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Key Points:

- Gypsum and the SOPHIA Mars simulant maintain their spectral features during cryodesiccation, aiding biosignature preservation
- Microbial mats and their biosignatures can survive exposure to the cold, low pressure Martian environment
- Predicting chemical changes in samples during operations provides accurate interpretations of past and present environmental conditions

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The Spectroscopic Impact of Sublimation Under Martian Surface Conditions: Implications for Sample Analysis by the Rosalind Franklin Rover and Biosignature Preservation

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Abstract

The 2028 ESA/NASA Rosalind Franklin Mission (RFM) will search for signs of past and present life in the shallow subsurface of Mars. It is crucial to understand how minerals and any biosignatures uncovered during these sampling activities might change and be identified under today's Martian conditions. This preliminary study explored the effects of cryodesiccation, induced by the sub-zero, near-vacuum conditions on the Martian surface, on Ca-sulfate, the SOPHIA Mars soil simulant and an Antarctic microbial mat collected during the Scott Expedition. Powdered samples were analyzed via Visible-Near-Infrared (Vis-NIR) and Fourier Transform Infra-Red spectroscopy to emulate future analyses by the PanCam and Enfys instruments and placed in a lyophilizer maintained at −63.4°C with a vacuum of 1.182 mbar for 1 hr and 72 hr. After 1 hr exposure, Mars-like sublimation processes began within the three Mars analog samples, increasing the spectral intensity of the mineralogical, hydration, and organic features within the samples. After 72 hr exposure, sublimation reactions were ongoing, with hydration- and organic-induced spectral bands observed to decrease in intensity and detectability, with some features now removed. Understanding how sampling activities and subsequent environmental exposure affect the mineralogical and organic content of samples, and how to spectrally identify these changes using rover instrumentation, is vital in assessing the reliability of the data uncovered, the differences between the subsurface and surface environments at Oxia Planum, and therefore the environmental and biological interpretations made.

Plain Language Summary

When the 2028 ESA/NASA Rosalind Franklin Mission arrives on Mars, it will drill up to 2 m into its surface and retrieve geological samples for analysis. These will be initially studied and imaged using multiple spectroscopic instruments. It is therefore crucial to understand the spectroscopic changes that will occur to these rocks, and any organic molecules contained within them, when they are exposed to the sub-zero, low pressure Martian environment. This study explored the sublimation effects on gypsum and Mars-soil simulants that are known to be good at preserving organic molecules and biosignatures of life, as well as a >120-year-old microbial mat from Antarctica. Initial results showed that after exposure to the Martian environment for up to 72 hr, gypsum and the clay-rich Mars soil simulant called SOPHIA, showed minimal water loss via sublimation and would be good mineral protectors for biosignatures. The Antarctic microbial mat organic signatures survived the cold and low pressure environment, with the loss of water actually amplifying the spectral visibility of the organic molecules present. This study highlights that perhaps the Martian environment is not as bad for astrobiology as once thought and may actually aid the spectral detection of biosignatures.

1. Introduction

The 2028 ESA/NASA Rosalind Franklin Mission (RFM) will search for signs of past and present life on Mars, and investigate the aqueous/geochemical environment as a function of depth in the shallow subsurface (Vago et al., 2017). As such, it is crucial to understand how minerals and any biosignatures preserved within them can be identified under today's Martian conditions. Minerals within the shallow subsurface of Mars are mostly shielded from the planet's harsh environment. However, when excavated by a rover through deliberate rock abrasion, drilling, and coring techniques or inadvertently during modes of operation and movement, geological materials and any associated organic matter can be newly exposed to the extreme surface environment, potentially for the first time since their formation. Understanding how this exposure affects the mineralogical and organic content of samples, and how to spectrally identify these features using rover instrumentation, is vital in assessing the reliability of the data uncovered, and the environmental and biological interpretations made.

Mars' habitability potential depends upon both its historical and present environmental conditions. The surface environment on Mars today is commonly understood to be inhospitable for life. Although certain aspects are useful for the long-term preservation of ancient organic molecules and possibly even biosignatures, such as the cold and dry surface environment, weak hydrological cycles, and lack of tectonic activity (Bada & McDonald, 1995), many others are detrimental. e.g., the thin atmosphere and lack of a global magnetic field have left the entire martian surface and shallow subsurface poorly protected against UV and ionizing radiation. Many studies have been conducted to understand the impact of this radiation environment on biosignature preservation on Mars (e.g., Dartnell et al., 2007; Kminek & Bada, 2006; Pavlov et al., 2012), however, little has been done to explore the dual effects of sub-zero temperatures and low atmospheric pressures, which will be immediately felt as soon as a rock sample is uncovered or removed during rover operations. Ice deposits in the subsurface and water held within pore spaces and crystal lattices may undergo sublimation when these buried geological materials and minerals are exposed to the low atmospheric pressure (6–7 mbar, a near-vacuum environment) and sub-zero temperatures on the surface, and are exposed to solar radiation during daylight hours (particularly in the Martian spring and summer). The removal of water/ice can transform the chemical structure, making this a significant geological process on Mars that requires further study.

On Earth, generations of arctic researchers have observed that ambient temperature has the strongest influence on the sublimation of pore ice within soils. Sublimation is most pronounced at around −1°C and as temperature decreases, the bond energy of the ice surface increases, suppressing the rate of ice sublimation (Mangold, 2011 and references therein). The second most influential factor was found to be relative humidity (Huang & Aughenbaugh, 1987), which as it increases, pore-ice sublimation decreases. On Mars, the effects of relative humidity are particularly significant, as the atmospheric water vapor pressure is very low, creating a frost point at 198K (−75.15°C). Given that the average temperature on Mars is −63°C, there is a net ice loss by sublimation observed for all regions where the mean temperature rises above 198K. As such, sublimation-related landforms are ubiquitous on Mars, dominating in the polar and mid-latitudes, as documented by Mangold (2011) and references therein. The process of sublimation has been visually documented on Mars at the Phoenix Landing Site in 2008, when out of 12 trenches dug, eight displayed exposed subsurface water ice at around 4 cm depth (Mellon et al., 2009). Phoenix found a dark ice in the Snow White trench and a relatively bright ice observed in the Dodo-Goldilocks trench, which were observed to sublimate over 2 and 5 to 60 sols respectively (Morris et al., 2008). Exposed sublimating ice patches have also been observed in new impact craters in the mid-latitudes of Mars, presenting as areas a few meters across located on crater floors or within ejecta (Byrne et al., 2009). They were observed to sublimate over several months; visible at Ls 126 (12 September 2008) and Ls 162 (22 November 2008) but not at Ls 180 (25 December 2008).

1.1. The Search for Biosignatures

A significant amount of organic carbon could have accumulated in the regolith and surface rocks of Mars over billions of years. This is supported by the findings of organic molecules in conjunction with areas displaying evidence of past water activity in both Gale and Jezero craters. A variety of organic molecules such as chlorobenzenes, dichloroalkanes, thiophenes, and other volatile aliphatic and aromatic hydrocarbons of Martian origin have been found in abundances of parts per billion, within ancient mudstones in Gale crater (Eigenbrode et al., 2018; Freissinet et al., 2015, 2025; Millan et al., 2022; Stern et al., 2022; Szopa et al., 2020), and aromatic organic compounds within sulfate minerals and mudstones in Jezero crater (Hurowitz et al., 2025; Sharma et al., 2023). The organic molecules observed on Mars are possibly contributed by life but are most likely produced by nonbiological in situ chemical reactions and exogenous delivery by comets, asteroids and meteorites.

