



# Miniaturised Instrumentation for the Detection of Biosignatures in Ocean Worlds of the Solar System

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This review of miniaturised instrumentation is motivated by the ongoing and forthcoming exploration of the confirmed, or candidate ocean worlds of the Solar System. It begins with a section on the evolution of instrumentation itself, ranging from the early efforts up to the current rich-heritage miniaturised mass spectrometers approved for missions to the Jovian system. The geochemistry of sulphur stable isotopes was introduced for life detection at the beginning of the present century. Miniaturised instruments allow the measurement of geochemical biosignatures with their underlying biogenic coding, which are more robust after death than cellular organic molecules. The role of known stable sulphur isotope fractionation by sulphate-reducing bacteria is discussed. Habitable ocean worlds are discussed, beginning with analogies from the first ocean world known in the Solar System that has always being available for scientific exploration, our own. Instrumentation can allow the search for biosignatures, not only on the icy Galilean moons, but also beyond. Observed sulphur fractionation on Earth suggests a testable “Sulphur Hypothesis”, namely throughout the Solar System chemoautotrophy, past or present, has left, or are leaving biosignatures codified in sulphur fractionations. A preliminary feasible test is provided with a discussion of a previously formulated “Sulphur Dilemma”: It was the Galileo mission that forced it upon us, when the European sulphur patches of non-ice surficial elements were discovered. Biogenic fractionations up to and beyond  $\delta^{34}\text{S} = -70\text{‰}$  denote biogenic, rather than inorganic processes, which are measurable with the available high sensitivity miniaturised mass spectrometers. Finally, we comment on the long-term exploration of ocean worlds in the neighbourhood of the gas and ice giants.

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## REVISITING THE “SULPHUR DILEMMA”

### Information on Ocean Worlds that is Coded in Stable Isotopes

We should take a look at what the Galileo mission taught us, regarding the search for life. In the near future, with the JUPITER ICY moons Explorer (JUICE) mission Grasset et al. (2013a) and the NASA proposed Europa Clipper mission (Howell and Pappalardo, 2020), there are several options for interpreting the information that is coded in the sulphur isotopes that have been deposited on the Galilean moons.

The epoch-making Galileo Mission was responsible for the discovery of intriguing surficial deposits of sulphur (patches) on Europa's frozen surface. Subsequent measurements ratified this discovery. It was the first proposal that was put forward, that these chemical elements may be exogenous, namely that their origin may have been from the neighbouring satellite Io. Sulphur was detected by the Galileo mission on the European surficial patches: The presence of sulphur compounds on the European surficial ice was confirmed by NIMS measurements, Near-Infrared Mapping Spectrometer (Carlson et al., 2002). The data matches the distribution of an ultraviolet absorber that had been suggested earlier McEwen (1986), and confirmed later on (Grundy et al., 2007). A suite of measurements, still from Galileo have led us to the conclusion that the source of the surficial sulphur is endogenous, including, Solid-State Imaging (SSI), NIMS and the Ultraviolet Spectrometer (UVS) (Fanale et al., 1999).

## A Europa Lander Mission Concept for Solving the Sulphur Dilemma

The European endogenous surficial sulphur could have been metabolically processed by a submarine biota. This hypothesis is testable, as at the level of isotopic modifications the sulphur could have left measurable traces. They would be detectable with the sensitivity of the available instrumentation that has already been approved for the forthcoming missions. All of these queries can be summarised in a *Sulphur Dilemma*, which was first formulated soon after the Galileo mission ended its activities on September 23, 2003 (Chela-Flores, 2006):

What is the source of the S patches? Could they be endogenous and at the same time biogenic?

A NASA Europa lander, which at present is only a proposed astrobiology mission concept Pitesky and Hand (2020) has, nevertheless, been advocated for over two decades (Phillips and Chyba, 2001). Such a lander could search for the biosignatures, which we have pointed out in earlier publications and especially in this review. Likely sites for can be retrieved from the NIMS data (cf., *Information On Ocean Worlds that is Coded in Stable Isotopes*). These measurements suggest that a Europa lander be placed especially on the area close to 0–30°N and longitudes 240 and 270, in correspondence with the S patches, as suggested by our comments above (McCord et al., 1998).

