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Detection of organic matter on Mars, results from various Mars missions, challenges, and future strategy: A review

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This review paper summarizes the literature on the organic matter detection by various Mars lander/rover missions, in order to understand the progress towards dealing with methodological challenges in the analysis of the Martian regolith and drilled mudstone samples. This paper shows that Martian missions are so far successful in detecting simple and some complex organic molecules, but their origin i.e., whether sourced by cosmic dust, meteoric bombardment, geochemical reduction of inorganic carbon during hydrothermal or igneous activity, or produced biologically in the ancient habitable Martian deposition environment, remains unknown. The preservation of organic matter in the Martian depositional realm has also been found as one of the biggest hurdles in its search. Therefore, upcoming ExoMars mission has been equipped with the instruments that would be able to drill and retrieve 2 m subsurface cores for organic matter analysis, with the assumption that the subsurface samples would have better chances of preserving original organic matter from the disintegration by ultraviolet (UV) radiation, galactic cosmic rays, and solar energetic particles. In addition to the method used for organic matter detection in previous missions [simple pyrolysis-GCMS and the use of combination of thermal combustion and derivatization (thermochemolysis)-GCMS], other alternative organic matter detection methodologies i.e., Raman spectroscopy (laser 523) plus deep resonant Raman and fluorescence spectroscopy are used in Mars 2020 Perseverance rover and will be used in ExoMars mission as well. Learning from the past and upcoming Mars missions will help in developing strategies and tools for the future Martian missions with goal to better understand it is ancient habitability.

KEYWORDS

Mars, organic matter detection, Vikings, Phoenix, Curiosity, ExoMars, extraterrestrial life, Perseverance

Introduction

There is compelling evidence that during the first half-billion years (4 to 3.5 Ga), Mars was wetter i.e., its surface and shallow subsurface hosted liquid water (Nisbet and Sleep, 2001; Baker, 2006; Greenwood et al., 2008). As a result, Mars has become the most promising target for astrobiological studies. However, the major question is how long this water must persist for life to evolve. Based on the Earth's geological record the estimated upper limit for the origins of life is considered 500 million years (Davis and McKay, 1996). Using a simple climate model, Davis and McKay (1996) determined that liquid water habitats on Mars could have survived for up to 500 million years under relatively thin ice covers with an atmospheric temperature below freezing point. Thus, the timeframe for liquid water on early Mars appears to be equivalent to the maximum timeframe for the emergence of life on Earth (Davis and McKay, 1996). In the last 20 years, the scientific search for life on Mars has been taken on two major aspects: 1) exploring the Martial geological records for probable evidences of extinct life, 2) looking for signs of extant microbial life on Mars surface and subsurface environments. Progress has been made in both the directions. However, the search for extinct life on Mars has received more attention (Carrier et al., 2020) mainly due to the fact that early Martian condition was relatively more hospitable for life (Fairén et al., 2010).

There is a general consensus that life, if it exists elsewhere, is based on carbon chemistry, needs nitrogen, highly information-rich organic compounds, energy, substrates that allow for the synthesis of the organic compounds, and liquid water (Marais and Walter, 1999; Schulze-Makuch et al., 2002; Stern and Jedrzejas, 2008). Therefore, understanding how organic substances are synthesized abiogenically throughout the universe also piques our intrinsic curiosity (Oparin, 1965; Lemmon, 1970; Becker et al., 1999; Sephton and Hazen, 2013). Organic molecule signatures of early life on Earth are largely destroyed by tectonic recycling. Such tectonic recycling of early biotic or pre-biotic organic signatures on Mars seems unlikely as no evidence of past tectonic activity has been recorded on this planet (Mahaffy, 2008). However, the presence of superoxide radicals (Yen et al., 1999; Yen et al., 2000), oxidized halides (Zent and McKay, 1994; Hecht et al., 2009), and radiation (Kminek and Bada, 2006) on the Martian surface may have transformed organic molecules, reducing the diversity of such compounds from earlier periods and limiting our ability to describe their origin. It is nonetheless important to note that the type of organic material found on Mars has a direct bearing on two most important scientific questions: 1) how life arose on Earth and, 2) how life in the universe may have originated. For this reason, several missions have been sent or are under preparation to Mars for the detection of organic compounds in surface/subsurface sediments and the atmosphere.

Several Martian meteorites and Martian surface sediments have been found to contain organic carbon, but their origin remains unclear (Biemann et al., 1977; Mazur et al., 1978; Steele et al., 2012; Glavin et al., 2013; Freissinet et al., 2015; Eigenbrode et al., 2018; Franz et al., 2020; Millan et al., 2022a; Millan et al., 2022b; Stern et al., 2022). There have been a number of sources proposed for the detected organic compounds: 1) terrestrial contamination (Biemann et al., 1977; Mazur et al., 1978; Jull et al., 1998); 2) chondritic meteoric inputs (Becker et al., 1999); 3) direct precipitation from aqueous fluids (Steele et al., 2007; Ming et al., 2014; Eigenbrode et al., 2018; Franz et al., 2020; House et al., 2022; Stern et al., 2022); and, 4) biotic remains (McKay et al., 1996). By confirming and understanding the origin and formation of organic carbon on Mars, we will be able to improve our understanding of its putative carbon cycle, the availability of carbon for biotic chemistry, life detection, and how to detect organic compounds on future extraterrestrial missions (McKay et al., 1996). This review article is focused on the published results of Martian hydrocarbon detection missions: Vikings, Phoenix, Curiosity, and Perseverance, highlighting the challenges in detecting indigenous organic carbon on Martian surface, determining their origin, and developing strategy for the future missions.

Existence of water and its role in the evolution and persistence of life on ancient Mars

In contrast to contemporary Mars, which is an aeolian planet containing intermittent liquid water on its surface (likely brines), ancient Mars appears to have had localized habitats that were compatible with the needs of putative early life similar to that existed on Earth (Grotzinger et al., 2014; Grotzinger et al., 2015). Based on crater counts, water channels on the Martian surface are estimated to have formed intermittently between 0.5 and 3.5 billion years ago (Malin, 1976; Masursky et al., 1977). This ancient fluvial areas are unlikely to have been relevant to the current life but might have played a significant role in the evolution of organic compounds and the possible existence of past life. However, the existence of liquid water on the Martian surface was probably sporadic and might have been too brief to allow life to emerge and flourish. So even if a large quantity of water might have flowed during these episodes, it would have vanished in a matter of weeks due to high evaporation rates (Masursky et al., 1977). However, the observations do not rule out the possibility that, in local oases, a steady production of liquid water could have counterbalanced the high evaporation rates and permitted the long-term existence of liquid water (Mazur et al., 1978; Grotzinger et al., 2015).

