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The preservation of fluid inclusions in diverse surface precipitates: the potential for sampling palaeo-water from surface deposits on Mars

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Abstract: A wide range of surface deposits have been suggested as targets for the search for evidence of life on the surface of Mars. We show that duricrusts, biogenic lacustrine precipitates, hydrothermal and chemosynthetic precipitates, speleothems, travertines and evaporites all contain low-temperature fluid inclusions which represent surface/very-near-surface fluids. These fluid inclusions have good preservation potential. The recording of abundant inclusions in sulphate crusts is particularly important as they may be widespread on Mars. The inclusion fluids represent the surface waters from which the precipitates were deposited, so they may contain biomolecules from any ambient life in the surface environment. As problems of analytical sensitivity and contamination are overcome, such surface deposits have the potential to yield samples of Martian palaeo-water and any entrained biomolecules.

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Introduction

As the prospects for further analyses on the surface of Mars, and eventually for analysis of returned Martian samples, become more tangible, speculation about the possibility of finding evidence for life through these analyses is rife. Such speculation is fuelled by the continuing debate about the putative evidence for life in meteorite ALH84001 (McKay *et al*. 1996; Gibson *et al*. 1999). Evidence for life in the Martian rock record could include physical remains in the form of microfossils (Westall 1999), organic molecules that might be detected by chemical extraction (Cabane *et al.* 2001), or through biogenic response to non-destructive techniques such as Raman spectroscopy (Wynn-Williams & Edwards 2000) or time-of-flight secondary ion mass spectrometry (Brinckerhoff & Cornish 2000).

The most viable deposits in which to search for this evidence are those which were precipitated at or just beneath the planetary surface, where conditions suitable for life (by terrestrial analogy) probably pertained in the past. Most types of terrestrial surface deposit have been suggested as targets for the search for life on Mars, which is reasonable enough as microbes can colonize almost any substrate within normal terrestrial temperature ranges. The targets identified include lake deposits in general and evaporites in particular, algal deposits (stromatolites), cave deposits (speleothems), travertines, 'hot' spring deposits, 'cold' seep (chemosynthetic) deposits and duricrusts (see Fig. 1 and Table 1, including references).

The purpose of this paper is to show that the deposits of all of these terrestrial environments contain water in the form of fluid inclusions, and that the water survives within samples in the geological record. Therefore, if deposits of any one of them could be accessed on/from Mars, they should contain micro-samples of Martian water, susceptible to a range of analyses including the high-resolution detection of biomolecules, assuming that Mars possessed surface water in its earlier geological history.

The case for astrobiological exploration in surface deposits on Mars

A brief summary of the case for the occurrence of such deposits on Mars is given below.

Evaporites

An extensive literature on prospective evaporite deposits on Mars (see discussions in Forsythe & Zimbelman 1995; Ori *et al.* 2000), focused on palaeolacustrine environments, suggests that site selection should include these deposits (Rothschild 1990). Evidence for evaporites includes Martian albedo data (Cabrol & Grin 2001), their occurrence in meteorites of Martian origin (Bridges & Grady 2000b), morphological evidence for ponding of water (Forsythe & Zimbelman 1995) and direct observations at the Opportunity Mars Exploration Rover landing site. The occurrence of

Table 1. *Surface/near-surface environments suggested as targets for exploration for life on Mars*

Environment	Predominant minerals	Deposit style	References
Subaqueous/desiccating	halite, gypsum, epsomite	evaporites	Rothschild 1990
Subaqueous	carbonate (silica)	stromatolites	Westall *et al.* 2000
Flowing water	carbonate	travertine	Wynn-Williams *et al.* 2001
Hot spring (subaqueous or subaerial)	silica, carbonate	sinters	Farmer 2000
Cold seep (generally sea floor)	carbonate	chemosynthetic crusts	Barbieri *et al.* 2001
Cave	carbonate	speleothem crusts	Boston *et al.* 2001
Soil zone	carbonate, silica, gypsum	evaporative/algal duricrusts	Knauth 2001

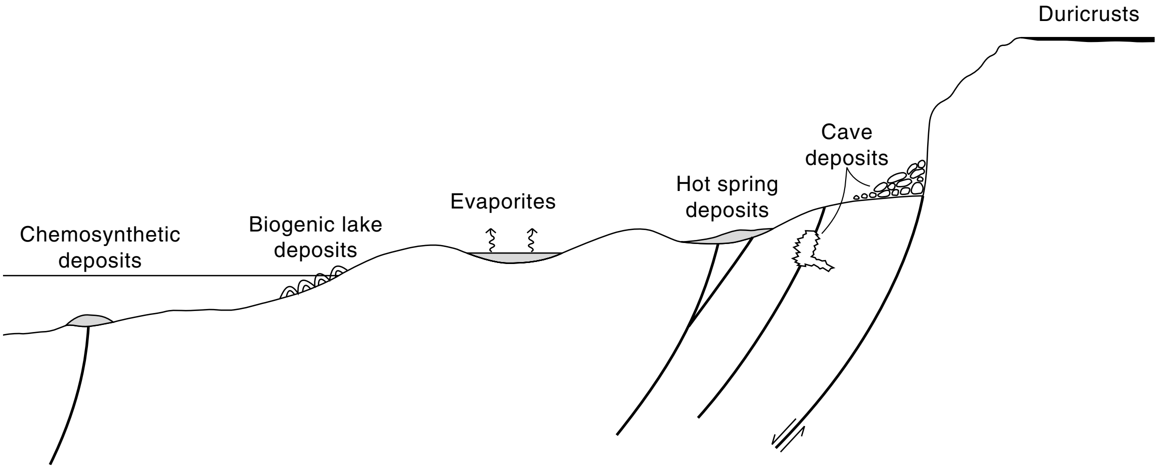

Fig. 1. The range of surface environments that astrobiologists have proposed should be targeted in the search for life on Mars. The schematic cross section shows scenarios in the vicinity of the fault-bound margin of a crater.

halophilic bacteria on Earth makes evaporites an attractive target in the search for life on Mars (Stan-Lotter *et al.* 2001).

Duricrusts

Evidence for cemented soil (duricrust) at the Viking lander sites, combined with geochemical data, suggests that the surface may contain sulphate-rich precipitates, most likely epsomite or gypsum, precipitated from concentrated brines (Jakosky & Christensen 1986; Clark 1998). Cid & Casanova (2001) recommend them as a priority for astrobiological exploration on Mars. Terrestrial duricrusts particularly involve calcrete (caliche): Knauth (2001) suggests that similar carbonate crusts could develop on basalt surfaces on Mars.

Biogenic lacustrine precipitates

Paleolake deposits in general are advocated as an astrobiological target (Doran *et al.* 1998). By analogy with the terrestrial record of life, simple microbial populations may have precipitated a mineral record with a distinctive and recognizable morphological character, like stromatolites (Westall *et al.* 2000). These precipitates would most likely be a feature of standing bodies of water or fluid seepage zones.

