International Journal of Astrobiology 14 (3): 427–434 (2015)
doi:10.1017/S1473550414000391

Biogeochemical fingerprints of life: earlier analogies with polar ecosystems suggest feasible instrumentation for probing the Galilean moons

J. Chela-Flores[1,2], A. Cicuttin[3], M.L. Crespo[3] and C. Tuniz[3]

[1] *Applied Physics Section, The Abdus Salam ICTP, Trieste, Italia*
e-mail: chelaf@ictp.it
[2] *IDEA, Instituto de Estudios Avanzados, Caracas, República Bolivariana de Venezuela*
[3] *MLab, The Abdus Salam ICTP, Trieste, Italia*

Abstract: We base our search for the right instrumentation for detecting biosignatures on Europa on the analogy suggested by the recent work on polar ecosystems in the Canadian Arctic at Ellesmere Island. In that location sulphur patches (analogous to the Europan patches) are accumulating on glacial ice lying over saline springs rich in sulphate and sulphide. Their work reinforces earlier analogies in Antarctic ecosystems that are appropriate models for possible habitats that will be explored by the European Space Agency JUpiter ICy Moons Explorer (JUICE) mission to the Jovian System. Its Jupiter Ganymede Orbiter (JGO) will include orbits around Europa and Ganymede. The Galileo orbital mission discovered surficial patches of non-ice elements on Europa that were widespread and, in some cases possibly endogenous. This suggests the possibility that the observed chemical elements in the exoatmosphere may be from the subsurface ocean. Spatial resolution calculations of Cassidy and co-workers are available, suggesting that the atmospheric S content can be mapped by a neutral mass spectrometer, now included among the selected JUICE instruments. In some cases, large S-fractionations are due to microbial reduction and disproportionation (although sometimes providing a test for ecosystem fingerprints, even though with Sim – Bosak – Ono we maintain that microbial sulphate reduction large sulphur isotope fractionation does not require disproportionation. We address the question of the possible role of oxygen in the Europan ocean. Instrument issues are discussed for measuring stable S-isotope fractionations up to the known limits in natural populations of $\delta^{34} \approx -70‰$. We state the hypothesis of a Europa anaerobic oceanic population of sulphate reducers and disproportionators that would have the effect of fractionating the sulphate that reaches the low-albedo surficial regions. This hypothesis is compatible with the time-honoured expectation of Kaplan and co-workers (going back to the 1960s) that the distribution range of $^{32}S/^{34}S$ in analysed extra-terrestrial material appears to be narrower than the isotopic ratio of H, C or N and may be the most reliable for estimating biological effects. In addition, we discuss the necessary instruments that can test our biogenic hypothesis. First of all we hasten to clarify that the last-generation miniaturized mass spectrometer we discuss in the present paper are capable of reaching the required accuracy of ‰ for the all-important measurements with JGO of the thin atmospheres of the icy satellites. To implement the measurements, we single out miniature laser ablation time-of-flight mass spectrometers that are ideal for the forthcoming JUICE probing of the exoatmospheres, ionospheres and, indirectly, surficial low-albedo regions. Ganymede's surface, besides having ancient dark terrains covering about one-third of the total surface, has bright terrains of more recent origin, possibly due to some internal processes, not excluding biological ones. The geochemical test could identify bioindicators on Europa and exclude them on its large neighbour by probing relatively recent bright terrains on Ganymede's Polar Regions.

Received 19 March 2014, accepted 15 August 2014, first published online 10 October 2014

Key words: biogeochemistry, habitability of Europa, isotope composition measurements, miniature laser ablation TOF mass spectrometer, the JUICE mission, the NASA proposed Europa lander.

Introduction

A variety of terrestrial ecosystems are analogues of the Jovian moon Europa. They have been discussed in the past in order to anticipate its potential habitability conditions and, especially, whether Europa may be inhabited (Lorenz *et al.* 2011). In this context, we should highlight, firstly the Canadian Arctic at Ellesmere Island, where sulphur patches are accumulating on glacial ice lying over saline springs that are rich in sulphide and sulphate (Gleeson *et al.* 2012). Secondly, an additional ecosystem is in the McMurdo Dry Valleys that has been identified on the microbially produced icy patches of Blood Falls (Mikucki *et al.* 2009; Fisher & Schulze-Makuch 2013).

