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

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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.

1. 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 et al., 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 (S^0) 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 S^0 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 S^0 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 1a). At this site, extensive deposits of S^0 derived from sulfide-rich supraglacial springs form on ice surfaces and have been observed during summer field campaigns over many years (Grasby et al., 2003; Gleeson et al., 2010; Gleeson et al., 2011; 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.

2. 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 and 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 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 supraglacial springs that form at Borup Fiord Pass and discharge from the glacier’s surface. Elemental sulfur,

gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), 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, 2003; Grasby et al., 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 (CaSO_4) and halite (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. Sulfur Allotropes

Elemental sulfur has more well-characterized solid allotropes than any other element (Steudel and 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 $\alpha\text{-S}_8$, $\beta\text{-S}_8$, and $\gamma\text{-S}_8$ (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 and Eckert, 2003). Alpha-cyclooctasulfur is the most common allotrope found in natural systems, while beta-cyclooctasulfur has been found in high-temperature fumarolic settings ($\beta\text{-S}_8$ is only predicted to form above $\sim 96^\circ\text{C}$; 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 ($\alpha\text{-S}_8$, $\beta\text{-S}_8$, and $\gamma\text{-S}_8$) 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 $\beta\text{-S}_8$ and $\gamma\text{-S}_8$ are usually found in high-temperature systems, they are not expected to be found at this cold, glacial site. In particular, our finding of $\beta\text{-S}_8$ in the sulfur bubble sample described above is, to our knowledge, the first detection of $\beta\text{-S}_8$ 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 $\beta\text{-S}_8$ and $\gamma\text{-S}_8$. 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 $\beta\text{-S}_8$ and $\gamma\text{-S}_8$ can be mineralized at low temperatures through direct interactions between sulfide and organic matter.

4. Materials and Methods

Ice, mineral, and fluid samples were collected at Borup Fiord Pass ($81^\circ 01'\text{N}$, $81^\circ 35'\text{W}$; 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). Bubbles of sulfur that had formed on top of one of the melt pools (Figure 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 2 and SI.1). Cryovials of sulfur bubbles and cryoconite material were stored in a liquid nitrogen (LN) dewar 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 10.0 mA as Cu K α radiation. Data were collected from 10° to 80° coupled 2 θ / 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 CO_2 and H_2O 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_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_3N_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 $1s \rightarrow \pi^*$ 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 5.3). We had initially intended to collect sulfur L-edge data for this sample as well, however absorption by the Si_3N_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 $\text{L}_{2,3}$ -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 $2 \times 12 \text{ mm}^2$ 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.

5. Results

5.1 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 $5 \times 10^4 \text{ m}^2$ in area and up to ~5 meters thick (Figure 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 ($\sim 10^4 \text{ m}^2$ 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 1b). While exploring the aufeis, we noted the odor of H_2S 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 SI.2). This discoloration is indicative of the reaction of the silver with dissolved sulfides to form Ag_2S (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 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 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 $0\text{--}1^\circ\text{C}$ (both measurements were collected at one time-point on 21 June 2014, at the same time that the sulfur bubbles were sampled).

5.2 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 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 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.

5.3 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 SI.5 and SI.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 3a): $\alpha\text{-S}_8$ (COD 9008577), $\beta\text{-S}_8$ (COD 9009891), and $\gamma\text{-S}_8$ (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 $\alpha\text{-S}_8$ in the diffractogram (Figure 3b), suggesting the instability of the rarer forms of S^0 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 $\alpha\text{-S}_8$, $\beta\text{-S}_8$, and $\gamma\text{-S}_8$ (Figure SI.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 SI.4). Interestingly, the diffractogram for this sample also includes a very good fit for rapidcreekite, a rare hydrated sulfate carbonate mineral with formula $\text{Ca}_2(\text{SO}_4)(\text{CO}_3) \cdot 4\text{H}_2\text{O}$. 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 (Roberts, 1986; Onac et al., 2013).