Hydrothermal precipitates

A particular type of fluid seepage is the hot spring, which is an attractive target on Mars as it represents a means of introducing liquid water to the planetary surface. Inhabitant primitive life could be thermophilic, and a record of life could be preserved in mineral precipitates from the cooling waters (Walter & Des Marais 1993; Farmer 2000).

Chemosynthetic precipitates

'Cold' seepages represent another type of seepage that may reach the surface, unrelated to hydrothermal activity, and they are also a prospective environment for primitive life. Chemosynthetic communities do not need photosynthesis or oxygen, drawing energy directly from compounds like methane that emerge at cold seepage sites. Terrestrial chemosynthetic communities precipitate distinctive carbonate crusts, which are also proposed as targets on Mars, where there is some morphological evidence for cold outgassing (Komatsu & Ori 2000; Barbieri *et al.* 2001).

Speleothems

A wide diversity of primitive life colonizes sub-surface void spaces ('caves'), a potential environment that offers protection from harmful radiation on the surface. Water in these spaces precipitates crusts (speleothems), which may entrap the ambient life (Boston *et al.* 2001), and which are therefore a plausible environment for exploration on Mars (Grin *et al.* 1998).

Travertines

Travertines are deposits from springs, rivers and lakes where degassing of carbon dioxide from waters enhances carbonate precipitation. The recognition of probable water seepage features on Mars suggests these may be sites for mineral precipitation where evidence for life should be sought (Wynn-Williams *et al.* 2001).

Inevitably, the types of deposit listed do not all constitute clearly distinct categories. Some deposits could be described differently using different nomenclatures (e.g. Pentecost & Viles 1994; Riding 2000). For example, duricrusts could be viewed as a type of evaporite, some duricrusts contain laminae precipitated by algae, some travertines might be described as hot spring deposits and hot spring deposits commonly incorporate algal deposits. The deposits examined in this paper are described according to existing local practice.

Fluid inclusions

Fluid inclusions are micrometre-scale volumes of ambient fluid, usually water, that are entrapped in minerals as the minerals grow. Entrapment occurs during mineral precipitation (primary inclusions) and during healing of microfracture post-precipitation (secondary inclusions). Their response to heating and cooling in the laboratory provides information on the temperature of entrapment and the chemistry of the fluid (see, e.g., Roedder 1984a; Shepherd *et al.* 1985; Goldstein & Reynolds 1994 for detailed methodologies). Prior to the 1980s, most studies of fluid inclusions were undertaken in ore deposits, where relatively large-sized (of the order of 10 μm) inclusions occur in quartz and other mineral veins. Subsequently, studies in sedimentary rocks became widespread, although the inclusions in sandstones are typically an order of magnitude smaller and therefore more difficult to detect and manipulate. Inclusions of this size have been detected in some meteorites (e.g. Zolensky *et al.* 1999; Bridges & Grady 2000a). At this scale most inclusions are detectable because they contain a vapour bubble at room temperature, which is a consequence of the reduction in pressure from entrapment to laboratory conditions and entry into P–T (pressure–temperature) space where vapour becomes stable. A few studies have detected fluid inclusions in surface precipitates, but these inclusions also tend to be very small and do not have the tell-tale vapour bubble, as they have not experienced a significant change in P–T conditions compared to those of entrapment. The detection of fluid inclusions in surface precipitates is therefore difficult without experience. Additionally, the most common objective of fluid inclusion studies is determination of the temperature of entrapment, which depends on heating to eliminate the vapour bubble (homogenization temperature), and as this is not possible in monophase (liquid only) inclusions in surface precipitates, they are not so extensively examined. However, we show here that liquid fluid inclusions do occur in all types of surface precipitate and are therefore a potential source of information in astrobiological exploration. Previous case studies that have reported inclusions entrapped during early diagenesis include those by Barker & Halley (1988), Johnson & Goldstein (1993), Benison & Goldstein (1999) and Dennis *et al.* (2001).

Fluid inclusions rarely comprise more than 0.5% by volume of a sample. Samples of white calcite or quartz contain of the order of 10^9 inclusions cm^{-3}, but as the inclusions average 1 μm in size the total fluid content is about 0.1 wt.% (Roedder 1984a).

Methodology

Samples were collected from terrestrial surface environments where mineral precipitates have formed in the recent past, and from the geological record where the context clearly shows that precipitates formed at the surface.

Samples were prepared as doubly-polished thick wafers and examined using a Linkam THM600 heating–freezing stage attached to an Olympus BH-2 petrographic microscope. Wafers were cooled and reheated to determine the temperature of final melting of ice within inclusions, which can be equated with fluid salinity, expressed as wt.% equivalent NaCl (Bodnar 1993).

Samples have been selected in which the predominant mineral phase, usually calcite or aragonite, is sufficiently coarsely crystalline to allow detection of fluid inclusions. As the wafers are 100 to 130 μm thick and optimum optical conditions require a minimum of crystal domain boundaries within the wafer, crystal domains of 200 μm or larger are preferred. This is readily achieved in most materials, but does exclude samples which are wholly or largely micritic (fine-grained). This does not mean that micritic samples do not contain micro-inclusions and can yield water, but they are not susceptible to observation of individual inclusions.

Carbonate precipitates were examined under cathodoluminescence using a Citl 8200 Mark 3 instrument operating at approximately 20 kV and 600 μA. The response under cathodoluminescence of early carbonate is very weak, whereas diagenetically recrystallized carbonates exhibit brighter luminescence and patterns of crystal distribution distinct from the primary depositional fabric (see, e.g., Walkden & Williams 1991).

Samples

Fluid inclusions are widely documented in evaporite minerals and sub-surface hydrothermal deposits (see below). The following samples of other deposit types were examined for inclusions.

Duricrusts

(1) The Eocene Bembridge Limestone, Isle of Wight, England, contains pedogenic horizons with laminar fabrics and root moulds (Armenteros *et al.* 1997). The root moulds are infilled with sparry calcite.

(2) Carboniferous calcrete in South Wales contains fibrous sparry calcite crystals believed to represent the primary growth fabric (Dixon & Wright 1983).

(3) The Eocene Hertfordshire Puddingstone of southern England is a conglomerate of pebbles cemented by chalcedony and quartz, interpreted as a silcrete (Summerfield & Goudie 1980).

(4) Miocene gypcretes (indurated gypsum soils) occur in the Calama Basin, northern Chile, where they are preserved from dissolution by an arid climate (Hartley & May 1998). The gypcretes cement surface detritus and include nodular and vein-form crystal growths.

Biogenic lacustrine precipitates

(5) White hydromagnesite deposits in Salda Lake, Turkey, are suggested as a possible analogue for the 'White Rock' in Sabaea Terra, Mars (Russell *et al.* 1999). The hydromagnesite includes biogenic mounds and is locally sparry.

