N-alkane biosignatures in High Arctic Mars analogue gossan deposits

By

Hiba Aoid

Department of Earth and Planetary Sciences McGill University Montreal, Quebec, Canada

December 2023

A thesis submitted to McGill University in partial fulfillment of the requirements of the degree of Master of Science

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Abstract

If past life ever existed on Mars, what are the multiple ways it could have been preserved in the Martian geological record? This crucial question is becoming especially relevant the more we uncover about the planet's ancient wet history. Different acidic and sulfur-rich analog environments have been proposed that are comparable to the alteration environments of iron oxides and sulfate minerals on Mars. However, some authors have hypothesized that these past Martian environments might have been cold and semi-dry, similar to polar regions on Earth. As part of the T-MARS project, we studied reactive gossans in the Canadian High Arctic, on Axel Heiberg Island, as an analog environment to similar deposits on Mars. We hypothesized that nalkane lipids could potentially be an important form of molecular fossils entombed in varying mineral assemblages of sulfates, iron oxides, and phyllosilicates in Arctic gossans, because of their excellent preservation potential relative to most other forms of organic molecules. To determine the preservation potential of lipids in mineralogically varying acidic sulfur-rich gossan deposits, this study extracted and quantified n-alkane biomarkers from three different Arctic gossans using gas chromatography-mass spectrometry (GC-MS). Samples were characterized by x-ray diffraction for mineralogy, as well as by pH and elemental analysis of carbon and nitrogen. Organic matter was found to be very low in all samples (<1% wt.%). N-alkane analysis also revealed preserved even-over-odd distribution patterns in short-chain n-alkanes, most likely from a microbial source, along with evidence for long-chain n-alkanes with odd-over-even distribution from higher plant sources. The presence of these unique chemical biosignatures in low organic, highly acidic, and sulfur-rich Mars analog gossans of varying maturity provides evidence that sulfur deposits linked to paleo hydrothermal systems on Mars can be promising targets for preserved organic biosignatures, specifically lipid n-alkanes. The significant diversity in

biosignature patterns across samples of varying mineralogy, pH, and oxidation levels within each gossan suggests that n-alkane preservation varies on a small scale in these environments. These factors alone do not definitively account for the variability of n-alkane concentrations and distributions in this study, and additional investigations of these and other influencing factors are needed to determine which specific targets to choose for biosignature search on Mars in future space missions. This exploratory study provides novel insights into the lipid biosignature content in high Arctic Mars analog gossan deposits.

Résumé

Si une vie passée avait jamais existé sur Mars, quelles seraient les multiples façons dont elle aurait pu être préservée dans les archives géologiques martien? Cette question cruciale devient de plus en plus pertinente à mesure que nous en découvrons davantage sur l'histoire aqueuse ancienne de la planète. Divers environnements analogues acides et riches en soufre ont été proposés, qui sont comparables aux environnements d'altération des oxydes de fer et des minéraux de sulfate sur Mars. Cependant, certains auteurs ont émis l'hypothèse que ces anciens environnements martiens passés auraient pu être froids et semi-arides, similaires aux régions polaires de la Terre. Dans le cadre du projet T-MARS, nous avons étudié les chapeaux de fer, « gossans », réactifs dans le Haut-Arctique canadien, sur l'île Axel Heiberg, comme environnement analogue à des dépôts similaires sur Mars. Nous avons émis l'hypothèse que les lipides n-alcanes pourraient potentiellement constituer une forme importante de fossiles moléculaires enterrés dans divers assemblages minéraux de sulfates, d'oxydes de fer et de phyllosilicates dans les gossans de l'Arctique, en raison de leur excellent potentiel de préservation par rapport à la plupart des autres formes de molécules organiques. Afin de déterminer le potentiel de préservation des lipides dans des dépôts de gossans acides riches en

soufre, qui varient sur le plan minéralogique, cette étude a extrait et quantifié des biomarqueurs en n-alcanes à partir de trois gossans arctiques différents en utilisant la chromatographie en phase gazeuse couplée à la spectrométrie de masse (GC-MS). La minéralogie a été déterminée à l'aide de la diffraction des rayons X, ainsi que le pH et l'analyse élémentaire du carbone et du nitrogène. La matière organique s'est avérée de concentration très faible dans tous les échantillons (<1 % en poids). L'analyse des n-alcanes a également révélé des modèles de distribution conservés, alternant entre pairs et impairs les n-alcanes à chaînes courtes, très probablement d'origine microbienne, et les n-alcanes à chaînes longues avec une distribution alternée entre impairs et pairs, provenant probablement de sources végétales. La présence de ces biosignatures chimiques uniques dans les gossans analogues à Mars à teneur très faible en matière organique, hautement acides et riches en soufre, de maturité variable, suggère que les dépôts de soufre potentiellement liés à d'anciens systèmes hydrothermaux sur Mars constituent des cibles prometteuses pour les biosignatures organiques préservées, en particulier les n-alcanes lipidiques. La diversité significative de la distribution de biosignatures entre les échantillons de minéralogie, de pH et de niveaux d'oxydation variables au sein de chaque gossan suggère que la préservation des n-alcanes varie à petite échelle dans ces environnements. Ces facteurs seuls n'expliquent pas de manière définitive la variabilité des concentrations et des distributions des nalcanes dans cette étude, et des enquêtes approfondies sur ces facteurs et d'autres facteurs influents sont nécessaires pour déterminer les cibles spécifiques à choisir pour la recherche de biosignatures sur Mars lors de futures missions spatiales. Cette étude exploratoire apporte de nouvelles perspectives sur le contenu des biosignatures lipidiques dans les dépôts de gossans analogues à Mars en haute Arctique.

Preface

The thesis presented here is the culmination of the author's original research at the Earth and Planetary Science Department of McGill University from 2021 to 2023. The article is intended to be submitted for review for the purpose of submission to complete the author's master's degree in the program, where the author is the primary contributor and Dr. Peter Douglas and Dr. Richard Léveillé are the author's primary co-supervisors. This study is conducted as a part of the Terrestrial Mineral Analysis by Remote Sensing (T-MARS) project funded by the Canadian Space Agency's *Flights and Fieldwork for the Advancement of Science and Technology* (FAST) program.

Acknowledgements

There are many people to thank for the submission of this thesis. First and foremost, I need to thank my incredible supervisors Dr. Richard Léveillé and Dr. Peter Douglas for their invaluable supervision and support during the course of my Master's degree. Thank you both for dedicating so much of your time to discussing and encouraging me through every step of this project. Dr. Richard Léveillé, I'm especially thankful for the opportunity to be a part of the T-MARS team, to conduct my own research, and to continue to learn. Dr. Peter Douglas, thank you for welcoming me into your lab group and providing constant support, along with your constructive feedback and encouragement.

I would like to thank all the members of the T-MARS project who played an integral role in the successful completion of this research: Dr. Marie-Claude Williamson, Dr. Myriam Lemelin, Dr. Cassandra Marion Beauchamp, Eloïse Brassard, Stephanie Lachance, and Sean

Clark. Thank you for your support in and out of the field. I could not have asked for a better team to tackle the harsh Arctic with.

I appreciate the dedicated individuals who played a pivotal role in the laboratory work and development of research methodologies for this thesis. I am grateful to Thi Hao Bui at McGill University for guiding me through the lipid extraction and separation protocol. To Dr. Yves Gelinas at Concordia University for guiding and mentoring me through the GC-MS analysis. To Victoria Jarvis at McMaster University for all the guidance with conducting XRD analysis. To Agnieszka Adamowicz-Walczak at UQAM for guidance with conducting elemental analysis. I also want to express my appreciation to my lab group mates, Erin Gibbons, Estelle Allan, and Yunfeng Wang, who were always there to answer my questions.

Finally, I want to thank every one of my friends and family members for their endless encouragement and understanding of the time and effort I devoted to this research.

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1. Introduction

Cumulative evidence in the literature suggests that there was a period during Mars' early history when it resembled Earth much more than it does today (Baker, 2001). The remnant lakebeds, deltas, and massive outflow channels that can be seen on Mars's present surface are evidence that this ancient period, which lasted approximately from 4.1 billion to 3.5 billion years ago, was characterized by widespread surface waters and significant rain near the equator during the late Noachina period (Baker, 2001; Ehlmann et al., 2011; Harrison et al., 2005; Howard et al., 2005; Salese et al., 2016). This also mineralogically distinct era is identified with the regional deposition of sulfates in aqueous environments and with the potential to host microbial life (Squyres et al., 2004; Gaidos et al., 2007; Gailliard et al., 2013; Vago et al., 2017; Tan et al., 2018). The combination of a universal solvent like water, which is fundamental for all life as we know it, paired with the discovery of all the major elemental building blocks of biomolecules, sources of energy, and evidence of a paleo magnetic field, is consistent with a habitable Martian world (Chassefiere et al., 2007; Irwin et al., 2010; Grotzinger et al., 2014; Hays et al., 2017). This habitability contrasts with the present-day surface of Mars, which is dry, cold, and probably uninhabitable (Baker, 2001). Evidence of life on Mars during the Noachian habitable period is yet to be established. To find and effectively identify potential Martian microbial biosignatures produced during this habitable period, it is necessary first to understand how they can be preserved in terrestrial analog environments.

On this basis, terrestrial analog studies can play a significant role in preparing for and exploring the major question of whether life ever existed beyond planet Earth. Terrestrial analog environments that have conditions similar to those of past or present-day Mars are used to investigate the potential for various Martian environments to host preserved microbial

biosignatures. These analog studies are, therefore, a fundamental basis for research aimed at understanding how biology might have left its traces on Mars in a comparable geologic record on Earth because they allow us to develop and test hypotheses on Earth before investing in interplanetary missions (Hays et al., 2017). They also allow us to understand the distribution and limits of life and predict where we are most likely to find it on Mars (Foing et al., 2011; Hays et al., 2017). Data collected from orbital spacecraft, landers, and rovers informs us of the environmental conditions of Mars, both past and present. This knowledge can be used to identify high-fidelity analog environments to Mars on Earth in planetary studies to help prepare and direct current and future space missions (Williamson et al., 2011). Such a high-fidelity Mars analog environment can be terrestrial gossans, which are weathered and oxidized rock formations typically overlaying massive sulfide deposits. (Peterson et al., 2014; Williams et al., 2015).

