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Review

Instrumentation for Detecting Sulphur Isotopes as Biosignatures on Europa and Ganymede by Forthcoming Missions

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Abstract: There has been remarkable progress in identifying a certain type of biosignature, both from the point of view of the payloads of forthcoming missions, and from the point of view of biogeochemistry. This progress has been due to the evolution of miniaturized mass spectrometry that can be used, under certain circumstances and for certain samples, to distinguish between putatively abiotic and biotic sulphur isotopes. These specific types of biosignatures are discussed in the context of Europa and Ganymede. Such instruments are sufficiently precise to differentiate between abiotic and biotic signatures. We reflect on new possibilities that will be available during this decade for exploring the nearest ocean worlds: Europa and Ganymede. We review arguments that point out the presence of intriguing sulphur patches on Europa's icy surface that were discovered by the Galileo mission. These patches lead to a "sulphur dilemma", which suggests not to focus future measurements exclusively on organics. We comment on the possibility of measurements of sulphur isotopes, as one kind of biosignature, to be complemented with additional biosignatures, in order to fully test biogenicity. These suggestions are intended to point out the best use of the available spacecrafts' payloads during the planning of the forthcoming Jovian missions.

Keywords: excursions of isotope fractionation; the JUICE mission; Europa clipper; Europa lander mission concepts

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1. A Sulphur Dilemma in the Jovian System

A sulphur dilemma can be formulated as follows: What is the origin of sulphur stains discovered by the Galileo mission? Are they due to cryovolcanism, or has the sulphur been processed by micro-organisms? To understand it we must go back to the Galileo mission. The Europa Ocean Conference was an early occasion to discuss topics that would be relevant for the return missions to the Jovian system, including its habitability [1]. One of the Galileo mission's most remarkable discoveries was the sulphur patches of non-ice elements on Europa's icy surface, which has led to the discussion of the above-mentioned sulphur dilemma: Is the source of surficial sulphur on Europa endogenous or exogenous? To address the question of endogenicity versus exogenicity, we should recall that even before the Galileo mission was launched it had been argued that the sulphur contamination, the patchiness of the surficial ice, was due to the implantation of sulphur from the Jovian magnetosphere [2]. Later on, with spectral reflectance data from various instruments on the Galileo payload, including the Solid-State Imaging (SSI) experiment, together with the Near-Infrared Mapping Spectrometer (NIMS) and Ultraviolet Spectrometer (UVS), it began to be realized that the non-water-ice materials are endogenous in different terrains [3]. Effusive cryovolcanism is a preliminary possibility as an endogenous source of the chemical elements on the icy surface [4]. The most visible aspect of the surficial elements different from water is their distribution in patches—their patchiness. If this were not such a dominating feature, implantation should have produced a more uniform surface distribution if the source had been entirely the ions from the plasma associated with Jupiter.

A similar presence of surficial sulphur was detected on Ganymede. These patches have been confirmed over a twenty-year period after the discovery by the NASA Galileo mission [5]. The present understanding of Europa and Ganymede can be taken as a first approach to a wider context of other ocean worlds [6].

2. Sulphate Reduction: Has there Been Evolution of Life on Ocean Worlds?

2.1. Isotopic Compositions

As it is possible to trace biologic fractionation into the geologic past, it is worthwhile to dwell on the biogeochemistry of stable sulphur isotopes; here are four stable sulphur isotopes: ^{32}S (94.93%), ^{33}S (0.76%), ^{34}S (4.29%), and ^{36}S (0.02%) [7]. The ratio of the two most abundant sulphur isotopes is taken as 22.22. This numerical value has been taken to coincide with the Canyon Diablo meteorite (CDM), a troilite (FeS) that was found in a crater north of Phoenix, AZ, USA.

