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Volatile organic compounds (VOCs) in terrestrial extreme environments: implications for life detection beyond Earth

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Covering: 1961 to 2024

Discovering and identifying unique natural products/biosignatures (signatures that can be used as evidence for past or present life) that are abundant, and complex enough that they indicate robust evidence of life is a multifaceted process. One distinct category of biosignatures being explored is organic compounds. A subdivision of these compounds not yet readily investigated are volatile organic compound (VOCs). When assessing these VOCs as a group (volatilome) a fingerprint of all VOCs within an environment allows the complex patterns in metabolic data to be unravelled. As a technique already successfully applied to many biological and ecological fields, this paper explores how analysis of volatilomes in terrestrial extreme environments could be used to enhance processes (such as metabolomics and metagenomics) already utilised in life detection beyond Earth. By overcoming some of the complexities of collecting VOCs in remote field sites, a variety of lab based analytical equipment and techniques can then be utilised. Researching volatilomics in astrobiology requires time to characterise the patterns of VOCs. They must then be differentiated from abiotic (non-living) signals within extreme environments similar to those found on other planetary bodies (analogue sites) or in lab-based simulated environments or microcosms. Such an effort is critical for understanding data returned from past or upcoming missions, but it requires a step change in approach which explores the volatilome as a vital additional tool to current 'Omics techniques.

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1 Introduction

Finding evidence of life elsewhere in the Solar System is dependent on the discovery of unique biosignatures that are produced by biological activity.[1–4] These biosignatures must be sufficiently abundant and/or complex in an environment to display measurable attributes that indicate life and be unlikely to be formed by a non-biological (abiotic) process.[5] Understanding the production and modification of potential biosignatures can inform strategies for research pathways, missions, and observations with life detection as a key objective.[6]

Biosignatures have been defined as '*any phenomenon for which biological processes are a known possible explanation and whose potential abiotic causes have been reasonably explored and ruled out*'.[7] They can be divided into two distinct categories: (1) inorganic, which include isotope fractionations, morphological fossils, mineral alterations, and sedimentary structures formed from microbial activity;[1,8–10] and (2) organic, which includes biomolecules produced as cellular structures and/or metabolic activity.[11–14] One sub-division of organic compounds that has yet

to be fully explored as viable biosignatures in this context are Volatile Organic Compounds (VOCs).

VOCs are compounds that readily evaporate at room temperature and are low molecular weight[15] (below 900 Dalton – but usually in the range 50–200 Daltons).[16] They can be further subdivided into 3 main groups as illustrated in Table 1. They have high vapour pressures and low boiling points, that facilitate the evaporative process.[18,19]

For this reason, on Earth, VOCs are intrinsically linked to the atmosphere and play a crucial role in global atmospheric chemistry; they can undergo gas phase oxidation with atmospheric oxidants such as hydroxyl radicals (OH), ozone (O_3), and nitrate radicals (NO_3) as well as other reactive processes to form volatile organic species such as carbonyls, carboxylic acids, alcohols, esters, organo-sulphates, and organo-nitrates.[20] These species can then condense or react with particle phase compounds to form secondary organic aerosols (SOA).[21–23] VOCs are necessary for the global cycling of essential elements; for example, oceans release a range of biogenic VOCs (containing carbon, nitrogen, sulfur, and halogens), which are transferred to land, *via* the atmosphere.[24] They are also primary and secondary metabolic by-products of microbial life, used to fulfil a variety of roles in their communication, survival, and persistence,[25] along with other volatile gases, for example: methane (CH_4) produced *via* methanogenesis through anaerobic respiration,[26,27] ammonia (NH_3), which is produced from the metabolism of peptide and amino acids; hydrogen cyanide (HCN), which has been detected in some *Pseudomonas*, catalysed by the enzyme HCN synthase and forming HCN and carbon dioxide (CO_2) from glycine; nitric oxide (NO), which is

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Geraint (Taff) Morgan spent the first half of his career conceiving, designing, building, and validating instruments for the Rosetta and Beagle2 space missions and working on the development of instrumentation to constrain the global budget of terrestrial atmospheric methane. He works with end-users to develop novel VOC solutions for a diverse range of commercial partners, from SMEs to global multi-nationals. He is still active in Space research, having been a co-author of the 2022 Science article, that analysed the volatile components of the UK Winchcombe meteorite. He is also an Associate Director and Commercialisation Lead of AstrobiologyOU Research Group.

Table 1 Classification of VOCs (adapted from WHO[17])

Description	Abbreviation	Boiling point range (°C)
Very volatile organic compound	vVOC	<0 to 50–100
Volatile organic compound	VOC	50–100 to 240–260
Semi-volatile organic compound	sVOC	240–260 to 380–400

produced mostly from L-arginine, and hydrogen sulfide (H_2S), usually produced from the degradation of cysteine.[28] The bioproducts of any biotic activity (including volatile) are therefore, prime targets as biosignatures.[28–31]

In planetary exploration, it is assumed that life will select chemical compounds that are useful to it (*e.g.*, that allow it to perform chemical processes), creating a disequilibrium; with the acceptance that extra-terrestrial life, could utilise different chemical building blocks and ways to facilitate chemical reactions.[32] Indeed, chemical disequilibrium in planetary atmospheres (including exoplanets) has been deemed a plausible biosignature for searching for life elsewhere in the Universe.[33,34] The disequilibrium balance and diversity of VOCs produced by phytoplankton has also been explored at the sea–air interface by Halsey & Giovannoni. Here, ecosystem shifts in phytoplankton caused by physical and biological events can lead to a state of surface ocean disequilibrium and VOC accumulation.[35] The shifting turnover of VOCs at this interface highlights the importance of investigating VOCs as a group alongside singular compounds as biosignatures.

