# Hidden in plain sight? Some challenges and needs for practical planetary biosignature exploration, both home and away-A Mini-Review.

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**Abstract:**

Identifying organic molecular biosignatures for life is challenging. Most current analytical methods were developed on Earth sediments rich in total organic carbon (TOC), and these methods struggle when dilute organic matter is situated within reactive, mineralogically complex astrobiological samples. Diverse geological alteration processes degrade biomarker signals, often concealing some chemical structures within hybrid species. Thermal maturation progressively destroys biomarker chirality and primary molecular signatures at moderate burial temperatures ($\leqslant$150 °C). Radiolysis, diagenesis, and maturation can eliminate reactive species and produce both lower and complex higher molecular weight products that may retain partial biological structures that are likely analytically obscured. Detecting low concentrations of such molecular biosignature structures hidden in composite reaction products presents a promising research focus. Selecting samples for return missions is crucial, necessitating an effective field screening system to assess organic carbon content and thermal history in potentially low TOC samples. Enhanced automated image-based detection of microbial structures, such as stromatolite analogs, is also a promising avenue for technological advancement, as is searching for gas transportable, resilient molecular markers, such as adamantanes, at seep locations.

# 1. Introduction

## 1.0 High stakes astrobiological sample collection

Sample selection poses a classic dilemma for field geologists in new terrain. With finite backpack capacity and limited sampling time, how does one choose which samples to take? Accessibility and geology limit options, but available samples often far exceed (metaphorical) backpack – and analytical – capacity. Early sample selection may be systematic, based on general interest and reconnaissance, but later stages of expeditions – or those with specific (e.g., fossil-finding) goals – will likely focus on specific sample features for follow-on analyses. Prior information on the geological character of the setting and macroscopic features of outcrops and boulders (including colour, grain size, and structure) can guide sample choice for further analysis. However, when the character of the rocks is poorly known or study goals relate to trace components that are not macroscopically detectable, sample selection often relies on intuition and chance as much as fact-based decisions.

In astrobiology, a sample's quantity and composition of organic carbon is a highly sought-after feature. However, the geologic behavior of organic carbon is heavily environment dependent. On Earth, the search for organic-rich samples typically focuses on fine-grained rocks with darker colours or enhanced gamma ray signals, suggestive of high total organic carbon (TOC) contents. In the absence of visible macroscopic fossil structures (e.g., stromatolites), there are currently no robust external criteria for selecting samples for organic biosignature assessment except based on TOC contents. On Mars, locating TOC-rich samples is challenging due to the dark mafic mineralogical composition of many sediments, dust coverings, and low carbon contents of characterized samples.

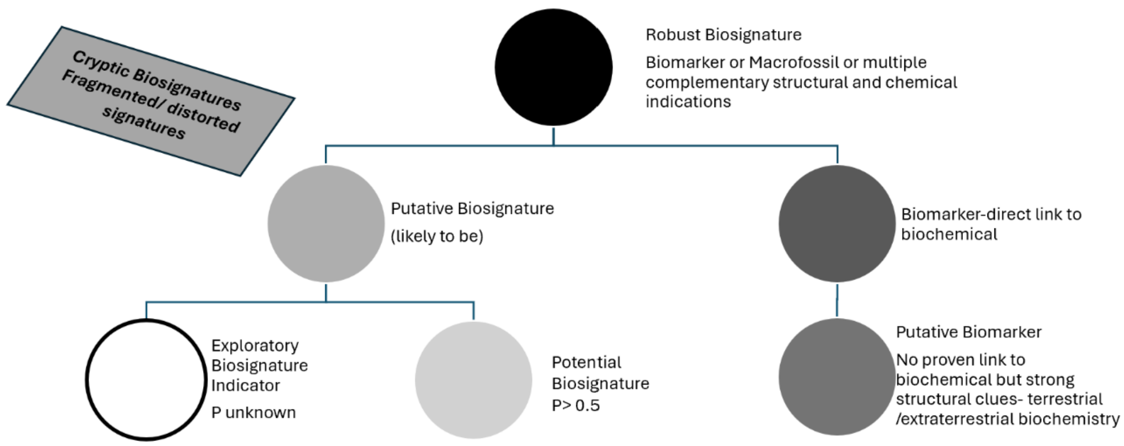
On Earth, field-selected samples undergo reconnaissance carbon analyses in the lab, with those exceeding 0.5 wt% TOC put forth for detailed molecular analysis, potentially including advanced pyrolysis screening for preliminary assessments of organic matter type and thermal maturity. None of these approaches is suitable in extraterrestrial settings (e.g., Mars), yet pivotal decisions must still be made on which samples to choose for the costly sample return to Earth. Here, we review the challenges of detecting biosignatures and molecular markers for life in astrobiological samples and outline analytical needs for practical biosignature exploration.

**1.1 Biosignatures**

A challenging aspect of Astrobiology is the lack of a universally accepted and constantly evolving definition of a biosignature. We use the definition of a BIOSIGNATURE as "Any object, substance, or pattern that provides scientific evidence of past or present life; it must be unlikely to arise from non-biological processes. This includes cellular structures, biogenic minerals, and organic molecules" (Paraphrased from Summons et al., 2011). A hierarchy of biosignature value can evolve with knowledge (Fig 1).