This meteorite has been taken as a universally accepted standard, which is called δ = 0.00. Deviations from the CDM are written as $\delta^{34}S$, ratio per mil (‰). Increased abundance of the heavier ^{34}S are inferred from positive values of $\delta^{34}S$. We express isotopic compositions with the conventional δ-notation for a given sample (sa), compared to the CDM standard (st):

$$\delta^{34}S = [(^{34}S/^{32}S)_{sa}/(^{34}S/^{32}S)_{sts} - 1] \times 10^3 \text{ (CDM, ‰)}. \quad (1)$$

The ^{34}S content of the sample (sa) is given as per mil difference from the standard CDM. When the sample coincides with the standard CDM:

$$\delta^{34}S = 0. \quad (2)$$

Among the oldest microbial life on Earth there are bacteria and archaea that consume sulphate and produce sulphide as a waste product [8,9]. However, the possibility of the preference for elemental sulphur has been given careful consideration [10]. Since the evidence is from fossils of ancient microorganisms, it is not the microbial life that has been detected, but an excursion in sulphur fractionation. Since the Galileo mission there has been evidence on Europa that has been interpreted as surficial sulphur patches, possibly originating from the ocean underneath the icy surface (e.g., Section 1), rather than entirely from the nearby volcanic moon Io. The Ulysses solar mission [11] discovered the emission of streams of volcanic particles, which could have been the exclusive source of the sulphur on Europa's icy surface, except that the surficial sulphur is patchy and does not evenly cover the complete moon's surface. Testing for excursions of sulphur fractionation will be within the capabilities of mass spectrometers both in Europa Clipper, as well as in the JUpiter ICy moons Explorer (JUICE), as we shall see later on.

2.2. δ^{34} S as an Index of Biogenicity in a Terrestrial Context

The possibility of using $\delta^{34}S$ as an index of biogenicity has a long history [12]. If sulphate-reducing bacteria have been present, and ^{32}S is consequently more abundant, then we would expect negative values of $\delta^{34}S$. For the distribution of $\delta^{34}S$ in terrestrial sedimentary sulphide and marine sulphate, the largest isotopic fractionation should be included: $\delta^{34}S$ extends from $-70‰ < \delta^{34}S < +20‰$. Up to the Permian this distribution is well documented [13], differing from the present situation, in so far as the marine sulphate had a Permian value of +10, instead of today's +20. Sulphate-reducing microorganisms are capable of fractionating sulphur isotopes by more than $\delta^{34}S = -70‰$ [14], which is fortunately within reach of the accuracy of the latest improvement of mass spectrometry that is now available for the forthcoming exploration of the moons of the Jovian system (cf., Sec.5).

Even though additional distributions of $\delta^{34}S$ in other terrestrial, meteoritic and lunar materials are known [12], we should underline that for the forthcoming missions, just the distribution of $\delta^{34}S$ in terrestrial sedimentary sulphide and marine sulphate are the only relevant ones.

It is reasonable to accept the contemporary sedimentary environment evidence that there is a difference in $\delta^{34}S$ of −30 to −50‰ between biogenic-processed sulphide and marine sulphate. There has been a gradual increment of $\delta^{34}S$ in geologic time, ranging from $\delta^{34}S = 0$, for instance, in the banded iron-formation from Isua, West Greenland [15], to higher values as life on Earth appeared at a later geologic time, for instance, in Michipicoten and Woman River iron formations in the Superior Province of the Canadian Shield [16]. In these environments there is evidence that sulphate-reducing bacteria have been responsible for substantial values of $\delta^{34}S$. The presence or absence in sedimentary sulphur of these fractionation excursions are correlated with the time of emergence of biogenic processes, the so-called dissimilatory sulphate reduction, in which sulphate reducers generate hydrogen sulphide from sulphate [12]. The point to underline is the isotopic composition of sedimentary sulphide and sulphate through time: fractionation excursions of $\delta^{34}S$ have been firmly established in contemporary sedimentary environments between sulphide processed by sulphate-reducing bacteria and marine sulphate. Similar fractionations in ancient sedimentary rocks may be interpreted as certain evidence of the activity of sulphate-reducing bacteria some 2.7 billion years before the present.

Detecting biogenically processed sulphur is becoming gradually more accessible with miniaturized mass spectrometry. The miniaturization for terrestrial geologic samples has been an effort of considerable interest, since their development has kept in mind its eventual use for the in situ exploration of planetary bodies in the solar system. Nevertheless, substantial improvements can be expected in the near future [17–21].

Biomarker environmental effects have to be kept in mind, such as of photolysis, as well as alternative abiotic fractionation pathways for sulphur, such as hydrolysis. Atmospheric photochemical reactions may result in mass-independent fractionation (S-MIF) [22]. Experiments with cultures reveal generally reduced S-MIFs [23]. Similarly contained are fractionation effects due to the hydrolysis of elemental sulphur; $\delta^{34}S$ values for product sulphide and sulphate and for parent elemental sulphur at reaction temperatures of 50–200 °C differ by less than 3‰ and demonstrate that only minor sulphur isotope fractionation accompanies hydrolysis [24]. Moreover, the rates of sulphate reduction by non-bacterial processes are also dependent on T and pH. However, these rates appear to be fast enough to become geochemically important at temperatures above about 200 °C [25]. In addition, processes, such as photolysis and hydrolysis, that limit the sulphate abiotic reductions are generally smaller than the above-mentioned large biogenic ones [26].