A broadscale method for group VOC analysis is in the form of the 'volatilome'. The 'volatilome' is a term used to describe all volatile compounds with unique complexity found in an organism, an ecosystem, or a matrix – including those from microbial metabolic processes and exogenously derived compounds.[36–38] This method could help to ensure that an unambiguous biosignature is ultimately detected.[39] This volatilomic fingerprint of all VOCs within an environment – would allow complex patterns in metabolic data to be unravelled, as has been applied in numerous biological and ecological fields and can be used as a tool for biomonitoring that is non-invasive, non-destructive, and rapid.[40] The human volatilome is regularly investigated in health and disease,[41–43] for example wound profiling in chronic wounds,[44] the gut–brain axis,[45,46] clinical medicine,[47–49] and diagnostics[50] as well as pathogenic microbes such as ampicillin-resistant and -susceptible *Escherichia coli*,[51] for exhaled signs of infection in multiple pathogenic species[52] and to help identify bacteria implicated in pneumonia.[53] VOCs have been shown to help differentiate groups of subjects[54] and identify markers for diseases such as tuberculosis.[55]

The plant volatilome has been explored by Rhinnan *et al.* in relation to extreme terrestrial and marine environments.[56] It has also been extensively characterised, including the rhizosphere and its interactions with microbes and insects,[57–59] and the volatilome has been identified as an essential piece of the soil metabolome.[60] As plant diseases caused by phytopathogens cause huge economic loses in agriculture, finding ways to characterise or identify patterns in VOCs as diagnostic markers or to develop strategies for biocontrol could have huge benefits to sustainability in agriculture.[61,62] Even research into conditions such as sick building syndrome have shown the value of VOC identification,[63] but in many cases each individual VOC chromatogram can contain hundreds, if not thousands of features to identify and classify, making them perfect for chemometric analysis approaches.[64] When then combined with metagenomic and metabolomic data, a volatilome could help elicit a holistic perspective on microbial processes[30] and offer a new avenue in astrobiology to help enhance current exploration techniques. An ongoing challenge with these techniques however, is that biological variability can be high. For example, variations in VOC concentrations can change with environment, genetics, species, and which communities of microbes exist together.[65] There could also be different enzymatic sources for the same volatile signatures, which a chromatogram would not be able to differentiate.[66] The complexity of these factors therefore requires the production of multi'Omics data with high precision and robust quality control (QC) protocols to allow for elucidation of multi-level, real-time interactions, that reflect biochemical pathways and highlight any dysregulations.[67]

Volatilomics can encompass large, untargeted (evaluation of all detectable compounds in the sample)[68] or small, targeted (evaluation of compounds that are predetermined by the researcher) analyses of a range of metabolites and explores the characterisation, detection, and quantification of these metabolites in a biological system.[37,69] It has also been suggested that microbial VOC data should be integrated into metabolic profiling (metabolomics) to enhance our understanding of microbial systems.[30,70,71] In these studies, the overlooked volatile component can lead to incomplete interspecies, and interspecies-to-ecosystem interactions.[30] By adding metagenomic analysis, (that characterises the diversity and function of micro-organisms at a genetic level[72]), we can combine volatilomics, metabolomics and metagenomics to give a holistic view of the dynamics between microbes.[73] Although this offers an opportunity for future work, it is not detailed in this review.

The key focus for establishing a volatilome to use as a biosignature is to understand the occurrence of VOCs and organic species in an environmental setting, including how that environment evolves or changes, and how potential atmospheric, geological, and stellar processes/interactions, may suppress, enhance, or mimic a biosignature at different times.[74] In this paper we review the production of VOCs from microbial sources (mVOCs) and how they may be produced and interact in extreme environments similar to those on other planetary bodies. We will explore how a volatilome can be used as a putative biosignature for life.

2 Microbial VOCs

Microbial VOCs (mVOCs) are those VOCs produced as a physiological response to environmental conditions.[75,76] This can include stresses such as extremes of pH, salinity, desiccation, or temperature, all of which require microorganisms to adapt for survival.[77,78] A single organism will emit or utilise a selection of

VOCs depending on environmental conditions, for example, nutrient source, pH, growth stage, moisture content, humidity, and aeration.[79–81]

A broad range of compounds can be released by microbes, including alcohols, ketones, nitrogen- and sulfur-containing species, esters, hydrocarbons, carbonyl groups and halogenated compounds.[82,83] Further, microbes can utilise VOCs generated anthropogenically,[84,85] through intra-and inter-kingdom interactions, *e.g.*, quorum sensing,[61,79,86] or biosynthesis, such as *via* the terpene pathway and fatty acid biosynthesis.[87]

mVOCs have highly diverse structural variations[88] and can move and interact with other volatiles easily because they diffuse well in the gas phase and move readily within the liquid phase (faster than polar compounds) as illustrated in Weisskopf *et al.* 2021.[89] They can interact within many environments, whether within an organism or as part of a complete ecosystem.[40,75,90] Subsequently, this affects cell membrane fluidity (by creating membrane expansion through the accumulation of VOC molecules[91]) or induces disruptions such as leakage of intracellular components. This changes the permeability, allowing VOCs to penetrate interior cell structures and interact with intracellular sites.[92] This can allow interaction between microbial groups to promote or reduce communication,[93] allow stress alleviation,[94] or improve/reduce defence.[95] For example, dimethyl disulfide (DMDS) can induce plant growth promotion,[96] 2-butanone and 2-octanone can affect microbial motility in biofilm formation,[97] and 3-carene can affect the production of other metabolites.[89] Microbial terpenoids (geosmin, 2-methylisoborneol) have also been shown to promote host health during growth, cell differentiation and rhizoid formation.[95,98] Many of these features could create a huge competitive advantage and support micro-organisms to survive large variations in physicochemical conditions within extreme environments.