(6) The Jurassic Purbeck Limestones, England, contain decimetre-scale stromatolitic bioherms (Pugh 1968). The stromatolites contain filament moulds infilled with sparry calcite. These rocks are lagoonal/marginal marine, but nevertheless represent a shallow water precipitate.

(7) The Devonian Stromness Group, Orkney Islands, Scotland, contains numerous lacustrine stromatolitic horizons. Some stromatolites contain diapiric fenestrae that appear to represent gas bubbles similar to those seen in living mats (Hoehler *et al.* 2001), probably from the decay of organic matter. The fenestrae are mineralized by sparry calcite (Parnell & Janaway 1990).

(8) A locality in the Devonian of northern Scotland exposes lake sediments that were exposed to develop a fissured surface which became colonized by filamentous microbes (Trewin & Knoll 1999). The filaments were preserved by early calcite mineralization.

Chemosynthetic precipitates

(9) Chemosynthetic carbonate crusts occur around methane seepages on the sea floor of the Vøring Plateau, offshore Norway. The crusts contain a bivalve-dominated fauna cemented by sparry aragonite (Mazzini *et al.* 2001).

(10) Chemosynthetic carbonate nodules occur in a palaeo-oil seepage on the Tertiary sea floor in Barbados, including a bivalve- and worm-rich assemblage (Parnell *et al.* 1994, 2002).

Speleothems

(11) Speleothem carbonates of Permian age occur in Oklahoma, where they are known to incorporate traces of oil from a contemporary seepage (Elmore *et al.* 1989).

(12) A modern speleothem occurs in a former limestone mine in the Carboniferous near Glasgow, Scotland (for the locality see Lawson & Lawson 1992). The deposit consists of laminated calcite containing microbial structures (G. Walkden, personal communication).

Travertines

(13) Recent laminar travertine has been precipitated in a stream bed in Gordale, England, and incorporates microbial colonies (Pentecost 1993).

(14) Recent algae-rich travertine has been precipitated by hot springs at BagnoVignoni, Italy (Pentecost 2001).

The literature on fluid inclusions in evaporites is very extensive (see Roedder 1984b for a review) and there is no requirement to prove that such inclusions occur. Several studies have undertaken quantitative inorganic analyses of the inclusion waters in halite samples from the geological record in order to reconstruct the evolution of seawater chemistry (Kovalevich *et al.* 1998; Timofeeff *et al.* 2001) and palaeoclimate data (Roberts & Spencer 1995; Benison & Goldstein 1999). Inclusions in halite are often abundant and can be large enough (of a millimetre scale) to allow extraction of the contents of an individual inclusion (Lazar & Holland 1988). Other evaporite minerals similarly contain inclusions. Evaporites are also of interest as it has been claimed that they host microbes that have survived entrapment, in inclusion fluids or the solid crystal, over a geological timescale (Norton & Grant 1988; Vreeland *et al.* 2000). Given the abundance of existing data on inclusions in evaporitic halite, we have chosen to examine gypsum in the form of gypcrete, classified as a duricrust above. Gypcretes are valuable analogues for Mars, where sulphate-rich duricrusts are inferred. On Earth they tend to be dissolved following burial beneath the water table, but on Mars would have long-term stability at the surface due to lack of water and subsidence.

Similarly, there is a substantial literature on fluid inclusions in hydrothermal deposits, particularly through studies of metalliferous mineralization. While fossil mineralizing systems mostly developed deep in the crust (at several kilometres depth), some were at shallow levels and even at the surface where they precipitated as sinters. The sinters typically yield fluid inclusion temperatures in the range 200–300 °C (e.g. Berger 1985; White *et al.* 1989). The hot spring precipitates classified as travertines above represent hydrothermal systems that emerged at the surface.

Data

Fluid salinities

Fluid inclusions were identified by optical examination in all of the samples (see Fig. 2 and Table 2). They are sufficiently large that their freezing behaviour could be measured and equated to fluid salinities, except in the case of chemosynthetic carbonates, where the presence of methane influences the freezing behaviour, and in the one case where only oil inclusions are present (see below). The salinities measured are mostly in the range 0–5 equiv. wt.% NaCl. These values are relatively low for fluids in sedimentary basins, which may be up to 25 equiv. wt.% NaCl (Goldstein & Reynolds 1994). This is not surprising as most surface environments are dominated by meteoric (surface) fluids of low salinity (although even seawater is only about 3 wt.% NaCl). The more saline samples (up to 14 equiv. wt.% NaCl) are from the magnesite and gypcrete deposits precipitated in arid environments, where the surface waters would be expected to be saline, and the Carboniferous calcrete, which is from an evaporite-bearing basin. Thus, the salinities measured appear to reflect their parent environments. Data from the two travertines were reported by Baron *et al.* (2003).

The aqueous inclusions are either exclusively monophase or are a mixture of monophase and two-phase with