To date on Mars, there is an observed association between these organics and sulfates, phosphates, perchlorate, carbonates, and amorphous silicates including alteration textures, and ancient lacustrine mudstones composed of basaltic minerals mixed with phyllosilicate, sulfate, iron oxide, and x-ray amorphous components (Rampe et al., 2017). The range of water-related minerals with the potential to support biosignature preservation is growing and the analysis of these on Mars is key to understanding past water interactions and habitability potential (e.g., Sutter et al., 2017, 2022). Water can be bound in minerals within their crystal structures, incorporated into their crystal lattice during their formation or chemically bonded to the mineral ions, forming a thin molecule-thick surrounding film of water. It can also exist as free water not chemically bonded to the mineral structure but held in pores and spaces within the mineral structure and is therefore more mobile. It is important to conduct laboratory experiments on these types of minerals together with biotic and abiotic organics to understand how they will change over time once exposed on the surface, and how these changes can be detected using rover instrumentation.

1.2. The Rosalind Franklin Rover

Due to the known association between organic molecules and water-related minerals such as phyllosilicates, Oxia Planum–situated at approximately 18.20°N, 335.45°E on the northern margin of Arabia Terra - was chosen as the landing site for the 2028 ExoMars RFM. The area shows strong evidence for past habitability potential, as it preserves a record of geological processes and environments that have occurred in the region and has conditions suitable for the preservation of physical and chemical biosignatures. Oxia Planum is a mostly flat plain formed in an alluvial or a lacustrine/deltaic environment, which was later altered by groundwater (Fawdon et al., 2024). The area is characterized by a shallow basin with Noachian-aged recently exposed Fe/Mg phyllosilicate-bearing bedrock (Carter et al., 2015, 2023; Favaro et al., 2024; Noe Dobrea et al., 2010; Riu et al., 2023) and records at least two distinct aqueous environments. In addition, there is an unaltered mafic-rich dark resistant unit likely of Amazonian age that caps the other units and possibly originated from volcanism.

The ExoMars Rosalind Franklin rover, named after Rosalind Franklin (1920–1958), will drill up to 2 m into the subsurface of Mars to extract these geological samples and then deliver them to the Analytical Laboratory Drawer (ALD) instruments. Rosalind Franklin will carry a suite of instruments—the Pasteur payload—operating at all scales and including several imaging and spectroscopic instruments (the focus of this study) designed to chemically identify and characterize the rocks, minerals and organics at the landing site of Oxia Planum. This includes (a) the PanCam (Coates et al., 2017) and Enfys (Grindrod et al., 2025) mast-mounted wide-angle and high-resolution multispectral visible wavelength cameras, and near infrared spectrometer, respectively; (b) Ma-MISS, an infrared spectrometer in the head of the subsurface drill (De Sanctis et al., 2017, 2022), (c) CLUPI, a close-up high resolution imager (Josset et al., 2017), and (d) MicrOmega, a visible and near infrared micro-imaging spectrometer (Bibring et al., 2017) housed within the ALD. The ALD also contains the RLS (a Raman Laser Spectrometer) (Rull et al., 2017), and MOMA (a Mars Organic Molecule Analyzer) (Goesmann et al., 2017).

To remain protected from the sublimating surface environment of Mars and to increase the survivability and detectability of organic molecules, including potential biosignatures, materials need to be investigated that have remained protected in the cold martian subsurface (e.g., Kminek & Bada, 2006; Vago et al., 2017). The Rosalind Franklin rover is equipped with a rotary drill (without percussion capability) and can acquire samples, either small cores, fragments, or loose regolith, from depths ranging between 0 and 2 m from multiple holes (Altieri et al., 2023). The rover drill is tasked with bringing these samples (typically 3 cm long by 1 cm diameter) to the surface and providing them for imaging before transferring them to the ALD. These subsurface samples will be critical for achieving the science goals of the RFM; however, the changes these samples may undergo once exposed to the surface environment need to be understood to enable researchers to accurately establish their composition, organic make-up, and origin on Mars. This will support correct interpretations of past, present and future data from multiple Martian missions, and aid operations planning and target selection for the Rosalind Franklin rover.

2. Materials and Methods

2.1. Sample Suite

In this preliminary investigation, three different analog materials known or postulated to exist on Mars and at Oxia Planum via orbital reconnaissance have been used to instigate the process of mineralogical and biological interpretations via spectral responses to surface conditions that will be encountered during drill core extraction processes; in particular, how infrared spectral fingerprints as seen by sample triage instruments PanCam and Enfys might change due to these environmental interactions.

Sample 1–Natural samples of pure massive gypsum were collected from the Bantycock Mine in Newark, Nottinghamshire, UK (Figure 1a). These are from the Mercia Mudstone Group, a red-brown clay and mudstone

Figure 1. (a) Massive gypsum veins within Mercia mudstone collected from the Bantycock Mine by Preston. (b) SOPHIA simulant jars from which the sample of this study was subsampled (image adapted from Dugdale et al., 2023). (c) Whole Scott microbial mat sample from which the sample of this study was removed. Image taken by Preston within the Natural History Museum London Herbarium. (d) Powdered samples within test tubes within the lyophilizer based at The University of Westminster.

formation that extends across northern to southern England, originally deposited on land by distant river floods and in sabkha environments during the Triassic period (Armitage et al., 2013). This was chosen as Ca-sulfates are more stable under martian conditions compared to other varieties and have been found in veins and the lower strata of Mount Sharp at Gale Crater (Grotzinger et al., 2012; Nachon et al., 2014; Rapin et al., 2016; Vaniman et al., 2014), at Endeavor Crater, the Columbia Hills at Gusev Crater (Squyres et al., 2006; Yen et al., 2008), and as gypsum dunes in the North Polar Cap. On Earth, sulfate-rich sediments are often formed from liquid water and organic matter is often co-deposited and can be preserved for geological periods of time (Aubrey et al., 2006).

Sample 2–An artificial mineralogical sample was used to mimic the local mineralogy of the Oxia Planum landing site (Figure 1b). SOPHIA (Simulant for Oxia Planum: Hydrated, Igneous, and Amorphous) was developed by Dugdale et al. (2023) at The Open University, UK, using orbital observations of Oxia and its catchment, combined with orbital data from Arabia Terra and Mawrth Vallis and in situ data collected from Gale crater. The simulant is rich in Fe/Mg phyllosilicates with additional primary igneous and alteration minerals (Dugdale et al., 2023).