Microbial metabolism regulation contributes significantly to the complexity and characterisation of their volatilomes, and this varies between species- and strain.[99] Tracking species- and strain-level volatilomic diversity across a genus results in a comprehensive understanding of VOCs for specific microbes and microbial groups.[100] Strain-level volatilomes have been explored in some pathogenic bacterial species where, at the compound level, the primary metabolites (described in next section) such as alcohols, ketones, and acids, varied between different glucose-dependent volatilomes (*e.g.*, brain heart infusion and tryptone soy broth media). The differences were detected in *E. coli* and *P. aeruginosa*, which assisted in the identification of the cellular origin of individual metabolites, and illustrated the complexity in the core (compounds emitted by all strains across all media) and accessory (compounds emitted by at least one strain in at least one medium) volatilomes.[99] *Bacillus subtilis* (a bacterium that has consistently demonstrated its resistance to space related extremes[101]) has been studied for its volatile emissions but mainly in isolates from soil and food sources.[82] Interestingly, although many wild-type strains have been analysed for non-volatile metabolites,[102] only a few studies have characterised their volatile profile.[82,103]

At a community level, mVOC profiles differ depending on the community's diversity and the dominant microbial groups.[104,105] These volatilomes provide an opportunity to study biochemical pathways, synergetic interrelationships (*e.g.*, quorum sensing), and allow investigation of the unique complexity found either in an organism, an ecosystem, or a matrix – including those from microbial metabolic processes and exogenously derived compounds.[37,38,106]

2.1 VOCs as metabolic products

Through primary metabolism, biota capture energy from the environment by catalysing complex redox reactions[107,108] to build the basic molecules of life, essential for reproduction and growth.[30] This process requires no addition of energy[109] and produces primary volatile metabolites such as the VOCs acetic acid, acetone, or ethanol.[109,110] These are usually produced by microbes in the exponential phase of growth.[111] In contrast, secondary metabolism provides another important source of metabolites (called secondary – or specialised – metabolites), which are usually diverse, biologically active, and low molecular weight molecules including mVOCs.[112,113]

In microbes, co-regulation of specialised metabolites has evolved for competitive advantage, where the evolution of traits optimises the retention and production of chemical diversity (at minimal energy cost to the microbe) to allow biomolecular activity.[114] Their specialised metabolites also play key roles in metabolic co-regulation between biosynthetic pathways, therefore influencing microbial interactions.[115] These enhancements can include, for example, the production and secretion of secondary metabolites as biosurfactants, which can decrease the surface tension of the surrounding liquid.[116] Biosurfactants are crucial in cellular communication, and quorum sensing,[117] both of which are utilised by microbes using VOCs.[87,118,119] The VOC dimethylhexadecylamine has also been shown to affect bacterial growth and swarming motility.[120] Utilising VOCs can therefore enhance survival/evolutionary advantages to a population.[116] This aids individual microorganisms[121] but also benefits the whole community in their quest for survival.[116]

Specialised metabolites are usually produced during late growth phase[122] during transition from active growth to stationary phase.[123] They are thought to play no direct part in growth[62] and are not essential for at least short-term survival[123] but could be a competitive advantage for ongoing microbial survival.[124–126] Many specialised metabolites have been identified despite the full biosynthetic pathways being unknown.[30] Recent genome sequencing has highlighted that genes involved in specialised metabolite biosynthesis are more abundant than first thought.[127] For example, biosynthesis mechanisms for specialised metabolites, are often encoded in biosynthetic gene cluster (BGCs) regions within the genome.[128] In the case of most *Pseudomonas* spp., there are also 'orphan' BGCs (loci encoding secondary metabolites) where the products are yet unknown.[129] Also, in *Streptomyces*, there is a higher number of BGCs that expected in relation to production of specialised metabolites, many of which are not expressed under laboratory conditions; hence their products remain unknown.[130] As genome

sequencing identifies new biosynthetic pathways, more volatilomes that have yet to be fully determined may be discovered. This is an important feature when studying extremophiles.

Specialised VOCs have been the subject of recent interest due to their potential application in biotechnology drug discovery.[82,131] Although their diversity has been investigated, however, in *Bacillus subtilis* isolates,[82] *Acinetobacter johnsonii* XY27,[131] and in Actinomycete communities,[130] they are still relatively unexplored as microbial metabolites.[82,130]

2.2 Metabolic diversity of microbes

Microorganisms have evolved many different metabolic strategies to obtain energy, as illustrated in Fig. 1. This means the volatilome of differing environments can be complex and combining primary and specialised VOC metabolites from a range of organisms and metabolisms. It is important, therefore, to understand the VOC contributions from the different metabolic pathways before considering the complexity of combining those in an environment.

Phototrophs are organisms such as photosynthetic bacteria, algae or plants that acquire energy from light.[132] Cyanobacteria (blue-green algae) can survive in numerous environments, including cold deserts, oceans, hypersaline waters, and hot springs[133,134] and produce VOCs such as aliphatic alcohols, aldehydes, and monoterpene alcohols.[135] For example, the cyanobacterium *Synechococcus* sp. GFB01, isolated from a freshwater lagoon in the Amazon, synthesises five VOCs including 6-pentadecanol and octadecyl acetate which had not previously been described for the phylum.[133] Several VOCs such as 3-methyl pyruvate, stearic acid and biuret have been identified to play a critical role in regulation of the composition, and diversity of other prokaryotic communities in hypersaline sediments,[136] an environment that could be prevalent on other planetary bodies.

Chemotrophs are organisms such as bacteria that obtain energy by oxidising reduced compounds. They are subdivided into chemoorganotrophs (using organic compounds) and chemolithotrophs (using inorganic compounds), as shown in Fig. 1.[137,138]

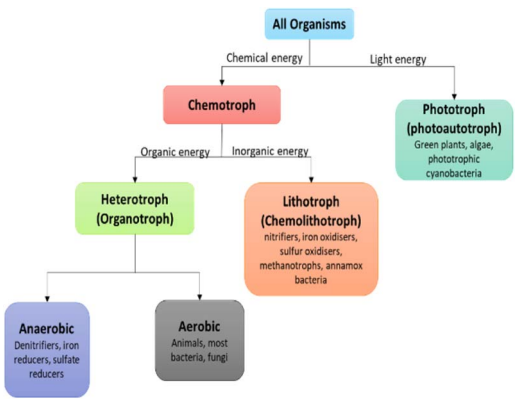

Fig. 1 Metabolic diversity of microbes – based on primary source of energy as compared with higher plants and animals (other anaerobic microbial metabolism *e.g.*, fermentation is included in text below) (Adapted from Burgin *et al.* 2011).[107]