Findings from Martian meteorites

The presence of organics in meteorites apparently ejected from Mars has been investigated in several studies (McSween Jr, 1994; McKay et al., 1996; Sephton et al., 2002; Steele et al., 2007; Steele et al., 2012; Steele et al., 2016; Eigenbrode et al., 2018). These include reports of organic volatile substances such as benzene, toluene, C2 alkylbenzene, and benzonitrile found by pyrolysis GCMS in Nakhla (Sephton et al., 2002) and polycyclic aromatic hydrocarbons (PAHs) in the Antarctic Martian meteorite ALH 84001 (McKay et al., 1996). Sephton et al. (2002) identified no organic pyrolysis products in their samples of ALH 84001, although they did discover aromatic organics in EET A79001. In this type of study, the amount of terrestrial contribution to Martian meteorites' organic matter during their residence on Earth (102–104 years) was a primary concern. For PAHs (Becker et al., 1997), amino acids (Bada et al., 1998), and acid-insoluble organic material (Jull et al., 2000), this issue has received considerable attention. Nevertheless, the extent of terrestrial contamination can be assessed by analyzing the environment from which the meteorite was collected, looking for molecules that appear to have been produced abiotically, and measuring carbon and hydrogen isotopes accurately (Mahaffy, 2008; Elsila et al., 2011; Aponte et al., 2014; Elsila et al., 2016; Glavin et al., 2021).

There has been evidence of macromolecular carbon (MMC) in Martian meteorites dating back from 4.2 Ga to 190 Ma (Borg and Draper, 2003; Lapen et al., 2010). Hirschmann and Withers (2008) postulated that carbon cycling in the Martian environment was dominated by its consumption in the reduced mantle which would have limited the release of CO_2 to the Martian atmosphere. The presence of MMC species in reduced igneous rocks (Steele et al., 2012) supported the central tenet of Hirschmann and Withers (2008). In contrast, the absence of MMC in inclusions in the most oxidized

TABLE 1 Major Mars Lander missions and their organic analysis results.

Mission	Year of landing	Experiment site	Instrument	Pyrolysis temperature	Method	Detected organic molecules	References
Viking	1975	Chryse Planitia, Utopia Panitia	GCMS	up to 500°C	Pyrolysis	No trace of hydrocarbons	Biemann et al. (1977), Mazur et al. (1978)
						0.7–6.5 ppm organic carbon	Reanalysis by Navarro-González et al. (2010)
Phoenix	2008	Vastitas Borealis, the arctic plains of Mars	GCMS	up to 820°C	Pyrolysis	No trace of hydrocarbons	Lauer et al. (2009)
Curiosity	2011	Rocknest aeolian deposits, Gale Crater	GCMS and Tunable Laser Spectrometer (TLS)	up to 835°C	Derivatization + Pyrolysis	Chloromethane, Dichloromethane, Trichloromethane, Chloromethylpropene, and Chlorobenzene	Glavin et al. (2013), Leshin et al. (2013), Ming et al. (2014)
		Sheepbed Lacustrine mudstones, Murray Formation, Pahrump Hills, Gale Crater	GCMS and TLS	up to 820°C	Derivatization + Pyrolysis	Dichloroethane, Dichloropane, Dichlorobutane, Thiophene, Methylthiophene, Benzene, Chlorobenzene, Toluene, Benzoic Acid, Menthanethiol, Dimethylsuplhide	Eigenbrode et al. (2018), Freissinet et al. (2015), Szopa et al. (2020)
		Glen Torridon, Gale Crator	GCMS and TLS	up to 850°C	Derivatization + Pyrolysis	Benzoic Acid, Phenol, Benzene, Toluene, Trimethyl- and Tetramethylbenzene, Naphthalene, Methylnaphthalen, Pentamethylbenzene, Benzoic Acid Methylester, Dimethyl-, Trimethyl-, and Tetramethylbenzenamine, Dihydronaphthalene, 2-Butylthiophene, and Benzothiophene	Millan et al. (2022a); Millan et al. (2022b)
Perseverance	2020	Jezero Crater, Nili Fossae region	Deep Ultraviolet Fluorescence and Raman spectrometry	No-pyrolysis	Deep Ultraviolet Fluorescence and Raman spectrometer scanning	Benzene, Naphthalene	Scheller et al. (2022)

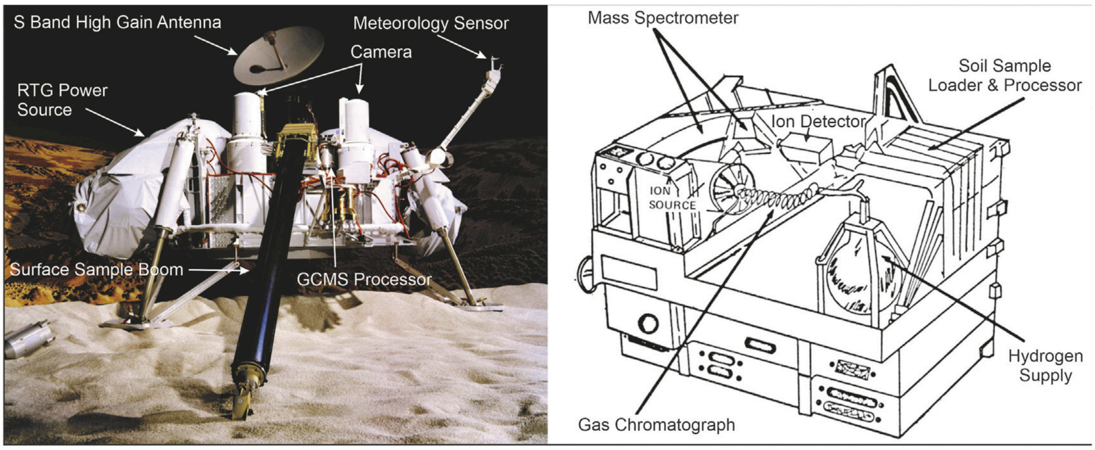
sample (Nakhla) illustrates the possibility that the redox state of the Martian magmas might affect the preservation of these carbon species during crystallization (Sephton et al., 2002). This has implications for the distribution of MMC on Mars surface and within its crust (Michalski and Niles, 2010; Morris et al., 2010).

No evidence of CH_4 or CO_2 has been reported from igneous inclusions of Martian Meteorites (Steele et al., 2012). Although there is some skepticism about its existence at all (Zahnle et al., 2011), CH_4 has been found in the Martian atmosphere and has been explained by both abiotic and biotic processes (Atreya et al., 2007; Mumma et al., 2009; Webster et al., 2018). According to Steele et al. (2012), occurrence of MMC in igneous rocks could be used as a supporting evidence for abiotic generation of CH_4 (Atreya et al., 2007; Mumma et al., 2009). The discovery of ~190 million years old MMC-containing Martian meteorite, suggests that reduced organic carbon production on Mars has been active in the recent past and it is possible that the Martian carbon cycle may still be active (Steele et al., 2012). Furthermore, according to Steele et al. (2012), primary organic carbon is almost always present in Martian basaltic rocks. It was transported to the surface over the majority of Martian geologic history, as recently as ~190 million years ago, through igneous mechanisms rather than biological ones. Photolysis of organic carbon (MMC) in the surface sediments or rocks can be a possible abiotic source of CH_4 in Martian atmosphere (Keppler et al., 2012; Schuerger et al., 2012).

Findings from various Martian missions

Viking mission

The main goal of the Viking mission was to look for signs of current or past life on Mars (Biemann et al., 1977; Mazur et al., 1978). Viking found clear evidence of the presence of water vapour and water ice, as well as strong inferences that there was once a significant amount of underlying permafrost on Mars. But it found no indication of existing liquid water with the high chemical potential necessary for the survival of terrestrial life, which is in line with the known pressure-temperature relations on the planet's surface (Mazur et al., 1978). The elemental analysis of the atmosphere and regolith revealed that the chemical elements typically thought to be necessary for terrestrial life are present (Mazur et al., 1978). Viking's GCMS studies carried by Biemann et al. (1977) and Mazur et al. (1978) found no unambiguous indigenous organic compound. According to Biemann et al. (1977) and Mazur et al. (1978), minor traces of volatile chloro-hydrocarbons detected in Martian regolith samples (Table 1) by the Viking's GCMS



Viking Lander

Viking's GCMS

FIGURE 1
Viking Lander and GCMS instruments [sources: Huidobro et al. (2022) and NASA (2010)].

