International Journal of Astrobiology

cambridge.org/ija

Surface mineral crusts: a potential strategy for sampling for evidence of life on Mars

Connor Brolly, John Parnell and Stephen Bowden

Department of Geology & Petroleum Geology, University of Aberdeen, AB24 3UE, UK

Research Article

Cite this article: Brolly C, Parnell J, Bowden S (2019). Surface mineral crusts: a potential strategy for sampling for evidence of life on Mars. *International Journal of Astrobiology* **18**, 91–101. https://doi.org/10.1017/S1473550418000034

Received: 27 March 2017
Revised: 4 January 2018
Accepted: 6 January 2018
First published online: 15 February 2018

Key words:
Astrobiology; ExoMars 2020; Mars; surface mineral crusts

Author for correspondence:
Connor Brolly, E-mail: connor.brolly@gmail.com

Abstract

Surface mineral crusts on Earth are highly diverse and usually, contain microbial life. Crusts constitute an attractive target to search for life: they require water for their formation, they efficiently entrap organic matter and are relatively easy to sample and process. They hold a record of life in the form of microbial remains, biomolecules and carbon isotope composition. A miniaturized Raman spectrometer is included in the ExoMars 2020 payload as it is sensitive to a range of photosynthetic pigments. Samples from the Haughton Impact Structure, Canadian High Arctic and others, shows the preservation of pigments in a range of crust types, especially supra-permafrost carbonate crusts and cryptogamic crusts. The Raman spectral signatures of these crusts are shown along with biomarker analysis to showcase these techniques prior to the ExoMars 2020 mission. Carotenoids and other photoprotective microbial pigments are identified in the Haughton surface crusts using Raman spectroscopy. Gas chromatography-mass spectrometry analyses show a distribution of fatty acids which are most likely from a cyanobacterial source. The successful demonstration of these analyses in the Haughton Impact structure shows the biosignature of surface mineral crusts can be easily extracted and provides an excellent target for sampling evidence of life on Mars.

Introduction

Mineral crusts are a widely developed feature at the rock or sediment surface, wherever there is a flux of water. They occur in all climatic zones on Earth, from tropical to polar desert, although their chemistry and morphology vary with surface hydrology, temperature and substrate. Where surface evaporation in the soil zone is an important and regular process, as in semi-arid environments, crusts tend to be well developed. The range of deposits includes duricrusts (calcrete, silcrete, gypcrete, ferricrete-laterite), rock (desert) varnish, crusts above permafrost and salt crusts. This list is much greater if mineral precipitates from flowing fluids are included, such as speleothems, travertine and other hot spring deposits, tufa, sea spray deposits and chemosynthetic deposits. Crusts occur on present-day bedrock surfaces and many types are also evident in the geological record. Even in the Precambrian, crusts have been identified of duricrust (Watanabe *et al.* 2000; Beukes *et al.* 2002) and hot spring (Melezhik & Fallick 2001) origin. This discussion will focus on precipitates associated with surface moisture.

Stromatolites are distinct, as they involve biological trapping of mineral grains rather than inorganic precipitation. However, they are certainly crust-like in nature, have a geological record back to the early Archean and offer a similar prospect of holding a record of life. The close relationship of mineral crusts and biogenic stromatolites is reflected in descriptions of various crust types as stromatolitic, including calcretes (Krumbein & Giele 1979), supra-permafrost crusts (Clark *et al.* 2004) and rock varnish (Perry & Adams 1978). In practice, the distinction would be of secondary consideration during planetary exploration, as any crust-like feature would merit serious investigation. Stromatolites have been repeatedly highlighted as a potential indicator of biogenic activity on Mars (e.g. Westall *et al.* 2004) and there is a very extensive literature on their biological significance (Riding & Awramik 2000 and references therein). There is some debate about whether a stromatolite-like morphology (laminar fabric, commonly with concentric domed elements) necessarily represent a biological origin, or could alternatively be abiogenic (Grotzinger & Rothman 1996). In a broader strategy to analyse mineral crusts, this distinction becomes immaterial, as a crust of biogenic origin may still be a host to ambient microbial life. A range of definitions of stromatolites is in use, variably including laminate algal structures, concentric algal lamination and permineralized algal lamination. Where algal deposits are permineralized, typically with calcite or silica, it is reasonable to regard them as a variety of mineral crust.

Mineral crusts are potentially sources of both extant (living, recently dead) and fossil biomarkers. As most studies of life in mineral crusts have been undertaken on recent material, the evidence involves microbiology or molecular biology. Organic geochemistry is of lesser value when these kinds of evidence are available and is therefore not routinely applied to recent

© Cambridge University Press 2018. This is an Open Access article, distributed under the terms of the Creative Commons Attribution licence (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted re-use, distribution, and reproduction in any medium, provided the original work is properly cited.

CAMBRIDGE UNIVERSITY PRESS

samples, but it becomes of increasing value back into the geological record. However, extant biomarkers can be readily detected in recently formed crusts. In addition to the detailed case study given below, molecular studies have been undertaken in a range of crust types including salt crusts (Ionescu *et al.* 2007), rock varnish (Perry *et al.* 2003) and hot spring deposits (Pancost *et al.* 2005). Fossil biomarkers are more difficult to determine, as their chance of survival becomes progressively less with age. Nevertheless, in favourable circumstances, where organic matter is sealed within a mineral matrix and dry conditions limit subsequent alteration, they may survive. Examples in the terrestrial fossil record are very few, although this partly reflects limited attempts to find them. The limited data are mostly from the Cenozoic, including determination of archaeal biomarkers in Miocene chemosynthetic carbonates in Italy (Thiel *et al.* 1999). A rare pre-Cenozoic example describes biomarkers from Mesozoic chemosynthetic deposits in California (Birgel *et al.* 2006).

Diversity of crusts

The range of crusts discussed is summarized in Table 1, including examples of studies undertaken on evidence for life within them. We address eight types of crust that have been proposed as candidate environments in the search for life on Mars.

Hot spring (hydrothermal) systems commonly precipitate minerals as the waters cool, particularly carbonate- or silica-rich crusts. The springs are usually found in regions of anomalous heat, such as above/around magmatic systems. Many are also nutrient-rich and support a flourishing biota. The mineral precipitates thus can contain organic remains. Modern hydrothermal precipitates yield biomarkers on analysis (Pancost *et al.* 2005) and there is some evidence for biomarker preservation in ancient hydrothermal deposits (Bowden & Parnell 2007).They have been strongly advocated for astrobiological exploration (Farmer 2000) and the recent identification of possible hydrothermal sites on Mars (Schulze-Makuch *et al.* 2007) has renewed interest in their potential for life.

The evaporation of salt-rich waters at the land surface produces salt crusts. Their mineralogy is dominated by relatively soluble minerals such as gypsum, halite and calcite. They can accumulate rapidly, given a continuous flux of water, so may entrap surface-dwelling organisms. Gypsum and halite crusts in particular seal organic remain effectively (Tehei *et al.* 2002). The widespread occurrence of sulphates at the Martian surface makes these a target to investigate (Mancinelli *et al.* 2004).

Duricrusts are similarly precipitated from evaporating water but are distinctively characterized by precipitation within the surface detritus ('soil'), to form a crust of mixed mineral precipitate and sediment particles. According to mineralogy, they are described as calcrete, dolocrete, silcrete, gypcrete and ferricrete. In laterites (ferricretes), terrestrial biomass may be essential to the mobilization and concentration of iron under oxidizing atmospheric conditions (Beukes *et al.* 2002). They form slowly (hundreds to thousands of years), so organic matter usually decays before entrapment. However, there are exceptions, including organic carbon concentrations in Archean duricrust (Watanabe *et al.* 2000). Proposed Martian scenarios include duricrust formation on weathered basalts (Knauth 2001).

Rock varnish is a thin (sub-millimetre) coating on exposed bedrock surfaces and clasts in arid/semi-arid environments. It is rich in manganese and silica and appears to have developed by evaporative concentration, gelling and hardening of opaline silica (Perry *et al.* 2006). Rock varnish is known to contain amino acids and DNA (Perry *et al.* 2003), although whether these are included incidentally or by active microbial precipitation (Dorn & Oberlander 1981; Nagy *et al.* 1991) is debated. Regardless, rock varnish is proposed as a target in the search for life on Mars (DiGregorio 2002; Perry & Sephton 2006).