Chemoorganotrophy can occur aerobically (*e.g.*, oxygenic respiration) where VOCs such as methanethiol, DMDS and acetoin are produced, and anaerobically (*e.g.*, fermentation) where VOCs such as alcohols, ketones, and fatty acids[139] are produced. Chemoorganotrophic microorganisms obtain energy from the oxidation and reduction of carbon/organics, including VOCs; for example, *Pelagibacter* HTCC1062 a marine bacterium, can consume and metabolise isoprene (C_5H_8) and acetone (C_3H_6O), which are prime climate-active (*e.g.*, can alter atmospheric chemistry) VOCs.[140] Chemoorganotrophs can also produce smaller organic compounds that can be used for biosynthesis or other assimilatory pathways.[141,142] In the case of soil systems, bacterial acetone metabolism occurs *via* several biochemical pathways, utilising the acetone monooxygenase enzyme to produce different VOCs such as acetaldehyde and formaldehyde (Fig. 2). Methyl acetate, the alternative product of the monooxygenase, can also be further converted to the VOCs methanol and acetic acid.[140,143]

In sub-surface environments on Earth, where photosynthesis is inhibited, *e.g.*, deep-sea hydrothermal vents,[144,145] primary production is driven by chemolithotrophic microorganisms. Hence, they can be used as candidates for putative life on other planets, given most extraterrestrial surface environments have detrimental radiation conditions.[146–148] Chemolithotrophic microorganisms catalyse inorganic chemical reactions that are in disequilibrium with their environment and drive the reactions towards equilibrium through redox reactions utilising, for example, manganese, iron, nitrogen, or sulfur.[107] Chemolithotrophs in hydrothermal vents, for example, utilise volatile H_2S as an electron source for growth[145] but also produce organic acids as specialised metabolites.[149,150] Iron and sulfur oxidising bacteria such as *Acidithiobacillus ferrooxidans*, *Leptospirillum ferriphilum*, and *Acidithiobacillus caldus* – considered to have substantial roles in oxidative dissolution of sulfide minerals in acidic environments – have been shown to produce the VOC glycolic acid in cell free culture liquors.[151]

This review focuses exclusively on chemolithotrophs since they are the most likely candidates for primary production on other planetary bodies and are common in the more extreme environments on Earth.[152,153]

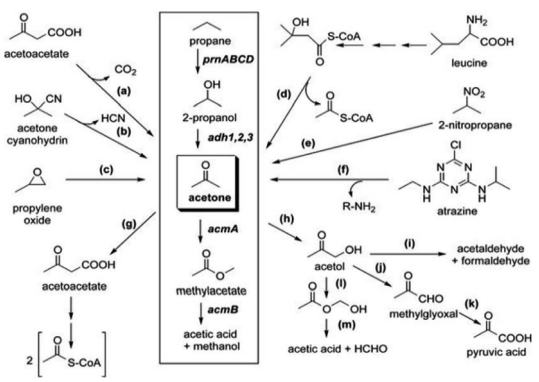

Fig. 2 Overview of acetone metabolism.[143]

3 Detecting VOCs

3.1 Detecting VOCs in extraterrestrial environments

In searching for life beyond the Earth, volatile analysis has predominately been achieved *via* remote sensing, including characterising exoplanet atmospheres. A range of volatile trace gases have been targeted in this context, such as oxygen (O_2), O_3, nitrous oxide (N_2O) and CH_4[154–156]. CO_2 and CH_4 have been recently detected remotely by the James Webb Space Telescope (JWST) in the atmosphere of the candidate exoplanet K2-18b,[157] where the VOC dimethyl sulfide (DMS) has also been tentatively identified.[142] However, at the astronomical distances involved in these contexts, VOCs are unlikely to be harnessed as biosignatures remotely: the concentration within an entire atmosphere would be too low to detect effectively.[154] Even if detected over shorter distances, there is a further limitation on using these molecules as biosignatures: owing to the inherent nature of gases, and the extreme environments that exist beyond Earth (*e.g.*, extreme in pH, temperature, salinity, radiation, water availability, and pressure[158]), VOCs detected on the surface or in the atmosphere of planetary bodies are unlikely to be indicative of any past life. Any VOCs would have rapidly dissipated or been affected on some bodies by UV/ionising radiation, leading to their destruction or transformation to a form that is not readily detectable by current remote or lander instrumentation.[159–161] Furthermore, many can be generated abiotically, for example, CH_4 can be created by rock–water interactions,[156] spallation (*e.g.*, lunar regolith[162,163]). O_2 can be produced by H_2O photolysis,[164,165] CO_2 photolysis, or an extreme hydrogen escape event with subsequent O_2 build up.[156] DMS has also been identified on comet 67P using data from the Rosetta spacecraft suggesting it may not be a robust indicator for life due to its potential abiotic production.[166,167] All these abiotic sources can then lead to a 'false-positive' detection or over-impose those that may be produced by life.[168]

VOC analysis is predominantly useful for detecting current life, including life that may exist in the subsurface environment. However, fluids and/or gases can also become entrapped in minerals in rocks or ice (as inclusions), providing a valuable archive of their preserved chemistry.[169,170] For example, halite can entrap gases that record ancient chemistry, climate, or evidence of past micro-organisms that may have decomposed to produce CO_2, CH_4 and VOCs such as aldehydes, alcohols, or ketones.[169] Miβbach *et al.* (2021) showed the presence of volatile compounds within fluid inclusions in 3.5-billion-year-old rocks (*e.g.*, H_2S, carbonyl sulfide (COS), methanedithione (CS_2), CH_4, acetic acid, organic (poly-)sulfanes, and thiols), which could have been important substrates for sulfur and methanogenic metabolisms by the earliest life on Earth. However, thiols are unstable in aqueous medium and tend to oxidise to disulfides[171] with the -SH group also causing challenges with chromatographic separation even when the thiol is well preserved[172]). These inclusions pose an analytical challenge with detection and sensitivity owing to their low abundances[173] and are not the focus of this paper.