Sample 3–To maximize the number of organic biosignatures of known biological origin available for study, a >120-year-old dried cyanobacterial mat, collected from a meltwater pond on the McMurdo Ice Shelf on 2

December 1902, was used. This sample was acquired during the 1902–1903 National Antarctic Expedition, led by Captain Robert Falcon Scott (Fritsch, 1912). It has been preserved and naturally dried in acid-free paper folders under controlled conditions in the herbarium at the Natural History Museum in London (e.g., Preston et al., 2024) and Figure 1c. Microbial mats (specialized biofilms comprising many microbial groups laterally compressed into a thin multilayered mat, ranging from several millimeters to a centimeter thick) are self-sustaining ecosystems dominated by photosynthetic bacteria, particularly cyanobacteria. The physical structure of cyanobacterial mats provides essential benefits to the microorganisms within them, such as protection from UV radiation, retention of water, and facilitation of nutrient transport (Martin-Andres et al., 2024). These properties make cyanobacterial mats especially resilient, allowing them to survive and thrive in harsh conditions, including in theory those conditions experienced on Mars (Qin et al., 2014), making them interesting analogs for studying potential ancient Martian life and its biosignatures.

2.2. Experimental Method

To mimic the cold and low atmospheric pressure conditions currently experienced on Mars, a technique to mimic cryodesiccation was used. While commonly associated with food preservation and pharmaceuticals, freeze-drying (lyophilization) is a process that removes water from a substance by freezing it, placing it under vacuum and then sublimating the created water ice directly into vapor. On Earth, this process commonly occurs in periglacial environments where water is removed from soils and sediments by freezing and subsequent sublimation. Lyophilization was applied in this study to emulate the sublimation-supportive Martian surface conditions - temperature around −63°C and atmospheric pressure around 6–7 mbars.

All samples were used in powdered form and analyzed via Fourier Transform Infra-Red (FTIR) and Visible-Near Infra-Red (Vis-NIR) spectroscopy at room temperature prior to the onset of the cryodesiccation procedure. FTIR was carried out using an Agilent 4,300 Handheld FTIR spectrometer docked onto a bench-top setup and equipped with a Diamond-ATR sampling module. The spectral range covers the Mid-IR region from 650 cm^{-1}–4,500 cm^{-1} with a spectral resolution of 4 cm^{-1}. Vis-NIR was conducted using an RxSpec 700Z spectrometer manufactured by ASD, Inc. with a spectral range of 350–2500 nm and a spectral resolution of 3 nm in the visible region and 10 nm in the NIR. There are spectral joins at 1,000 nm and 1,830 nm. For each sample, five spectra were taken.

To simulate Martian surface conditions, the powdered samples of gypsum, SOPHIA simulant and Scott microbial mat were first placed in test tubes in a freezer at −20°C for 30 min. This was to ensure any water within the sample powders was frozen before insertion into the lyophilizer to ensure sublimation of water ice, to avoid boiling of the water when exposed to the vacuum and to mimic the frozen state of Martian samples in the subsurface. The frozen samples were then transferred to a Labconco FreeZone 6L Console Freeze Dryer (Figure 1d), with a collector temperature maintained at −63.4°C and a vacuum of 1.182 mbar. All test tubes were placed with the lid left on but loosened so that the samples were directly exposed to the lyophilization environment but remained contained within the test tube. The samples were initially subjected to cryodesiccation conditions for 1 and 72 hr periods, designed to represent the possible minimum and maximum time intervals that could occur on Mars between core sample removal and sequestration into the ALD in Rosalind Franklin. Once removed from the lyophilizer, they were immediately sealed and only opened for subsampling and re-analysis via FTIR and Vis-NIR spectroscopy. Samples were analyzed via both Vis-NIR and FTIR spectroscopy again within 1 hr of removal from the lyophilizer.

3. Results

Representative Mid-IR and Vis-NIR spectra were averaged from five analyses of each original sample and after 1 hr and 72 hr cryodesiccation, and are compared below and in Figures 2–4.

3.1. Gypsum

The IR spectra of gypsum exhibit distinct features that correspond to various vibrational modes of water (H_2O) and sulfate (SO_4) and are shown in Figure 2.

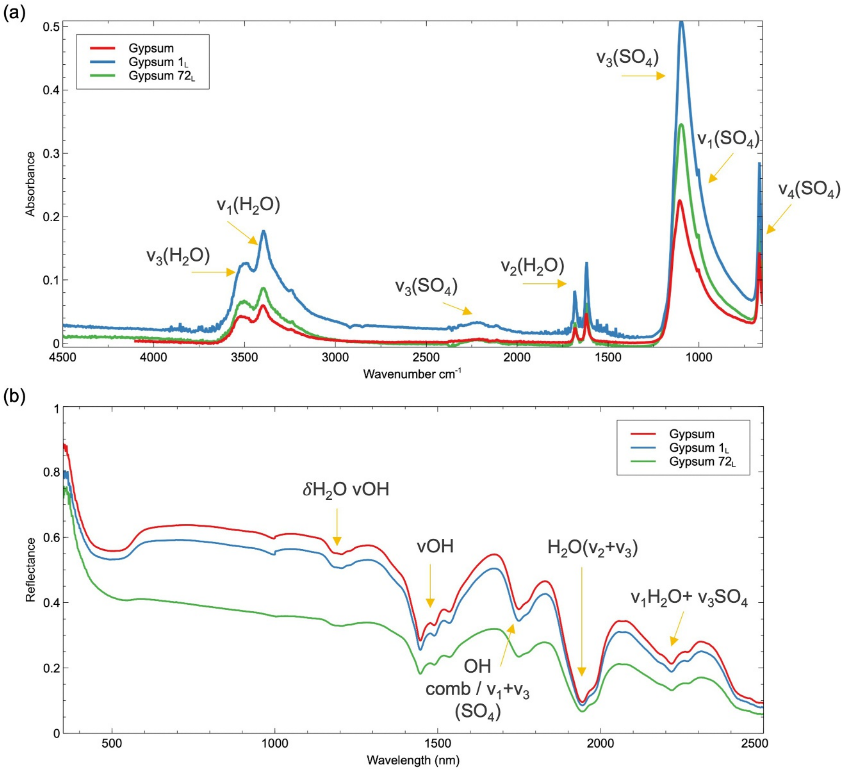

Figure 2. (a) A Mid-IR spectrum displaying averaged spectra of the original gypsum powder, the powder after 1 hr lyophilization, and after 72 hr lyophilization. (b) A Visible-Near Infra-Red spectrum of gypsum, and after 1 hr and 72 hr lyophilization.

3.1.1. Mid-IR

The fundamental vibrational modes of gypsum ($CaSO_4.2H_2O$) were found to correspond to the main peaks in the Mid-IR spectra and the overtone and combinational modes to the absorption bands in the Vis-NIR. The assignments for the mineralogical components of the samples are consistent with previous studies such as Liu (2018) and Preston et al. (2019). In the Mid-IR, the strongest absorption bands are found at around 1,108 cm^{-1} which corresponds to the v3 asymmetric stretching vibrational modes of SO_4 tetrahedra whilst a shoulder absorption located at 1,007 cm^{-1} is due to the SO_4 v1 symmetric stretching vibrational modes. The antisymmetric v4 bending vibration of SO_4 tetrahedra was also observed around 665–669 cm^{-1}. Given the cryodesiccation goal of the experiment, the presence of water in the gypsum was tracked and can be discerned by exploring peaks in the region near 3,500 and 1,600 cm^{-1}. The v1 symmetric stretching vibrational modes of H_2O are located around 3,404-3,408 cm^{-1} and the v3 antisymmetric stretching vibrational mode at 3,530 cm^{-1}. There are two peaks caused by the O-H bending vibrational modes located at 1,682 and 1,620 cm^{-1}. This double peak indicates that there are two distinct crystallographic types of water in the samples — one hydrogen bonded to the sulfate ions and one linked to calcium ions.

