

Research Article

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Testing S isotopes as biomarkers for Mars

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Abstract

We suggest testing S isotopes as biomarkers for Mars. An analogous robust biosignature has recently been proposed for the forthcoming exploration of the icy surface of Europa, and in the long term for the exploration of the surfaces of other icy moons of the outer solar system. We discuss relevant instrumentation for testing the presence of life itself in some sites, whether extinct or extant in order to complement a set of other independent biosignatures. We pay special attention to the possible early emergence of sulphate-metabolizing microorganisms, as it happened on the early Earth. Fortunately, possible sites happen to be at likely landing sites for future missions ExoMars and Mars 2020, including Oxia Planum and Mawrth Vallis. We suggest how to make additional feasible use of the instruments that have already been approved for future missions. With these instruments, the proposed measurements can allow testing S isotopes on Mars, especially with the Mars Organic Molecule Analyzer.

Introduction

A second genesis is a suggestive term introduced to denote the emergence of life in places other than Earth (McKay, 2001), a possibility searched for both with perseverance and with suitable instrumentation (Grotzinger *et al.*, 2012; Goesmann *et al.*, 2017). This is a fundamental phenomenon of astrobiology that could be detected on several locations inside our Solar System, including Europa (Grasset *et al.*, 2013; Phillips and Pappalardo, 2014; Chela-Flores *et al.*, 2015), Enceladus (Guzman *et al.*, 2018), possibly on several icy moons of the outer solar system (Husmann *et al.*, 2006; Christophe *et al.*, 2012; Arridge *et al.*, 2014; Turrini *et al.*, 2014 and Bocanegra-Bahamon *et al.*, 2015). The special case of Mars will be discussed in the present paper.

In the short term such detection is more likely to be successful inside the solar system than on thousands of exoplanets that are expected to exist in our Galaxy (Crossfield *et al.*, 2015), and in other galaxies, where they are in the process of being detected (Dai and Guerras, 2018).

A biosignature has been proposed in a recent publication for the future exploration of Europa in the 2020s. For ocean worlds in the decade 2030–2040 there are some possibilities for the detection of life during the eventual exploration of the icy moons and of the giant and icy planets (Chela-Flores, 2017). Likewise, in the present work, we discuss the possibility of searching for evidence of life on Mars with the suggested biosignature. On the Red Planet, the additional advantage is that the search is independent of either the present harsh environmental conditions or even of the depths that may eventually be reachable with future rovers.

On Mars detection has significant and favourable advantages, since neither plate tectonics, nor several billion years (Gyrs) of hydrology have hidden the original surface that consisted predominantly of basalt and the volcanic rock komatiite (Meunier *et al.*, 2010). These terrains are exposed most evidently in Noachis Terra in the Martian southeastern hemisphere.

The advantage of the present approach is that a biogeochemical biosignature is more robust after death than the alternative search for a statistically anomalous distribution of biotic organic molecules (amino acids, nucleic acids and membrane lipids). To ascertain that biological organics are distinct from organic material of non-biological origin is a complex problem (McKay, 2008): Indeed, while they are alive, organisms will maintain their original distribution of organics that are different from distribution of organics from abiotic sources, for instance in the over 70 amino acids that were present in the Murchison meteorite (Kvenvolden *et al.*, 1970).

Physical factors after death will slowly alter this life-like distribution and turn it into a statistically smooth one that is indistinguishable from the background. In this sense, the biogeochemical perspective may be an attractive and more reliable complementary biosignature or even it may be a valid alternative for the search of the emergence of life independent of searching for transitory molecular biomolecules (Johnson *et al.*, 2018).

Chemical evolution of the early dense Martian atmosphere

We focus on the geological system of the Noachian. In the early part of the corresponding period (4.6 to 3.7 Gyrs before the present, BP) there must have been a reduced amount of sulphur

compounds. Later on, due to volcanism, likely candidates for the dense atmospheric components (towards the later Noachian/Hesperian transition) were SO_2 and H_2 , (Greely, 2013). The resulting high atmospheric pressure may have inhibited SO_2 outgassing while allowing H_2O and CO_2 (Gaillard *et al.*, 2013). In addition, it is only until the Noachian/Hesperian transition that widespread sulphate compounds appear when the valley networks were formed (Bibring *et al.*, 2006). For surficial sulphur minerals, biogeochemistry yields large negative values for isotopic fractionation. This should not be confused with the results of photolysis experiments involving the atmospheric components SO_2 and H_2S (Farquhar *et al.*, 2000) that can produce analogous fractionation.

The significant relevance of these experiments demonstrate exclusively that sulphur was indeed one of the chemical elements that were present in the early atmosphere. For that reason, Farquhar and coworkers suggest isotopic fractionation of sulphur isotopes in Martian meteorites. However, the period of Martian geologic evolution that concerns us in the present paper is the Early Noachian, rather than the period of formation of those SNC meteorites that were available to the experimenters. Unlike the SNC meteorites, which are of a younger age, the photolysis experiments did not include the oldest known sample of Mars' crust – the approximately 4.1 Gyr-old meteorite Allan Hills 84001.

The emergence of abundant Martian surficial sulphates

Sulphates were abundant towards the Noachian/Hesperian. However, in the later Noachian, more precisely, towards the Noachian/Hesperian transition and later, volcanic activity argues in favour of sulphur compounds playing a significant role, either maintaining a warm and wet period (Halevy and Schrag, 2009), or subsequently working as a factor contributing to general cooling that ended the wet warm period (Kite *et al.*, 2014; Kerber *et al.*, 2015).

