formed directly from magmatic sources, where sulfides are essentially smelted from intrusive magmas, often consist of pyrrhotite, pentlandite, and chalcopyrite (Barnes et al., 2017), while hydrothermal deposits of sulfide minerals can be enriched in pyrite and other sulfide minerals as well (Fontboté et al., 2017). Meanwhile, sedimentary pyrite emplacements are common in myriad environments on Earth and constitute some 95% of the sulfide on the surface of our planet. Furthermore, it is estimated that 96% of this pyrite in sedimentary deposits is formed through biological sulfate reduction (BSR) and subsequent titration of geologically available ferrous iron (Rickard et al., 2017). Such pyrite deposits form a critical record of the evolution of the global biogeochemical sulfur cycle on Earth.
The acidic weathering of minerals in pyrite-rich, near-surface systems can drive the creation of redox gradients, produce recognizable alteration mineral assemblages, and provide habitable, though perhaps relatively extreme, environments for life (e.g., Mcguire et al., 1999; Edwards et al., 2000; Zolotov and Shock, 2005; Amils et al., 2007; Amils, 2016). For instance, the oxidation of ferrous iron and sulfur within sulfide minerals to form sulfates, ferric (oxyhydr)oxides, and acidity is driven by biological processes in a variety of systems on Earth, including acid mine/rock drainage systems like those at Iron Mountain, California, USA (e.g., Mcguire et al., 1999; Edwards et al., 2000) and the Rio Tinto system in Spain (e.g., Fernández-Remolar et al., 2005; Amils et al., 2007; Amils, 2016). The weathering of the primary minerals in these settings is often catalyzed by biological activity, producing mineral assemblages that are diagnostic of the potential role of biology. Furthermore, the oxidative leaching of pyrite in near-surface veins forms geological structures known as gossans. Gossans produce recognizable, stratified alteration features, with circular red staining from iron oxides overlying the region of the sulfide vein. Also known as “red caps”, gossans have long been a target for ore exploration in mining interests (e.g., Taylor and Eggleton, 2001; West et al., 2009; Percival and Williamson, 2016).

Terrestrial systems with sedimentary pyrite emplacements as well as the products of the acidic alteration of pyrite are important analogs for our explorations of Mars. Iron and sulfur are both enriched in the Martian crust (Toulmin, III et al., 1977; Gellert and Clark, 2015), and the weathering of iron sulfide ores may be a key piece to understanding iron and sulfur mineralogy on Mars’ surface (Burns and Fisher, 1990a). Though limited thus far, iron sulfide minerals have been detected on Mars through rover-based instrumentation (Morris et al., 2008; Vaniman et al., 2014), while sulfates have been identified globally through remote sensing (Ehlmann and Edwards, 2014). Iron and sulfur rich environments may represent habitable systems on past and present-day Mars (Hays et al., 2017).
Building upon our understanding of the role that biology plays in pyrite alteration systems, as well as constraining which signatures of such life form and persist in these systems, is necessary for our future exploration of Mars. However, many such analog systems on Earth exist in regions with much higher temperatures and levels of precipitation than have occurred through most of Mars’ history. Furthermore, many of these terrestrial systems are also surrounded by abundant plant and animal life, obscuring some otherwise observable features. Given the low-temperature, low-moisture conditions through much of Mars’ history, pyrite alteration under similar conditions on Earth may serve as a more appropriate analog system. The pyrite alteration features entrained in carbonate rock and permafrost at Borup Fiord Pass present such analogs in a region with low-moisture and low-temperatures (e.g., Grasby et al., 2003). Grasby et al. (2012) have showed from x-ray diffraction (XRD) of surface materials that these features are primarily composed of gypsum with visibly red staining from minor concentrations of goethite and jarosite. The red staining also marks the transition from the gypsum-rich features to the calcite-rich rock of the valley floor.

In this work, we set out to further characterize these features, specifically with regard to their potential relationship to modern sulfide-rich, supraglacial springs that form at a nearby glacier (Grasby et al., 2003; 2012). We demonstrate the co-localization of pyrite with elemental sulfur ($S_0$) and sulfates in the features, providing a range of sulfur redox states throughout. Pyrite had not previously been detected in these features, and this detection provides a new consideration of the nature of these conspicuous structures in the Canadian High Arctic. This writing details the chemistry and mineralogy of materials from two of the features. We use geochemical and spectroscopic methods (including XRD, Raman microspectroscopy, and scanning electron microscopy (SEM)) to detail the bulk and microscale mineralogy of the features and to discern the redox speciation of sulfur within these materials. We also consider the importance of organic carbon and potential biosignatures (such as filamentous materials and geometric etchings of the pyrite) as signs of the role of biology in the alteration of pyrite within these structures. We consider
the potential sources of the pyrite in these structures and the habitability of such systems on Earth and on Mars. Furthermore, we examine these features for their relevance to Mars exploration and for their implications for the potential role of biology in controlling the expression of products from the weathering of pyritic materials in low-temperature settings.

4.2. Materials and Methods

Borup Fiord Pass is a north-south trending valley located at ~81°N, 81°W, on Ellesmere Island in the Canadian High Arctic (Figure 4.1). The geology of this region was first described by Thorsteinsson and Tozert (1957), and further characterization of the valley’s stratigraphy was provided by Gleeson et al. (2011) and Hill (2014). Borup Fiord Pass occurs within the Krieger Mountains, in the deformed eastern portion of the Sverdrup Sedimentary Basin, a Carboniferous to Eocene depocenter (Embry and Beauchamp, 2008). The valley’s surface is composed primarily of Carboniferous to Permian carbonate units. A right-lateral strike-slip fault crosses this valley roughly 100 m from the toe of a coalescence glacier (“Borup Fiord Pass Glacier”) which forms from the merger of local alpine glaciers (Grasby et al., 2003; Gleeson et al., 2011). Modern-day sulfide-rich springs and spring derived ices (aufeis) form at the toe of this glacier and have been the focus of previous research due to the presence of extensive deposits of elemental sulfur that form at this site (Grasby et al., 2003; Gleeson et al., 2012; Wright et al., 2013). These sulfur deposits have also revealed rare mineral occurrences, including vaterite (a polymorph of calcium carbonate; Grasby, 2003) and metastable allotropes of elemental sulfur (β-S₈ and γ-S₈; Lau et al., 2017). The valley where these sulfur deposits and the red-stained mineral features are located is a polar desert region, with mean annual rainfall <100 mm and mean annual air temperatures of -19.7°C reported at the Eureka meteorological station ~140 km to the southwest (Fig. 4.1a; Grasby et al., 2003).
Figure 4.1: Location and regional geology of Borup Fiord Pass

A line drawing (a) shows the location of Ellesmere Island, in the Canadian High Arctic (black-and-white inset). The bottom inset in a shows the location of Borup Fiord Pass as well as the location of the Eureka weather station. Borup Fiord Pass is a north-south trending valley (b). The satellite image in b was collected on 21 June 2014 by the Operational Land Imager (OLI) onboard Landsat 8 (image credit: NASA Earth Observatory/USGS/J. Allen/R. Simmon). The dashed box in b shows the location of the geological map in (c). The regional geology includes primarily Permian to Triassic units with Cretaceous igneous intrusions and Quaternary glacial deposits (c; adapted from Hill (2014)). Features in c include: a black dashed line showing the location of a strike-slip fault running across the valley; a yellow arrow showing where the modern sulfur spring system forms at the surface in some years (including in 2014); and a red dotted circle showing the region where the alteration features, pyrite veining, and general red staining of rocks has been observed.
Materials for this study were collected during a summer field campaign in 2014. Two of the conspicuous red-stained features were selected for surface sampling, one of which was also selected for subsurface sampling (Fig. 4.2). For subsurface samples, a trench was dug by shovel to provide deeper samples (Fig. 4.2c,d). Three samples were collected from ~30 cm below the surface from the side of the wall of the trench. In addition, a core drill was used to collect material from the permafrost-hosted material below the trench (which had been dug until permafrost hindered hand-powered action, at ~60 cm below the surface). Cores were wrapped in aluminum foil and placed on ice during transport back to the laboratory. Other samples were collected using plastic bags and polyethylene tubes and were stored at ambient temperatures during transport. After transport to the laboratory, all materials were stored at -70°C until needed for analyses. The feature in Figure 4.2a is located near the fault crossing the valley and so was named “Fault Feature”. Samples from this structure are called FF1, FF2, and FF3. The other feature (Fig. 4.2b-c) is located ~400 m to the south of the fault. Samples from this feature are named relative to their position in the shovel-dug trench; these samples are named T1 and T2 (for the samples of the top material from the center and rim of the trench, respectively); S1, S2, and S3 (for the three samples from the “side wall” of the trench); and C1 through C4 (for the four core samples that were collected).

The materials used in this study were not conducive to direct pH measurement (as they are mostly solids), however 1:1 mixtures of sample material and deionized water enabled comparison of the relative acidity of each of the samples (1:1 sample:water pH measurements are common for measuring the acidity of soils; e.g. Carter and Gregorich 2008). For this, dried sample material was ground and sieved (<180 μm), and then a mass of sample material was mixed with an equivalent mass of deionized water. The sample was mixed on a vortex mixer for one minute. Ten minutes after fluid addition a pH measurement was collected. Measurements were also collected one hour after fluid addition to ensure consistency of results. All measurements were conducted in triplicate.
Figure 4.2: Alteration features and sampling locations
Samples were collected from two of the alteration features (a,b). Samples FF1, FF2, and FF3 are labeled in a (with human for scale). A shovel and core drill (shown in b) were used to dig a trench and take samples from the permafrost (c) of the feature in b. Goggles are shown in c for scale. The locations of samples collected from this feature are shown in a representation of the trench in d. Sample names from the trench samples are included. Approximate lengths along the long axes of the features in a and b are 4 m.
This method was modified from those found in Carter and Gregorich (2008), though similar methods can be found elsewhere. A 1:1 sample:water mixture was selected to reduce the necessary amount of water (a pH microelectrode was used for the measurements). A 0.01 M CaCl₂ solution was first used, but did not show inherent differences in pH to measurements made in deionized water alone. Measurements of acidity were collected 10 minutes and 1 hour after addition of water. These time measurements varied by an average of 0.1 pH units per sample, with a greatest variation of 0.2 pH units. The measurements collected after 10 minutes are reported here.

Samples for total organic carbon (TOC) analysis were prepared by repeat washing with concentrated HCl to remove carbonate carbon followed by centrifugation and removal of supernatants. TOC measurements were made in the Arikaree Environmental Laboratory (AEL) at the Institute for Arctic and Alpine Research (INSTAAR) at the University of Colorado Boulder using a FLASH EA 1112 Series CHN Analyzer (Thermo Finnigan, LLC.; San Jose, California, USA). Data were calibrated using an atropine standard.

Isotopes of sulfur (³²S and ³⁴S) were analyzed through elemental analyzer isotope ratio mass spectrometry (EA-IRMS) in the Isotope Science Laboratory at the University of Calgary. δ³⁴S values were standardized against V-CDT (Vienna Canyon Diablo Troilite). Sulfur isotopes were measured in sulfides and sulfates from submitted samples. Sulfide was first extracted through washing of material with acidified water and then sieving to select reflective grains greater than 425 μm. Sulfates were extracted from samples by the Isotope Science Laboratory prior to analysis.

X-ray diffraction (XRD) data were collected on either a D2 PHASER desktop diffractometer (Bruker Corporation; Billerica, Massachusetts, USA) at the University of Colorado Boulder or a D500 diffractometer (Siemens AG; Berlin, Germany) at the United States Geological Survey (USGS). X-rays were generated as Cu Kα radiation and data were collected with 1- to 2-second dwell times per step and steps of 0.02° 2θ. Ranges of data collection vary for some samples, but all cover at least 15° to 60° 2θ. Prior to data collection, samples were dried and then ground to a fine powder.
Samples were packed on Si-wafers for reduced background and rotated during data collection to reduce common orientation effects. XRD patterns were analyzed using Jade 9 (Materials Data Inc.; Livermore, California, USA) and the JCPDS PDF-2 database, 2001 release (ICDD: Newtown Square, PA, USA, 2001).

Raman microspectroscopy of samples was performed at the University of Colorado Boulder using a LabRAM HR Evolution Raman spectrometer (Horiba, Ltd.; Kyoto, Japan) with reflected light microscopy for imaging and a 532 nm green laser for Raman spectroscopy. Data collection and analysis was conducted using Horiba’s LabSpec 6 (v6.4.1.63) spectroscopy suite. Raman spectra were processed using LabSpec and peaks were fit with reference compounds from the RRUFF database (Lafuente et al., 2015), either manually or by using the program Know-It-All (Bio-Rad Laboratories, Hercules, California, USA). Spectral maps, where collected, were processed using LabSpec. Map data were corrected using the Instrument Correction System (ICS) process and then were subtracted to baselines using 3rd degree polynomial functions applied over 100+ data points. Noise points were added into baselines with low signal data. Map data were analyzed using the classical least squares (CLS) and multivariate curve resolution (MCR) applications within LabSpec to spatially resolve components within map regions and to detect the range of components within map data.

Material for scanning electron microscopy (SEM) was thoroughly dried and then placed on carbon tape over an aluminum stud. Samples were sputter coated with Au to decrease charging artifacts. Electron microscopy was conducted at the Nanomaterials Characterization Facility (NCF) at the University of Colorado Boulder using a JEOL JSM-6480LV SEM outfitted with an energy dispersive spectroscopy (EDS) x-ray detector. SEM was conducted in secondary electron mode with accelerating voltages from 2-5 kV for imaging and 15 kV for EDS.

Scanning transmission x-ray microscopy (STXM) was conducted at the S L-edge and C K-edge at the soft x-ray spectromicroscopy (SM) beamline, 10ID-1, at the Canadian Lightsource (CLS)
in Saskatoon, Saskatchewan, Canada. The monochromator was calibrated using the standard 3p Rydberg transition of gaseous CO$_2$ at 294.96 eV. STXM was used to map the distribution and characterize the speciation of sulfur and carbon in the sample at a 35 nm spatial resolution. STXM data were collected on samples which were prepared through repeated washings with ultrapure water to remove salts. Samples were then mixed with ultrapure water and allowed to settle. Supernatants were then sampled with micropipettes and deposited on gold TEM grids. Material was then thoroughly dried before analysis. The sample was placed in a vacuum chamber for STXM collection; the chamber was evacuated to ~13 Pa and then back-filled with He to standard atmospheric pressure before data acquisition. Scanning transmission x-ray images were collected for sulfur at four energies (160, 163, 170, and 173 eV). These energies were selected to target variations in x-ray transmission intensities for reduced and oxidized sulfur compounds (160 vs. 163 eV and 170 vs. 173 eV, respectively; e.g., Jalilehvand, 2006). For carbon, images were collected at 280.0 eV (below the C K-edge) and 288.2 eV (the absorption energy of 1s→π* electronic transitions of carbon in amide groups; Benzerara et al., 2004). STXM data were processed using the aXis2000 software package (Hitchcock, 2015). Transmission intensity data for images were converted to optical densities (OD). The differences in OD between images was used to generate maps of sulfur and organic carbon distribution within sample materials. These maps were then used to select regions for collections of stacks of images, using small steps in incident energy over a region of energies through either the sulfur L-edge (155 to 190 eV) or the carbon K-edge (260 to 340 eV). These image stacks were used to generate x-ray absorption near edge structure (XANES) spectra, which were then analyzed with aXis2000 and compared to the literature for functional group interpretations.
4.3. Results

4.3.1. Field Observations and Sampling

The red-stained, gypsum-rich features at Borup Fiord Pass are located on a hill, standing ~50 m above the surrounding valley and having a diameter of ~1000 m (Figs. 4.1c & A3.1). While the Fault Feature lies along the fault in the valley, the other features all occur ~300 m to the south and lie within ~50 m from each other. The red-stained features stand out against the grey carbonate rocks of the surrounding valley (Figs. 4.2 & A3.2-3). The material within the features is crystalline, but also friable. Although these mineralized features sit relatively level with the immediate surrounding rock, they are located in a region that is notably topographically higher than the surrounding valley (Figs. 4.1 & A3.1). This topographically high region presents itself as a roughly circular hill, just to the south of the strike-slip fault that crosses the valley. Mapping in this region has revealed that the exposed materials on this hill are mostly Quaternary glacial deposits and exposed limestone rock of the Permian-aged Nansen Formation (Grasby et al., 2003; Hill, 2014; Fig. 4.1). Six red-stained elliptical regions have been identified to-date, with two of these revealing white central regions composed primarily of gypsum (Fig. A3.2). All of the features are 1-5 m in diameter and show apparent red staining from iron oxides. Also, abundant red staining of rocks can be observed on the hill where the features are located. For instance, a small lake (which can be seen in satellite imagery; Fig. A3.1) roughly 100 m from most of the alteration features has abundant red-stained rocks (Fig. A3.3). In addition, to the west of the alteration features on the hill is a drainage, informally referred to as "pyrite canyon", where carbonate rocks are marked by veins of pyrite (identified visually; Fig. A3.3). These observations suggest that oxidation of iron from subsurface pyrite throughout the region surrounding the mineralized features has occurred.

Two of the red-stained features were selected for sampling in this work. One, where samples were collected from a trench that was dug into the feature, is the same one that was used for surface mineralogy characterization in a previous study by Grasby et al. (2012). This previous
work only included sampling from the surface materials, where transects showed the calcite from the limestone rock of the valley giving way to gypsum-rich material, with goethite and jarosite in the red-stained outer region and the interior white region containing up to 15% S\textsuperscript{0}. However, these samples of materials in the active zone above the permafrost of the valley may not be entirely representative of the subsurface chemistry of the features (due to constant exposure to the atmosphere and annual freeze-thaw cycles). For this reason, in the current work, we sampled from the surface as well as from deeper within the active zone and from the permafrost layer below for this feature. Sampling from multiple depths into the structure provided a spatially resolved suite of samples for chemical and mineralogical analyses. As we collected our permafrost core samples during the summer, we believe these samples represent the true perennial permafrost material (as thawing of the active zone should be maximal at this time).

4.3.2. Geochemical Measurements and Bulk Mineralogy

Total organic carbon (TOC) averaged 0.10% over all measured samples (Table 4.1). Sample T2 yielded the highest TOC value at 0.37%. Without this high value from the rim material, the average TOC is 0.03%, showing that the material from the surface edge of the white-centered feature skews the total organic carbon data. All of the core samples were below the detection limit for the instrument of 0.01% TOC. TOC in Fault Feature samples FF2 and FF3 has not been measured.

The pH measurements ranged from 1.2 to 7.2 units, with a mean of 3.5 (Table 4.1 and Fig. 4.3). The least acidic sample was T2, with a 1:1 water pH of 7.2. The most acidic samples within the trench were the sidewall samples (S1, S2, and S3; Fig. 4.3).

X-ray diffraction (XRD) was used to probe the bulk mineralogy of sample materials. XRD data show that gypsum is the primary component of nearly all bulk powder samples, by relative
### Table 4.1: Acidity, TOC, and components detected with XRD and Raman spectroscopy

Acidity measurements are given with an error of ±0.2 pH units (and measured as 1:1 sample:water pH). For TOC measurements, “DL” indicates below detection level of the instrument (see text), while “NM” indicates where no measurement was collected. XRD data are ordered by dominant peak heights; questionable mineral components are indicated in parentheses. Raman spectroscopic results are split into the most common and less common phases observed (most common are observed in nearly every observed region of the sample material, while less common phases are sparsely located within the materials). S\(^0\) indicates elemental sulfur while OC indicates organic carbon.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>TOC (%)</th>
<th>XRD Mineralogy</th>
<th>Raman Spectroscopic Results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Common</td>
</tr>
<tr>
<td>T1</td>
<td>2.8</td>
<td>0.02</td>
<td>Gypsum, S(^0), (pyrite)</td>
<td>Gypsum, pyrite, S(^0), OC</td>
</tr>
<tr>
<td>T2</td>
<td>7.2</td>
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<td>Quartz, gypsum, goethite</td>
<td>Goethite, gypsum</td>
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<td>S1</td>
<td>1.2</td>
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<td>Gypsum, S(^0), pyrite</td>
</tr>
<tr>
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<td>0.06</td>
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<td>Gypsum, pyrite, goethite</td>
</tr>
<tr>
<td>S3</td>
<td>2.8</td>
<td>0.02</td>
<td>Gypsum, S(^0), anhydrite</td>
<td>S(^0), gypsum, OC</td>
</tr>
<tr>
<td>C1</td>
<td>3.7</td>
<td>DL</td>
<td>Gypsum, pyrite, S(^0)</td>
<td>Pyrite, gypsum, anhydrite, S(^0), quartz</td>
</tr>
<tr>
<td>C2</td>
<td>5.2</td>
<td>DL</td>
<td>Gypsum</td>
<td>Gypsum, pyrite, S(^0), hematite, iron oxides</td>
</tr>
<tr>
<td>C3</td>
<td>4.3</td>
<td>DL</td>
<td>Gypsum, (pyrite)</td>
<td>Gypsum, anhydrite, pyrite, S(^0), OC</td>
</tr>
<tr>
<td>C4</td>
<td>3.0</td>
<td>DL</td>
<td>Pyrite, gypsum, quartz S(^0)</td>
<td>Gypsum, pyrite</td>
</tr>
<tr>
<td>FF1</td>
<td>4.1</td>
<td>0.19</td>
<td>Gypsum, quartz, jarosite</td>
<td>Gypsum, goethite, jarosite, pyrite, OC</td>
</tr>
<tr>
<td>FF2</td>
<td>3.6</td>
<td>NM</td>
<td>Gypsum, quartz, pyrite</td>
<td>Gypsum, pyrite, goethite, jarosite, pyrite, OC</td>
</tr>
<tr>
<td>FF3</td>
<td>2.0</td>
<td>NM</td>
<td>Gypsum, goethite, quartz, jarosite</td>
<td>Gypsum, goethite, jarosite, quartz, OC</td>
</tr>
</tbody>
</table>
Figure 4.3: Acidity measurements from the trench samples
Relative acidity measurements were collected as 1:1 water:sample pH. See Table 1 for numerical pH values.
XRD peak heights (Table 4.1). XRD data for samples T1, S1, C1, and C4 all reveal pyrite, elemental sulfur, and gypsum co-occurring. Quartz was identified in several samples (T2, C4, FF1, FF2, and FF3). Jarosite was detected in FF1 and FF3, but not in any samples from the trench. X-ray diffractograms for each sample are reported in §A3.2 (Figs. A3.4-A3.15).

Sulfur isotopes (δ34S) in sulfides and sulfates were measured for three alteration feature samples. Core samples C1 and C2 were analyzed to reveal sulfur isotope values within the permafrost. δ34S values in sulfides from these samples are 6.5 and 8.5‰, respectively, while δ34S in sulfates are 7.7 and 8.0‰, respectively. One Fault Feature sample, FF1, was measured as well and revealed 11.7‰ δ34S in sulfides and 12.7‰ δ34S in sulfates. Figure 4.4 shows these isotopic values compared to data for other relevant sulfur-bearing materials in the valley. For instance, a sample from the fault that was collected in the eastern portion of the valley, far from the region of the alteration features, revealed δ34S of 16.2‰ in sulfide and 15.2‰ in sulfate. Sulfur isotope data for dissolved sulfide and sulfate in spring-derived ice (aufeis) in the modern sulfur spring system are also reported. These samples, also collected in 2014, have ranges of 9.7-13.2‰ and 26.0-30.1‰ in sulfide and sulfate δ34S, respectively.