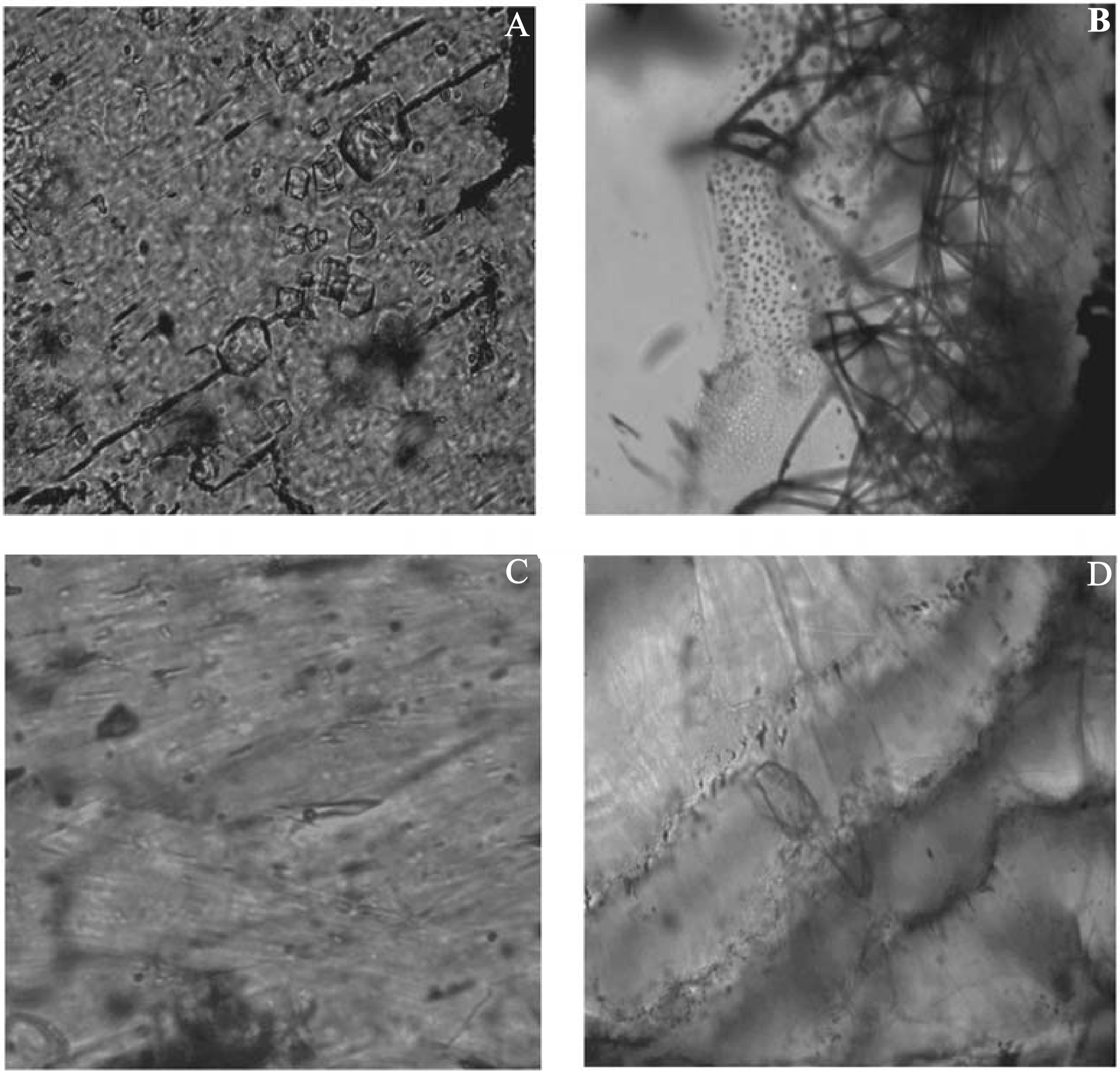

Fig. 2. Photomicrographs of surface precipitates containing: A, equidimensional monophase inclusions in gypsum, gypcrete, Miocene, Chile; B, a dense plane of inclusions in calcite containing microbial filaments, lacustrine low-stand crack-fill, Devonian, Scotland; C, single two-phase inclusion in aragonitic chemosynthetic crust, Recent, offshore Norway; D, parallel arrays of small inclusions marking growth zones in travertine calcite, Recent, England. Field widths: 190 μm. © courtesy of A. Mazzini.

varying amounts of vapour. The variable two-phase inclusions are assumed to represent trapping of air–water mixtures.

Oil inclusions

Oil inclusions occur in the samples from Oklahoma and the Orkney Islands. The Oklahoma speleothem contains a population of aqueous inclusions and two populations of hydrocarbon inclusions distinguished by their fluorescent colour under ultraviolet light. The aqueous inclusions are monophase or two-phase but clearly stretched (see below). Yellow-fluorescing hydrocarbon inclusions occur in both primary and secondary settings and they are both monophase and two-phase. Blue-white fluorescing hydrocarbon inclusions are secondary and two-phase. As a general rule, blue-white fluorescence reflects a greater maturity than yellow fluorescence (Bodnar 1990). Our interpretation of these observations is that the aqueous inclusions and some yellow-fluorescing oil inclusions represent the fluids in the depositional environment, which is consistent with the model of precipitation in the vicinity of an oil seep (Elmore *et al.* 1989). Further yellow-fluorescing oils and the blue-white fluorescing oils reflect continued oil migration after precipitation of the speleothem.

Table 2. *Primary inclusion fluids determined in surface precipitates*

Environment	Provenance (locality, age)	Inclusion size (µm)	Salinity (equiv. wt.% NaCl)	Other populations
Duricrusts				
1. Calcrete	Tertiary, England	3–6	0–2	none
2. Calcrete	Carboniferous, Wales	2–4	6–14	abundant secondary
3. Silcrete	Tertiary, England	2–5	0–5	abundant secondary
4. Gypcrete	Miocene, Chile	2–10	10–13	none
Lake/Sabkha				
5. Magnesite	Recent, Turkey	2–3	4–9	none
6. Stromatolite	Jurassic, England	2–10	0–3	rare secondary
7. Stromatolite	Devonian, Scotland	2–5	(organic)	abundant secondary
8. Low-stand crack-fill	Devonian, Scotland	2–5	2–5	rare secondary
Chemosynthetics				
9. Seafloor crust	Recent, Norway	2–6	(methanic)	none
10. Seafloor crust	Tertiary, Barbados	2–6	(methanic)	none
		2–13	(organic)	
Speleothem				
11. Cave carbonate	Recent, Milngavie	4–15	0–0.4	none
12. Cave carbonate	Permian, Oklahoma	2–6	1–5	abundant secondary
		2–40	(organic)	
Travertine				
13. Stream carbonate	Recent, England	2–4	0–3	none
14. Hot spring carbonate	Recent, Italy	2–3	0–3	none

The fenestrae in the Devonian stromatolite contain only liquid hydrocarbon inclusions. As the host is a kerogen-rich rock, in a succession that has entered the oil window (Parnell 1985), this fluid record is not surprising but is clearly related to deep burial rather than the original, shallow mineralization of the fenestrae. The homogenization temperatures for the hydrocarbon inclusions are in the range 50–80 °C. Very few aqueous inclusions were observed. The calcite exhibits a more pronounced fluorescence than the other samples, which is consistent with precipitation during deep burial. In this case, although the original fluid record has not been preserved, the study nonetheless shows that the deposit type is capable of yielding a fluid record.

Water in skeletal carbonates

For completion it should be noted that skeletal carbonates (corals, mollusc shells, echinoderm tests, etc.) contain water in fluid inclusions, up to 3 wt.% (Gaffey 1988; Gaffey *et al.* 1995). Although we do not expect to find such advanced bioclasts on Mars, this does emphasize the potential of surficial carbonates to preserve significant amounts of water. Two particular points are evident from studies of the water in skeletal carbonates. Firstly, when the primary aragonite or high-magnesium calcite is altered during diagenesis, the volume of included water may be substantially decreased (Gaffey 1988). Secondly, the water in the skeletons is a metabolic fluid, so does not represent the ambient environment (Lecuyer & O'Neil 1994). However, during diagenetic alteration, new inclusions may be trapped which do consist of ambient pore water.

Discussion

The preservation of early fluids

The conclusion that early, depositional or shortly post-depositional fluids are preserved in samples from the geological record is the fundamental basis of this account. There are several reasons to believe that this conclusion is justified.

(i) They are consistently monophase inclusions, characteristic of inclusions trapped at temperatures less than about 50 °C. Where samples from the geological record have experienced burial to more than 2 km, later, deeper fluids would have left consistently two-phase inclusions.

(ii) In five of our cases, later fluid populations are recorded in the same samples as the early fluids in cross-cutting secondary planes, but have not displaced the early fluids from their inclusions.