Some proposed biosignatures, like stable carbon isotopic distributions linked to life on Earth, are merely indicators of potential consistency with known life-associated mechanisms: they may also have abiotic sources (both known and unknown). We term such signals POTENTIAL BIOSIGNATURES. Small molecule signatures, such as dimethyl sulfide (DMS; Madhusudhan et al., 2025) or combinations of other volatile species detectable in exoplanetary atmospheres (Schwieterman et al., 2018), are of great interest. However, geochemistry suggests that small volatile molecules are most likely to have multiple chemical origins, including through abiotic processes like radiolysis and photolysis. In the case of DMS, where evidence exists of a biological source on earth, but little is known of other possible origins, we term it a POTENTIAL BIOSIGNATURE. Signals speculated to be biosignatures without evidence of any connection to life anywhere are termed EXPLORATORY BIOSIGNATURES, requiring substantiation.

Fig 1. A hierarchy of biosignature terminology




The most robust biosignatures are morphologically based, whether on unambiguous chemical structural information (e.g., chemical biomarkers), or fossilized biological structures (macrofossils or complex microfossils). Less robust are PUTATIVE BIOSIGNATURES, which have a higher probability of utility based on experience and inference but lack a proven link to a specific biological process. These are best illustrated through the biomarker concept.

The classical organic geochemical BIOMARKER concept, where molecules in terrestrial samples have close chemical structural relationships with specific known biomolecules in organisms, is well-tested on Earth. The discovery of a rigorously evaluated

BIOMARKER, such as derivatives of a steroid carbon skeleton for example, must be placed at the top of any hierarchy of biosignatures. However, with unknown extraterrestrial biochemistry and inevitable alteration of carbon skeletons during diagenesis and thermal maturation, such strict definitions are of limited value, and PUTATIVE BIOMARKER is a more apt term for molecules that are strong candidates for BIOMARKER status but lack a final, crucial link to biochemistry. Observing a limited subset of possible stable carbon skeletons with some structural isomer bias in a complex molecular suite is the essence of molecular biosignature detective work. Many Earth biomarkers started as PUTATIVE BIOMARKERs - for example, hopanes were discovered in crude oils before the identification of the diagnostic biological precursor hopane-tetrol membrane species in microorganisms (Ensminger et al., 1978; Ourisson et al., 1979).

Geological processing inflicts both chemical change and physical deformation through burial and tectonic forcing. Relevant molecular degradation processes altering biosignature molecular structures are primarily temperature-driven and include loss of primary stereochemistry at chiral centers, alkyl group migrations, carbon skeleton aromatization, and fragmentation during thermal maturation (Huang et al, 2022). Importantly, partial biosignature structural fragments can be incorporated into new condensed organic structures. We refer to altered, partial hints of biosignatures, whether based on molecular skeleton or fragmented fossil evidence, as CRYPTIC BIOSIGNATURES. Assessment of biosignatures will continue to involve interpretation and deconvolution processes. Traditionally such approaches are manual, but future approaches will likely be more algorithmic and artificial intelligence/ML methods will no doubt feature strongly in the future detective’s toolkit and may help resolve issues related to analytical artefacts with techniques such as pyrolysis (e.g., Cleaves et al., 2023).

Morphological evidence of fossilized microbial mats, stromatolites, microfossil indications, and other preserved biological structures in rock formations are considered biosignatures (e.g., Summons et al., 2011) and seem to be the most robust putative or potential biosignature field indicators. Imaging systems are critical in such analysis. Sheared partial fragments of fossils would be macroscopic analogs of those altered molecular CRYPTIC BIOSIGNATURES. The significance of cryptic biosignatures is reflected below, as we hypothesise, they may represent the bulk of the molecular signal in ancient, altered samples.

In many cases, especially with molecular signals, detailed analysis with multiple techniques in an Earth laboratory will be needed to validate any biosignature indications in the field and translate biosignature-consistent signals into more definite biosignatures. A conspicuous, statistically unlikely co-occurrence of multiple putative biosignature signals will enhance the net biosignature comfort level. As a footnote, some individual species of what might be termed prebiotic chemicals technically fit the structural definition of biomarkers. Prominent examples are amino acids and purine bases in asteroid samples. They are typically excluded based on contextual information relating to the entire collection of species found and sample origins. However, caveat emptor is always wise in astrobiology!