Included in Figure 4.4 are previous sulfur isotope measurements from relevant materials in the valley. These include δ34S values for S⁰ and gypsum in the modern spring system sampled in 2000 and previously reported by Grasby et al. (2003), values for S⁰ and gypsum at the surface of the trench-sampled alteration feature (revealing δ34S of 7.4-14.2‰ and 7.3-13.0‰, respectively) as reported by Grasby et al. (2012), and measurements for the sulfates in local anhydrite-bearing geological units (proposed as the potential sources of the sulfur in the system). These anhydrite-bearing units, the Otto Fiord Formation and the Mount Bayley Formation, have average δ34S values of 14.6 and 13.1‰, respectively (Davies and Nassichuk, 1975; Wallace et al., 1994; Grasby et al., 2003). Furthermore, pyrite within the fault was also measured by S.E. Grasby in previous years (Grasby et al., 2003), with the average δ34S value of 9.1‰ reported here in Figure 4.4.
Figure 4.4: Sulfur Isotopes

Sulfur isotopes are reported as $\delta^{34}S$ (‰) against V-CDT. Ranges of $\delta^{34}S$ values for anhydrite in local evaporite units are from the Mount Bayley Formation (reported in Wallace et al., 1994) and the Otto Fiord Formation (reported in Grasby et al., 2003); lines show ranges while average values are shown as filled markers. Data for deposits from the modern spring system include dissolved sulfide and sulfate from melted aufeis (2014) as well as elemental sulfur (S0) and gypsum (2000; reported by Grasby et al., 2003). Sample data from the strike-slip fault (dotted line in Fig. 4.1c) include sulfide and sulfate from a 2014 sample as well as an average value reported for 2000 samples in Grasby et al. (2003). Isotope data for alteration feature samples include sulfide and sulfates in core samples C1 and C2 as well as Fault Feature sample FF1. A range of $\delta^{34}S$ values from S0 and gypsum from a surface transect (reported in Grasby et al., 2012) are reported as a solid black line (ranges overlap; $\delta^{34}S$ of S0 ranges from 7.4 to 14.2‰, while $\delta^{34}S$ of gypsum ranges from 7.3 to 13.0‰).
4.3.3. Raman Microspectroscopy

Raman microspectroscopy allows for probing through materials to find the most common mineral phases, but also allows for more spatially resolved analyses that can reveal the discrete spots containing less common materials within a sample, underpinning sample heterogeneity. Also, while XRD discriminates based on concentration and crystallinity of bulk mineral components, some compounds are more or less Raman active (or not at all) and so Raman spectroscopy can be very useful for targeting certain mineral phases that are highly Raman active even at low concentrations, including S\textsuperscript{0} and organic carbon. Raman microspectroscopy analyses revealed S\textsuperscript{0} and organic carbon in nearly all of the sample materials, even though they were not detected with XRD (Table 4.1; §A3.3).

Raman microspectroscopy of sample T1 showed primarily tabular crystals of gypsum, with large pyrite grains (tens to hundreds of microns in width) and smaller spots containing elemental sulfur (S\textsuperscript{0}; Figs. 4.5 & 4.11). Organic carbon is also detected in association with the pyrite and S\textsuperscript{0} in this sample (see Figs. 4.11 & A3.16-17). Sample T2, meanwhile, consists primarily of gypsum heavily stained in red/orange from the occurrence of iron (oxyhydr)oxides, including goethite (Figs. 4.5 & A3.18). This sample also revealed the presence of calcite, likely from the carbonate rock of the surrounding region, as well as one conspicuous filamentous structure (see Fig. 4.5).

The sidewall samples (S1, S2, and S3) show primarily tabular gypsum crystals. Sample S1 had an abundance of gypsum grains with associated sulfur and pyrite (Fig. 4.6a). Sample S2, while similar, also had many regions containing red/orange stained gypsum grains with goethite and pyrite (Fig. 4.6b). The pyrite grains in S1 and S2 also revealed associations with globules of elemental sulfur and organic carbon (Fig. 4.6c; §A3.3.2). Sample S3 appears to be composed primarily of gypsum and elemental sulfur with abundant organic carbon (Fig. 4.7). The Raman spectral map for sample S3 in Figure 4.7 shows that organic carbon is associated with globular sulfur in this sample. No pyrite has been detected in sample S3.
Figure 4.5: Raman microspectroscopy of trench surface materials
Sample T1, from the central surface region of the trench, primarily shows tabular crystals of gypsum (a) with grains of pyrite and smaller spots containing elemental sulfur (smaller dark ovoids in a). The reflected light image in b shows mostly red/orange goethite and gypsum in sample T2. A filament in this sample is highlighted with a white arrow (see Fig. 12f).
The core samples show similar mineral morphologies and compositions to the sidewall samples, with an abundance of gypsum, pyrite, elemental sulfur, and organic carbon (Figs. 4.8-9 & A3.21-23). Sample C1 contains large sulfide and gypsum grains (tens to hundreds of microns in width) with micron-sized spots bearing $S^0$ and quartz (Fig. 4.8a,b). Sample C2 also contains large grains of pyrite and gypsum. One region from sample C2 contains tabular gypsum grains with spots of $S^0$, pyrite, and organic carbon (Fig. 4.8d). This region also appears to have the red/orange staining indicative of iron (oxyhydr)oxides, though these phases are not observed in the Raman map for this region (Fig. 4.8c,d). Other regions of this sample show tabular gypsum grains encrusted in iron (oxyhydr)oxides, including hematite ($\text{Fe}_2\text{O}_3$). Sample C3 revealed pyrite and gypsum together with iron (oxyhydr)oxide, while a large grain of pyrite (~50 microns by 80 microns) revealed associated gypsum, and hematite. This pyrite grain also had associated organic carbon, which is compared to organic carbon from a dark spot in/on a gypsum crystal in the same sample in Figure 4.9. C3 also had a region (~6 microns by 8 microns) that is rich in elemental sulfur. Furthermore, a Raman map of the large pyrite grain in Figure 4.9b revealed the presence of micron-sized spots bearing mackinawite (see Figs. A3.24-26). Sample C4 contains primarily pyrite, $S^0$, gypsum, and organic carbon. There are $S^0$- and OC-rich regions of the sample that are up to 10 $\mu$m in width.

Reflected light microscopy and Raman microspectroscopy reveal that the Fault Feature samples are very similar to the materials from the trench-sampled feature (Table 4.1; Fig. 4.10). All Fault Feature samples are primarily composed of tabular grains of gypsum with goethite, jarosite, and pyrite found in many places (Fig. 4.10). In many ways, the Fault Feature samples are indistinguishable from those of the other feature, except for that jarosite is abundant in the Fault Feature samples and was not detected in the other samples in these analyses (although jarosite was previously identified in alteration feature surface materials through XRD by Grasby et al., 2012).
Figure 4.6. Raman microspectroscopy of samples S1 and S2

A gypsum grain with associated dark grains of micron-sized pyrite from sample S1 is shown in a, while b shows a region of red/orange stained gypsum with iron oxide globules and larger pyrite grains within sample S2. Spectra presented in c show data for a pyrite grain from S1 (green circle in a) which bears pyrite as well as elemental sulfur (S0) and also reveals gypsum. Spectra for a globule of goethite from S2 (blue diamond in b) and a pyrite grain from S2 with peaks for organic carbon (red box in b) are also shown. A spectrum is presented bearing peaks for S0 and organic carbon, which comes from micron-sized spots on the pyrite grain in the red square in b. Reference spectra for pyrite, S0, gypsum, and goethite are also shown.
Figure 4.7. Raman spectromicroscopy of sample S3
A reflected light microscope image of sample S3 (a) shows tabular grains of gypsum surrounded by globules of elemental sulfur. The tri-colored Raman spectral map in b shows fits for elemental sulfur (red; fit to primary S0 peak from 210-225 cm$^{-1}$), gypsum (green; fit to primary peak from 1000-1020 cm$^{-1}$), and organic carbon (blue; fit to G-band of OC from 1500-1650 cm$^{-1}$). Map data were collected in 5 µm steps with 6 iterations of 2 seconds of collection per step.
Figure 4.8: Raman microspectroscopy of samples C1 and C2
Microscope images and Raman spectral maps are shown for samples C1 (a,b) and C2 (c,d). The white rectangles in microscope images show where maps were collected. The map for sample C1 shown in b is colorized to match fits for pyrite (red; 375-380 cm\(^{-1}\)), gypsum (green; 1000-1020 cm\(^{-1}\)), and the G-band of organic carbon (blue; 1500-1650 cm\(^{-1}\)). Quartz, S0, anhydrite, hematite, calcite, and silicon were also found in this map region (see text). The map for sample C2 shown in d is colorized to match fits for pyrite (red; 365-375 cm\(^{-1}\)), S0 (green; 205-225 cm\(^{-1}\)), and gypsum (blue; 1000-1020 cm\(^{-1}\)). This map region also contains anhydrite and organic carbon.
Figure 4.9: Organic carbon in sample C3
Organic carbon was detected in a dark granule on/in a tabular gypsum crystal (a) as well as on a pyrite grain (b) in sample C3. Spectra for organic carbon are shown in (c). The spectrum from the dark grain in (a) was collected from one spot with 3 iterations at 3 seconds each. The spectrum from the pyrite grain in (b) (taken from the region shown in green) is an average of 6 spots with 4 iterations of 4 seconds each. The D1- and G-bands in (c) derive from peak fitting of the spectra. Peaks for gypsum (Gyp; 1008-1010 cm$^{-1}$) and for pyrite (Pyr; 342, 377, & 429 cm$^{-1}$) are also labeled.
Organic carbon is detected throughout the FF material, including in darker, isolated spots as were detected in the trench samples as well as one ~200 µm² region of organic carbon associated with two globules of S⁰ (Figs. 4.10 & A3.30).

Raman microspectroscopy revealed regions rich in organic carbon in all of the samples (Table 4.1, §A3.3.4). Organic carbon compounds are Raman active and can be detected through the presence of the D- and G-bands ("disordered" and "graphitic" bands, located at ~1350 and 1550-1600 cm⁻¹, respectively; sometimes a series of D-bands can be discerned around 1150, 1350, 1500 and 1620 cm⁻¹ depending on the carbon compounds and the quality of the spectra; Ferrari and Robertson, 2000; Beyssac et al., 2002; Beyssac et al., 2003; Sadezky et al., 2005). These bands derive from the level of disorder among aromatic sp²-bonded carbon atoms. For instance, stretching vibrations in well-ordered aromatic carbon in the graphite arrangement will produce the G-band, while disorder in the structure of the organic compounds from in-plane defects, heteroatoms, and tetrahedral carbon interactions outside of the plane give rise to the D-bands (Beyssac et al., 2002; Beyssac et al., 2003; Brolly et al., 2016). Most of the organic carbon detected in the alteration feature materials appears to be associated with pyrite, S⁰, and/or iron (oxyhydr)oxides within the samples; Figure 4.11 shows associations of organic carbon with both pyrite and S⁰ in sample T1.

A comparison of the disordered (D) bands of organic material to the graphitic (G) bands can yield useful information regarding the alteration of the carbon (through thermal alteration and graphitization). For instance, the broad and overlapping D and G bands in organic carbon from the pyrite alteration features (Table A3.1) is generally indicative of disordered carbonaceous matter with low levels of carbonification and structural organization (e.g., Spötl et al., 1998; Ménez et al., 2012). Also, the R1 ratio and R2 ratio, defined by Beyssac et al. (2002), have been used to determine the maturity of organic carbon through Raman spectroscopy of metamorphic sediments. The R1
Figure 4.10. Raman microspectroscopy of fault feature samples
Sample FF1 shows an abundance of gypsum with grains of pyrite, jarosite, and goethite throughout (a-c). The dark grain in a appears to be a grain of pyrite, which also reveals dispersed goethite, discrete granules of jarosite, anatase, and organic carbon, all set within gypsum. The microscope image in b and corresponding Raman spectral map in c show tabular grains of gypsum (green in c; 1000-1020 cm\(^{-1}\)) with smaller grains of jarosite/natrojarosite (red in c; 425-435 cm\(^{-1}\)) and various organic carbon-rich spots (blue in c; 1500-1650 cm\(^{-1}\)). Anatase and goethite were also detected in this map region. Pyrite grains are apparent within the gypsum matrix of FF2 (d). A yellow box in d highlights a region where a “goop” of organic material adhered to a gypsum crystal was detected. This material, shown in e and f, revealed two globules of elemental sulfur (red in f; 205-225 cm\(^{-1}\)) with a large clump of organic carbon (blue in f; 1500-1650 cm\(^{-1}\)). The green in f signifies gypsum (fitting intensities from 1000-1020 cm\(^{-1}\)). Sample FF3 showed a greater abundance of red/orange staining from goethite (g). A low-resolution spectral map of the region in g revealed the presence of anatase, quartz, goethite, and gypsum in this region. One region showed a grain of gypsum along with abundant goethite and jarosite as well as organic carbon and anatase in sample FF3 (h).
Figure 4.11: Organic carbon in sample T1
Two regions from sample T1 are shown in reflected light microscopy in a and b; white rectangles in a and b show locations where Raman maps were collected (maps are presented in c and d, respectively). The map in c shows fits for pyrite (red; 375-380 cm$^{-1}$), gypsum (green; 1000-1010 cm$^{-1}$), and the G-band of organic carbon (blue; 1500-1650 cm$^{-1}$). The map in d shows fits for S$^0$ (red; 205-220 cm$^{-1}$), gypsum (green; 1000-1020 cm$^{-1}$), and the G-band of organic carbon (blue; 1500-1650 cm$^{-1}$). Averaged organic carbon spectra from the regions in the white rectangle in c and the white circle in d are plotted in e and f, respectively; results from peak fitting of organic carbon D and G bands are also shown. Raman peaks from gypsum are also indicated (“Gyp”).
ratio is defined as the peak intensity of the D1 band compared to that of the G band (D1/G intensities), while the R2 ratio is defined as the area of the D1 band over the sum of areas of D1, D2, and G bands (D1/(D1+D2+G) areas). These ratios are generally used for analyzing maturity of carbon in higher-temperature regimes. For instance, Beyssac et al. (2002) infer that the R2 ratio is useful for identifying carbon maturity in the ranges of 330-650°C, while below 330°C the R2 ratio should remain fairly constant at 0.7 to 0.8. Table A3.1 shows the D1 and G band locations and the R1 and R2 ratios for several samples from the pyrite alteration features. R1 in all samples averaged 0.7 (ranging from 0.5 to 1.0) while R2 averaged 0.6 (ranging from 0.4 to 0.7). This indicates lower-temperature formation of the organic carbon in these samples, but makes it difficult to further constrain the thermal maturity of these materials.

A number of filamentous materials have also been observed within these materials (specifically, in samples C2, C3, C4, and T2). Several spiral-shaped filaments were detected in sample C2 (Fig. 4.12a-c). These filaments are ~1 µm in width and tens of µm in length. Unfortunately, attempts to collect Raman spectra for these filaments were unsuccessful, as the filaments were so thin that the spectra returned showed only the glass slide in the background. A thicker filamentous structure (~10 µm width) was also detected in C2 and appeared to contain gypsum (see Fig. 4.12d). Thicker filaments (~5-10 µm widths) were also detected in samples C4 and T2 (Fig. 4.12e,f). The filament in sample C4 was highly fluorescent to the laser, but peaks for organic carbon were still discernible. Small spheroids of pyrite were attached to this filamentous structure. The filament in T2 was also fluorescent, but also revealed the presence of organic carbon. This filament appeared to be embedded in materials rich in goethite, quartz, and organic carbon (Fig. A3.18).
Sample C2 contains a number of filamentous structures (a-d). No adequate spectra were produced for the thin spiral filaments in a-c, while the thicker filamentous structure in d appeared to be composed of gypsum. A filamentous structure in sample C4 (e) was highly fluorescent but appears to contain organic carbon while small spheroids attached to it (e.g., yellow arrow in e) are composed of pyrite. The image in f shows the filament in sample T2 marked with the white arrow in Figure 4.5b. This structure was also fluorescent while producing peaks for organic carbon. A Raman map of the region shown in f showed goethite, quartz, and organic carbon through the material as well (Fig. A3.18).
4.3.4. Electron Microscopy

SEM/EDS analyses were used for imaging and elemental analysis on samples C2, C3, and C4. Outside of the expected tabular grains of gypsum, sample C2 revealed a large number of filamentous materials, which appear to be composed of, or coated in, aluminum-rich material (Fig. 4.13). This material also contains oxygen, sulfur, and calcium. This sample also shows many gypsum crystals that are encrusted in materials that were determined to be aluminum and iron rich. Sample C3 materials included an aluminum-rich filament as well. Sample C4 contains abundant pyrite grains from 10s to 100s of microns in size. These pyrite grains in many places appear to be geometrically etched, leaving grooves and polygonal holes (Fig. 4.14). Figure 4.14e shows one grain of iron and sulfur, presumed to be pyrite, with polygonal etchings, with what appear to be two grains of other minerals within a cavity. These other grains contain aluminum, iron, sulfur, calcium, and silicon. Furthermore, Sample C4 also contains filaments and encrusted materials that contain aluminum and iron (not shown).

4.3.5. Scanning Transmission X-ray Microscopy (STXM)

STXM allows for element-specific, nanoscale imaging of x-ray transmissive materials paired with nanoscale x-ray absorption spectroscopy. STXM was used to map the distribution and characterize the speciation of carbon and sulfur in samples due to absorptions at the C K-edge and S L-edge. Samples that were analyzed using STXM include samples S2 and C4 (sidewall and core samples, respectively) as well as sample FF1. STXM data revealed the association of organic carbon with sulfate particles in the materials (Figs. 4.15 & 4.16). Sulfate, matching spectra for gypsum (Jalilehvand, 2006), was identified in micron-sized grains in all three samples; no other form of sulfur was detected in these materials using this sample preparation and analysis approach. Although organic carbon was detected using STXM, an issue with data quality, potentially resulting
Figure 4.13: SEM/EDS of filaments in core sample C2
Several encrusted filamentous structures were detected in sample C2 (a-d). The red inset in d shows a higher magnification image of two filaments. A spectrum was collected at the spot in the yellow square and shows O, Al, S, and Ca (as well as the Au which was used as a coating).
Grains of pyrite with polygonal etchings were observed throughout sample C4 (a-e). EDS spectra were collected from two regions (blue and green rectangles) of the round grain in e (inset spectra).
Sulfate and organic carbon were detected in sample FF1 (a-c). An image collected at 280.0 eV shows a chain of particles (a). A STXM map of this region in b shows sulfur (172 vs. 170 eV) and carbon (288.2 vs. 280.0 eV), colorized as yellow and white, respectively. Spectra from these species revealed organic carbon and gypsum (orange and purple spectra in c, respectively). The carbon spectrum in c revealed peaks for aromatic and/or ketone carbon-oxygen bonds (C-OH and/or C=O; highlighted with a dotted vertical line at 286.3 eV) as well as carboxylic carbon (C=O; highlighted with a solid vertical line at 288.6 eV; Brandes et al., 2004; Chan et al., 2010; Liu et al., 2013). Dips in the carbon spectrum around 284 and 291 eV derive from instrumental issues (see text). The sulfur spectrum in c reveals the presence of gypsum in a & b (a reference spectrum for gypsum is also shown in c; adapted from Jalilehvand, 2006). A STXM image of material in sidewall sample S2 is shown in d (image collected at 160 eV). Particles of sulfates with associated organic carbon rich regions from this sample are shown in the spectral map in e (yellows are sulfur (172 vs. 170 eV); blues are organic carbon (288.6 vs. 280.0 eV)). Sulfur in e was identified to be gypsum, while organic carbon spectral data suffer from instrumental errors (see text).
Two regions of core sample C4 are presented (a,b), showing the colocation of sulfur and organic carbon (identified with sulfur and carbon XANES spectra in c and d, respectively). A STXM image collected at 320.0 eV (a) shows particles identified as gypsum (see representative yellow spectrum in c, collected from the location in a of the yellow circle). The blue circle in a shows the location of collection of the solid blue carbon spectrum at the top of d (the dashed blue spectrum represents organic carbon from smaller spots distributed around the largest gypsum-rich grain). A STXM map of sulfur and carbon is presented in b, where green represents the difference in sulfur absorptions between 170 and 172 eV, and magenta represents the difference in carbon absorptions between 280 and 288.2 eV. The green spectrum in c represents gypsum detected throughout the green regions in b. The white circle in b highlights the location of collection of the solid magenta carbon XANES spectrum shown in the middle region of d (the dashed magenta spectrum represents organic carbon from smaller spots distributed throughout the material in b). A reference spectrum for gypsum is shown in c (data adapted from Jalilehvand, 2006). Reference spectra for multiple organic carbon compounds are also shown in d. These reference data are reported by Chan et al. (2010) and are as follows: a protein (bovine serum albumin; BSA), alginate (an acidic polysaccharide), agarose (a neutral polysaccharide), a sample of DNA, and a lipid (1,2-dipalmitoyl-sn-glycero-3-phosphoethanolamine). Vertical lines, included to highlight the carbon functional groups in the sample spectra, represent the following carbon functional groups: unsaturated or aromatic carbon (1s→π* C=C; solid line at 285.2 eV and dotted line at 285.4 eV); aliphatic carbon, aromatic carbonyl, ketones, and/or phenols (1s→σ; dashed line at 287.6 eV); and carboxyl (1s→π* C=O; double lines; 288.6 eV; see references in the text).
from an issue with the beamline optics, has made it difficult to infer the speciation of the organic carbon in most materials. However, interpretable data from one region in sample FF1 (Fig. 4.15a-c) showed defined carbon XANES peaks for carbon and oxygen bonds in aromatic and/or ketone functional groups as well as carboxylic groups (Brandes et al., 2004; Chan et al., 2010; Liu et al., 2013). In addition, organic carbon detected in two regions within sample C4 revealed the presence of two potentially different forms of carbon in this sample (Fig. 4.16). One region (shown in the blue circle in Fig. 4.16a and the blue spectra in Fig. 4.16d) has a strong carbon XANES peak indicative of carboxyl functional groups \((1s\rightarrow\pi^* C=O)\). The associated dashed blue spectrum in Figure 4.16d (averaged over multiple small spots around the edges of a large gypsum grain in Fig. 4.16a) may reveal further carbon XANES peaks, however these potential peaks may also be errors in data and are not interpreted further. Another region (shown in magenta in Fig. 4.16b and the magenta spectra in Fig. 4.16d) reveals the presence of unsaturated or aromatic carbon \((1s\rightarrow\pi^* C=C)\) as well as aliphatic and/or aromatic carbonyl groups, ketones, and/or phenols \((1s\rightarrow\sigma; \text{e.g., Brandes et al., 2004; Chan et al., 2010; Liu et al., 2013})\). Figure 4.16d includes several spectra for organic carbon compounds, adapted from Chan et al. (2010). These spectra include a protein (bovine serum albumin; BSA), alginate (an acidic polysaccharide), agarose (a neutral polysaccharide), a sample of DNA, and a lipid \((1,2-dipalmitoyl-sn-glycero-3-phosphoethanolamine)\), and are used for comparisons with carbon functional groups from the material analyzed in sample C4.