VOC analysis is a non-invasive, quick, and economical method to detect potential biosignatures and it could, with improvements in analytical capabilities, be deployed in future life detection missions. VOCs and organic compounds on Earth can be identified and quantified using a variety of analytical techniques including ion mobility spectrometry (IMS), gas chromatography mass spectrometry (GC-MS), gas chromatography with flame ionisation detection (GC-FID), fourier transformation infrared spectrometry (FTIR), proton transfer mass spectrometry (PTR-MS), Selective Ion Flow Tube Mass Spectrometry (SIFT-MS), Raman spectroscopy, non-selective gas sensors, photoionisation detectors (PID), and fluorescence spectroscopy.[174–181] Some of these instruments have been deployed on past and planned spaceflight missions to search for evidence of life, with GC-based instruments dominating payloads.[182–184] For example, fluorescence spectroscopy, Raman spectroscopy and GC-MS are utilised on the Sample Analysis on Mars (SAM) instrument onboard NASA's Mars Science Laboratory (MSL) Curiosity rover,[185] and fluorescence and Raman spectroscopy are deployed on the Perseverance rover within its Scanning Habitable Environments with Raman and Luminescence for Organics and Chemicals (SHERLOC) instrument.[186] A GC-MS was also deployed on the Mars Viking landers,[187] and on the Cassini–Huygens probe, which determined the composition of Titan's atmosphere as the Huygens lander descended.[188] The Rosetta orbiter spectrometer for ion and neutral analysis (ROSINA) was deployed on the Ptolemy instrument which was deployed to chase and analyse the comet 67P which included a GC/MS with an ion trap mass spectrometer.[189] The Mars Organic Molecule Analyser (MOMA) onboard ESA's ExoMars 'Rosalind Franklin' rover (due for launch in the late 2020s) will have a GC instrument with four columns to allow *in situ* analysis of organic molecules and enantiomers, including VOCs and semi volatiles (sVOCs).[190] Similarly, the Europa Clipper mission, launching in October 2024, and will combine spectroscopy and GC-MS techniques to detect organics including VOCs with its 'MAss Spectrometer for Planetary Exploration' (MASPEX) instrument[191,192] in its search for biosignatures on Jupiter's moon Europa.[193] With the presence of subsurface oceans seen and predicted on other planetary bodies in our solar system (icy moons)[194] exploration using submersibles in future missions may become a reality.[195] Although VOCs are usually detected directly in the gas phase they can be detected in liquids or in the headspace above the liquid. For example, on Earth deep sea ramen spectrometers have been developed to detect variations in H_2S, CH_4 and CO_2,[196] a solid phase micro extraction (SPME) sampler has been used on a submersible analysing hydrothermal deep see vents,[197] and a hydrothermal organic geochemistry sampler has been developed for deployment on deep sea submersibles.[198]

It is critical to validate approaches used when seeking VOCs as biosignatures, *e.g.*, gain baseline data, and test instrumentation on Earth. For this, analogue sites are used – sites on Earth that exhibit geological, chemical, or biological similarities to those of the target of a mission. These are habitats that have environmental conditions that are harsh, and beyond the optimal range for humans.[199,200] Organisms that have adapted to survive and thrive in these conditions are known as extremophiles (extreme-loving).[199,201–203] Identifying and exploring how these extremophile microorganisms survive and interact with

their environment through monitoring organic species such as VOCs is therefore vital for determining the potential volatilomes that might be established for equivalent extraterrestrial environments.

3.2 Detecting VOCs in terrestrial environments

There has been limited work relating to mVOC production in terrestrial extreme environments, with most focus instead on mVOCs related to pathogenic species, plant, and soil microbes.[204–207] However, in the cold desert environment of the Antarctic, the genera *Pseudoalteromonas* (in particular the Antarctic bacterium *P. haloplanktis* TAC125 – a model example of cold-adapted bacteria) has been shown to produce bioactive specialised metabolites including anti-biofilm molecules, compounds that promote antiproliferative action, and antimicrobials.[206] These functional responses in the bacterium can then give a competitive advantage to some community members[208] or create disadvantages for competing communities,[209] since cells in biofilms survive harsh growth conditions[210] and are more resistant to UV, toxicity from metals, acid exposure, and desiccation.[211] pH has also been shown to influence the mVOCs produced and their utilisation. For example, microalgae, when exposed to acid conditions in a marine environment, produced different VOCs compared to diatoms, and these changes in VOCs altered the behavioural responses of benthic invertebrates.[212] Further, *Streptomyces venezuelae* produces the VOC trimethylamine (TMA), which increases the pH to a more alkaline state (pH 9.5), subsequently acting as a 'Streptomyces communication cue' (causing the microbes to initiate exploration into separate *Streptomyces* colonies) as well as acting as a weapon to reduce the survival of other soil bacteria such as *Bacillus subtilis*.[213]

The analytical methods for characterising VOCs from natural sources have been well documented by Rowan (2011)[16] and Li (2023).[214] To increase the breadth of environments characterised for their volatilomes, there has been steady progress in the technology of portable field instruments and their applications, offering a wide range of organic and inorganic analysis in multiple matrices.[215] In addition, techniques that can give a snapshot of the volatiles present at a timepoint, or a real-time/near real-time representation over time have been developed.[216–218] Due to the huge diversity of these volatile compounds, no 'one single' analytical method can detect them all, which then leads to challenges in the identification or characterisation of certain compounds of interest[214] and therefore any determination of an entire volatilome. Especially within dynamic processes such as metabolism. Working in extreme field sites also requires staying in remote locations far away from a regular source of power, from lab-based analytical equipment, and laboratory supplies. This somewhat limits the type of equipment that can be used in the field, especially if it is also heavy or bulky. Some areas of exploration have access only by foot with challenging hiking in very high or low temperatures, or with variable terrain to navigate. With local pH or salinity also in the extreme, some equipment may become compromised or dysfunctional.