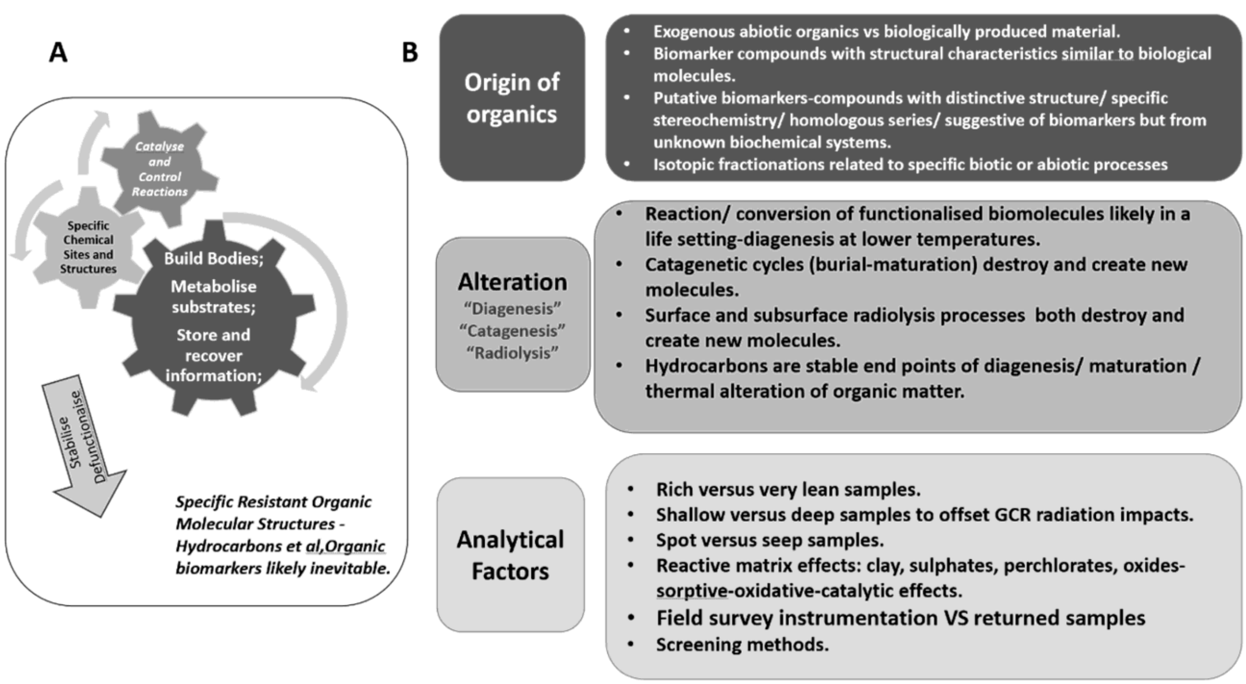
Where sample selection for return missions is critical, additional data from the outcrop provide necessary context, including the ability to leverage serendipity (many key fossil occurrences were discovered by accident - e.g., Walcott's discovery of the Burgess shale; numerous novel dinosaur discoveries), with signal detectability and intelligent analysis of both novel and expected signals in the field being key criteria in managing exploration programs. Thus, detectability of biosignature indications at outcrop becomes primary, as does understanding the preservation of biosignatures and the occurrence of cryptic biosignatures—hidden in plain sight—along with the artifacts introduced by the field analytical packages deployed. Detection and quantification of organic carbon, at low levels, in the field is a practical primary criterion for assessing samples for further organic molecular chemical analysis.

**1.2 What are geologic putative biomarkers and how do they relate to life?**

Clearly, identifying organic molecular markers for life (as we know it or not; Bartlett and Wong, 2020) is deeply challenging. Key processes relevant to generating and assessing biomarkers are illustrated in Figure 2(A). Life requires building structures, metabolizing substrates, and having an information storage and recovery system. This combination of functions necessitates specific chemical sites and structures to catalyze and control reactions. Most biochemical species degrade or cross-react upon the death of their host, but some resilient biomolecule carbon skeletons do survive diagenesis and maturation, becoming classical carbon skeleton-based molecular life markers, primarily hydrocarbons. The term hydrocarbon is inconsistently used in planetary geology/astronomy and petroleum literature. For clarity, we define hydrocarbons as chemical species made solely of hydrogen and carbon.

Relevant organic matter domains for assessing biomarkers and potential biosignatures in planetary samples are shown in Figure 2B. The figure also identifies alteration domains (discussed in Section 2) and analytical factors (discussed in Section 3), crucial for determining what is detectable in any sample. Some criteria for assessing biological origin, as opposed to abiotic organic matter production, have been detailed in prior literature (e.g., Summons et al., 2008). The classic biomarker concept, where environmental molecules closely relate structurally to specific biomolecules, is well-established on Earth (Treibs, 1937; Peters et al., 2005) and can extend to "putative biomarkers" on alien worlds where no biological precursor is identified, but general specific structural relationships suggest a biological origin.

**Figure 2.** A) Life processes and requirements resulting in the production of specific molecular structures that, if preserved, can function as biosignatures. B) OM domains relevant to the assessment of biosignatures in planetary samples.



Structural specificity is crucial for assessing biomarker status, with chirality often serving as a key criterion. Chiral centers in biomolecules play critical roles and indicate biological inheritance, yet isomerization over geological timescales in cyclic and acyclic structures limits this application. For instance, Patience et al. (1978) demonstrated that isomerization of pristane chiral centers occurs below 100 °C on geological timescales. Biological processes also fractionate isotopes of major elements, with depleted carbon isotope signatures widely regarded as indicators of biological origin. Consequently, biological signals can persist even when molecular structures are altered through diagenesis and maturation. However, many other processes, including radiolysis, can also cause significant carbon isotopic depletion (Silva et al., 2019), making isotopic signals at best potential biosignatures. Organic biosignature assessments are most effective when based on collective structural inferences, considering the alteration impacts on organic structures in the geosphere.