We draw our insights on the assumption—capable of being falsified by the instruments on JUICE—that the Europan waters have been turned into a reservoir of S stable isotope fractionation.

2.3. *δ^{34} S as an Index of Biogenicity in the Context of Astrobiology*

To extrapolate to astrobiology $\delta^{34}S$ as an index of biogenicity, we first realize that there is an overwhelming amount of data indicating the role of bacteria consuming sulphate and yielding sulphide as a waste product. These microorganisms leave a clear trace of their presence in sulphur fractionation excursions that are measurable with instrumentation that is available. On the other hand, sulphur is prominent on the icy surface of an ocean world that is a major objective for astrobiology: Europa. There are solid arguments that the patchiness suggests that a source of the sulphur layer is from the subsurface ocean. If the ocean is inhabited by sulphur-processing microorganisms, some traces of their presence ought to be detectable by probing the surficial patches [27]. This exploration will be possible in the forthcoming missions to Europa and Ganymede: the hydrated salt minerals on the Ganymedean icy surface have already been interpreted as being similar to the Europan surficial non-water chemical elements. Their origin is from the subsurface ocean [28].

3. Testing for Excursions on the Surfaces of Icy Worlds

We have sufficient information on the Galilean moons of a non-ice surficial chemical element—sulphur—to allow using stable isotope geochemistry [13,29]. With this branch of the Earth sciences, we can orient ourselves on the question of whether the Jovian ocean worlds are not only habitable, but actually currently inhabited [30,31]. Achieving this objective is within our possibilities with the available instrumentation in the payloads of JUICE, or the Europa Clipper's MASPEX [32].

Significant variations of $\delta^{34}S$ were suggested from culture experiments [33]. This level of sulphur excursions is within the possibility of the instruments in the JUICE mission, especially for larger values (−70‰). A similar situation is feasible with the Europa Clipper mission. Using sulphur isotopes as a biosignature requires knowledge about abiotic systems as well. We should keep in mind abiotic isotopic fractionation, for instance, the thermochemical reduction of sulphate, which is sulphate being reduced to sulphide under the influence of heat [34,35]. It has been argued that such thermal reductions, which are typical of high temperatures, in some cases could proceed at temperatures just above the activity of bacteria reductions [36]. In any case, bacterial sulphate reduction tends to be larger than thermogenic sulphate reduction, namely, smaller ^{34}S depletions. This reinforces the interpretation of larger values of the $\delta^{34}S$ parameter as one of the possible (biogeochemical) biosignatures. As repeatedly mentioned before, sulphur isotopes are strong indicators of being considered a biosignature, but are not unambiguous, as they should be complemented by other biosignatures not necessarily related to biogeochemistry.

4. Evolution of Instrumentation for Testing Biosignatures

The work with landers and melt-probe concept studies for Europa began 25 years ago following a proposal by the Jet Propulsion Laboratory, JPL [37]. Since 2016 a NASA Science Definition Team has intended to answer questions about the icy surface and subsurface ocean [38]. As a consequence, a lander on Europa mission concept is currently under consideration [39], which could look for evidence of life while sampling the surface composition and possibly performing seismic studies of the subsurface structure. The above-mentioned suggestion to land on the icy surface of the smallest Jovian icy moon was triggered soon after the arrival of the Galileo mission: two components, a hydrobot and a cryobot, were coupled in its objective to search for life. A vehicle dubbed a "cryobot" was suggested to carry a small deployable submersible (a "hydrobot") equipped with a complement of instruments.

In the future this mission may present opportunities for the exploration of the solar system. Even though at the closing of last century it was unlikely to receive financial support, when we consider long-term plannings, e.g., [40], it is conceivable that among future mission concepts, the cryobot, remains an open question. For the first time, a conceivable technology that was suggested for the search for microorganisms in Europa's ocean may eventually be feasible.