4.4. Discussion

4.4.1. Mineralized Alteration Features at Borup Fiord Pass

Using XRD and Raman microspectroscopy, we detected pyrite, \(S^0\), gypsum, and organic carbon in nearly all of the samples from the trench (Table 4.1). Also, while the red staining of the outer region of this feature is visually apparent and goethite is detected in sample T2 through XRD, iron (oxyhydr)oxides (primarily goethite and hematite) were detected through Raman
microspectroscopy within the interior of the trench and in the permafrost (samples S2 and C1-C3). Although jarosite was detected at low concentration in the outer region of the surface of the trench-sampled feature by Grasby et al. (2012), we did not detect jarosite in any of the samples from the trench, even at the surface. Also, while the transect of samples from Grasby et al. (2012) did not contain detectable pyrite, quartz, or anatase, these minerals are detected in several samples throughout the trench (Table 4.1).

The pyrite alteration feature that lies close to the strike-slip fault crossing the valley, which has been called “Fault Feature” in this work, has not been previously reported from this site. The Fault Feature is on the edge of the topographically high region and appears to have a definitively similar mineralogy to the other red-stained structures (Table 4.1; Fig. A3.1). The Fault Feature has developed a similar zonation with a rim of staining from iron (oxyhydr)oxides, but does not bear the familiar gypsum-rich white core of the two larger alteration features. Instead, the Fault Feature appears to have a central region of red-staining as well as pebbles and cobbles of carbonate rock. However, there are some noticeable dissimilarities in the surface mineralogy of the Fault Feature. As well as pyrite and gypsum, the Fault Feature also contains abundant jarosite, detected through both XRD and Raman microspectroscopy (Table 4.1; Figs. 4.10 & A3.13-15). Also, quartz and goethite were detected in each Fault Feature sample, while S\textsuperscript{0} was only detected in FF2 (through Raman spectroscopy; observed to be scarce in sample material). The detections of anatase (TiO\textsubscript{2}) and quartz (SiO\textsubscript{2}) in these features in intriguing. Anatase is commonly found in hydrothermal and metamorphic systems (Banfield et al., 1993; Tilley and Higgleton, 2005). Also, titanium (in anatase) is usually considered an immobile reference element in alteration processes, though solubility is strongest at very low and very high pH (much like aluminum; Tilley and Higgleton, 2005). Indeed, titanium mobility at the meter-scale has only been documented in hydrothermal and metamorphic systems (Tilley and Higgleton, 2005). TiO\textsubscript{2} minerals (e.g., anatase, rutile, brookite) often occur as fine crystals in other minerals and can be difficult to study through XRD (Banfield et al., 1993),
however the implementation of Raman microspectroscopy in our study allowed for the microscale identification of anatase in these samples.

While pyrite was not detected in previous work on surface materials (Grasby et al., 2012), we’ve demonstrated the presence of pyrite in surface and near-surface samples (T1, S1-2, and FF1-3) within the active zone. Furthermore, pyrite was detected in all four of the core samples from the permafrost region. In addition, when extracting grains for submission for sulfur isotopes, it was observed that opaque, metallic grains >425 μm in diameter made up ~45% of sample C1 (these grains were later confirmed by EA-IRMS to bear 54% sulfur, roughly the expected concentration of sulfur in pyrite). This suggests that pyrite may be abundant in the central regions of these features.

**4.4.2. Weathering of Pyrite: Gossans in Permafrost**

Given the extent of red staining from iron (oxyhydr)oxides in the alteration features at Borup Fiord Pass, the low relative acidity of the materials within the features (Fig. 4.3), and the red staining of rocks and pyrite veining in the surrounding region, it is here, again, inferred that pyritic ore has been emplaced beneath the surface of this region and subsequently weathered. The oxidation of pyrite by oxygen and ferric iron (often driven and accelerated by biology) produces ferric iron (oxyhydr)oxides, sulfates, and acidity.

The nearly identical δ34S values for sulfides and sulfates in the alteration features suggests that the sulfates (primarily in gypsum) formed from the oxidation of the sulfide, a process that does not impart a significant fractionation of sulfur isotopes (this is also supported through oxygen isotope systematics; see Grasby et al., 2012). The production of sulfates from the oxidation of pyrite also releases acidity, as can be observed in the 1:1 water:sample pH measurements (Table 4.1 and Fig. 4.3). Also, the discovery through SEM/EDS of filamentous materials that appear enriched in aluminum (Figs. 4.13) reveals the importance of acidity in alteration feature formation. The fact that there are aluminum-rich materials suggests that aluminum had at one time been mobilized in
this system, and aluminum is only stable in solution at significant concentrations when pH is very low (or, to a lesser degree, very high; e.g., Hem, 1985). Furthermore, the mineralogical suite we detect in the alteration feature materials, with an abundance of iron (oxyhydr)oxides in the presence of pyrite and gypsum (e.g., Table 4.1), are reminiscent of acid mine drainage systems (e.g., Mcguire et al., 1999; Fernández-Remolar et al., 2005; Taylor and Konhauser, 2011). The detections of minerals common in such systems of pyrite oxidation (e.g. iron (oxyhydr)oxides, goethite, quartz) suggest to us that the alteration features represent emplacements of pyrite that have since been altered to form their current oxidized iron and sulfur mineralogical structure. Also, lowered pH does not increase silica solubility, explaining the abundances of quartz in gossans (Taylor and Eggleton, 2001), where silicate minerals are often leached in the acidic system leaving behind quartz. This may explain the abundance of quartz detected in these features.

Gossan sites on Victoria Island (Northwest Territories, Canada) present materials indicative of pyrite alteration including gypsum, goethite, jarosite, and hematite, all in a permafrost-rich environment (Percival and Williamson, 2016). In particular, the site called Gossan Hill is topographically high compared to the surrounding region, possibly due to the presence of pyritic sand and erosion resistant iron oxides in the soil (Peterson et al., 2014), and is similar to the topographically high region at Borup Fiord Pass that hosts the alteration features in this study (Figs. 4.1, A3.1, A3.3). Gossan Hill also bears concentric gossan features, with interior regions dominated by gypsum and quartz, a yellow-stained border with gypsum, quartz, and jarosite, and then a brown colored rim with quartz and ferric (oxy)hydroxides. Below the surface, the central regions also contain quartz and pyrite along with S
. Also in common with the alteration feature region at Borup Fiord Pass, Gossan Hill is underlain by carbonate with inter-bedding of sulfate evaporites (Peterson et al., 2014).

Peterson et al. (2014) hypothesized sulfide ore emplacement at Gossan Hill was driven by hydrothermal fluid migration. Intriguingly, the presence of this gossanous system over sulfate-rich
evaporites in a similar environment to what is found at Borup Fiord Pass may be useful in determining the source of pyrite in such gossanous systems. However, Peterson et al. (2014) indicate that no other features of hydrothermal systems are locally detected at the Gossan Hill site, and they also did not report sulfur isotope values for their materials compared to the sulfate evaporites of the underlying Kilian Formation (which may reveal potential BSR as a sulfide source as compared to thermal reduction of sulfate).

Due to the presence of permafrost at Borup Fiord Pass, it is likely that little oxidation of the pyrite can occur at depth in this gossanous system. In terrestrial gossans at lower latitudes, iron oxides are often leached downward through the gossan from infiltration by meteoric waters (e.g., Taylor and Eggleton, 2001; Fig. 4.17a). However, a pyrite vein in permafrost will not see infiltration of fluids and rather will likely leach horizontally along the active zone (Fig. 4.17b). This may be the reason for the white central regions rich in gypsum in the two largest alteration features, as well as for the anatase and quartz that were detected within these materials.

The question arises as to what fluid source allows for pyrite alteration in these features. Even though Borup Fiord Pass receives a minor amount of precipitation annually, the melt and refreezing of snow and ice likely imparts a significant volume of water into the alteration features and surrounding region. For instance, during the process of digging the trench and drilling cores for this study, we encountered several cavities within the features. Deployment of a camera into some of these cavities revealed significant amounts of water ice around the rims of the cavities. Furthermore, summertime temperatures at the site of the alteration features can be quite mild, allowing for the melt of glacial ice and snow locally and providing a source of fluid for pyrite alteration. This was observed by glacial melt streams, lakes, and water-logged sediments throughout the region of the alteration features.
Figure 4.17. The structure of gossans

Terrestrial gossans often present as region of sulfide leaching through the influx of meteoric waters, leaving behind red-staining from ion oxides and sometimes building a leach cap of sulfates and quartz near the surface (a). However, in a permafrost setting, where the influx of meteoric water is hindered, the leaching zone may develop horizontally (b).
4.4.3. Source of the Pyrite in Features and the Relationship to the Modern Sulfur Spring System

The conspicuous red-stained features at Borup Fiord Pass were previously described and discussed by Grasby et al. (2003, 2012) and Scheidegger et al. (2012). These features have been implicated as remnants of springs similar to those that currently form sulfur-rich deposits and spring-derived ices (aufeis) at the toe of the glacier to the north of the features (Grasby et al., 2003; 2012; Lau et al., 2017). The source of sulfur for this modern spring system has been proposed to be biological sulfate reduction (BSR) of subsurface anhydrite-bearing evaporite formations, as evidenced through sulfur isotope data (Grasby et al., 2003; see Fig. 4.4). Grasby et al. (2012) proposed a model of sulfuric acid speleogenesis (SAS) for the formation of these structures from the spring system that forms these modern-day sulfide springs. In this model, spring conduits carrying sulfide-rich fluid from the subsurface, as in the modern spring system, formed beneath the local coalescence glacier when it was further south in extent. The re-oxidation of reduced sulfur species in such springs, forming sulfates as well as acidity, was then hypothesized to lead to the dissolution of local carbonates and replacement with sulfate minerals in the pipes carrying the spring fluids. After glacial retreat, permafrost advance would eventually cut off such spring conduits. The model of Grasby et al. (2012) then suggests that the mineral suite of the spring conduits would be “trapped” by being frozen in-place. These authors posited that the surface expression of the features, with their friable gypsum-rich materials, at the same topographic relief as the immediately surrounding native valley rock suggests that the features formed (at least partly) after the recession of ice from this region. This led for a constraint on the age of the surface formation of the features to sometime within the last ~7,500 years (when glaciers in this region began to significantly retreat).

Our findings here provoke a reinterpretation of the nature of these iron- and sulfur-rich mineralized features. For instance, while Grasby et al. (2012) did not detect pyrite in the surface materials used in their study, we find abundant pyrite throughout the features, especially within
the core material closest to the center of the trench in one feature (sample C1). We propose here that a mechanism driving pyrite emplacement formed veins of pyrite in the near-surface, and the emplaced pyrite was subsequently oxidatively weathered releasing acidity and forming the current suite of oxidized iron and sulfur minerals. Furthermore, the extensive red staining of the region and smaller pyrite veining in nearby carbonate rocks suggests that pyrite emplacement in the region was more extensive than just in the alteration features alone. Three potential mechanisms that may have led to the emplacement of the pyrite in this region include: 1) magmatic sulfide ore derived directly from regional Mesozoic igneous intrusions; 2) pyrite derived from a hydrothermal system in conjunction with such igneous intrusions, with sulfur sourced from contact of a sill or dyke with a local, anhydrite-bearing evaporite unit; and 3) the low-temperature emplacement of sedimentary pyrite from sulfide-rich fluids titrating ferrous iron from subsurface sources (where sulfide is derived from BSR of evaporite anhydrite).

4.4.3.1. High-Temperature Pyrite Emplacement

Regional igneous intrusions are potential sources of thermal energy as well as iron and sulfur for the subsurface system that formed the pyrite in the structures under consideration (see Fig. 4.1c). These intrusions are part of the High Arctic Large Igneous Province (HALIP), a predominantly intrusive, Cretaceous to Paleogene magmatic emplacement spanning much of the circum-Arctic region (e.g., Evenchick et al., 2015; Deegan et al., 2016; Saumur et al., 2016). Sills and dykes from these intrusions can be observed in the valley of Borup Fiord Pass (Fig. A3.3a; Grasby et al., 2003; Hill, 2014). Although it is not known if an intrusion directly underlies the region of the pyrite alteration features (and at what depth such an intrusion may be found), such magmatism may have been a source of thermal energy driving high-temperature emplacement of sulfide in veins around and within the local strike-slip fault in the valley (dashed line in Fig. 4.1c).
Magmatic intrusions can source sulfide ore deposition through concentration of sulfur within the melt or through interaction with crustal sources of sulfur, though the latter is predominant (Barnes et al., 2017). In the region of the Sverdrup Basin, evaporite deposits are a likely source of crustal sulfur for such magmatic sulfide mineral formations. Crustal sulfur can be incorporated into intrusive magmas from surrounding sulfides (in pyrite and pyrrhotite) and also evaporites containing sulfates (Robertson et al., 2015). Another potential source of the pyrite within the red-stained features could have been hydrothermal deposition, likely related to the intrusive magmatism discussed above. While high temperatures of metal sulfide formation in magmatic sulfides leads primarily to pyrrhotite and pentlandite, hydrothermal sulfide deposits most commonly consist of pyrite (Barnes et al., 2017; Fontboté et al., 2017). The sulfur for such hydrothermal deposits could come from reduced magmatic sources but also from the abundant sulfate available in local evaporite deposits. The latter requires that sulfate be reduced to sulfide. In most hydrothermal temperature regimes (>100°C), this is likely to proceed via thermochemical sulfate reduction (TSR), a process that does not impart a significant fractionation of sulfur isotopes (Machel, 2001). If this were the case, then it would be expected that the sulfur isotopes of known evaporite units underlying Borup Fiord Pass would match closely to those of the pyrite within the features. There are two known anhydrite-rich evaporite units regionally, the Otto Fiord and Mount Bayley Formations.

The Otto Fiord Formation is a Carboniferous evaporite formation composed primarily of anhydrite (CaSO₄) and halite, with variable amounts of gypsum, limestone, and shale (Davies & Nassichuk, 1975; Grasby et al., 2003). This formation outcrops ~20 km to the north of Borup Fiord Pass (Davies & Nassichuk, 1975; Grasby et al., 2003). Stratigraphic constraints on the subsurface depth of the Otto Fiord Formation at Borup Fiord Pass range from hundreds of meters below the valley floor (Hill, 2014) to as much as 1.5-2 km in depth (Gleeson et al., 2010; Grasby et al., 2003). Meanwhile, the Mount Bayley Formation, which outcrops 19 km to the east of Borup Fiord Pass, is a
Lower Permian evaporite unit of anhydrite, shale, and both fossiliferous and non-fossiliferous carbonates (Wallace et al., 1994). If the Mount Bayley Formation underlies Borup Fiord Pass then it may be within 200 m of the valley floor, however, it has been suggested that the formation appears to “pinch out” stratigraphically east of the valley (Gleeson et al., 2010; 2011). The Otto Fiord Formation has been shown to have a gradient of $\delta^{34}$S values ranging upward through the bed from 16 to 12‰ (Davies and Nassichuk, 1975), with an average $\delta^{34}$S of 14.6‰ (Grasby et al., 2003; these authors also reported a range of 12.2 - 17.0‰ for Otto Fiord anhydrite $\delta^{34}$S measurements; Fig. 4.4). Meanwhile, sulfur isotopes in the Mount Bayley Formation have $\delta^{34}$S values from 12.0 to 14.3‰, with an average $\delta^{34}$S of 13.1‰ (Wallace et al., 1994; Fig. 4.4). The lowest $\delta^{34}$S values from these formations (12.0‰ in both cases) is higher than those measured for pyrite in the features (6.5‰ in C1, 8.5‰ in C2, and 11.7‰ in FF1; Fig. 4.4).

4.4.3.2. Low-Temperature Pyrite Emplacement

As the Otto Fiord and Mount Bayley Formations are the only known sulfur-rich geological units locally, these evaporite formations have previously been implicated as the sources of sulfur for the modern-day, low-temperature spring system at Borup Fiord Pass (Grasby et al., 2003). However, both evaporite formations are only known to bear oxidized sulfur in anhydrite (and some gypsum), driving the need for sulfate reduction to be the source of the high levels of sulfide observed in the modern-day springs. TSR and BSR occur in much different thermal regimes. TSR often requires minimum temperatures from 100-140°C (although in some systems TSR requirements of 160-180°C have been observed; Machel, 2001). As described by Grasby et al. (2003), permafrost from an oil well 43 km to the south of Borup Fiord Pass has been measured at 540 m (suggesting potentially even deeper permafrost at Borup), and, with the local geothermal gradient of 22°C km$^{-1}$ beneath the base of the glacier/permafrost (Grasby et al., 2012), this suggests that TSR could require sulfate-enriched fluids from the dissolution of the Otto Fiord or Mount
Bayley Formations to travel as much as 5 to 6 km into the subsurface. Lithostatic pressure at this depth precludes fluid flow, and, thus, this physically precludes TSR as a likely source of reduced sulfur from the Otto Fiord and Mount Bayley Formations; this leaves BSR as the likely pathway for reduced sulfur in the modern sulfur springs as no known source of high temperatures exists in the modern system (Grasby et al., 2003).

Sulfate reducing bacteria tend to pair sulfate reduction with either organic carbon or hydrogen oxidation; either way, the process of BSR is known to produce fractionations of sulfur isotopes, where biological reactions favor use of $^{32}$S over $^{34}$S (e.g., Thode, 1991). BSR of Otto Fiord or Mount Bayley Formations is thus expected to result in sulfide that is depleted in $^{34}$S relative to the source anhydrite. Sulfur isotopes in samples of the spring-derived aufeis at the toe of the glacier in 2014 reveal a depletion in $^{34}$S for sulfides relative to that of sulfates. The average $\delta^{34}$S for sulfides in these samples was 12.1‰ while average $\delta^{34}$S for sulfates was 28.6‰ (Fig. 4.4). These findings are similar to previously reported $\delta^{34}$S values for deposits of $S_0$ and gypsum in the active spring system (Grasby et al., 2003; Fig. 4.4). The $\delta^{34}$S of these reduced sulfur species in the modern spring system are also lower than the average $\delta^{34}$S values reported for the Otto Fiord and Mount Bayley Formations (Fig. 4.4). These data support a model of BSR from subsurface anhydrite deposits driving the $^{34}$S-depleted sulfide and $S_0$ in the modern-day spring formations relative to the average values measured for the geological formations (see Grasby et al., 2003). Furthermore, the greatly $^{34}$S-enriched population of dissolved sulfates in the aufeis samples relative to the anhydrite deposits also fits with some degree of closed-system Rayleigh-type fractionation from BSR (whereby the discrimination toward lighter isotopes in the biological reduction of sulfate develops $^{34}$S-depleted sulfide and $^{34}$S-enriched sulfate products relative to the reactant sulfate; e.g., Canfield, 2001; Detmers et al., 2001; Grasby et al., 2003; Thode, 1991).

Should the pyrite (and other sulfur species) in these features be derived from low-temperature BSR of the evaporite units, it is necessary that reduced sulfur in these structures be
depleted in $^{34}$S relative to the Otto Fiord and/or Mount Bayley Formation anhydrite. The $\delta^{34}$S values for the materials in the alteration features are similar to those for reduced sulfur species in the modern spring system and are less than the average $\delta^{34}$S values of the evaporites (Fig. 4.4). The average $\delta^{34}$S for sulfides and sulfates (from pyrite and gypsum, respectively) in the core materials are 7.5 and 7.9‰, respectively. Meanwhile, $\delta^{34}$S for pyrite and gypsum in Fault Feature sample FF1 are 11.7 and 12.7‰, respectively. These values also fall within the range of $\delta^{34}$S previously reported for $S^0$ and gypsum in the alteration feature surface materials (7.4-14.2‰ and 7.3-13.0‰, respectively; Grasby et al., 2012; Fig. 4.4). If local anhydrite-bearing evaporite units are the source of the sulfur in the features, then these isotope data support the interpretation that the pyrite formed at low-temperature subsequent to subsurface BSR. However, this necessitates a geological source of iron and a mechanism for iron titration forming pyrite at low-temperature. The local Cretaceous igneous intrusions and the Permian-aged Esayoo Bay lavas at Borup Fiord Pass (Fig. 4.1c) may provide a source of ferrous iron for the formation of pyrite in the alteration features.

4.4.4. The Role of Biology in the Formation of the Alteration Features

There are two potential roles for biology in the cycling of sulfur and the formation of materials in the alteration feature region at Borup Fiord Pass: the production of sulfide in the subsurface through BSR and the alteration of the pyrite at the surface to form the gossanous suite of minerals. As previously discussed, BSR is presented as a potential mechanism for the production of the sulfide in the spring fluids in the modern spring system. Although we cannot fully infer BSR as the source of sulfide for the pyrite in the alteration features based upon our current data, sulfur isotope data do appear to potentially support low-temperature formation of biologically-derived sulfide. It’s currently unknown which electron donors may be present for BSR in the subsurface, however local intervening shale units in the valley have up to 4% organic carbon (Grasby et al.,
2003), and there may also be other sources of organic carbon for sulfate reducing microbes to act upon.

It is currently unknown what fraction of the organic carbon inventory in these features may derive exogenously (e.g., from BSR or other organic carbon sources in the subsurface) and how much, if any, of the organic carbon may have formed in situ through biological processes involved in the alteration of the pyrite. Beyond potential subsurface sources, organic carbon may be present in the surface materials from the interactions of tundra plants and animals (muskox and Arctic hare were observed at the site in 2014) and soil microbial processes of the valley. Also, pre-glacial soils may have imparted a significant fraction of organic matter regionally (for instance, glacial till at the toe of the glacier in 2014 had 2.5 wt.% TOC; unpublished data). In the alteration features, sample T2 had the highest TOC at 0.37%, but also is close to nearby tundra plants and soil. However, we cannot infer how much of that carbon may come from surface sources and how much is primary. Given the pyrite in the features, we hypothesize that much of the carbon either comes from subsurface sources or was formed in situ. Although we cannot preclude exogenous sources of organic carbon in the alteration features, Raman microspectroscopy reveals an apparent association of the organic carbon with pyrite, S⁰, and iron (oxyhydr)oxides in the materials (though conspicuous dark grains of OC either on or in grains of gypsum are also detected). The Fault Feature material (sample FF2) also has an organic carbon-rich region of ~200 µm², identified through Raman microspectroscopy, where the organic carbon is associated with two globular regions of elemental sulfur (Figs. 4.10d-f, A3.30). These elemental sulfur regions are 2 and 4 µm in diameter and, together with the organic carbon glom, are found in a region of tabular gypsum crystals and large grains of pyrite. These co-associations of organic carbon and S⁰ in a region of pyrite and gypsum may indicate biological activity in the formation of the elemental sulfur regions.

Our STXM data also show associations of organic carbon with sulfates in these materials (Figs. 4.15 & 4.16). For instance, a carbon spectrum derived from one region in sample FF1 showed
the presence of carbon and oxygen bonds in aromatic and/or ketone functional groups as well as carboxylic groups (Brandes et al., 2004; Chan et al., 2010; Liu et al., 2013). These C-OH and C=O bonds are found in many forms of organic carbon, but may be indicative of in situ biological activity. For instance, these carbon functional groups are common in polysaccharides, aromatic proteins, and lipids (e.g., Chan et al., 2010; Liu et al., 2013). Organic carbon functional groups were also identified through STXM within the core material of sample C4 (Fig. 4.16). We show that two regions of this sample bear organic carbon and that two different carbon spectra can be derived from these materials. Of these two spectral forms, one shows carbon XANES peaks indicative of unsaturated or aromatic carbon as well as aliphatic and/or aromatic carbonyl groups, ketones, and/or phenols (see magenta carbon XANES spectra in Fig. 4.16d). These carbon functional groups can also be found in proteins, DNA, and lipids. The other carbon spectral form in sample C4 reveals the presence of carboxyl functional groups (blue spectra in Fig. 4.16d). As we show in Figure 4.16d, these carbon functional groups are also found in some lipids and polysaccharides (e.g., Chan et al., 2010; Liu et al., 2013).