Recently, metrics for evaluating molecular complexity, such as assembly theory (Sharma et al., 2023), have been proposed for recognizing biosignatures. Such algorithmic approaches are very welcome, but current versions are contentious, as some minerals exhibit complexity comparable to biomarkers (Hazen et al., 2024). Additionally, organic materials in sediments undergo diagenesis and thermal maturation (catagenesis), degrading materials into lower molecular weight fragments while producing higher molecular weight condensates and diverse cross-reaction products, complicating assembly theory applications. Many surviving structures in typical samples are complex, hybrid structures with both biological and geological affinities, concealed in heterogeneous composite reaction products — CRYPTIC BIOSIGNATUREs. We suggest that assessing and decrypting these complex alteration products becomes a research priority for astrobiologists.

## 2. Alteration processes that affect organic biomarkers

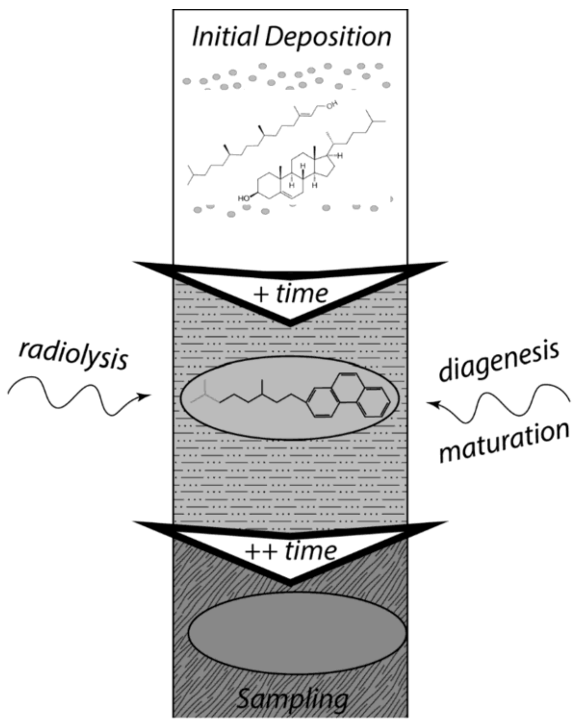
### *Diagenesis and thermal maturation*

Biochemicals on Earth are primarily reactive components, and many biochemicals from other life systems are likely to be similarly reactive, degrading through cross-reaction or being consumed/modified by indigenous biota. Early diagenesis, largely driven by microbiological and chemical reactions at low temperatures (<80°C), substantially scrambles carbon skeletons such that many cross-reaction products no longer show biologically derived structures. For example, Maillard type reactions, likely important during diagenesis, produce complex and diverse products with few remaining indications of the parent biochemicals (e.g. Oldenburg et al., 2021).

Complications dramatically increase when applying our biomarker knowledge to rocks from the Precambrian Earth or those from other planets. For example, burial temperatures for sediments in Gale Crater on Mars may exceed 100 °C (Borlina et al, 2015), necessitating consideration of diagenesis and advanced thermal maturation of organic matter as risk factors for biomarker detection. Thermal maturation of organic matter degrades biomarker structures into lower molecular weight fragments and complex hybrid structures in asphaltenes, kerogens, and other higher molecular weight fractions (Huang et al., 2022). Chiral centers are crucial in many biochemicals but can easily isomerize at low thermal maturity (cf. Patience et al., 1978). While biomarkers in hydrothermally altered rocks on Earth can retain some biogenic signatures despite thermal overprinting (Simoneit, 2004), at burial temperatures ⩾150 °C, classical biomarkers (e.g., hopanes and steranes), often decrease in concentration by two orders of magnitude or more, compared to thermally immature sections (Huang et al., 2022). The remaining structures are dominated by more biologically ambiguous, lower molecular weight fragment species, with acyclic isoprenoid species being more resilient. We contend that many modified biomarker structures are likely preserved (but currently unrecognised) in organic matter as hybrid cryptic biosignatures, containing fragments of original biomarker structures linked to rearranged carbon skeletons. These cryptic biosignatures are not easily analyzable, and even advanced techniques like multidimensional GC-MS (Ventura et al, 2008) struggle to analyze or quantify these hybrid structures. This molecular pool likely represents a large, unexplored, hidden biosignature resource, with some early attempts to examine highly altered derivative molecular signatures (Pehr et al, 2021), moving in that direction.