3.1.2. Vis-NIR

The assignments for overtone and combinational modes in the Vis-NIR spectral range are shown in Figure 2b. A prominent sharp spectral feature around 1,900 nm, caused by the v2 + v3 (H_2O) band produced by structural water molecules in the mineral lattice is observed. The band at 1,750 nm is due to an OH combination mode and the v1 + v3 (SO_4), and at 1,180 nm due to the combination of the H_2O bending fundamental and the first overtone of the OH stretching fundamental. The characteristic complicated triplet band shape of gypsum is observed near 1,400 nm created by the first overtone of the OH stretching of water–v3 + 2v2 (H_2O). Reflectance minima were observed at 2,220, 2,270, and 2,330 nm due to the combinational mode of v1H_2O + v3SO_4.

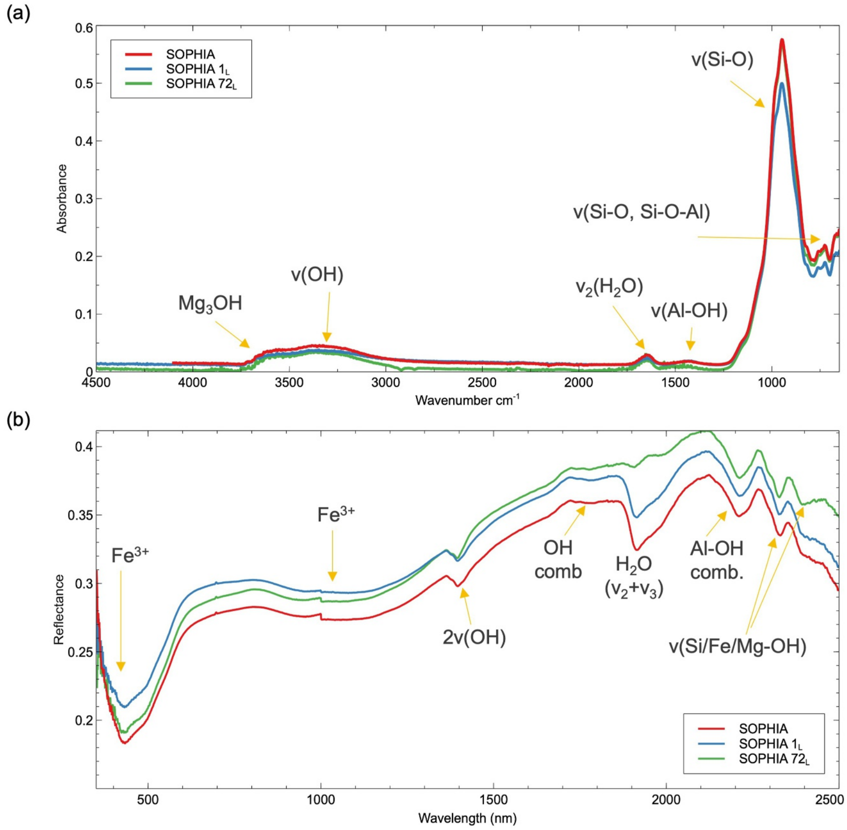

Figure 3. (a) A Mid-IR spectrum displaying averaged spectra of the original SOPHIA simulant, the simulant after 1 hr lyophilization, and after 72 hr lyophilization. (b) A Visible-Near Infra-Red spectrum of the SOPHIA simulant, and after 1 hr and 72 hr lyophilization.

3.1.3. Gypsum Cryodesiccation

In the Mid-IR, gypsum retains all of its key spectral features after cryodesiccation for both 1 hr and 72 hr. No absorbance bands are lost and no new ones are observed, and the shape of the bands remains the same. However, after 1 hr exposure to Mars-like conditions in the lyophilizer, the intensity of the absorbance bands has increased across the spectrum. After 72 hr the intensity of the spectra has decreased below that observed after 1 hr but is still relatively more intense when compared to the original unexposed gypsum.

In the Vis-NIR region, after 1 hr exposure there is very little change observed in the spectra other than a slight overall decrease in reflectance. All bands are still present and maintain the same band depth positions. After 72 hours however, and unlike in the Mid-IR region, there is a distinct change observed. There is a decrease in relative intensity across the whole spectrum. In addition, all observed bands exhibit a pronounced decrease in band depth and less distinct features. There is no loss or gain of spectral features and despite the overall relative “flattening” of the spectrum, it is still clearly that of gypsum and resembles the original sample.

3.2. SOPHIA Simulant

3.2.1. Mid-IR

The Mid-IR spectral response of the SOPHIA simulant has relatively few absorption bands (Figure 3). The strongest absorption is at 952 cm^{-1} within the fingerprint region and is due to the v(Si-O) stretching vibrational mode of the silicate minerals within the simulant. Another strong mineralogical absorbance band is at 738 cm^{-1} and is assigned to the stretching v(Si-O, Si-O-Al) vibrational mode. A shallow broad band assigned to v(Al-OH) is found at 1,509 cm^{-1} and a shoulder at 3,632 cm^{-1} is assigned to an Mg_3OH vibrational mode. The water present

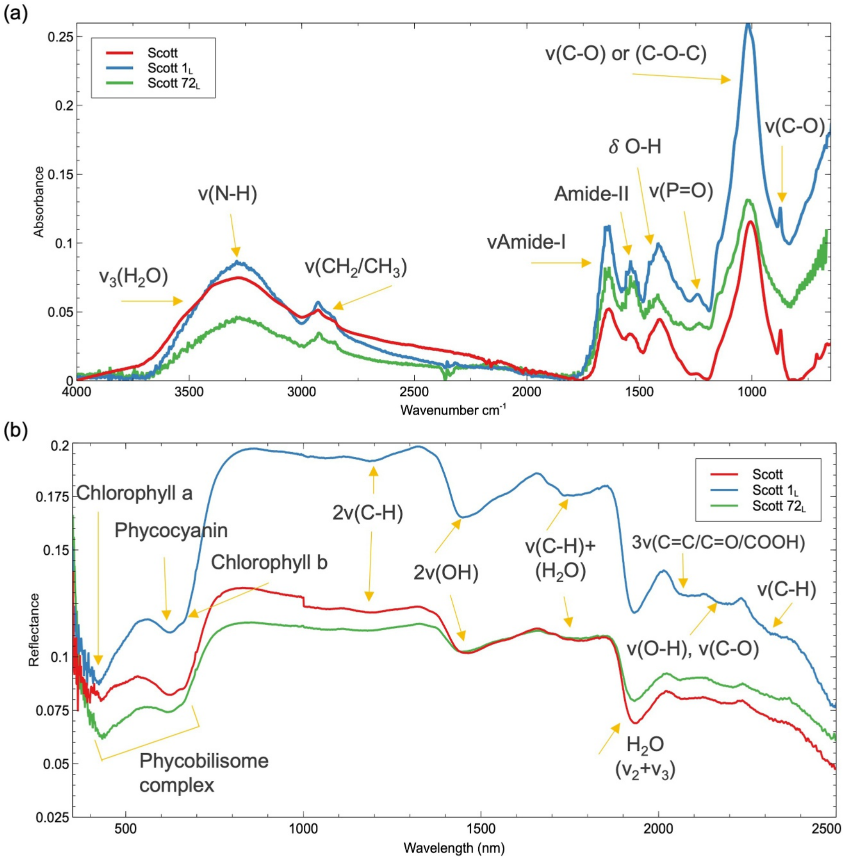

Figure 4. (a) A Mid-IR spectrum displaying averaged spectra of the original Scott microbial mat sample, after 1 hr lyophilization, and after 72 hr lyophilization. (b) A Visible-Near Infra-Red spectrum of the Scott sample after 1 hr and 72 hr lyophilization.

within the simulant is visible through the broad v1 symmetric stretching vibrational mode of H_2O at 3,384 cm^{-1}, and the v2 stretching vibrational mode of H_2O at 1,664 cm^{-1}.