These two examples are well-understood analogies that motivate the main thrust of the present work. Our main aim is to discuss possible tests of biogenicity on the Galilean moons, especially on Europa that are feasible with the instrumentation that has been approved by the forthcoming mission to the Jovian system. The geochemical tests to be discussed could identify bioindicators on Europa and exclude them on its large neighbour by probing relatively recent bright terrains on Ganymede's Polar Regions. For example, the sulphates known to be present in the low-albedo regions should by micrometeorite bombardment produce a quantity of sulphur atoms in the thin Europa atmosphere as will be discussed in the following sections. But we hasten to underline, as we did in an earlier work (Chela-Flores 2010) that geochemical tests could identify bioindicators on Europa and exclude them on its large neighbour, Ganymede. This remark arises from probing relatively recent bright terrains on its polar regions. For example, the sulphates known to be present in the Europan low-albedo regions should by micrometeorite bombardment produce a quantity of sulphur isotopes in the thin Europa atmosphere, but exclude them form Ganymede due to the different nature of their respective oceans.

Various geophysical insights that are evident from Archaean hydrothermal vents can orient us into what may be similar biotopes on the Galilean moons. Even though there is evidence for an ocean on Ganymede (McCord *et al.* 2001), it is not expected to be in contact with its silicate core. In two of the Galilean satellites that the JUICE mission intends to explore in some detail, mass spectrometry either on a lander or inferred from orbital measurements from JGO should yield different results for fractionated sulphur according to our hypothesis: the biogenically processed icy patches of Europa should give substantial depletions of ^{34}S, whereas Ganymede measurements should give significantly lower values for the depletion of ^{34}S. In other words, a large minus δ^{34}S for Europa and small minus δ^{34}S for Ganymede, would test the origin of habitable ecosystems in two of the Galilean moons (Chela-Flores & Kumar 2008; Chela-Flores 2010). The relevance of this result should be seen in the light of more recent research (Grassett *et al.* 2013a), where the authors do not exclude that current knowledge of Ganymede's ocean may possess all the requisites for being habitable. The proposed stable isotope fractionation result would be more relevant for testing the nature of icy surfaces of Galilean moons, where biogenic activity from the internal oceans may have altered a relatively young surface measured in tens of millions of years. This is the case of Europa estimated to be 30–70 Myr old (Zahnle *et al.* 2003).

Besides the case of the Europan ocean, the work presented in this paper is potentially applicable to the other oceans that may be present in the outer Solar System. These are Ganymede (Vance *et al.* 2014) and Callisto (Spohn & Schubert 2003), where the conditions for life appear to be less favourable on Europa. The main rationalization is the lack of contact with silicate cores (Lipps *et al.* 2004). Other possible oceans have been suggested: Firstly, among the Saturn satellites our work may apply to Enceladus (McKay *et al.* 2014). Secondly, in the Neptune system Triton is yet another potential example of a moon ocean that will eventually be explored (Gaeman *et al.* 2012; Turrini *et al.* 2014). Even though specific missions to all of them have not been endorsed at present by the various space agencies, the habitability tests mentioned in this work will eventually be relevant.

Is there an Europan population of sulphate reducers and disproportionators?

Stable isotopic fractionation in atmospheric studies

We should first recall that the sulphur isotopic interpretation of biosynthetic pathways is a time-honoured subject that deserves attention, even if space limitation constrains us to highlight only a few significant contributions (Canfield & Thamdrup 1994; Canfield & Raiswell 1999; Johnston 2011). These works embody some of our current understanding of the relevance of sulphur isotopes and the evolution of the terrestrial surface sulphur cycle. The point we wish to underlie here is that within the last decade, this information has been supplemented by new data derived from the less abundant isotopes [^{33}S and ^{36}S] (Farquhar *et al.* 2003). Indeed, multiple sulphur isotope geochemistry has expanded our insights of biological evolution and activity, and several fields related to Earth surface processes. For earlier references, we refer to the detailed review of Hoefs (2009). These robust bases support the feasibility of extending terrestrial geochemistry to other worlds in our Solar System.