Although we cannot here determine the source(s) of organic carbon that we’ve identified in the alteration feature materials, some potential indicators for biological activity in the process(es) of pyrite alteration are demonstrated in this work. For instance, pyrite grains within the alteration features are geometrically etched (Fig. 4.14), similar to etchings which have been identified in microbial leaching patterns in pyrite (e.g., Edwards et al., 2000; Rojas-Chapana and Tributsch, 2004). Also, the abundance and variety of filamentous structure detected in the alteration feature materials (Figs. 4.12 & 4.13) may indicate potential biological activity. For instance, the aluminum-rich filaments in the alteration features (Fig. 4.13) resemble similar structures that have been implicated as forming through microbial processes from a variety of low-temperature, subsurface sites globally (e.g., Hofmann and Farmer, 2000). If such filaments formed through biological processes, they may then have later served as sites for precipitation of aluminum oxides from
aluminum which had been mobilized in the low-pH system caused by the oxidation and alteration of the pyrite. However, recent work by Cosmidis and Templeton (2016) shows that systems rich in organic carbon and sulfide can abiotically form carbon and sulfur rich microstructures, reminiscent of filaments previously identified and implicated as forming from biological processes in the Borup Fiord Pass sulfur spring system (Gleeson et al., 2012). The filaments identified in the alteration feature materials share some sizes and morphologies with these abiotic filaments presented by Cosmidis and Templeton (2016), though this does not preclude biological activity in formation of filamentous materials within the alteration features.

These detections of organic carbon functional groups are not themselves positive identification of active microbial processes occurring in the alteration feature materials, but they do warrant further consideration of the role of biology in surface processes acting upon the pyrite. These potential signs of microbial processing of the materials in the features are intriguing. Fortunately, our attempts to extract DNA from these materials has not yet proven successful. In addition, during the course of field work, the materials that were collected from the alteration features were not collected in a manner that would allow for a well-resolved extraction and characterization of the organic carbon through a method such as gas chromatography mass spectrometry (GCMS). Future work on these features should include sample collection and analyses through such a method, to allow for characterization of the organic carbon molecules present and to potentially target lipids that may reveal the activity of iron- and/or sulfur-oxidizing microbes in the alteration features.

4.4.5. Mineralized Paleohydrological Features on Mars: The Alteration Features as Analogs for Potential Pyrite Alteration Systems on Mars

High concentrations of iron and sulfur in the Martian regolith were first detected by the Viking XRF instrument (Toulmin, III et al., 1977) and have since been confirmed with APXS
instruments onboard multiple Mars rovers (e.g., Gellert and Clark, 2015). The potential for the emplacement of iron sulfide ores in the Martian subsurface and subsequent oxidative leaching via gossanous systems has been considered by Burns (1987) and Burns and Fisher (1990a,b). They have proposed that komatiitic basalts on Mars likely host sulfide deposits rich in pyrrhotite and pentlandite (similar to known Earth-based analogs). Also, sulfides formed from sulfate reduction through thermochemical and potentially biological processes may also have happened on Mars. Oxidative weathering of Martian sulfide ores in near-surface environments would follow pathways similar to those for known gossanous systems on Earth, and may have provided habitable systems for life. Sulfide minerals have been identified from two specific locations on Mars through surface rover instrumentation (Morris et al., 2008; Vaniman et al., 2014). There are also abundant oxidized iron and sulfur minerals identified through remote sensing and from surface observations (e.g., Ehlmann and Edwards, 2014), though it’s unknown yet if these may indicate pyrite alteration.

The presence of sulfates associated with hematite spherules at Meridiani Planum, as detected by the Opportunity rover, have been implicated as having formed through the emplacement of sulfide ore followed by later oxidative leaching, creating the jarosite-goethite-gypsum assemblage observed (Zolotov and Shock, 2005; though other interpretations also exist, c.f. Squyres et al., 2004; McCollom and Hynek, 2005). The emplacement of parent pyrite in such a system was hypothesized by Zolotov and Shock (2005) to have formed through hydrothermal input of sulfide, however it is also possible that low-temperature pyrite emplacements exist on Mars. Although the preservation potential for organic materials in acidic iron-rich systems on Mars may be limited (e.g., Sumner, 2004), the potential for the prevalence of such systems on Mars and for their forming a habitable refuge for life make them a key target for Mars exploration (Hays et al., 2017). Meridiani Planum and other sulfur- and iron-rich regions of Mars should be further explored with future robotic instrumentation and human missions to the Red Planet. For instance, relevant to our work here, the upcoming ExoMars and Mars 2020 missions will both use Raman
spectrometers to probe Martian materials for mineralogy and organics (Mustard et al., 2013; Vago et al., 2016; Rull et al., 2017). Raman spectra collected from the pyrite alteration features at Borup Fiord Pass may serve as references for iron- and sulfur-rich mineral assemblages and potential associated organic material if detected on Mars with these upcoming missions. Although a Martian gossan has not yet been detected, it is quite possible that mineral assemblages that are diagnostic of pyrite alteration will be detected in the future.

4.5. Conclusion

We show that pyrite is abundant in the alteration features from Borup Fiord Pass, especially within cores taken from below the permafrost. Although isotopic data may suggest that the sulfide in the pyrite could have come from BSR of subsurface anhydrite, we also present two other potential mechanisms for the emplacement of the pyrite in the system, specifically magmatic pyrite and hydrothermal pyrite related to the intrusion of Mesozoic dykes and sills regionally (part of the High Arctic Large Igneous Province; HALIP). Mineralogical analyses reveal pyrite, S\textsuperscript{0}, and gypsum co-localized within these features. Also, we find a mineralogical suite including iron (oxyhydr)oxides indicative of pyrite alteration. Abundant red-staining and pyrite veining in materials within the alteration feature region also suggest large-scale pyrite alteration. As demonstrated here, the oxidative weathering of pyrite (either abiotic or biologically driven) in these features form gossanous structures. The erosion resistant nature of iron oxide minerals may contribute to the topographically high nature of the alteration feature region, similar to that seen for Gossan Hill on Victoria Island (Peterson et al., 2014). We report that organic carbon in abundant in these materials, as are geometrically etched pyrite grains and aluminum-encrusted filamentous materials. Such features serve as easily accessible windows into the subsurface, where practicality can often make sample and data collection difficult. To go further in such considerations, we must gain a better understanding of how these features were formed and what information they
preserve with regard to subsurface processes. The emplacement of sulfidic ore and subsequent leaching to form an alteration mineralogy (potentially through biological action) presents a unique target for our future geological and astrobiological explorations of Earth and Mars. Our future exploration of the Red Planet may thus target gossanous systems for the ability to preserve large-scale sulfide mineral emplacements as well as for their potential in preserving signatures of biological processes that occur during the oxidative alteration of such emplaced pyrite, forming alteration mineral assemblages that are rich in sulfur and iron and preserving indications of past processes.

4.6. Acknowledgements

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CHAPTER 5:

FUTURE WORK: UNRAVELING THE MYSTERIES OF BORUP FIORD PASS

5.1. Overview

This dissertation builds upon our previous knowledge of the Borup Fiord Pass sulfur spring system and pyrite alteration features. However, there is much that remains to be explored with regard to this dynamic, sulfur-dominated, low-temperature system. Some of these explorations require further field-implemented measurements, such as deployment of specific instrumentation to study sulfur springs, aufeis, and mineral deposits in situ. Meanwhile, other future work should include lab-based studies of the sulfur deposits, ices, melt pool minerals, organic carbon, and microbial communities. Furthermore, the pyrite alteration features remain as an intriguing target for better understanding the subsurface hydrology, pyrite mineralization, and pyrite weathering in permafrost. This chapter serves to guide future researchers working on the sulfur spring system and the nearby pyrite alteration region at Borup Fiord Pass in determining some of the remaining questions and targets for future endeavors.

Beginning with field work, a more thorough collection of in-field data for the springs and aufeis should include measurements of temperature, pH, redox potential, oxygen saturation, conductivity, and alkalinity across various materials and distances from the site of spring emergence. This will allow for better physical constraints to be placed on the potential geochemical reactions and mineralogy of samples. Also, in-field measurements of several dissolved chemical species in the fluids and ices is warranted. These species include sulfide, nitrite, nitrate, ammonium, ferrous and total iron, and total dissolved solids (TDS). Some of these species are chemically reactive and should be measured in-field (such as sulfide and ammonium) while others will help guide field researchers to finding the best samples for further in-lab analyses. Along the same lines, in-field utilization of portable instrumentation is highly valuable in guiding sample collection and in providing a thorough analysis of the field site. This is especially important for a site like Borup
Fiord Pass, where the springs (when present), aufeis, and melt pools are highly dynamic and present variations in chemistry over time (as was determined in this dissertation for melt pool samples). VNIR had previously been taken into the field and used for comparisons of surface materials (including S⁰, gypsum, and bassanite) to hyperspectral satellite data (Gleeson et al., 2010). VNIR is a useful tool for exploring surface materials, especially since VNIR is used for spacecraft based missions, allowing Borup to serve as a more useful analog environment. Another technique that would be highly useful for in-field analyses is Raman spectroscopy. Raman microspectroscopy has been used extensively for the work of this dissertation and is becoming a more widespread method in geochemical sciences. Also, Raman spectrosopes are being developed for upcoming missions to Mars and may be used for a Europa lander in the future (e.g., Beegle et al., 2014; Pappalardo et al., 2013), again allowing for comparisons of field data from Borup to other planetary environments. Field portable Raman instruments are becoming cheaper and more easily deployed (for instance, one engineering team in the undergraduate design competition The University Rover Challenge, for which I have been the Director of Logistics, developed and implemented their own in-field Raman spectroscope for analysis of materials in a desert environment). Bringing together this greater level of field characterization and in-field measurement will improve the results from future field seasons to Borup Fiord Pass. For instance, using field deployed Raman spectroscopy to prove the sulfur-rich materials for the presence of organic carbon and, potentially, for beta-cyclooctasulfur (see Chapter 3) may allow us to further unravel the potential for in situ microbial activity to be involved in the formation of rare allotropes of sulfur (or to determine that the microbes in the system truly do not have any relationship to these rare mineral occurrences). The following sections address some of these potential future endeavors, highlighting where data was lacking from the 2014 field campaign, but also highlighting some as-of-yet unexplored considerations for Borup Fiord Pass.
5.2. Aqueous Chemistry and Gases

During the 2014 field expedition, we attempted to use microsensors for measuring dissolved oxygen, pH, dissolved sulfide, and redox potential in the melt pool fluids. However, issues with sensor calibration hindered these measurements. Such measurements are crucial to a better understanding of the thermodynamic constraints on mineral formation as well as on microbial metabolism within melt pools fluids and sulfur deposits. If I were given an opportunity to return to the field, one key point of interest would be preliminary testing of microsensors in fluids with similar chemistry to those known for the springs and ices to ensure that the sensors could be properly utilized in the field. Also, the microsensors we took along were suited to measurements of microbial mats and soft sediments. The ices were dangerous for the sensors, hindering some potential probing of cryoconite that could have been important. Future in-field deployment of chemical sensors could be better implemented with a suite of sensors that can probe soft sediments (i.e. thick sulfur deposits) but also ices and mineral deposits within cryoconite holes. Also, fluids that couldn’t be tested at the glacial site should then have been removed and tested back at the field camp, to determine if the low temperatures and high sulfide levels hindered measurement at the glacier. This was not done previously, but would have been a helpful test of the microsensor system in-field.

We had initially intended to bring along a Chemetrics field-portable colorimeter with test kits for measuring such aqueous chemical parameters as dissolved nitrate, ammonium, alkalinity, phosphate, and dissolved iron. These measurements would have vastly improved the results of my work (see for instance, issues with CBE and lacking analytes in Chapter 2). Unfortunately, the airline we had shipped our materials through had confiscated all of our hazardous chemicals, thus hindering us from employing some of these measurements and sample prep methods in the field. Measurements of reactive species, such as ammonium, should be conducted in-field and would have crucially benefited the field work in 2014.
In 2014, John Spear employed a bubble stripping method to capture some of the gases in melt pool fluids from three of the melt pools (labeled as MP2, MP3, and MP4 in Chapter 2). The gases were analyzed for the presence of ethylene, acetylene, and hydrogen (Table A1.3). Although ethylene and acetylene were below quantitation limits in all three samples (<0.01 µ L⁻¹ and <1.0 µ L⁻¹, respectively), hydrogen gas was detected in all three samples. MP3 and MP4 had 1.5 and 2.2 nM H₂, respectively, while MP2 (the site of the collection of sulfur bubbles where rare allotropes of sulfur were discovered) had 29 nM hydrogen. Although these measurements were important, I think future gas phase analyses on the Borup springs, melt pools, and ice should include measurements for H₂S, CH₄, CO, and CO₂ to build upon our understanding of the sulfur and carbon chemistry, as well as the biological processes, in these materials.

5.3. Microbial Communities

Future work considering the microbial community composition and activity at Borup Fiord Pass may reveal a potential connection between the mineral assemblages in the cryoconite and aufeis samples and biology, though it may be possible that the primary controls on mineralogy are solely abiotic in nature. An analysis of the microbiological communities and biological functions occurring at Borup Fiord Pass in 2014 is being conducted by Christopher Trivedi of the Colorado School of Mines. Mr. Trivedi’s work thus far has used 16S rRNA gene analyses to examine the microbial communities within the melt pool fluids and aufeis materials. Dominant organisms in these materials include members of the Epsilonproteobacteria (e.g., *Sulfurimonas* sp., *Sulfuricurvum* sp., *Sulfurovum* sp.) and Flavobacteria, all of which had previously been detected in mineral deposits. For instance, *Sulfurovum* sp. and *Sulfuricurvum* sp. were identified as dominant members of the community within a thick deposit of sulfur downstream from an active stream in 2009 (the spring in that year occurred on the glacier, just above the location of the ice blister in 2014). Sulfur lithotrophy by these organisms has been proposed as the main driver of primary productivity in the
system (Wright et al., 2013). Mr. Trivedi is now assessing the role of these organisms in 2014 samples, especially of *Sulfurimonas* sp., which appear to be more abundant than other members of the Epsilonproteobacteria in the melt pool site from which rare forms of elemental sulfur were found in sulfur bubbles and rapidcreekite was identified in cryoconite. Current work at the Colorado School of Mines includes culturing of representatives of the Epsilonproteobacteria to determine if they play a role in the formation of the rare, monoclinic allotropes of elemental sulfur that have been detected and also to determine if these organisms are able to oxidize the monoclinic allotropes. These studies by Mr. Trivedi should tie in to the geochemical and mineralogical findings presented in this dissertation and will yield a greater characterization of the biogeochemical cycling of sulfur at Borup Fiord Pass.

Further characterizations of the microbial communities, functional genes, and microbial exudates in the system are necessary. For instance, it is still unknown which microbial populations dominate the spring fluids below the surface. Although Ralstonia and Burkholderia have been detected in spring fluids (Gleeson et al., 2011; Grasby et al., 2003; Wright et al., 2013), further sampling for microbiology should be conducted deep with the spring fluids or sites of aufeis formation. For instance, should another large aufeis be detected at Borup Fiord Pass, coring the ice to collect samples from depth may be useful in understanding the microbes that were emplaced by the spring fluids that formed the ice, and may teach us more about the subsurface communities. As the aufeis form as layerings, it may also be possible that variations in the microbial complement of the fluids (based upon changes in chemistry, temperature, seasonal fluctuations, etc.) may drive variations in the microbial communities in aufeis layers. This may form a testable hypothesis for future field endeavors.

Also, Flavobacteria are found to dominate nearly all of the surface samples from aufeis and sulfur deposits at Borup (Wright, 2012; Trivedi et al., in prep.), however it's not yet known if Flavobacteria are present at all times and only opportunistic aerobic heterotrophs that take over
once exposed to the atmosphere or if they are a common component of the local tundra soil biology. The work of Christopher Trivedi, who is working on characterizing the 2014 microbial communities, will help us unravel the background populations of microbes in the valley (samples collected from tundra). However, a full workup of the microbial populations in tundra, glacial till, and from the region will still be necessary for constraining how the microbial community in the surface materials of the sulfur deposits and aufeis relate to the microbial populations in the subsurface and in regional materials. Furthermore, if I had unlimited funding for sampling, I would want to get better samples on englacial and subglacial microbial communities, especially from the till directly below the glacier, to better constrain the microbial processes occurring in the springs as they are delivered to the glacial environment.

Furthermore, preparation of samples for electron microscopy and other methods should be conducted in future field work. In 2014, we had intended to take along glutaraldehyde and formaldehyde for the preservation of microbial biomass for electron microscopy, however these chemicals were confiscated by the airline and were not available for use in the field. Future work should endeavor to prepare samples in such way as to allow fixed samples to be analyzed and imaged upon return from the field.

5.4. Minerals and Organic Carbon

Further interrogations of materials from 2014 and future samples will be necessary to better constrain the geochemical constraints on the formation of rare minerals that have been detected, including vaterite, beta- and gamma-cyclooctasulfur, and rapidcreekite. One major finding from this dissertation that remains to be further developed is the detection of rapidcreekite in the cryoconite of one of the melt pools (MP2 as presented in Chapter 2). This hydrated sulfate carbonate mineral has only been detected a hand-full of times in nature (e.g., Onac et al., 2013; Roberts, 1986) and may be important for future studies regarding Borup Fiord Pass. Two things
can be done in the near-future using Borup 2014 samples to better understand the role of rapidcreekite in these materials. Firstly, only a limited number of samples were analyzed using XRD and Raman microspectroscopy during the course of this research. A new graduate student, “getting their feet wet”, could begin by surveying the many remaining samples for their general mineralogy using XRD. They could then use Raman microspectroscopy for the samples that appear to warrant further analysis. Not only may rapidcreekite be discovered in more of the sample materials, but it may be that beta- and gamma-cyclooctasulfur as well as vaterite may be detected in some of these materials (all of which have been detected in Borup samples in this dissertation or previously). Such a mineralogical inventory will serve in the next step, which would be to model the formation of rapidcreekite in the cryoconite sample (and more if detected) by calculating the saturation index (SI) for gypsum and then constraining the potential dissolved carbonate and calculating the SI for calcite. This can then be used to characterize the formation of rapidcreekite, and, given the limited number of previous studies, could become a short publication of an intriguing environmental detection of rapidcreekite.

Beyond the potential microbial controls on the mineralogy and geochemistry of the Borup aufeis materials, the current analyses show that origin, abundance, and reactivity of organic carbon in these materials is important for understanding this system and warrants further study. Although we cannot currently constrain the source(s) of organic carbon in the materials (whether from the subsurface, picked up from glacial till in the near-surface, or formed in situ through microbial autotrophy), these analyses show that organic carbon is associated with a variety of mineral forms in the Borup samples. Further analyses of the organic carbon composition and functional groups will be important for understanding the dynamics of this cold, sulfur-rich system. This may include FTIR for organic functional groups characterizations but should also include mass spectrometric methods. For instance, pyrolysis gas chromatography mass spectrometry (pyGCMS) is a technique which had been intended for this work. PyGCMS is a useful method for studying the organic
components of a sample without much sample preparation before-hand and has been used on Mars in the search for life with the Viking Mission (e.g., Mukhopadhyay, 2007). The sample is thermally decomposed, and volatile organic groups are then characterized through GCMS. However, other forms of mass spectrometry may also be useful in studying samples from Borup and in characterizing the organic carbon.

5.5 The Alteration Features

More work is also warranted for the pyrite alteration features and associated region. The detection of abundant pyrite in the mineral features led to the interpretation from Chapter 4 that either a high-temperature magmatic, hydrothermal, or low-temperature hydrological system working at Borup Fiord Pass has previously emplaced a large amount of near-surface pyrite in the topographically high region to the south of the glacier. This interpretation and the source of the pyrite should be further tested with mineralogical characterizations and probing deeper into the subsurface. A future field excursion should include digging/coring deep into the permafrost below the surface expression of the features to determine if sulfide minerals are also abundant at depth, and also to characterize the materials at greater depths. A thorough analysis of each of the pyrite alteration features as well as sampling from multiple materials around the region is necessary. For instance, pyrite in “pyrite canyon” to the west of the features should be sampled and analyzed for sulfur isotopes to determine if all of the pyrite in the region shares the signature of sulfur isotopes seen in the reduced sulfur of the red-stained features.

Beyond greater sampling and isotope measurements, a more thorough characterization of the organic carbon in the region is necessary to determine the remnant signatures, if there are any, from biological processes. Specifically, material collected from depth, below the surface of the permafrost, may serve as an indicator of whether the pyrite was sourced from a low-temperature system with biological sulfate reduction (BSR) or came from a high-temperature system with
thermochemical sulfate reduction (TSR) from some unknown pool of geological sulfate (sulfur isotopes of the feature materials are depleted in $^{34}\text{S}$ relative to known deposits of Otto Fiord and Mount Bayley Formations, though, as Davies & Nassichuk (1975) pointed out, a gradient upward through the Otto Fiord Formation of $\delta^{34}\text{S}$ from 16 to 12‰ has been detected. This may implicate an even lower $\delta^{34}\text{S}$ signature remains in some unexposed portion of the formation). Also, sampling from greater depth may provide more information on potential sources of organic material in the subsurface.

Also, it is possible (and perhaps likely) that biological processes have been involved in the oxidation of the pyrite in the near-surface. An abundance of organic matter was observed through the analyses presented in Chapter 4. The next step should be to examine that organic carbon in the samples by using techniques such as micro-FTIR and cryo-STXM, as well as to extract the organic material and analyze the carbon through techniques such as FTIR and GCMS. This will allow for a thorough inventory of the organic constituents of the pyrite alteration features and surrounding region. Furthermore, although multiple samples were collected for DNA extraction, Chris Trivedi does not trust any data yet returned from these collections. Future work should seek to characterize the microbial community and possible function within this region through in-lab testing of extraction procedures on material made to simulate the acidic, iron-rich features before fieldwork is conducted. Testing of DNA extraction techniques before field work may allow a future researcher to collect the necessary data to characterize not just the organic carbon but also the microbial community (and potentially the activity of microbes in the near-surface if they are involved in the oxidation of the pyrite).

5.6. Other Potential Targets for Future Research

One major missing component in previous research at Borup Fiord Pass is a more thorough exploration of subsurface samples and studies of subsurface structure. Bringing to bear geophysical
measurements of the subsurface structure of the valley may aid in determining the nature of the hydrological network(s) that form the modern-day sulfur spring system and that may have been involved in sourcing the pyrite in the topographically high region to the south of the glacier. Although Borup Fiord Pass is a remote valley, driving up costs for field-implemented instrumentation and techniques, geophysical measurements of the valley are warranted to better understand the nature of the spring system.