Crusts may develop above permafrost because the surface water cannot percolate downwards so becomes ponded at the surface and gradually evaporates. Crusts of this origin occur in the Arctic and may involve microbial matter (Lauriol & Clark 1999). The low temperatures and evidence of surface fluid seepage (Luo & Howard 2008) make this type of crust a possibility on Mars. The formation of indurated crusts from moisture movement through aeolian dust above ice has been inferred by Farrand & Lane (2007) from THEMIS data.

Speleothems are crust-like deposits formed in cave environments, including dripstone structures like stalagmites and stalagtites. Modern speleothems show evidence for incorporation of microbial matter (Barton, Spear & Pace 2001). Proposals that they should be astrobiological targets (Boston *et al.* 2001) have gained new significance with observations of possible cave skylights on Mars (Cushing *et al.* 2007).

Stromatolites are laminated sediments, representing algal (cyanobacterial) mats deposited in shallow water environments,

Table 1. Types of mineral crust: predominant mineralogy and case studies of evidence for life

		Fossil record Case studies		
Crust type	Mineralogy	Organic geochemistry	Isotopic data	Microbial
Hydrothermal	Ca, Si, Gyp, Fe	Pancost *et al.* (2005)	Zhang *et al.* (2004)	Lin *et al.* (2016)
Salt crusts	Gyp, Hal	Ionescu *et al.* (2007)	Finstad *et al.* (2016)	Canfora *et al.* (2016)
Duricrusts	Ca, Si, Gyp, Fe	Connon *et al.* (2007)	Robinson *et al.* (2002)	Verrecchia *et al.* (1995)
Rock varnish	Si, Fe	Perry *et al.* (2003)	Dorn & Deniro (1985)	Esposito *et al.* (2015)
Supra-permafrost	Ca, Gyp	Parnell *et al.* (2006)	Clark *et al.* (2004)	Lauriol & Clark (1999)
Speleothem	Ca	Xie *et al.* (2003)	Paulsen *et al.* (2003)	Northup et al. (2000)
Stromatolite	Ca, Si	Allen *et al.* (2010)	Kakegawa & Nanri (2006)	Riding & Awramik (2000)
Chemosynthetic	Ca	Birgel *et al.* (2006)	Campbell *et al.* (2002)	Barbieri *et al.* (2002)

Ca, carbonate; Si, silica; Gyp, gypsum; Fe, iron/manganese minerals; Hal, halite.

https://doi.org/10.1017/S1473550418000034 Published online by Cambridge University Press

permineralized by carbonate or silica. Modern cyanobacterial mats can be rich in lipid compounds (e.g. Jahnke *et al.* 2004), but the permineralized equivalents often lack organic matter. Nevertheless, they are sought on Mars as an indicator of microbial life (Westall *et al.* 2004).

Chemosynthetic deposits are carbonate-rich crusts developed where seeping hydrocarbons, especially methane, emerge at the surface and fuel a localized biota and produce carbonates by oxidation of organic carbon. They are generally sea-floor deposits, but subaerial deposits are feasible. They inherently involve organic matter which can be trapped within the carbonate (Campbell *et al.* 2002). Suggestions that they should be sought on Mars (Komatsu & Ori 2000) may be given impetus by the discovery of methane in the Martian atmosphere (Formisano *et al.* 2004).

The focus of this paper is on mineral crusts, but it is notable that biological materials may themselves form a firm crust with the admixed mineral matter, known as cryptogamic crusts and variably including lichens, cyanobacteria, algae, mosses and fungi (Stradling *et al.* 2002). Cryptogamic crusts inherently contain large quantities of labile organic compounds: An example of an organic geochemical study of such material is given by Cockell *et al.* (2007).

Suitability of mineral crusts for record of life

Mineral crusts are strong candidates in the search for evidence of life, both in terrestrial extreme environments and during planetary exploration. There are several reasons for their suitability:

(1) The growth of any mineral precipitate implies an active flow of water to transport the solutes for mineral growth. Water is also a vector for life, so crust development is a direct indicator of a potential environment for life.
(2) The precipitation of mineral from water also implies that the water has a high load of dissolved ions, which should include nutrients for living matter. Dissolved ions also provide redox-based energy sources that can be exploited by simple life.
(3) As the mineral precipitates, the growing crystals can entrap and thereby preserve, organic matter. This can range from different types of biomolecules to whole cells with morphological form, i.e. the evidence entrapped can be both chemical and physical.
(4) Mineral precipitates can also incorporate an inorganic record of life, including microbially mediated crystal growths and isotopic evidence for microbial metabolism.
(5) In addition to entrapment of ambient life, mineral precipitation may create a new microenvironment (microporosity) for an active biota.

In the particular case of Mars:

(6) The philosophy of searching for evidence of life on Mars has been 'follow the water' (Kargel 2004; Tokano 2005). Any surface crusts on Mars are likely to represent the most recent mineral precipitation from water.
(7) We already have evidence of crust formation in Martian soil through precipitation of sulphate salts. Crust-like surfaces were observed by both the Viking missions (Guinness & Arvidson 1989) and at the Mars Pathfinder landing site (Moore *et al.* 1999).
(8) Observations of fog/frost in several contexts on Mars (Kargel 2004) suggest that mineral dissolution and reprecipitation on a micro-scale could be still occurring in some surface crusts.

The impact crater environment, widespread on Mars, is an especially favourable case for crust development, because:

(9) Active circulation of water follows the impact event due to hydrothermal activity. Many terrestrial impact craters show evidence for hydrothermal circulation and in the biggest craters this might last for up to a million years or longer (Abramov & Kring 2004).
(10) Ponding of water may occur temporarily in the crater depression. Some craters in the geological record have infillings of lacustrine sediments, including the Haughton impact structure(Osinski *et al.* 2005; see below). These successions indicate long-term trapping of water.
(11) The impact detritus presents a substantial surface area for mineral dissolution, to create saturated ground waters which can reprecipitate as crusts.
(12) The anomalous heating in a crater allows chemical reactions (including solution, reprecipitation), to proceed at a faster rate than ambient, as well as favouring any organic metabolism.

In terms of sampling, additional advantages are:

(13) Minerals precipitating at the surface tend to be relatively soluble and soft, making them amenable to processing by both chemical and physical methods. Gypsum and halite can be dissolved in water and carbonates in acid. Each of these can be readily cored and crushed to a powder for ease of handling.
(14) Deflation of crusts by the wind, which is likely in dry surface environments, releases abundant crust detritus into the surrounding soil, where it is easy to sample.

Analysis by Raman spectroscopy

A miniaturized Raman spectrometer is part of the payload instrumentation on the ESA ExoMars mission, set to fly in 2020. It is sensitive to most rock-forming minerals including oxides hydroxides, silicates and sulphates, therefore it can be used for petrographic analysis (Haskin *et al.* 1997; Wang *et al.* 1998). Previous work by Jehlička *et al.* (2014) shows the range of microbial pigments that can be detected by Raman spectroscopy, promoting its use for the analysis of crusts on Mars. Crusts from the Haughton impact crater and other modern crust samples will be analysed by Raman spectroscopy to determine if a biosignature can be identified.

Haughton Crater case study

A case study was undertaken based on samples collected in the Haughton Impact Structure, Devon Island, Canadian High Arctic. The location is especially suitable for research because it is used as a site for analogue studies for Martian exploration (Lee & Osinski 2005) and consequently the surface environment and microbiology are well documented (e.g. Cockell *et al.* 2001). A preliminary report on the potential of Haughton crusts to yield evidence of life is given by Parnell *et al.* (2006).

The Haughton Impact structure was formed about 39 Ma ago (Sherlock *et al.* 2005) in a ~1880 m thick series of Lower Palaeozoic sedimentary rocks dominated by carbonate facies overlying Precambrian crystalline basement (Robertson & Sweeney 1983; Osinski *et al.* 2005). The structure's interior contains lithic breccias and impacts melt breccias. Limited Miocene-age lacustrine sediments overlie the melt breccia in places within the crater. Country rocks around the crater are predominantly brown dolomites with a sucrosic, porous texture. Four main formations are exposed within

https://doi.org/10.1017/S1473550418000034 Published online by Cambridge University Press

the impact structure, in descending stratigraphic order: the Allen Bay Formation (spanning the Ordovician-Silurian boundary), as well as the Thumb Mountain and Bay Fiord Formations of the Cornwallis Group and the Eleanor River Formation (all of Ordovician age). As the bedrock is predominantly carbonate, the groundwaters are bicarbonate-rich (Lim & Douglas 2003).