To mitigate this, sampling techniques have been developed to entrap or isolate volatile gases. This also ensures targeted sampling, and not just the 'air' around it. Several types of containers – gas-tight syringes, stainless steel canisters, or borosilicate glass bulbs/containers – can be utilised[219,220] but these can be fragile, with limited volume. Pre-evacuated canisters are robust and provide good sample stability but are bulky, heavy and require rigorous cleaning between samples.[219] A solution to this is food grade polymer bags (for example made of Nalophan® (polyethylene terephthalate), or more expensive bags made from Teflon® (polytetrafluoroethylene) or Tedlar® (polyvinyl fluoride) materials). These are chemically inert, have low permeability to VOCs,[221] are economical and more convenient for field analysis[220] being foldable, low weight, resistant to breakage, and available in various sizes.[222]

These bagging methods are well established[222] and are extremely useful in many contexts, including enclosing stems and leaves on living plants,[223] in breath analysis,[219,224] for the enclosure of a huge variety of biological samples,[225–227] and biofilms[97,228,229] or sediment samples.[230–232] These approaches allow for a more volatile rich, and specific sample to be collected, which helps equilibrate VOCs between sample and headspace, and create a larger dynamic headspace to sample from ref. 233 and 234. Dynamic enclosure techniques are also being utilised to enclose larger areas such as to study fluxes in sub-artic tundra plants[235] and permafrost affected peatland.[236] By applying an enclosure over an item of interest, a snapshot of VOCs can be collected. This can also be applied over a gas emanation source (Fig. 3a), biofilms (Fig. 3b), or by placing sediment samples or biofilms into a fully enclosed bag/container (Fig. 3c).

There are some disadvantages to bagging methods: limited time to keep the sample in the bag – suggested up to 6 hours before loss of volatiles *via* diffusion through the material,[237] loss of sample through wall adsorption, leaking, or potential loss of organics *via* partitioning into water vapour.[222] Some gas sampling bags (*e.g.*, reusable ones such as Tedlar®) may also need to be cleaned or conditioned extensively prior to use as they can produce and adsorb VOCs, such as phenol.[238] To counteract this in the field, samples can be analysed either directly from the bags or by concentrating the VOCs onto a solid adsorbent, such as those in a thermal desorption (TD) tube or

Fig. 3 (a) Using Nalophan® bags to collect gas emanating from a shallow water bubbling pool (b) example of a thick biofilm where gases had collected underneath and formed bubbles in the biofilm (c) area of drier biofilms which had become firm and easy to place inside a Nalophan® bag.

trap, and then purging and/or heating within the 6 hours window to remove excess water vapour.[234]

Analytical tools such as TD tubes,[239,240] or pocket diffusive (POD) samplers,[241,242] are useful as they are portable, small, light, and contain sorbent material such as Tenax™ or Carbotrap™. These sorbents are hydrophobic and preconcentrate VOCs onto them[243,244] making them easy to carry to and use in a remote site. Electronic nose[245] has a multi sensor array that can respond to numerous chemical classes that are then identified by artificial neural network (ANN) software.[246] The type of sensor used in portable versions can be more specific to measuring low-concentration gases but struggle with high concentration environments.[247] However, recent developments have helped create a more stable system, with reduced interference from humidity and temperature, that has been deployed successfully in the VOC analysis of whitefly infestations on tomato plants.[248] Portable commercial gas sensors (*e.g.*, electrochemical, infra-red, photo ionisation detectors[249]) provide specific detection for individual or small groups of gases,[250] and are often tailored to gas leak detection, fire detection, or control of ventilation.[251] They have recently become smaller, more affordable, and easier to use[250] making them a useful tool when in the field.

In many extreme environments, the variety and concentration of gases emitted are likely unknown, so broad VOC detection is a necessity. However, many of these analyses are complicated to achieve in the field, as they require sensitive non-portable equipment. Physical samples such as sediments or biofilms can be collected on site and transferred back to a laboratory. However, metabolic changes may occur within the time frame of transportation, or the samples may be subjected to contamination. To minimise this, cooling and freezing samples as soon as possible is essential[252] so they can be returned to laboratory conditions for further analysis and potential culturing. Using microcosms which reproduce conditions as close to those in analogue environments, it is possible to measure VOCs under controlled conditions. This technique has been proven effective with terrestrial samples from boreal peatland[253] and in reproducing the behaviour of VOCs in subsurface materials.[254]

There is also analytical equipment that is becoming more portable for in-field analysis. Ion mobility spectrometry (IMS) is an established technique for VOC detection in military security (detection of chemical warfare agents and explosives) and air quality control and monitoring in industrial processes.[255–257] IMS does not require the addition of bulky vacuum pumps and can detect down to ppb levels;[257,258] it is robust and has a rapid response and wide application.[255] However, IMS can have limited selectivity alone (*e.g.*, to separate and characterise compounds) and requires coupling with a GC, MS or with liquid chromatography (LC).[257,259] For example, it has been deployed alongside GC (GC-IMS) by NASA to function as the volatile organic analyser (VOA) on the International Space Station (ISS) to monitor air quality for outgassing material, contaminants from human excretion, containment breaches of utility chemicals (fuels, coolants *etc*), and thermal degradation by products.[260]

An 'in the field' portable GC-MS has also been developed but in practice was bulky, fragile, and required a significant power supply.[261] More recently, military units have utilised portable GC-MS to rapidly confirm chemical warfare agents (CWAs) at very low concentrations, but these systems proved complex from both a hardware and software perspective making them difficult to use in harsh and dangerous environments[262] and subject to continued testing.[263] For example, a needle trap system has been incorporated into one portable GC-MS design to allow dynamic or static headspace analyses, but this could only detect 31 volatile compounds, with a sensitivity too low for full characterisation. In addition, deploying such a system in the field would require key processes such as calibration curves and method development to also be carried out, increasing the demand and duration of use.[264] For example, an internal ion trap mass library must be generated using standards to allow for proper compound identification. Compound resolution can also be an issue in complex samples as column lengths in field-based kits are usually short, making it more likely to need deconvolution due to more complicated overlapping resolutions.[265] These issues continue to be problematic for portable equipment, however the reduction in storage or transportation issues can outweigh the need for ultimate sensitivity.[215]

A further compromise needed with vVOCs and other trace gas species, as many cannot be collected or stored on a sorbent or in containers unless under cryogenic conditions. This requires either large heavy cylinders/canisters to collect the sample in or liquid nitrogen which is difficult to transport to remote field sites. For example, CH_4 cannot be retained on traditional sorbents in a TD tube, so this method is not viable for CH_4 detection.[266] Recent developments in photoacoustic spectroscopy gas sensors for trace gases such as CH_4 and C_2H_6 have led to a range of highly sensitive, fast sensors that are reliable and chemically sensitive.[267] Optical fibre sensors based on absorption, which incorporate LED, hollow core waveguides (HCW) and photodiodes, have also been developed.[268] They can also be coated with layers of nano-assembled ultrathin films to allow for specificity to certain VOCs[269,270] and are small, portable, resistant to harsh environments and corrosion, and immune to electromagnetic interference.[270,271] These have not yet been tested in extreme environments, but the hope is that a broad range of portable, affordable devices will allow the fullest analysis of volatiles from trace gases to sVOCs and aerosols.