(Figure 1) was a result of terrestrial contamination. Furthermore, they stated that if volatile organic compounds were present in the regolith samples, they were either limited to substances like methane, which were undetectable or only detectable at low sensitivity levels, or they were present in concentrations below the detection limit of the instrument.

The reasons for the negative results of Viking's GCMS in detecting the presence of indigenous organic compounds were debated in subsequent studies (Benner et al., 2000; Glavin et al., 2013). According to Benner et al. (2000) and Glavin et al. (2013) the Viking's GCMS design was not optimized for the detection of certain potential hydrocarbons found in Martian meteorites (Sephton et al., 2002) which could have been present in the Martian samples. Benner et al. (2000) re-examined the Viking's GCMS results in light of what is known about the oxidation of organic compounds more generally as well as the makeup of organics that are likely to arrive on Mars *via* meteorite. They came to the conclusion that non-volatile salts of benzenecarboxylic acids, as well as possibly oxalic and acetic acid, should be metastable intermediates of meteoritic hydrocarbons under oxidizing conditions. For the Viking's GCMS, the salts of these non-volatile organic acids would have been largely undetectable, as the organic molecule must first go through a GC in order to access the MS, which is only possible for volatile molecules. Under pyrolysis, oxalic acid produces carbon dioxide, carbon monoxide, and water (Lewis et al., 2021). In fact, all of these were detected in the Viking's GCMS, but all these molecules are also present in the Martian atmosphere. Thus, Benner et al. (2000) and Mahaffy (2008) presented three possible reason for the failure of Viking's GCMS in detecting indigenous organic matter in the Martian regolith's: 1) the design of the gas-processing system that safeguarded the vacuum ion pumps decreased the GCMS's sensitivity for light organic compounds by a factor of 1,000; 2) the Viking GC column would not have transmitted numerous kinds of polar organic compounds, such as carboxylic acids, which are probably oxidation products of aliphatic and aromatic hydrocarbons; 3) instead of less permeable materials that would have been better protected from oxidants, the Viking sample-acquisition device could only collect loosely consolidated particles samples.

After the discovery of perchlorate in the Martian arctic soils by the Phoenix lander (Hecht et al., 2009), Navarro-González et al. (2010) ran an analogous experiment in which they heated the Mars-like soil from the Atacama desert containing 32 ppm of organic carbon with 1% magnesium perchlorate and demonstrated that nearly all of the organic present in the samples were decomposed to CO_2 and water, with the production of chloromethane and dichloromethane in trace amounts. Navarro-Gonzalez reconsidered the analysis results and suggested the burning of Martian soil sample would essentially decompose all the organics into water and CO_2. Based on this experiment they developed a chemical kinetics model for the degree of oxidation and chlorination of organics in the Viking oven and re-analysed the Viking results. According to Navarro-González et al. (2010) re-analysis results, ≤0.1% perchlorate and 1.5–6.5 ppm organic carbon were present in the sample of Viking landing site 1, and ≤1% perchlorate and 0.7–2.6 ppm organic carbon were present in the sample of Viking landing site 2 (Table 1).

Phoenix mission

Phoenix mission touched down on Mars' polar surface in March 2008 on a valley floor covered by the Scandia Formation, which is thought to be an ancient deposit from the Amazonian period (Arvidson et al., 2008; Smith et al., 2009). This formation encircles the northern edge of a shield volcano called Alba Patera (Arvidson et al., 2008). Phoenix heated soil and ice samples in the Thermal and Evolved-Gas Analyzer (TEGA) (Figure 2) in order to look for organic compounds (Boynton et al., 2009). For a mass range of 2–140 daltons, TEGA was made up of eight differential scanning calorimeter (DSC) ovens that were connected with a mass spectrometer (Boynton et al., 2009). The TEGA DSC monitored endothermic and exothermic processes when samples were heated from ambient temperature to roughly 1,000°C. Throughout the heating process, the mass spectrometer simultaneously detected all evolved gases, including any organic compounds and their byproducts.

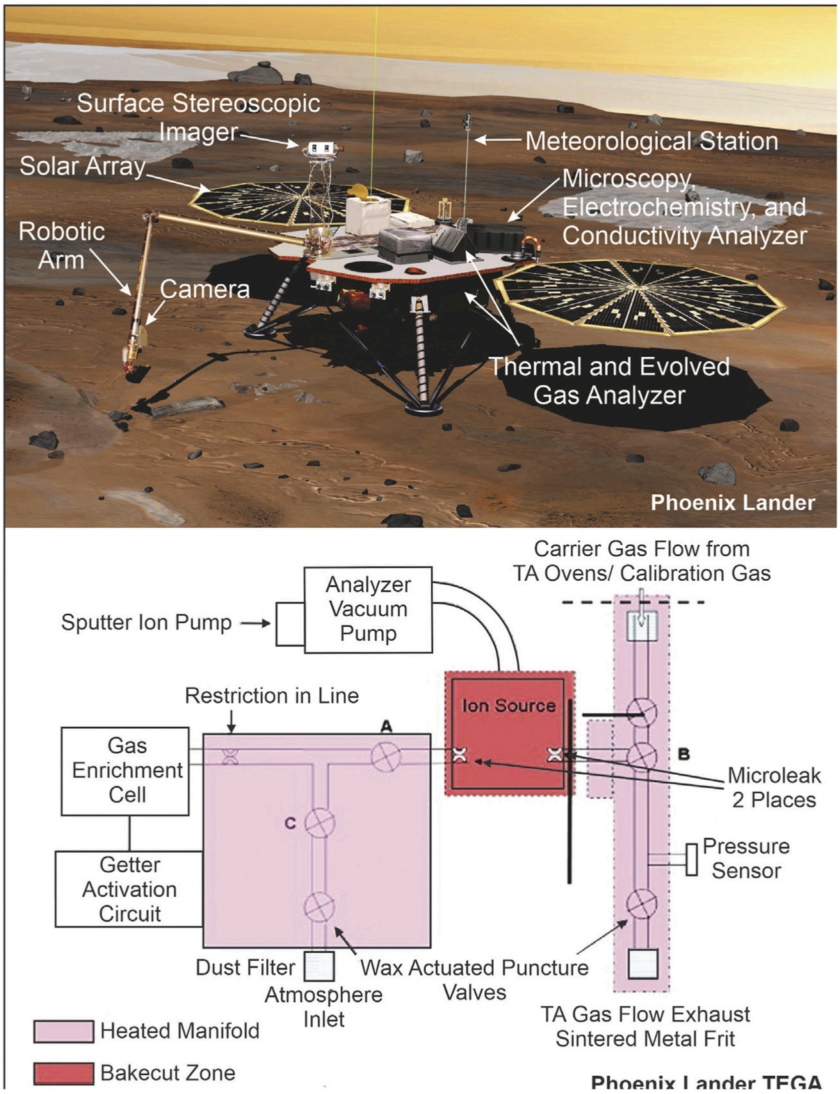


FIGURE 2
Phoenix Lander and TEGA instruments [sources: Huidobro et al. (2022) and NASA (2008)].