5. Recent Work in Instrumentation for Testing Biosignatures

The payload of the JUICE Mission is capable of measuring sulphur excursions with the required accuracy [41]. The Europa Clipper's instrumentation is also adequate: the SUrface Dust Mass Analyzer, SUDA [42,43], and the MAss SPectrometer for Planetary EXploration, MASPEX [44].

A significant preparatory series of experiments by means of pyrolysis-gas chromatography-mass spectrometry has been performed in order to analyse some Archaea and Bacteria as potential analogues of icy moons microorganisms [45]. Their data have been converted into mass spectra of the type that would be obtained by MASPEX and the Particle Environment Package (PEP) for the JUpiter ICy moons Explorer (JUICE) [46,47]. With MASPEX the ability to measure any given element is sufficient to unambiguously measure S-isotope fragment ions. It is also capable of measuring excursions of sulphur fractionations.

There has been recent progress in miniaturised laser ablation ionization mass spectrometry (LIMS) for in situ measurements of sulphur isotope fractionation on planetary or icy surfaces of ocean worlds [48]. In situ measurements of sulphur isotopic fractionation excursions on Europa's icy surface have now been shown to be feasible, having identified a trend of the $^{34}S/^{32}S$ ratio, which allows them to derive isotope fractionation with an estimated $\delta^{34}S$ accuracy of ~2‰. However, since sulphate-reducing microorganisms are capable of fractionating sulphur isotopes by more than $\delta^{34}S = -70‰$, the accuracy achieved by Riedo and co-workers [48] is sufficiently precise to differentiate between abiotic and biotic signatures.

6. The Relevant Payloads of Europa Clipper and JUICE

Measurements have provided some evidence for various salts and other chemical elements on the icy moon surfaces including sulphur on Europa [49,50]. The possibility of its oceanic source has been discussed [51]. As a part of the Europa Clipper mission, SUDA will measure the composition of small solid particles ejected from the icy surface of Europa [44]. The SUDA instrument will not sample Europa's surface directly. It will sample only Europa's exosphere. However, it has been observed elsewhere that with a neutral mass spectrometer in a 100 km orbit above the icy surface of Europa, the detection of sulphur compounds would be feasible, as well as the averaged densities [52]. With PEP such measurements would be possible in the icy Jovian moons' exospheres.

Measurements have provided some evidence for various chemical elements in the surface composition of Ganymede, including sulphur [53]. Surficial effects on Ganymede [54] could provide additional opportunities for testing sulphur biogeochemical biosignatures, which may arise for Ganymede with the forthcoming mission to the Jovian system [55,56]. However, Europa flybys will also present additional occasions to test sulphur excursions with the required accuracy of ‰.

7. Final Comments

The sulphur dilemma might be solved in the near future, possibly yielding biogeochemical biosignatures. Some forthcoming efforts are conceived, or conceivable. Firstly, the programmed missions to the nearest of the Jovian ocean worlds are a possibility. Secondly, some additional help might come from with the eventual success of a first Europa Lander [39], after our early proposal of a mission concept in 1997 [37]. It is reasonable to fully exploit instruments that are already on payloads that will fly: PEP on JUICE and MASPEX and SUDA on Clipper. We have argued that in both missions it is worth searching for agnostic biosignatures on the icy surface of Europa. We will take as an agnostic biosignature a geochemical anomaly, which makes no reference to "life as we know it" (amino acids, DNA, or phospholipids). Sulphur fractionations are agnostic in so far as no mention is made of organics; it is emphasized that the missions should consider putative biosignatures other than organics.

We should especially keep in mind the need to measure large negative excursions of sulphur isotopic fractionation (and, eventually, other ocean worlds). We have included a careful discussion of what we may eventually expect regarding the habitability of both Europa and Ganymede.

The biogeochemical information that has been provided in this paper is intended to help during the exploration plans to make the best possible use of spacecrafts' payload.

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Abbreviations

The following abbreviations are used in the manuscript:

JUICE: JUpiter ICy moons Explorer;
LIMS: miniaturised laser ablation ionization mass spectrometry (general use);
MASPEX: MAss SPectrometer for Planetary EXploration (for Europa Clipper);
NIMS: Near-Infrared Mapping Spectrometer (Galileo mission);
PEP: Particle Environment Package (for JUICE);
SSI: Solid-State Imaging (Galileo mission);
SUDA: SUrface Dust Mass Analyzer (for Europa Clipper);
UVS: Ultraviolet Spectrometer (Galileo mission).

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