The claim that Mars had environments that are analogous to terrestrial gossans is supported by datasets collected by Mars missions and Mars meteorite studies which link terrestrial gossan sulfide deposits to certain Martian environments (Burns, 1987; Burns & Fisher, 1990; Klingelhofer et al., 2004; Gendrin et al., 2005; Morris et al., 2006; Williams et al., 2015). Multiple studies have explored how gossans capping oxidized sulfide deposits can serve as mineralogical analogs to ancient environments on Mars (Fernández-Remolar et al., 2008; West et al., 2009; Sobron & Alpers, 2013; Peterson et al., 2014; Williams et al., 2015; Hays et al., 2017). Gossans are mineral deposits that form close to the surface due to the weathering and oxidation of sulfide minerals (Harris et al., 2015; Percival & Williamson, 2016). Their exact mineralogy varies widely, but it generally shows a predominance of iron oxides, sulfates, alteration minerals such as jarosite, some carbonates, silica minerals, and a host of other secondary minerals (Dill,

2010; Percival & Williamson, 2016). These mineral assemblages have been suggested as astrobiologically relevant in the search for preserved microbial life in the Martian record both for the use of some as indicators of aqueous and, therefore, potentially habitable conditions and for their positive preservation potential of organics (Klingelhofer et al., 2004; Lalonde et al., 2012; Keil & Mayer, 2014; Parenteau et al., 2014; Hays et al.; 2017; Tan et al., 2018; Stromberg et al., 2019; Bosak et al., 2021). Arctic gossans can be of particular interest as few studies have explored this analog environment despite studies showing how mineralogically different sulfate species can vary in colder temperatures and how an early habitable Mars might have been cold and icy, similarly to the polar regions on Earth (West et al., 2009; Lacelle and Leveille; 2010; Wordsworth et al., 2015; Woodley et al., 2022). Arctic gossans can therefore represent an acidic and sulfur-rich site in a low-temperature environment that is comparable to Martian conditions in which sulfate and iron-oxide minerals precipitate (West et al., 2009).

Biosignatures in the context of Mars analog studies can be a variety of different measurable and quantifiable indicators of biological processes (Simoneit et al., 1998; Hays et al., 2017). This study targets n-alkane lipid biomarkers as the molecular indicator of choice. Lipids are commonly produced by a wide range of microorganisms and are established as a universal biomarker in the literature (Georgiou & Deamer, 2014). N-alkanes specifically are more resistant to degradation by common environmental processes, such as microbial or chemical breakdown, due to their relatively simple, saturated hydrocarbon structure (Eckmeier et al., 2009). They can provide a promising target for detecting remnants of ancient life, as some of the earliest evidence of life on Earth found in the Archaean sedimentary record have been n-alkane lipid biomarkers (Brocks et al., 2003a,b). Lipids have therefore been essential for identifying our planet's earliest bacterial processes due to their highly resistant nature that can survive in the geologic record for

hundreds of millions to billions of years (Summons & Walter, 1990; Brocks et al., 2003a,b; Johnson et al., 2020). Lipid biosignatures, specifically n-alkanes, are, therefore, invaluable in Martian astrobiological studies due to their remarkable stability and resistance to degradation (Georgiou & Deamer, 2014; Johnson et al., 2020).

Investigations of biosignatures have been conducted in terrestrial gossans, including the investigation of preserved morphological evidence of microbial biosignatures (Williams et al., 2015). Additionally, Mars analog studies have also been conducted in massive sulfide deposits or gossans such as the Iron Mountain gossan in California, the Rio Tinto gossan in Spain, and Gossan Hill at Victoria Island, NW territories (Fernández-Remolar et al., 2008; Sobron & Alpers, 2013; Peterson et al., 2014; Williams et al., 2015; Hays et al., 2017). Concurrently, numerous lipid preservation studies have already been conducted in other iron and sulfur-rich environments such as iron hot springs, acidic salt lake sediments, and sulfur streams (Parenteau et al., 2014; Tan et al., 2018; Johnson et al., 2020; Williams et al., 2021). However, no studies have been conducted on lipid preservation as evidence of microbial biosignatures in terrestrial gossans, and few Mars analog studies have been conducted in Arctic gossans (West et al., 2009). This study addresses this gap in the current literature by investigating the lipid, specifically nalkane, preservation pattern and resilience in a highly acidic and sulfur-rich polar environment. We hypothesized that deposits and mineral assemblages associated with gossans are a viable target for the preservation of a molecular microbial signal. This exploratory study therefore aims to provide novel insights into the lipid biosignature content in high Arctic Mars analog gossan deposits. Additionally, this project conducted a mineralogical study using X-ray Diffraction (XRD) to characterize the mineral profile of the sampled areas to investigate any potential relationship between specific mineral assemblages and lipid preservation.

Axel Heiberg Island in Nunavut, Canada, has been shown to be particularly enriched in gossans and evaporite domes consistent with the presence of a paleo hydrothermal system (Percival & Williamson, 2017; Harrington et al., 2019; Zentilli et al., 2019). On this basis, we selected gossans on Axel Heiberg Island as appropriate analogous terrestrial environments to investigate potential Martian biosignatures. This study explored three different Arctic gossans by characterizing and quantifying their mineralogical profiles and investigating their lipid biomarker content for biogenic patterns associated with microbial life.

2. Literature Review

2.1. Gossans & Mineralogical Context

Gossans are highly oxidized ferruginous rock or soil that cap sulfide-rich deposits. These rust-colored superficial deposits form through the alteration of primary sulfides in the host bedrock by oxidizing fluids leaching to produce secondary iron-oxide and sulfate minerals (Harris et al., 2015; Percival & Williamson, 2016). Terrestrial gossans can be found in a diverse range of climates worldwide and represent a natural acid drainage site (West et al., 2009; Percival & Williamson, 2016). They have a deep orange-red coloration, and when present in a vegetation-free environment like the Arctic, they can be clearly detected by the naked eye or through satellite remote sensing (Burns, 1988; Burt et al., 2006; West et al., 2009; Percival & Williamson, 2016; Clabaut et al., 2020; Lemelin et al., 2020).

On Victoria Island, NT, Canada, Percival & Williamson (2016) studied the mineralogy and spectral signature of two reactive high Arctic gossans. The two gossans were a classic gossan and a gossan that had its morphology flipped in which the unoxidized, grey pyrite-rich zone sits on top of the oxidized Fe-rich orange soil. The findings showed that the classic gossan had a predominant composition of sulfates and iron oxides, including gypsum, goethite, and jarosite, in

addition to quartz, illite, and feldspar. While the inverted gossan showed a predominance of sulfates jarosite and gypsum with varying amounts of iron oxides and iron sulfide minerals: goethite, hematite, pyrite, in addition to chlorite, calcite, and feldspar.

Many of these minerals have been shown to be highly relevant to astrobiology both because they occur on Mars, and because they can preserve biosignatures. Evaporite minerals such as gypsum and calcite are considered to be some of the most astrobiologically critical deposits for the potential preservation of biosignatures on Mars and for the context of Martian habitable paleoenvironments (Stromberg et al., 2014; Hays et al., 2017; Stromberg et al., 2019). This is because organic carbon deposited in interbedded evaporites can be preserved over long periods of time (Lalonde et al., 2012; Hays et al.; 2017). Moreover, iron oxides and iron sulfates such as goethite, hematite, and jarosite have also been suggested to help isolate organic lipid biomarkers from degradation processes such as heterotroph enzymatic degradation during initial preservation (Parenteau et al., 2014; Tan et al., 2018). Lastly, phyllosilicates such as chlorite and smectites are important for the preservation of organics by preventing fluid flow and diagenesis by chemically stabilizing organic matter (Keil & Mayer, 2014; Hays et al., 2017; Stromberg et al., 2019; Bosak et al., 2021).

Furthermore, the presence of alteration minerals like jarosite, a hydrous ferric sulfate that precipitates in acidic, sulfate-rich environments, requires the presence of water during its formation and is, therefore, a mineralogical indicator of past aqueous processes on Mars (Klingelhofer et al., 2004). Jarosite is, therefore, a prime target mineral for the search for life as the most likely places to discover evidence of previous life on Mars are the mineralized remnants of aqueous and shallow subsurface hydrothermal systems on Mars (Farmer, 2002; Martinez-Frias et al., 2004; Williamson et al., 2011). This aligns with one of the three models proposed for the

history of deposition of sulfate mineral assemblages on Mars, and that requires the presence of near-surface water. This model hypothesizes that sulfates formed in an acidic, oxidizing, and briny environments during the Noachian Epoch (3.9-3.5 Ga) (Grotzingeretal.,2005; McLennan et al.,2005; West et al., 2009). The model is based on observations made by the Mars Exploration Rover Opportunity at Erebus Crater, Olympia outcrop, in the Meridiani Planum region that identify sedimentary structures formed by aqueous processes preserved in sulfate-rich bedrock (McLennan et al., 2005; Grotzinger et al., 2006; West et al., 2009). Because this model requires the presence of liquid water, an essential parameter for habitability on Mars, it asserts this gossanous environment as an appropriate geochemical analog for the potentially habitable period in Mars history (Farmer, 2002; West et al., 2009; Williamson et al., 2011).

Additionally, previous studies done in Northern Yukon, Canada, suggest that certain sulfate mineral assemblages similar to those observed on Mars could have formed in a periglacial climate. Lacelle & Leveille (2009) investigated an active acid drainage zone in the Canadian subarctic as a potential analog for low-temperature sulfide formation on Mars; a zone that precipitates gypsum, jarosite, schwertmanite, and hematite from acidic sulfate-rich waters. The same alteration minerals have been identified near the Martian northern polar ice cap in Olympia Undae dune field. The study's findings support the hypotheses that the formation of sulfate deposits on Mars did not take place in a warm climate through evaporation, but rather that these mineral assemblages precipitated through the freezing of Ca-Fe-Mg-SO4 rich acidic waters in a periglacial cold and semi-dry climate environment. This illuminates the potential of using arctic terrestrial environments as Mars analog sites to better understand the low-temperature hydrogeochemical processes under which sulfate, and iron-oxide-rich deposits would have formed. This also promotes the idea of investigating gossans in an Arctic setting, rather than in

warmer climates as has been previously investigated (Preston et al., 2011; Peterson et al., 2014; Williams et al, 2015; Tan et al., 2018). Climate model studies suggesting that early Mars was cold and icy rather than warm and wet also support this hypothesis (Wordsworth et al., 2015; Woodley et al., 2022).

Arctic gossans have been proposed as an appropriate analog for ancient Martian conditions under which sulfates and iron-oxide deposits formed. These environments have been shown to record the processes that form alteration minerals similarly found in Terra Meridiani in Mars in seasonally wet cold climates (West et al., 2009). That study's findings also suggest that Arctic gossans significantly differ from similar gossan and acid mine drainage (AMD) sites in warmer climates in the way they lack diversity in sulfate species and in their significantly smaller sulfate crystalline size. These differences, which are caused by the slower reaction rates at low temperatures, can be significant parameters to consider when choosing a high-fidelity geochemical and mineralogical terrestrial analogue environment.