A wide variety of mineral crusts occurs in and around the structure. These include carbonate, gypsiferous and ferruginous crusts. The carbonate crusts (Fig. 1) are varieties of a phenomenon that occurs across the Arctic region from Canada, Greenland and Spitzbergen (Swett 1974; Bunting & Christensen 1978; Forman & Miller 1984; Clark *et al.* 2004; Pellerin *et al.* 2009), but include crusts that occupy fractures relating to the impact event. For the purposes of this study, we have sought to show:

(i) that the biosignature can be obtained following relatively simple analysis.
(ii) that the organic compounds are in sufficient detail to make inferences about the type of life present.

Methodology

Samples

Samples of crust were collected from *in situ* exposures in the Haughton Impact Structure at Pete Conrad Valley and Lowell Oasis (Fig. 2) and transported to the laboratory wrapped in aluminium foil.

Gas chromatography-mass spectrometry (GC-MS)

As microbiological studies have shown that cyanobacteria are prevalent in rock samples in the Haughton Impact Structure (Cockell *et al.* 2002; Parnell et al. 2004), we particularly sought compound classes that are present in and have been the subject of numerous previous studies on, cyanobacteria, namely fatty acids. Examples of such studies are described by Bowden & Parnell (2007).

The GC-MS analysis was performed on an Agilent Technologies 5975 inert Mass selective Detector, fitted with a 30 × 250 μm internal diameter film, 0.25 μm in thickness, fused capillary column with helium as the carrier gas.

Raman spectroscopy

Raman spectra were obtained using a Renishaw InVia H36031 confocal Raman microscope operating at a wavelength of 514.5 nm green monochromatic laser light, which is similar to the 2020 ExoMars flight instrument wavelength of 532 nm. 5% power (1.5 mW) was used with 10 accumulation and 2 s exposure time, giving a good signal-to-noise ratio. A 50× objective lens was used giving a laser 'footprint' of 1–3 mm, with a static spectral range centered at 1200 cm^{-1}.

Petrography of crusts in High Arctic

In the High Arctic region, there is widespread evidence of the dissolution of carbonate bedrock. The permafrost ensures only limited drainage, so the surface waters become bicarbonate-saturated and a diversity of carbonate precipitates form including above and below pebbles, lining the walls of fractures, speleothems and crusts on the sediment surface. Precipitation on the underside of pebbles and cobbles is particularly widespread (Bunting and Christensen, 1978; Forman & Miller, 1984). The underside precipitates are composed of calcite and aragonite, which form

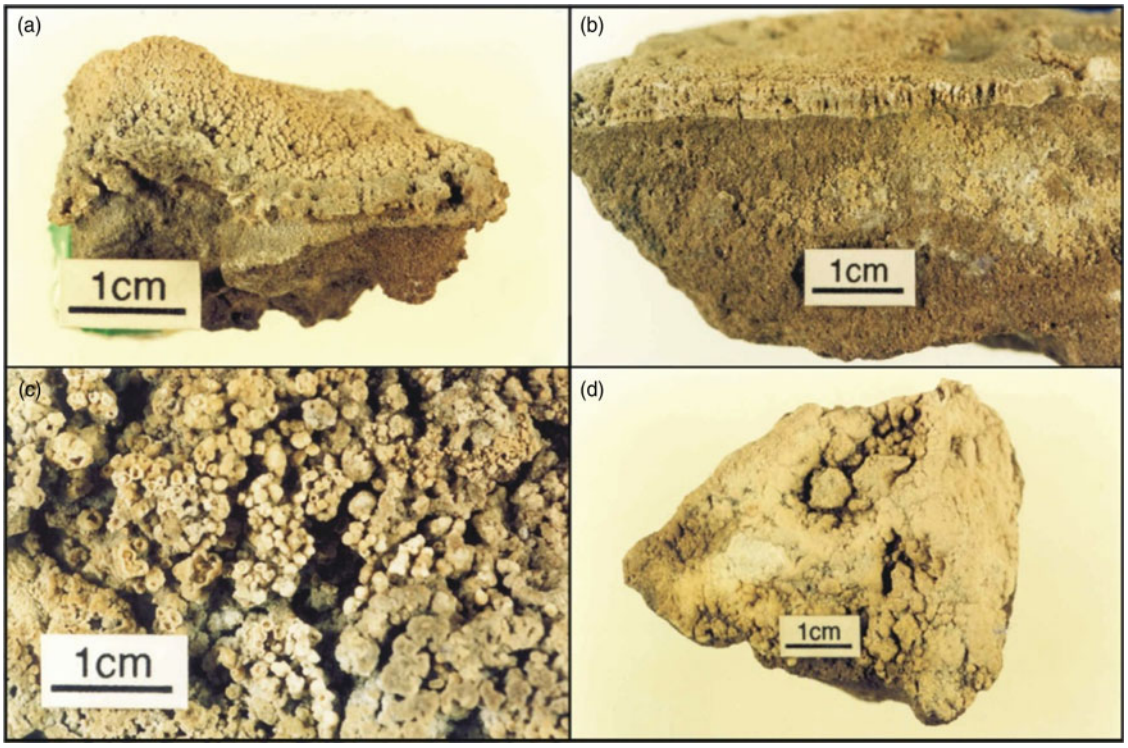


Fig. 1. (a) Typical hand specimen of carbonate crust growing over the top surface of dolomite bedrock. (b) The carbonate crust sits upon an uneven erosion surface above the brown dolomite. (c) Plan view of the crustal structure shows that tubular structures are interconnected, but where they have broken off they are hollow inside. (d) Where a tubular structure has not fully formed a white precipitate covers the dolomite. (Photos courtesy of J. Whelan).

https://doi.org/10.1017/S1473550418000034 Published online by Cambridge University Press

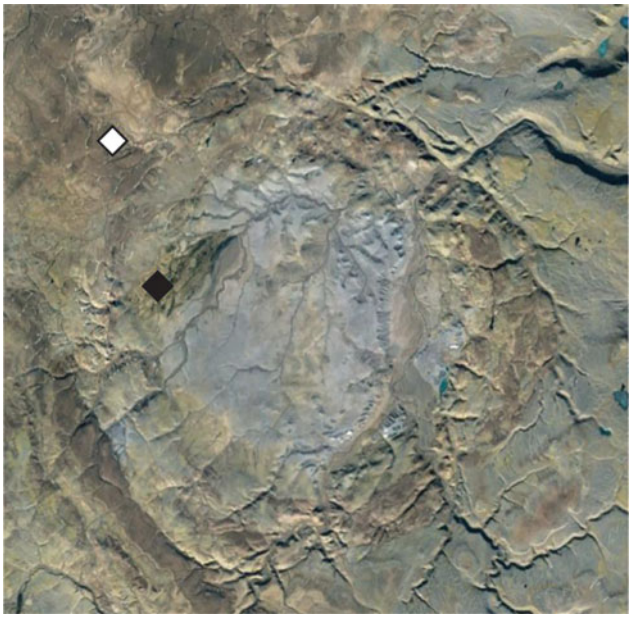


Fig. 2. Google Earth image of the Haughton impact crater, Devon Island. Black marker depicts Lowell Oasis sample location (H1). White marker depicts Pete Conrad Valley sample location (H2).

pendant growths with an internal laminate structure. The laminae are 10–100 μm thick and reflect variations in crystal size and organic matter content during continuous growth. The crusts develop a microcolumnar structure similar to some stromatolites (Clark *et al.* 2004; Pellerin *et al.* 2009).

Another case study (Swett 1974) reports carbonate precipitation particularly on the *upper* sides of pebbles and cobbles. This suggests local variations in the relative importance of water draining the undersides, or evaporation off the upper sides, which may, in turn, be related to a height above the water table, surface temperature gradient and clast permeability.

Haughton crater crusts

In the Haughton crater, carbonate crusts occur in each of the settings described above, i.e. below pebbles, on the upper surfaces of pebbles and in fractured bedrock. The mineralized fracture systems are related to deformation during the impact event. The carbonate crusts are up to 3 cm thick, developed particularly on the underside of blocks of bedrock, which are most commonly granular dolomites of the Ordovician-Silurian Allen Bay Formation. On a megascopic scale, the crusts are composed of coalesced microdigitate structures. On a microscopic scale, the carbonate exhibits a mixed radial and laminar fabric. There is a predominant radial fabric of outward (downward) growth, on which a laminate fabric is superimposed by variations in crystal size and breaks between successive phases of radial growth. Each column in the microdigitate structure reflects a separate domain of radial outgrowth, but the laminate fabric is common to all columns. The radial crystals also contain scattered dolomite grains, with rhombic form, upon which the radiating crystals are nucleated. There are also small masses and discontinuous layers of micrite between the radial growths, which contribute to the laminate fabric (Fig. 3(a)). Tower-like shrubs on the outer parts of crusts, forming the microdigitate structure, have a high (up to 50%) content of micrite. Some microporosity remains between individual crystal bundles, and between the columns and is partially infilled with dark organic matter (Fig. 3(b)).