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, including the detected organic carbon (Figure 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 section SI.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 $\sim 1160\text{ cm}^{-1}$ 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; section SI.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 $\sim 1367\text{ cm}^{-1}$ may be indicative of geminal dimethyl group splitting of the symmetric C-H bend, while a small, broad feature at $\sim 1469\text{ cm}^{-1}$ 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 $\text{C}=\text{C}$ stretches of olefinic carbon groups, though multiple features on the shoulder of that peak are interpreted as deriving from sulfates and/or thiosulfate (section SI.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 μm in scale within the sulfur bubble material. We also observe a component of the sulfur material that appears smooth and, in some cases, euhedral (Figure 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, micron-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 5a). EDS data revealed that sulfur and carbon are present in all globular materials from this sample (Figure SI.4). The unidentified, smooth phase is observed within the sulfur bubble materials in Figure 5b,c. When analyzed with EDS, even at lower accelerating voltages, the electron beam destroys this smooth material (see Figures SI.7 and SI.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 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 6b). A smaller region of one such carbon map was then selected for stack collection and C XANES analyses (Figure 6d). Two representative C K-edge XANES spectra from the carbon-rich material are shown in Figure 6c; XANES spectra have been normalized below and above the carbon edge for visual comparison. The top spectrum in Figure 6c (Spectrum 1; solid red line) represents the majority of the carbon-rich material in this region while the bottom spectrum in Figure 6c (Spectrum 2; dashed green line) represents the carbon-rich material surrounding the opaque globules. Figure 6d shows how the carbon-rich material in the map has been fitted using Spectra 1 and 2 from Figure 6c.

Peaks in the two C XANES spectra shown in Figure 6c have been assigned to carbon functional groups by comparisons to peak energy positions of carbon standards reported in the 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 π^* resonance at 290.2 eV as well as three σ^* 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 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; Brandes et al., 2010; Chan et al., 2010). Absorptions at 288.4 eV in both of the spectra in Figure 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 6c does not have the characteristic carbonate peaks except for a small peak at 290.2 eV that might be from the typically strong π^* 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 (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 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).

6. Discussion

We interpret the aqueous geochemical data reported here (Table 1) to show that the sulfidic auferis observed in 2014 was derived from the sulfide-spring system at Borup Fiord Pass. 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 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 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 S⁰ of the same size were observed in FE-SEM images (Figure 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 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 S⁰ 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 5b,c). This smooth phase was extremely sensitive to beam damage, precluding

thorough examination using EDS (see Figure SI.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 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 β - S_8 in a low-temperature environment. We find this β - S_8 co-existing with two other sulfur allotropes, α - S_8 and γ - S_8 . The finding of actively forming β - S_8 is surprising, as the monoclinic β - S_8 form of elemental sulfur is not expected to form below $\sim 96^\circ\text{C}$ (Steudel and 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 β - S_8 has a much broader environmental stability than previously recognized.

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

For instance, Moon et al. (2013) created α - S_8 nanowires encapsulated in ~ 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 β - S_8 . Moon et al. (2013) report that β - 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 - S_8 in their nanowires. However, other recent endeavors have shown formation and stabilization of β - S_8 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 S^0 was of the β - S_8 form. Their β - S_8 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 - S_8 nanoparticles.

More recently, Choudhury et al. (2013) used a modification of this water-in-oil microemulsion technique to prepare β - S_8 nanoparticles (identified with XRD) using only a rotary vacuum evaporation step for drying. These authors report formation and stabilization of β - S_8 at room temperature for at least the 3-month duration of their experiments. Although the authors

484 did not identify their β -S₈ again using XRD, the size of their monoclinic sulfur nanoparticles
485 (characterized through TEM), when stored at 4°C, remained almost unaltered. The results of
486 Guo et al. (2006), Choudhury et al. (2013), and Moon et al. (2013) show the formation and
487 room-temperature stabilization of β -S₈ (at least temporarily) through an as-of-yet unknown
488 interaction of sulfur with inorganic and organic forms of carbon.