## Autochthonous Microbes Could Alter the Surface of Europa

It is possible to answer the question whether the early Earth microbial life could mirror the emergence of European microorganisms, at least as far as their biochemistry is concerned. Metabolism of autochthonous microbes could alter substantially the S surficial deposits. The answer lies encoded in the isotopic fractionation of the sulphur atoms that would have been involved. Such alterations are measurable with the accuracy that is available in the latest miniaturised mass spectrometers that would be compatible with payloads allowed for a Europa lander.

## OCEAN WORLDS PAST AND PRESENT

### Past Ocean Worlds on Venus and Mars

Both Venus and Mars were possible hosts of ancient oceans, probably not unlike the terrestrial ones. Firstly, the possibility of an early Venusian life-friendly environment was raised earlier on (Donahue et al., 1982). In addition, on the question of habitability of Venus, additional papers were published in the early 1980s: Firstly, numerical simulations suggested that habitability of Venusian oceans was not excluded in its first billion years, with oceans persevering for possible up to twice that time (Grinspoon and Bullock, 2007). There is evidence that initially Venus was an ocean world (Kasting et al., 1984; Kasting, 1988; Donahue and Russell, 1997; Grinspoon and Bullock, 2003).

In addition to the early approaches to the question of an early Venusian ocean, a recent three-dimensional model militates in favour of the ocean lasting until recent geological times, including potential habitability conditions (Way et al., 2016). The possibility of some form of extremophilic life has also been discussed in a variety of possible environments and the possibility of panspermia to and from our own planet (Schulze-Makuch and Irwin, 2004).

Secondly, on a second terrestrial planet—Mars—there could have been a global ocean in its northern hemisphere, so that the Red Planet can be added to the list of (past) ocean worlds (Clifford and Parker, 2001; Fairén et al., 2003).

Volcanic eruptions, contemporary with the presence of the early ocean, were possible sources of abundant sulphur compounds. These chemical elements would be expected to have been deposited on the ancient Martian surface. An early ecosystem can be tested by ruling out, or detecting, fractionation codified in the sulphur compounds that were deposited. Testing S isotopes as biosignatures is a possibility that has already been raised for Mars (Chela-Flores, 2018). Such identification of biosignatures will be in a more favourable position with the forthcoming landing missions Tianwen-1 (CNSA, landed on May 14, 2021), Perseverance (NASA, landed on February 18, 2021) and Rosalind Franklin (Roscosmos and ESA, expected to land in 2023).

### Analogies From the First Ocean World Known in the Solar System

Some of the confirmed ocean worlds (OWs) have icy surfaces over subsurface oceans. On Earth we have a valuable analogy in Antarctica's McMurdo Dry Valley Lakes (DVL). These lacustrine environments (Doran et al., 2010; Chela-Flores and Seckbach, 2011) have biotopes that are known to survive under difficult constraints, including being permanently covered by ice (cf., **Tables 1–3**).

Lake Joyce is an interesting lake, also ice covered all the year-round. An analogous water environment lying underneath an icy cover is Lake Untersee, whose maximum depth is 169 m (Wand et al., 1997). Being in central Queen Maud Land in East Antarctica, Untersee is significant as an analogy for the ocean worlds: The lake ice cover is 2–6 m thick which may have

**TABLE 1** | Statistics of the Dry Valleys lakes in Antarctica.

Lake or pond	Maximum depth (meters)	Elevation (meters above sea level)	Lake type	References
Lake Hoare	34	73	Perennial ice cover; liquid water	Chela-Flores and Seckbach, (2011)
Lake Vanda	69	123	Perennial ice cover; liquid water	Chela-Flores and Seckbach, (2011)
Lake Joyce	37	1677	Perennial ice cover; liquid water	Chela-Flores and Seckbach, (2011)
Lake Untersee	169	563	Perennial ice cover; liquid water	Wand et al. (1997)

**TABLE 2** | Microbial life in the Dry Valleys lakes, Antarctica (Chela-Flores, and Seckbach, 2011).

Organism	Domain	Habitat
Cyanobacteria	Bacteria	Lakes Chad, Fryxell, and Vanda
<i>Leptothrix</i>	Bacteria	Lakes Fryxell and Hoare
<i>Achronema</i>	Bacteria	Lakes Fryxell and Hoare
<i>Clostridium</i>	Bacteria	Lakes Fryxell and Hoare
<i>Chlamydomonas subcaudata</i> (Phylum chlorophyta)	Eucarya	Lakes Bonney (east lobe) and Hoare
Diatoms (Phylum bacillariophyta)	Eucarya	Lakes Bonney, Chad, Fryxell Hoare and Vanda
<i>Bryum</i> (a moss)	Eucarya	Lake Vanda