Figure 3 shows a schematic of the cryptic molecular biosignatures concept showing the schematic evolution of molecular markers from deposition to deep burial settings (more details in Huang et al, 2022), and ultimately sampling and analysis. Biochemicals such as isoprenoid and steroidal alcohols (as indicative terrestrial examples), are deposited and microbial and other low temperature diagenetic transformations and cross reactions produce altered products. These occur, both as free molecules such as alkanes and isomerised and aromatised biomarker derivatives and such species also react to become incorporated into condensed phases such as kerogens. Over time, and at higher temperatures (>80$^{o}$C), processes including thermal maturation and radiolysis, further alter carbon skeletons with alkyl group migrations, aromatisation, cross reaction and movement of species to and from free to condensed phases, producing a range of complex species. These include hybrid skeletons with both biomarker fragments and more scrambled carbon skeletal components (aka cryptic biosignatures). The quantitative distribution of biosignature skeletons between free and condensed phases is not well reported and is not easily analytically accessible on earth, let alone other planets. We hypothesise such hybrid, and fragmented structures may dominate biosignature populations in many planetary settings.

**Figure 3.** Schematic evolution of molecular markers from deposition to deep burial settings (more details in Huang et al, 2022).




Biochemicals such as phytol and cholesterol (as indicative terrestrial examples in the figure) are deposited and microbial and other low temperature diagenetic transformations produce altered products. These occur, both as free molecules such as isoprenoid alkanes, cholestanes and isomerised derivatives, such species also reacting to become incorporated into condensed phases such as kerogens. Over time, burial, and at higher temperatures (>80$^{o}$C), processes including thermal maturation and radiolysis, further alter carbon skeletons with alkyl group migrations, aromatisation, cross reaction and movement of species to and from free to condensed phases, producing a range of complex species with partial biosignature skeletons (cryptic biosignatures) as illustrated in the middle panel of the figure.

***Radiolysis***

Radiolysis is another significant source of alteration of organic species on weakly shielded and/or very old planetary domains like Mars. Radiolysis of organic species can occur via radiation from various sources, including host rock radionuclide decay, cosmic rays, stellar winds, or secondary radiation. Compton scattered electron avalanches, derived from high energy photon interactions, can produce reactive oxygen species in rocks, degrading common organic species, with aromatic hydrocarbons being more resistant and biomarker alkanes more readily degraded (Larter et al., 2019; Roussel et al., 2024). However, detectable levels of biomarkers survive in organic-rich settings like crude oils, even after a 10 MGy dose (Larter et al., 2019). Roussel et al. (2024) studied the impact of organic matter abundance on the extent of radiolysis in model terrestrial sediments, concluding that alteration is strongest in samples low in organic matter. This likely relates to the impacts of reactive oxygen species from water radiolysis being greatest in samples with lower organic contents, while richer samples have more organic matter remote from water-filled pores.

Radiolysis products of alkylated organic species include $^{12}C$ enriched methane with a 40‰ fractionation factor (Silva et al., 2019), indicating that isotopically light methane is not exclusively indicative of biological activity. Radiolytic polymerization/degradation cycles of $CO_2$/$H_2O$/$CH_4$ (Court et al., 2006) could, speculatively, also produce very isotopically depleted alkylated organic phases. Upon further radiolytic degradation these phases generate methane with isotopically light carbon and/or provide isotopically light condensed organic phases that may confuse Martian geochemists (Yin et al., 2023; Larter et al., 2023). Isotopic signatures can be powerful supporting evidence, but too often are ambiguous! This highlights the need for biosignature detection to be a multiproxy effort, where accumulating evidence can overcome reasonable skepticism.

### 3. Approaches to characterizing biosignatures in organic matter

Even under optimal conditions, biomarkers are trace components of sedimentary organic matter. Table 1 shows concentrations of some molecular species in a $C_6$+ fraction of crude oil from marine algal kerogens buried and heated to ~130 °C over geological time (sample described in Larter et al., 2019). The crude oil's $\delta^{13}C$ value is -28‰, supporting evidence that most carbon in the sample is from biological sources, yet major biomarker fractions (78 compounds including C19, 20 isoprenoid alkanes + $C_{20}$–$C_{35}$ terpenoid, hopanoid and steroid alkane and aromatic hydrocarbons), account for <1% of the sample mass. The most abundant cyclic biomarker compound ($C_{30}$ hopane) has a concentration of only 405 ppm! Other more abundant hydrocarbon fractions, like alkylated aromatic hydrocarbons, share the same carbon source as biomarkers, but their carbon is no longer in biological structures due to diagenesis and maturation rearranging the carbon skeletons. Crude oils contain many thousands of components (Marshall and Rogers, 2004), and largely through habit and partly due to mixture complexity, the bulk of the molecules are typically not characterised using current protocols! In general, today, most organic geochemical analytical protocols of geological samples leave much potential molecular data on the table (Radovic and Silva, 2024). Many biosignatures likely remain hidden in plain sight!

**Table 1. Concentration of molecular markers in a crude oil (wt% of sample): -**

**C9-C35 n-alkanes 3.36 wt%; C20-C35 Cyclic Biomarkers 0.61 wt%; C19-20 acyclic isoprenoid alkanes 0.26 wt%; C0-C5 alkyl-naphthalenes 1.63 wt%; C0-C2 alkyl-dibenzothiophenes 0.10 wt%; C0-C2 alkyl phenanthrenes 0.25 wt %**

In summary, original biological signals may be dilute, as with ancient samples on Earth (Brocks et al., 2023), and likely Mars, or altered by processes like diagenesis, thermal maturation (Huang et al., 2022), and, in unprotected or ancient environments, radiolysis (Larter et al., 2019; Roussel et al., 2024; Bernard et al., 2025). These processes can degrade and polymerize organic species, producing complex mixtures with numerous individual species at low concentration. Within these complex products, there are moieties (distinct fragments of larger molecules) that could retain biologically specific structures. These hybrid structures (cryptic biosignatures) may not readily appear biological with current analytical methods.