Another intriguing potential for future work comes in the realm of the deployment of time-lapse infrared cameras in the field and remote sensing from orbital observations to better constrain the timing of spring flow, aufeis formation, and sulfur formation at this site. A time-lapse camera was left in the field in 2014, and was used to monitor the melting of the aufeis that year. An infrared time-lapse camera would also be valuable in that it should be able to observe the formation of springs/auseis even when there is snow, as the springs have been measured to be slightly warmer than the surrounding glacial ice (Gleeson et al., 2011; Grasby et al., 2003). Also, while remote sensing was previously implemented for observing the timing of sulfur formation at Borup Fiord Pass (Gleeson et al., 2010), this approach could be further developed to aid in monitoring the evolution of the spring system and aufeis formation over multiple years. Paired with ground-based sample collection and in-field measurement, this would allow for a much fuller characterization of biological and geochemical sulfur cycling at this unique Arctic site.
CHAPTER 6: RECAPITULATION AND CONCLUDING REMARKS

“...Before I go, I just wanna tell you, you were fantastic. Absolutely fantastic. And do you know what? So was I!”
-Doctor Who (S1:E13; 2005; written by Russell T. Davies & Terry Nation)

6.1. Overview

Borup Fiord Pass, a valley in the Canadian High Arctic, bears a system with the northernmost occurring sulfide springs on Earth. These cold springs emerge at the toe of a coalescence glacier in the valley, and yellow deposits rich in elemental sulfur form as the sulfide undergoes oxidation and mineralization. A key point of interest that has driven myself and others to further explore this system is the potential for life, for biological activity, to drive the formation and stabilization of the elemental sulfur that forms at this site. The surface expressions of these springs provide windows into the (bio)geochemistry of the subsurface processes at this intriguing site. This graduate dissertation has significantly expanded our knowledge of the sulfur spring system by presenting results from research conducted on materials from Borup Fiord Pass, collected during a field excursion in the summer of 2014. We’ve discovered that extensive, sulfide-rich aufeis forms from spring fluids and that active (bio)geochemical processes actively occur on this ice and in melt pools of fluid that form on its surface. The research has revealed the intriguing existence of rare crystallographic forms of sulfur and carbonate minerals, including beta- and gamma-cyclooctasulfur and rapidcreekite, forming within sulfur bubbles at the surface of melt pools as well as within cryoconite from those melt pools. Also, this dissertation has presented detailed mineralogical characterization of mineralized pyrite alteration features in the valley, potentially revealed a larger system of pyrite emplacement than was previously understood, and determined that the unique elliptical features in the valley likely formed from leaching of pyritic ore to form mineral suites reminiscent of terrestrial gossans. The potential for a topographically high region around these features to represent one relatively large sulfide (bio)mineral deposit, visible from
orbit, is explored in Chapter 4. The conclusion of the dissertation presented here will review the findings from the 2014 field season and the work conducted in completing my graduate degree. The overarching questions regarding Borup Fiord Pass as presented in the introduction will again be considered here in light of the preceding research in Chapters 2-4. I will present a conceptual overview for the large-scale processes occurring at Borup Fiord Pass, further developing ideas that have been building through time and through the efforts of many people before me. This will include graphic representations of the field site that are intended to provide a visual demonstration of these processes for use in future research talks and publications as well as in videos and talks for communicating this research with the broader public. Finally, I will briefly consider the implications of this research for geobiological and astrobiological investigations elsewhere and will conclude with a final thought about my next steps in sharing this work.

6.2. A Brief Review of Findings from this Dissertation

Although no active sulfide springs were detected during the 2014 field excursion to Borup Fiord Pass, the existence of the aufeis and melt pools containing rare minerals of sulfur and carbonate are intriguing and will lead to a better understanding of the sulfur spring system. Our geochemical and isotopic analyses from the aufeis reveal that the ice derives from the sulfide spring system, emplacing the materials from the spring but also providing a new target for exploring (bio)geochemical sulfur cycling in the form of the spring-derived, sulfide-rich aufeis itself. The formation of melt pools with sulfur bubbles at the surface and mineral-rich cryoconite filling sun cups at the bottom, as well as the daily freeze-thaw cycles and changes in gas exsolvation (suggesting changes in the ice below the melt pools), suggested that these melt pools may be a key target in further understanding the aufeis (bio)chemistry. Furthermore, we observed fresh sulfur-rich deposits forming on the surface of the aufeis, especially apparent when material was scraped away or fresh ice had fallen on the surface and then new yellow material was observed to form
within one day. Our measurements of temperature and pH (0-0.2°C and 5.5-6.0 units, respectively) from the aufeis melt pools agree with the data previously presented for spring-derived ice and sulfur deposits (Gleeson et al., 2011; Grasby et al., 2003; Wright et al., 2013), though pH is much less (more acidic) than that previously reported for the flowing sulfide springs (spring pH has ranged from 7.29 to 9.50 in previous measurements; Gleeson et al., 2011; Grasby et al., 2003; Wright et al., 2013). Sulfide measurements, ranging from 0.22 to 2.25 mM in 2014 materials, roughly the same order-of-magnitude as previous measurements for the sulfide springs in 2006 and 2009, which had dissolved sulfide as high as 4.2 mM, the highest reported in any cold sulfide-spring system (Gleeson et al., 2011; Wright et al., 2013). Sulfur isotope data also support that the aufeis was derived from sulfide springs, as the $\delta^{34}S$ values for dissolved sulfides and sulfates (against V-CDT) are similar to those previously measured for reduced sulfur (S$^0$) and oxidized sulfur (gypsum) species in the spring system. As Chapter 2 showed, our sulfur isotope data further support the hypothesis that the sulfide in the springs derives from biological sulfate reduction (BSR) in the subsurface. BSR is likely acting on sulfate introduced to subsurface fluids from the anhydrite of the Otto Fiord or Mount Bayley evaporite units, the only two sulfur-rich geological units in the region. This sulfate, once reduced, forms the sulfide that is then observed in springs and, now, in large spring-derived aufeis. The active formation of elemental sulfur and of exotic minerals on the surface of the aufeis during the two weeks that we spent in the field have completely changed our views of how this system functions. While previous reports had discussed the formation of sulfur-rich mineral deposits on glacial ice and in at least three previous years (2000, 2006, 2007) spring-derived ice has been observed (Gleeson, 2009; Gleeson et al., 2010, 2011; Grasby et al., 2003; Wright, 2012), formation of such sulfide-rich aufeis along with subsequent alteration of this aufeis as is observed in the active formation of elemental sulfur and of rare minerals in the cryoconite of the melt pools has not been reported previously.
X-ray diffraction (XRD) data for sulfur bubbles that formed on one of the melt pools revealed the presence of three known crystalline forms of elemental sulfur ($S^0$). These three allotropic forms of sulfur are known as $\alpha$-$S_8$, $\beta$-$S_8$, and $\gamma$-$S_8$ (alpha-, beta-, and gamma-cyclooctasulfur, respectively). As $\beta$-$S_8$ and $\gamma$-$S_8$, the two monoclinic forms of elemental sulfur, are usually found in high-temperature systems, they are not expected to exist at a cold, glacial site like Borup Fiord Pass. In particular, finding $\beta$-$S_8$ in the sulfur bubble sample appears to be the first detection of $\beta$-$S_8$ in any cold, natural system (Lau et al., 2017). As Chapter 3 shows, detection of organic carbon associated with the rare monoclinic forms of sulfur (beta- and gamma-cyclooctasulfur) led to the hypothesis that formation of mineralized elemental sulfur from sulfide in the presence of organic carbon may drive the formation (and temporary stabilization) of the rare forms of cyclooctasulfur. Some preliminary characterization of the organic carbon was developed using Fourier transform infrared (FTIR) spectroscopy and scanning transmission x-ray microscopy (STXM). These analyses revealed aliphatic and aromatic organic functional groups associated with the $S^0$ in the sample. Unfortunately, the origin of the organic carbon is unknown: organic carbon in the sulfur bubbles may derive from the relict carbon preserved in subsurface rocks or may be a product of in situ microbial metabolisms. Since there is yet no direct evidence of biomineralization of the elemental sulfur, the rare mineral forms of elemental sulfur are thus not inherently biosignatures. However, future work may further determine if specific functional groups in the organic carbon constituent are required in forming beta- and gamma-cyclooctasulfur and whether the microorganisms in the deposits are actively producing such forms of organic matter. For instance, Christopher Trivedi at the Colorado School of Mines is actively exploring the microbial communities that were present in these samples during the 2014 field season, and part of his work includes a consideration of the potential role these microbes may play in producing beta- and gamma-cyclooctasulfur as well as in consuming these rare forms of sulfur. Furthermore, it may be possible that Raman microspectroscopy can be applied to these types of materials to detect beta-
cyclooctasulfur vs. alpha-cyclooctasulfur in the field (see §3.6.4 and §6.4). Only one study of Raman spectroscopy detection of β-S₈ has been undertaken, to my knowledge (Gautier & Debeau, 1976; also reviewed by Eckert & Steudal, 2003), however, as I show in §3.6.4 and Figure 3.7, I may have detected the β-S₈ in the sulfur bubble material using Raman microspectroscopy (though that result has not yet been rigorously confirmed). Applying Raman spectroscopy to the samples from Borup Fiord Pass may thus reveal further connections between the geochemistry and microbiology of the deposits and the pathways of formation of beta- and gamma-cyclooctasulfur.

Another rare mineral form, Rapidcreekite (Ca₂(SO₄)(CO₃)•4H₂O), was detected by XRD as well as Raman microspectroscopy within the cryoconite of one of the melt pools (see Chapter 2). This carbonate sulfate has only been shown to form in systems with far more dissolved sulfate than carbonate (otherwise, formation of gypsum and calcite are thermodynamically favored; unfortunately, we are missing alkalinity/DIC data from the 2014 samples, as is discussed in Chapter 2). This finding may reveal the dominance of dissolved sulfate over carbonate in the melt pool fluids. However, this finding should also be further explored to determine if processes of sulfur and carbon cycling by the microbial community effect rapidcreekite formation. As will be discussed in §6.4, following completion of this dissertation, the rapidcreekite finding will be further considered to determine its importance in the mineralogical suite produced within materials from the Borup Fiord Pass spring system.

Exploration of the region just south of the glacial terminus at Borup Fiord Pass has revealed the presence of the Fault Feature, a newly reported mineralized feature, as well as more extensive red-staining and pyrite deposition (in veins within carbonate rocks) in the region connecting to the pyrite alteration features than had previously been reported (Chapter 4). For instance, pyrite veining in a region called “pyrite canyon” (§A3.1), which lies ~100 m from the mineralized features, suggested a large amount of pyrite emplacement in this region, far more than had previously been considered. New analyses of the materials from the mineralized features, including those collected
at depth and from the permafrost layer, revealed an abundance of pyrite. This pyrite is hypothesized to have been emplaced in the near surface, though the mechanism of emplacement, thermal regime, and timing are as-of-yet unknown. Chapter 4 discussed three potential processes of emplacement of pyrite in the region and the subsequent alteration of pyritic ore forming the current mineralogical suite expressed in these features. Co-localizations of pyrite, $S^0$, and gypsum, the three most common oxidation states of sulfur, were considered along with the abundance of iron (oxyhydr)oxides, iron sulfate (jarosite), anatase, and quartz. Also, organic carbon, which was found to be abundant in these materials was explored through elemental analysis, Raman microspectroscopy, and STXM. We found organic carbon functional groups that may be indicative of biological activity, perhaps from subsurface processes or perhaps through \textit{in situ} biological activity in an acidic pyrite alteration system. For instance, STXM of some materials showed aliphatic and aromatic carbon as well as carboxylic carbon functional groups (e.g., §4.5.2 and Figures 4.15 & 4.16). In this way, the pyrite alteration features and surrounding area at Borup Fiord Pass present two potential expressions of biological activity: biological activity involved in the emplacement of subsurface sulfides and then subsequent surface oxidation of these sulfides to form a gossanous mineral suite around regions of spring conduit formation.

6.3. The Current Conception of Biogeochemical Processes in Borup Fiord Pass Sulfur Springs

The work from this dissertation builds into our current understanding of biogeochemical dynamics at Borup Fiord Pass by more explicitly considering subsurface processes (i.e. distribution of sulfidic fluids and emplacement of sulfide mineral deposits) as well as surface processes occurring where we observe the formation and stabilization of sulfur in the modern springs and aufeis (such as the formation of rare forms of elemental sulfur). The work presented in this graduate dissertation will feed directly into the current efforts in identifying the microbial communities and their associated biological activities in Borup 2014 samples. Such efforts are
being conducted by Christopher Trivedi at the Colorado School of Mines, who will soon produce his own research papers and graduate dissertation, tying his work together with the geochemical and mineralogical work from this dissertation. By integrating the findings from this dissertation along with previous published works and observations, the overall conceptual scheme for processes occurring at Borup Fiord Pass can be further developed. In the overview that follows, additions to the overall conceptual model from my work are expressed in bold font, though all figures were created by me as well:

- Subglacial melt water infiltrates into the subsurface (Figure 6.1). Alpine glacial ice covering the Kreiger Mountains to the east and west of the valley provides meltwater for infiltration into the subsurface aquifer. Groundwater meets with anhydrite-bearing geological units in the subsurface, where dissolution of the anhydrite (and other evaporite minerals) occurs. The Carboniferous-aged Otto Fiord Formation and Permian-aged Mount Bayley Formation are the only known potential geological sources of sulfur (Davies & Nassichuk, 1975; Gleeson et al., 2010; Grasby et al., 2012; Wallace et al., 1994), and both are composed primarily of anhydrite (CaSO₄). Dissolution of this anhydrite is hypothesized to drives the high concentrations of dissolved calcium and sulfate in subsurface fluids (Figure 6.1). Also, high concentrations of chloride in subsurface fluids may derive from halite in the evaporite units.

- Biological sulfate reduction (BSR) occurs in the subsurface of Borup Fiord Pass (Figure 6.2), as first hypothesized by Grasby et al. (2003). Sulfate-rich fluids provide the electron acceptors for BSR. The electron donors for this process are not well constrained, though organic carbon inputs are likely given the intervening shale units in the valley (Grasby et al., 2003) and the marine depositional history of local geological units (as well as known shales
Figure 6.1. Meltwater infiltration and dissolution of sulfates
A conceptual view of the valley (looking at an east-west cross-section). Glacial meltwater from the Kreiger Mountains to the west and the east infiltrates into the subsurface. Subsurface waters meet with local anhydrite-bearing geological units, where anhydrite (CaSO₄) is dissolved, forming aqueous Ca²⁺ and SO₄²⁻. Borup Fiord Pass Glacier (BFP Glacier) lies in the central region of the valley. The subsurface here is shown as anhydrite-bearing evaporite units (pink) while the rest of the geological strata are included in one unit (see Figure A3.2 for surface exposures of geological units in the valley).
within the Otto Fiord and Mount Bayley Formations; Davies & Nassichuk, 1975; Embry & Beauchamp, 2008; Hill, 2014; Wallace et al., 1994). **High concentrations of organic carbon** were also detected within the glacial till of the valley (TOC in till directly below the aufeis was measured at 2.49%), also potentially sourcing electron donors for BSR. It is currently unknown to what level waters interacting with this organic rich glacial till are involved in recharging the aquifer. Furthermore, this leads to the need for future work to address the electron donors for BSR, the subsurface geology/hydrology and where BSR may be occurring, and to determine if organic material from various sources at this site can be discriminated using organic geochemistry methods.

- **Subsurface BSR drives** the high concentrations of sulfide in subsurface fluids (as observed when springs and aufeis form at the surface) and also produces a diagnostic isotopic signature of $^{34}$S-depletion in dissolved sulfide relative to the source anhydrite (as well as $^{34}$S-enrichment in remaining dissolved sulfate relative to the source anhydrite; Figure 6.2b).

- **Although physicochemical constraints** as presented in Chapters 2 and 4 show that thermochemical sulfate reduction (TSR) can be precluded in this system, it has not yet been constrained at what depth(s) sulfate reduction occurs. The potential depths to the anhydrite-bearing geological units are several hundred meters to 2 km (see Chapter 2). From this, BSR may occur at any point in the subsurface, perhaps primarily dependent on the availability of electron donors (such as organic carbon-rich deposits). For now, it is assumed that BSR occurs at or near the interface with the anhydrite-bearing units (Figure 6.2).
Figure 6.2. Biological Sulfate Reduction in the Subsurface

Although it is currently unknown where biological sulfate reduction (BSR) occurs in the subsurface, it is presented here as occurring at the interface with anhydrite-bearing evaporite deposits (a; evaporate deposits are shown in pink). Sulfate (SO$_4^{2-}$) serves as the electron acceptor in BSR. Two typical reactions for BSR are shown in the bracket, one using organic carbon (expressed here as CH$_2$O, though several forms of organic carbon are known to be used) and the other using hydrogen (H$_2$) for electron donors. This process is known to drive fractionations in sulfur isotopes (b). Figure 2.5 has been adapted here in b to show the sulfur isotope data (as $\delta^{34}$S vs. V-CDT) for source anhydrite (from both Otto Fiord and Mount Bayley Formations; yellow square and orange triangle show average values for each, while black lines show known ranges of values) as well as for the product dissolved sulfides and sulfates measured in 2014 aufeis fluid and ice samples.
• Hydrological gradients driven by topography to the north, east, and west and permafrost confinement to the south produce an artesian spring system at the base of Borup Fiord Pass Glacier (Figure 6.3a). Subsurface fluids, enriched in sulfide, may reach the surface through high permeability faults and fractures (Figure 6.3b). The main strike-slip fault running across the valley at Borup Fiord Pass, along with fracturing orthogonal to the fault, may provide a system for the release of stored fluids. These sulfide-rich fluids then work their way either between unfrozen ground and the bed of the glacier or, as has been observed in some field seasons, through the glacier itself (freezing of the bed near the terminus may force fluids to form conduits through the glacier). The sulfide springs are then observed emerging from the glacier or at its toe (Figure 6.3b).

• As the springs discharge, the microbial community from the subsurface is released into the surface environment as well. Then sulfur oxidation reactions can occur in the flowing spring system or on the ices surrounding the springs. The sulfide from the springs most certainly interacts with atmospheric oxygen at the ice surface, forming elemental sulfur, though this process may be driven by some degree of biological processes as well. For instance, metagenomic analyses from a sulfur deposit in 2009 revealed that genes for biological sulfur oxidation are dominant metabolic genes within the deposit (Wright et al., 2013). The roles microorganisms play in oxidizing sulfide to form elemental sulfur and then in further oxidizing elemental sulfur to form other sulfur intermediates and, eventually, sulfate is currently unknown, but is currently being explored.

• As is shown in Figure 1.2, thermodynamic calculations of sulfur stability over reduction potential and pH conditions in the springs and aufeis at Borup Fiord Pass suggest that $S^{0}$ is
Figure 6.3. Formation of Sulfide-Rich Artesian Springs

Confinement of fluids due to topography to the north, west, and east as well as permafrost to the south forces subsurface fluids to the toe of Borup Fiord Pass Glacier (BFP Glacier; a). In a, glacial meltwater from the Kreiger Mountains infiltrates the subsurface, where biological sulfate reduction (BSR; red circle) of subsurface anhydrite (pink) drives high levels of dissolved sulfide. Fluids are focused to the toe of the glacier where sulfide springs and sulfidic aufeis (shown in yellow) form from an artesianal flow system. The conceptual cross-section in a is presented as an east-to-west cut of the valley. Meanwhile, a north-to-south cross-section is shown in b, where the confining permafrost to the south (grey), evaporite units (pink), and Permian carbonates of the Nansen Formation (brown) are shown. The right-lateral strike-slip fault is shown (the fault has a minor component of dip; Hill, 2014), and orthogonal fracturing is suggested. The fault and fractures force fluid flow, driving the spring system to emerge at the toe of the glacier. Not shown in is the topography of the region to the north of the glacier (where it slopes upward; see Figure A3.2). The scale bar in b is estimated based on the known horizontal distance from the toe of the glacier to the expression of the fault, on the south side of the meltwater channel. The depth to anhydrite-bearing evaporite units is approximated here (see Chapter 2).
only stable over a narrow range of these conditions in the ice (and not at all in the springs). It still cannot be determined if sulfide is being oxidized to $S^0$ through biological or abiotic processes (though it may likely be both), however this does raise the question of whether the formation and long-term stability of sulfur at this site is impacted by the formation of metastable sulfur intermediates through microbial processes. Future work will seek to characterize the full range of sulfur species present in the yellow deposits at the site.

- The previously identified microbial communities and functional genes within the sulfur deposits support sulfur metabolism as a key driver of the changes in the sulfur chemistry at the surface of the glacier (Gleeson et al., 2011; Grasby et al., 2003; Wright et al., 2013). Microorganisms may be involved in a dynamic cycle of the oxidation, disproportionation, and potentially even further reduction of a variety of intermediary sulfur compounds (those of oxidation states between those of $S^{2-}$ and $SO_4^{2-}$) such as polysulfides, elemental sulfur, reduced and oxidized organothiols, thiosulfate and other polythionates, and sulfite (e.g., Canfield & Farquhar, 2012; Gleeson et al., 2011; Wright et al., 2013; Wright, 2012; Zerkle et al., 2010; Zopfi et al., 2004).

- When the springs flow in the winter, perhaps under light cover of snow, large aufeis are formed, emplacing sulfide-rich ice in the valley (Figures 6.3a & 6.4). The aufeis forms at the site of spring emergence and spreads down the canyon to the south and east of the glacier and then follows the local riverine flow down the valley (the flow is constrained by the hill where pyrite alteration features are located). During the 2014 field season, a large ice blister on the aufeis near the glacier formed, likely as the site of spring emergence (Figure 6.4c). Fluid flow under and around this site likely caused
Figure 6.4. Formation of the Aufeis and Ice Blister

A schematic representation of the processes that occurred during the formation of the aufeis and ice blister in 2014 is shown in a-c. First, the site of spring emergence drives sulfide-rich fluid to emerge at the toe of the glacier, covering over the glacial till at the terminus and flowing into a local meltwater channel (a). Then, freezing of these sulfide-rich fluids forms the aufeis (b). During this time, fluid continues to flow under/over the frozen ices that have formed (frozen, sulfur-rich ice is represented in yellow in the images). Finally, flow of the spring fluids at the glacial terminus drives the uplift and cracking of the ice blister, which is shown forming in c. The scale bars are estimated based on the known distance from the strike-slip fault and the terminus of the glacier (roughly 100 m in horizontal distance).
the uplift and cracking identified in the ice blister, which is commonly observed on aufeis and other iced-over regions where fluids from streams and rivers flow beneath the ice (e.g., Gosnell, 2007). This ice blister was uplifted ~2-3 m above the roughly level region of aufeis at the toe of the glacier (Figure 6.5). When Steve Grasby revisited the field site in the summer of 2015, a large hole in the glacial till was observed where the ice blister had been, further supporting the ice blister as the site of spring emergence that created the 2014 aufeis (Figure 6.5). The hole in 2015 at the ice blister site was observed to have muddy fluid in the bottom as well.