The evolved gas analysis (EGA) using Phoenix TEGA data did not reveal any organic fragments (Lauer et al., 2009; Ming et al., 2009). A perchlorate salt was found in the soil of Mars by the Microscopy, Electrochemical and Conductivity Analyzer (MECA) and Wet Chemistry Lab (WCL) (Hecht et al., 2009). It is probable that the O_2 generated during the thermal decomposition of the perchlorate salt ignited organic fragments evolved in the temperature range of 300°C–600°C. During the heating, CO_2 was produced as a byproduct of the burning of organic molecules. According to Ming et al. (2014), the possible causes of low temperature release of CO_2 in Phoenix TEGA could be desorption of adsorbed CO_2, thermal breakdown of Fe- and Mg-carbonates, and combustion of organic molecules in the Martian soils.

Curiosity mission

This is one of the strongest and long-standing missions which landed on Mars (in August 2012) in Aeolis Palus area inside Gale Crater. The main goal of Curiosity is to search the possible traces of life on Mars using the Sample Analysis Mars (SAM) lab suite it carried (Figure 3). SAM onboard the Curiosity rover has the capability to detect complex hydrocarbon molecules having astrobiological implication, by coupling the EGA and GCMS with two type of wet chemistry methods: 1) organic derivatization by adding N-methyl-N-(ter-butyldimethylsilyl) trifluoroacetamide (MTBSTFA) and dimethylformamide (DMF) in 4:1 by volume, 2) organic derivatization by adding 25% tetramethylammonium hydroxide (TMAH) in methanol (Millan et al., 2022a; Millan et al., 2022b). Glavin et al. (2013) reported first SAM-EGA-GCMS data of a Martian solid sample, from Rocknest aeolian deposit of Gale Crater and provided an extensive discussion on the possible origins of chlorinated hydrocarbons detected by SAM. Their studies detected several chlorinated chemical species above EGA background concentration including hydrochloric acid, chloromethane, and dichloromethane (Table 1). As these chlorinated organic species were not detected in the blank EGA

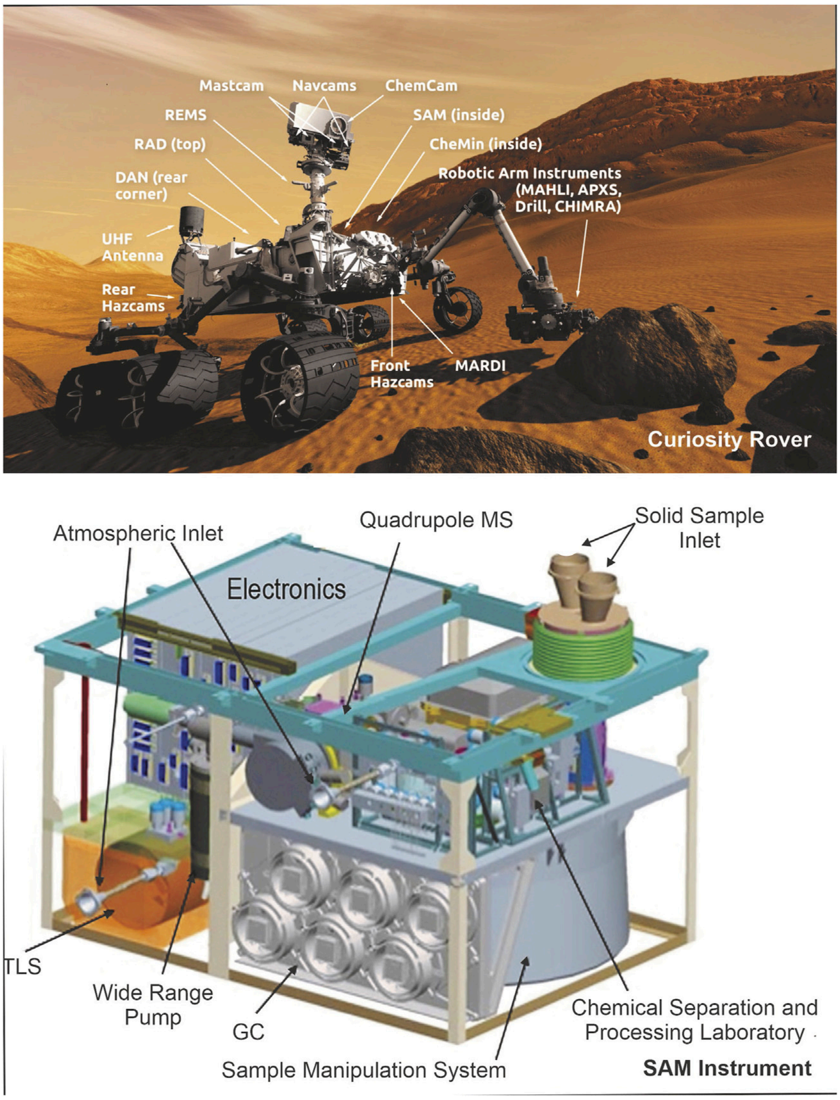


FIGURE 3
Curiosity Rover and SAM instruments [sources: Huidobro et al. (2022) and NASA (2012)].

run of SAM, the source of this organic carbon was combustion of reduced carbon in the presence of oxygen from oxychlorine. In the blank run 1,3-bis (1,1-dimethylethyl)-1,1,3,3-tetramethyldisiloxane and tert-butyldimethylsilanol were detected by GCMS. These two compounds are the fragmentary products of MTBSTFA (Glavin et al., 2013; Leshin et al., 2013; Millan et al., 2022a; Millan et al., 2022b). Therefore, it is assumed that the MTBSTFA and DMF vapor was perhaps leaked and reacted either with terrestrial or Martian water during the pyrolysis. A major difference between the peaks of 1,3-bis(1,1-dimethylethyl)-1,1,3,3-tetramethyldisiloxane for blank run and Rocknest sample run was that during the pyrolysis of the Rocknest sample, the peak intensity of 1,3-bis(1,1-dimethylethyl)-1,1,3,3-tetramethyldisiloxane sharply decreased with increase in O_2 peak. This according to Glavin et al. (2013) was a result of MTBSTFA decomposition along with the chlorate minerals present in the samples which may have contributed to some chlorinated hydrocarbons. However, GCMS analysis of Rocknest samples after pyrolysis detected chlorinated hydrocarbons such as chloromethane, dichloromethane, trichloromethane, choromethylpropene, and chlorobenzene (Table 1) significantly above the background level recorded in black run (Glavin et al., 2013). The concentration of chlorohydrocarbons detected by EGA-GCMS was more than 50 times higher than detected by the Viking-GCMS (Biemann et al., 1977). But, this comparison of detected concentration by the Viking and SAM is less relevant as unlike SAM, Viking did not carry derivatizing agent MTBSTFA. Nevertheless EGA-GCMS analysis at various pyrolysis temperature cut (>500°C) demonstrated that light chlorinated hydrocarbons can be effectively purged from SAM gas processing unit between the analyses. Chlorobenzene was also detected in the blank GCMS run of SAM and to some level above in the Rocknest samples. Its most likely source has been traced to thermal degradation of SAM organic trap (Tenax TA) containing 2,6-diphenylphenylene oxide which can produce Benzene, Toluene, and lesser amount of biphenyl. Hence its sourcing from Rocknest sample was suggested unlikely (Glavin et al., 2013).