3.2.2. Vis-NIR

Given the range of minerals mixed to create this simulant, identifying specific fingerprints of these in the Vis-NIR is challenging. A strong band at 432 nm and a broad shallow band centered around 1,100 nm are assigned to Fe^{3+} potentially contributed by the Fe-silicates, hematite and siderite present in the simulant. An absorption at 1,398 nm is created by a 2vOH overtone and one at 1,917 nm is associated with the H_2O stretch common to phyllosilicate minerals, probably arising from the vermiculite present, and/or the siderite and serpentine. Further bands at 2214 nm are assigned to an Al-OH combination, and two at 2332 nm and 2422 nm are assigned to the v (Si/Fe/Mg-OH) band arising from the olivine, serpentine, vermiculite and Fe-silicate present.

3.2.3. SOPHIA Simulant Cryodesiccation

In the Mid-IR, the effects of cryodessication appear minimal. Aside from a slight decrease in the relative intensity of the main silicate band at 952 cm^{-1} after 1 hr and 72 hr exposure, there is very little change observed.

In the Vis-NIR this trend is also observed. The relative reflectance increases after both lyophilization periods and, except for one band, the positions, shapes and band depths of all features remain the same. The exception is the band at 1,917 nm associated with the H_2O stretch common to phyllosilicate minerals, which after 72 hr exposure is barely visible.

3.3. Scott Microbial Mat

Due to the known biological provenance of this sample, the organic absorption bands are assumed here to have a biotic origin, which has been proposed below and shown in Figure 4.

3.3.1. Mid-IR

In the Mid-IR, several organic absorption bands have been identified and were previously documented from another subsample of the microbial mat in Preston et al. (2024). A shoulder at 3,489 cm^{-1} is the v3 antisymmetric stretching vibration of water. The v1 symmetric stretching vibrational mode of H_2O is located at 3,395 cm^{-1} as another slight shoulder on the strong N-H stretching vibrational mode of amines-nitrogen-containing organic compounds at 3,292 cm^{-1}. Absorption bands of aliphatic C-H_x moieties, assigned to aliphatic hydrocarbons found in phospholipids, are observed at 2,955 cm^{-1} and 2,921 cm^{-1} derived from the asymmetrical stretching vibrational modes of CH_3 (methyl) and CH_2 (methylene) respectively, and at 2,864 cm^{-1} and 2,846 cm^{-1} due to the symmetric stretching vibrational mode of CH_3, and the symmetric CH_2 stretching vibrational mode. A strong absorption band at 1,640 cm^{-1} could be assigned to the Amide-I $C = O$ band, in particular a β-pleated protein sheet structure, or the O-H stretching vibration of residual water in the mat. An absorption band at 1,530 cm^{-1} is assigned to the Amide II vibrational mode of proteins, and at 1,402 cm^{-1} to the O-H bending vibrational mode within polysaccharides. There is a shallow peak at 1,232 cm^{-1} caused by the asymmetrical $P = O$ stretching of PO_2 within nucleic acids. The most intense absorbance is located at 1,009 cm^{-1} and is assigned to the C-O or C-O-C stretching vibrational modes of carbohydrates within polysaccharides. A shoulder at 1,150 cm^{-1} could be assigned to the C-O stretching from cellulose. Finally, an absorbance peak observed at 870 cm^{-1} is assigned to the C-O stretching vibration, potentially caused by chlorophyll in the microbial mat.

3.3.2. Vis-NIR

Within the Scott microbial mat, key bands are created due to overtones and combinations of the organic molecules present and residual water within the mat and possibly within the cells themselves. In the visible region there are a number of bands present due to the phycobilisome light harvesting complex within the microbial communities; observed at 440, 503, 626, and 657 nm created by chlorophyll-a, carotenoids, phycocyanin and chlorophyll-b respectively. The absorption band at 1,203 nm is associated with the second overtone stretching vibration of C-H bonds. A relatively strong band around 1,400 nm is created by a 2vOH overtone of structural water and the strong band at 1,930 nm is due to the $v2 + v3$ (H_2O) band produced by structural water molecules. A shallow band at 1,766 nm is proposed to be due to the first overtone of aliphatic v(C-H) + H_2O, commonly found in cellulose. The shallow band at 2057 nm corresponds to the third overtone stretching vibrations of aromatic $C = C$, COO-hydrogen bonds, or $C = O$ bonds, which can be linked to cellulose, and finally reflectance minima at 2188 and 2315 nm are assigned to the v(O-H) and/or v(C-O) and combination band of v(C-H), respectively.

3.3.3. Scott Microbial Mat Cryodesiccation

The Mid-IR spectra of the microbial mat follows a similar trend to the gypsum–after 1 hr cryodessication the overall spectral intensity increases, and then decreases after 72 hr–however the intensity of the absorption bands above 2,000 cm^{-1} drops below the original sample, but those below 2,000 cm^{-1} remain stronger than the original. A few absorption bands appear to disappear after lyophilization. The v3 antisymmetric stretching vibration of water at 3,489 cm^{-1} is not visible after 1 hr and a further 72 hr cryodesiccation. In addition, the 870 cm^{-1} C-O stretching vibrational mode was absent from the 72 hr spectrum. In general however, all organic absorption bands appear sharper after the onset of cryodessication, in particular the v(N-H) band at 3,292 cm^{-1}, the C-H_x aliphatic hydrocarbon region, the Amide region, the P=O stretch at 1,232 cm^{-1} and the C-O main peak of polysaccharides. After 72 hours these are still sharper in shape, but relatively less intense in line with the rest of the spectrum, and have smaller band depths and an overall less smooth profile—spectra are more “fuzzy.”

In the Vis-NIR spectra, after 1 hr the relative intensity of the spectra increases in all areas with all key bands highlighted in Section 3.3.2 increasing in band depth and becoming sharper. After 72 hr the relative intensity has decreased again, sitting close to that of the original sample, yet most of the organic bands are still present and have similar profiles and bands depths to the original sample. A key biosignature region is the Phycobilisome complex in the visible range of the spectra. After 1 hr exposure the bands associated with chlorophyll-a and -b, carotenoids and phycocyanin are still present, although the carotenoid feature at 503 nm is hard to discern. After 72 hr all these features are less clear with the carotenoid feature now absent and the two phycocyanin and chlorophyll-b bands harder to differentiate between. Additionally, after 72 hours the band depths of the 1,400 nm feature created by a 2vOH overtone and that at 1,930 nm due to the v2 + v3 (H_2O) band produced by structural water molecules have decreased, and are less than observed in the original samples.