High-fidelity terrestrial analog sites are chosen to be similar to targeted Martian landing sites, based on a combination of geological and astrobiological interests (Martinez-Alonso et al., 2005; Williamson et al., 2011). Data collected by early Mars landers as well as Mars meteorite studies suggest the presence of gossanous sulfate deposits on the surface of Mars (Burns, 1987; Burns & Fisher, 1990). Later missions to Mars also resulted in datasets suggesting the presence of different mineral species on the Martian surface, namely iron oxides, sulfates, and alteration minerals (Klingelhofer et al., 2004; Gendrin et al., 2005; Morris et al., 2006; Williamson et al., 2011), and the presence of acid-sulfate weathered outcrops, such as the Burns Formation at Meridiani Planum (Squyres et al., 2004). The presence of these iron oxide and sulfate minerals, along with hydrous iron sulfates and acid-sulfate weathered formations on Mars, characteristic of

gossanous oxidizing sulfur deposits, support the assertion that Mars likely had environments that are analogous to terrestrial gossans, effectively making them an appropriate mineralogical analog environment to study these deposits (Squyers et al., 2004; Karunatillake et al., 2014; Williams et al., 2015; Lane et al., 2015). On this basis, this study suggests high Arctic gossans on Axel Heiberg Island in Nunavut, Canada, as appropriate mineralogical and geochemical analog terrestrial environments to investigate the preservation potential of biosignatures during the habitable period in Mars history.

2.1. Lipid Biomarker Detection

Biomarkers can be defined as tracers or measurable organic indicators of biological activity (Simoneit et al., 1998; Hays et al., 2017). They can be molecular markers/fossils or chemical fossils, and they are the by-products of reductive and oxidative processes that are indicative of biochemistry, as they cannot be products of any known abiogenic processes (Simoneit et al., 1998). The four major biomolecules of life are carbohydrates, nucleic acids, proteins, and lipids. Lipids stand out as they are highly resistant to degradation over long timescales, making them good molecular fossils in contrast to the other biomolecules that degrade more readily (Aerts et al., 2014; Georgiou & Deamer, 2014). Lipids are generally defined as biomolecules that are insoluble in water but soluble in nonpolar solvents. This term can encompass a range of compounds, including fats, oils, waxes, sterols, and phospholipids (Ahmed & Ahmed, 2021). More specifically, the group of organic compounds that compose the bio-membranes of cellular life are excellent biomarkers, as their preserved remains and chemical pattern can survive geologic times on the scale of millions to billions of years (Simoneit et al., 1998; Aerts et al., 2014; Georgiou & Deamer, 2014).

A universal biomarker to expect in extraterrestrial life is the compositional patterns of hydrocarbon derivatives associated with biogenic lipids (Georgiou & Deamer, 2014). This assumption is based on a set of rules: first, cells are the fundamental unit of life, even in the case of potentially extinct extra-terrestrial forms of life, and second, there must be a boundary structure to regulate the permeability and diffusion of solutes. From what we know from life on Earth, this boundary shares a common structural organization: a membrane composed of a lipid bilayer, and the same is assumed for potential extraterrestrial life (Georgiou & Deamer, 2014). This lipid bilayer fulfills the requirement for a universal biomarker based on its specifically defined parameters relating to permeability, stability, and fluidity, which are required by the aqueous nature of molecules of life (Georgiou & Deamer, 2014). However, the presence alone of hydrocarbon derivatives, a class of lipid molecules, is not indicative of a biogenic source, as there are instances where they can be abiotically synthesized by Fischer-Tropsch-type reactions that can happen in high-pressure and high-temperature conditions. For instance, hydrocarbon derivatives found in the Murchison meteorite or abiotic hydrocarbons found in mid-ocean ridge vents (Naraoka et al., 1999; Proskuowski et al., 2008; Georgiou & Deamer, 2014). So, the presence alone of lipids cannot be interpreted as a definitive biomarker, but the unique chemical pattern of lipid distribution that can only result from universal biosynthetic pathways can be considered a reliable biosignature for extraterrestrial life (Summons et al., 2008; Georgiou & Deamer, 2014; Summons et al., 2022).

The way to differentiate between abiotic and biotically synthesized hydrocarbon derivatives is by looking at the distribution of their different chain lengths (Georgiou & Deamer, 2014). For instance, the pattern of monocarboxylic fatty acids from a bacterial source shows a clear predominance in its even-numbered carbon chains (Hartgers et al., 2000). This preference is due to the addition of two carbon atoms at once during biotic synthesis (Georgiou & Deamer, 2014). This odd-even pattern would not be observed in lipids from an abiotic source such as Fischer-Tropsch alkanes (McCollom & Seewald, 2007). This clearly distinguishable chemical pattern in hydrocarbons has been demonstrated to be preserved on a timescale of hundreds of millions to billions of years (Hatch et al., 1989; Georgiou & Deamer, 2014). Their chemical patterns are a chosen biomarker for the search for life on Mars because they are easily analyzed and stable over long timescales (Georgiou & Deamer, 2014).

A diverse range of lipids have been studied and utilized as biomarkers for preserved ancient life on Earth, including n-alkanes, sterols, fatty acids, and their associated alcohol groups (Table 1) (Brocks et al., 1999; Xie et al., 2003; Brocks & Pearson, 2005; Eigenbrode, 2008; Georgiou & Deamer, 2014). However, on Earth, n-alkanes are the most prevalent lipids in ancient sedimentary bitumen from the late Archean eon, which spanned approximately 2.8 billion years to 2.5 billion years ago (Brocks et al., 2003a,b; Georgiou & Deamer, 2014). One of the most noteworthy examples is the n-alkanes found in some of the oldest known sedimentary rocks in Pilbara, Australia, which are dated to be at least 2.7 billion years old (Brocks et al., 2003a). More recently, other examples also include n-alkanes found in crude oil that date as far back as 200 million years and have a preserved odd-even chemical pattern indicative of bacterial origin (Cai et al., 2005). These studies provide insight into the ability of lipid hydrocarbons, and more specifically alkanes, to be preserved over billions of years. Additionally, n-alkanes are more resistant to microbial decomposition than other lipid compounds such as fatty acids and alcohols (Eckmeier et al., 2009). Furthermore, investigations of early life's membrane compartment's capability to endure a stable structural state in extreme temperatures and pressure conditions (up to 100 °C/800 bar) found that n-alkane-enriched structural membranes are significantly less

affected by harsh conditions and suggest n-alkane enrichment as a potential survival strategy for the earliest living forms on Earth (Misuraca et al., 2021). This is crucial to consider considering that the general agreement for the origin of life is theorized to be under extreme conditions, in hot springs or hydrothermal environments (Martin et al., 2008; Damer & Deamer, 2020). Overall, the current literature demonstrates the use of n-alkane lipids as molecular fossils and biomarkers for ancient life in a diverse range of environments and settings.

The Sample Analysis at Mars (SAM) suite instrument on NASA's Curiosity rover has characterized complex organic matter using evolved gas analysis and GC-MS at Pahrump Hills and the Glen Torridon region of Gale Crater (Eigenbrode et al., 2018; Millan et al., 2022). The earlier study reported organic matter in the 3.5-billion-year-old Murray formation (Eigenbrode et al., 2018). These results included the identification of alkane compounds in sedimentary lacustrine mudstones. Most recently discovered sulfur-bearing organics in Glen Torridon included medium-chain length alkanes made from organic materials preserved in the mudstones and sandstones of Gale Crater (Millan et al., 2022). Although further analysis is required to determine if they have a biogenic origin, these findings are an important clue in the direction of what further biosignatures to target for the search for ancient life on Mars. They also show that organic molecules, specifically alkane compounds, are preserved in materials on Mars over long geologic times.

 Table 1: Classification and Structural Characteristics of Various Lipids. Based on Ball et al.

 (2011).

Lipid	Lipid Group	Composition & Structure	
Fatty agids	Fatty acids	Saturated or unsaturated hydrocarbon chains with a	
Fatty actus	Fatty acids	carboxyl group (COOH) at the end.	
n-Alkanes	Nonglyceride lipids	Saturated hydrocarbons of single-bonded carbon	
n-Aikanes		and hydrogen.	
		Lipids with characteristic structural components	
Sterols	Nonglyceride lipids	consisting of a "steroid nucleus," a fused four-ring	
		system.	
Alaahala	Nonglyceride lipids	Hydrocarbon chains with a hydroxyl (-OH)	
AICOHOIS		functional group at the end.	

Multiple studies have also targeted lipids as biomarkers in iron-rich Mars analog environments (Georgiou & Deamer, 2014; Marshall & Cestari, 2015; Tan et al., 2018; Johnson et al., 2020; Williams et al., 2021). Some of these studies suggest microbial lipids are a potentially significant reservoir of fossilized organic carbon on Mars (Tan et al., 2018; Williams et al., 2021). Despite the previous widespread thought that iron-rich sediments do not preserve lipid biosignatures well, more recent studies suggest the opposite (Sumner et al., 2004; Klein et al, 2005; Parenteau et al., 2014), it's proposed that the preservation of lipid biomarkers is rather enhanced due to the encrustation of cells in iron oxide minerals, which can shield lipids from initial degradation processes (Parenteau & Cady, 2010; Parenteau et al., 2014; Tan et al., 2018). Other studies also suggest that specific mineral assemblages of sulfates, iron oxides, and phyllosilicates, similar to what is found in gossan deposits, are favorable for lipid preservation and are, therefore, a good target for biomarker search on Mars (Johnson et al., 2020). Layers containing alteration minerals, such as goethite, which can be a product of the transformation of jarosite in gossans, have also been suggested as targets for fossilized lipids due to their association with highly aqueous environments and, therefore, habitable environments (Tan et al., 2018). But although there are studies which utilized gossans as a Mars analog environment and looked at potential biosignatures, the sought-after indicators have mainly been textural or morphologic biosignatures in gossans (Fernández-Remolar et al., 2008; Williams et al., 2015, 2016, Hays et al., 2017). This study therefore aims to bridge this gap by investigating the preservation potential of n-alkane lipids in high Arctic Mars analog gossan deposits.

3. Methodology

3.1.Sampling Location and Collection

Field sampling was carried out in July 2022. The sampling sites were located near Expedition Fiord on Axel Heiberg Island, Queen Elizabeth Islands, Nunavut, in the Canadian Arctic Archipelago, latitude 79°24'N (Figure 1). Two base camps were set up near the WGVA site and the McGill Arctic Research Station (M.A.R.S), where multiple gossans were previously identified (Percival & Williamson, 2016; Lemelin et al., 2019; Zentilli et al., 2019). The first gossan was sampled near the White Glacier Vein Array (WGVA) site, the second at Color Peak Diapir, and the last near the M.A.R.S station (Table 2). The three sites were chosen based on multiple factors, including logistical considerations, geological characteristics, and the presence of gossans in the area.

Table 2:	Geographic	coordinates	of the sa	ampled	gossans'	locations.
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Gossan	Longitude	Latitude	Altitude (m)
WGVA	N 79° 26' 36.6426"	W 090° 42' 19.8"	368
Color Peak	N 79° 23' 49.1172"	W 091° 15' 28.6668"	279
НТС	N 79° 25' 22.0542"	W 090° 43' 33.1566"	198



Figure 1: Map showing the location of the three sampled gossans adjacent to the McGill Arctic Research Station (M.A.R.S) in Axel Heiberg Island, Nunavut, Canada. Background from ESRI imagery, co-created with T-MARS member Eloïse Brassard.