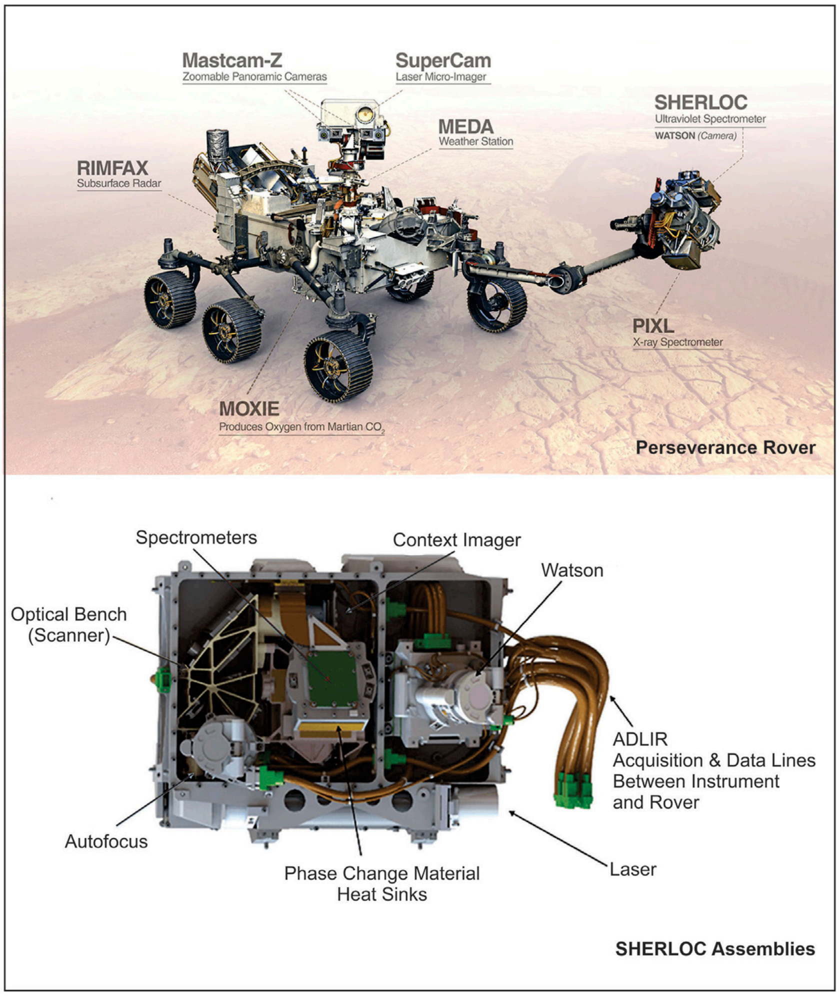


FIGURE 4
Perseverance Rover and SHERLOC instruments [Huidobro et al. (2022) and NASA (2020)].

Based on the results from EGA-GCMS, Freissinet et al. (2015) reported detection of 150–300 ppb chlorobenzene and up to 70 ppb C2-C4 dichloroalkanes in several locations of the Cumberland drill hole in the Sheepbed Mudstone at Yellowknife Bay (Table 1). Their findings indicate that when combined with EGA-GCMS data from multiple scooped and drilled samples, blank runs, and laboratory analogs, the relatively high concentrations of dichloroalkanes and chlorobenzene cannot be a result of the instrument's internal sourcing. The Sheepbed Mudstone may contain chlorohydrocarbons as such (Szopa et al., 2020), but they are thought to be the products of chemical reactions occurring during pyrolysis between Martian oxychloride and the sample's organic compounds. The finding of chlorinated organic molecules close to the surface indicates that reduced organic material with covalent bonds has endured despite the presence of several oxidants and high-energy radiation exposure due to the thin Martian atmosphere. Thus, the outcomes of the Freissinet et al. (2015) studies made a significant contribution to identifying possible preservation windows for reduced organic molecules on the Martian surface. In addition, this perspective on ancient Mars offers some context for a potentially habitable environment and represents a first step toward comprehending the existence and variety of potential prebiotic or biotic chemical fingerprints.

To circumvent the perchlorate degradation product of organic matter in the Martian sample analysis, Eigenbrode et al. (2018) analyzed the gases produced exclusively above 400°C, as salt present in the Martian regolith breakdown during heating to a temperature of 200°C in the SAM. Their results provided unambiguous evidence of organic molecules such as thiophenic, aromatic, and aliphatic hydrocarbon from the drill samples of Gale Crater. These sulfur-bearing hydrocarbons are considered to have originated from Mars surface (i.e. igneous, hydrothermal, atmospheric, or biological) and indicates presence of refractory organic materials in the samples (Freissinet et al., 2015; Eigenbrode et al., 2018).

The MTBSTFA derivatization experiment on Mars performed on Ogunquit Beach dune samples of Gale Crater detected several molecules containing benzoic acid, phenol, ammonia and phosphoric acid structures (Millan et al., 2022a; Millan et al., 2022b). Such molecules were either sourced from organic molecules on surface and subsurface environment due to strong oxidizing condition or from MTBSTFA present in SAM

TABLE 2 Lab based flash pyrolysis (at > 500°C) products of derivatization agents MTBSTFA and DMF (He, 2021).

Derivatization agent	Pyrolysis temperature (°C)	Derived organic compound	Reference
MTBSTFA	600	Difluorodimethylsilane, 4-methyl-1-hexene, Tert-Butyldimethylsiyl fluoride, Tert-Butyldimethyksilyl 2,2,2- trifluoroacetate, O-(trimethylsilyl)phenol, Tert-Butyl-isocyanatodimethylsilane, N-methyl-N-(trimethylsilytrifluoroacetamide, 1,3-ditert-butyl-1,1,3,3,- termethyldisiloxane, Pentamethyldisiloxane, Bis(trimethylsiloxy)methylsilane, Tris (trimethylsilyl) borate, Bis [tert-butyl (dimethyl)silyl]oxalate	He (2021)
	850	Methyltrifluorosilane, Tert-Butyldimethylfluorodilane, Fluorobenzene, 1, 4-difluoro-Benzene, Benzene, Trifluoromethybenzene, N-methyltrifluoroacetamide, Pyridine, Toluene, Isocyanatotrimethylsilane, O-(Trimethyl)phenol, Ethylbenzene, Tert-Butyl-isocyanatodimethylsilane, Styrene, 2-Propenylbenzene, 3-methyl-Benzonitrile,2 -Methyl-naphthelene, Biphenyl, Acenaphthylene, Phenanthrene, Pyreneetc.	
DMF	600	N, N-Dimethylformamide, Trimethylamine, Dimehtylamine, Ethanolamine, N,N,N′,N′-Tetramethylmethanediamine, Dimethylaminoacetonitrile, Styrene, Hydracrylonitrile, Benzene, Naphthaleneetc.	
	800	N, N-Dimethylformamide, Styrene, Hydracrylonitrile, Benzene, Naphthaleneetc.	

background or both (Millan et al., 2022a; Millan et al., 2022b). First TMAH experiment on Mars was performed at Mary Anning (MA) drill site in the Glen Torridon region of Gale Crater that detected a range of hydrocarbons e.g., benzene, toluene, trimethyl- and tetramethyl-benzene, naphthalene, methylnaphthalene, pentamethyl-benzene, benzoic acid methyl ester, dimethyl-, trimethyl-, and tetramethyl-benzenamine, dihydronaphthalene, 2-butyl-thiophene, and benzothiophene (Millan et al., 2022a; Millan et al., 2022b) (Table 1). As TMAH is a methylating agent that break polar bonds and methylate pyrolysis products *in situ*, suggests that hydrocarbons might have derived from macromolecules which was methylated by TMAH thermochemolysis. In this way pentamethyl benzene could be a product of multimethylation during TMAH reaction. Benzoic acid is detected both in SAM background and Mars samples, therefore its TMAH methylated product benzoic acid methyl ester is of currently unknown sources. The benzenamine may have originated on Mars or it could be a result of benzene reacting again with the N in TMAH. In addition, thiophene has been found in both refractory and mature organic phases in Martian meteorites (Steele et al., 2016; Eigenbrode et al., 2018). Hence, thiophenes found on Mars are thought to be pyrolysis breakdown products from various macromolecules.