- When an aufeis has formed, summertime melting can create melt pools on the surface of the aufeis (Figure 6.6). Hydrogen sulfide and other gases exsolving from the aufeis bubble their way up through the melt pools, forming the sulfur bubbles (Chapter 3). As organic carbon is present in the melt pools, either from exogenous delivery with the springs or from endogenous microbial activity, its presence is hypothesized to be involved in the formation of beta- and gamma-cyclooctasulfur when sulfide is oxidized in the sulfur bubbles (Lau et al., 2017). As more melt occurs and gases in the aufeis below the melt pool are reduced (observed in the decrease in bubbling and decreased sulfur bubble formation in melt pools over time), cryoconite precipitation from melt pools fluids increases. The cryoconite forms primarily from precipitation of gypsum and calcite, but also from rapidcreekite. The melt pools thus present dynamic microcosms for microbial activity (the work of Chris Trivedi and the Spear Lab will further inform on the microbial community dynamics in melt pools).

- The (bio)geochemical dynamics that may be involved in the development of the current
Figure 6.5. The Ice Blister Region: 2014 vs. 2015

During the 2014 field expedition, the ice blister appeared as an uplifted and cracked region of ice near the toe of the glacier (a). This ice blister was ~2-3 m in height (b; Steve Grasby gives scale). When Steve Grasby returned to the site in 2015, a sulfidic aufeis was present (b), but the region of the ice blister had eroded and presented a depression filled with fluid (c). Images in b and c were collected by Steve Grasby.
Figure 6.6. Sampling for a Melt Pool Beside the Ice Blister

One of the melt pools closest to the ice blister on the 2014 aufeis is shown. Graham Lau is sampling fluid while Steve Grasby (left) and Christopher Trivedi (right) look on. The melt being samples in sample site MP3 in Chapter 2. The presence of yellow sulfur deposits can be seen at the edges of the melt pool and on the surfaces of the aufeis.
mineralogical suite observed in the pyrite alteration feature region has built upon our past knowledge and serves to develop our conceptual understanding of sulfur (bio)geochemical cycling in this system and beyond. Chapter 4 presented an overview of potential mechanisms for emplacement of near- and sub-surface pyrite as well as the processes that lead to alteration of the pyrite, forming the mineral features as they appear at the surface.

6.4. Connecting Borup Fiord Pass to Other Worlds through Astrobiology

The chemical and mineralogical characterizations of the cold spring deposits and pyrite alteration features presented in this dissertation are useful for our studies of sulfur cycling in other cold hydrological systems on Earth as well as for our astrobiological exploration of the Solar System and beyond. For instance, another intriguing environment dominated by geobiological sulfur cycling is the Blood Falls spring system, at Taylor Glacier in Antarctica. This system presents an active spring environment where visibly red precipitates from iron-rich fluids emerge at the toe of Taylor Glacier (Mikucki et al., 2009; Mikucki & Priscu, 2007). At Blood Falls, a subglacial brine reservoir provides an environment for active microbial sulfur cycling and resultant reduction of ferric iron. Microbial consortia in the brine fluids pair the oxidation of carbon with the reduction of sulfate. The reduced sulfides produced from this sulfate reduction are then scavenged by ferric iron in the brine, driving the re-oxidation of sulfur along with the reduction of iron (Mikucki et al., 2009; Mikucki et al., 2004; Mikucki, 2005). Blood Falls presents a useful comparison system for Borup Fiord Pass, given the mineralized spring features in both systems (indeed, at Borup Fiord Pass in 2014 the “sulfur falls” region of the aufeis presents an intriguing yellow icefall similar to the red icefall of Blood Falls). Similarly, there are other cold springs across the planet which may serve as key sites of comparison for the biological communities and processes occurring at Borup Fiord Pass (e.g., Andersen et al., 2002; Douglas & Douglas, 2001; and references presented in Chapters 2-4).
Studies from these sites and Borup Fiord Pass are important for better understanding global sulfur biogeochemical cycles or, at least, the biogeochemical cycling of sulfur in low-temperature systems.

Sulfur biology may also have had a role to play if life ever originated and evolved in other regions of our Solar System, including Venus, Mars, and outer solar system moons, such as Europa and Enceladus. Specifically, Mars and Europa, two current targets for astrobiological investigations, may have had past or even present sulfur metabolisms and/or interactions of living processes with sulfur chemistry. As Chapter 4 shows, the sulfur-rich pyrite alteration features and surrounding region at Borup Fiord Pass may be an ideal analog for our exploration of Mars. Sulfates of calcium and magnesium have been identified globally on Mars through remote sensing, and ferric iron sulfates (e.g. jarosite) have also been detected in certain Martian localities through robotic exploration (see King and McLennan (2010) for review). Schopf et al. (2012) have considered the potential for sulfate deposits on Mars to contain morphological signs of past life, and Norlund and colleagues (2010) have suggested that jarosite minerals on Mars may be relics from biological sulfur oxidation processes similar to those seen in some Acid Mine Drainage (AMD) systems on Earth. The oxidation of sulfide and other forms of sulfur in the Martian past to form the sulfates detected in modern times may have been driven by Martian biological systems. If this has been the case, then sulfate deposits on Mars may hold biosignatures of such past activities. The future exploration of Mars should include work to determine whether biological mechanisms have been involved in processing sulfur on that planet. Banfield et al. (2001) have reviewed a plethora of the potential mineralogical biosignatures from Terran environments that may be utilized for such astrobiological analyses of Mars. Included are mineral phases indicative of biogenic processes; variations in crystallinity and surface morphology that indicate biological mediation during formation; and the presence of organic molecules within minerals. Some of these potential signs of biological activity have been detected in the pyrite alteration features and are discussed in Chapter 4. The Borup Fiord Pass alteration features thus present one of the mineralizing hydrological
environments which have been proposed to be ideal systems for studying relevant to Mars exploration (e.g., Cady et al., 2003; Farmer & Des Marais, 1999). For instance, light-toned deposits (LTDs) have been observed on the surface of Mars that may be representative of large-scale spring deposition through past hydrological activity (Rossi et al., 2008). These deposits have been seen in regions such as Valles Marineris, around “chaotic terrain” in Martian equatorial regions, and within crater bulges (such as in Gale Crater, where the rover Curiosity is currently operating). Furthermore, modern spring systems on Mars may be able to exist within the permafrost and still show surface expression (Andersen et al., 2002). The modern spring system at Borup Fiord Pass thus provide one potential analog for the exploration of mineralized hydrological systems on Mars, both past and present.

It is now widely accepted that Europa, the smallest of the Galilean Moons, likely has a subsurface ocean under its thick, icy crust. Although the physicochemical dynamics of Europa’s ocean and icy crust are different from those at Borup Fiord Pass Glacier, the potential for geobiological sulfur cycling within Europa and the likelihood of future astrobiological investigations on that moon demand that processes affecting the production and preservation of biosignatures in geochemically-unique, cold environments on Earth be better characterized. For instance, Borup Fiord Pass has previously been discussed as one of the best analogs for Europa on Earth (Gleeson et al., 2010; Grasby et al., 2012). This is due to the connections that are made possible between subsurface and surface processes through glacial ice; in some years, the sulfur springs have produced conduits through the glacier itself. The presence of the sulfur deposits on the surface of the glacier at Borup may serve as analogs for the potentially sulfurous material concentrated within the lineae on Europa (see Chela-Flores, 2006; Hand et al., 2007; and references therein). Continued research at Borup could thus play an important role in the development of instrumentation to explore the materials that develop at the dynamic boundaries between surface ices and subsurface
anoxic fluids. Furthermore, the materials in the mineral deposits at Borup may serve as test beds for the instrumentation that may one day be sent to Europa on a surface mission.

6.5. Conclusion

Borup Fiord Pass provides a unique system for studying processes involving sulfur (bio)geochemical cycling at low-temperature. The connections between subsurface processes and surface mineral expressions in the modern spring system and in the paleopipe region present an intriguing system for characterizing geochemical and mineralogical signatures of biological sulfate reduction, sulfide oxidation, the formation and stabilization of elemental sulfur, the oxidation of elemental sulfur, and the formation of exotic mineral forms that are not common in most terrestrial systems (such as rapidcreekite and monoclinic allotropes of elemental sulfur). I conducted the research for this dissertation to better characterize the geochemistry and mineralogy of the modern sulfur spring system as well as of the red-stained mineral features and I feel that I have been successful in such a characterization. My detections of the monoclinic allotropes of sulfur, specifically beta-S\(_8\), open up new questions about the potential for organic carbon to be involved in the formation of these rare allotropes of S\(^0\) in sulfide oxidizing systems at low temperature. This detection also warrants further research into the potential for biological processes to not only form monoclinic sulfur allotropes, but also to use these forms of sulfur for sulfur oxidation pathways. Similarly, the detection of rapidcreekite (a very rare mineral on Earth) may present another avenue for future research to constrain the geochemical and biological processes happening in sulfide-rich spring-derived aufeis. My work in characterizing the pyrite alteration features, which includes the first analyses of samples collected below the surface, has revealed a large amount of subsurface pyrite is likely present in the region and led us to the hypothesis that the entire region represents a large-scale emplacement of pyritic ore in the subsurface delivering sulfide from deeper regions. The alteration features and nearby region also present a possible connection for studying gossanous
systems on Earth and beyond, as the oxidation of the near-surface pyrite appears to have developed a mineralogical suite of oxidized sulfur and iron minerals similar to other leached ore emplacements on Earth. This dissertation sought to identify which features at Borup Fiord Pass may have been influenced by biological activity. Chapters 2-4 present the results of this work and shows how the mineral features at Borup Fiord Pass may relate to such biological processes. While the research work on Borup Fiord Pass will hopefully continue, especially as there are still questions remaining unanswered about the processes occurring there, my portion of the work is not yet complete, as I will continue to develop videos, blog posts, and delivering public talks related to the research. Hopefully, that continued portion of my work will bring more renown to the efforts that will proceed in the field and in the laboratory to better understand life and geochemistry in this dynamic, cold environment in the High Arctic.
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APPENDIX 1:
SUPPLEMENTARY INFORMATION FOR CHAPTER 2

A1.1. Further Field Observations

The field campaign to Borup Fiord Pass in 2014 took place from 19 June to 2 July of that summer (with the first and last days dedicated to setting up and taking down camp and travel). No active sulfide springs were observed in 2014, but on first flying into Borup Fiord Pass on 19 June a large aufeis stained in yellow was observed at the toe of the glacier. Aufeis are a common feature formed by High Arctic perennial springs and are formed by freezing of spring fluids released during winter months (e.g. Grasby et al., 2003; 2014). The aufeis was at its greatest extent near the toe of the glacier, where it was later estimated to cover an area of \( \sim 10^4 \text{ m}^2 \) (Lau et al., 2017). This portion of the aufeis has been informally called “the ice blister region”, as it sits just at the toe of the glacier and presented an elliptical region of uplifted and fractured ice which was called the “blister”. This blister is very reminiscent of ice blisters which commonly form in icy and glacial landscapes from confined fluid flow. For instance, other, smaller ice blisters were observed in the valley, toward the southernmost extent of the aufeis (Figure A1.1), and likely formed from confined flow in this region.

As presented in Chapter 2, the large ice blister in the ice blister region of the aufeis is hypothesized to be the original region of spring emergence which formed the aufeis. The blister region appeared to sit atop till at the toe of the glacier with the yellow aufeis ice dropping down the side of a small hill into a canyon that runs west-to-east just to the south of glacier's toe. Due to the yellow staining (likely from sulfur) and similarities with ice waterfalls, regions where the aufeis dropped into the canyon were termed “sulfur falls”. The aufeis below the sulfur falls then filled the floor of the canyon just to the south of the ice blister region and ran along with the canyon to the east, where after about 1 km the canyon ended and the aufeis turned south, traveling along with local riverine flow in the valley. The aufeis, marked by the ice and yellow staining, has been
Figure A1.1. Ice blisters at Borup Fiord Pass
The main ice blister that is believed to be the site of spring emergence shows cracking from uplifted ice as well as deposits of yellow sulfur-rich material (a). Meanwhile, ice blisters on the ice further south have less coloration from sulfur precipitation (b), but still show the cracking from uplift.
estimated to have covered a total area of \( \sim 5 \times 10^4 \text{ m}^2 \) (Lau et al., 2017). In the ice blister region, the aufeis is estimated to have been \( \sim 5 \) m thick, at most, while the rest of the icing in the canyon and along the valley to the south was up to \( \sim 2 \) m in thickness. While exploring the aufeis, we noted the odor of \( \text{H}_2\text{S} \) gas apparently emanating from the ice, suggesting the release of trapped \( \text{H}_2\text{S} \). We also observed that after being cleared, fresh surfaces of the aufeis were covered by yellow precipitates that formed within one day (e.g., Figure A1.2).

Multiple melt pools at various areas around the aufeis were sampled and studied (including sample locations MP1-5 in Chapter 2). These melt pools formed from the melting of the aufeis, but then bubbles of gases, likely including \( \text{H}_2\text{S} \) based on scent, were observed to be coming up through the melt pools from the ice below. In some places, goopy yellow agglomerations of sulfur appeared to form on and around the bubbles where they met the water-air interface at the surface of a melt pool. Also, a large amount of yellow precipitates formed around the edges of the melt pools. Through two weeks of observations, it was seen that the smaller melt pools would freeze over in the evening hours and then re-melt every day. This intriguingly appeared to be a process that drove the yellow precipitates to the edges of the melt pools and appeared to affect their overall structure over time. Also, from visual and olfactory observations, the release of gases (including \( \text{H}_2\text{S} \)) appeared to be a process that occurred early in the formation of a melt pool and then appeared to dwindle after several days. Silver foil, which had been placed within the melt pool at site MP2, reacted with this dissolved sulfide, forming noticeable black silver sulfide on the foil (Figure A1.3).

Another intriguing discovery with the aufeis melt pools was the formation of subaqueous cryoconite. Cryoconite from areas high on the glacier appeared to be dark brown and grainy, while much of the cryoconite in the melt pools appeared finer and mostly white in coloration. Multiple cryoconite holes within melt pools in the blister region and in the canyon to the south were sampled. The cryoconite holes grew in their extent during the field campaign, and the cryoconite
Figure A1.2. Yellow deposits forming on top of freshly deposited ice
In multiple places, fresh yellow deposits of material were seen to form on top of glacial ice within as little as one day (a,b).
A large piece of silver foil was deployed in site MP2, using two metal rods to hold the foil (a). The foil reacted immediately with the sulfide in the melt pool, forming a dark surface of silver sulfide (b). Where the metal rods had been in contact with the film, the silver sulfide formation was seen to move up the surface of the foil, likely from fluid surface tension.
appeared to grow more extensive in volume within the melt pools during the course of the field campaign, suggesting continual precipitation of material from the melt pool fluids.

During the course of the field campaign, it was determined that an understanding of the chemistry and microbial populations below the surface of the aufeis may be important for understanding the Borup sulfur spring system. To achieve this, multiple sampling locations were selected from the blister region and down the canyon. The upper surface of material was cleared away and then a shovel was used to remove the top ~10-20 cm of ice. The ice below was then shoveled into large metal buckets (2 per site) and allowed to sit until thawed. This bucket fluid was then filtered for collection of biological material and some samples were taken for geochemical analysis as well. Samples in Chapter 2 that came from these ice buckets include samples I1 and I3-6.

In-field analyses during the 2014 field campaign included the use of pH strips (Carolina Biological Supply Co.; Burlington, North Carolina, USA) and an HQ40d field portable multimeter (Hach Company, Loveland, Colorado, USA), which was used to measure pH, conductivity, and temperature of some of the selected sites. However, the pH probe on the HQ40d appeared to provide questionable results early during the field campaign and so pH values were then collected using pH strips solely. Also, a field portable multimeter (Unisense, Aarhus, Denmark) was taken into the field. However, the pH probe and hydrogen sulfide sensors for this multimeter appeared to have trouble calibrating, perhaps due to interferences from hydrogen sulfide gas and low temperatures while on the glacier. Following is a list of some other general observations and findings while in-field, organized chronologically:

- 20 June: we used the HQ40d pH probe to take multiple measurements of pH and temperature around the ice blister. All measurements of temperature were ~0.2°C. The measured fluids were neutral to basic, though two attempted measurements could not be collected as the pH probe did not stabilize. These pH measurements appeared to agree with
measurements from active springs in previous field seasons. However, it was immediately following these measurements that a glacial outburst occurred, and a large amount of fluid and ice was ejected onto the aufeis to the northwest of the blister, covering these previous sites of pH measurement. Measurement attempts within the next day using the HQ40d began producing questionable, if not unreadable, results. No further basic measurements of pH were observed and the previous results from the pH probe were then considered dubious.

- **21 June**: Measurements of conductivity were made where a stream flowed onto the aufeis from a crevasse to the northeast corner of the ice blister region. Conductivity of the incoming outflow was measured at 4 $\mu$S cm$^{-1}$, at a location where the ice surrounding the water had a visually blue appearance. Just below this, the ice surrounding water had a greenish appearance by eye (suggesting the location of the aufeis). Just past this change in ice color, the conductivity was measured at 40 $\mu$S cm$^{-1}$.

- **21 June**: pH paper was used and read pH $\approx$ 5.5 for waters sampled in melt pools and the stream in the canyon as well as in fluids on the valley aufeis. These measurements were repeated multiple times and always showed pH $\approx$ 5.5-6.0 for melt pools and fluids. Melt pool fluid and stream water temperatures were consistent around 0-1°C.

- **Early during the 2014 field campaign**, it was noticed that fresh icy material carried onto the aufeis by the outburst flood or by water flow from a glacial crevasse could be covered in yellow precipitates within one day. Furthermore, areas where aufeis was cleared of yellow precipitates, the ice would again be covered with yellow deposits within one day.
21 June: It was noticed that the top of the glacier was covered in cryoconite holes and cryoconite appeared brown and grainy. The “grains” in this glacial cryoconite were easily broken when touched with a polyethylene pipette.

22 June: While sampling from fresh sulfur on snow (Figure A1.2), I wondered if it was from H$_2$S from below forming S$^0$ on the snow (perhaps mediated by biological processes), or if it could be S$^0$ migrating up through the snow and depositing at the surface (or both). Later that same day, a “snow cone” in the canyon aufeis region was sliced in half and observed. Even though the ice had been layered in growth (or melting), the yellow precipitates only occur at the surface where the ice and air interface.

23 June: While sampling from site I4, it was noted that the ice removed for the bucket had distinct cryoconites in new layers down below. This suggested that the formation of the ice is a process that is dynamic and some ice is formed as an aufeis, some of that melts and then fills over other parts of the aufeis (or there is a new insurgence of flow from the spring), and that new fluid is frozen over on top of the older cryoconite holes below.

28 June: By this point in time, the streams in the canyon and valley aufeis had started to become very deep and widened, making travel more difficult. It was determined that the active melt in the summer would likely eventually melt out all of the aufeis.

30 June: To the west of the ice blister region on the aufeis, there is a canyon cutting back into the glacier (and presumed to lead to the north of the glacier and connect with the glacial lake that is dammed by Borup Fiord Pass Glacier). On 30 June, three of us hiked a small way into this canyon, to see if there was unobserved spring flow within. Though no
spring was observed, it was noted that there were at least 3 circular regions, maybe 20-80 cm in diameter, of visibly yellow circles on the wall of the glacial ice in the canyon. These circles are roughly the size of the spring conduit previously imaged and reported by Grasby et al. (2003). Moreover, the location of these circles of yellow material are within the same region where those previous springs were observed in 2000.

A1.2. Samples Discussed in Chapter 2

The samples presented and discussed in Chapter 2 only represent a fraction of the total sampled sites at Borup Fiord Pass in 2014. Only a subset of the full sample list was reported for brevity, though the samples selected for consideration appear to represent the majority of the samples collected. Also, the samples and sites that were presented in Chapter 2 are those for which samples were subjected to the greatest number of analyses and/or for which the CBE was the most acceptable (closest to zero percent error). Table A1.1 presents some general site descriptions and images for each of the sites discussed in Chapter 2.

A1.3. Charge Balance Error (CBE)

Charge balance was performed by converting concentrations of aqueous anions and cations to molar equivalents of charge per kilogram of sample. For charge balance, nitrite and phosphate were removed (as they weren’t detected); bromide and thiosulfate were included; manganese was assigned an assumed charge of 2+ (the most common oxidation state in most systems); iron was assigned a 2+ charge (the most probable oxidation state for dissolved iron in the fluids at Borup); and SiO$_2$ was removed as it does not contribute to the overall electronic charge. All analytes below detection level were considered as zeroes (assuming concentrations to be at detection level did not
Table A1.1. Sample sites presented in Chapter 2

The sites (as presented in Chapter 2) are highlighted to give their locations and some sample information. Descriptions include the types of samples collected and intended analyses for those materials. Images of each sampling location are also shown. Where present, GPS coordinates are in NAD83 units. (Table continues for multiple pages.)

<table>
<thead>
<tr>
<th>Site</th>
<th>Description</th>
<th>Image</th>
</tr>
</thead>
<tbody>
<tr>
<td>GMW1</td>
<td>Highest point sampled on the glacier; north of site where glacial cryoconite was collected (Fig. 2.11). Meltwater from surface glacial ice in large pores sampled for aqueous geochem. Collected on 23 June.</td>
<td><img src="image1.jpg" alt="Image" /></td>
</tr>
<tr>
<td>GMW2</td>
<td>On top of the glacier, just above the aufeis. Noticed lines of yellow precipitates higher on the glacial ice. Sampled for DNA and material collected on 28 June.</td>
<td><img src="image2.jpg" alt="Image" /></td>
</tr>
<tr>
<td>MP1</td>
<td>On top of ice blister on the aufeis. Sampled for DNA and aqueous geochem on 27 June. Fluids also collected filtered and unfiltered into vials on 27 June. Sulfide precip on 28 June. Fluid collected on 30 June. Material of cryoconite sampled on 30 June. DNA and aqueous geochem samples collected on 30 June.</td>
<td><img src="image3.jpg" alt="Image" /></td>
</tr>
<tr>
<td>Site</td>
<td>Description</td>
<td>Sampled for DNA and aqueous chem and cryoconite material collected</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>---------------------------------------------------------------------</td>
</tr>
<tr>
<td>MP3</td>
<td>Blister region, southwest of MP2. Sampled for DNA and aqueous chem and cryoconite material collected on 21 June. Fluid collected on 30 June. Material of cryoconite sampled on 30 June. DNA and aqueous geochem sampled on 30 June.</td>
<td></td>
</tr>
<tr>
<td>MP4</td>
<td>Between and southwest of sites MP2 and MP3.</td>
<td></td>
</tr>
<tr>
<td>MP5</td>
<td>In the canyon below the aufeis and ice blister, just beside lower sulfur falls. Large melt pool with copious cryoconite 2-8 cm in depth. Sampled for DNA and aqueous geochem and cryoconite collected on 22 June. DNA sampled and cryoconite collected on 30 June.</td>
<td></td>
</tr>
<tr>
<td>I1</td>
<td>~10 m east of the ice blister on the aufeis. Collected on 27 June.</td>
<td></td>
</tr>
<tr>
<td>I2</td>
<td>Upper sulfur falls. Sampled for DNA and aqueous geochem and material of surface and ice below sampled on 22 June.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Between glacial till exposed on auifeis near ice blister and waterfall. Collected on 27 June.</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>In the canyon, just below the waterfall. N81°01.638’ W81°37.472’ Collected on 23 June. Sulfide Precip on 28 June.</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>At the mouth of the canyon. N81°01.621’ W81°36.687’ Collected on 23 June. Sulfide Precip on 28 June.</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Far downstream on valley auifeis. N81°01.621’ W81°36.687’ Material collected and sulfide precip on 28 June.</td>
<td></td>
</tr>
<tr>
<td>Lysimeter</td>
<td>In a small melt pool to the east of MP5 in the canyon. Material inside the lysimeter sampled on 1 July, after 1 day of sitting in a pool of fluid (roughly in the region of the yellow circle in the image).</td>
<td></td>
</tr>
</tbody>
</table>
significantly improve charge balance). Also, sulfide values were added for samples where the sample for ICP-OES and IC was collected at the same time as the sulfide precipitation sample. The error in charge balance was then determined using the conventional charge balance error (CBE). The CBE for each sample was calculated as:

$$CBE = \frac{\sum[cation\ charge] + \sum[anion\ charge]}{\sum[cation\ charge] - \sum[anion\ charge]} \times 100$$

CBE allows for a consideration of the error in the charge balance, including whether the charge balance is dominated by negative charges contributed by anions (a negative CBE) or positive charges contributed by cations (a positive CBE). Such considerations of CBE for the sample data are presented in §2.3.1.