4 Simulations, data analytics and beyond

4.1 Simulated environments

With the high costs of directly sampling planetary environments and their access limited to specific missions, a wide variety of simulation chambers have been developed to mimic conditions that have either previously been measured by spacecraft or are predicted to exist on certain planetary bodies such as different radiation environments, varying temperature/pressure conditions, or water/rock ratios. These can provide insights into conditions expected on rocky planets (*e.g.*, Mars[272,273] or Venus[274–276]), icy worlds,[152,277] or early-Earth conditions.[278] The stability of organics and interactions with

organisms can be observed in such simulated environments.[275,279] These data type will be invaluable to elaborate on for future missions.[280] For example, by understanding multiple biochemical pathways and potential transformational processes, it may be possible to predict the behaviours of organics in certain environments, as well as understanding how they are affected by different parameter changes, or the addition of microbial life.

Identifying VOCs or other trace gases over a wide simulated parameter space could provide insights for understanding data returned from future subsurface exploration or lander missions.[278] By coupling VOC analysis to simulation experiments we can understand how VOCs behave within these environments, how they chemically change under differing conditions, and how they could be used to help make decisions about future mission targets. If organisms are active or can survive under the simulated planetary simulation conditions, including the subsurface environment,[281] this could inform habitability studies immensely.[280]

4.2 Maximising lab-based studies

In current laboratory settings, techniques to analyse VOCs such as TD, GC-MS, SIFT-MS, and PTR-MS are gold standard or are becoming a gold standard.[174,282,283] These techniques are being successfully applied to planetary science and will be essential to lab-based experiments in astrobiology. For example, the recent Winchcombe meteorite analysis in the UK included SIFT-MS analysis, which yielded a number of volatile species, including alcohols (C_1–C_6), carboxylic acids, aldehydes, and ketones.[284] While organic species have been identified in meteorites for several decades, the application of SIFT-MS was novel and yielded a greater understanding of the volatile component of this type of meteorite, which has been difficult to elucidate.[285] Evolved gas analysis (linear heating of material to release volatile gases that are then detected by gas chromatography, infrared spectroscopy, or mass spectrometry) is a well explored technique that has been successfully applied to studies of meteorites, including Winchcombe[286,287] and lunar samples from the Apollo missions. Other methods such as smartphone based, SPME, and adsorbent traps are detailed in Tholl *et al.* (2021).[265] HiSorb® is also a recently developed technique which is compatible with aqueous samples and requires no solvent extraction. It also allows for a larger volume of sorbent than SPME (HiSorb® 65 μL *vs.* SPME 0.5 μL), improving the extraction capabilities.

Samples collected in field sites or from return missions will include many complex matrices (for example a combination of sediments, microbial mats, and gases in hydrothermal fluids[288]). This added complexity can be hard to completely unravel with the previously mentioned analytical techniques. A more expensive but advanced tool for analysis of these complex signatures is using two-dimensional gas chromatography (GCxGC) where compounds are separated in two dimensions, allowing overlapping peaks to be separated.[289] GCxGC can not only be coupled with multiple detectors (FID[290]/sulfur chemoluminescence detector (SCD)[291]/Time of flight MS[292]) but also handle complex samples at low limits of detection (LOD).[293] It can also be coupled with TD systems allowing it to be utilised in the lab after field sampling of VOCs.[294] 2D GCxGC-ToFMS has already been applied to the analysis of extraterrestrial samples.[295]

4.3 Analysing VOCs as a whole unit

Volatilomics targets a small or large range of metabolites and explores the characterisation, detection, and quantification of these metabolites in a biological system.[37,69] It has been highlighted that VOCs should be integrated into metabolic profiling to enhance our understanding of microbial systems. In metabolomic studies, overlooked volatile components can lead to an incomplete understanding of the interspecies- and intraspecies-to ecosystem interactions.[30] To get a greater insight into the function and diversity of volatile compounds as, for example, secondary metabolites, it is vital to follow workflows that are well documented, as well as look at production of VOCs at a single cell level, to potentially attribute metabolites to certain developmental stages or cell forms.[82] As the volatilome has not readily been explored within astrobiology, this is a key area to focus on in future.

An advantage to studying the whole volatilome is that you can perform targeted and untargeted analyses, as is undertaken in traditional metabolomics.[30] In targeted analyses, compounds that are predetermined by the researcher are selected for analysis. The untargeted analysis involves the evaluation of all the detectable compounds in the sample[68] including chemical unknowns and is the current preference for analysis.[296] The untargeted method can be particularly useful when studying unknown environments or micro-organisms, such as those that could be present on other planetary bodies, as many different VOCs could be identified. Untargeted volatilomics focuses on the dynamic adjustments of small molecules in response to subtle disruption made by organisms.[297] These methods can also be performed in 'real-time or near real-time', which allows non-invasive monitoring, particularly on microbial communities.[30]

In astrobiology, being able to analyse a group of compounds and their relationships to each other, rather than relying on a single gas, could provide a wealth of information as has been shown successfully with other 'omics techniques within astrobiology such as exploring the diversity of microbial mats in the Makgadikgadi Salt Pans,[298] and genomic modelling of extremophiles.[299,300] Alone, gene-based tools are currently insufficient to explore the full plethora of chemical reactions and small molecules that compose a living cell.[301] Different 'omics techniques have provided insights into the survivability of microbes living in terrestrial environments that resemble potentially habitable environments on other worlds.[302] By analysing a variety of small metabolic products of living organisms including combining with volatilomics, we can help target the search for biomarkers and their interactions.[301]

4.4 Data analytics

To explore the volatilome, complex robust statistical analysis is becoming more commonplace[303] but it is a complex technique

that has numerous dimensions (compounds), and different magnitudes of each dimension.[304] Consequently, evaluating these data can be challenging and requires specialist expertise. Chemometric methods are used to retrieve greater information from the chemical information. Primary goals often include differentiation of compounds between different groups.[305] With advances in computer technology, statistical software, and analytical techniques, the chemometric approach has supported analytical chemists to obtain more robust, quicker results for analyses.[306] Typically, a full spectrum of data is imported, pre-processed, and then subjected to numerous different data analysis techniques or machine learning to tease out the interesting information.[64] For extensive reviews of these processes see Eisen *et al.*,[305] and Lubes & Goodarzi,[307] and references therein.