Against this background, sulphur stable isotopic fractionation applied to terrestrial atmospheric studies, has an excellent track record. In particular, the related mass-independent effects in planetary atmospheres, other than the terrestrial one have been considered. If we focus our attention on probing Europa's ice to test the hypothesis that substantial processing of seafloor sulphur by sulphate-reducing micro-organisms might have taken place, measuring a large effect (for instance, $\delta^{\mathbf{34}} \approx -70‰$ has been reached in euxinic seas, cf., Section 'The biogenic hypothesis'). If after biogenic activity over geologic time turned the Europan ocean into a condition close to terrestrial euxinic seas, we will argue that the biogenic signal would not be ambiguous. Recalling that $^{32}\mathrm{S}/^{34}\mathrm{S} = 22.6$ (Kaplan 1975), in the usual notation the sulphur fractionation has been denoted as:

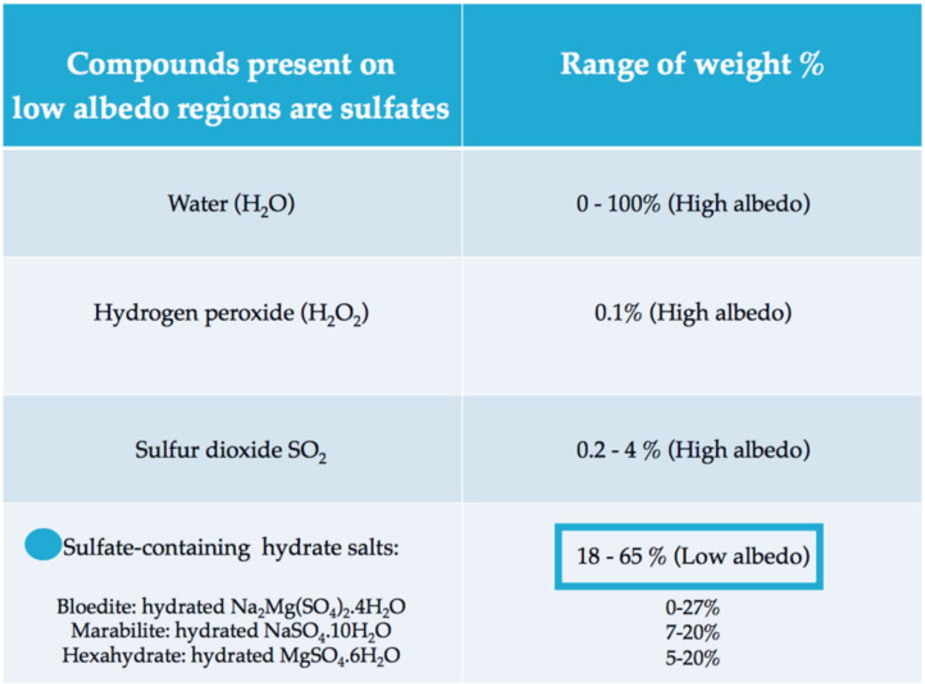
$$\delta^{34}\mathrm{S} = \left[\left(^{34}\mathrm{S}/^{32}\mathrm{S}\right)_{\mathrm{sa}}/\left(^{34}\mathrm{S}/^{32}\mathrm{S}\right)_{\mathrm{CDT}} - 1\right] \times 10^{3}\left[^{0}/_{00}\right]. \qquad (1)$$

Its value is close to zero when the sample coincides with the corresponding value of the standard Canyon Diablo meteorite (CDT), which is a triolite (FeS) that was found in a crater north of Phoenix, Arizona, a long-time standard that has recently been replaced. This parameter allows a comparison of a sample (sa) with the standard CDT. The relevant terms are the dominant sulphur isotope (^{32}S) and the next in abundance (^{34}S).

Testing sulphur isotopic fractionation imprinted by a microbial ecosystem

Difficulties may arise on two accounts: thickness of the atmosphere and the abundance of sulphur. Determining the S

Table 1. *The albedo of the icy surface of Europa. The suggested abundances of sulphur compounds on Europa based on analogous terrestrial systems (Shirley* et al. *2010).*



Compounds present on low albedo regions are sulfates	Range of weight %
Water (H_2O)	0 - 100% (High albedo)
Hydrogen peroxide (H_2O_2)	0.1% (High albedo)
Sulfur dioxide SO_2	0.2 - 4 % (High albedo)
● Sulfate-containing hydrate salts:	18 - 65 % (Low albedo)
Bloedite: hydrated $Na_2Mg(SO_4)_2.4H_2O$ Marabilite: hydrated $NaSO_4.10H_2O$ Hexahydrate: hydrated $MgSO_4.6H_2O$	0-27% 7-20% 5-20%

abundance required for detecting up to the order of $\delta^{34} \approx -70$‰ is a challenge. The ability to make S isotope measurements have to answer two questions. Firstly, are they possible due to the presence of a very thin atmosphere? Secondly, is the abundance of the ejected surficial sulphur sufficient for the instruments available now? Cassidy and co-workers (Cassidy *et al.* 2009) find that the instrument, a neutral mass spectrometer (NMS) orbiting at a height of 100 km above the surface is capable of performing the relevant measurement, and secondly, that the globally averaged densities at the orbital height for SO_2 is 110–600 cm^{-3}. The NMS is capable of detecting these species with surface concentrations above 0.03%.