Site description. All three of our sampling sites lie within the Sverdrup Sedimentary Basin, a 1,000 km by 350 km base that contains up to 13 km of Carboniferous to Paleogene rocks (Embry et al., 2008; Zentilli et al., 2019). Gossans were sampled from sites near two prominent salt diapirs in the Expedition fiord area, namely Color Diapir and Expedition Diapir, which are associated with perennial spring activity and acidic brine fluid leeching that links them to the local hydrothermal network (Zentilli et al., 2019).

The first gossan sampled belongs to the set of gossans associated with the White Glacier vein array (WGVA). WGVA is a network of minerals discovered to be of hydrothermal origin, where brightly colorful gossans have been observed (Zentilli et al., 2019). WGVA sits at the intersection of a Cretaceous diabase unit overlaying Triassic-Jurassic sedimentary rocks and a prominent fault (Figure 2) (Zentilli et al., 2019). The first sampled gossan is part of the WGVA system, near the intersection of a rusty diabase ridge and White Glacier. The nearby glacial activity is responsible for the carving of the Jurassic and Triassic units, which exposes the White Glacier vein array. Gypsum Hill is its closest associated salt diapir (Zentilli et al., 2019). Nine samples were subsequently collected from a \sim 30 cm trench.

The second sampling site was a bi-layered gossan at Color Peak. Color Peak is a diapiric body that is part of the carboniferous evaporites unit, the oldest exposed rock in the area (Figure 2). Color Peak is heavily associated with perennial springs situated in its periphery and has been reported and extensively studied in the literature (Perreault et al., 2007; Battler et al., 2013; Zentilli et al., 2019). Samples were collected from two layers: the bright orange top layer at a 5 cm depth and the dark grey bottom layer at a 35 cm depth.

The third and last site was a reactive gossan located north of the M.A.R.S station. This site was observed to be in a mineralized zone in a hydrothermal chimney structure. It is situated

at the intersection of the Cretaceous diabase and the Jurassic to Triassic strata and is located near Gypsum Hill (Figure 2). The gossan appeared to stretch up vertically alongside the exposed side of a dried stream bank. The host rock observed on site was fractured breccia. This gossan had no apparent stratigraphy but had distinct alteration zones based on color and texture. Three samples were collected from three mineralogically and texturally distinct zones. This was observed to be a relatively active system, with apparent active alteration, precipitation, and oxidation.



Figure 2: Generalized geological map showing the location of the three sampled gossans in relation to local geology. Geology modified from Harrison and Jackson, 2010 and created by T-MARS member Eloïse Brassard.

Sampling protocol. From initial observations, the sampling areas appeared to be a loworganic environment with limited surrounding vegetation. The sampling protocol was therefore designed to minimize contamination from extraneous organic material during every step of the process: during the pre-treatment of the sampling equipment, during sampling, and while handling samples during laboratory analysis. The sampling protocol was modified from Williams et al. (2021). Before the expedition, clean and sterile sampling equipment was pre-treated to remove organic contamination. 120 mL amber glass jars were combusted at 550°C for 12 hours. Their accompanying PTFE-lined polypropylene jar caps were solvent rinsed (3x methanol, 3x DCM, 3x, hexane). Aluminum foil was baked at 550°C for 12 hours. Clean metal scoopulas were solvent washed (3x DI water, 3x methanol, 3x DCM, 3x hexane), then wrapped in ashed aluminum foil. The metal shovel and trowel hand tools were cleaned and solvent washed similarly, then packed in ashed aluminum foil. At the gossan sampling sites, samples were collected vertically along the apparent gossan stratigraphy that spans varying mineral assemblages and levels of alteration and oxidation to be analyzed for their lipid content. At the WGVA and Color Peak sites, ~30 cm trenches were dug using hand shovels (Figure 3,4). The HTC site was sampled based on its distinct alteration zones (Figure 5). Pre-cleaned metal scoopulas wrapped in ashed foil were then used to collect samples. After collecting a sample, the cap was screwed onto an ashed foil-topped jar. Sealed samples were then kept in a commercial freezer at the M.A.R.S station until return, where they were stored in a -40°C freezer. The samples were freeze-dried for 24 hours prior to laboratory analysis. Returned samples were divided into two sections, one for elemental analysis and lipid extraction and analysis and one for mineralogical analysis using X-ray diffraction (XRD).



Figure 3: Field observations at the WGVA gossan. (A) Overview of WGVA gossan looking north showing the rust-colored cap.(B) View of the alteration layers exposed in a 30 cm trench showing layers-stained different shades of orange and grey. (C) Enlarged view of a brecciated bedrock fragment shows rust-colored staining, gypsum, and barite precipitates. The scale card measured 12 centimeters (cm).



Figure 4: Field observations at the Color Peak gossan. (A): Overview of the gossan showing the bi-layered rust-colored cap.(B): View of the two alteration layers sampled. The scale bar measured 12 centimeters (cm).



Figure 5: Field observations at the HTC gossan. (A) Overview of HTC chimney structure. (B) View of rust-colored alteration zones. (C) Close-up of sample 22HA-04-1-B. (D) Close-up of 22HA-04-1-A and 22HA-04-1-B samples. The scale card measured 8 centimeters (cm).

3.2. X-ray Diffraction (XRD)

A mineralogical analysis was conducted using XRD to characterize the mineral profile of the area more in depth and to correlate it with our lipid findings. Samples were prepared for XRD analysis using an XRD McCrone Mill. They were first crushed lightly to be homogenized, then reduced to less than 0.5mm particles using a stainless-steel percussion mortar. 4 mL volumes of each sample were then pulverised using corundum grinding elements and isopropyl alcohol wet grinding for 5 minutes in the McCrone Mill. Powders were subsequently dried at a 50° C in an oven. The McCrone Mill was used due to its gentle size reduction process that preserves the crystal lattices of softer minerals despite harder minerals. This way, samples are powdered and reduced to submicrometric particles needed for XRD analytical methods (O'Connor et al., 1986).

The XRD analysis was performed at the McMaster Analytical X-Ray Diffraction Facility (MAX). Powders were pressed into sample holders using a sample-mounting method for random powder X-ray diffraction. XRD data was then analyzed on a Bruker D8 DISCOVER with DAVINCI.DESIGN diffractometer equipped with an Eiger2R 500K area detector in 2D mode and a Cobalt Sealed Tube Source (λavg = 1.79026 Å) set at 35kV and 45mA. Data were collected with DIFFRAC—measurement Centre Version 7.5 software. Qualitative and semi-quantitative analysis was completed using DIFFRAC.EVA software. Mineral phases were identified by their characteristic peaks and diffraction patterns.

3.3. Elemental analysis and pH measurements

The total carbon (TC), total nitrogen (TN), and total organic carbon (TOC) content were analyzed using a Carlo Erba NC2500 Elemental Analyzer at the Geotop-UQAM laboratory. 15-20 mg of each sample was weighed into tin cups to be analyzed for %TC and %TN, and 12-15 mg of the sample was weighed into silver cups and reacted with HCl for 24h to be analyzed for %TOC. Total organic carbon concentrations were determined using the high-temperature catalyst combustion analysis. This was performed using an acidification by 24-hour fumigation as a decarbonation method to remove inorganic carbon (Helie, 2009). Analytical uncertainty for TOC and TN measurements is 0.07% for TC and \pm 0.01% for TN.

Sample pH was measured using a cleaned and calibrated benchtop pH probe at McGill University. Samples were air-dried and ground to <2 mm. 10g of each sample was mixed with 10 mL of DI water to create a slurry that was let to stand for 1 hour. Samples were then analyzed for pH immediately.

3.4. Lipid Analysis

3.4.1. Lipid Extraction

Frozen samples were freeze-dried for 24 hours prior to extraction. Approximately 10 g of each sample was powdered and homogenized using a ceramic mortar and pestle that was combusted at 550° C and was cleaned with solvents (methanol and dichloromethane) between samples. The total lipid extract (TLE) was extracted from freeze-dried sediments by microwave extraction using a CEM MARS 6 solvent extraction system alongside an extraction blank to detect any traces of contamination. Microwave extraction vessels were pre-cleaned by running a cleaning program using 18 mL 9:1 DCM:methanol mixture for 40 min at 80°C. Then, approximately 10 g of samples were transferred to clean extraction vessels with ~20 mL of a 9:1 DCM:Methanol mixture and was heated using the program ran previously at 80°C for 40 min. The slurry mixture was then transferred into 50 mL centrifuge tubes, vortexed for 5 min, and

centrifuged for 10 min to separate solvent and sediment. The liquid phase containing the TLE was pipetted into pre-combusted test tubes, and the process was repeated 3 times, each time adding 9:1 DCM to methanol solvent to the solid phase. To remove elemental sulfur present in the samples, copper pellets were solvent cleaned with a 9:1 DCM:Methanol, acid activated in HCl solution for 2 hours, and around 5 mg of it was added to the TLE. The test tubes were then placed in the RapidVap® Vertex[™] Dry evaporator at 40°C overnight.

3.4.2. Alkane Separation

The TLE of the gossan samples alongside the extraction blank was separated into different fractions using silica gel chromatography. 10-cm silica gel columns were built for each sample alongside the extraction blank. In pre-combusted pipettes, burnt glass wool was added at the bottom, then \sim 5 cm silica gel and \sim 1 cm sodium sulfate was added respectively to each column. Columns were rinsed respectively with methanol, DCM, and hexane. \sim 5 mL of hexane was added to the evaporated TLE, then pipetted through the column and collected in a pre-combusted vial, with the process being repeated three times to separate and collect the alkane fraction from the TLE. The 15 mL alkane fraction was then gently evaporated under N₂ gas and transferred into 1 mL GC-vials. Further concentration of the alkane fraction was needed so the 1 mL alkane fraction was further evaporated under N₂ gas and was transferred into 150 μ L GC-inserts.

3.4.3. GC-MS Conditions & Peak ID

An injection volume of 1 μ L from each sample was analyzed on an Agilent gas chromatograph model 7890B coupled to an Agilent mass spectrometer model 5977B MSD at the Organic Geochemistry Environmental Laboratory at Geotop-Concordia. The GC is equipped

with an Agilent DB-5ms, 25 m, column, with 0.200 mm ID, and 0.33 um thickness. The temperature was set initially at 75° C, held for 10 min, then ramped at 10° C/min to 320° C, then held at 320° C temperature for 10 min. The injector was kept at a 300° C temperature, with a pure helium flow rate of 1.3 mL/min, and septum flow rate at 5 mL/min. The same GC temperature program was used for all samples analyzed. Chromatograph data and the mass spectra for each sample was then viewed using Agilent MassHunter software. Peak identification was based on retention time comparison with external standards coupled with NIST Spectral Library software matches. We used external standards for the following straight-chain alkanes: docosane (C22), heptacosane (C27), and tricontane (C30), along with the ASTM® D2887 quantitative calibration solution with components ranging from pentane (C5) to n-tetratetracontane (C44) at a 20-ppm concentration.