4. Discussion

The stability of any organic molecule or biosignature, and ergo its identification potential, is dependent on its initial form, the matrix in which it is hosted, and the chemical and physical processes it is subjected to over geological time. On Earth, entombment of biosignatures within mineral matrices constitutes one of the most efficient preservation mechanisms against degradation; however, the persistence of the geological material is the limiting factor—if this is altered or fails, then the biosignatures it protects are compromised. Based on observations of terrestrial analog sites, there is a general consensus that sediments, evaporites, and hydrothermal minerals provide the best matrix and highest preservation potential for biosignatures.

4.1. Gypsum

Ca-sulfate hydrates, such as the gypsum described in this study, are of great importance due to their significance in both terrestrial and planetary environments and have been observed to offer fossil stabilities for timescales of up to 1×10^6 years (Farmer & Des Marais, 1999) and more, given the right conditions, and can preserve organic carbon and amino acids for 40 million years (Aubrey et al., 2006). However, they are susceptible to dissolution and phase transitions when exposed to increasing temperatures, removing the water molecules and causing the formation of either bassanite ($CaSO_4 \cdot ½H_2O$) or anhydrite ($CaSO_4$). But what happens to the gypsum, and in theory any associated biosignatures preserved within it, when exposed to the sub-zero, near-vacuum Martian surface environment?

In this study, the Mid-IR spectra of gypsum indicated that no significant changes occurred following the inducement of cryodesiccation. The pure gypsum samples mostly retained their hydrated state and remained fully spectrally identifiable. In the Vis-NIR region however, after 72 hr there is a decrease in relative intensity across the whole spectrum and a pronounced decrease in band depth and less distinct hydration features. This could be due to the loss of non-structural loosely bound water found within small pores that may have been introduced in the natural environment before the samples were collected. Lyophilization did not cause significant changes in the spectra because gypsum's bound water is integral to its crystal structure and the hydrogen bonds fight against water molecules evaporating during lyophilization. Spectra were compared to those of bassanite and anhydrite from the RUFF database and published in Liu (2018) to see if any phase transitions had occurred during the sublimation process. The spectra are still clearly gypsum after lyophilization and show no evidence of any other phases present.

The findings of this study on gypsum's behavior under Martian conditions are well-supported by existing research on its stability under Martian temperatures. Schofield et al. (2000) confirmed the stability of gypsum at low temperatures through neutron diffraction, highlighting that the essential hydrogen bonding and water molecule interactions in gypsum remain largely unaffected by the Martian temperature. This is also consistent with findings by Robertson and Bish (2013), who noted that below 323 K significant dehydration of gypsum on Mars is unlikely to occur via diurnal or seasonal cycles unless influenced by external factors. Cloutis et al. (2007) found that minerals such as gypsum that contain structural H_2O are more resistant to H_2O loss under Martian conditions than phyllosilicates. In a spectral study on gypsum endoliths exposed to the UV, anoxia, low pressure and desiccating conditions of Mars, Stromberg et al. (2014) found there was little change in the NIR spectra of the samples, with all major spectral features of both gypsum and chlorophyll preserved after exposure to the equivalent of ~300 years at present martian surface conditions. The current study highlights that gypsum cored out from the subsurface by Rosalind Franklin and newly exposed to the martian surface will remain stable and detectable during operation timescales of at least 72 hr, which also bodes well for the preservation of any biosignatures or organics that may be held within them.

4.2. SOPHIA

There is very little to no change in the SOPHIA simulant throughout the experiment, indicating that little to no water is being sublimated from the material. After 72 hours only the 1,917 nm band in the Vis-NIR spectra, associated with the H_2O stretch, has decreased in band depth. This slight reduction in water content could be due to the loss of loosely bound or adsorbed water in small pores, which is more mobile and easily removed under the lyophilization conditions. The minimal changes in water content suggest that the simulant is already very dry, potentially due to its artificial nature and a lack of free water having been introduced from the terrestrial environment. The water present is tightly bound to the minerals present, in particular the phyllosilicates. Additionally, the grain size of the SOPHIA simulant is <212 μm having undergone crushing, milling and sieving, and has been more processed than the gypsum and Scott microbial mat samples.

The dominant phyllosilicate mineral in the simulant is vermiculite. Clay minerals have a layered structure consisting of aluminum oxide sheets and silicon oxide sheets. Due to the replacement of some metal atoms, these layers carry a negative charge balanced by positively charged ions between the layers. When humidity increases, these positively charged interlayers attract water, which is inserted between the aluminum and silicon layers, forming distinct layers (Malikova et al., 2006). These layers are connected by van der Waals bonds, which are relatively weak compared to the stronger hydrogen bonds found in gypsum, making the water held between the layers of clay minerals more susceptible to evaporation under Martian-like conditions. As a result, any loosely bound hygroscopic water (Chen et al., 2014) likely evaporated, leading to a slight reduction in water content in the Vis-NIR spectra while the more tightly bound water within the molecular structure remained detectable. This indicates that while some water was lost during exposure, the essential hydrated nature of the simulant minerals was preserved. Separate analyses of pure vermiculite before and after 72 hr lyophilization (non-published data) also display a decrease in band depth in the 1,900 nm hydration band after 72 hr exposure, but the overall spectral profile of the mineral is preserved. Due to the lack of changes observed within the SOPHIA simulant, it can be postulated that the composition of the Oxia Planum regolith and dust might be mostly stable under Martian surface conditions and might therefore be a good geological shield.

4.3. Scott Microbial Mat

The Scott microbial mat has been air-dried and protected from the terrestrial environment for the past >120 years since collection (to the best of our records). Despite this, while some free water may have already been lost during storage in the herbarium, residual bound water within the mat, from within the Extracellular Polymeric Substance (EPS), and from the cells themselves is likely drawn out and frozen when it was subjected to Martian-like conditions. As such after the 1 hr lyophilization, Vis-NIR and Mid-IR spectra increase in overall intensity and the hydration bands become relatively stronger. The organic absorption bands also become relatively more intense and sharper. After 72 hr, the overall intensity then decreases as the water is partially sublimated and is starting to be removed, yet the organic absorption bands are still present despite also decreasing in relative intensity.

The organic absorption bands remain visible during cryodesiccation. These might be the result of the cyanobacterial cells making up the mats and the presence of Extracellular Polymeric Substances (EPSs)–matrices of biomacromolecules including exopolysaccharides, proteins, lipids and nucleic acids–which assist the microorganisms to endure extremes of temperature (Casillo et al., 2017), salinity (Bemal & Anil, 2018; Moshabaki Isfahani et al., 2018), and desiccation (Knowles & Castenholz, 2008; Tamaru et al., 2005). Antarctic microbial and algal communities are known to secrete EPS, which serves a number of different functions and can assist these microbes to survive under harsh extreme conditions for example, by acting as a cryoprotectant preventing the breakdown of cell membranes during freezing (Caruso et al., 2019; Madigan et al., 2017); and helping to retain water that prevents cells from undergoing desiccation (Krembs et al., 2002) in the dry Antarctic climate (and potentially herbarium storage drawers). EPS composition in Antarctic mats is dominated by carbohydrates, in particular glucose and mannose, followed by proteins and uronic acids (Nagar et al., 2021), which reflects the strongest and main absorptions identified within the Mid-IR spectra of this study. This EPS, despite its age, might be helping to protect the Scott microbial mat samples and the associated organic absorption bands during the lyophilization process and as such bodes well for the likelihood of microbial biosignatures surviving within similar mats and being identifiable on Mars if brought up from beneath the surface.