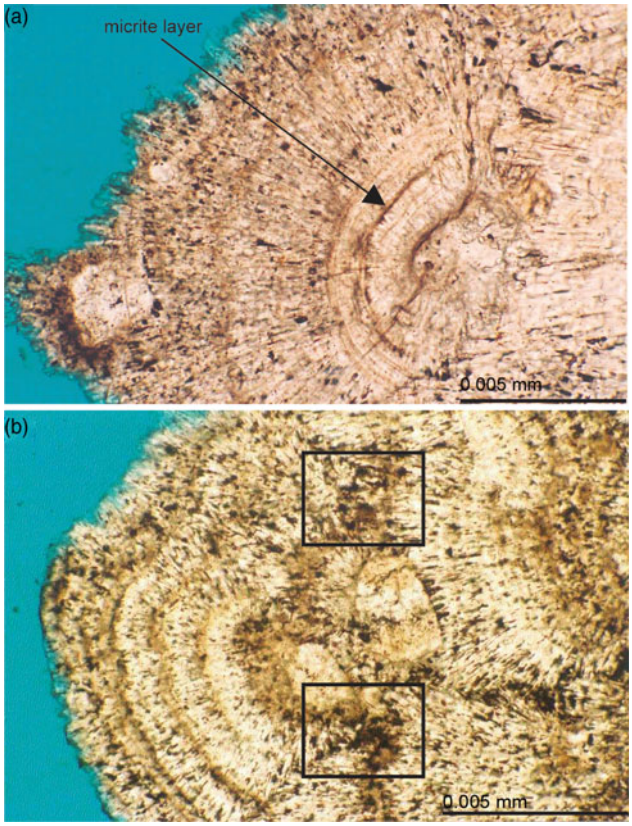


Fig. 3. (a) Discontinuous layers of micrite create a laminate fabric within the crust. (b) microporosity partially infilled with the dark organic material, highlighted by the black boxes.

Where carbonate precipitated on the *upper* surfaces of pebbles, it is laminate rather than microdigitate, or may just occur as structureless microcrystalline carbonate. Locally, these deposits have an upper yellow patina. The components of the carbonate crusts probably have mixed inorganic-organic origins. The micritic material and the shrubs in which it is concentrated is comparable with microbial shrubs in hot spring systems (Pentecost, 1990; Guo and Riding, 1994). The radiating crystals may be inorganic, but the micritic shrubs would provide nucleation sites for precipitation. The scattered dolomite grains are identical to water-borne/air-borne dust grains at the sample site and are assumed to be incorporated into the crusts incidentally.

Gypsum crusts up to 2 cm thick are developed on the lacustrine sediments of the Haughton Formation that infilled the crater and the present-day silty soils derived from them. The gypsum exhibits a fibrous structure normal to the growth surface and is coloured brown due to the incorporation of abundant crystals of iron oxide (Fig. 4).

The underlying Haughton Formation sediments contain pyrite, oxidation of which explains the mixture of gypsum and iron oxides. The crusts also exhibit localized efflorescences of jarosite, as also recorded by Léveillé (2007). The mineral assemblage is therefore comparable with that encountered on Mars at Meridiani Planum (Squyres & Knoll 2005). The Meridiani Planum sulphates have been proposed as a potential target for astrobiological investigation (Knoll *et al.* 2005; Aubrey *et al.* 2006).

https://doi.org/10.1017/S1473550418000034 Published online by Cambridge University Press



Fig. 4. Fibrous gypsum crust coloured brown due to incorporated iron oxide. From 'weather station', Rhino Creek.

Black cryptogamic crusts were sampled from the slopes around active water courses. Such crusts are widespread on Devon Island (Bliss & Gold 1999), and are rich in cyanobacteria (Dickson 2000). The cryptogamic crusts are 1–2 mm thick, consisting of the desiccated black microbial mat with an adhering substrate of sand composed of dolomite grains derived from weathering of the local bedrock. Moist, pliable equivalents of the crusts occur at the margins of active streams. The black mats also coat pebbles and cobbles. They occur over regions of thousands of square metres, evident in aerial photographs.

Data

Raman

Figure 5 shows the Raman spectrum of two samples from the Haughton crater, two samples from North Scotland and one sample from Spain. The carbonate band (1085 cm^{-1}) is present in Wick and Pete Conrad valley samples. Bands associated with β-carotene (1006, 1157, 1517 cm^{-1}) are present in Wick and Ebbro Basin samples. Salinixanthin is a major carotenoid pigment produced by *Salinibacter (Bacteroidetes)* and is present in Wick, Lowell Oasis and Achmelvich. The Raman spectrum of this pigment is characterized by three bands at 1003, 1155 and 1512 cm^{-1}. Parietin is often observed in combination with Salinixanthin displaying bands at 1671, 1575 (1595 shoulder), 1197, 914, 464 cm^{-1}. Scytonemin, a UV protective pigment is surprisingly not present as expected given the dark coloration of the crusts.

GC-MS

The analyses of H1 and H2 samples are shown in Fig. 6, below. Palmitic (16 : 0) and stearic (18 : 0) fatty acids dominate the polar fraction and are the most abundant compound that was extracted from the carbonate crust. The presence of *cis*-vaccenic acid (18 : 1) in both samples, indicates a biological source derived from bacteria (Volkman *et al.* 1998). The absence of polyunsaturated fatty acids (C_{18} and above) suggest a prokaryotic source, which is supported by the presence of C_{15} and C_{17} methyl-branched fatty acids, which are present in higher proportions in bacteria (Volkman *et al.* 1980). Higher plants are not common in the Arctic polar desert of Devon Island, therefore a bacterial origin for the lipid signatures is the most likely. Cyanobacteria are common as communities of *Chroococcidiopsis, Aphanothece, Gloeocapsa* and *Nostoc commune* are observed (Cockell *et al.* 2002; Parnell *et al.* 2004). It is possible that some of the lipids derive from fungi as the saturated C_{16} and C_{18} *n*-alkanoic acids are also held in fungi (Harwood & Russell 1984). The chromatograms shown below are comparable with that shown in Fig. 1 from Bowden & Parnell (2007).

Discussion

Crusts on Mars

Observations by previous Mars missions (Banin *et al.* 1992) show that the surface has a widely developed salt-rich crust, dominated by sulphates (Cooper & Mustard 2002), which have been identified by both Mars Exploration Rovers (MER), Spirit and Opportunity (Gellert *et al.* 2004; Squyres *et al.* 2004). Spirit encountered ferric sulfate-rich crusts in Gusev crater, which are likely to be associated with the hydrothermal activity (Arvidson *et al.* 2010) and are evidently accessible by a rover. On Earth, hydrothermal activity is commonly associated with microbial life (Walter & Des Marais 1993).

Sublimation could play a role in crust formation on Mars, but this is restricted to higher latitudes (>60°) and is unlikely to be a major mechanism for crust formation in equatorial regions (Mangold 2011), where the two remaining ExoMars landing sites are located.

Wind erosion could be an important factor for the preservation of crusts, including a range of other exploration targets on Mars. Although wind erosion on Mars is complex, net erosion occurs mainly in lowland regions, such as the northern plains and the southern mid-latitudes and is controlled by topography (Armstrong & Leovy 2005). Chryse is highlighted as an area which could experience net erosion by Armstrong & Leovy (2005) and given the proximity to Oxia Planum and Mawrth Vallis, these sites could experience similar erosion rates. The formation and preservation of evaporitic crusts on Mars is controlled by wind erosion and water-table fluctuations. For crusts to develop, erosion rates must match the rate of water-table lowering, which would control the preservation of strata including crusts (Grotzinger *et al.* 2005). Given that Spirit and Opportunity rovers both encountered crusts during their missions, crusts are regarded as a valuable exploration target.

Thermal inertia mapping suggests that a significant proportion of the planet surface may be indurated (Mellon *et al.* 2000), including about 50% of the terrain from 0° to 60° N. The ejecta around craters in the Terra Meridiani region is rich in high-thermal inertia indurated material (Hyneck 2004). At Meridiani Planum, rock surfaces exhibit weathering rinds that are relatively resistant to erosion (Jolliff *et al.* 2006). If extant life could tolerate the Martian surface, crusts could be a good habitat. Palaeo-crusts may exist within Noachian sedimentary successions, but these are likely difficult to distinguish from other sulphate-rich rocks.