Sulphur is a key non-icy contaminant of the Europan surface

Galileo magnetometer data suggested the existence of an induced moment that requires a layer of a highly electrically conductive material in Europa's interior that appears to originate from an ocean containing ions. The most plausible candidate for this role is a large subsurface ocean of liquid saltwater (Kivelson *et al.* 2000). But some constraints on the composition of Europa's ocean have been discussed concerning the nature of the ocean saltwater (Zolotov & Shock 2001, 2004). The icy surficial patches were investigated by Galileo near-infrared spectrometry: the sulphate group (SO_4^{2-}) was detected (Carlson *et al.* 1999; McCord *et al.* 1999). The source of hydrated sulphate salts detected on low-albedo regions is likely from the ocean beneath (Fanale *et al.* 2000). Magnesium sulphate, for instance epsomite $MgSO_4.7H_2O$ that is highly soluble in water at low temperatures suggests that it is a leading candidate for being present in the saltwater that was discovered by the Galileo magnetometer data (McCord *et al.* 2002; cf., also Table 1, first column).

Even though the magnesium sulphate is very soluble and the surface of Europa is recent on a geological scale, separating endogenic and exogenic material is of paramount importance. If endogenous populations of sulphate-reducing bacteria are present in the Europa Ocean, surficial locations, such as Castalia Macula (0°N, 225°W), provide ideal places to sample material that has recently been erupted from the subsurface and may have been in communication with Europa's ocean (Prockter & Schenk 2005). The tests we are proposing in the present paper can feasibly detect, or rule out, the presence of a significant biogenic signal in sulphate that has been processed by microbial life.

Oceanic origin of possibly fractionated sulphate in hydrated surficial salts on Europa

To address the question of the oceanic origin of surficial sulphate, one issue is relevant and has to be answered to begin with: What is the importance of the young age of the surface of Europa for the age of the sulphate patches? The age of the sulphate patches is geologically young, constrained by the highly resurfaced icy cover itself. But in some places the hypothesis of an oceanic biota can be tested to illustrate the relative contributions of endogenic (from Europa's conjectured biota) and exogenic processes, for instance, the sulphur originated for Io's volcanic activity. Castalia Macula, once again, points to the way ahead. The low albedo has suggested it to be a site of non-ice materials, including hydrated minerals (Carlson *et al.* 1999; McCord *et al.* 1999), which appear to have originated from the underlying ocean. If such is the case, the conjectured biota may have fractionated the sulphur, unlike the exogenic contribution from Io, where no biota is possible due to its high temperatures.

Experimental work supports the interpretation of the surficial low-albedo contaminants as a variety of salts, since aqueous leaching of salts from carbonaceous chondrites suggests this possibility (Fanale *et al.* 2001). Europa silicate mantle has been conjectured to have been formed from these small bodies in the early Solar System. The composition of ordinary and carbonaceous chondrites, CM (volatile rich) and CV type (volatile poor) was suggested as a possible primary material that gave rise to the ocean.

Besides, Galileo gravity measurements and magnetometer data can explain the existence of a salty ocean (Kargel *et al.* 2000). Having justified the origin of the ocean, the 2001-leaching/freezing experiments of Fanale and co-workers mentioned above argue in favour of estimates of Europa's ocean composition that is independent of Galileo orbital remote sensing. Together with this significant experimental work, some theory (Zolotov & Shock 2001) has supported the predominance of magnesium and sodium sulphates formed from freezing oceanic water. This scenario is in agreement with the Galileo near-infrared spectral region.