Perseverance

The Perseverance rover (Figure 4) was launched by NASA in 2020 (Farley et al., 2020) in an effort to determine the potential habitability of Mars and possible evidence of past life. This mission landed (on February 2021) at Jazero Crater, a 45 km diameter impact structure in the Nili Fossae region of Mars, where a lake and river delta existed approximately 3.5 billion years ago (Mangold et al., 2007; Goudge et al., 2012; Goudge et al., 2015; Goudge et al., 2017; Farley et al., 2020). The main instrument onboard Perseverance to detect signs of past life is SHERLOC (Scanning Habitable Environments with Raman and Luminescence for Organics and Chemicals) (Hollis et al., 2021; Hollis et al., 2022). SHERLOC (Figure 4) uses a deep ultraviolet (DUV) laser to detect fluorescence emissions from aromatic compounds, as well as Raman scattered photons to identify organic functional groups, chemicals, and minerals (Bhartia et al., 2021). This enables SHERLOC to improve Martian studies by analyzing the abundance and variety of organic matter at the fine scale in different minerals to comprehend the potential for organic matter preservation in the Martian surface soils/outcrops, and help resolving organic biosignatures such as hopanes, steranes, and other organic macromolecules (Abbey et al., 2017; Bhartia et al., 2021). SHERLOC's micro-mapping mode allows non-destructive, sub-picogram sensitive organic detection (Bhartia et al., 2010) to identify smaller-scale features. In order to confirm that all the observed spectral characteristics are intrinsic to the material, the spectrometer's dust cover will occasionally be opened, and the instrument laser will be fired into the starry night sky (Bhartia et al., 2021). This method makes it possible to assess and eliminate any slight spectrum contamination from the optics or signature from Mars dust pollution deposited on optics from the data processing pipeline. Raman and Fluorescence data from first 208 Martian days of Perseverance on Mars has recently been published by Scheller et al. (2022). These analysis were conducted on three rock targets in two lithological units of the Jazero Crater floor. Reports of detailed scanning of the three samples by Scheller et al. (2022) demonstrated presence of carbonate, sulfate, phosphate, amorphous silicate bearing minerals in association with aromatic organic compounds most likely single- and double-ring aromatics. Carbonation of olivine in presence of briny water has been interpreted as an origin of carbonate minerals, whereas sulfate and perchlorate in the subsurface samples are indicated to have formed by precipitation from briny water. Presence of aromatic organic compounds in all the three targeted rocks is suggested by DUV analysis however, Raman analysis was unable to detect presence of organic compounds most likely due to insufficient organic matter concentration.

Future Mars sample return

For more than 4 decades, the planetary science community has placed a high focus on Mars Sample Return (MSR) (Beaty et al., 2019). By analyzing Mars samples in terrestrial laboratories, we could gain a greater understanding of Mars than we could achieve with just *in situ* missions. Perseverance is capable of collecting samples to return to Earth. In support of its goal to collect sample for possible future Earth return, Perseverance carries an entirely new sampling and catching subsystem (SCS) (Townsend et al., 2022). SCS is used to collect rock core and regolith samples into individual ultraclean and sterile tubes, to photo-document and assess the collected volume of each sample, and to hermetically seal each tube. The sample tube can be manipulated through a sophisticated internal robotic mechanism called the Adaptive Catching Assembly (ACA) (Townsend et al., 2022), which can place the tube on the surface individually, at any time, and in one or more locations from which they can be retrieved. To maximize the likelihood of success of the Mars Sample Return (MSR) campaign duplicates have been collected for each particular target rock. One copy will be deposited at the end of the prime mission in the Jazero deposit identified at Three Forks, to ensure their availability for return to Earth in case Perseverance fail in the future. The second copy will be carried in the rover during its extended mission, with aim of collecting additional samples that the rover will directly deliver to the lander of the retrieval mission. The Mars 2020 science team has identified two hypothetical sample caches in order to examine: 1) the geology of the Jezero Crater, which will be collected during the prime mission, and, 2) the ancient crust outside of the Jezero Crater, which will be collected during a potential extended mission (Herd et al., 2022). The recent successful sample collection by the Perseverance rover and ongoing work by the National Aeronautics and Space Administration (NASA) and European Space Agency (ESA) on developing missions that could retrieve and transport the samples to Earth have put MSR on track to become a reality (Kminek et al., 2022).

Preservation of organic matter on Mars surface

Comets, asteroids, meteorites, and interplanetary dust particles deliver organic compounds to planetary surfaces abiotically (Chyba and Sagan, 1992; Ehrenfreund et al., 2011). Based on scaling the terrestrial influx to a Martian scenario and measurements of the Martian atmosphere, the estimated current influx of abiotic organic molecules to the surface of Mars is around 100–300 tons per year (Eigenbrode et al., 2018). Given that majority of the Martian surface is covered by billions of years old rocks (Carr and Head, 2010), it must have received abundance of organic molecules over this time span. But various Mars lander missions so far found it challenging to detect organic molecules unambiguously on the Martian surface. This suggests a more rapid degradation (by ionic radiation or oxidizing agents) of organic matter than accumulation. However, the crystal structures of minerals found on Mars, such as sulfates and clay minerals, may retain organic molecules, shielding them from the hostile environment (Keil and Mayer, 2014).

The results of the Mars missions to date mostly point to the existence of powerful oxidants and ultraviolet light, which can significantly shorten the residence period of organic matter on the Martian surface and represent the biggest barrier to its identification using *in situ* techniques. However, recent evidences of organic compounds from SAM observations (Glavin et al., 2013; Freissinet et al., 2015; Eigenbrode et al., 2018; Millan et al., 2022a; Millan et al., 2022b) demonstrate the possibilities and ways to detect *in situ* organic matter on Mars. Moreover, Applin et al. (2015) found that oxalate minerals are particularly susceptible to accumulation at the surface, as their experiments indicate they are as stable to UV radiation as sulfates and carbonates. Other significant degrading agents for organic materials on Mars are solar energetic particles and galactic cosmic rays which are more powerful than UV as its influence can extends much deeper (up to 9 m) in the subsurface than UV light (Pavlov et al., 2002; Dartnell et al., 2007b; a; Pavlov et al., 2012; Pavlov et al., 2022).