4. Results

4.1. Description of Gossan Sampling Sites

The pH, depth, and color of each sample are presented in Table 3. Gossan layers were sampled to select different colours. Ex-situ pH measurements varied widely between the different gossan layers but were acidic across all samples, ranging from 6 to 1.7. In the WGVA gossan, pH varied from 6 to 3.8. The lowest pH of 3.8 was the value of the deepest light brown layer 22HA-01-3-F at 16 cm. For Color Peak gossan, the pH levels were uniform across both layers at a low pH of 3.9. The HTC gossan pH measurements were also highly acidic and varied from 1.7 to 2.1.

Gossan	Sample	Depth (cm)	Descriptive Color	рН
WGVA	22HA-01-2-A	1	Brown	5.8
	22HA-01-2-C	6	Bright orange	6.1
	22HA-01-3-A	2	Brown	6.0
	22НА-01-3-В	2	Light grey	6.0
	22HA-01-3-C	5	Bright orange	5.9
	22HA-01-3-D	1	Grey	4.9
	22НА-01-3-Е	16	White	-
	22HA-01-3-F	16	Light brown	3.8
	22HA-01-4-A	1	White	5.3
Color				
Peak	22HA-02-1-A	1	Bright orange	3.9
	22HA-02-1-B	30	Dark grey	3.9
НТС	22HA-04-1-A	-	Light yellow grey	1.7
	22HA-04-1-B	-	Bright orange	2.1
	22HA-04-1-D	-	Dark grey	1.9

 Table 3: Sample, depth, color, and pH.

4.2. X-ray Diffraction mineralogy

X-ray diffraction analysis was conducted to reveal qualitative and quantitative mineralogical differences between the gossan layers. Table 4 and Figure 6 show the phase identifications and quantifications derived from XRD analysis.

Sulfates dominated the mineralogy of the WGVA site. Barite, gypsum, quartz, and kaolinite were all identified in varying weight percentages. Barite was the dominant mineral in all samples, making up 71.9 wt.% of the combined samples' weight and ranging from 30.9 to 100.0 wt% in all samples. Gypsum was the second most common phase at 21.2 wt.% of the combined samples' weight and was found in seven out of the nine samples varying from 9.5 to 53.7 wt%. Quartz was identified in four out of nine samples ranging from 4 to 15.5 wt% and making up 4.9 wt.% in the combined sample's weight %. Lastly, one sample contained kaolinite at 17.5 wt%.

The Color Peak gossan site had a different mineralogy that was primarily composed of silicates and phyllosilicates. Quartz was the dominant phase, making up 80 wt.% of the combined samples' weight. Other phases identified in minor amounts in this gossan were, respectively, kaolinite (8 wt.%), albite (7 wt.%), jarosite (3 wt.%), gypsum (2 wt.%), and trace amounts of barite.

The HTC gossan mineralogy was more variable between samples. The first sample, 22HA-04-1-A, appeared to be dominated by clays. Semi-quantitative results showed the presence of barite, gypsum, and minor amounts of jarosite. This sample, however, could not be properly quantified by XRD using the standard Rietveld refinement method due to the poorly crystalline nature of clays and their potential preferred orientation in the random orientation

sample method. The second sample, 22HA-04-1-B, was quartz-rich (78.1 wt. %) and contained gypsum (14.3 wt.%) and albite (7.6 wt.%). The last sample had more mineral phases and was also dominant in quartz (59.7 wt.%), with other minerals including albite (18 wt.%), jarosite (10.7 wt.%), hedenbergite at (7.5 wt.%) and gypsum (4 wt.%).

All samples throughout the three sampled gossans had unidentified broad peaks at low angles $< 10^{\circ} 2\theta$. These broad peaks can be attributed to various sources, namely, due to amorphous material, small particle size, lattice distortion, or, most likely, because of clays whose unique layered crystal structure can result in low-angle reflections.
Table 4: Phase Identifications and semi-quantitative XRD analysis (wt%) using Rietveldrefinement (Diffrac.Eva software).

WGVA Gossan	Quartz	Gypsum	Barite	Jarosite	Kaolinite	Albite	Hedenbergite
22HA-01-2-A	15.5	53.7	30.9	-	-	-	-
22HA-01-2-C	-	31.4	68.6	-	-	-	-
22HA-01-3-A	13.9	-	68.5	-	17.5	-	-
22НА-01-3-В	-	43.7	56.3	-	-	-	-
22HA-01-3-C	4.0	30.3	65.7	-	-	-	-
22HA-01-3-D	11.1	14.6	74.3	-	-	-	-
22НА-01-3-Е	-	7.9	92.1	-	-	-	-
22HA-01-3-F	-	9.5	90.5	-	-	-	-
22HA-01-4-A	-	-	100.0	-	-	-	-

Color Peak	Quartz	Gypsum	Barite	Jarosite	Kaolinite	Albite	Hedenbergite
22HA-02-1-A	92.8	-	0.6	1.2	5.4	-	-
22HA-02-1-B	67.3	4.7	-	3.7	9.9	14.4	-

НТС	Quartz	Gypsum	Barite	Jarosite	Kaolinite	Albite	Hedenbergite
22HA-04-1-A	-	-	-	-	-	-	-
22HA-04-1-B	78.1	14.3	-	-	-	7.6	-
22HA-04-1-D	59.7	4	-	10.7	-	18	7.5



Figure 6: Pie charts showing the combined bulk mineralogy of: (A) the WGVA gossan. (B) Color Peak gossan. (C) HTC gossan.

4.3. Elemental Analysis

The percentages of total nitrogen (TN), total carbon (TC), total organic carbon (TOC), and the organic carbon to nitrogen ratios (C/N) are shown in Table 5. Total nitrogen was either below detection levels or very low across all samples, ranging from 0.00-0.03 w/w %. Total carbon percentages were also very low but more variable. In the WGVA gossan, TC contents are the lowest, ranging from 0.01 to 0.23 w/w %. TC values were highest in the Color Peak gossan samples, ranging from 0.90 w/w % in the deeper layer to 0.97 w/w % in the surface layer. TC values range more considerably between the HTC gossan, ranging from very low levels in the first two levels (0.04-0.03 w/w %) to higher TC in the dark grey layer (0.92 w/w %).

TOC levels measured in the WGVA gossan are close to the TC levels, indicating that almost all of the carbon is organic. TOC concentrations in the Color peak gossan are also high relative to TC, with 85.7-89.5 w/w % of TC being TOC. TOC levels in the HTC gossan also indicate that 100 w/w % of the carbon present is also originating from organic carbon. All sampled gossans show less than 1 w/w % TOC, which is considered a low organic environment.

Due to the extremely low TN values in most samples, the organic carbon to nitrogen atomic ratio (OC/N) could only be calculated for five out of fourteen samples. The first surface layer at the WGVA gossan has an OC/N ratio of 24.13. Both layers at the Color Peak gossan have OC/N ratios ranging from 41.79 at the top layer to 51.08 at the bottom layer. The first sample at the HTC gossan has a low OC/N ratio of 1.98, and the last sample has an OC/N ratio comparable to the 2nd gossan at 53.84. Given the very low %TN values, the OC:N values are subject to a large amount of uncertainty, ranging from ± 2.3 to ± 22 , corresponding to relative errors between 50 to 200%.

Gossan	Sample	%TN	%TC	%TOC	OC/N
WGVA	HA-01-2-A	0.01	0.23	0.21	24.13
	HA-01-2-C	0.00	0.06	0.04	-
	HA-01-3-A	0.00	0.06	0.06	-
	HA-01-3-B	0.00	0.05	0.06	-
	HA-01-3-C	0.00	0.04	0.05	-
	HA-01-3-D	0.00	0.09	0.08	-
	НА-01-3-Е	0.00	0.01	0.02	-
	HA-01-3-F	0.00	0.01	0.01	-
	HA-01-4-A	0.00	0.02	0.02	-
Color	HA-02-1-A	0.02	0.97	0.84	
Peak					41.79
	HA-2-1-B	0.02	0.90	0.81	51.08
НТС	HA-04-1-A	0.03	0.04	0.04	1.98
	HA-04-1-B	0.00	0.03	0.03	-
	HA-04-1-D	0.03	0.92	1.25	53.84

Table 5: Percentages of total nitrogen (TN), total carbon (TC), total organic carbon (TOC), and atomic OC/N ratios of all samples.

 $^{\textit{Note}}:$ Analytical uncertainties for TC were $\pm 0.07\%$ and for TN $~\pm~0.01\%.$

4.4. N-alkane Abundances

Straight-chain n-alkanes were characterized at each gossan layer of the three sampled sites. The relative concentrations of each n-alkane carbon chain were calculated by subtracting the measured blank concentrations from the measured sample concentrations and normalizing them to the total organic carbon present ($\mu g/gOC$) (see Appendix). Absolute n-alkane abundances are also presented in micrograms of n-alkanes per gram of dry weight (ug/gdw) (see Appendix). All n-alkane abundances are color-coded to visually compare values in a range. The n-alkanes were grouped into two groups: high molecular weight n-alkanes (HMW), which are n-alkanes that range from nC_{25} to nC_{36} , and low molecular weight n-alkanes (LMW), which range from nC_{11} to nC_{24} (Cui et al., 2021). They were grouped separately to account for shorter chain alkanes' preferential production by algal and bacterial sources, compared to longer chain alkanes' preferentially production by higher plants (Han & Calvin, 1969; Silva et al., 2012; Imfeld et al., 2019). Graphs plotting the relative abundances of n-alkanes in each sample can be found in Figure 7.

At the WGVA gossan, both relative and absolute n-alkane abundance values indicate large variations between samples. The normalized alkane concentrations ranged from 110.29 ug/gOC in the surface sample HA-01-2-A which has the highest TOC content, to 12708.68 ug/gOC in the grey 2 cm subsurface sample HA-01-3-B. The highest n-alkane concentrations were followed by 22HA-01-3-E, then by 22HA-01-3-C, and 22HA-01-3-D, a bright orange, and a grey sample, respectively. There is no apparent trend regarding n-alkane abundances and any inferred oxidation based on color. In the Color Peak gossan samples, the total alkane concentrations ranged from 184.29 to 519.73 ug/gOC, with the first orange sample HA-02-1-A having the

highest normalized concentration compared to the underlying grey layer HA-02-1-B. In the HTC gossan samples, the total alkane concentrations ranged from 344.91 to 1282.91 ug/gOC. The third dark grey sample HA-04-1-D with the highest TOC content between the gossan layers (1.25 wt %) has the lowest normalized n-alkane concentrations (344.91 ug/gOC). Similarly, the first yellow sample HA-04-1-A that has the highest n-alkane concentrations (1282.91 ug/gOC), has the lowest total organic carbon content (0.04 w/w %).