The capabilities of analytical systems for characterizing OM, either remotely on planetary surfaces or from returned samples, set the boundaries for biosignature detection in astrobiological samples. The best approaches stem from fundamental work on biomarkers by Treibs (Treibs, 1934; Peters and Moldowan, 2005), and key developments like Gas Chromatography – Mass Spectrometry (GC-MS) and legacy analytical pyrolysis (Py) techniques such as Py-GC-MS, as well as bulk flow pyrolysis methods like Rock-Eval driven by the petroleum industry during the 1970s and 80s (Espitalié et al., 1985; Larter and Horsfield, 1993). These methods were developed for organic-rich samples like source rocks with several wt% TOC. In contrast, the Sample Analysis at Mars (SAM) analysis suite on the Mars Science Laboratory Curiosity rover (Eigenbrode et al., 2018; Mahaffey et al., 2012) successfully detected organic carbon in Mars Gale crater sediments present at just nanomolar concentrations. Molecular analysis of this material was complicated for various reasons, including low levels of OM and reactive mineralogy in the host sediments (Sephton et al., 2025).

The legacy of academic and industrial research into sedimentary OM, which has been dominated by petroleum system interests, has had both positive and negative impacts on the current state of molecular assessment of astrobiological materials. Petroleum systems and astrobiology may seem disparate, but Cockell (2012; 2025) suggested that petroleum biodegradation constraints on Earth (e.g. Wilhelms et al., 2001) place comparable temperature boundaries for microbial life on planetary bodies. Ultimately, petroleum systems studies have provided significant understanding of organic signature alteration during diagenesis, maturation, and more recently, radiolysis (Larter et. al., 2019, Silva et. al., 2021).

Organic carbon compounds occur widely in planetary materials, and various methods have been used to analyse OM in extraterrestrial samples (Kebukawa et al., 2024;

Glavin et al., 2025). The analytical deficits of these approaches have been reviewed for analysis of returned samples (cf. Sephton et al., 2025). Remote detection and characterization of OM on planetary bodies, such as Ceres and Mars, have largely been achieved through remote spectroscopy (e.g. De Sanctis et al., 2017) and direct, on-site sampling and analysis (Eigenbrode et al., 2018; Freissinet et al., 2025). The SAM instrument suite was designed to assess OM composition at a molecular level using Py-GC-MS and evolved gas analysis (EGA) coupled to spectroscopy and thus be capable of examining biomarker compounds or alteration products indicative of life processes (Mahaffy et al., 2012; Stern et al., 2022). Recently, UV Raman and luminescence for OM detection was deployed on the Mars Perseverance rover via the SHERLOC instrument (Bhartia et al., 2021). This instrument suite has faced challenges from background mineral luminescence, which may complicate OM characterization in organic-lean samples (Scheller et al., 2024). The difficulties of such analyses on Martian samples are compounded by low carbon contents (Stern et al., 2022), reactive and oxidative sample matrices (Eigenbrode et al., 2018), and OM alteration from irradiation levels on candidate bodies like Mars or Ceres, where near-surface doses are in the megagray (MGy) range sufficient to degrade organic species (Pavlov et al., 2012; Larter et al., 2019; Nordheim et al., 2022; Roussel et al., 2024).

**Applications and limits of PY-GC-MS on Mars**

Whole rock thermal evolution/pyrolysis-GC-MS is a rapid technique that provides data—with minimal sample preparation—for organic-rich samples. It also offers molecular data on biomarkers in both volatile and bound species in involatile (kerogen) fractions. Variants of this approach have been widely used for sample analysis on several Mars missions—including Viking, Phoenix, and Curiosity (Huidobro et al., 2022; Ansari, 2023; Sephton et al., 2025). However, pyrolysis GC or evolved gas analysis (EGA) methods coupled to MS in organic-lean samples are affected by reactive minerals like iron oxides/perchlorates, which are highly reactive under pyrolysis conditions and oxidize pyrolysates. Additionally, minerals such as clays that sorb pyrolysates aid in cracking products to gases, aromatic species, and chars, which can eliminate useful biological signals.

There is a long history of study on the effects of sample richness and reactive matrix effects on Py-GC-MS analysis of whole rock samples. Lean samples (<1 wt% TOC) show dramatic loss and chemical modification of primary pyrolysis sample signal from isolated OM (Larter, 1985; Larter and Horsfield, 1993; Royle et al., 2022; Salter et al., 2023). Sephton et al. (2025) describe many challenges faced by remote analysis of Mars samples via evolved gas analysis and Py-GC-MS, where reactive minerals both alter pyrolysate composition and reduce usable signal intensity. Despite these challenges, Py-GC-MS and EGA-MS have been used to successfully detect organic carbon on Mars at very low levels (Eigenbrode et al., 2018; Freissinet et al., 2025) – a remarkable achievement!