Survivability of biomarkers

A major concern in the search for evidence of life on other planetary surfaces is that molecular evidence could be severely compromised by irradiation (Kminek & Bada 2006). Living organic matter within crusts should have adequate protection from

https://doi.org/10.1017/S1473550418000034 Published online by Cambridge University Press

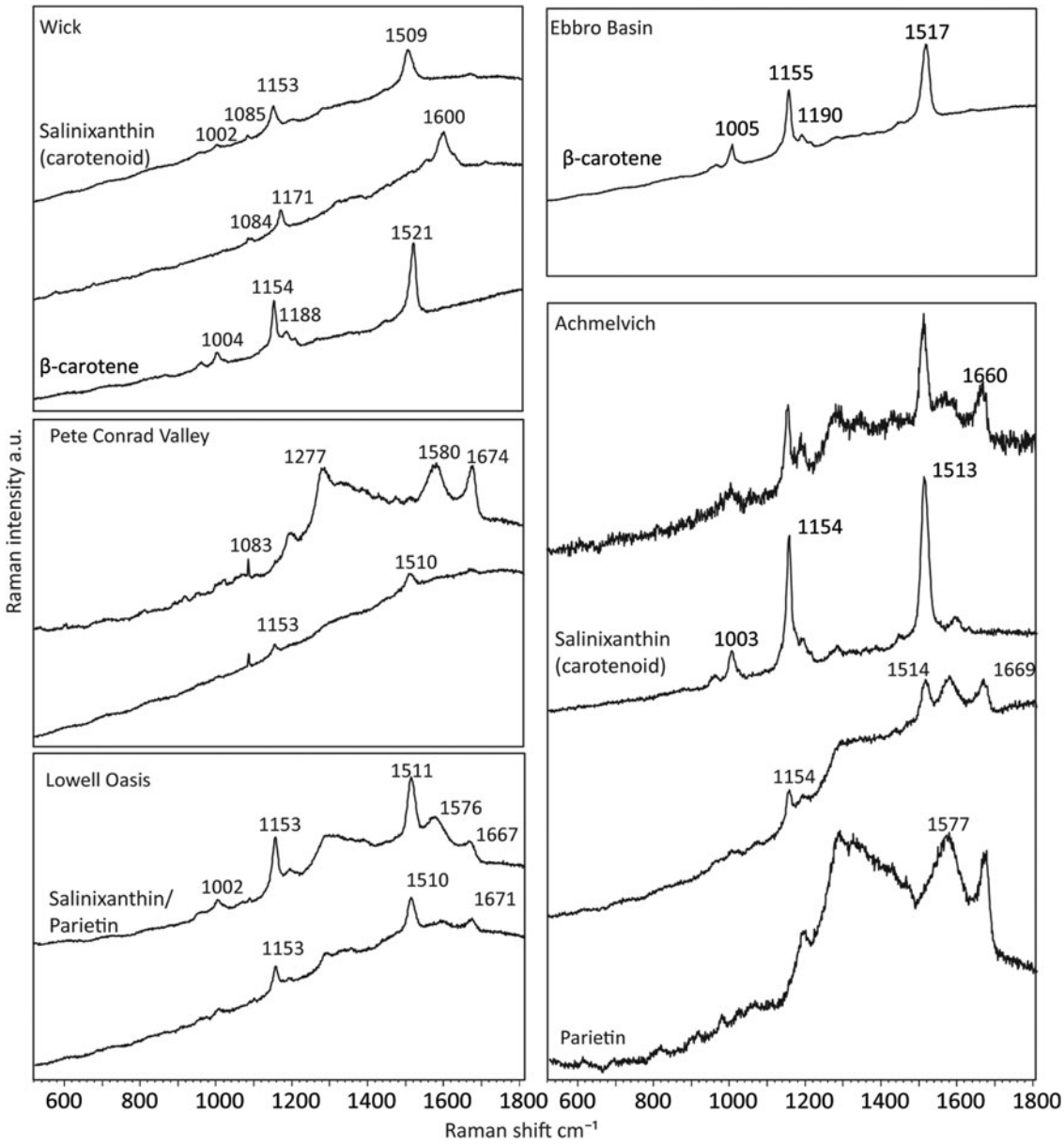


Fig. 5. Raman spectra of crust samples from Wick, Scotland; Ebbro Basin, Spain; Pete Conrad Valley, Haughton; Lowell Oasis, Haughton; Achmelvich, Scotland. The *x*-axis is in reciprocal centimeters (cm^{-1}), the *y*-axis is the relative Raman intensity. Notable Raman bands are depicted with the band position.

ultraviolet irradiation, as only a few microns of shielding is required. Although other forms of irradiation (solar energetic particles, galactic cosmic radiation, mineral radiation) penetrate rocks further, living organisms may have developed genetic damage repair systems that can cope with it, however in the shallow subsurface (<2 m depth) the biomolecules in fossil organic matter in crusts would experience progressive degradation (Kminek & Bada 2006; Dartnell *et al.* 2007). Fossil organic matter is best sought where shielded from long-term irradiation (recently excavated channels or craters, or sampled by coring).

A further note of caution is appropriate. Despite the extensive evidence for the microbial matter in terrestrial mineral crusts, there is no guarantee that we would be able to detect it during a remote mission, particularly if it is a fossil sample. If any rock looking vaguely similar to a stromatolite was encountered on Mars, it would become a priority target for analysis. But would we make a successful analysis of a similar rock on Earth? If it was recent, probably. If it was a fossil, the successful analysis is by no means certain, as organic matter is progressively oxidized and otherwise altered until it leaves no molecular record. Success is more likely when the organic matter is tightly sealed within the mineral matrix.

Other signatures

Although the focus of this discussion is on molecular evidence, several types of crust do preserve morphological evidence of microbial life. For example, biological structures are evident in case studies of speleothems (Northup *et al.* 2000), supra-permafrost crusts (Lauriol & Clark 1999) and chemosynthetic deposits (Barbieri *et al.* 2002) and in each case would be evident

https://doi.org/10.1017/S1473550418000034 Published online by Cambridge University Press

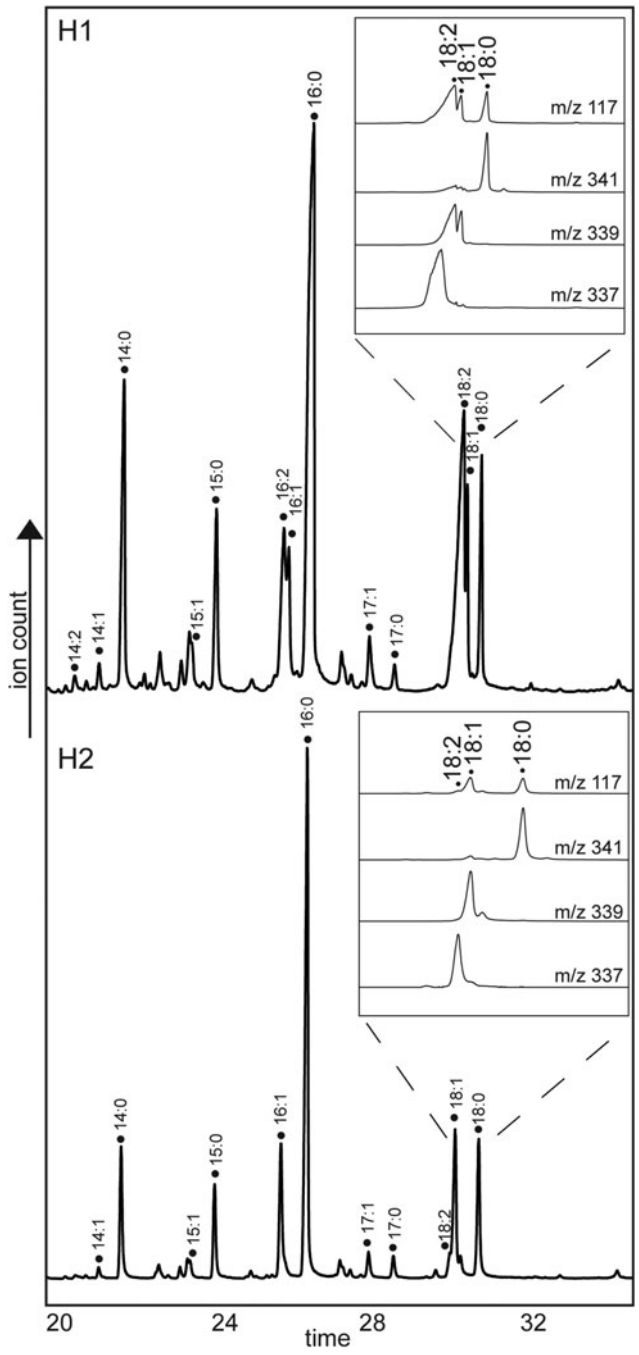


Fig. 6. GC-MS trace of the *m/z* 117 ion chromatograms of the polar fractions, derivatized with BSTFA. Expanded sections show *m/z* 337 339 & 341 ions. The fatty acids are denoted as e.g '16 : 0'; the number before the colon specifies the number of carbon atoms, the number after the colon specifies the number of double bonds.

in a field of view of 50 μm. Morphological evidence can also include the microporosity left by microbial degradation.