(iii) In most cases, the host mineral is carbonate, which can be shown petrographically to be an early precipitate. All of the carbonate samples used in this study were examined under cathodoluminescence. Excepting the Devonian stromatolites, the samples exhibit very low luminescence, indicating a lack of recrystallization.

Those samples which are from modern surface environments obviously contain a record of the ambient surface fluid in the inclusions.

Although the carbonates used in this study do not exhibit evidence of recrystallization, many carbonates in the geological record do show such evidence (Walkden & Williams 1991), and therefore are likely to contain a mixture of included fluids from the depositional environment and one or more later diagenetic events. Any interpretation of the composition of fluids extracted from bulk samples would be complex, and it is clearly preferable to select samples for this kind of analysis whose petrography indicates a lack of alteration. In a similar manner, evaporites are particularly prone to dissolution–reprecipitation, recrystallization and mineral transformation (e.g. gypsum to anhydrite), but careful petrography and identification of inclusions along crystal growth zones can confirm the primary origin of inclusions (Rosenzweig *et al.* 2000). As stated, fluid inclusions in surficial and early diagenetic precipitates are normally monophase liquid, which is interpreted to represent entrapment at temperatures below 50 °C (Goldstein & Reynolds 1994). However, two-phase inclusions are commonly encountered in these precipitates, due to heterogeneous trapping of an air–water mixture, necking down (alteration of shape) during inclusion entrapment (Goldstein 1986), the exsolution of gas from water (Barker & Halley 1988), re-equilibration by burial heating (Bodnar & Bethke 1984), heating during sample preparation and fluid leakage (Schwartz *et al.* 1976). The homogenization temperatures determined from such two-phase inclusions would yield misleading information, but the salinity measurements from their cooling behaviour are unaffected. In the present study, we have observed and measured monophase inclusions in almost all of the precipitates examined. Those samples that contain populations of consistently two-phase inclusions can reasonably be inferred to have incorporated them during burial to temperatures above 50 °C. Furthermore, the main premise of this paper, that the precipitates hold a fluid record which could be extracted to obtain chemical data, is unaffected by these modifications.

Some samples from the geological record only yield an inclusion record representative of deep burial. However, in the context of planetary exploration, obtaining any fluid record would be invaluable, and it is encouraging that the majority of samples of surface precipitate examined in this study have yielded such a record.

Application to Mars

Surface precipitates are the proposed targets of several strategies in the search for life on Mars (Table 1). The observations of layered deposits (Malin & Edgett 2000b) and surface seepage sites (Malin & Edgett 2000a) give us confidence that there is a realistic chance of encountering such precipitates. Morphological evidence will be supported by planetary spectroscopic techniques capable of detecting hydrothermal deposits, carbonates and evaporites (Swayze *et al.* 1999). Of the various types of deposit discussed, hydrothermal deposits and evaporites may be the most widespread on Mars (Farmer & Des Marais 1999). This is fortuitous, as deposits from these environments on Earth readily incorporate microbial remains (Schultze-Lam *et al.* 1995; McGenity *et al.* 2000).

Evaporitic deposits include evaporite-cemented soils: As the surface detritus at both the Viking and Pathfinder landing sites is probably sulphate-cemented (Jakosky & Christensen 1986; Cid & Casanova 2001), this type of precipitate should offer readily accessible samples. In fact spectroscopic data suggest that sulphate-rich crusts are widespread on Mars (Cooper & Mustard 2002), making our record of water inclusions in gypcrete crusts particularly significant. The occurrence of aqueous fluid inclusions in evaporite minerals in meteorites (e.g. Bodnar & Zolensky 2000; Bridges & Grady 2000a), including those whose ages imply preservation since early in the history of the solar system (Zolensky *et al.* 1999; Whitby *et al.* 2000), also offers encouraging support for the possibility of accessing inclusion water samples on Mars.

Hydrothermal deposits should be more localized, but as hydrothermal activity is a predictable consequence of impact events (Newsom *et al.* 2001), they may nevertheless be widespread on Mars. Hydrothermal deposits should also be sought in regions of inferred magmatic activity (Gulick 1998), where heating of subsurface water/ice could have opened up subterranean fluid conduits and vent systems suitable for colonization by primitive life.

Potential preservation of biomolecules

Having shown that early fluids can be preserved in surface crusts, it would be very valuable to show that the chemical record that they contain includes biomolecules. This is desirable both for improving our knowledge of biological evolution on Earth and in the search for a record of life on Mars. On Earth, encouragement stems from the very-long-term survivability of biomolecules in some cases (e.g. Brocks *et al.* 1999), the preservation of biomolecules within hydrothermal sinters in particular (Guidry *et al.* 2000), the possible preservation of microbes within evaporites in the geological record (McGenity *et al.* 2000; Vreeland *et al.* 2000), the nucleation of many carbonate crusts upon biological templates (Riding 2000) and the preservation of organic breakdown products within diagenetic mineral precipitates (Banfield & Nealson 1997).

All surface waters on Earth should contain trace concentrations of biomolecules, produced by the metabolism or degradation of the ambient life inhabiting those waters. The most abundant classes of organic compound in natural waters are carbohydrates, amino acids and other organic acids, all products of biological activity (Thurman 1985). The ubiquity of biomolecular material in surface waters is exemplified by the flux of microorganisms from water surfaces into the atmosphere and their subsequent precipitation from aerosols in meteoric waters (Weber *et al.* 1983; Blanchard 1989).

Detection of biomolecules

The methodology for identification of biomolecules will be dominated by the need to detect extremely low concentrations, with the associated problem of eliminating contamination. The absolute concentration of biomolecules could be higher in deposit types which contain a relative abundance of inclusions, such as evaporites (Roedder 1984b) and speleothem carbonates (Dennis *et al.* 2001). We will discuss potential technology for extraction of the inclusion fluids and delivery to an analytical system elsewhere, but it is likely to involve a mechanical crushing system and a microfluidic handling and analytical system. Crushing of speleothem crusts to release inclusion fluids for isotopic analysis is a well-established procedure (Schwartz *et al.* 1976; Dennis *et al.* 2001) and shows that the general goal of extracting fluids from surface precipitates is a viable one though application to Mars presents a number of technological challenges. Upon liberation of the inclusion fluids, they could be analysed using a number of approaches advocated for the sensitive determination of organic compounds on Mars, including gas chromatography–mass spectrometry (Cabane *et al.* 2001), liquid chromatography, immunoassay (Steele *et al.* 2001), electrospray ionization high-resolution ion mobility spectrometry (Beegle *et al.* 2001) or polymeric sensors (Cullen *et al.* 2001). However, given the limited quantities of fluid involved, it may be advantageous to incorporate the analytical process within a microfluidic handling system. Such a procedure has been designed for surface-enhanced resonance Raman spectroscopy (Keir *et al.* 2002), with the prospect of detecting femtomoles of organic compounds from picolitres of fluid. This kind of technology, undertaken on a 'lab-on-a-chip', is ideally suited to the need for miniaturization of instrumentation on Mars. However, before application to Mars, analyses will be undertaken on terrestrial material, where laboratory-scale instrument configuration is possible. In fact, the search for biomolecular data from inclusions within surface deposits of the Archean and Proterozoic age should itself yield exciting data. Also, the analysis of metabolic water trapped in fluid inclusions in skeletal carbonates on Earth should offer valuable information to palaeobiologists, especially in rare examples where the primary mineralogy has survived alteration for a long period back into the geological record. In addition to samples from the geological record, analytical development may make use of model crystals grown in the laboratory to incorporate organic compounds and/or microbes that can act as standards to test resolution of measurements and comparison of techniques (Wilkins *et al.* 2003).