**TABLE 3** | A few examples of eukaryotes present in Antarctica.

Organism	Domain	Habitat	References
Diatom shells	Eucarya (bacillariophyta)	Lake Vostok (ice core, at depth of 2375 m)	Chela-Flores, and Seckbach, (2011)
<i>Caloneis ventricosa</i>	Eucarya (bacillariophyta)	Lakes Chad, Fryxell, Hoare, and Vanda	Chela-Flores, and Seckbach, (2011)
<i>Navicula cryptocephala</i>	Eucarya (bacillariophyta)	Lakes Bonney, Fryxell, Hoare, and Vanda	Chela-Flores, and Seckbach, (2011)
<i>Chlamydomonas subcaudata</i>	Eucarya (chlorophyta)	Lakes Bonney and Hoare	Chela-Flores, and Seckbach, (2011)
<i>Tetracystis sp.</i>	Eucarya (chlorophyta)	Lakes Fryxell, Hoare, and Vanda	(Chela-Flores, and Seckbach, 2011)
Yeast	Eucarya (Ascomycota)	Lake Vostok (ice core)	Chela-Flores, and Seckbach, (2011)

persisted for over 100,000 years. Below 80 m hydrogen sulfide is present, associated with decreased sulfate concentrations, probably arising from bacterial reduction of sulfate. It is known that stromatolites are present in the lake bottom (Andersen et al., 2011). But resurfacing also hints at submerged geologic activity. The icy Galilean moons cryovolcanism may resemble terrestrial silicate volcanism. Earth-like geologic activity includes a candidate for the origin of life, namely, hydrothermal vents (Wächtershäuser, 1990).

## Confirmed Ocean Worlds in the Jovian System

Going beyond the Martian orbit, we could persevere with a systematic search for sulphurous material on the surface of the Galilean icy worlds. We may assume a testable “Sulphur Hypothesis” (throughout the Solar System chemoautotrophy, past or present, has left, or are leaving biosignatures codified in sulphur fractionations).

Under this hypothesis, the non-ice chemical elements may have their source in the moon’s interior biota; for a test we should identify surficial locations, where it is most likely to detect chemical elements arising from the subsurface ocean. One prominent spot is undoubtedly the dark and red-coloured

material in the young depression Castalia Macula (0°N, 225°W), which has been pointed out by Louise Prockter and Paul Schenk in the first decade of this century (Prockter and Schenk, 2005). The tests we have proposed earlier (cf., *Stable Isotopes From Ore Genesis Can Be Used as Biosignatures*) can detect, or rule out, the presence of a significant biogenic signal if surficial sulphur has been processed by oceanic microbial life.

One of the natural phenomena that could contribute to yield the ocean chemical contents in places like Castalia Machia is cryovolcanism (Fagents, 2003). The patchy nature of the surficial S deposits argues strongly against the possible source being from the neighbouring volcanic Galilean moon, Io (Carlson et al., 1999).

In the foreseeable future, direct geochemical tests on the furthest ocean worlds are not possible, but as we will see in this section much information has been gathered for including their moons, as either confirmed, or candidate ocean worlds.

## Confirmed Ocean Worlds in the Saturnian System

Two satellites of Saturn have been the focus of attention for several missions including the two confirmed ocean worlds Enceladus and Titan (Hendrix et al., 2018). Enceladus

**TABLE 4** | Mass spectrometers for studying ocean worlds of the Solar System.

Miniaturised instrumentation	Details	References
NGMS: Neutral Gas (NG) Mass Spectrometer MS Laser-Induced Breakdown Spectroscopy (LIBS)	A Time of Flight (TOF) MS Can be used to distinguish bacteria with few constraints, which has advantages when adopted for space research	Wurz et al. (2012) Multari et al. (2010)
Laser Desorption Mass Spectrometry	Potentially applicable for the detection of amino acids on the icy surfaces of ocean worlds	Ligterink et al. (2020)
Laser Ionization Mass Spectrometry (LIMS)	Adopted for space research	(Riedo et al., 2012), 2013b)
The MAss SPectrometer for Planetary EXploration/ Europa (MASPEX)	Incorporated in the payload for Europa clipper	Howell and Pappalardo, (2020)

Explorer is a mission concept by the German Aerospace Center together with German universities for an unprecedented coupled system for probing this moon's exterior, orbiter and its interior, at least its surficial ice (cf., **Table 4** for references and full names of all the missions referred to below). In addition, coming from NASA, Christopher McKay, and colleagues have proposed to measure biosignatures on Enceladus, the ELSAH mission, with a payload that would include a sophisticated instrumentation, for mass spectrometry (McKay, 2008). On the other hand, and once again focusing on the same intriguing ocean world, the ELF mission hopes to probe its subsurface ocean. Instead, not only for Enceladus, but also for Titan, the E2T mission is an international collaboration between two major space agencies dedicated to both Enceladus and Titan.