Molecular signals are the hardest to detect and validate, and detection and quantitative assessment of organic carbon itself is a baseline measurement for assessing sample validity for advanced analysis on Earth. Currently, we lack robust methods for sensitive and accurate screening of organic carbon content at low levels in the field. Even if we return appropriate samples to Earth, we argue that we lack methods capable of detecting very low concentrations of highly altered biomarker skeletons dispersed in complex reaction products. There is work to be done!

**4. Geological reconnaissance to improve biosignature detection**

Characterizing organic matter (OM) at low concentrations is challenging, yet screening for potential sample return is crucial for deploying advanced methods in Earth labs. Despite numerous reports of ancient biomarkers, the oldest sediments with proven indigenous biomarkers are only about 1.7 billion years old (Brocks et al, 2023). There is fossil evidence for life older than 3.4 billion years (Dodd et al., 2017; Schopf and Packer, 1987), but this is often disputed as artefactual (e.g., Brasier et al, 2002). Claims of biotic signals from isotopically light carbon ($\delta^{13}C$ −24 per mil) in Hadean age (>4 billion years) graphite inclusions in zircons (Bell et al, 2015) are also contested (Javaux, 2019). Isotopically light carbon in ancient, metamorphosed rocks may originate from biotic sources or hydrothermal alteration of inorganic carbon (McCollom and Seewald, 2006; Bernard and Papineau, 2014). Localities like the Eoarchaean Saglek-Hebron Gneiss Complex (Canada) are believed to contain graphitic carbons from both biotic and inorganic sources (Guo et al, 2024).

In astrobiology, the most reliable biosignatures of ancient terrestrial life are microbialite structures, such as stromatolites from the ca. 3.5-billion-year-old Dresser Formation, Pilbara, Western Australia (Walter et al., 1980; Van Kranendonk, 2006). The 3D structure and scale of these stromatolites could be visible in rover images (Hickman-Lewis et al, 2022). While these features are plausible biosignatures, some stromatolite reports have been contested as deformation structures in metasediments (Nutman et al, 2016; Allwood et al, 2018). The investigation of the Isua supracrustal belt serves as a cautionary tale in the search for past life on Mars, emphasizing the need for integrated analysis of morphology, rock fabrics, and geochemistry, as well as enhancing remote detection methods. We speculate that high-frequency acoustic petrophysics, LIDAR, and AI image processing in the field could aid in sample selection for return missions.

Sampling fluid seepage sites could provide access to large subsurface volumes and improve detection of life signals. Gas and liquid seeps are common on Earth, and sampling seep plumes is crucial in the search for biosignatures on Enceladus and other gas giant moons (Soderland et al, 2020). On Mars, gas or water seepage sites are plausible, and we speculate that volatile diamondoid hydrocarbons (adamantane and derivatives), could be targets for assessing isotopic signatures of deeply sourced mobile carbon. These hydrocarbons, derived principally from thermal cracking at temperatures over 150°C (Dahl et al, 1999; Fang et al, 2013; Walters et al, 2024), are resistant to microbial degradation and radiolysis (Larter et al, 2019), and carry isotopic signals similar to source organic matter in petroleum systems.

Looking ahead, more accurate and simpler methods for initial OM assessment would facilitate sample screening before detailed analysis, reducing wasted sampling time and increasing average TOC yields per returned sample. The lack of a practical remote method for quickly measuring organic carbon in challenging lithologies hampers planetary investigation. Ideally, such a system would also provide basic chemical information on thermal maturity for sample return assessment.

Roving and stationary spacecraft on Mars have achieved remarkable success, with imaging capabilities leading to key geological discoveries and impressive inorganic and mineralogical analysis tools linked to drilling and sample recovery systems. This has enabled crucial findings about early Mars and its atmosphere, including evidence of ancient lacustrine systems (e.g., Grotzinger et al., 2014) and the recent, surprising discovery of abundant iron carbonates in Gale crater sediments that had not been detected in previous, thorough orbital mineralogical investigations (Tutolo et al, 2024; 2025). Detecting and characterizing OM on Mars is more challenging than inorganic material analysis, as OM is a trace constituent of near-surface samples, like Precambrian Earth rocks (Brocks et al., 2023), and organic molecules are generally much less well behaved and harder to analyse than crystalline mineral structures.

**5. Analytical needs and changes in strategy**

What routes exist for reliably assessing key parameters of OM content and type in lean samples on planetary bodies? Planetary rovers have been designed with a "Jack-of-all-trades" strategy, which is reasonable given the uncertainty of what to look for. On the human side, while incredibly successful, the (inter)national composition of instrument teams may have led to less optimal integration of approaches than might be possible. Now that we understand some realities of detecting organic species extra-terrestrially, specific rovers or strategies focused on organics, with enhanced mobility and higher sample throughput, seem more prudent. A revised approach could involve larger numbers of small, mobile systems (e.g., short-range aerial spacecraft like *Ingenuity*) linked to base units such as landers with complex instrumentation. Basic and rapid screening of organic carbon content could become essential for sample selection and time-intensive analysis. Given the complex mineralogy of some Martian sediments, whole rock pyrolysis methods, while practical in many ways, are not ideal, and while reagent-modified analyses have seen some operational success (Milan et al, 2022), they complicate remote operation and to date do not resolve key matrix effect issues. Innovation is needed in terms of analytical objectives and systems and the associated engineering solutions! In that sense, design should be based on objective needs rather than inheritance of prior analytical approaches.