At this stage in the evolution of the Martian atmosphere, there is ample evidence of large emissions of SO_2 due to volcanism. In the section 'Can stable isotopes ratios yield biomarkers of sulphate-reducing microorganisms?', we are mainly concerned with effects from the early atmosphere and the corresponding required sensitive instrumentation that could detect a sulphur biomarker in sulphur minerals. There are possible testing sites at Mawrth Vallis and Oxia Planum, which are probable landing sites for the forthcoming missions: ExoMars and Mars 2020.

Can stable isotopes ratios yield biomarkers of sulphate-reducing microorganisms?

We have seen that at a terrestrial time contemporary with the transition Hadean/Archean, there is ample evidence that Noachian Mars was in the presence of liquid water on its surface. There were also possible hydrothermal vents, environments where life emerged, as it did in the analogous terrestrial case. At least if life did originate elsewhere, we expect that it would likely prosper near vents (Baross and Hoffman, 1985; Reysenbach and Cady, 2001), or at any rate, near the sedimentary layer between oceanic crust and seawater, given the convincing evidence from the terrestrial Hadean Eon. On the Martian surface, it is possible to test biosignature detection with miniaturized mass spectrometry that has already reached a significant degree of development, but we expect some feasible improvements in the foreseeable future (Tulej *et al.*, 2015; Wiesendanger *et al.*, 2018).

To answer with confidence whether variations of stable isotopes ratios could be indicative of biogenic origin, certain questions have to be taken into account, especially the possible effects of diagenesis and thermochemical sulphate reduction on sedimentation. Terrestrial sulphate reducing bacteria are of Archean time (Kaplan, 1975). Some reliable estimates for their first emergence are available. Indeed, some of these chemosynthesizers have been detected in sediments of approximately 3.47 Gyrs BP (Shen *et al.*, 2001).

These early microbes have demonstrated that on Earth isotopic fractionation δ^{34} exceeds by some 20‰ of the standard value. This data may be interpreted as the result of sulphate reduction, in spite of diagenesis and sedimentation. Such geologic measurements place sulphate reducers low in the phylogenetic tree, among the most ancient of our ancestors (Philippot *et al.*, 2007). To constrain our search for the first appearance of life on Mars, we should consider the evidence so far in our own planet: It is possible that life had already established a terrestrial habitat near submarine-hydrothermal vents before 3.77 Gyrs BP and, possibly as early as 3.95 Gyrs BP, or even 4.28 Gyrs BP (Dodd *et al.*, 2017; Tashiro *et al.*, 2017). These events may have taken place not long after the earliest evidence for a continental crust and oceans (Wilde *et al.*, 2001). Hadean zircons suggest that liquid water was present at the surface of the Earth, possibly already by 4.36 Gyrs BP, the age of the oldest zircons (Mojzsis *et al.*, 2001; Wilde *et al.*, 2001; Nemchin *et al.*, 2006; Bell *et al.*, 2015). In any case, the bounds for the emergence of terrestrial life are most likely to be constrained to the time range of 4.5 to 3.9 Gyrs BP, as it has been recently discussed (Pearce *et al.*, 2018). Such early genesis of life on Earth strongly suggests constraining our search for an early emergence of life on Mars to the Noachian before the transition to the Hesperian.

Where are the best sites for testing isotopes as biomarkers?

The southern hemisphere may still retain analogous conditions to those that led to the origin of life on Earth, where they have totally disappeared, due to the harsh effects of metamorphism and plate tectonics. In any case, the early geological history of Mars has left a window for testing the emergence of life, whereas it has disappeared on Earth (cf., the section 'Can stable isotopes ratios yield biomarkers of sulphate-reducing microorganisms?'). While there are numerous factors that militate in favour of present uninhabitability of the Red Planet, or even simply contemporary habitability, there is no evidence yet for uninhabitability, or ancient uninhabitability that could be detectable with biosignatures of reliable microbial fossils.

But we have argued that focusing on testing for the more robust S isotopes as biosignatures will lead to useful information with a careful analysis of the changes that the first sulphur metabolizing bacteria may have made in isotopic ratios on Mars.

However, a possible eventual search is suggested due to the newly discovered lake of liquid water that is 20 km across buried 15 km beneath Mars surface close to the southern polar ice cap (Orosei *et al.*, 2018). It is not deeper than the analogous subterranean lake Vostok in Antarctica (Siebert *et al.*, 2001). Fortunately, it is known that the ice above the terrestrial lake is a testimony of great diversity of single-celled organisms: yeast, actinomycetes, mycelian fungi, the alga *Crucigenia tetrapodia* and diatoms (Siebert *et al.*, 2005). Besides, it appears that in Vostok, water temperatures do not drop too far below zero centigrade, with the possibility of geothermal heating raising the temperatures above this

level. In the Martian lake, there are also conditions that keep the water liquid (Orosei *et al.*, 2018). This suggests a search for isotope biomarkers closely beneath the surface of the polar cap in Planum Australe (reachable by future rovers), in order to test whether biomarkers of fossilized microbes or even multicellular microorganisms may have emerged from the interior of the Martian lake.

The detection of biosignatures awaits the challenge of innovative use of approved instrumentation for forthcoming missions. We conclude that with so much valuable and appealing potential astrobiological information to be retrieved, rovers should also use their approved instrumentation for testing isotopic biomarkers (Goesmann *et al.*, 2017).

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