In spite of the rich assortment of options, in 2019 NASA gave a priority in their New Frontier Programme to the mission Dragonfly to Titan to characterize the habitability of Titan. The Dragonfly would use a lander with rotors to take off, fly, and land at new sites to characterize the habitability of Titan's environment and to search for biosignatures.

Finally, there is a set of another four Saturnian satellites that are presently candidate ocean worlds: Mimas, Tethys, Rhea, Iapetus, where there is only basic foundation for this possibility (Hendrix et al., 2018). However, new missions for the Saturnian system is required to promote these four Saturnian moons to the rank of confirmed ocean worlds. Exceptionally, at the end of 2004 and in 2007, there were close flybys of Iapetus during the Cassini mission.

## THE EVOLUTION OF INSTRUMENTATION UP TO MINIATURISED MASS SPECTROMETERS

### The Exploration of Confirmed or Candidate Ocean Worlds

In the long-term planning, the search of biosignatures should focus mainly on two of the Galilean moons, Europa and Ganymede (cf., *The Robustness of Geochemical Biosignatures*), since there are missions by ESA and NASA that in the short term will be equipped with appropriate instrumentation. The case of Mars as a previous ocean world is also discussed. Clearly, it is instructive to review the evolution

of instrumentation towards a stage when they have been approved by the space agencies.

### Cryobots and Hydrobots for the Exploration of Ocean Worlds

Soon after the Galileo mission arrived in the Jovian system, it was suggested that for icy moons with internal oceans coupled instruments could be useful. The hydrobot-cryobot intended to melt through the icy surface into the ocean underneath (cf., **Figure 1A**).

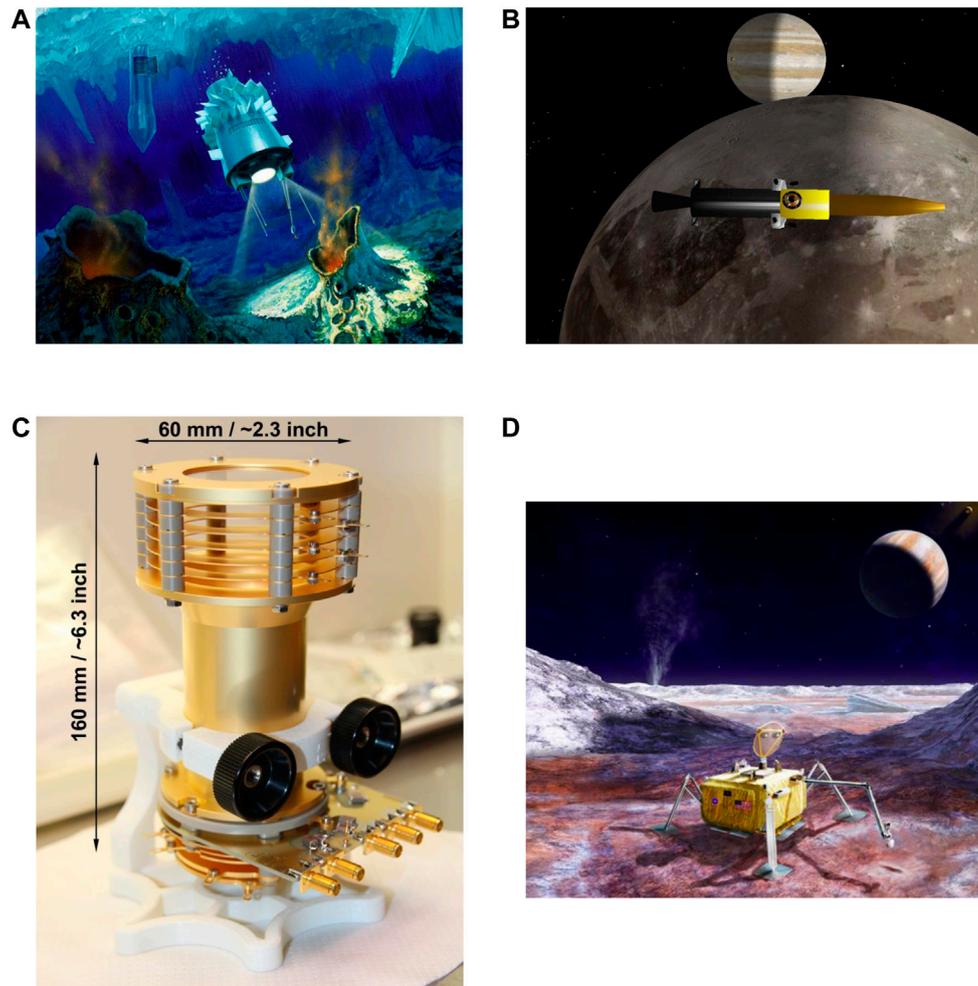
It is at present no longer being considered feasible as we proposed it. However, we should underline that the cryobot-type of instrumentation, as a melting drill head for the exploration of subsurface planetary ice layers has subsequently attracted the attention of researchers (Weiss et al., 2008).