What are the alternatives and complications of such methods, assuming organic carbon contents are low? The most direct route to OM detection would be complete oxidation to carbon dioxide. However, the Martian environment presents challenges, particularly with abundant sulfate and carbonate minerals. Fluid inclusions likely contain ancient carbon dioxide from the hydrosphere and atmosphere. Inclusion decrepitation during OM oxidation could complicate analysis, so methods must eliminate thermal processing and decrepitation of minerals. A more functional route would be low-temperature oxidation of OM, where $CO_2$ is detected by proven detectors. Generating oxidant reagents on Mars is ideal and likely sustainable. With abundant oxy-chlorine minerals, generating hypochlorite or reactive oxygen species (ROS) from water radiolysis in on-board nuclear power systems is plausible. Electrochemical oxidation is also possible, as shown by MOXIE aboard the Perseverance rover (Hecht et al., 2021).

Many approaches can be envisaged, and while spectroscopic and colorimetric methods are appealing, they must pass engineering accuracy and false positive tests. Sephton et al. (2025) summarized the need for radically new analytical systems, likening the current research and development window to that following the Apollo program announcement before lunar samples arrived. We are in a similar period of innovation if new approaches to assessing OM abundance and occurrence, both remotely and on Earth, are to be developed. Table 2 summarizes needs for remote screening methods for organic biosignatures and indicators in planetary samples, along with development areas for improved sample selection for return missions. Once again, there is work to be done!

**Table 2: Needs for remote sample screening methods for organic matter assessment in planetary samples for improved selection of samples for return missions.**

| **Screening methods-Need to have!**<br>**Assessment of:** | **Methods-Nice to have properties!** |
|---|---|
| Sample organic carbon content at trace levels and above, with enough sampling throughput for functional mapping and extrapolation of local area organic carbon content. | Quick-screening approach-preferably ex situ or remote acting. Highly mobile, potentially with flight capability and/or multiple small surface surveyors. Sample caching capability for return to lander or more complex rover-based laboratory |
| Needs mechanism for clearing surface fines to access geologically representative materials (e.g., brush or high-powered fan) | Can handle samples with labile minerals including $CO_2$ bearing inclusions. Sustainable use of local geochemistry (e.g., perchlorate salts, water radiolysis products) for oxidation chemistry. |
| Assess sample thermal maturity. | Can also assess sample organic matter type and general molecular composition. |
| Assess mineralogical complexity to assess chemical interference challenges for screening methods, as well as host-phase context. | Existing tools provide a fantastic mineralogy/ inorganic chemistry platform for next generation developments |
| Automated intelligent optical/ petrophysical imaging systems that can assess sample petrographic fabric and macroscopic structure characterisation at a scale appropriate for microbialite and fossil detection. | |

## 6. Summary and Outlook

Experience from Earth shows that even under optimal conditions, organic molecular biosignatures in ancient, altered rocks are typically present at low concentrations in planetary samples. Diagenesis, thermal maturation, and radiolysis degrade primary signals but may create secondary hybrid species that retain fragments of original biomarkers or their alteration products—CRYPTIC BIOSIGNATURES. These species could be quantitatively more viable biosignature targets, and calibrating their detection within composite reaction products should be a key focus of future research.

Selecting samples for return missions is vital. A high-volume, mobile, rapid screening system to measure total organic carbon (TOC) and thermal maturity is essential for screening samples for return or time-intensive in situ analysis. This system must function at low TOC levels amid complicating reactive mineralogy. Current organic geochemistry methods were designed around Earth sediments rich in TOC, necessitating a new suite of methodologies with enhanced sensitivity, resilient to interference and artifacts in real samples.

Examining the challenging record of biosignatures on ancient Earth is sobering. With current methods and samples, reliable molecular biosignatures are only found in relatively young sections (<2Ga), with the oldest, most plausible biosignatures being the physical evidence of stromatolites at around 3.5 Ga. The oldest claimed biosignatures on Earth are isotopically light carbon condensed phases, like graphite, found in very old rocks (Bell et al., 2015). While the origin of these isotopic signals is often contested, they represent valuable reconnaissance targets. For remote missions, less wasteful sampling strategies are needed. Searching for volatile, gas-transportable molecular markers, such as adamantanes (diamondoid hydrocarbons) at seep locations, could improve isotopic and molecular sampling of organic carbon in larger rock volumes.

The analytical capabilities of current generation rovers are impressive, but the next step in planetary research should involve dedicated and strategic chains of organic analytical systems focused on reliable and comparatively rapid screening and, through sample return, detailed molecular characterization of organic matter. New, more resilient methods for organic carbon biosignature detection are essential, and the best place to develop these is on Earth.

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