According to Fornaro et al. (2018), it is extremely difficult to develop a general mechanism to predict the behavior of Martian minerals. However, an accurate simulation of Martian environment considering all the key factors would contribute significantly to understanding the trends. Studies of organic matter association with different mineralogy have shown that some minerals aid in organic preservation while others speed up their degradation (Fornaro et al., 2018; Brucato and Fornaro, 2019). For instance, Poch et al. (2015) found that when adenine and glycine molecules were exposed to mid-UV irradiation in iron (III) smectite clay and non-tronite at very high molecule-mineral mass ratios, the effectiveness of the two organic molecules' photodecomposition was reduced by a factor of 5. This suggests not only physical shielding by non-tronite but also organic molecules stabilization by their interaction with the minerals allow recombination of dissociated organic molecule fragments (Poch et al., 2015). Furthermore, dos Santos et al. (2016) studied preservation of 25 amino acids in various minerals like olivine, enstatite, goethite, hematite, gypsum, jarosite, labradorite, augite, montmorillonite, non-tronite, and saponite, as well as basaltic lava. In their studies, clay minerals were found to exhibit amino acid-protective properties. The typical characteristics of clay minerals, such as their high surface area, which promotes molecular adsorption, their small pore sizes, which prevent radiation from penetrating, and their ideal interlayer sites for the accommodation of organic compounds, which create a shielded environment against external agents, were used to explain this behavior (dos Santos et al., 2016). Such minerals have been detected at several sites on Mars (Bishop et al., 2008; Ehlmann et al., 2009; Ehlmann et al., 2011a; Ehlmann et al., 2011b; Noe Dobrea et al., 2012; Carter et al., 2013; Ehlmann and Edwards, 2014; Vaniman et al., 2014; Adeli et al., 2015; Michalski et al., 2015) which has also been seen as a trace of past active hydrosphere. Millan et al. (2022b) discovered that highest diversity of organic molecules in Martian soil was associated with samples having highest proportion of clay and calcium sulfate minerals. These results comply with the recent findings that phyllosilicate clay minerals show better preservation potential for organic molecules, especially in active Fe-Mn redox environment (Gasda et al., 2022).

Detection of high abundance of thiophenic and other sulfur containing organic carbon in the Murray Formation mudstone (Confidence Hills) infer the possibility that sulfurization of organic matter during deposition or during early diagenesis would also have added their preservation (Eigenbrode et al., 2018). Observations from Earth's natural environment have indicated that sulfurization of organic matter increases their refractory properties by reducing reactive functional groups and adding small cross links between small unstable molecules (Aubrey et al., 2006; Kotler et al., 2008). Incidentally, studies of terrestrial organic-mineral interaction have demonstrated better preservation of organic molecules by entrapment within the crystal structure (Aubrey et al., 2006; Kotler et al., 2008).

Significant capacity to store organic molecules has also been seen in terrestrial hypersaline halite- and perchlorate subsurface deposits, which are common on Mars (Fernández-Remolar et al., 2013).

Applin et al. (2015), who reinterpreted the results collected by various pyrolysis-based instruments aboard Viking, Phoenix, and Curiosity, have recently reported the potential existence of oxalates on Mars in various regions (Biemann et al., 1977; Boynton et al., 2009; Mahaffy et al., 2012; Ming et al., 2014). Furthermore, a re-analysis of a Martian mudstone by Applin et al. (2015) using X-ray diffraction (XRD) of the Mars Science Laboratory (MSL) onboard Curiosity rover revealed that the data are compatible with the existence of refractory Ca, Fe, or Mg oxalates at low levels. It has been shown that oxalates can be produced from other organic compounds through both biological (Johnston and Vestal, 1993; Baran, 2014) and abiotic pathways (Durand and Nicaise, 1980; Peltzer et al., 1984). By interacting with aqueous cations, oxalate in solution forms weddellite, whewellite, and glushinskite, which are extremely resistant to chemical and physical degradation (Wilson et al., 1980; Chen et al., 2000; Frost and Weier, 2003; Frost, 2004). According to Cheng et al. (2016) oxalate formation may be a widespread process in the Martian surface condition and potentially play a key role in global carbon cycling and organic matter geochemistry.

Challenges in distinguishing between biogenic and abiogenic hydrocarbons

Various hydrocarbons can be formed abiotically in terrestrial and extraterrestrial environments by high temperature and pressure Fischer-Tropsch synthesis (McCollom, 2003). Aliphatic hydrocarbons and amino acids are among the byproducts of Fischer-Tropsch type synthesis, according to laboratory investigations; these substances may be oxidized at the surface to more stable molecules. Other abiotic processes may also result in the formation of organics, possibly even in the current Martian environment. Through photolytic or catalytic reactions triggered by light at ultraviolet and visible wavelengths, many organic compounds can be produced, for examples photolysis of water and CO_2 mixtures (Franz et al., 2020). Formic acid, formaldehyde, and oxalate, as well as methane and alcohol, have been produced in laboratory studies by these processes. It has also been demonstrated that ultraviolet irradiation of siderite in the presence of water produces formate, formaldehyde, and its derivatives (Franz et al., 2020). These organic compounds may be oxidized on the Martian surface to form oxalate minerals (Benner et al., 2000; Eigenbrode et al., 2018).

SAM stepped combustion experiment study on Yellowknife Bay Mudstone at Gale Crater, Mars by Stern et al. (2022) demonstrated that CO_2 evolved at $< 550^{\circ}C$ was enriched in ^{13}C ($\delta^{13}C = +1.5‰ \pm 3.8‰$), based on the mass balance calculation they suggested that 431 μg C/g of the released CO_2 represented indigenous organic and inorganic Martian carbon. At $> 550^{\circ}C$ released CO_2 was enriched in ^{12}C ($\delta^{13}C = -32.9$ to $-10.1‰$) which represented 273 ± 30 μg C/g of mineral-bound refractory organic carbon. This amount of organic carbon is 40 times more than reported by Eigenbrode et al. (2018) and even higher than reported in Martian meteorites (Steele et al., 2016). Franz et al. (2020) found the isotopic composition to be compatible with macromolecular organic carbon derived from igneous sources, meteoritic infall, diagenetically-altered biomass, or a mix of these. Therefore, the source of high-temperature organic carbon cannot be conclusively identified.

Before 2003, all efforts to find statistically significant methane on Mars were unsuccessful (Maguire, 1977; Krasnopolsky et al., 1997; Lellouch et al., 2000). Subsequently four research groups claimed CH_4 detection (Formisano et al., 2004; Krasnopolsky et al., 2004; Mumma et al., 2009; Webster et al., 2018; Giuranna et al., 2019). Using Thermal Emission Spectrometer onboard Mars Global Surveyor, Fonti and Marzo, (2010) suggested presence of CH_4 on the Martian surface, however, later re-analysis of the data could not reproduce unambiguous evidence for CH_4 (Fonti et al., 2015). Many other researchers failed to detect CH_4 on Mars (Krasnopolsky, 2007; Villanueva et al., 2013; Aoki et al., 2018; Korablev et al., 2019). More recently House et al. (2022) reported anomalously ^{13}C depleted methane ($-137‰ \pm 8‰$) in the drilled samples from multiple horizons of the Gale Crater of Mars using SAM instruments and skeptically suggested three possible scenarios for its production: 1) photolysis of biological methane, 2) photoreduction of CO_2, and 3) deposition of cosmic dust. Nevertheless, they concluded that identifying which of the three scenarios most likely represented the condition that existed on the 3 billion years old Martian surface is not possible based on the current knowledge.