Prevalent methods in chemometrics include unsupervised pattern recognition (UPR), supervised pattern recognition (SPR), and exploratory data analysis (EDA). Unsupervised methods include principal component analysis (PCA), and cluster analysis (CA) and focus on the interconnectedness of the data and the intrinsic structure and relationship of the different features (*e.g.* peak area).[307] Supervised methods (often termed predictive models) for example classification models, partial least squares (PLS), discriminant analysis (DA), and neural networks[267,307] require training the data. This allows the development of classification models that are built on prior information about the samples. These models are then tested and validated on a known independent sample set, before then being applied to unknown samples.[307]

Classification models have been widely used in VOC research within many medical and food-based studies. For example, for differentiating air–liquid interface cultures after *Staphylococcus aureus* infection,[308] separating healthy and infected mushrooms *via* microbial VOCs,[309] differentiating VOCs associated with security issues (*e.g.*, drug trafficking, explosives, or the presence of humans in forbidden areas),[310] identifying microorganisms in pulmonary bacterial infections,[311] assessing microbial and mite contamination in cereal grains and coffee beans,[312] or profiling the faecal metabolome in horses with colic.[313] They have also been used in many metabolomic studies on individual or groups of microbes,[314] including NMR metabolomics of bacterial extracts,[315] in combination with proteomics, to analyse the effect of spaceflight on rice progeny,[316] and the identification of microbes using their metabolomic profiles.[317] These studies all highlight that by applying multivariate techniques to both untargeted environmental volatile profiles, and microbial volatile profiles, large amounts of complex data can be integrated and compared. Subsequently, analysis time is also shortened by the reduction in manual processing, human errors are minimised and there is less need for analytically trained experts.[318]

By using these classification techniques, data analysis can be expanded within astrobiology to distinguish differences or similarities between VOCs in environments, microbial communities, or can even assist in searching for contamination. Exploring volatile compounds and their interactions within environments that could hold biological systems, rather than just searching for individual compounds of interest produced by abiotic processes, could allow subtle changes in VOC dynamics produced by life to be tracked. The amount, ratio, or diversity of emitted VOCs are part of a microbe's phenotype,[319,320] so when their volatilomic data are then also combined with metabolomic, transcriptomic and genomic data, a more complete picture of metabolic pathways, and the potential routes VOCs are produced and utilised through this. This is useful to astrobiology because it helps to elucidate a clear picture of a whole system. If only parts of it are investigated, subtle elements could be missed in the relationship between rock, environment, and potential life. By understanding how they fit into complex systems could also help predict how they may evolve or be detectable in places where the immediate surface environment is too harsh to sustain life.

4.5 Future missions

Real-time measurements, miniaturisation, automation, reliability, portability, accuracy and sensitivity and low power consumption are all pre-requisites for analytical techniques that may be deployed on a spacecraft.[321] This provides a great challenge to analysts without even considering the finer points of landing a mission or running equipment that is millions of miles away.[321,322] Technical innovation has allowed technology such the mass spectrometer to be mobilised and miniaturised to allow *in situ* and field deployment.[323] In the context of VOCs, an OrbitrapTM cell-based mass spectrometer termed OLYMPIA (Orbitrap anaLYser MultiPle IonisAtion) is being developed for spaceflight, as well as a laboratory instrument for high-resolution studies of space-relevant chemical processes.[324]

Application of high throughput 'omics' analysis and deployment of omics instrumentation into space is also coming to the fore in relation to *in situ* biological analysis in locations such as the International Space Station (facilitating life science research and enabling dynamic biological studies in low gravity environments).[325] However, when samples from planetary bodies, such as Mars or the Moon, are returned to Earth, VOC analysis, including high throughput 'omics', would be beneficial in the search for life and for planetary protection.[326–328] For example, in the planned NASA/ESA Mars sample return programme, a sample receiving facility (SRF) will be in place for curation, where sample tubes will be opened and initially processed.[329] Preliminary stages of this processing will include safety protocols to avoid backward contamination (release of extraterrestrial material into Earth's biosphere).[330] All material collected (which includes samples of gas, rock, and sediments[329,331]) needs to be carefully stored, handled, and analysed with minimal alteration or contamination from the Earth, while also ensuring the samples are non-hazardous and sterilised before distribution.[329] Initial volatile analysis of the collected gases and rocks offers a way to minimally interact with the samples prior to sterilisation[332] since harsh chemicals are not required for compound extraction, and the gas can be gently removed from sample containers to establish its indigenous volatilome. This allows the collection of valuable initial data with minimal interference, acting as a robust precursor to the

wealth of other analyses likely to be conducted on extraterrestrial samples where sample alteration or destruction will be required.

For now, researching volatilomics in astrobiology requires time spent characterising patterns of VOCs and differentiating these from abiotic signals within analogue or simulated environments. Such an effort is critical for understanding the data returned from past or upcoming missions, but it requires a step change in approach. Exploring the volatilome in astrobiology offers this step change.

5 Author contributions

Claire Batty: conceptualization, writing – original draft, writing – review & editing. Victoria Pearson: conceptualization, writing – review & editing. **Karen Olsson-Francis**: conceptualization, writing – review & editing. Geraint Morgan: writing – review & editing.

6 Conflicts of interest

There are no conflicts to declare.

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