Absolute n-alkane concentrations (ug/gdw) follow a similar trend as the normalized concentrations (ug/gOC) for the WGVA and the Color Peak gossan, but not for the HTC gossan. In the HTC gossan, the first sample, HA-04-1-A, which has the lowest TOC content, has the highest normalized concentrations but the lowest absolute n-alkane concentrations. This suggests preferential preservation of n-alkanes over other organic molecules. The third sample, HA-04-1-D, conversely, which has the highest TOC content, has the lowest normalized concentrations but the highest absolute n-alkane concentrations but the first sample as the lowest normalized concentrations but the highest absolute n-alkane concentrations. This implies that n-alkanes constitute a smaller fraction of the bulk organic matter in this sample comparatively because it is less biodegraded.







Figure 7: Concentrations and distribution of normalized n-alkanes concentrations in ug/gTOC in samples of the three sampled gossans in this study. (A) WGVA gossan. (B) Color Peak gossan.(C) HTC gossan.

4.5. CPI & ACL molecular proxies

We calculated two molecular proxies: the Carbon Preference Index (CPI) and Average Chain Length (ACL). CPI is a molecular ratio used to identify the biological source and characterize the maturity of organic matter (Marzi et al., 1993). ACL is a measure that represents the average number of carbon atoms in the chain of n-alkanes and is used to characterize the distribution of n-alkanes chain lengths within each sample (Poynter & Eglinton, 1990). These two proxies are commonly used in geochemistry to interpret the sources and processes that contribute to the formation of the present n-alkanes and organic matter (Poynter & Eglinton, 1990; Marzi et al., 1993; Peters et al., 2005).

4.5.1. Indices Equations

Carbon preference index (CPI): Calculations for CPI are based on equations from Teece et al., (2020). Parameters are the following: C: Carbon-chain, n: lower endpoint of the carbon chain range, m: Upper endpoint of the carbon chain range.

$$CPI_{n-m} = \frac{2.(C_n + C_{n+2} + \dots + C_m)}{C_{n+1} + 2.C_{n+3} + \dots + 2.C_{m-3} + C_{m-1}}$$

Average chain length (ACL): Calculations for ACL are based on equations from Poynter and Eglinton (1990). Parameters are the following: C: Carbon-chain, n: lower endpoint of the carbon chain range, m: Upper endpoint of the carbon chain range.

$$ACL_{n \to m} = \frac{\sum (n. C_n \to m. C_m)}{\sum C_n \to C_m}$$

CPI and ACL values presented in Table 6 show a variation in calculated carbon preference indices and chain lengths preferences. First, at the WGVA site, there is a distinct even over odd carbon number preference in the short-chain n-alkanes in all samples other than the surface 1 cm deep sample HA-1-02-A and the 2 cm deep HA-1-03-B sample, as can be observed on Figure 7. These results are supported by calculated LMW CPI indices with values < 1 ranging from 0.39 to 0.81. For the HMW n-alkanes, the calculated CPI values in the majority of WGVA samples, for the exemption of samples HA-01-2-C and HA-01-3-D, are higher than 1 and ranging from 1.11 to 8.49, indicating an odd-over even pattern in the HMW n-alkanes. ACL values ranged from 19.08 to 27.55 for WGVA samples, which generally shows a predominance of HMW n-alkanes.

At the Color Peak gossan, the overlying sample 22HA-02-1-A has no distinguishable odd/even pattern as supported by CPI values of 1.04. In contrast, the underlying sample 22HA-02-1-B, shows a strong even-over odd preference in its LMW n-alkanes as supported by a low CPI value of 0.51. This deeper sample also had more overall enrichment in shorter chain nalkanes as indicated by a lower ACL value. The ACL values ranged from 21.92 in the underlying sample to 23.10 in the overlying oxidized sample.

Lastly, at the HTC gossan, two out of the three samples (HA-04-01-B and HA-04-01-A) showed a clear even-over-odd preference in the LMW n-alkanes. These patterns were coupled with relatively low ACL values ranging from 16.74 in HA-04-1-B, to 22.70 in HA-04-1-A.

Table 6: Calculated carbon preference index (CPI) and average chain length (ACL) values of all three gossan samples. This table uses color grading to visually represent data, with darker colors indicating higher values.

		СРІ			ACL		
Gossan	Sample ID	LMW	HMW	All	LMW	HMW	All
WGVA	HA-01-2-A	1.09	8.49	2.51	19.05	28.81	24.63
	HA-01-2-C	0.81	0.16	0.32	18.46	32.72	27.55
	HA-01-3-A	0.76	1.38	0.87	19.31	28.73	23.04
	НА-01-3-В	1.03	1.11	0.94	18.99	29.43	23.97
	HA-01-3-C	0.68	2.34	1.21	19.44	29.06	25.07
	HA-01-3-D	0.78	0.79	0.72	19.87	30.01	26.80
	НА-01-3-Е	0.73	1.62	0.97	20.38	28.49	24.97
	HA-01-3-F	0.39	1.62	0.51	17.33	28.60	19.43
	HA-01-4-A	0.42	1.47	0.51	17.04	27.99	19.08
Color Peak	HA-02-01-A	1.07	1.28	1.04	18.89	29.37	23.10
	HA-02-01-B	0.51	1.56	0.67	18.78	28.95	21.92
HTC	HA-04-1-A	0.87	4.80	1.39	19.38	28.43	22.70
	HA-04-1-B	0.09	2.18	0.16	15.63	27.17	16.74
	HA-04-1-D	1.08	1.57	1.07	18.82	28.19	21.78

5. Discussion

5.1. Mineralogy

Astrobiological studies suggest that if life were ever present on Mars, it could be preserved as microbial lipids (Parenteau et al., 2014; Georgiou & Deamer, 2014; Hays et al., 2017; Tan et al., 2018). Furthermore, studies investigating lipid preservation in acidic and sulfurrich environments suggest that mineral assemblages of sulfates, along with iron oxides and phyllosilicates, can present favorable conditions for the long-term preservation of organics and should therefore be targeted in future Mars missions (Aubrey et al., 2006; Tan et al., 2018; Johnson et al., 2020). Thus, our study targeted several sites comparable to these mineral assemblages in an acidic to highly acidic and polar Mars analog environment to characterize the presence of organic biosignatures.

On Earth, studies have shown how organic molecules are often well-preserved when deposited with sulfate-rich sediments (Parnell et al., 2004; Aubrey et al., 2006). Our three sites' mineralogy comprises varying assemblages of sulfates, phyllosilicates, and silicate minerals. Clays are assumed to be underrepresented in our results as some clay phases might not have been fully characterized due to the parameters of the randomly oriented XRD technique, as this method is not as effective for clay minerals. The characteristic reddish color of many samples also suggests the presence of oxidized iron phases that may not have been characterized by XRD, potentially due to poor crystallinity, nano-sized particles, or overlapping peaks (Zhou et al., 2018).

Sulfates dominated the first WGVA site, with precipitates such as barite and gypsum, while it contained lower amounts of quartz and the phyllosilicate mineral kaolinite in isolated samples. This site is spatially associated with the White Glacier Vein Array system, a network of veins of hydrothermal origin (Zentilli et al., 2019). This gossan site can potentially be one of the mineralized sites proposed to result from the fluid expulsion phenomenon, which similarly formed the WGVA (Zentilli et al., 2019). Therefore, fluid mixing and cooling are theorized to play an essential role in the mineralization of such deposits (Zentilli et al., 2019). By association, our sampled gossanous deposit can therefore be inferred to be the result of hydrothermal processes, as sulfates likely deposited from hydrothermal fluids, which later oxidized to form the gossan. Therefore, this site likely formed in an acidic, oxidizing environment.

Barite, often associated with metallic ore deposits formed by hydrothermal mineralization (Staude et al., 2011), comprised an average of 72 wt.% of the samples from the WGVA gossan site. While specific formation conditions might vary in a hydrothermal setting, barite potentially resulted from the precipitation of barium and sulfate ions from circulating hydrothermal fluids into spaced fractures, forming the observed vertical white veinlets on the field (Kontak et al., 2006). Similarly, cooling of circulating hot hydrothermal fluids would have catalyzed the reaction of calcium and sulfate ions to precipitate gypsum (Parnell et al., 2004).-The precipitated sulfates likely have then undergone mixing with detrital matrix mineralogy through the effects of mass-wasting (Percival and Williamson et al., 2016).

White Glacier Vein Array and Colour Peak Diapir have been proposed to have a kinship due to their mineralogical, textural, and compositional similarities (Zentilli et al., 2019). They have been proposed to be heavily influenced by the same Eurekan Orogeny 50 million years ago, which created the local network of hydrothermal system (Zentilli et al., 2019). Regarding the

sampled gossan sites, in contrast to WGVA, the Color Peak gossan's mineralogical analysis indicated the dominant mineral present to be quartz at 80 wt.%. Additionally, XRD data show the presence of minor phases such as albite, kaolinite, sulfates such as gypsum and jarosite, and trace amounts of barite. Additionally, the rust-colored top layer strongly indicates the presence of iron oxides that were potentially undetected by XRD.

This Color Peak gossan is located adjacent to Color Peak, which is a salt diapir that is known for its colorful rust-colored appearance and its extensively studied perennial spring system (Zentilli et al., 2019; Battler et al., 2013; Perreault et al., 2007). It is a unique site that is one of a few known to host cold and nonvolcanic spring activity in a permafrost-dominated environment (Zentilli et al., 2019). These spring sites are also locally associated with the underlying hydrothermal system in Expedition Fjord (Zentilli et al., 2019). Color Peak mineralogy is heavily associated with perennial spring discharge and might be linked to the local hydrothermal development. This Color Peak gossan we sampled possibly had been influenced in the past by hydrothermal alteration and formation of sulfides.

The Color Peak gossan lies adjacent to the Carboniferous evaporite and Cretaceous strata juncture. Previous studies of gossans in the Canadian Arctic have discovered many other gossans on Axel Heiberg Island located within different comparable evaporitic diapir to Color Peak, such as Agate North Diapir, East Fiord North Diapir, and East Fiord South Diapir (Williamson et al., 2015; Percival & Williamson, 2016). These gossans were determined to be associated with relict sulfide chimneys of basaltic breccia embedded in the salt diapirs. They have the characteristic visible ochre-colored alteration zones and were confirmed to contain sulfates such as jarosite, copiapite, and fibroferrite. Our XRD results are the most closely comparable to some of the gossans described to consist of a poorly preserved mafic breccia structure, a silica-rich 'apron,' and gossanous soil (Williamson et al., 2015). Similarly, our Colour Peak samples, sampled along a 30 cm depth, were dominated by silicious material, with quartz as the dominant phase (80 wt.% average) and minor amounts of sulfates and clays. The quartz is likely from the residual silica left behind as other minerals are dissolved or altered during the weathering and oxidation process of the gossan, as gossans are also commonly associated with quartz due to the release of silica during this oxidation process (Pirajno et al., 2010).