The question remains open whether in the future the exploration of ocean worlds may benefit from a more advanced version of hydrobots. For instance, the proposal of a hydrobot submersible has been used subsequently by the concept mission ENDURANCE. This probe could eventually be used for the direct exploration of an ocean world, such as Europa (Bortman, 2010). The possibility of extremophiles that are known on terrestrial conditions to persevere and survive in anoxic conditions, can be thought of as models of possible European biota that a hydrobot-type of probe could eventually detect with an appropriate payload.

### Penetrators as Alternative Instruments for Ocean Worlds

A second suggestion that we found as an attractive instrument for probing the icy surfaces of the ocean worlds was called a penetrator (Gowen et al., 2011, cf., **Figure 1B**), which had previously been suggested for use in the context of lunar exploration (Smith et al., 2009).

These mini-missiles would have been delivered from orbit to reach and penetrate the icy surface. In spite of its advantages some subsequent variations the main space agencies have not included them in payloads of future missions. Yet, at present there is still considerable interest in penetrators (Bagrov et al., 2021).



**FIGURE 1** | A vehicle referred to as a cryobot was intended to carry a small submersible (a hydrobot) equipped with a relevant payload. The hydrobot was based on previous submersible experience for research in oceanography (Horvath et al., 1997). Image courtesy NASA/JPL-Caltech. As an alternative to landers in space exploration, penetrators were high speed impacting projectiles designed to investigate the subsurface of icy moons, including Europa, advocated by the UK Penetrator Consortium and European proposers, besides our Abdus Salam International Centre for Theoretical Physics, Trieste, Italy (Gowen et al., 2011), a technological initiative to overcome challenges of the standard exploration, carried on in 2021, but more significantly still, the strategy has been advocated for the direct exploration of the icy surface of Europa and other Galilean worlds in our cosmic neighbourhood. Image published with permission of the Mullard Space Science Laboratory (UCL, UK). The miniature mass analyzer of the LIMS system of the University of Bern is displayed. The mass analyzer is held by a structure for bench testing before it will be integrated into the vacuum chamber. CC the University of Bern, Switzerland. An artist conception of a mission concept, for a first lander on an extraterrestrial ocean world, a Europa lander (Pitesky and Hand, 2020). Image courtesy NASA/JPL-Caltech.

It should not escape our attention that the basic idea of the penetrator, as a means to deliver an impacting descent probes for the Galilean moons has subsequently been extended. The alternative projectile has been suggested in order to simplify the costs and technological challenges of direct exploration of the icy surfaces of ocean worlds with landers (Wurz et al., 2017). But the possible alternative impacting probe would be an implementation of an earlier Europa Descent Probe of approximately cubic shape, unlike the traditional cylindrical penetrator.

After these pioneering efforts for exploring the ocean worlds, which we have illustrated in **Figure 1A,B**, a significant string of publications has followed with the view of participating in the forthcoming missions to the Galilean moons. We have presented

the corresponding evolution of instrumentation as the timeline in **Table 5**:

### Heritage of Miniaturised Instruments for Forthcoming Missions

The most successful instruments that have been selected for forthcoming space missions are mass spectrometers. From the point of view of probing the ocean worlds for biosignatures, they have many advantages to which we shall return in ***Biosignatures From the Geochemistry of Stable Isotopes***. Their most attractive feature is the degree of miniaturisation that has been achieved (Tulej et al., 2015).