Conclusions

The examination of the fluid inclusion record in precipitates from a range of surface environments shows that:

(i) low-temperature inclusions occur consistently within the precipitates;

(ii) the inclusions are well-preserved and thus contain a record of the ambient fluid of the precipitating environment;

(iii) inclusions are preserved in several precipitates which also contain microbial remains or other evidence of life; the entrained fluids may contain biomolecules derived from this biological activity.

This offers encouragement to the development of a strategy to use surface precipitates as a source of data on the composition of surface waters in the geological record on both Earth and Mars.

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References

Armenteros, I., Daley, B. & Garcia, E. (1997). Lacustrine and palustrine facies in the Bembridge Limestone (late Eocene, Hampshire Basin) of the Isle of Wight, southern England. *Palaeogeog. Palaeoclimatol. Palaeoecol.* **128**, 111–132.

Banfield, J. & Nealson, K. (1997). Geomicrobiology: interactions between microbes and minerals. In *Reviews in Mineralogy*, vol. 35. Mineralogical Society of America, Washington.

Barbieri, R., Ori, G.G. & Taviani, M. (2001). Phanerozoic submarine cold vent biota and its exobiological potential. In *Proc. First European Workshop on Exo-/Astro-Biology, ESA Spec. Publ.*, vol. 496, pp. 295–298. European Space Agency, Noordwijk.

Barker, C.E. & Halley, R.B. (1988). Fluid inclusions in vadose cement with consistent vapor to liquid ratios, Pleistocene Miami Limestone, southeastern Florida. *Geochim. Cosmochim. Acta* **52**, 1019–1025.

Baron, M., Pentecost, A. & Parnell, J. (2003). Hot and cold spring deposits as a source of palaeo-fluid samples on Mars. *Lunar Planet. Sci.* **XXXIV**, 1184.

Beegle, L.W., Kanik, I., Matz, L. & Hill, H.H. (2001). Electrospray ionization high-resolution ion mobility spectrometry for the detection of organic compounds, 1. *Amino Acids. Anal. Chem.* **73**, 3028–3034.

Benison, K.C. & Goldstein, R.H. (1999). Permian paleoclimate data from fluid inclusions in halite. *Chem. Geol.* **154**, 113–132.

Berger, B.R. (1985). Geologic-geochemical features of hot-spring precious-metal deposits. *Bull. U.S. Geol. Surv.* **1646**, 47–53.

Blanchard, D.C. (1989). The ejection of drops from the sea and their enrichment with bacteria and other materials: a review. *Estuaries* **12**, 127–137.

Bodnar, R.J. (1990). Petroleum migration in the Miocene Monterey Formation, California, USA: constraints from fluid-inclusion studies. *Mineralog. Mag.* **54**, 295–304.

Bodnar, R.J. (1993). Revised equation and table for determining the freezing point depression of H_2O-NaCl solutions. *Geochim. Cosmochim. Acta* **57**, 683–684.

Bodnar, R.J. & Bethke, P.M. (1984). Systematics of stretching of fluid inclusions. I: fluorite and sphalerite at 1 atmosphere confining pressure. *Econ. Geol.* **79**, 141–161.

Bodnar, R.J. & Zolensky, M.E. (2000). Fluid inclusions in meteorites: are they useful and why are they so hard to find? *Meteor. Planet Sci.* **35**, A29.

Boston, P.J. *et al.* (2001). Cave biosignature suites: microbes, minerals, and Mars. *Astrobiology* **1**, 25–55.

Bridges, J.C. & Grady, M.M. (2000a). Petrography and fluid inclusion studies of Zag. *Meteor. Plan. Sci.* **35**, A33.

Bridges, J.C. & Grady, M.M. (2000b). Evaporite mineral assemblages in the nakhlite (martian) meteorites. *Earth Planet. Sci. Lett.* **176**, 267–279.

Brinckerhoff, W.B. & Cornish, T.J. (2000). Elemental, isotopic and organic analysis on Mars with laser TOF-MS. *Concepts and Approaches for Mars Exploration*, abstract 6027. Lunar and Planetary Institute, Houston.

Brocks, J.J., Logan, G.A., Buick, R. & Summons, R.E. (1999). Archean molecular fossils and the early rise of eukaryotes. *Science* **285**, 1033–1036.

Cabane, M. *et al.* (2001). In situ inorganic and organic analysis (Pyr/CD-GC/MS) of the Martian soil, on the Mars 2005 mission. *Planet. Space Sci.* **49**, 523–531.

Cabrol, N.A. & Grin, E.A. (2001). The evolution of lacustrine environments on Mars: is Mars only hydrologically dormant? *Icarus* **149**, 291–328.

Cid, A. & Casanova, I. (2001). Sulphates in Martian soils: a clear exobiological target. In *Proc. First European Workshop on Exo-/Astro-Biology*, ESA SP-496, pp. 201–202. European Space Agency, Noordwijk.

Clark, B.C. (1998). Surviving the limits to life at the surface of Mars. *J. Geophys. Res.* **103**, 28 545–28 555.

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

Cullen, D.C., Grant, W.D., Piletsky, S. & Sims, M.R. (2001). Proposed biomimetic molecular sensor array for astrobiology applications. In *Proc. First European Workshop on Exo-/Astro-Biology*, ESA SP-496, pp. 329–332. European Space Agency, Noordwijk.

Dennis, P.F., Rowe, P.J. & Atkinson, T.C. (2001). The recovery and isotopic measurement of water from fluid inclusions in speleothems. *Geochim. Cosmochim. Acta* **65**, 871–884.

Dixon, J. & Wright, V.P. (1983). Burial diagenesis and crystal diminution: the origin of crystal diminution in some limestones from South Wales. *Sedimentology* **30**, 537–546.

Doran, P.T., Wharton, R.A., Des Marais, D.J. & McKay, C.P. (1998). Antarctic paleolake sediments and the search for extinct life. *J. Geophys. Res.* **103**, 28 481–28 493.