Future Mars mission strategy to detect hydrocarbons

The prerequisites for a future Mars rover mission that would look for organic chemicals on the Martian surface and address their biogenic or abiotic origin must be understood by researchers based on the outcomes of previous Mars missions. So far organic matter search on Mars has achieved moderate success by demonstrating the release of simple organic molecules (i.e., aliphatic hydrocarbons) and some larger molecules (thiophenic and aromatic hydrocarbons) during the pyrolysis of drilled samples from the sedimentary outcrops (Freissinet et al., 2015; Eigenbrode et al., 2018). However, there is still no information about the source organic material present in sedimentary rocks. Also, it is unknown whether that organic matter is linked with a specific mineral phase. Given these uncertainties, combining previously used experimental techniques with new ones to analyze samples collected at a future landing site using both old and new approaches is the most meaningful strategy for continuing the *in situ* research of organic Mars. This will assure continuity throughout all landed Mars missions until samples are returned from Mars and new data can be compared to that from earlier missions.

The ExoMars rover mission, which will launch in the near future, is a component of the ExoMars project, which also includes the 2016 ExoMars orbiter mission. The ExoMars rover's high-level scientific objectives are: 1) to look for evidence of past and extant life on Mars, and 2) analyze geochemical and water conditions with increasing depth in the shallow subsurface of Mars. The most important capability of the ExoMars rover payload instrument is to drill and retrieve a 2 m deep core that will be crushed and analyzed for organic matter using Mars Organic Matter Analyzer (Goetz et al., 2016). According to experimental and modeling research (Kminek and Bada, 2006; Pavlov et al., 2012), Martian rocks at a depth of 2 m are expected to remain less affected by UV radiation and galactic cosmic radiation (Pavlov et al., 2002; Pavlov et al., 2012; Pavlov et al., 2022).

In the case of a complicated depositional scenario, where the deposition and denudation cycle takes place, determining whether the subsurface Martian samples were unaffected throughout its history is extremely challenging. For example, given that generally Mars underwent low volcanic activity during the past two billion years, the deposition scenario in which sediment was rapidly deposited, and subsequently exposed for long-term denudation (Gale Crater) might also be a common process on the surface of Mars. However, it is conceivable that the rover could find organic-bearing strata that primarily underwent insignificant exposure to high particle radiation over the geological timescale and may have preserved near original signature of ancient organic deposit. Thus, drilling down to a depth of 2 m would be a huge step toward gaining access to such least altered organic molecule containing Martian rock samples. In order to search the ancient life on ancient Mars, the ExoMars rover requires this insight back in time.

Derivatization/thermochemolysis-GCMS, Laser Desorption and Ionization (LDI)-MS, and Pyrolysis-GCMS are the three operational modes of MOMA. MOMA-MS is not made to identify light molecules (e.g. CO_2, N_2, O_2, CH_4, and HCl) that are either a part of Martian atmosphere or change during pyrolysis, even though that mass threshold of MS can be modified during operations (Goetz et al., 2016). In MOMA, derivatization agent (DA) will be chosen during surface operations on Mars based on the kinds of organic residues that are anticipated to be found in the sample. Based on the success of SAM derivatization experiments MTBSTFA seems to be the most versatile DA and it is expected to be used in MOMA. Amino acid or carboxylic acid with chiral centers will be separated using dimethylformamide dimethylacetal (DMF-DMA) that preserves the asymmetrical center and is used with the enantio-selective GC column onboard MOMA to achieve chiral separation. For example, since biology on Earth specifically uses left-handed amino acids, one of the main goals of ExoMars mission will be to determine the homochirality or enantiomeric excess of potential Martian amino acids. Another selected DA is TMAH that will be helpful in volatilizing non-soluble refractory kerogen fraction. In addition, laser techniques such as MOMA-LDI and Raman spectroscopy can be used to avoid thermal decomposition of organic matter (Li et al., 2015).

Discussion and conclusion

From Viking to Mars 2020, rover missions searching for signatures of extinct life in Martian surface rocks and sediments have moderately advanced our knowledge of challenges lying ahead in finding organic molecules of biological origin. These challenges also include understanding the carbon cycling of Mars, identifying sites with better preservation potential for hydrocarbons, developing more refined methods for improved extraction of indigenous organic molecules with minimum contamination. The lack of a non-ambiguous detection of organic molecule by pyrolysis-GCMS method onboard Viking and Phoenix missions (Biemann et al., 1977; Mazur et al., 1978; Lauer et al., 2009) made researchers to reevaluate the design and methods of the corresponding units for the subsequent missions. These findings prompted the use of derivatization wet chemistry in the subsequent rover mission i.e., Curiosity and the future ExoMars mission to enhance the chances of organic molecule detection. This method uses derivatization agents such as MTBSTFA, DMF, and TMAH to improve the thermal stability of compounds and ameliorate volatility by substituting their active polar functional groups (Schummer et al., 2009). Using the derivatization/thermochemolysis method Curiosity detected several Cl, S, and, N containing aliphatic and aromatic compounds (Table 1) above the background level of the instrument (Glavin et al., 2013; Leshin et al., 2013; Ming et al., 2014; Freissinet et al., 2015; Eigenbrode et al., 2018; Millan et al., 2022a; Millan et al., 2022b). There are, however, some unanswered questions about the origin of the detected organic compounds: 1) How much of the detected organic compounds represent Martian indigenous organic compounds? 2) Which and how much of the detected organic compounds are derived from indigenous biogenic/abiogenic hydrocarbons?

MTBSTFA, DMF, and TMAH have been generally employed as derivatizing agents for organic compound studies on Earth with GCMS temperature ramping up between 50°C and 200°C at which the derivatization agents are found relatively stable (Molnar-Perl and Katona, 2000; Schummer et al., 2009). But the MTBSTFA, DMF, and TMAH derivatization experiments by Curiosity on Mars has been conducted at a higher temperature (generally >200°) at which the degradation product of these derivatization agents is not properly known. Recently, a lab based simple flash pyrolysis study of MTBSTFA and DMF demonstrated that both the derivatization agent degrade at higher temperature to produce several organic products including dimethylamino-acetonitrile, styrene, benzene, phenol, entylbenzene, 3-methylebenzonitrile, toluene, napthalene, methyl-naphthalene, naphtonitrile, pyrene, above ≥500°C (Table 2) (He, 2021). Thus, results from Martian missions employing derivatization agents can have contaminant complex organic compounds and need to be interpreted with caution. A systematic study of high temperature degradation products of MTBSTFA, DMF, and TMAH in Martian analog conditions can be helpful in resolving such issue and in refining our current understanding of complex hydrocarbons and their origin in Martian surface and subsurface samples.

The use of non-destructive techniques, such as the Raman and fluorescence spectroscopy currently employed by Perseverance, and the Raman and infrared spectroscopy plus the laser desorption techniques that will be employed by the future ExoMars mission, will minimize possible alteration and contamination of the original organic material due to the measurements themselves. This is essential to provide more insights into the nature of the organics detected in the Martian samples, while we wait for their return to Earth and analysis with more sensitive techniques.

Author contributions

AA: Conceptualization, writing an original draft, data Curation, reviewing and writing the final draft.

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Conflict of interest

The author declares that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher's note

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