**TABLE 5 |** Timeline: instrumentation for ocean worlds. The early preliminary efforts (1997–2011), in which the author participated, are illustrated in **Figures 1A,B**. The more recent miniaturised instruments that are meant to contribute to the exploration of the nearest Galilean ocean worlds, are available in several papers mainly from the University of Bern, Switzerland, have been cited in *Heritage of Miniaturised Instruments for Forthcoming Missions* and illustrated in **Figure 1C**.

1997	2011	2015	2020	2022	2024	>2027
Cryobot-hydrobot <b>Figure 1A</b>	Penetrators for Europa <b>Figure 1B</b>	Mass spectrometers <b>Figure 1C</b>	Origin instrument <i>Heritage of Miniaturised Instruments for Forthcoming Missions</i>	NIM instrument <i>Heritage of Miniaturised Instruments for Forthcoming Missions</i>	MASPEX <i>Heritage of Miniaturised Instruments for Forthcoming Missions</i>	Europa lander <b>Figure 1D</b>

Miniaturisation of mass spectrometers has been developed specifically for space exploration. In various previous applications, miniaturised mass spectrometers have been used in the payload of space orbiters, as well as in rovers. There are many studies aiming at the exploration of the Solar System (Tulej et al., 2011; Tulej et al., 2016; Wiesendanger et al., 2017; Wiesendanger et al., 2018a; Wiesendanger et al., 2018b).

In **Figure 1C**, we illustrate a recent example of the process of miniaturisation of mass spectrometry. It shows one of its components—a mass analyzer—which takes ionized masses and separating them according to charge to mass ratios. This instrument is responsible to deliver the information received to the detector, where it is converted into a digital output.

Some more exciting recent research is relevant in this context. Firstly, cutting-edge instrumentation that is currently ready for the flight on the PEP JUICE mission (including the NIM instrument), which will fly in 2022. The NIM instrument is designed to measure exospheres of Jupiter satellites during flyby (Lasi et al., 2020). This work addresses instruments designed for a future Europa lander. Secondly, miniaturized mass spectrometry with the intention of being included in future payloads is also being considered (Föhn, et al., 2021). Finally, some work now is focusing on a lander instrument on Europa, particularly on a coupling of the mass analyser with sample introduction/laser ablation/desorption ion source (Origin instrument). This instrument is more like LMS with the laser ablation/desorption ion source (Ligterink, et al., 2020).

To implement the experimental tests on biogeochemical biomarkers on Europa and Ganymede, we have to wait some time for the results of two forthcoming missions.

There are two possibilities for the use this instrumentation in the exploration of the icy Galilean moons. The first of the two missions to launch will be the ESA mission JUPITER ICy moons Explorer (JUICE), whose main objective will be on Ganymede (Grasset et al., 2013b). In this mission there has been significant progress in relevant miniaturised mass spectrometry. In fact, JUICE will include in its payload a Particle Environment Package, which includes a Neutral and Ion Gas Mass Spectrometer (Abplanalp et al., 2009; Meyer et al., 2017). Potentially, this new instrumentation is capable of testing whether isotopes of sulphur can be used as biomarkers, as explained in *Biosignatures From the Geochemistry of Stable Isotopes* below.

The second mission to launch will be the NASA Europa Clipper mission. After the major work achieved by the Galileo mission, it intends to investigate habitability of Europa. It has the

capability to measure biogenic stable S-isotope fractionation. Besides, a mission concept for a landed spacecraft to the surface of Europa is under consideration. The MASS Spectrometer for Planetary EXploration/Europa (MASPEX) will be included in the Europa Clipper scientific payload (Pappalardo et al., 2013).

Even as a mission concept, a Europa lander remains an appealing project of NASA (**Figure 1D**).

This lander has been discussed in the scientific community for a long time, going back at least to the Sixth Trieste Conference (Phillips and Chyba, 2001). The possibility of including a mass spectrometer in its payload Pitesky and Hand (2020) would add significantly to the first possibility of testing the Sulphur Hypothesis, a critical question in efforts to search for biosignatures (cf., *Biosignatures From the Geochemistry of Stable Isotopes*).