Similar to Color Peak, mineralogy results at the HTC gossan site show that it was also dominated by quartz (69 wt.%). XRD analysis additionally revealed varying amounts of sulfates, such as gypsum and jarosite, as well as albite and hedenbergite. This site was observed to be a part of a vertical chimney-like structure of weathered and oxidized minerals. This gossan is, therefore most likely the result of hydrothermal activity. The primary sulfate mineral deposits of gypsum in this site likely precipitated from the cooling of hot fluid migration through fractures and faults (Tang et al., 2014; Zentilli et al., 2019). Jarosite, a secondary mineral, likely formed from the oxidation of hydrothermally produced iron-sulfides, which is commonly found in rocks that have undergone hydrothermal alteration. Jarosite in this context can indicate our site's past hydrothermal origin as it is often associated with hydrothermal alteration (West et al., 2009; Grasby et al., 2022). The presence of jarosite in both these gossans also indicates highly acidic formation conditions (West et al., 2009; Percival & Williamson, 2016). Albite, another secondary mineral that forms through the alteration of primary feldspars, likely resulted from mineral replacement through fluid-rock interactions associated with hydrothermal alteration (Hövelmann et al., 2010). The lack of sediment and debris accumulated over the chimney structure might suggest that HTC is a young system. Though this site differed greatly from the

first two gossans in its mineral and alteration patterns, it contained comparable mineralogy to the Color Peak gossan and a comparable hydrothermal origin to WGVA.

5.2. Implications of n-alkane lipid distributions

N-alkane lipid molecules are a small fraction of bulk sedimentary organic matter. However, they can be used as a proxy to understand sedimentary organic matter's source, preservation, and diagenetic alteration (Meyers, 1997). Our study detected the presence of nalkane lipids ranging from nC₁₁ to nC₃₆ in the gossan sediment records throughout the sampled gossan layers. N-alkanes alone cannot constitute definitive evidence for life (Sherwood et al., 2002). However, when used in a comprehensive study that examines its distribution patterns and the relative proportion of n-alkane chain lengths, it can give us supporting lines of evidence on the source input of the organic matter, including biotic sources (Peters et al., 2005).

Interestingly, we found a predominance of even-over-odd numbered carbon chains in the distribution of shorter chain n-alkanes ranging from nC₁₁-nC₂₃, with a maximum at nC₁₄ in all three gossans. Even-over-odd predominance is not a typical pattern observed in n-alkane lipids. N-alkanes commonly preserved in sedimentary samples rather have an odd-over-even carbon chain distribution due to how carbon atoms are added during biosynthesis (Tissot & Welte, 1984; Wang et al., 2010). The unique pattern of short-chain n-alkanes with a predominance for even-over-odd carbon chains was observed in 71% of the total gossan samples. Notably, at the WGVA gossan, we observed this pattern in 77% of samples. We also see this pattern in the deeper sample at Color Peak gossan and 2 out of 3 samples at HTC gossan. This even-over-odd predominance, although uncommon, has been previously observed in numerous aqueous depositional environments. Namely, it has been reported in lacustrine sediments (Wang et al.,

2010), marine sediments (Nishimura & Baker, 1986), estuarine and riverine systems (Grimalt et al., 1985; Wang et al., 2014), and hydrothermal systems (Elias et al., 1997). This pattern is, therefore, not strictly attributed to a singular sedimentary environment or a distinct reaction, as it has been observed in a diverse set of sedimentary and depositional environments. Rather, it is attributed to a likely microbial source, inferred to represent direct input from bacteria in complex depositional environments (Wang et al., 2010). Gossan formation often involves exposure to flowing or standing water, underground water, or leaching fluids, which contribute to the oxidation of sulfide deposits and the subsequent formation of sulfates (Burns et al., 1988; Burt et al., 2006; West et al., 2009). This is consistent with the observed even-over-odd predominance microbial signal that is primarily reported in aqueous environments.

Notably, in all three gossan sites, we observed this even preference in short-chain nalkanes in the samples with the lowest organic carbon concentrations. N-alkanes, especially long-chain n-alkanes, are relatively resistant to biodegradation (Medic et al., 2020), which suggests that this pattern is associated with samples that have undergone the highest levels of microbial biodegradation. This further validates the possibility that the observed n-alkane distribution is likely preserved from an active microbial community in situ. The overall distribution patterns and relative proportion of n-alkane chain lengths found strongly point to the presence of preserved biogenic markers. The unique pattern of even predominance in short-chain n-alkanes is most likely from a microbial source, from the product of microbial degradation of algal organic matter or longer-chain n-alkanes by acidophilic microorganisms that are associated with gossans (Elias et al., 1997; Langdahl et al., 1997; Wang et al., 2010; Hedrich et al., 2021).

The even-over-odd predominance in short-chain n-alkanes is also associated with the samples bearing the highest levels of sulfates, particularly gypsum. WGVA gossan, which

demonstrates the strongest signal, is dominated by the sulfates barite and gypsum. At the same time, the deeper sample in Color Peak that preserves this n-alkane pattern has 4.7 wt.% gypsum compared to none in the overlaying sample. At HTC, the sample that shows the strongest microbial signal has the highest levels of gypsum at 14.3 wt.% compared to 4 wt.% in the other sample of known mineralogy. However, our limited data is non-conclusive, and no significant correlation can be made between n-alkane measurements and distribution and mineralogy. The large pH range difference from 6.1 to 1.7 between all three gossans also suggests that pH alone is not a strong indicator of preservation.

Major differences in n-alkane distributions between samples were seen in the LMW vs. HMW concentrations and CPI values in the longer-chain n-alkanes. N-alkanes ranging from C_{20} to C₂₈ generally indicate higher plant input (Eglington & Hamilton, 1967). We observed the predominance of longer-chain n-alkanes in 78% of the samples. CPI values higher than 3 generally indicate higher plant epicuticular waxes (Chen et al., 2014). This high CPI signal is especially prominent in 2 samples: the surface sample from WGVA and the first sample from HTC gossan, with HMW CPI values of 8.49 and 4.80, respectively. These values can be compared to values from modern soils collected around the McGill Arctic Research Station (M.A.R.S) on Axel Heiberg Island during the 2018 field season by a previous student (Chen, 2020). These surface samples exhibited high CPI values across the board, ranging from 1.10 to 5.26 for n-alkanes within the range of nC_{16} - nC_{30} . The average ACL values ranged from 25.44 to 27.24, indicating that the background signal of the soil in the area also predominantly reflects a signal indicative of higher plant material (Chen, 2020). Some of our other gossan samples also exhibit long-chain n-alkane distributions without a distinct odd-over-even pattern, as evidenced by CPI values closer to 1. This can indicate a source input from petroleum contamination

through anthropogenic inputs (Marzi et al., 1993; Chen et al., 2014; Imfeld et al., 2022), though this is not likely as anthropogenic contamination in this remote and high-latitude arctic environment should be minimal. Alternatively, it can be attributed to a biological source from the diagenesis of long-chain molecules in significantly altered plant matter (Kennicutt et al., 1987; Imfeld et al., 2022). This combination in n-alkane patterns points to a mixture of multiple sources of organic matter.

The n-alkanes patterns detected on-site can confirm the preservation of organic matter during at least the early stages of degradation. However, our data does not constrain the ages of the biogenic sources of n-alkanes. Furthermore, given that our findings point to more than one source for organic matter, diagnostic indices such as CPI and ACL alone do not provide diagnostic source identification (Imfeld et al., 2022). To further constrain the origins of n-alkanes detected in this study, isotopic measurements could help unravel the provenance and age of the n-alkane molecules. For instance, carbon-14 isotopic analysis of the bulk organic matter, or the n-alkanes themselves, can provide insight into the age of the n-alkane carbon chains through radiocarbon dating, which would give us an approximate age of the preserved organic material if it is younger than 50,000 years old (Eglinton et al., 1996; van der Voort et al., 2017; Makou et al., 2018). This will allow us to determine if the microbial signal discovered is derived from recent or active microbial communities on-site or from ancient ecosystems. However, it is important to note that if contemporary microbes are consuming fossil carbon, their lipids would have a fossil 14C signature. Stable isotopic studies focusing on isotopic fingerprinting using compound-specific δ^{13} C and δ^{2} H analysis of n-alkanes could be used to further validate the results from molecular diagnostic ratios by differentiating between the different sources of organic matter and determining anthropogenic input (Hou et al., 2007; Imfeld et al., 2022).

5.3. Implications for detecting biosignatures on Mars.

This study is based on the claim that Mars likely had environments that are analogous to terrestrial oxidizing massive sulfide deposits (Burns et al., 1978; Dehouck et al., 2012; Macey et al., 2020; Wong et al., 2022). At all three sampled sites, conditions resembling ancient and current Martian conditions, such as low temperatures, permafrost, and arid weather, prevail. Gossans like the ones we studied on Axel Heiberg Island, although undetected to date, likely could have existed on Mars, making them an appropriate mineralogical and geochemical analog to the conditions under which some sulfates possibly formed on Mars (Burns et al., 1978; West et al., 2009; Williams et al., 2015). Sulfate minerals have been detected by Martian landers and Martian meteorites in various regions on Mars, including Terra Meridiani and Gale Crater (Gendrin et al., 2005; Dehouck et al., 2012; Ehlmann et al., 2014). Notable examples include gypsum found in Gale Crater, Margaritifer Terra, Valles Marineris, and Terra Meridiani (Gendrin et al., 2005; Nachon et al., 2014; De Toffoli et al., 2020), as well as jarosite and acidsulfate weathered outcrops observed in the Burns formation at Meridiani Planum (Squyres et al., 2004). Of particular interest to this study is the Meridiani Planum region, whose sulfate-rich outcrops were proposed to bear a resemblance to the High Lake gossans (West et al., 2009).

In the study of the origin of life, hydrothermal systems are an important model of potential sites for the early origins of biochemistry on Earth (Martin et al., 2008). Similarly, hydrothermal systems provide environments that could have initiated the chemistry of life and subsequently sustained thriving microbial communities on Mars (Martin et al., 2008). They are, therefore, primary targets for the search for life on Mars as they possess the necessary conditions to sustain

it (Martin et al., 2008; Ojha et al., 2021). Mars could have hosted hydrothermal circulation over a prolonged period (100–1000 Ma) during the Noachian. Such systems could have been important in Martian biological and geological history (Ojha et al., 2021). Gossans in the exposed High Arctic Large Igneous Province on Axel Heiberg Island, including the ones we sampled, are suggested as analogs to reactive gossans that can serve as indicators of ancient hydrothermal activity on Mars (Lemelin et al., 2020). Geomorphic studies suggest that some sulfate deposits and associated gossans in this area likely resulted from the same regional fluid expulsion phenomenon associated with the hydrothermal system that developed during the Eurekan Orogeny (Zentilli et al., 2019). The link between gossans and ancient hydrothermal systems has led to the hypothesis that fluids from paleo-hydrothermal systems on Mars could have thawed the deep permafrost and formed nearby associated gossans (Lemelin et al., 2020). Gossans, therefore, can be prime targets for biology potentially preserved in the mineralized remnants of ancient hydrothermal activity on Mars. Our results show biotic signals preserved in the lipid remnants in the gossan mineralogy, including likely microbial signatures, suggesting that gossanlike deposits can potentially be viable targets for biosignatures on Mars.