Elmore, R.D., McCollum, R. & Engel, M.H. (1989). Evidence for a relationship between hydrocarbon migration and diagenetic magnetic minerals: implications for petroleum exploration. *Bull. Assoc. Petrol. Geochem. Explor.* **5**, 1–17.

Farmer, J.D. (2000). Hydrothermal systems: doorways to early biosphere evolution. *GSA Today* **10**(**7**), 1–9.

Farmer, J.D. & Des Marais, D.J. (1999). Exploring for a record of ancient Martian life. *J. Geophys. Res.* **104**, 26 977–26 995.

Forsythe, R.D. & Zimbelman, J.R. (1995). A case for ancient evaporites on Mars. *J. Geophys. Res.* **100**, 5553–5563.

Gaffey, S.J. (1988). Water in skeletal carbonates. *J. Sed. Petrol.* **58**, 397–414.

Gaffey, S.J., Zabielski, V.P. & Bronnimann, C. (1995). Roles of organics and water in preneomorphic and early neomorphic alteration of coralline aragonites from San Salvador Island, Bahamas. *Geol. Soc. Amer. Spec. Paper* **300**, 233–250.

Gibson, E.K., McKay, D.S., Thomas-Keprta, K., Westall, F. & Romanek, C.A. (1999). It's dead Jim. But was it ever alive? *Ad Astra* **11**(**1**), 1–5.

Goldstein, R.H. (1986). Reequilibration of fluid inclusions in low-temperature calcium-carbonate cement. *Geology* **14**, 792–795.

Goldstein, R.H. & Reynolds, T.J. (1994). *Systematics of Fluid Inclusions in Diagenetic Minerals, SEPM Short Course*, No. 31. SEPM, Tulsa.

Grin, E.A., Cabrol, N.A. & McKay, C.P. (1998). Caves in the Martian regolith and their significance for exobiology exploration. *Lunar Planet. Sci.* **XXIX**, abstract 1012.

Guidry, S.A., Chafetz, H.S., Steele, A. & Toporski, J.K.W. (2000). A preliminary ToF-SIMS assessment of preservation potential of organic biomarkers in modern siliceous sinter and core, Yellowstone National Park, Wyoming. *Lunar Planet. Sci.* **XXXI**, abstract 1100.

Gulick, V.C. (1998). Magmatic intrusions and a hydrothermal origin for fluvial valleys on Mars. *J. Geophys. Res.* **103**, 19 365–19 388.

Hartley, A.J. & May, G. (1998). Miocene gypcretes from the Calama Basin, northern Chile. *Sedimentology* **45**, 351–364.

Hoehler, T.M., Bebout, B.M. & Des Marais, D.J. (2001). The role of microbial mats in the production of reduced gases on the early Earth. *Nature* **412**, 324–327.

Jakosky, B.M. & Christensen, P.R. (1986). Global duricrust on Mars: analysis of remote-sensing data. *J. Geophys. Res.* **91**, 3547–3559.

Johnson, W.J. & Goldstein, R.H. (1993). Cambrian sea water preserved as inclusions in marine low-magnesium calcite cement. *Nature* **362**, 335–337.

Keir, R., Igata, E., Arundell, M., Smith, W.E., Graham, D., McHugh, C. & Cooper, J.M. (2002). SERRS. In situ substrate formation and improved detection using microfluidics. *Anal. Chem.* **74**, 1503–1508.

Knauth, L.P. (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.

Komatsu, G. & Ori, G.G. (2000). Exobiological implications of potential sedimentary deposits on Mars. *Planet. Space Sci.* **48**, 1043–1052.

Kovalevich, V.M., Peryt, T.M. & Petrichenko, O.I. (1998). Secular variation in seawater chemistry during the Phanerozoic as indicated by brine inclusions in halite. *J. Geol.* **106**, 695–712.

Lawson, J. & Lawson, J.D. (1992). Baldernock and Blairskaith. In *Geological Excursions around Glasgow and Girvan*, eds Lawson, J.D. & Weedon, D.S., pp. 77–82. Geological Society of Glasgow, Glasgow.

Lazar, B. & Holland, H.D. (1988). The analysis of fluid inclusions in halite. *Geochim. Cosmochim. Acta* **52**, 485–490.

Lecuyer, C. & O'Neil, J.R. (1994). Stable isotope compositions of fluid inclusions in biogenic carbonates. *Geochim. Cosmochim. Acta* **58**, 353–363.

McGenity, T.J., Gemmell, R.T., Grant, W.D. & Stan-Lotter, H. (2000). Origins of halophilic microorganisms in ancient salt deposits. *Environ. Microbiol.* **2**, 243–250.

McKay, D.S. *et al.* (1996). Search for past life on Mars: possible relic biogenic activity in Martian meteorite ALH84001. *Science* **273**, 924–930.

Malin, M.C. & Edgett, K.S. (2000a). Evidence for recent groundwater seepage and surface runoff on Mars. *Science* **288**, 2330–2335.

Malin, M.C. & Edgett, K.S. (2000b). Sedimentary rocks of early Mars. *Science* **290**, 1927–1937.

Mazzini, A., Belenkaya, I., Parnell, J., Cronin, B. & Chen, H. (2001). Evidence for modern and ancient fluid flow in the seafloor crusts: implications for understanding the plumbing of submarine sediments. In *Geological Processes on Deep-Water European Margins, Intergovernmental Oceanographic Commission Workshop Report* No. 175, pp. 51–52. Paris.

Newsom, H.E., Hagerty, J.J. & Thorsos, I.E. (2001). Location and sampling of aqueous and hydrothermal deposits in Martian impact craters. *Astrobiology* **1**, 71–88.

Norton, C.F. & Grant, W.D. (1988). Survival of halobacteria within fluid inclusions in salt crystals. *J. Gen. Microbiol.* **134**, 1365–1373.

Ori, G.G., Marinangeli, L. & Komatsu, G. (2000). Martian paleolacustrine environments and their geological constrains on drilling operations for exobiological research. *Planet. Space Sci.* **48**, 1027–1034.

Parnell, J. (1985). Hydrocarbon source rocks, reservoir rocks and migration in the Orcadian Basin. *Scott. J. Geol.* **21**, 321–336.

Parnell, J., Geng, A. & Veale, C. (1994). Petrology of the bitumen (manjak) deposits of Barbados: hydrocarbon migration in an accretionary prism. *Marine Petrol. Geol.* **11**, 743–755.

Parnell, J. & Janaway, T. (1990). Sulphide-mineralized algal breccias in a Devonian evaporitic lake system, Orkney, Scotland. *Ore Geol. Rev.* **5**, 445–460.

Parnell, J., Mazzini, A. & Chen, H. (2002). Fluid inclusion studies of chemosynthetic carbonates: Strategy for seeking life on Mars. *Astrobiol.* **2**, 43–57.

Pentecost, A. (1993). British travertines: a review. *Proc. Geol. Assoc.* **104**, 23–39.