The biogenic hypothesis

Against the observations from Galileo's orbit, the experimental work of Fanale and co-workers and the above-mentioned theoretical work of Zolotov and Shock, in our paper we add an additional significant contribution to Europa's ocean, namely we conjecture the presence of an oceanic anaerobic population of biological sulphate reducers and disproportionators. This hypothesis is subject to experimental refutation (cf., below 'Testing the biogenic hypothesis'). In view of the history shared by the early Solar System, up to 4 Gyr before the present (BP), not only the Earth, but also other large bodies, such as growing planets and their satellites were subject to the Early Heavy Bombardment that seeded significant carbon inventories (Chyba & Sagan 1992). Around this time the first steps leading to the emergence of earliest terrestrial micro-organisms (both autotrophic and later heterotrophic – the precise dates remain uncertain). The geochemical evidence needs to be confronted with geochronology (Schildowski 1988; Moorbath 1994). Europa is no exception: if there is an oceanic biota the earliest autorophs and, later, heterotrophs would be able to obtain their carbon.

Our proposed Europan microbial ecosystem would have the effect of fractionating the sulphate that reaches the low-albedo regions, whose spectra was observed by the IR-Galileo spectrometer. Just as the geological record of stable sulphur isotopes is a real archive of insights about Earth's history (Detmers *et al.* 2001), we can also expect the same with the coming era of exploration with the JUpiter ICy Moon Explorer (JUICE), which is a Large-class mission in ESA's Cosmic Vision 2015–2025 programme. It will probe the Jovian system, including, but note exclusively: Ganymede and Europa (Grasset *et al.* 2013b). We should aim at retrieving as far as possible the geological record of the Europa's stable sulphur isotopes. In the case of S mass-dependent fractionations (S-MDF), advances in the understanding of the metabolism of sulphate-reducing bacteria lead to the conclusion that for the largest S-MDF bacterial sulphate reduction can be of the order of –70‰ (Wortmann *et al.* 2001; Brunner *et al.* 2005). This is in excess of –46‰, previously considered to be the theoretical maximum (Rees 1973) that had been confirmed in the laboratory with pure cultures of sulphate-reducing bacteria (Kaplan & Rittenberg 1964).

Yet, for 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) (Thamdrup 2007). Experiments with cultures reveal generally reduced S-MIFs (Franz *et al.* 2013). Similarly contained are fractionation effects due hydrolysis of elemental sulphur, δ^{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 (Smith 2000). 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 euxinic ocean, a reservoir of S stable isotope fractionation. Our analogy has a terrestrial counterpart in the Black Sea (known to the early Romans as Pontus Euxinus, its waters are consequently have been called 'euxinic'). Such sulphur-reducing populations are capable to turn seas into dark sulphur-laden waters (Grice *et al.* 2005). Naturally occurring sulphides in sediments, and in euxinic waters, can be depleted in ^{34}S by as much as – 70 per mil. With a repeated cycle of sulphide oxidation to elemental sulphur, followed by a reaction in which a single compound is simultaneously oxidized and reduced (disproportionation), these microbes can generate large fractionations that go well beyond the Rees upper bound of 46 per mil (Canfield & Thamdrup 1994). If sulphur fractionations (by sulphate reducers and disproportionators) are present in the Europan patches on its icy surface (the main hypothesis of this work), then detecting large fractionations would be a fingerprint of life. It should be underlined that the biomarkers we have singled out in our work for the extreme case of an Europan euxinic ocean may provide an example of distinguishing life from non-life (processes, such as photolysis and hydrolysis that limit the sulphate abiotic reductions, are generally smaller than the above-mentioned large biogenic ones).

A separate question has a parallel between terrestrial geochemistry and Europa's characteristics: a sufficiently oxygenated terrestrial Archaean ocean was needed to support sulphate reduction, as well as disproportionaiton: indeed, cosmic rays impacting on Europa's surface may convert some water ice into free oxygen (O), which could then be absorbed into the ocean below as water wells up to fill cracks (Greenberg 2009). Via this process, Europa's ocean could eventually achieve an oxygen concentration greater than that of Earth's Archaean oceans within just a few million years.

This would enable Europa to support anaerobic microbial life, including sulphate reducers and disproportionators, namely our hypothesized Europan biota. Only experiment can either confirm of reject our biogenic hypothesis of an anaerobic oceanic Europan biota.