Surface precipitates have similarly been advocated as a potential source of fossil fluid samples from Mars, whereby the minerals contain fluid inclusions trapping the water from which they precipitated (Parnell & Baron 2004). Such fluid samples can also be valuable in the recording of terrestrial palaeoenvironments and the mineral precipitates may hold other compositional data (e.g. isotopic) that can be used for the same purpose, for example, inference of an organic contribution to carbonate precipitation. Indeed most of the crust types discussed in this paper yield evidence for a role of organic matter in their formation, through carbon isotope composition (Table 1), in calcrete (Watanabe *et al.* 2000), supra-permafrost crusts (Clark *et al.* 2004) and chemosynthetic deposits (Campbell *et al.* 2002). Cyanobacterial mats forming in mineralizing hot springs readily yield lipid biomarkers (Jahnke *et al.* 2004, and references therein)

Conclusions

Mineral crusts are strong candidates in the search for evidence of life during planetary exploration and should be an important target for examination on Mars. The pilot study in the Haughton Impact Structure shows that they can readily yield a biological signature. In terms of the specific objectives of the analysis, the study showed that:

(i) The biosignature of the crusts can be obtained by normal extraction techniques and spectral analyses.
(ii) The organic compounds can be resolved sufficiently to make deductions about the nature of the life that was trapped in the crusts.

Acknowledgements. The research was under the auspices of the NASA Haughton-Mars Project. J. Whelan is acknowledged for photomicrographs taken from undergraduate laboratory projects. This work was funded by STFC grant ST/L001233/1. The University of Aberdeen Raman facility was funded by the BBSRC grant BBC5125101.

References

Abramov O and Kring DA (2004) Numerical modelling of an impact-induced hydrothermal system at the Sudbury crater. *Journal of Geophysical Research* **109**, E10007. doi: 1029/2003E002213.

Allen MA, Neilan BA, Burns BP, Jahnke LL and Summons RE (2010) Lipid biomarkers in Hamelin Pool microbial mats and stromatolites. *Organic Geochemistry* **41**, 1207–1218.

Armstrong JC and Leovy CB (2005) Long term wind erosion on Mars. *Icarus* **176**, 57–74.

Arvidson RE, Bell JF III, Bellutta P, Cabrol NA, Catalano JG, Cohen J, L Crumpler S, Des Marais DJ, Estlin TA, Farrand WH, Gellert R, Grant JA, Greenberger RN, Guinness EA, Herkenhoff KE, Herman JA, Iagnemma K D, Johnson JR, Klingelhöfer G, Li R, Lichtenberg KA, Maxwell SA, Ming DW, Morris RV, Rice MS, Ruff SW, Shaw A, Siebach KL, de Souza PA, Stroupe AW, Squyres SW, Sullivan RJ, Talley KP, Townsend JA, Wang A, Wright JR and Yen AS (2010) Spirit Mars Rover Mission: overview and selected results from the northern home plate winter haven to the side of Scamander crater. *Journal of Geophysical Research: Planets (1991–2012)*, **115**, E00F03.

Aubrey A, Cleaves HJ, Chalmers JH, Skelley AM, Mathies RA, Grunthaner FJ, Ehrenfreund P and Bada JL (2006) Sulfate minerals and organic compounds on Mars. *Geology* **34**, 357–360.

Banin A, Clark BC and Waenke H (1992) Surface chemistry and mineralogy. In Kieffer HH, Jakosky BM, Snyder CW and Matthews MS (eds). *Mars*. Tucson: University of Arizona Press, pp. 594–625.

Barbieri R, Cavalazzi B and Westall F (2002) Microbial fossilization potential in chemosynthetic (cold seep) carbonate rocks: exopaleontological implications. *Lunar and Planetary Science* **XXXIII**, abstract 1319.

Barton HA, Spear JR and Pace NR (2001) Microbial life in the underworld: biogenecity in secondary mineral formations. *Geomicrobiology Journal* **18**, 359–368.

Beukes NJ, Dorland H, Gutzmer J, Nedachi M and Ohmoto H (2002) Tropical laterites, life on land, and the history of atmospheric oxygen in the paleoproterozoic. *Geology* **30**, 491–494.

https://doi.org/10.1017/S1473550418000034 Published online by Cambridge University Press

Birgel D, Thiel V, Hinrichs K-U, Elvert M, Campbell KA, Reitner J, Farmer JD and Peckmann J (2006) Lipid biomarker patterns of methane-seep microbialites from the Mesozoic convergent margin of California. *Organic Geochemistry* **37**, 1289–1302.

Bliss LC and Gold WG (1999) Vascular plant reproduction, establishment, and growth and the effects of cryptogamic crusts within a polar desert ecosystem, Devon Island, N.W.T., Canada. *Canadian Journal of Botany* **77**, 623–636.

Boston PJ, Spilde MN, Northup DE, Melim LA, Soroka DS, Kleina LG, Lavoie KH, Hose LD, Mallory LM, Dahm CN, Crossey LJ and Schelble RT (2001) Cave biosignature suites: microbes, minerals, and Mars. *Astrobiology* **1**, 25–55.

Bowden SA and Parnell J (2007) Intracrystalline lipids within sulfates from the Haughton impact structure–implications for survival of lipids on Mars. *Icarus* **187**, 422–429.

Bunting BT and Christensen L (1978) Micromorphology of calcareous crusts from the Canadian high Arctic. *Geologiska Föreningen i Stockholm Förhandlingar* **100**, 361–367.

Campbell KA, Farmer JD and Des Marais D (2002) Ancient hydrocarbon seeps from the Mesozoic convergent margin of California: carbonate geochemistry, fluids and palaeoenvironments. *Geofluids* **2**, 63–94.

Canfora L, Vendramin E, Vittori Antisari L, Lo Papa G, Dazzi C, Benedetti A, Iavazzo P, Adamo P, Jungblut AD and Pinzari F (2016) Compartmentalization of gypsm and halite associated with cyanobacteria in saline soil crusts. *FEMS Microbiology Ecology* **92**(6), 1–13.

Clark I, Lauriol B, Marschner M, Sabourin N, Chauret Y and Desrochers A (2004) Endostromatolites from permafrost karst, Yukon, Canada: paleoclimatic proxies for the Holocene hypsithermal. *Canadian Journal of Earth Sciences* **41**, 387–399.

Cockell CS, Lee P, Schuerger AC, Hidalgo L, Jones JA and Stokes MD (2001) Microbiology and vegetation of micro-oases and polar desert, Haughton impact crater, Devon Island, Nunavut, Canada. *Arctic, Antarctic and Alpine Research* **33**, 306–318.

Cockell CS, Lee P, Osinski G, Horneck G and Broady P (2002) Impact- induced microbial endolithic habitats. *Meteoritics & Planetary Science* **37**, 1287–1298.

Cockell CS, Kennerley N, Lindstrom M, Watson J, Ragnarsdottir V, Sturkell E, ott S and Tindle AG (2007) Geomicrobiology of a weathering crust from an impact crater and a hypothesis for its formation. *Geomicrobiology Journal* **24**, 425–440.

Connon SA, Lester ED, Shafaat HS, Obenhuber DC and Ponce A (2007) Bacterial diversity in hyperarid Atacama Desert soils. *Journal of Geophysical Research*, **112**, G04S17, doi: 10.1029/2006JG000311.

Cooper CD and Mustard JF (2002) Spectroscopy of loose and cemented sulphate-bearing soils: implications for duricrust on Mars. *Icarus* **158**, 42–55.

Cushing GE, Titus TN, Wynne JJ and Christensen PR (2007) THEMIS observes possible cave skylights on Mars. *Geophysical Research Letters* **34**, L17201. doi: 10.1029/2007GL030709.