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

508 We hypothesize that the presence of organic matter in the melt pool fluids during the
509 oxidation of sulfide and formation of S⁰ at Borup Fiord Pass gives rise to the formation of both
510 β -S₈ as well as γ -S₈. There is a clear co-association of organic carbon with the sulfur in the sulfur
511 bubbles. This hypothesis for the formation of monoclinic sulfur (β -S₈ and γ -S₈) under
512 environmental conditions is also supported by the experimental studies that have shown that
513 β -S₈ can be formed and temporarily stabilized at temperatures below 96°C in the presence of
514 carbon (Guo et al., 2006; Choudhury et al., 2013; Moon et al., 2013). Our present data do not
515 inherently suggest that β -S₈ and γ -S₈ are formed by the action of microorganisms, since the
516 organic carbon in the melt pool may be from exogenous sources (i.e. organic rich shales in the
517 subsurface), and we cannot at this time constrain the mechanism through which the association
518 of organic carbon and sulfur drives the formation of the monoclinic allotropes of elemental
519 sulfur. Although previous research has hypothesized rosickyite (γ -S₈) to be a possible
520 biosignature of microbial sulfide oxidation (Meisser et al., 2000; Douglas and Yang, 2002;
521 Gleeson et al., 2012), it may simply be that microbial activity commonly generates appropriate
522 dissolved organic carbon that participates in the precipitation and the stabilization of γ -S₈. Thus
523 microbial processes may be only indirectly involved and not inherently necessary for organic
524 carbon and sulfur to interact and form monoclinic sulfur allotropes in cold natural systems. For
525 instance, recent laboratory work by Cosmidis and Templeton (2016) has shown that reactions
526 of sulfide and organic carbon in opposing gradients of sulfide and oxygen can drive the
527 formation of S⁰ 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 $\alpha\text{-S}_8$ in many of these samples, but this is the first time that $\beta\text{-S}_8$ has been detected. However, the $\gamma\text{-S}_8$ 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_2S in the laboratory and in the field will be necessary to determine the physicochemical constraints on the formation of $\beta\text{-S}_8$ and $\gamma\text{-S}_8$ in natural systems. Furthermore, although our current research suggests that the formation and stabilization of $\beta\text{-S}_8$ and $\gamma\text{-S}_8$ 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 $\beta\text{-S}_8$ and $\gamma\text{-S}_8$ in unexpected localities is needed.

7. 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 $\beta\text{-S}_8$ and $\gamma\text{-S}_8$ is inferred to occur through interaction of organic carbon and sulfur. This is the first detection of the $\beta\text{-S}_8$ form of S^0 in a cold, natural setting and suggests that the formation and stabilization of $\beta\text{-S}_8$ may be more commonplace and over a much wider range of environmental conditions than previously thought. Intriguingly, $\beta\text{-S}_8$ and $\gamma\text{-S}_8$ in our sample of sulfur bubble material appeared metastable, reverting to $\alpha\text{-S}_8$ in less than two weeks at room temperature. This may suggest that $\beta\text{-S}_8$ and $\gamma\text{-S}_8$ 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 $\beta\text{-S}_8$ and $\gamma\text{-S}_8$, 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.

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Figure 1. Borup Fiord Pass: Site location and sulfur bubble collection. **a)** Line drawing and map showing the location of Ellesmere Island in the Canadian High Arctic. Inset shows the locations of Borup Fiord Pass and nearby Eureka. **b)** The sulfidic aufeis with yellow S^0 deposits at the toe of the glacier. 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. **c)** Collection of sulfur bubbles on top of melt pool. A human hand gives relative scale. **d)** The melt pool designated by the blue star in (b) and the site of collection in (c). Co-authors Trivedi and Templeton give relative scale.

Figure 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.

Figure 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-dash-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.

Figure 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 SI.5.

Figure 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 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 .

	2009	2014	
	Spring	Melt Pool	Glacial Melt
Na⁺	51.8	38.2	0.470
K⁺	0.302	0.210	(DL)
Mg⁺	12.9	9.17	0.121
Ca²⁺	17.3	12.6	0.150
Fe_T	0.0050	0.0007	0.001
Mn_T	0.0010	0.0005	0.010
SiO₂	0.0411	0.0541	(DL)
SO₄²⁻	13.0	18.6	0.4
S₂O₃²⁻	0.103	0.172	(NM)
Cl⁻	39.2	86.0	0.9
F⁻	0.0542	0.0621	(DL)
Br⁻	0.0330	0.0212	(DL)
NO₃⁻	0.0030	0.0908	(DL)

Table 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 SiO₂. 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 (SiO₂), 1.1 μM (F⁻), 0.6 μM (Br⁻), and 0.8 μM (NO₃⁻)).