Testing the biogenic hypothesis: instrument issues

The Galileo Mission heritage for the Europan tenuous exoatmosphere

Sulphuric acid hydrate abundance is linked to the magnetospheres' charged particle energy flux, and could result from radiolytic processing of implanted sulphur from Io, or of sulphur emplaced as part of the surface deposits that came from the interior (Grasset *et al.* 2013b). We should underline that the potential significance of the S influx from Io is not being able to yield sufficiently large fractionations, due to its surficial high temperature. Their exogenic nature could be recorded in the isotopes by smaller values of $\delta^{34}S$. The first of the two mutually exclusive regimes where sulphate reduction takes place is low-temperature diagenetic environments with $0 < T < 60$–80 °C. The second regime is high-temperature diagenetic environments with $80–100 < T < 150–200$ °C (cf., Machel *et al.* 1995).

Thermochemical sulphate reduction is an abiotic process, in which sulphate is reduced to sulphide, due to heat, rather than due to biology. However, the above two thermal regimes overlap in some cases (Krouse *et al.* 1988), when aqueous sulphate can be reduced by organic compounds at temperatures close to the water boiling point. A major difficulty for an unambiguous biogenic signal fortunately is once again avoided, since sulphate abiotic reductions are generally not as large as the biogenic ones. For instance, experiments have yielded fractionations in the range 10–20‰ for temperatures in the range of 100–200 °C (Kiyosu & Krouse 1990).

Destruction of large molecules by radiation, however, suggests that there may be equilibrium between creation and destruction that varies based on sulphur content and radiation flux. O_3 is not as obvious in Europa as in Ganymede, but signatures of O_2 and H_2O_2 are evident (Hall *et al.* 1995; Carlson *et al.* 1999; Fanale *et al.* 1999; Hand *et al.* 2007; Johnson *et al.* 2009). As the surface material is ejected by micrometeoroid bombardment, it can be expected that the dust particles around Europa will be composed of water ice, sulphate salts and their decomposition products, including potential organic compounds (Miljković *et al.* 2012). In addition, the Galileo Mission showed us an approach to study the atmosphere of Europa: the Dust Detector Subsystem (DDS) was used to measure the mass, electric charge, and velocity of incoming particles. Detection of the dust around Europa can provide information about its surface and in turn about its ocean (Milković 2011). Both a DDS type of instrument, as well as the miniaturized mass spectrometers already in the payload of JUICE (discussed below) are sufficiently accurate to allow measuring S isotopes in atmospheric particles.

The JUpiter ICy Moon explorer

The main science objectives for Europa are the chemistry essential to life, including the composition of the non-water – ice material. JUICE, will carry a total of 11 scientific experiments to study the gas giant planet and its large ocean-bearing moons. They include two that are of special interest for our work: PEP (package to study the particle environment) addresses all scientific objectives of the JUICE mission relevant to particle measurements. The relevance of this instrument is evident from the following question: *What are the governing mechanisms and their global impact of release of material into the Jupiter magnetosphere from Europa and Io?* (Barabash *et al.* 2013).

With the heritage of the Galileo Mission that we have just described, it is rewarding to realize that a Dust Orbitrap Sensor (DOTS) for *in situ* Analysis of Airless Planetary Bodies has been considered in response to the Announcement of Opportunity of the European Space Agency (ESA) for the JUICE mission (Briois *et al.* 2013). If we had a dust detector on board JUICE, the search for biomarkers would be enhanced, not only with the miniaturized mass spectrometer, but also with DOTS we could further analyse the ejected surface fragments.

Assuming that the internal material circulates inside the moon reaches very close to the surface (Greenberg 2005), it is possible to have both surface and subsurface material ejected from Europa's surface by micrometeoroid bombardment. The composition of the ejected dust fragments should be very similar to the actual surface material of the regions from which they were ejected. The JUICE Mission has been provided with instruments to make analogous measurements.

A possible NASA landing mission

This accuracy of the orbital tests should be compared with the expected accuracy that will be needed with the proposed study of the lander that has been commissioned: NASA intends to implement its science goals for a landed spacecraft mission to the surface of Europa, including the investigation of the composition of its icy surface and the likelihood of its habitability (Pappalardo *et al.* 2013).

If this option was realized, the well-tested miniature laser ablation time-of-flight mass spectrometers (TOF-MS) would be ideal instruments to take into consideration for the payloads (Riedo *et al.* 2012, 2013a, b). In this context, the laser-ionization mass spectrometry (LIMS) are especially relevant. They are capable of detecting almost all elements, including sulphur. This is demonstrated in the mass spectrum of the lead isotopic pattern in a standard sample, for ^{208}Pb the mass resolution $m/\Delta m$ is such that isotopic analysis in the required per mill accuracy can be achieved. The results for sulphur are of the same order of magnitude (Riedo *et al.* 2013a, Figs. 13 and 15).