Dartnell LR, Desorgher L, Ward JM and Coates AJ (2007) Modeling the surface and subsurface martian radiation environment: implications for astrobiology. *Geophsical Research Letters* **34**, L02207.

Dickson LG (2000) Constraints on nitrogen fixation by cryptogamic crusts in a polar desert ecosystem, Devon Island, N.W.T., Canada. *Arctic, Antarctic and Alpine Research* **32**, 40–45.

DiGregorio BE (2002) Rock varnish as a habitat for extant life on Mars. In Hoover RB (ed) *Instruments, Methods and Missions for Astrobiology IV*. Califotrnia, USA: Proceedings SPIE, **4495**, 120–130.

Dorn RI and Deniro MJ (1985) Stable carbon isotope ratios of rock varnish organic matter: a new paleoenvironmental indicator. *Science* **227**, 1472–1474.

Dorn RI and Oberlander TM (1981) Microbial origin of desert varnish. *Science* **213**, 1245–1247.

Esposito A, Ahmed E, Ciccazzo S, Sikorski J, Overmann J, Holmström SJM and Brusetti L (2015) Comparison of rock varnish bacterial communities with surrounding non-varnished rock surfaces: taxon-specific analysis and morphological description. *Microbial Ecology* **70**(3), 741–750.

Farmer JD (2000) Hydrothermal systems: doorways to early biosphere evolution. *GSA Today* **10**, 1–9.

Farrand WH and Lane MD (2007) "Blebby" terrains and domes on the northern plains of Mars: evidence of ancient ice ages? *Lunar and Planetary Science* **XXXVIII**, abstract 1972.

Finstad K, Pfeiffer M, McNicol G, Barnes J, Demergasso C, Chong G and Amundson R (2016) Rates and geochemical processes of soil and salt crust formation in Salars of the Atacama Desert, Chile. *Geoderma* **284**, 57–72.

Forman SL and Miller GH (1984) Time-dependent soil morphologies and pedogenic processes on raised beaches, Bröggerhalvöya, Spitsbergen, Svalbard Archipelago. *Arctic and Alpine Research* **16**, 381–394.

Formisano V, Atreya S, Encrenaz T, Ignatiev N and Giuranna M (2004) Detection of methane in the atmosphere of Mars. *Science* **306**, 1758–1761.

Gellert R, Rieder R, Anderson RC, Brückner J, Clark BC, Dreibus G, Economou T, Klingelhöfer G, Lugmair GW, Ming DW, Squyres SW, d'Uston C, Wänke H, Yen A and Zipfel J (2004) Chemistry of rocks and soils in Gusev Crater from the Alpha Particle X-ray spectrometer. *Science* **305**(5685), 829–832.

Grotzinger JP and Rothman DH (1996) An abiotic model for stromatolites morphogenesis. *Nature* **383**, 423–425.

Grotzinger JP, Arvidson RE, Bell JF III, Calvin W, Clark BC, Fike DA, Golombek M, Greeley R, Haldemann A, Herkenhoff KE, Jolliff BL, Knoll AH, Malin M, McLennan SM, Parker T, Soderblom L, Sohl-Dickstein JN, Squyres SW, Tosca NJ and Watters WA (2005) Stratigraphy and sedimentology of a dry to wet eolian depositional system, burns formation, Meridiani Planum, Mars. *Earth and Planetary Science Letters*, **240**, 11–72.

Guinness EA and Arvidson RE (1989). Viking optical and thermal evidence for widespread duricrust substrate on Mars. Lunar and Planetary Science Conference, XX, 367-368.

Guo L and Riding R (1994) Origin and diagenesis of Quaternary travertine shrub fabrics, Rapolano Terme, central Italy. *Sedimentology* **41**, 499–520.

Harwood JL and Russell NJ (1984) *Lipids in Plants and Microbes*. London: Allen & Uwin, 35–59.

Haskin LA, Wang A, Rockow KM, Jolliff BL, Korotev RL and Viskupic KM (1997) Raman spectroscopy for mineral identification and quantification for in situ planetary surface analysis: a point count method. *Journal of Geophysical Research* **102**(97), 19293–19306.

Hyneck BM (2004) Implications for hydrologic processes on Mars from extensive bedrock outcrops through Terra Meridiani. *Nature* **431**, 156–159.

Ionescu D, Lipski A, Altendorf K and Oren A (2007) Characterization of the endoevaporitic microbial communities in a hypersaline gypsum crust by fatty acid analysis. *Hydrobiologia* **576**, 15–26.

Jahnke LL, Embaye T, Hope J, Turk KA, van Zuilen M, Des Marais DJ, Farmer JD and Summons RE (2004) Lipid biomarker and carbon isotopic signatures for stromatolites-forming, microbial mat communities and *Phormidium* cultures from Yellowstone National Park. *Geobiology* **2**, 31–47.

Jehlička J, Edwards HGM and Oren A (2014) Raman Spectroscopy of Microbial Pigments. *Applied and Environmental Microbiology* **80**, 3286–3295.

Jolliff BL and McLennan SM and the Athena Science Team (2006) Evidence for water at Meridiani. *Elements* **2**, 163–167.

Kakegawa T and Nanri H (2006) Sulfur and carbon isotope analyses of 2.7 Ga stromatolites, cherts and sandstones in the Jeerinah Formation, Western Australia. *Precambrian Research* **148**, 115–124.

Kargel JS (2004) *Mars: A Warmer, Wetter Planet*. London: Springer, 557pp.

Kminek G and Bada JL (2006) The effect of ionizing radiation on the preservation of amino acids on Mars. *Earth and Planetary Science Letters* **245**, 1–5.

Knauth LP (2001) Isotopic biosignature in calcite formed during weathering of basalt: implications for past life on Mars, early life on Land, and ALH 84001. *Astrobiology* **1**, 363–364.

Knoll AH, Carr M, Clark B, Des Marais DJ, Farmer JD, Fischer WW, Grotzinger JP, McLennan SM, Malin M, Schröder C, Squyres S, Tosca NJ and Wdowiak T (2005) An astrobiological perspective on Meridiani Planum. *Earth and Planetary Science Letters* **240**, 179–189.

Komatsu G and Ori GG (2000) Exobiological implications of potential sedimentary deposits on Mars. *Planetary and Space Science* **48**, 1043–1052.

Krumbein WE and Giele C (1979) Calcification in a coccoid cyanobacterium associated with the formation of desert stromatolites. *Sedimentology* **26**, 593–604.

https://doi.org/10.1017/S1473550418000034 Published online by Cambridge University Press

Lauriol B and Clark I (1999) Fissure calcretes in the Arctic: a paleohydrologic indicator. *Applied Geochemistry* **14**, 775–785.

Lee P and Osinski GR (2005) The Haughton-Mars Project: overview of science investigations at the Haughton impact structure and surrounding terrains, and relevance to planetary studies. *Meteoritics and Planetary Science* **40**, 1755–1758.

Léveillé RJ (2007) Mars-like minerals in a cold, water-limited environment, Haughton Impact Crater, Devon Island. GAC NUNA Conference, The Pulse of the Earth & Planetary Evolution, Proceedings volume p.87.

Lim DSS and Douglas MSV (2003) Limnological characteristics of 22 lakes and ponds in the Haughton Crater region of Devon Island, Nunavut, Canadian High Arctic. *Arctic, Antarctic, and Alpine Research* **35**, 509–519.

Lin TJ, Ver Eecke HC, Breves EA, Dyar MD, Jamieson JW, Hannington MD, Dahle H, Bishop JL, Lane MD, Butterfield DA, Kelley DS, Lilley MD, Baross JA and Holden JF (2016) Linkages between mineralogy, fluid chemistry, and microbial communities within hydrothermal chimneys from the Endeavour Segment, Juan de Fuca Ridge. *Geochemistry, Geophysics, Geosystems* **17**(2), 300–323.

Luo W and Howard AD (2008) Computer simulation of the role of groundwater seepage in forming Martian valley networks. *Journal of Geophysical Research* **113**, E05002. doi: 10.1029/2007JE002981.

Mancinelli RL, Fahlen TF, Landheim R and Klovstad MR (2004) Brines and evaporites: analogs for martian life. *Advances in Space Research* **33**, 1244–1246.

Mangold N (2011) *Water ice Sublimation-Related Landforms on Mars*, vol. **356**. London: Geological Society, Special Publications, pp. 133–149.

Melezhik VA and Fallick AE (2001) Palaeoproterozoic travertines of volcanic affiliation from a ^{13}C-rich rift lake environment. *Chemical Geology* **173**, 293–312.