A1.4. Saturation Index Calculations for Gypsum and Calcite

The SpecE8 package of Geochemist’s Workbench (Aqueous Solutions, LLC.; Champaign, Illinois) was used to calculate saturation indices (SI) for gypsum (CaSO$_4$$\cdot$2H$_2$O) and calcite (CaCO$_3$) in samples of melt pool fluid and ice from the aufeis (see Chapter 2 and §A1.2 above). Charge balance error (CBE), total dissolved solids (TDS), and carbonate alkalinity were also calculated. These calculations were made assuming T=0°C and pH=6.0 and using only data for the following chemical species: F$^-$, Cl$^-$, Br$^-$, NO$_3^-$, SO$_4^{2-}$, Mn$^{2+}$, Ca$^{2+}$, Na$^+$, and K$^+$. As bicarbonate (HCO$_3^-$) was not measured in-field, the calculation assumed bicarbonate equal to a value near the maximum observed in the sulfide springs from previous research at Borup Fiord Pass ([HCO$_3^-$] was set at 1.0 mM; see §2.3.1). Setting [HCO$_3^-$] to 0.001 mM did not significantly affect gypsum saturation, but greatly decreased calcite saturation (as dissolved carbonate is one of the primary controls on calcite saturation). Calculations of SI for calcite may thus be considered maxima, within the constraints of setting bicarbonate concentrations to previously measured values in active springs. Where measurements for a chemical species was below detection, the value was set at the detection
level for calculation (see Tables 2.2 and 2.3). The data from these calculations is presented in Table A1.2. The CBE calculations use only the chemical species and values computed by the program and show that charge balance is greatly in error in most of these samples (see §2.3.1).

Saturation indices can be used to determine the saturation of minerals relative to a fluid composition. SI values close to zero represent a fluid that is near to saturation with a mineral, while SI > 0 is supersaturated and SI < 0 is undersaturated. The calculations show that the samples are mostly near to saturation with respect to gypsum but highly undersaturated with respect to calcite (calculations performed with lower bicarbonate concentrations are even more undersaturated). However, as the CBE values reveal poor charge balance in the chemistry (see §2.3.1), the results of saturation calculations, while informative, suffer from potential issues in aqueous chemical analyses.

**A1.5. Hydrogen, Ethylene, and Acetylene in Melt Pools**

Bubble stripping was conducted on samples MP2, MP3, and MP4 to collect dissolved gases within fluids. The sample for MP2 was collected on 22 June 2014, while MP3 and MP4 bubble stripped samples were collected on 27 June 2014. The concentrations of hydrogen, ethylene, and acetylene were measured by Microseeps/Pace Analytical Energy Services, LLC. (Pittsburg, PA) and analyzed on 18 October 2014. The data are reported below in Table A1.3. Only hydrogen measurements were above the practical quantitation limit.
Table A1.2. Saturation calculations for gypsum and calcite in melt pool and ice samples
Data were computed using the SpecE8 package of Geochemist’s Workbench (see text for details on constraints). Saturation indices (SI) for gypsum and calcite are shown only for melt pool and ice samples. Charge balance error (CBE), total dissolved solids (TDS), and alkalinity (as carbonate) were computed as well. As bicarbonate concentration was set at 1.0 mM, alkalinity is constrained to be close to this value and does not necessarily reflect the true chemistry of the samples (alkalinity was not measured in-field).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Date Collected</th>
<th>CBE</th>
<th>TDS (mg/kg)</th>
<th>Alkalinity (mg/kg as CO$_3^{2-}$)</th>
<th>SI$_{gypsum}$</th>
<th>SI$_{calcite}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP1</td>
<td>27</td>
<td>-5</td>
<td>756</td>
<td>11.6</td>
<td>-1.0</td>
<td>-2.5</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>-7</td>
<td>440</td>
<td>11.4</td>
<td>-1.4</td>
<td>-2.7</td>
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<tr>
<td>MP2</td>
<td>21</td>
<td>-3</td>
<td>3799</td>
<td>12.5</td>
<td>-0.5</td>
<td>-2.2</td>
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<td></td>
<td>23</td>
<td>-46</td>
<td>6308</td>
<td>12.7</td>
<td>-0.4</td>
<td>-2.3</td>
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<td></td>
<td>30</td>
<td>63</td>
<td>1529</td>
<td>12.0</td>
<td>-0.8</td>
<td>-2.3</td>
</tr>
<tr>
<td></td>
<td>30 (ice)</td>
<td>-17</td>
<td>4817</td>
<td>12.6</td>
<td>-0.4</td>
<td>-2.2</td>
</tr>
<tr>
<td>MP3</td>
<td>11</td>
<td></td>
<td>1631</td>
<td>12.0</td>
<td>-0.6</td>
<td>-2.3</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>-54</td>
<td>2111</td>
<td>12.0</td>
<td>-0.8</td>
<td>-2.5</td>
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<td>MP4</td>
<td>26</td>
<td>-18</td>
<td>2802</td>
<td>12.2</td>
<td>-0.5</td>
<td>-2.3</td>
</tr>
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<td></td>
<td>30</td>
<td>-19</td>
<td>1514</td>
<td>11.9</td>
<td>-0.8</td>
<td>-2.4</td>
</tr>
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<td>MP5</td>
<td>22</td>
<td>1</td>
<td>6211</td>
<td>12.8</td>
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<td>-2.1</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>-73</td>
<td>2271</td>
<td>12.1</td>
<td>-0.7</td>
<td>-2.5</td>
</tr>
<tr>
<td>I1</td>
<td>28</td>
<td>1</td>
<td>1897</td>
<td>12.0</td>
<td>-0.5</td>
<td>-2.2</td>
</tr>
<tr>
<td>I2</td>
<td>22 (crust)</td>
<td>10</td>
<td>250</td>
<td>11.2</td>
<td>-2.0</td>
<td>-2.9</td>
</tr>
<tr>
<td></td>
<td>22</td>
<td>-3</td>
<td>3449</td>
<td>12.4</td>
<td>-0.4</td>
<td>-2.2</td>
</tr>
<tr>
<td>I3</td>
<td>28</td>
<td>-12</td>
<td>2360</td>
<td>12.1</td>
<td>-0.6</td>
<td>-2.3</td>
</tr>
<tr>
<td>I4</td>
<td>25</td>
<td>23</td>
<td>607</td>
<td>11.5</td>
<td>-1.7</td>
<td>-2.8</td>
</tr>
<tr>
<td>I5</td>
<td>25</td>
<td>-3</td>
<td>639</td>
<td>11.5</td>
<td>-1.6</td>
<td>-2.8</td>
</tr>
<tr>
<td>I6</td>
<td>28</td>
<td>10</td>
<td>632</td>
<td>11.5</td>
<td>-1.2</td>
<td>-2.6</td>
</tr>
</tbody>
</table>
### Table A1.3. Dissolved gas analyses from melt pool samples

Concentrations of dissolved hydrogen, ethylene, and acetylene gases from bubble stripped samples of melt pool samples MP2, MP3, and MP4 are reported. “PQL” stands for Practical Quantitation Limit, while “MDL” stands for Minimum Detection Limit.

<table>
<thead>
<tr>
<th></th>
<th>Melt Pool Samples</th>
<th>PQL</th>
<th>MDL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MP2</td>
<td>MP3</td>
<td>MP4</td>
</tr>
<tr>
<td>Hydrogen (H(_2); nM)</td>
<td>29</td>
<td>2.2</td>
<td>1.5</td>
</tr>
<tr>
<td>Ethylene (Ethene; C(_2)H(_4); µg/L)</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
</tr>
<tr>
<td>Acetylene (Ethyne; C(_2)H(_2); µg/L)</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
</tr>
</tbody>
</table>
APPENDIX 2:
SUPPLEMENTARY INFORMATION FOR CHAPTER 3

A2.1. Material within cryoconite holes

Material that had precipitated and collected within cryoconite holes appeared light in color, had a fine texture, and was easily sucked up by a pipette for collection (we note the coloration and texture here as cryoconite on the glacier and down-valley, beyond the aufeis, appeared dark brown and clumped into grains). Figure A2.1 shows the cryoconite holes and collected material within the melt pool sampled for this study.

A2.2. Precipitation of sulfide on a silver film deposited in the melt pool

A film of silver was placed in the melt pool from this study (Figure A2.2). The film almost immediately reacted with sulfide in the melt pool, forming AgS.

A2.3. X-ray diffraction (XRD) of sulfur bubbles and cryoconite

To test the replicability of the finding of allotropes of elemental sulfur in our sulfur bubble sample, we thawed and ran more of the material with XRD. The original finding of monoclinic sulfur phases came from data collected in April 2015. Our test for replicability took place in September 2015 (Figure A2.3). Furthermore, cryoconite material from this same sample location was thawed and prepared in the same way as sulfur bubble material (see main text). DiffracEVA revealed the presence of gypsum, halite, and pyrite (Figure A2.4).
Figure A2.1. Picture shows cryoconite holes in melt pool

The cryoconite hole with material in shadow near the center of the image is ~2 cm in diameter.
Figure A2.2. Images of silver foil reaction with sulfide in the melt pool
The image at the left shows co-author Lau depositing a film of silver in the melt pool from this study. The image at the right shows co-author Templeton holding the film after reaction with sulfide. The darkening of the film from formation of AgS stand out along with two dark vertical lines where sulfide-rich fluid traveled along posts that were used to hold the film.
Figure A2.3. Sulfur bubble diffractograms from two separate runs

Normalized intensities (counts) vs. angle (2θ) for material from sulfur bubbles. Compare to Figure 3 in the main text.
Figure A2.4. Diffractogram for cryoconite

Normalized intensity (counts) vs. angle (2θ) for cryoconite material. Peaks identified as gypsum (red lines), rapidcreekite (green lines), halite (blue lines), and calcite (orange line) are shown. The gypsum peak at 11.6° has been cut to 30% of max intensity (indicated by open circle) to make other peaks apparent to the reader.
A2.4. Sulfur K-edge XANES of sulfur bubbles

Bulk sulfur K-edge x-ray absorption near edge structure (XANES) spectroscopy was performed on the sulfur bubbles using beamline (BL) 4-3 of the Stanford Synchrotron Radiation Lightsource (SSRL). The sample was coated onto a sulfur-free polypropylene tape and immediately placed into a liquid He cryostream. Data were collected using the following energies and steps:

<table>
<thead>
<tr>
<th>Energy Region (eV)</th>
<th>Increment (eV)</th>
<th># of Points in Region</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2400-2460</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>2460-2478</td>
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Three replicate spectra of the sulfur bubble sample were collected. The spectra were averaged and then normalized, setting the pre-edge region equal to zero absorption and the post-edge vacuum photoelectron emission region to unity. The normalized average spectrum was then compared to data previously collected for a variety of sulfur compounds on BL 4-3. The spectrum was best fit using solely a non-diluted sampled of precipitated sulfur (Fisher Scientific, Hampton, New Hampshire, USA) that was run under the same conditions as the sample. Figure A2.5 shows the comparison of the normalized average spectrum of the sulfur bubbles compared to the spectrum for precipitated sulfur. The two spectra correlate well, though a minor feature in the sulfur bubble spectra ~2482.7 eV likely derives from absorption due to sulfate within the sample.

Sulfur suffers greatly from self-absorption effects in fluorescence XANES spectroscopy. Manceau and Nagy (2012) propose a maximum limit of 20,000 ppm (2%) of sulfur within a sample to avoid self-absorption effects. The sulfur bubble material appears primarily to be composed of sulfur and so likely suffers from such self-absorption issues. However, since we are comparing it here to a sample of non-diluted precipitated sulfur, the standard spectrum is likely also self-absorbed.
Figure A2.5 Bulk S XANES spectra of sulfur bubbles and precipitated $S^0$
The S K-edge XANES spectrum of elemental sulfur is distinct and can be compared among various forms of elemental sulfur (e.g., Pickering et al., 2001; Foriel et al., 2004; George et al., 2008; Morgan et al., 2009; Almkvist et al., 2010). Figure A2.6 shows the spectrum from the sulfur bubbles compared against multiple forms of elemental sulfur. These include precipitated sulfur (same as in Figure A2.5), mineral sulfur (purchased from a local mineral supplier in Boulder, Colorado, USA), rosickyite (the mineral form of γ-S₈), and spectral data for elemental sulfur published online by the European Synchrotron Radiation Facility (ESRF; collected by Magnus Sandström, of Stockholm University, in 2005 and available online at http://www.esrf.eu/files/live/sites/www/files/UsersAndScience/Experiments/Imaging/ID21/php/sulfur/sulfur_tr.pdf).

The similarity between the sulfur bubble spectrum and that of precipitated elemental sulfur purchased from a chemical supplier can be observed here once more. It is interesting that these forms of sulfur show less pronounced primary absorption peaks than the crystalline forms of sulfur (mineral sulfur and rosickyite). George et al. (2008) have shown that changes in peak intensity and broadening for elemental sulfur can be due to particle sizes within a sample. This suggests that particle sizes between the sulfur bubbles and the precipitated sulfur are similar. The sulfur bubbles and precipitated sulfur spectra can be compared to the spectra modeled by George et al. (2008) for particles of elemental sulfur that have a spherical particle diameter of 10 μm, while mineral sulfur and rosickyite are more similar to the particles modeled at spherical diameters of 2.2 μm. Although we have not investigated the particle sizes of the precipitated sulfur, our SEM images (Figure 3.5) show that there are globular sulfur particles in our sample in the 5-10 μm size range. However, as mentioned previously, self-absorption effects may also alter S K-edge XANES spectra for sulfur-rich materials like these, and so some mixture of effects from particle size and self-absorption cause the spectra we see for our natural sample.

The ESRF Sulfur spectrum appears more similar to the spectra for mineral sulfur and
Figure A2.6. Sulfur K-edge XANES spectra for multiple sulfur models compared to data for the sulfur bubbles

The spectra presented have been offset. Spectra are as follows: Sulfur Bubbles (solid black line), Precipitated S0 (red dash line), Mineral Sulfur (green dash dot line), ESRF Sulfur (blue long dash line), and Rosickyte (purple long dash dot dot line). Models and spectra presented are further discussed in the text. A small, broad peak in the rosickyte spectrum ~2482.7 eV is likely caused by a trace amount of sulfate from this natural mineral sample.
rosickyite. This S0 sample is reported to have also been elemental sulfur purchased from a chemical supplier (Aldrich), though it is remarked to have been of “good” crystallinity. This sample may represent smaller particle sizes than the sulfur bubbles and precipitated sulfur (George et al., 2008). It should be noted though that this spectrum and was collected in transmission mode, as opposed to fluorescence mode for the other spectra in Figure A2.6, and may represent a more self-absorbed spectrum. Also, we note here that this spectrum was calibrated to the white line for sulfate at 2482.5 eV and not the leading edge of thiosulfate, which explains a slight offset in the absorption energy of the leading edge.

A2.5. Fourier transform infrared (FTIR) spectroscopy of sulfur bubbles and inorganic functional group interpretations

Fourier transform infrared (FTIR) spectra for the sulfur bubbles showed multiple peak absorptions that can be explained through comparison with inorganic salts of sulfate, thiosulfate, and carbonate, as well as elemental sulfur (Figure A2.7). For instance, the O-H stretch region shows an intense, broad peak centered at 3405 cm\(^{-1}\), most likely from a mix of absorptions from hydrated sulfate and thiosulfate salts. Shoulders on this broad peak around 3230 and 3550 cm\(^{-1}\) also match corresponding O-H stretch absorptions from hydrated sulfates (Figure A2.7). A small, sharp peak at 3676 cm\(^{-1}\) also indicates O-H stretching (though we do not further interpret that feature at this time). Multiple features throughout the spectrum support the presence of hydrated sulfates and thiosulfate. The sharp feature centered at 1631 cm\(^{-1}\) is interpreted as an olefinic -C=C- stretch, but the sharp shoulder feature at 1620 cm\(^{-1}\) and broad shoulder at 1695 cm\(^{-1}\) likely derive from inorganic sulfate and thiosulfate groups. Also, another shoulder feature at 1655 cm\(^{-1}\) is interpreted as deriving from thiosulfate absorptions.
Figure A2.7. FTIR absorbance for sulfur bubbles compared to relevant inorganic model compounds
Sulfur bubble FTIR data are compared to data collected for dried calcium sulfate dihydrate, sodium thiosulfate pentahydrate, calcium carbonate, and elemental sulfur. Corresponding absorbance peak locations are marked with dashed lines (and a dashed box in the inorganic sulfate absorbance region) and further discussed in the text. Spectra are offset for ease of viewing. The spectra for calcium sulfate dihydrate and calcium carbonate have been reduced by 40% and 60%, respectively, to more closely match the intensities of the corresponding peak features in the sample data.
The sharp absorption peaks at 1138 and 1124 cm\(^{-1}\), the associated shoulder around 1153 cm\(^{-1}\), and the sharp peaks at 658 and 604 cm\(^{-1}\) are interpreted here to be contributed from S-O stretching in inorganic sulfates (Coates, 2000; Lane, 2007). The peak at 1103 cm\(^{-1}\) and the dual peaks at 1016 and 994 cm\(^{-1}\) may also represent S-O stretching within a variety of sulfate minerals (Lane, 2007), but can also derive from S-O stretching in thiosulfate. For instance, Degenhardt and McQuillan (1999) used FTIR spectroscopy to analyze the adsorption of aqueous thiosulfate onto chromium oxide hydroxide colloids and identified peaks at 1104 and 994 cm\(^{-1}\) as deriving from absorptions by thiosulfate S-O bonds. This supports the interpretation of these absorption features as deriving from thiosulfate. We report 0.172 mM thiosulfate in the melt pool fluid (see Table 3.1), so it’s not surprising that thiosulfate may be present in the sulfur bubble material as well.

A pair of absorption bands in the sulfur bubble FTIR spectrum at 465 and 451 cm\(^{-1}\) may be indicative of S-S stretching within S\(_8\) molecules, as documented for low temperature studies of crystals of S\(_8\) by Eckert and Steudel (2003). Although these features are usually too weak to be of practical importance, the abundance of elemental sulfur (revealed through XAS; section A2.4) in this sample supports the interpretation that these features derive from S-S bond absorptions. We also interpret the presence of minor concentrations of carbonates in this material from diagnostic features at 1427 and 875 cm\(^{-1}\) (Figure A2.7). Carbonates generally have very intense absorptions, and the high transmission for these features in our data suggest that carbonates are only present in minor amounts.

In order to gain a better understanding of the possible contributions of hydrates sulfates and thiosulfates, carbonates, and elemental sulfur, we analyzed mixtures of these compounds (with additions of organic materials) and attempted to reproduce the FTIR spectrum for the sulfur bubbles. For instance, one mixture of 78.9% precipitated sulfur (S\(^0\)), 9.2% calcium sulfate dihydrate (CaSO\(_4\)-2H\(_2\)O), 8.6% sodium thiosulfate pentahydrate (Na\(_2\)S\(_2\)O\(_3\)-5H\(_2\)O), 3.1% agarose, and 0.2% calcium carbonate (CaCO\(_3\)) produced a spectrum that was very close in structure to the FTIR
spectrum for the sulfur bubbles (Figure A2.8), except for the organic functional groups we interpreted for the sulfur bubbles (see main text). Although we had added agarose to simulate organic material, the low concentration of agarose did not produce significant absorption peaks. The higher amounts of thiosulfate and sulfate in the model mixture appear surprising at first, as our XAS data appeared to show primarily elemental sulfur in this material with a minor peak for sulfate in the sulfur bubbles (Figure A2.5), however a consideration of the mole fractions of sulfur contributed by the model compounds is more revealing. In the mixture, elemental sulfur comprises ~95 molar percent of the total sulfur, while sulfate and thiosulfate account for ~2% and ~3%, respectively. Although we do not have bulk sulfur XAS data for a similar mixture of sulfur compounds, it is likely that such a mixture would reveal an XAS spectrum similar to the one for the sulfur bubbles.

**A2.6. EDS data from FE-SEM**

Energy dispersive spectroscopy (EDS) was performed on several regions within the sulfur bubble material. Figure A2.9 shows one of the regions where EDS was conducted. This region is the same as that shown in Figure 3.4b.

**A2.7. Images showing the destruction of the sulfur material under the EDS**

Figure A2.10 shows a region of the sulfur bubble material that was analyzed using EDS. In this region, two areas of the smooth material were analyzed and one area of sulfur globules was analyzed. After the EDS spectra were collected, the region was then imaged using secondary electron mode and an accelerating voltage of 15 kV. Here the sulfur globule material appeared undisturbed while the smooth phase appeared to be destroyed by the beam. Where the smooth material was removed, sulfur globules below and perhaps within can be observed.
Figure A2.8. FTIR transmission data for sulfur bubble material compared to a mixture of model compounds
The sulfur bubble FTIR spectrum was compared to a complex mixture of calcium sulfate dihydrate, sodium thiosulfate pentahydrate, calcium carbonate, elemental sulfur, and agarose. The structure of inorganic functional group absorptions was mostly replicated with this mixture (agarose did not appear to add appreciable absorptions from organic functional groups).
Figure A2.9. EDS of the sulfur bubbles
Top left shows the FE-SEM image from Figure 4c under secondary electron mode and an accelerating voltage of 3 kV. Top right shows the same region with an accelerating voltage of 15.0 kV and at a magnification of 7,500x. Two regions were used for EDS analysis. Bottom images show the EDS x-ray fluorescence counts vs. energy (keV) for the two regions from the top right image. Peaks have been identified.
Figure A2.10. EDS destruction of smooth material in the sulfur bubbles
Top left shows a region identified through EDS where some smooth material and some associated sulfur globule material were analyzed. The image was produced with an accelerating voltage of 15.0 kV and at a magnification of 7,000x. Top right shows the FE-SEM image for the same region as the top left after the EDS was conducted. Bottom images show the EDS x-ray fluorescence counts vs. energy (keV) for the three regions from the top left image. Peaks have been identified.
APPENDIX 3:

SUPPLEMENTARY INFORMATION FOR CHAPTER 4

A3.1. Satellite Imagery and Field Observations

The region bearing the alteration features is topographically high compared to the surrounding valley floor. This can be observed in Figure A3.1a, where a hillshade digital elevation model shows this topography. The hill can also be observed in Figure A3.1b, which highlights locations of key features on the hill.