Sulfates, specifically barite, gypsum, and jarosite, were a common thread between all three sites. Our interpretations deduced that the development of barite and gypsum was likely in a hydrothermal context, while jarosite was likely the result of the oxidation of sulfides. These minerals are all indicators of past aqueous environments (Burt et al., 2004; Elwood et al., 2004). Jarosite and gypsum have been mapped in multiple localities on Mars (Elwood et al., 2004; Ming et al., 2007; Vaniman et al., 2018). Jarosite formation requires wet, oxidizing, and acidic conditions (Elwood et al., 2004). Its presence on Mars has been proposed as mineralogical evidence for these conditions and highlighted for its potential to record evidence for biological

activity, especially in the case of biologically mediated jarosite formation (Loiselle et al., 2012; 2018). Gypsum, while primarily forming through non-biological processes, is also another indicator of aqueous alteration (Ming et al., 2007). Barite, although undetected to date on Mars, has been proposed as an exceptionally good target for the search of past aqueous environments due to its relatively low solubility, the relatively low geochemical abundance of Ba in mafic igneous rocks, its resistance to weathering, and its lack of polymorphs, making barite is a stable and unambiguous potential mineral indicator of past aqueous environments on Mars (Burt et al., 2004). Its crystallization is also associated with hydrothermal activity and biologically mediated precipitation, both of which are contexts with appropriate applications in biosignature search on Mars (Hanor, 2000; Veneranda et al., 2020). Barite deposits associated with hydrothermal fluids were also found to preserve organic molecules in fluid inclusions in 3.5 billion-year-old rocks on Earth in the region of Pilbara Carton, Western Australia (Mißbach et al., 2021). The preserved organic molecules are theorized to have been delivered by hydrothermal fluids, which would then fuel microbial communities associated with these barite deposits (Mißbach et al., 2021). This further highlights the durability and fitness of hydrothermally associated sulfates such as barite as a host mineral of organics over billion-year timescales. Our results therefore build on other findings that suggest that mineral assemblages containing sulfates have a good preservation potential for organics (Francois et al., 2016; Johnson et al., 2015, 2020).

The Mars Science Laboratory (MSL) Curiosity Rover's Sample Analysis at Mars (SAM) instrument, equipped with both a mass spectrometer and a gas chromatograph (GC-MS), was designed to identify a variety of organic substances on Mars (Mahaffy et al., 2012). Although of unknown origins, findings from SAM's wet chemistry experiment revealed the presence of short-chain n-alkanes ranging from C10-C12 at Gale Crater (Freissinet et al., 2019).

Additionally, the SAM instrument also revealed the first quantifiable bulk organic carbon in a 3.5-billion-year-old mudstone in Gale Crater (Stern et al., 2022). Previous findings also point to the presence of organics in the first 6 cm of the Martian surface (Freissinet et al., 2015; Eigenbrode et al., 2018; Millan et al., 2019; Millan et al., 2022; Williams et al., 2021). Tentative identification of alkanes linked to sulfates has also been made in Mars meteorites (Freissinet et al., 2019; Steele et al., 2022). Although a biotic source of these organics cannot be confirmed, the presence of n-alkanes as preserved organics from a past habitable Martian environment further reinforces our study's suggestion that potential ancient microbial life could have been preserved and its signal recorded in n-alkane distribution patterns.

A challenge to detecting organics such as lipid compounds on Mars is the low detection limits of the instruments used in space exploration missions and the very low organics content on Mars (Mahaffy et al., 2012; Azua-Bustos et al., 2023). This is evidenced by the work presenting the first quantification of bulk organic carbon in Mars surface sedimentary rocks (Stern et al., 2022). The SAM combustion experiment detected a range of 950 μ g C/g of organic carbon at low temperatures and a minimum of $273\pm 30 \mu$ g C/g at high temperatures, which is even lower than our Arctic Mars analog sites, which demonstrates a low abundance of organic carbon (TOC) (0.01 – 1.25 w/w %), and even lower amounts of nitrogen (0.00 – 0.03 w/w %), which were undetectable for most samples. Additionally, alkanes were detected in very low amounts using a commercial GC-MS, as absolute n-alkane abundances ranged from as low as 0.22 – 7.32 ug/gdw. In lower amounts and with less sensitive instruments, the n-alkanes might be below detection levels using instruments like SAM on Mars (Azua-Bustos et al., 2023). This further reinforces

the importance of a Mars Sample Return mission so that samples can be extensively examined using much more sensitive instruments on Earth (Beaty et al., 2019; Azua-Bustos et al., 2023).

Another challenge to the search of organics on Mars is the harmful effects of radiation and oxidants on organics (Summons et al., 2008). Although the microbial signal detected in this study is present in samples from a variety of depths, it is most likely that the deeper subsurface samples in gossans would be a better target for preserving lipid biomarkers on Mars. This is due to the reactive and harsh Martian surface, which is constantly bombarded with cosmic rays and UV irradiation, in addition to an array of non-aqueous chemical reactions over long timescales that degrade or corrupt potential molecular biosignatures (Summons et al., 2008; Johnson et al., 2020). Additionally, oxidation processes might still occur in near-surface rocks on Mars (Freissinet et al., 2015; Benner et al., 2000). The Curiosity and the Perseverance rovers can drill to a full depth of 6 and 7 cm, respectively, and the ExoMARS Rosalind Franklin rover to 2 m deep (Williams et al., 2021; Megivern et al., 2022). The n-alkane microbial signal detected in our study ranged from surface depths to 30 cm deep, indicating that the deeper subsurface samples in gossans might potentially preserve detectable undegraded n-alkane lipids on Mars.

Our findings also support the idea that although the Martian surface is highly oxidized, it is still possible that organic molecules could be preserved in certain oxidizing conditions, such as within subsurface layers in protected geological formations/mineral assemblages of sulfates, silicates, and phyllosilicates. While it is widely recognized that oxidized samples are less conducive to preserving organic matter over long periods of time compared to reduced environments (Sumner et al., 2004; Summons et al., 2011; Fernández-Remolar et al., 2021), our samples, which clearly show indications of oxidation similar to the Martian surface, clearly still have a preserved n-alkanes signal. This suggests that Martian targets for biosignatures do not

need to be reduced environments to retain evidence of n-alkanes, raising the prospect that even acidic and oxidizing environments on Mars might contain important evidence of these chemical molecules, which widens the search for exploration targets for past or present life on Mars.

Comparing terrestrial gossans to Mars reveals a notable contrast between the current Earth's O_2 rich atmosphere and Mars' CO_2 rich atmosphere (Mahaffy et al., 2013). Studies, however, suggest that Mars' current atmospheric oxygen levels, which fall below ~ 10^{-5} times present day Earth, may have been comparable to early Earth's O_2 concentrations during the Archean (Pavlov and Kasting, 2002; Mahaffy et al., 2013; Lanza et al., 2016). This raises the question of whether gossans that formed during this time in Earth's early history might serve as better high-fidelity analog environments to similar deposits on Mars. However, although studies have located gossans which formed on Archean sulfide deposits such as the High Lake gossans in Nunavut, Canada (West et al., 2009), preserved gossans specifically formed during the Archean era are yet to be discovered. Beyond the scope of this research, future studies might benefit from seeking and examining gossans from Earth's early history as Mars analogs.

6. Conclusion

Our study is among the first to investigate n-alkane biomarkers in an Arctic gossan Mars analog environment. By assessing the preserved lipid n-alkane load and distribution patterns in acid-weathered sulfate-rich gossanous soils, this preliminary work explored how a microbial signal can potentially present itself in the geologic record of this novel analog environment. Nalkane biomarker analysis revealed preserved long-chain n-alkanes with odd-over-even distribution from higher plant sources and, most interestingly, an even-over-odd distribution pattern in short-chain n-alkanes, most likely from a microbial source. This microbial pattern is clearly distinct from the background n-alkane distribution in modern soils collected around the MARS Station (Chen et al., 2020). Although an even-over-odd distribution pattern in short-chain n-alkanes is uncommon for n-alkane distributions, it has previously been observed in various aqueous depositional environments and is associated with complex depositional settings (Wang et al., 2010). The even-over-odd predominance in short-chain n-alkanes also correlated with higher sulfate levels in our study, particularly gypsum.

However, no significant correlation could be established between n-alkane measurements and specific mineralogy. Despite our initial hypothesis that mineralogy, acidity, or depth may be a driving force for controlling the preservation potential of organics in gossans, specifically nalkane lipids, the results of this study indicate no systematic difference in n-alkane abundances or signatures based on these factors alone. Additionally, the distribution of n-alkane abundances was highly variable on a small scale. Without a clear understanding of the factors that control these relationships, this could potentially pose challenges for analysis of samples rom Mars. Therefore, it is advisable to conduct further investigations into this small-scale variation. A broader dataset from further sampling of soil directly adjacent to the studied gossans and of other various reactive gossans in the Axel Heiberg area is needed to refine the conclusion drawn from our analyses and confine the unique parameters which control lipid biosignature preservation. The preserved n-alkanes need to also be further analyzed to identify exact biogenic sources of lipids and their ages beyond early stages of degradation. As this research was an exploratory work in an underexplored area, additional comparative studies need to be carried out on a larger scale to advance our current knowledge of how preserved microbial life presents itself in Arctic Mars analog gossan environment. Stable isotopic studies, carbon-14 dating, and analysis of other

molecular biomarkers such as fatty acids are needed to improve the accuracy and specificity of our assessment of biogenic sources.

Our study focused on gossans in the High Arctic Large Igneous Province on Axel Heiberg Island, which can serve as indicators of ancient hydrothermal activity. Our findings suggest that hydrothermally associated gossans have the potential to preserve organic matter and biotic signals within their sulfate-rich mineralogy, making them valuable analog environments for Mars missions. Our GC-MS analysis of gossans revealed the presence of mixed plant and microbial lipids, albeit in low abundances. This supports the idea that sulfate mineral assemblages, including silicates and phyllosilicates, are suitable for preserving molecular fossils on Mars (Aubrey et al., 2006; Tan et al., 2018; Johnson et al., 2020). These findings strengthen the hypothesis that ancient microbial life may have been preserved in oxidized, acid-weathered, sulfate-rich Martian environments. They also emphasize the potential of lipids and n-alkanes as organics of interest for detecting signs of life on Mars. However, challenges persist in detecting lipid biosignatures on Mars, including the low abundance of organics, instrument sensitivity limitations, limited rover coverage and sampling, and the harsh Martian surface conditions (Summons et al., 2008; Freissinet et al., 2015; Johnson et al., 2020).

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