## BIOSIGNATURES FROM THE GEOCHEMISTRY OF STABLE ISOTOPES

### The Robustness of Geochemical Biosignatures

The distribution of life in the Universe is the third “chapter” of astrobiology, which has been given a suggestive name, a Second Genesis (McKay et al., 2001). We are suggesting in this paper and some of our previous ones that one way to search for a second genesis is with the help of stable isotope biochemistry. Metabolic alteration of the environment, seems to be more robust than the alternative search for the biomolecules of life, amongst them the amino acids, lipids or the monomers of the nucleic acids, as it is often done (Zhang et al., 2021). To test for the difference between biogenic as opposed to abiogenic remains as one of the outstanding challenges in astrobiology (McKay, 2008).

### Stable Isotopes From Ore Genesis Can Be Used as Biosignatures

Ore is a term which applies to any mineral (metalliferous, or non-metal) from which the metallic, or non-metallic element may be profitably extracted. Ore genesis refers to mineral deposits formation underneath the terrestrial surface. Based on the analysis of ( $^{34}\text{S}/^{32}\text{S}$ ), petroleum geologists used the analysis of ore genesis for understanding the provenance of sulphur. Besides, the light stable isotopes, including S, have provided information about mineral deposition,

demonstrating that ore formation is a surficial phenomenon, rather than having their origin in magmas. This topic has been reviewed earlier (Ohmoto, 1986). As opposed to the above work on ore genesis, astrobiologists can use the experience of geochemists by taking advantage of an extraordinary phenomenon in microbiology that has been widely studied since the middle of last century (Kaplan, 1975): sulphur is highly fractionated by microbes, in such a way that biogenically processed S can readily be distinguished from terrestrial mantle sulphur (Ireland, 2013). This is a remarkable phenomenon in the context of astrobiology. Indeed, biogeochemical biomarkers have long been used in astrobiology (Chela-Flores, 2006). This approach for the detection of biologic, rather than inorganic fractionation processes, is currently being exploited in a terrestrial context (Kring et al., 2021). This work goes back to its roots based on the well-established studies of ore genesis.

We refer to our earlier discussions for details related to the introduction of the “delta parameter”  $\delta^{34}\text{S}$ . This term is significant for the search of geochemical biosignatures (Chela-Flores and Seckbach, 2011; Chela-Flores et al., 2015):

$$\delta^{34}\text{S} = \left[ \left( \frac{{}^{34}\text{S}/{}^{32}\text{S}}{\text{sa}} \right) = \left( \frac{{}^{34}\text{S}/{}^{32}\text{S}}{\text{st}} - 1 \right) \times 10^3 [0/00, \text{CDM}] \right]$$

where a standard is chosen referring to a troilite from the Barringer crater in the Canyon Diablo meteorite (CDM). To sum up, we already possess the technology which will facilitate the measurements with the necessary sensibility to test the icy surface for signs of life in the European ocean.

### Distribution of Sulphur in the Solar System

In spite of remarkable progress in chemical evolution since the landmark paper of Stanley Miller (1953), there is yet no consensus for a theory of life’s origin (Davis and McKay, 1996). This situation suggests that one possibility to make further progress in life’s emergence would be to make testable hypotheses to find pathways for deeper aspects of the origin of life in the Universe.

There is wide past experience in assessing the presence of biogenicity in terrestrial environments. (Canfield and Thamdrup, 1994; Kohn et al., 1998; Popa et al., 2004; Shen and Buick, 2004; Sim et al., 2011; Kring et al., 2021).

Motivated by the Solar System S abundances, we adopt a ‘Sulphur Hypothesis’:

*Throughout the Solar System, sulphur-processing microorganisms emerged early and have left, or are leaving, biosignatures codified in sulphur fractionations.*

This is a testable hypothesis with the available instrumentation. One motivation for the Hypothesis is the role in chemoautotrophy by a type of bacteria that consumes sulphate and produces sulphide, as a waste product. These microorganisms are ancient sulphate-reducers. We will return to them.

For a long time, we have known from the exploration of the inner Solar System that sulphur is ubiquitous (Gibson, 1982), examples of which have been given more recently. Sulphur is

present, not only on the Earth, but also on the other terrestrial planets: Mercury Weider et al. (2016), Venus Sandor et al. (2010) and Mars (McLennan and Grotzinger, 2009). But more significantly, the missions Galileo and Cassini support this view, since the giant planets have no less abundances of “metals” (elements heavier than helium), relative to hydrogen than the inner planets. Indeed, in those giant planets S abundances are much higher than observed in the Sun (Owen et al., 1999). In fact, the Jovian S abundance (measured by Galileo) exceeds Solar by a factor of three (Atreya et al., 2003).