Mellon MT, Jakosky BM, Kieffer HH and Christensen PR (2000) High-resolution thermal inertia mapping from the Mars Global Surveyor Thermal Emission Spectrometer. *Icarus* **148**, 437–455.

Moore HJ, Bickler DB, Crisp JA, Eisen HJ, Gensler JA, Haldemann AFC, Matijevic JR, Reid LK and Pavlics F (1999) Soil-like deposits observed by Sojourner, the Pathfinder rover. *Journal of Geophysical Research* **104**, 8729–8746.

Nagy B, Nagy LA, Rigali MJ and Jones WD (1991) Rock varnish in the Sonoran Desert: microbiologically mediated accumulation of manganiferous sediments. *Sedimentology* **38**, 1153–1171.

Northup DE, Dahm CN, Melim LA, Spilde MN, Crossey LJ, Lavoie KH, Mallory LM, Boston PJ, Cunningham KI and Barns SM (2000) Evidence for geomicrobiological interactions in Guadalupe caves. *Journal of Cave and Karst Studies* **62**, 80–90.

Osinski GR, Lee P, Spray JG, Parnell J, Lim DSS, Bunch TE, Cockell CS and Glass B (2005) Geological overview and cratering model for the Haughton impact structure, Devon Island, Canadian High Arctic. *Meteoritics and Planetary Science* **40**, 1759–1776.

Pancost RD, Pressley S, Coleman JM, Benning LG and Mountain BW (2005) Lipid biomolecules in silica sinters: indicators of microbial biodiversity. *Environmental Microbiology*, **7**, 66–77.

Parnell J and Baron M (2004) The preservation of fluid inclusions in diverse surface precipitates: the potential for sampling palaeo-water from surface deposits on Mars. *International Journal of Astrobiology* **3**, 21–30.

Parnell J., Bowden S.A., Cockell C.S., Osinski G.R. and Lee P. 2006. Surface mineral crusts: a priority target in search for life on Mars. *Lunar and Planetary Science* **XXXVII**, abstract 1049.

Parnell J, Lee P, Cockell C and Osinski G (2004) Microbial colonization in impact-generated hydrothermal sulphate deposits, Haughton impact structure, and implications for sulphates on Mars. *International Journal of Astrobiology* **3**, 247–256.

Paulsen DE, Li H-C and Ku T-L (2003) Climate variability in central China over the last 1270 years revealed by high-resolution stalagmite records. *Quaternary Science Reviews* **22**, 691–701.

Pellerin A, Lacelle D, Fortin D, Clark ID and Lauriol B (2009) Microbial diversity in endostromatolites (cf. Fissure calcretes) and in the surrounding permafrost landscape, Haughton impact structure region, Devon Island, Canada. *Astrobiology* **9**, 807–822.

Pentecost A (1990) The formation of travertine shrubs: Mammoth Hot Springs, Wyoming. *Geological Magazine* **127**, 159–168.

Perry RS and Adams JB (1978) Desert varnish: evidence for cyclic deposition of manganese. *Nature* **276**, 489–491.

Perry RS and Sephton MA (2006) Desert varnish: an environmental recorder for Mars. *Astronomy & Geophysics* **47**, 4.34–4.35.

Perry RS, Engel MH, Botta O and Staley JT (2003) Amino acid analyses of desert varnish from the Sonoran and Mojave deserts. *Geomicrobiology Journal* **20**, 427–438.

Perry RS, Lynne BY, Sephton MA, Kolb VM, Perry CC and Staley JT (2006) Baking black opal in the desert sun: the importance of silica in desert varnish. *Geology* **34**, 537–540.

Riding R and Awramik SM (2000) *Microbial Sediments*. New York: Springer.

Robertson PB and Sweeney JF (1983) Haughton impact structure; structural and morphological aspects. *Canadian Journal of Earth Sciences* **20**, 1134–1151.

Robinson SA, Andrews JA, Hesselbo SP, Radley JD, Dennis PF, Harding IC and Allen P (2002) Atmospheric pCO_2 and depositional environment from stable-isotope geochemistry of calcrete nodules (Barremian, Lower Cretaceous, Wealden Beds, England). *Journal of the Geological Society, London* **159**, 215–224.

Schulze-Makuch D, Dohm JM, Fan C, Fairén AG, Rodriguez JAP, Baker VR and Fink W (2007) Exploration of hydrothermal targets on Mars. *Icarus* **189**, 308–324.

Sherlock SC, Kelley SP, Parnell J, Green P, Lee P, Osinski GR and Cockell CS (2005) Re-evaluating the age of the Haughton impact event. *Meteoritics and Planetary Science* **40**, 1777–1787.

Squyres AH and Knoll AH (2005) Sedimentary rocks at Meridiani Planum: origins, diagenesis and implications for life on Mars. *Earth and Planetary Science Letters* **240**, 1–10.

Squyres SW, Grotzinger JP, Arvidson RE, Bell JF III, Calvin W, Christensen PR, Clark BC, Crisp JA, Farrand WH, Herkenhoff KE, Johnson JRKlingelhöfer G, Knoll AH, McLennan SM, McSween HY Jr, Morris RV, Rice JW Jr, Rieder R and Soderblom LA 2004. In situ evidence for an ancient aqueous environment at Meridiani Planum, Mars. *Science*, **306**(5702), 1709–1714.

Stradling DA, Thygerson T, Walker JA, Smith BN, Hansen LD, Criddle RS and Pendleton RL (2002) Cryptogamic crust metabolism in response to temperature, water vapour, and liquid water. *Thermochimica Acta* **394**, 219–225.

Swett K (1974) Calcrete crusts in an Arctic permafrost environment. *American Journal of Science* **274**, 1059–1063.

Tehei M, Franzetti B, Maurel N-C, Vergne J, Hountondji C and Zaccai G (2002) The search for traces of life: the protective effect of salt on biological macromolecules. *Extremophiles* **6**, 427–430.

Thiel V, Peckmann J, Seifert R, Wehrung P, Reitner J and Michaelis W (1999) Highly isotopically depleted isoprenoids: molecular markers for ancient methane venting. *Geochimica et Cosmochimica Acta* **63**, 3959–3966.

Tokano T (2005) *Water on Mars and Life*. Berlin: Springer, 331pp.

Verrecchia EP, Freytet P, Verrecchia KE and Dumont JL (1995) Spherulites in calcrete laminar crusts: biogenic $CaCO_3$ precipitation as a major contributor to crust formation. *Journal of Sedimentary Research* **65**, 690–700.

Volkman JK, Johns RB, Gilian FT and Perry GJ (1980) Microbial lipids of an intertidal sediment. I. Fatty acids and hydrocarbons. *Geochimica et Cosmochimica Acta* **44**, 1133–1143.

Volkman JK, Barrett SM, Blackburn SI, Mansour MP, Sikes EL and Gelin F (1998) Microalgal biomarkers: a review of recent research developments. *Organic Geochemistry* **29**, 1163–1179.

Walter MR and Des Marais DJ (1993) Preservation of biological information in thermal spring deposits: developing a strategy for the search for fossil life on Mars. *Icarus* **101**, 129–143.

Wang A, Haskin LA and Cortez E (1998) Prototype Raman spectroscopic sensor for in situ mineral characterization on planetary surfaces. *Applied Spectroscopy* **52**(4), 477–487.

Watanabe Y, Martini JEJ and Ohmoto H (2000) Geochemical evidence for terrestrial ecosystems 2.6 billion years ago. *Nature* **408**, 574–578.

Westall F, Hofmann B and Brack A (2004) The search for life on mars using macroscopically visible microbial mats (stromatolites) in 3.5-3.3 Ga cherts

https://doi.org/10.1017/S1473550418000034 Published online by Cambridge University Press

from the Pilbara in Australia and Barberton in South Africa as analogues. *Lunar and Planetary Science* **XXXV**, abstract 1077.

Xie S, Yi Y, Huang J, Hu C, Cai Y, Collins M and Baker A (2003) Lipid distribution in a subtropical southern China stalagmite as a record of soil ecosystem response to paleoclimate change. *Quaternary Research* **60**, 340–347.

Zhang CL, Fouke BW, Bonheyo GT, Peacock AD, White DC, Huang Y and Romanek CS (2004) Lipid biomarkers and carbon-isotopes of modern travertine deposits (Yellowstone National Park, USA): implications for biogeochemical dynamics in hot-spring systems. *Geochimica et Cosmochimica Acta* **68**, 3157–3169.

https://doi.org/10.1017/S1473550418000034 Published online by Cambridge University Press