5. Implications

5.1. Planning for Operations on Mars

The reliable acquisition of deep samples is key for the successful fulfillment of Rosalind Franklin's main science objectives; however, the stability of the geological samples once removed and understanding the changes that may occur before and during analysis is key to ensuring accurate interpretations. Samples in the 2 m subsurface will be kept at higher pressures than those experienced at the surface due to the weight of the overlying geological materials and the atmosphere. However, the lower atmospheric pressure on Mars means this effect will be less pronounced than observed on Earth, and will also depend on the density of the overlying geological materials. Packing of the buried substrates strongly reduces the porosity and eventually decreases the diffusion rates of water vapor (Clifford & Hillel, 1983). On Mars, while mean temperatures and water vapor pressure strongly control the sublimation rate, sublimation in the ground depends on diffusion and water adsorption, which are both very dependent on regolith porosity and composition (Mangold, 2011). As such, when buried up to 2 m geological samples will have undergone minimal alteration yet when brought to the surface through drilling and coring, will be exposed to a lowering of overlying pressure together with a change in air temperature and humidity, supporting sublimation processes to occur.

5.1.1. Timing

Rosalind Franklin is scheduled to land at Oxia planum in October 2030 during the northern hemisphere spring. This has been chosen to lessen the impact of Martian dust storms and ensure optimal sunlight for the rover's solar panels, but this timing will also have an impact on the samples being collected. It has been observed that sublimation on Mars is particularly noticeable during the Martian spring and summer due to increased solar heating. Measurements of groundwater activity at the Perseverance rover landing site in Jezero Crater taken over consecutive sols during summer, autumn and winter have indicated two periods when water activity tends to increase: (a) between $L_s = 100°$ (2/3 into the Martian spring) to $L_s = 150°$ (halfway through summer), and (b) around $L_s = 270°$, when the ground temperatures decrease with the arrival of winter and the relative humidity and water activity increase (Zorzano et al., 2024). The first period occurs when there is an increase in the atmospheric H_2O vapor mixing ratio due to the global circulation of atmospheric water; following the release of water vapor from the north polar cap.

Daily cycles are also observed, influenced by the seasonal changes on Mars. There is a strong rock- and regolith-atmosphere exchange mechanism on Mars (Hausrath et al., 2023). At Jezero Crater, the analysis of atmospheric data from one full Martian year suggests that the surface can act as a water sink at night as the temperature drops, with most of this water released back into the atmosphere after sunrise (Zorzano et al., 2024). This is also observed at Gale Crater, where the daytime water vapor abundance appears to run on a diurnal cycle. This would be expected if water is adsorbed to the cooling regolith in the evening via salt or mineral hydration—a solid-solid phase transition in which water molecules are incorporated into the crystal structure - and then released from the rapidly warming regolith in the morning (Savijarvi et al., 2016; Steele et al., 2017). These diurnal and seasonal water activity and temperature changes could impact Rosalind Franklins' newly cored samples. As well as having cryodesiccation reactions induced through core removal from the subsurface, cyclical cryodesiccation reactions involving water movement in and out of the samples when exposed to the pressure, temperatures and sunlight at the surface could also occur if the samples remain exposed on the surface for multiple sols.

In particular, for biosignature preservation, how the minerals of this study react to the Martian surface environment can provide a guideline for interpreting future analyses. Gypsum is very close to instability at the Martian equatorial surface. The CheMin team on the Curiosity Rover studied possible mineral dehydration reactions through exposure to post-drilling desiccating conditions and observed a small amount of gypsum within the sample Lubango at the Stimson fracture to decrease below detection limits after 7 sols, while at the same time bassanite increased. In the Oudam sample, they observed that there was no initial bassanite within the material but after 4 sols some of the gypsum was converted to bassanite, after 8 sols there was less gypsum and more bassanite, and after 37 sols a total transformation of gypsum to bassanite had occurred (Vaniman et al., 2018). The Zechstein sample, where the drill penetrated a gypsum vein with 18% gypsum abundance, showed the loss of gypsum and transformation to bassanite occurred over a period of 38 sols. Laser ablation measurements of hydrogen content at the surface with the ChemCam instrument on MSL also indicated that all exposed veins targeted so far at Gale Crater consist predominantly of bassanite, which is most likely formed by dehydration of gypsum (Rapin et al., 2016). The Perseverance Rover at Jezero crater is also at a near-equatorial site and has found low-hydration Ca-sulfates (anhydrite and bassanite) on the surface but, so far, very little gypsum (Lopez-Reyes et al., 2025; Siljeström et al., 2024).

Gypsum does not appear to occur as much as less hydrous Ca-sulfates, quite possibly due to its dehydration to bassanite and anhydrite (Vaniman et al., 2024), with all three of these Ca-sulfate phases often occurring together in mixed assemblages. However, under the right conditions, gypsum can survive on surfaces exposed at low latitudes, possibly influenced by crystal size, crystal habit, rock fabric, and other petrologic factors, with dehydration rates slowed by factors such as density and grainsize (Vaniman et al., 2018). Some evidence of surface gypsum is found at Gale crater, indicated by Mastcam near-IR spectral filters in veins of the Bradbury group (Vaniman et al., 2014). At the rim of Endeavor crater the MER rover Opportunity also identified a gypsum vein based on spectra (Squyres et al., 2012).

Phyllosilicates are mostly found in the oldest Noachian terrains on Mars, and are believed to be the dominant mineralogy at Oxia Planum. They hold clues to the planet's earliest aqueous and geologic history. Clay stability on the Martian surface today is evidenced by the presence of widespread clay deposits and reflected in this study as lyophilization for up to 72 hr did very little to the SOPHIA simulant samples. Sublimation occurs more rapidly in sand-sized materials than in silt-sized materials, and soils composed of very small particles (<10 μm) slow the sublimation process down. For Mars, the physical properties of the regolith or soil will be important. Porosity and tortuosity (the way by which water vapor molecules escape) will have a major influence on sublimation in fine-grained regolith as they control the diffusion processes that lead to sublimation of water ice (and the adsorption of water to mineral grains). Small grain sizes strongly reduce diffusion, thereby reducing the sublimation rate (Smoluchowski, 1968). Given the <212 μm grainsize of the simulant, this will contribute to the lack of changes observed after lyophilization whilst more changes are observed in the other samples whose grainsize is larger.