Although only two of the alteration features were sampled for this study, six of these features have been identified at Borup Fiord Pass (Fig. A3.2). Five of these features all occur within a small region (see white ellipse in Fig. A3.1b) while another, the Fault Feature from this study, occurs ~300 m to the north (yellow arrow in Fig. A3.1b), very close to where the strike-slip fault crosses the valley.

Figure A3.3 highlights the red staining and pyrite veining that was observed at Borup Fiord Pass in the summer of 2014. For instance, Figure A3.3b shows the mouth of “pyrite canyon” (the same location as is indicated with the blue arrow in Fig. A3.1b). The red staining of the rocks around the canyon mouth is apparent. Figure A3.3c shows more of this red staining in pyrite canyon. Although the pyrite veins are difficult to see in this image, they were observed in these same rocks, which are located just past the mouth of pyrite canyon in Figure A3.3b. Red staining of rocks in and around a lake close to the alteration features can also be seen in Figure A3.3d. These observations reveal that iron oxides are far more abundant in the region than has previously been reported (see Grasby et al., 2012).

A3.2. X-ray Diffraction (XRD) Data

X-ray diffraction (XRD) data were processed in Jade 9 through first applying a background
Figure A3.1. Satellite images
A digital elevation model (DEM) of the valley of Borup Fiord Pass in hillshade, as processed by ArcticDEM, shows the topography of the valley. The red circle highlights the topographically high region of the alteration features. The region is also shown in a satellite image in b, where the white circle shows roughly the region where most of the alteration features are located. The red arrow shows the location of the best exposure of the strike-slip fault within the central region of the valley. The yellow arrow highlights the location of the Fault Feature, at the edge of the hill. The green arrow shows the location of a lake where multiple red stained rocks were observed. The blue arrow shows the region of a canyon that cuts along the side of the hill (pyrite was observed in veins within carbonate rock in this canyon cut). Satellite images from Digital Globe (https://www.digitalglobe.com/). The DEM was created from DigitalGlobe, Inc., imagery and funded under National Science Foundation awards 1043681, 1559691, and 1542736, by Arctic DEM (http://www.pgc.umn.edu/arcticdem). Scales are 1 km in a and 200 m in b.
Figure A3.2. Alteration Features of Borup Fiord Pass
All six of the alteration features are shown. The features in c and f were sampled for this study. The elliptical features are stained red by the presence of iron oxides, with two of the features (in # and #) showing white, gypsum-rich interior regions. Approximate diameters of the features in a-f are 5, 2, 3, 1, 0.5, and 3 m, respectively.
Figure A3.3. Red staining and pyrite veining at Borup Fiord Pass
An image taken from the east side of the valley (a) shows the structure of the valley around the alteration feature region (circled in red; the hill is estimated to be 1 km in diameter). The black arrow points to the location of the sulfide-rich aufeis observed in 2014. The mouth of pyrite canyon, which opens to a small pool of water, is shown in b (human shown for scale), and c shows a close-up of rocks stained in red (and veined with pyrite, though not obvious at the scale of the image). The scale bar in c is estimated to be 30 cm. The lake which sits slightly below the alteration features on the hill is shown in d, with the yellow arrow indicating the location of the close-up shot of red-stained rocks shown in e (human for scale).
correction routine (the data were of high quality and backgrounds were minimal for all samples). Data were then visually shifted in $\theta$ to fit the maximum XRD lines of gypsum (a major component of all samples; JCPDS PDF #00-033-0311); shifts were no more than 1° $\theta$ (and often less), but improved results of the search/match routine within Jade 9 for potential mineral components. Components were determined visually as well as through search/match fitting routines. Although the XRD data were not collected in a manner which allows quantitative determination of mineral component fractions, the relative composition of each sample was qualitatively determined through comparisons of peak heights (where it was assumed that the component giving the highest intensity peak is also most likely the most abundant component). Figures A3.4-15 contain the XRD diffractograms for all of the samples from this work. Sulfur, abbreviated as “S”, indicates only the common alpha-cyclooctasulfur ($\alpha$-S$_8$) allotrope.

**A3.3. Raman Microspectroscopy Data**

Raman microspectroscopy maps were processed using LabSpec. The Horiba ICS Correction (an intensity correction calculation based on the laser source and optics) was applied to all data before processing. Automatic baselining was applied to all data by using polynomial fits (3$^{rd}$ or 4$^{th}$ degree) and fitting over a minimum of 100 points. In some cases, depending on noise, 10-100 noise points were added during baselining. Classical least squares (CLS) fitting was used to fit spectral maps with detected components. Multivariate curve resolution (MCR) was used to search for potential components of maps, though those operations were not performed for all data. Unknown peaks in Raman spectra were searched using Know-It-All and the RRUFF database (see Lafuente, Downs, Yang, & Stone, 2015; also, http://rruff.info/). Sections A3.3.1-4 present further figures from Raman microspectroscopy of samples from the alteration features.
Figure A3.4. X-ray diffractogram of sample T1

Figure A3.5. X-ray diffractogram of sample T2
Figure A3.6. X-ray diffractogram of sample S1

Figure A3.7. X-ray diffractogram of sample S2
Figure A3.8. X-ray diffractogram of sample S3

Figure A3.9. X-ray diffractogram of sample C1
Figure A3.10. X-ray diffractogram of sample C2

Figure A3.11. X-ray diffractogram of sample C3
Figure A3.12. X-ray diffractogram of sample C4

Figure A3.13. X-ray diffractogram of sample FF1
Figure A3.14. X-ray diffractogram of sample FF2

Figure A3.15. X-ray diffractogram of sample FF3
A3.3.1 Raman Mapping and Spectra for Top Samples (T1 and T2)

Figures A3.16 and A3.17 highlight the observations of grains from sample T1 that were used to show associations of organic carbon with pyrite and elemental sulfur ($S^0$) in Figure 4.11. Figure A3.16 highlights the detections of anatase, pyrite, $S^0$, gypsum, and organic carbon in the pyrite grain that was presented in Figure 4.11a,c. Figure A3.17, meanwhile, shows identification of pyrite, $S^0$, gypsum, and organic carbon in the spectral data from the mapped region presented in Figure 4.11b,d. Figure A3.18 shows a Raman spectral map and fitting for data collected within the region presented in Figure 4.11b. These data are highly noisy, but do show the presence of abundant goethite as well as anatase, quartz, gypsum, and potentially some organic carbon. The filament in this region (and highlighted with the white arrow in Fig. 4.11b) was highly fluorescent to the laser and did not return interpretable data.

A3.3.2. Raman Mapping and Spectra for Sidewall Samples (S2 and S3)

Further Raman microspectroscopy data are presented here for regions of samples S2 and S3. Figure A3.19 shows results of CLS fitting for a region of sample S2 (see Fig. 4.6). This region shows large pyrite grains (up to ~100 µm in width) surrounded by red-stained tabular grains of gypsum and round grains of goethite. Figure A3.19 reveals fits for gypsum, goethite, and pyrite spectral data throughout the region. Micron-sized spots of $S^0$ as well as organic carbon are found associated with the large pyrite grain in this region.

Figure A3.20 shows the results of fitting a Raman map for sample S3 (as shown in Fig. 4.7) using CLS fitting. The map fits showed the presence of $S^0$, gypsum, and organic carbon in this sample. Elemental sulfur appears to dominate the material in this mapped region. Grasby et al. (2012) had previously identified up to 15% $S^0$ within the white material of the central surface
Figure A3.16. Raman spectral mapping of the pyrite grain in Figure 4.11a

The pyrite grain is shown surrounded by tabular grains of gypsum in a. The yellow box in a shows the region of Raman spectral mapping, represented by the colorized Raman map in b. The map was collected with 1 μm steps and 3 iterations of 3 seconds each for data collection at each step. A 50x microscope objective was used and the 525 nm laser was reduced to 5% intensity to avoid burning of sample material. The spectral map shown in b is colorized for spectral fits as follows: red for pyrite (375-380 cm⁻¹), green for gypsum (1000-1010 cm⁻¹), and blue for the G-band of organic carbon (1500-1650 cm⁻¹), yellow for $S^0$ (210-220 cm⁻¹) and one dark blue spot for anatase (110-160 cm⁻¹). The arrows were included to highlight the spots containing the most $S^0$ (yellow arrow) and organic carbon (orange arrow) as well as the spot of anatase (white arrow). The spectra in d show fits of RRUFF reference spectra to the best spectra for $S^0$, anatase, and organic carbon in this region (shown as red, green, and blue spectra, respectively).
Figure A3.17. Raman spectral mapping of the pyrite grain in Figure 4.11b

The dark circular region reported in Figure 4.11 to contain organic carbon surrounded S\(^0\) is again shown in a, surrounded by tabular grains of gypsum and globular S\(^0\) (as shown in spectral map in b). The yellow box in a shows the location of the map in b. The map was collected with 1 \(\mu\)m steps and 2 iterations of 4 seconds each for data collection at each step. A 50x microscope objective was used and the 525 nm laser was reduced to 5% intensity to avoid burning of sample material. The spectral map shown in b is colorized for spectral fits as follows: red for S\(^0\) (205-225 cm\(^{-1}\)), green for gypsum (1000-1020 cm\(^{-1}\)), and blue for the G-band of organic carbon (1500-1650 cm\(^{-1}\)). The Raman spectra shown in c are the best representative spectra from the map in b for S\(^0\), gypsum, and organic carbon (red, green, and blue spectra, respectively). Also shown are RRUFF reference spectra for pyrite, S\(^0\), and gypsum (no pyrite was detected in the map in b).
Figure A3.18. Raman spectral mapping of the sample T2

The region of sample T2 with the filament (see Fig. 4.5) was mapped using Raman microspectroscopy (a,b). The map was collected with 1 µm steps and 3 iterations of 5 seconds each for data collection at each step. A 50x microscope objective was used and the 525 nm laser was reduced to 1% intensity to avoid burning of sample material (although sample materials rich in iron oxides tend to burn even at the lowest laser intensities). The spectral map shown in b is colorized for spectral fits as follows: red for goethite (360-400 cm\(^{-1}\)), green for gypsum (1000-1020 cm\(^{-1}\)), and blue for the G-band of organic carbon (1500-1650 cm\(^{-1}\)). The Raman spectra in c-f are the best representative spectra from the map in b for fitting with anatase (shown in red in c), gypsum (shown in green in d), goethite (shown in orange in e, though present in all spectra from this mapped region), and quartz and organic carbon (blue and yellow in f, respectively). The data were very noisy and the potential detection of peaks fit with organic carbon is considered dubious.
Figure A3.19. CLS fitting of a Raman map for sample S2

The region shown in the image (upper left) is a subset of the region presented in Figure 4.7. Raman map data were collected with 4 µm steps and 3 iterations of 5 seconds each for data collection at each step. A 10x microscope objective was used and the 525 nm laser was reduced to 5% intensity to avoid burning of sample material. Four of the images produced through CLS fitting were fit with RRUFF reference spectra: pyrite (R050190), S0 (R040135), goethite (R050142), gypsum (R060509). Organic carbon was fit using my own organic carbon spectra. Scale bars are 40 µm.
Figure A3.20. CLS fitting of the Raman map for sample S3 shown in Figure 4.7

Only S$^0$, gypsum, and organic carbon were detected in this mapped region. Raman map data were collected with 4 µm steps and 3 iterations of 5 seconds each for data collection at each step. Map data were fit with RRUFF reference spectra for S$^0$ (R040135; red map), gypsum (R060509; green map), 12.34%), and a lab standard for organic carbon (teal map). Scale bars in the map images are 50 µm. Spectral data on the right show matches of the best spectra for organic carbon in this region. The orange arrow in the OC map is the location of the spectrum titled “Best OC Spot in S3 Map”, and the circle is a region where spectra were averaged (the averaged spectrum is titled “Average of OC-rich Spots in S3 Map”). Reference spectra for S$^0$, gypsum, and organic carbon are also shown (in red, green, and blue, respectively).
region of one feature through XRD analyses, and our results show elemental sulfur to be present throughout the features. However, Raman microspectroscopy is far more sensitive to elemental sulfur than some other techniques (such as XRD), so we cannot here quantify the amount of S⁰.

**A3.3.3. Raman Mapping and Spectra for Core Samples (C1, C2, and C3)**

This section presents further images and Raman microspectroscopy data for regions of samples C1, C2, and C3 that are shown in Figures 4.8 & 4.9. Figure A3.21 shows all of the spectral reference fits which were used to identify the components in pyrite-rich region of sample C1. As the colorized map fitting images and associated colorized spectra show, Raman microspectroscopy identified the following components in this region of the sample: pyrite, gypsum, organic carbon, quartz, S⁰, anhydrite, hematite, and calcite. A region was also found which showed a fit for silicon. Silicon is almost never in pure metallic form in nature, so it’s assumed here that the finding of a silicon-rich region has two potential interpretations: 1) silicon wafers are sometimes used for samples that have been run through XRD before or after Raman microspectroscopy analysis. Although no silicon wafers were used for sample preparation for Raman microspectroscopy (samples were prepared on glass slides), it is possible that some silicon contamination from the instrument was introduced to the samples. However, as three spots (1 µm² each) were fit with this silicon and the peak is well resolved, a second possibility is presented. 2) Although the spectral data from the map fit nearly identically with a reference spectrum of pure silicon and no silicate mineral spectra was identified within the RRUFF database or our own reference database, it is likely that these spectral data do indicate the presence of silicate minerals in the sample.

Figure A3.22 shows a microscope image of sample C2, where red and white grains of gypsum were detected. The red/orange coloration has been detected as iron (oxyhydr)oxides. Figure A3.23 also shows Raman data for sample C2. This map region showed the presence of pyrite, S⁰, gypsum, anhydrite, and organic carbon in core sample C2.
Figure A3.21. Raman spectral maps and fits for the region shown in Figure 4.8a
Three RGB colorized maps are shown. In each case, reference spectra (presented in black) are shown along with the best spectral data for each component from the map (components are colorized to match the RGB maps). Scale bars are 10 µm.
Figure A3.22. Tabular grains of gypsum in sample C2
This microscope image shows two tabular grains of gypsum in sample C2. One of these grains (on the left) is stained in red due to the presence of iron (oxyhydr)oxides. Although data are not shown here, mapping of small regions on each of these grains revealed gypsum, anhydrite, anatase and iron (oxyhydr)oxides on/in the red-stained grain, while gypsum, anhydrite, S⁰, iron (oxyhydr)oxides, and organic carbon are on/in the white grain on the right in this image.
Figure A3.23. Raman maps and spectra for sample C2 region shown in Figure 4.8c
The Raman map of this region is colorized for spectral fits in a and b. The Raman map was collected using 1 µm steps with 3 iterations of 2 seconds of data collection per step. A 50x microscope objective was used with the 525 nm laser reduced to 5% intensity. The colorized map in a shows fits for pyrite (red; fit to 365-375 cm⁻¹), S⁰ (green; fit to 205-225 cm⁻¹), and gypsum (blue; fit to 1000-1020 cm⁻¹). The spectra in c for map data are colorized to match these components, with the specific spectral data coming from the regions shown in the circle, box, and diamond in a. Reference spectra are shown for pyrite, S⁰, and gypsum. The colorized map shown in b reveals map fits for anhydrite (red; fit to 1025-1030 cm⁻¹) and the G-band of organic carbon (green; fit to 1500-1650 cm⁻¹). The spectra in d for map data are colorized to match these components, with the specific spectral data coming from the regions shown in the pentagon and triangle in b. Reference spectra are shown for S⁰, gypsum, and anhydrite. Although not plotted here, the anhydrite spectrum in d from the pentagon region shown in b also appears to contain disordered (or laser damaged) hematite (the spectrum is very similar to an RRUFF database spectrum for burnt umber).
Figures A3.24-26 all show Raman microspectroscopy data relevant to the large pyrite grain in sample C3 shown in Figure 4.9b. This pyrite grain, which appears to potentially be an etched pyrite grain from microscope images (though resolution is not adequate for a definitive identification of etchings as are seen through SEM images in Figure 4.14), is surrounded by tabular grains of gypsum (Fig. A3.24) and showed well-resolved organic carbon peaks (see Fig. 4.9). Furthermore, a small Raman map collected on this pyrite grain revealed the presence of anatase, gypsum, anhydrite, and pyrite (Fig. A3.25). However, some pyrite spectra in this map region showed splitting of the pyrite Raman peaks (teal spectrum in Fig. A3.25). Figure A3.26 further explores this pyrite Raman peak splitting. Spectra were identified with peaks at lower energies (~336 and ~367 cm\(^{-1}\)), peaks at higher energies (~342 and ~377 cm\(^{-1}\)), or a mixture of both types of peaks. Furthermore, spectra with the lower energies for pyrite peaks also revealed the presence of Raman bands for mackinawite, a tetragonal iron/nickel sulfide mineral that can bear sulfide in divalent (2-) chemical oxidation state. It is not yet known if the presence of mackinawite is also the reason for the lower energy positions of Raman bands in this material.

**A3.3.4. Organic Carbon Analyses from Raman Microspectroscopy**

Figures A3.27-30 show the fits of mixed Gaussian/Lorentzian functions and peak locations for organic carbon in samples T1, S1, C3, and FF2. Figure A3.27 shows the fitting used for sample T1 organic carbon presented in Figure 4.11. Figure A3.28 shows a microscope image of a small region of organic carbon-rich grains arranged in a line on top of a gypsum grain in sample S1. This line, called “the dagger”, revealed S\(^0\), gypsum, and organic carbon (Fig. A3.28b). The analysis of the organic carbon in “the dagger” is shown in Figure A3.28c. Figure A3.29 shows the fitting used for sample C3 organic carbon presented in the 2 spectra in Figure 4.9. Meanwhile, Figure A3.30 shows the fitting used for the large glom of organic carbon (~200 µm\(^2\)) in sample FF2 as shown in Figure 4.10d-f. The results of these fits are presented in Table A3.1.
Figure A3.24. A large pyrite grain in sample C3

One sulfide grain within the matrix of tabular gypsum crystals (a,b) was mapped using Raman microspectroscopy over a small region of the grain (~16x36 \( \mu \text{m}^2 \); teal colored box in b). The map was collected using steps of 1 \( \mu \text{m} \) with 4 iterations of 4 seconds per spot. A 50x microscope objective was used to focus the 525 nm laser.
Figure A3.25. Raman spectra from the map region shown in Figure A3.24
The primary components of the map collected in the teal box shown in Figure A3.24b are anatase, gypsum, anhydrite, and pyrite (see fits with reference data above). The teal spectrum labeled “Strong splitting of sulfide peaks” was intriguing and led to further analyses that are shown in Figure A3.26.
Figure A3.26. Splitting of pyrite Raman bands in sample C3 and the presence of mackinawite

The splitting of pyrite peaks as observed in the teal spectrum in Figure A3.25 led to a refined map fitting using energy bands within the split peaks’ regions (a). The maps shown in b-d were created by mapping to energies shown in green and red regions in the spectra in a (and match the same area as the teal box in Fig. A3.24). Maps in b-d are colorized to fit these regions, where green is the lower-energy pyrite peak and red is the higher energy pyrite peak (a). Spectra in e were collected from maps b-d, where the brown and white star in b is the location of collection of the brown spectrum in e, the yellow circle in c is the location of collection of the red spectrum in e, and the yellow circle in d is the location of collection of the green spectrum in e. As is also shown in e, pyrite spectra with the lower-energy peaks also fit with Raman band positions of a reference spectrum of mackinawite.
**Figure A3.27.** Fitting of carbon in sample T1 in Figure 4.11c,d

**Figure A3.28.** “The Dagger” in sample S1 and fitting of organic carbon

A region revealing a linear arrangement of dark particles called “the dagger”, on top of a grain of gypsum, is shown in a. Raman microspectroscopy was used to map the region in the yellow box in a, using 1 μm steps and 2 iterations of 1 second per step. The 525 nm laser was reduced to 5% intensity to avoid laser damage of the sample. An organic carbon spectrum was created from the average of the spectra within the three white crosses shown in b. The fitting of mixed Gaussian/Lorentzian function for analyses of the D- and G-bands of this organic carbon spectrum is presented in c.
Figure A3.29. Fitting of organic carbon in sample C3 spectra from Figure 4.9
The spectrum on the left is the same as is presented at the top of Figure 4.9c, while the spectrum on the right is the same as the one presented at the bottom of Figure 4.9c.

Figure A3.30. Fitting of organic carbon from FF2
The glom of organic carbon shown in Figure 4.10d-f is shown here with applied Guassian/Lorentzian functions for fitting of the D- and G-bands of organic carbon.
Table A3.1. Organic Carbon Peak Fitting from Raman Microspectroscopy

Data for several samples that were analyzed by using peak fitting routines in LabSpec6 are presented. Organic carbon peaks were fit using assumed locations of the D1, D2, D3, D4, and G bands and then allowing the program to determine the best-fit. Displayed are the locations of the D1 and G bands (in Raman shift; cm\(^{-1}\)), the R1 and R2 ratios (where R1=(D1/G) and R2=(D1/(D1+D2+G)), as well as the standard error (%) and reduced chi-square values as determined from the fitting routine. Minimum, maximum, and average values, as well as the range of measurements, are also reported.

<table>
<thead>
<tr>
<th>Sample</th>
<th>D1 Band (cm(^{-1}))</th>
<th>G Band (cm(^{-1}))</th>
<th>R1</th>
<th>R2</th>
<th>Std. Error (%)</th>
<th>Reduced X(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1 - Grain 3 (see Fig. 11a,c)</td>
<td>1349</td>
<td>1594</td>
<td>0.6</td>
<td>0.5</td>
<td>4.7</td>
<td>2.4</td>
</tr>
<tr>
<td>T1 - Grain 5 (see Fig. 11b,d)</td>
<td>1347</td>
<td>1576</td>
<td>1.0</td>
<td>0.6</td>
<td>7.1</td>
<td>2.1</td>
</tr>
<tr>
<td>T2 - Grain 1</td>
<td>1359</td>
<td>1592</td>
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<td>0.7</td>
<td>8.3</td>
<td>2.7</td>
</tr>
<tr>
<td>S1 - “Dagger” (see Fig. A28c)</td>
<td>1352</td>
<td>1587</td>
<td>0.7</td>
<td>0.6</td>
<td>13.6</td>
<td>2.1</td>
</tr>
<tr>
<td>S2 - Pyrite in Map</td>
<td>1377</td>
<td>1574</td>
<td>0.8</td>
<td>0.6</td>
<td>1.8</td>
<td>1.1</td>
</tr>
<tr>
<td>S3 - Best OC Spot</td>
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<td>0.5</td>
<td>3.0</td>
<td>3.4</td>
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<tr>
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<td>0.6</td>
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<td>0.5</td>
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<td>1.6</td>
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<tr>
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</tr>
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<td>0.6</td>
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</table>
Table A3.2. Organic Carbon Peak Fitting from Raman Microspectroscopy, Part II
Similar to Table A3.1, data for organic carbon peak fitting are presented. Included here are D1-G band separation values and FWHM measurements for the D1 and G bands. All values are expressed in Raman shift of cm⁻¹.

<table>
<thead>
<tr>
<th>Sample</th>
<th>D1 Band</th>
<th>G Band</th>
<th>G-D1 Band Separation</th>
<th>D1 FWHM</th>
<th>G FWHM</th>
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<tr>
<td>T1 - Grain 3 (see Fig. 11a,c)</td>
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<td>1576</td>
<td>229.1</td>
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<td>1587</td>
<td>235.7</td>
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<td>1574</td>
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</tr>
<tr>
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