Pentecost, A. (2001). Microdistribution of algae in an Italian thermogene travertine. *Arch. Hydrobiol.* **152**, 439–449.

Pentecost, A. & Viles, H. (1994). A review and reassessment of travertine classification. *Geog. Phys. Quat.* **48**, 305–312.

Pugh, M.E. (1968). Algae from the Lower Purbeck limestones of Dorset. *Proc. Geol. Assoc.* **79**, 513–523.

Riding, R. (2000). Microbial carbonates: the geological record of calcified bacterial-algal mats and biofilms. *Sedimentology* **47**(suppl. 1), 179–214.

Roberts, S.M. & Spencer, R.J. (1995). Paleotemperatures preserved in fluid inclusions in halite. *Geochim. Cosmochim. Acta* **59**, 3929–3942.

Roedder, E. (1984a). Fluid inclusions. In *Reviews in Mineralogy*, vol. 12. Mineralogical Society of America, Washington.

Roedder, E. (1984b). The fluids in salt. *Amer. Mineral.* **69**, 413–439.

Rothschild, L.J. (1990). Earth analogs for Martian life. Microbes in evaporites, a new model system for life on Mars. *Icarus* **88**, 246–260.

Rosenzweig, W.D., Peterson, J., Woish, J. & Vreeland, R.H. (2000). Development of a protocol to retrieve microorganisms from ancient salt crystals. *Geomicrobiol. J.* **17**, 185–192.

Russell, M.J., Ingham, J.K., Zedef, V., Maktav, D., Sunar, F., Hall, A.J. & Fallick, A.E. (1999). Search for signs of ancient life on

Mars: expectations from hydromagnesite microbialites, Salda Lake, Turkey. *J. Geol. Soc. Lond.* **156**, 869–888.

Schultze-Lam, S., Ferris, F.G., Konhauser, K.O. & Wiese, R.G. (1995). In situ silicification of an Icelandic hot spring microbial mat, implications for microfossil formation. *Can. J. Earth Sci.* **32**, 2021–2026.

Schwartz, H.P., Harmon, R.S., Thompson, P. & Ford, D.C. (1976). Stable isotope studies of fluid inclusions in speleothems and their paleoclimatic significance. *Geochim. Cosmochim. Acta* **40**, 657–665.

Shepherd, T.J., Rankin, A.H. & Alderton, D.H. (1985). *A Practical Guide to Fluid Inclusion Studies*. Blackie & Son, Glasgow.

Stan-Lotter, H., Radax, C, Gruber, C., Legat, A., Pfaffenhuemer, M. & Wieland, H. (2001). Viable halobacteria from Permo-Triassic salt deposits and the possibility of extraterrestrial microbial life. In *Proc. First European Workshop on Exo-/Astro-Biology*, ESA SP-496, pp. 25–31. European Space Agency, Noordwijk.

Steele, A., Toporski, J., McKay, D.S., Schweitzer, M., Pincus, S., Perez-Mercader, J. & Garcia, V.P. (2001). Microarray assays for solar system exploration. In *Proc. First European Workshop on Exo-/Astro-Biology*, ESA SP-496, pp. 91–97. European Space Agency, Noordwijk.

Summerfield, M.A. & Goudie, A.S. (1980). The sarsens of southern England: their palaeoenvironmental interpretation with reference to other silcretes. In *The Shaping of Southern England, Spec. Publ. Inst. Brit. Geogr.*, 11, ed. Jones, D.K.C., pp. 71–100. Institute of British Geographers, London.

Swayze, G.A., Kokaly, R.F., Clark, R.N. & Livo, K.E. (1999). A strategy to use UV-NIR reflectance spectroscopy to search for mineralogical evidence of extant or past life on Mars. *Geological Society of America Abstracts with Programs*, A-304.

Thurman, E.M. (1985). *Organic Geochemistry of Natural Waters*. Nijhoff, Dordrecht.

Timofeeff, M.N., Lowenstein, T.K., Brennan, S.T., Demicco, R.V., Zimmermann, H., Horita, J. & von Borstel, L.E. (2001). Evaluating seawater chemistry from fluid inclusions in halite: examples from modern marine and nonmarine environments. *Geochim. Cosmochim. Acta* **65**, 2293–2300.

Trewin, N.H. & Knoll, A.H. (1999). Preservation of Devonian chemotrophic filamentous bacteria in calcite veins. *Palaios* **14**, 288–294.

Vreeland, R.H., Rosenzweig, W.D. & Powers, D.W. (2000). Isolation of a 250 million-year-old halotolerant bacterium from a primary salt crystal. *Nature* **407**, 897–899.

Walkden, G.M. & Williams, D.O. (1991). The diagenesis of the late Dinantian Derbyshire–East Midland carbonate shelf, central England. *Sedimentology* **38**, 643–670.

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

Weber, M.E., Blanchard, D.C. & Syzdek, L.D. (1983). The mechanism of scavenging of water-borne bacteria by a rising bubble. *Limnol. Oceanogr.* **28**, 101–105.

Westall, F. (1999). The nature of fossil bacteria: a guide to the search for extraterrestrial life. *J. Geophys. Res.* **104**, 16 437–16 451.

Westall, F. *et al.* (2000). An ESA study for the search for life on Mars. *Planet. Space Sci.* **48**, 181–202.

Whitby, J., Burgess, R., Turner, G., Gilmour, J. & Bridges, J. (2000). Extinct ^{129}I in halite from a primitive meteorite: evidence for evaporite formation in the early solar system. *Science* **288**, 1819–1821.

White, N.C., Wood, D.G. & Lee, M.C. (1989). Epithermal sinters of Paleozoic age in north Queensland, Australia. *Geology* **17**, 718–722.

Wilkins, A.D., Wright, A., Parnell, J. & Artz, R. (2003). Astrobiological use of model crystals containing biomolecules and microbes: testing analytical techniques and space exposure experiments. In *Proc. Second European Workshop on Exo/Astrobiology*, Graz, Austria, *European Space Agency Spec. Publ.* 518, pp. 567–568.

Wynn-Williams, D.D., Cabrol, N.A., Grin, E.A., Haberle, R.M. & Stoker, C.R. (2001). Brines in seepage channels as eluants for subsurface relict biomolecules on Mars? *Astrobiology* **1**, 165–184.

Wynn-Williams, D.D. & Edwards, H.G.M. (2000). Proximal analysis of regolith habitats and protective biomolecules in situ by laser Raman spectroscopy: overview of terrestrial Antarctic habitats and Mars analogs. *Icarus* **144**, 486–503.

Zolensky, M.E., Bodnar, R.J., Gibson, E.K., Nyquist, L.E., Reese, Y., Shih, C.Y. & Wiesmann, H. (1999). Asteroidal water within fluid inclusion-bearing halite in an H5 chondrite, Monahans (1998). *Science* **285**, 1377–1379.