5.1.2. Analysis

A drilling campaign on Mars could take up to several sols before a sample is acquired. Vertical drilling speeds depend on the characteristics of the material being penetrated and the harder the materials, the slower the drilling will take. For the RFM, it has been proposed that a daily progress of about 50 cm can be expected and as such, it could take four sols to reach the proposed maximum depth of 2 m. As the rover retracts the drill, the drill core or pellet (typically 1 cm in diameter and 2.5 cm long) is released into a special drawer at the front of the rover. Before transitioning into the crushing station in the body of the rover, however, the core will need to be imaged. First, this will be carried out by the PanCam Right Wide Angle Camera, followed by the High Resolution Camera and then CLUPI (as described later) who will obtain a z-stack of images at each position as the drawer is sequentially retracted. The duration of this process could vary. The goal is for this to occur within 30 min of the sample being exhumed from the subsurface; however, planning for what might happen to the sample should it take multiple days to complete the imaging cycle is paramount. The imaging of this first-of-a-kind sample cannot be rushed or skipped; therefore, the impact of this time window before crushing and chemical analysis in the ALD can occur, and the sample exposure to the surface environment of Mars during this time must be considered.

This study has shown that after 1 hr exposure to Martian-analog conditions, the sublimation process has begun in the samples but is in the early stages whereby residual or free water is mobilized and ice is formed, increasing the spectral intensity of the minerals, hydration features and organic absorptions within the samples, or in the case of the SOPHIA simulant having little impact. Therefore, 1 hr post drill core removal, at least in the sample suite of this study, no detrimental effects on the samples have been observed. In fact, the conditions experienced have improved the spectral intensity of the samples and in the case of the organic absorptions allowed them to be more visible and detectable. After 72 hr however, the hydration bands decrease in intensity as sublimation reactions progress, which means that the spectra obtained will not be truly representative of the original hydration state of the rock or perhaps its original chemical composition. Organic absorptions are also becoming less defined and as such are potentially showing signs of degradation; however, they are still mostly present and identifiable. Given the decreasing spectral intensities after 72 hr lyophilization, it is clear that sublimation reactions are progressing; however, they do not appear to be complete and further studies for increased timeframes would be needed to bookend how long the entire process might take on Mars and what the resulting spectral profiles will be.

The results of this study will begin to help us predict and ultimately understand the sublimation potential of drill cores and fines extracted at the Oxia Planum. Given the dominance of spectroscopic instruments involved in the imaging and analysis campaign before samples are moved to the ALD, this research will help these instrument teams in the interpretations of their results and environmental characterizations.

The spectral results from both PanCam and Enfys will be impacted by any sublimation reactions occurring in the drill samples and it is to help the interpretations of this data that this study was originally conceived. Enfys (Grindrod et al., 2025) and PanCam (Coates et al., 2017) will work together to provide a comprehensive mineralogical analysis. PanCam, with its visible and near-infrared capabilities, provides color and visual context, while Enfys, with its SWIR capabilities, focuses on mineral identification, specifically targeting clays and other minerals of interest. The PanCam high-resolution camera will obtain a total-view image of the core sample and PanCam will also image the growing accumulation of loose drill material around the borehole to examine its physical properties and mineralogical properties.

In concert with PanCam and Enfys, CLUPI (Josset et al., 2017) is a high-resolution camera system that can take color close-up images of outcrops, rocks, soils, drill samples, drilling areas and drill tailings. CLUPI has three different Field Of View (FOV) configurations. While drilling is being performed, CLUPI's third FOV - FOV3 - can be used to monitor the process and observe the mound of fines that is generated, effectively tracking any sublimation-related chemical changes occurring. Color and textural variations as well as mechanical properties, such as grain size, shape and cohesion can also be observed. It will also be used to image the collected core prior to delivery to Rosalinds' ALD. After the drilling operation has been completed and the drill has been retracted, FOV2 can then be used to image the state of the surface after drilling, the amount of dislodged fines, their color and physical properties, and 6 cm depth into the borehole given the right illumination. From a higher position, CLUPI will be able to observe the borehole to a depth of approximately 10 cm. As such, understanding the spectral signatures of the minerals CLUPI might observe and how they will change at each of these stages is of great importance.

Finally, Ma-MISS observations will be crucial as it is the only instrument on the rover that can study the sample material in its native condition before it has interacted with the surface environment. Ma-MISS (De Sanctis et al., 2017, 2022) is a visible and near infrared (VIS-NIR 0.4–2.3 μm) micro spectrometer hosted in the drill head that can create hyperspectral images of the borehole walls excavated by the rover drill. Two of its objectives are to determine the composition of subsurface materials; and to map the distribution of H_2O-bearing and OH-bearing minerals, including H_2O-ice at Oxia Planum. Ma-MISS will be a key method in helping us understand the pre and post-surface environmental exposure changes when working in conjunction with PanCam and Enfys. Rosalind Franklin will be the first rover on any planetary body able to investigate the shallow subsurface and provide contextual information to support the analysis of subsurface samples by ALD instrumentation (MicrOmega, RLS, MOMA). Samples extracted from the subsurface will be crushed to search for the possible presence of chemical biosignatures and it is noted that this operation will take place at a temperature higher than what the sample will have seen in the subsurface. As such, it is likely that the sample may experience some alterations (Altieri et al., 2023), as has been observed previously on Curiosity (Vaniman et al., 2018).

6. Conclusions

It is important to plan for the changing spectral responses of rover sampling activities. During this investigation, it was observed that after 1 hr, Mars-like sublimation processes were not fully completed within the three Mars analog samples. The drawing out of residual water and ice formation was observed and helped to increase the spectral intensity of the mineralogical, hydration, and organic features within the samples. After 72 hr of exposure, hydration- and organic-induced spectral bands began to decrease in intensity and detectability, with some features now removed. It can be postulated that under similar circumstances on Mars, the spectra obtained from recently exhumed geological samples may not be truly representative of the original composition, yet are still clearly identifiable. Gypsum maintains its spectral features throughout the lyophilization process, which supports its known stability on Mars' surface and is encouraging for biosignature preservation. The SOPHIA soil simulant seems to also withstand the effects of cryodesiccation, which supports the protection of subsurface biosignatures. Microbial mats and several of their associated biosignatures have shown that they can survive exposure to the cold, low pressure Martian environment even without added mineral protection. The added impact of UV radiation exposure across the sampling activity timeframes will be explored in future studies.

It is hoped that the results from this work and future studies will:

- Help researchers understand how rocks and minerals can respond to the sublimating effects of the Martian environment during exploration activities.
- Help develop planning and operations protocols, and predict the changes occurring during operations to enable more accurate interpretations of environmental conditions.
- Help change the view that the extreme Martian environment is always a bad thing for astrobiology—if we can predict its impact on samples, then perhaps it is something that can be used to aid and even amplify our observations.

Through the results obtained in this study and future Martian sublimation research, working together with all the Rosalind Franklin instruments that will contribute to the drill core and drill fines analyses, we can better understand and constrain the differences between the subsurface and surface environments at Oxia Planum, identify the organics and potential biosignatures within them, and ultimately discern the habitability potential of the area. In addition, we can also use this study to start planning for and predicting potential changes occurring to the Mars Sample Return samples, currently waiting on the surface of Mars for collection.

Inclusion in Global Research Statement

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Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Availability Statement

Infrared data (Preston, 2025) is available through the open access UCL Research Data Repository and can be accessed at https://doi.org/10.5522/04/30060709.v1.

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