Returning to our own planet, sulphur in the fossil record extends some three billion years before the present. There is evidence for the ancient emergence of sulphate-reducing microorganisms, which go back to the Archean: The phenomenon of sulphate reduction has been confirmed in terrestrial sediments 3.47 billion years before the present. At that time, in Australia they produced strong stable isotope depletions in pyrite embedded in barite (Shen et al., 2001; Shen and Buick, 2004).

## DISCUSSION OF INNOVATIVE MISSIONS FOR THE GAS AND ICE GIANTS

### Biogeochemical Biosignatures Beyond Mars and Jupiter

Due to the large distances involved, in the foreseeable future it will not be possible to apply the robust biogeochemical biosignatures discussed in *Biosignatures From the Geochemistry of Stable Isotopes* of the present review, but the planning still continues in the main space agencies. In spite of this handicap, the preliminary efforts of previous missions, Cassini, New Horizons and Dawn have given us a general view of the 19 confirmed and candidate ocean worlds of the Solar System, although, alas it will not be in the near future when we will have the first indications of an extant inhabited world in our cosmic neighbourhood.

In **Table 6** we have gathered information on the exploration of some of the possibly habitable worlds of the outer Solar System of which we have little information. Some mission concepts have been formulated for some time now. Even though they have not received support from the main space agencies, they should be considered amongst astrobiology’s most urgent future projects.

### Candidate Ocean Worlds Amongst the Moons of the Ice Giants

The search for biosignatures should be an objective for the Ice Giants Uranus and Neptune, especially the candidate ocean worlds amongst their moons: The Neptunian satellite Triton and the five Uranian moons, which are candidates for ocean worlds (Miranda, Ariel, Umbriel, Titania, Oberon). In spite of the fact that they are likely ocean worlds, in the future we still need orbiters around Uranus, as in the past it was the case for the

**TABLE 6** | Exploration of the ocean worlds of the Gas and Ice Giants.

Solar system bodies	Proposed missions	References
Enceladus	Enceladus explorer	Konstantinidis et al. (2015)
Enceladus	Enceladus Life signatures and Habitability (ELSAH)	Eigenbrode et al. (2018)
Enceladus	The Enceladus Life finder	Reh et al. (2016)
Enceladus and Titan	Explorer of Enceladus and Titan	Mitri et al. (2018)
Titan	Dragonfly to titan	Barnes et al. (2017)
Titan	OCEANUS	Mansell et al. (2017)

**TABLE 7** | Proposals of missions for Uranus and Neptune.

Solar system bodies	Proposed missions	References
Uranus	OCEANUS	Mansell et al. (2017)
Uranus	Orbital mission to uranus	Arridge et al. (2014)
Uranus	MUSE	Bocanegra-Bahamón et al. (2015)
Uranus and Neptune	ODINUS	Turrini et al. (2014)
Neptune	OSS	Christophe et al. (2012)

Saturnian system with its Cassini mission (Hofstadter et al., 2017).

In **Table 7** we have gathered some proposals of missions, not supported in the current programmes of the main space agencies, which may throw some light on additional ocean moons around and beyond Uranus and Neptune, for instance: the Neptunian moon Triton, Pluto, Ceres, and the Saturnian moon Dione.

## Candidate Ocean Worlds in Our Cosmic Neighbourhood

We have some remarkable moons in the outer Solar System, Triton being one of them (Gaeman et al., 2012; Nimmo and Spencer, 2014). It is conceivable that the geochemical biosignatures could eventually be applicable in those strange environments. The work of Hussmann and co-workers (2006) has taken into consideration, not only the above-mentioned satellite of Neptune, but in addition, moons of Saturn, Uranus, and Pluto as well (Rhoden et al., 2015).

Even tantalising opportunities are waiting in planetary science for deeper insights on the ocean worlds beyond the gas giants (Chela-Flores, 2017). But as mentioned in ***Biogeochemical Biosignatures Beyond Mars and Jupiter***, this aspect of the exploration of the Solar System has not been favoured by the space-faring nations. Some of the most significant proposals for future missions to the ice giants await the exploration of the least known ocean worlds of our cosmic neighbourhood.

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