In view of the multiple difficulties that fundamental geobiology presents (Knoll *et al.* 2012), in this work we advocate the combined efforts that an orbiter could implement together with a lander, such as the one conceived and discussed by NASA. In the foreseeable future a reliable detection of a large negative δ^{34} parameter imprinted on the icy surface of Europa could be the first reliable fingerprint of life elsewhere.

Biomarkers in the atmosphere

Measuring biomarkers in the atmosphere would be particularly challenging. At present there is no certainty of a possible landing on the icy surface of the Galilean satellites. Nevertheless, we discuss the PEP instrument from the point of view of possible ways for addressing the question of biomarkers. In fact, Europa's atmosphere is relevant, since it is normally considered as an extension of its surface (Johnson *et al.* 2009). Besides, if chemical elements in the exosphere are of endogenic origin, as for instance, sulphur compounds, the ultimate source must be regions having a young surface, where the upwelling of subsurface material may occur. This raises the possibility that the observed chemical element may be from the subsurface ocean (Leblanc *et al.* 2002). Consequently, in spite of the atmospheric biomarkers being particularly challenging, with the accuracy of the available instrumentation we have just discussed, the possibility arises to measure anomalous S isotope ratios that would test the biogenicity, or not of the surficial icy patches.

Biomarkers in the ionosphere

The erosion of the icy surface of Europa, also called 'sputtering', is due to energetic heavy ions from Jupiter's magnetosphere (sulphur and oxygen) that eject H_2O molecules. Other molecules representative of non-ice elements from the icy surface, such as the sulphur that is on the surficial icy patches, will be carried off with the ejecta at levels detectable using an ion mass spectrometer (IMS) on an orbiting spacecraft (Cassidy *et al.* 2009), just like JUICE's PEP that includes an orbital spacecraft with an IMS, such as the NIM Spectrometer. The atmosphere and ionosphere are populated by impacting heavy and energetic ions (100's keVs) that are provided by the Jovian magnetosphere. The yields of the impinging ions are large ($>10^2$ water molecules per incident ion, Johnson *et al*. 1998).

Miniaturized mass spectrometers

There is a new generation of instruments: a neutral gas mass spectrometer (NGMS) is a TOF-MS using a grid-less ion mirror (called a 'reflectron') for performance optimization (Wurz *et al*. 2012). One of the science goals of the Neutral Gas and NIM (a component of the PEP instrument) is the isotopic analysis of the Galilean satellites' atmospheres when the signal levels are sufficiently high, which is based on the heritage of instruments that were intended to measure the chemical composition of the terrestrial stratosphere (Abplanalp *et al.* 2009).

Searching biomarkers with a lander on the icy surface

Mass spectrometry is of utmost importance for the question of habitability. This concern forces upon us special care for the appropriate instrumentation that can serve to estimate the relevant geochemical measurements. Fortunately, there is long heritage of mass spectrometry in various previous and current missions: laser-induced breakdown spectroscopy (LIBS) and laser ionization mass spectrometry (LIMS) are experimental techniques that first come to mind since they have been adopted for space research. Highly miniaturized instruments have been developed (Riedo *et al.* 2013a).

Mass spectrometric analysis of elemental and isotopic compositions can be performed by a miniature laser ablation/ionization reflectron-type TOF-MS (LMS) using an fs-laser ablation ion source (Riedo *et al.* 2012, 2013b). The results of the mass spectrometric studies indicate that under certain conditions, the measurements of isotope abundances can be conducted with a measurement accuracy at the per mil level and at the per cent level for isotope concentrations higher and lower than 100 ppm, respectively.

The elemental analysis can be performed with a good accuracy. This accuracy should be compared with the expected accuracy that will be needed with the proposed study of the lander that NASA has commissioned a study for a landed spacecraft mission to the surface of Europa, including the investigation of the composition of its icy surface and the likelihood of its habitability (Pappalardo *et al.* 2013). In this context, separating the endogenic from the exogenic materials is of prime importance. But considering that the spacecraft itself may be a source of outgassed volatiles and organic compounds, this factor suggests the instrumentation sensitivity at, or below 1 ppb, to distinguish contamination of the samples that need to be probed.

Discussion

The low expected abundance of organic compounds at Europa based on terrestrial systems such as the oceans, hydrothermal vents and the Vostok Lake suggests that measuring organics on Europa will require high sensitivity such as the one provided by the ESA PEP technology (cf., Riedo *et al*. 2012, 2013a, b). From Table 1 ('range of weight %'), we appreciated that on Europan surficial icy materials sulphur is expected to be present at <1 wt% to even 50 of the weight per cent, depending on the species and on the surficial location. The considerations in this work make it likely that an eventual test for biogenicity proposed earlier should be feasible (cf., Conclusions). The large S-MDF 70 per mil δ^{34}S variations suggested for microbial sulphate reduction was discovered recently in pure culture experiments (Sim *et al.* 2011) and is only observed in a small handful of natural environments. This result does not exclude an Europan biota composed of sulphate reducers and disproportionators that over geologic time may lead to a euxinic ocean that can be tested with instruments on board of JUICE.

Instrumental issues have been discussed in this paper to ascertain that possibly biogenic stable S-isotope fractionation the order of up to $\delta^{34} \approx -70‰$ are not beyond the combined efforts of the NASA lander with the mass spectrometers that are available at present (Riedo *et al.* 2013a). We expect that bright terrain form from earlier dark terrain by some internal processes that may have changed its surface (Greely 2013); but, at this stage, we cannot exclude the participation of biogenic contributions. As in the case of Europa, the trailing hemisphere is darker, possibly due to external implantation, but not excluding hydrated brines, as the sulphate salts that we have mentioned earlier for the case of Europa (cf., Table 1, 'Sulphate-containing hydrate salts', in the first column).

The geochemical tests suggested in this paper could, in principle, discriminate the nature of the non-icy contaminants of Ganymede trailing hemisphere to exclude a biogenic component (small minus $\delta^{34}S$).

Conclusion

The present work suggests the way ahead to the following question: *How can we make some progress in the search for biomarkers?* We recall that besides the present knowledge of the Europan surface, the surface of Ganymede is known up to 80% from two preceding missions: Voyager (low-resolution images) and Galileo (middle-resolution images $\cong 10$ km px^{-1}, exceptionally reaching down to 100 m px^{-1}).

In contrast to these relatively low resolutions, JUICE is expected to provide some urgently needed high-resolution imaging <5 m px^{-1}. Firstly, dark, heavily cratered ancient terrain covers about one-third that can be dated to at least 1 Gyr BP (Schenk *et al.* 2010). *Galileo Regio*, is an outstanding example on the leading hemisphere: it is semi-circular in shape with over 3000 km across, largely covered by dark terrain (Greely 2013). Secondly, bright terrain covers the remaining two-thirds, consisting of ridges and grooves. It is on the average 2 Gyr BP (with large uncertainties ranging from 1 to 3.6 Gyr). Bright terrain covers, for example, polar areas.

Sadly, no Ganymede lander is under consideration by any of the space agencies. The major issue of discerning whether there are habitable Galilean satellites has been the core of this work. We have to rely eventually on careful consideration of the exosphere of Ganymede. Fortunately, even though a lander is still not under consideration, JUICE is expected to have a broad mission profile, including several orbits around the largest moon of the Solar System that will begin in September 2032, well before the Mission nominal end a year or so later, when the orbiter will be disposed of on Ganymede itself (Grasset *et al.* 2013b), yet not posing any significant planetary protection risk (Grasset *et al.* 2013a):

- First elliptic (10 000 × 200 km) 30 days.
- High-altitude circular (5000 km) 90 days.
- Second elliptic (10 000 × 200 km) 30 days.
- Medium-altitude (500 km) circular (102 days)
- Low-altitude (200 km) circular (30 days).

In addition, JUICE is also expected to include two close flybys around Europa. As argued in this paper, with these planned flybys the possibility of performing biogeochemical measurements is feasible with the required accuracy of ‰.

At a later date it is possible to discuss what would be required to analyse the isotopic sulphur content of the Ganymede exosphere (faithfully reflecting the surface contaminants), as well as in the exoatmospheres in other outer Solar System moons. Such studies are needed with analogous line of reasoning with the case of Europa that we have discussed above. Such studies would go a long way to complete the test of biogenicity of the known or hypothesized moon oceans. However, theoretical enquiries of this nature lie beyond the scope of the present work.

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