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Biogeochemical Fingerprints of Life: From Polar Ecosystems to the Galilean Moons (*)

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Abstract: We highlight two aspects of terrestrial Polar Regions that are relevant for astrobiology. We mention the Canadian Arctic at Ellesmere Island, where sulfur patches are accumulating on glacial ice lying over saline springs rich in sulfate and sulfide. Secondly, we discuss ecosystems in the McMurdo Dry Valleys of Victoria Land, Antarctica, where the microbially produced icy patch of Blood Falls is a clear analog of Europan patches. These ecosystems 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. The icy surfaces of Callisto, Ganymede and Europa are amongst JUICE's primary objectives, including the search for biomarkers. The extensive evidence for an ocean over a silicate nucleus makes Europa the leading candidate for the emergence of a second evolutionary pathway of autochthonous life in the Solar System. The Galileo orbital mission discovered surficial patches of non-ice elements on Europa, including sulfur, especially sulfate salts. These low albedo regions were found to be widespread and, in some cases possibly endogenous. Chemical elements on the Europa exosphere include SO_2. Its ultimate source must be regions having a young surface, where the upwelling of subsurface material may occur. This suggests the possibility that the observed chemical elements in the exoatmospheres may be from the subsurface ocean. Spatial resolution calculations are available, suggesting that the atmospheric S content can be mapped by a neutral mass spectrometer, now included amongst the selected JUICE instruments. As in terrestrial polar ecosystems, the largest known S-fractionations are due to microbial reduction and disproportionation, providing a test for ecosystem fingerprints. 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 sulfate reducers and disproportionators that would have the effect of fractionating the sulfate that reaches the low albedo surficial regions. We discuss the necessary instruments that can test our biogenic hypothesis. 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 exoatmosphere, ionosphere and, indirectly, surficial low albedo regions. Ganymede's surface, besides 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 neighbor by probing relatively recent bright terrains on Ganymede's polar regions.

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

Introduction

A variety of ecosystems are analogs 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., 2010). Beyond the much studied Lake Vostok (Christner et al., 2006), we should highlight the Canadian Arctic at Ellesmere Island, where sulfur patches are accumulating on glacial ice lying over saline springs that are rich in sulfide and sulfate (Gleeson et al., 2012). From the point of view of astrobiology additional ecosystems are in the McMurdo Dry Valleys of Victoria Land, Antarctica, especially on Taylor Valley, where biogenic icy patches are found on both Lake Hoare (Wharton et al., 1983; Simmons et al., 1979; Walton, 2013), as well as on the microbially produced icy patches of Blood Falls (Mikucki et al., 2009; Fisher and Schulze-Makuch, 2013).

In the context of the present work even a closer analogy may be drawn from vents under Antarctic ice (Dählmann et al., 2001). As subsurface, exothermic, mineral-fluid reactions are associated with the oxidation of iron in cooling mantle peridotite producing fluids rich in hydrogen and methane at temperatures up to 90°C. These fluids produce carbonate precipitation upon mixing with seawater, so that they may be considered an energy source for polar ecosystems, but also for ecosystems elsewhere.

There is a second general analogy, besides the terrestrial polar ecosystems, to guide our insights into what would be the nature of an Europan biota that could be tested with the forthcoming generation of instruments that can fly in the missions to the Jovian system. At the root of the phylogenetic tree of life, namely at the foot of the graphic representation of the evolutionary history of a group of organisms, there are many examples of microorganisms that are found in deep-ocean hydrothermal systems.

The biota may resemble an unusual ecosystem that has been discovered at the Lost City hydrothermal system (Von Damm, 2001). The vents are on the Atlantis Massif (a seafloor mountain), where reactions between seawater and upper mantle peridotite produce methane- and hydrogen-rich fluids with temperatures ranging from below 40° to 90°C. The Lost City analogs and the sulfide-rich high-temperature environments (Canfield and Raiswell, 1999) suggest, in a geochemical context that ecosystems of the early Earth are analogs of present-day sea-floor environments. In other worlds, if there is some form of hydrothermal venting, as on Europa, the hydrothermal system dependence on the sulfur cycle may provide appropriate guiding lines. Two terrestrial examples are the East-Pacific Rise at high temperature (Fornari et al., 2012, or at moderately lower temperatures the Atlantis Massif (Vance et al., 2004).

Both analogies, the polar ecosystems and the sea-floor bacterial communities lead us to pay special attention to the sulfur cycle, including dissimilatory sulfate reduction, as well as elemental S-processing by disproportionators, as we do in the present paper.

Is there an Europan population of sulfate reducers and disproportionators?

Stable isotopic fractionation in atmospheric studies

Sulfur 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 has been considered If we focus our attention on probing Europa's ice to test the hypothesis that substantial processing of seafloor sulfur by sulfate-reducing microorganisms may have taken place, measuring a large effect (for instance, $\boldsymbol{\delta^{34}} \approx -70$ ‰) would imply that the biogenic signal would not be ambiguous (Chela-Flores, 2010). Recalling that $^{32}S/^{34}S = 22.6$ (Kaplan, 1975), in the usual notation the sulfur fractionation has been denoted as:

$$\delta^{34}S = [(^{34}S/^{32}S)_{sa} / (^{34}S/^{32}S)_{CDM} - 1] \times 10^3 \ [^0/_{00}] \quad (1)$$

Its value is close to zero when the sample coincides with the corresponding value of the standard Canyon Diablo meteorite (CDM), 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 CDM. The relevant terms are the dominant sulfur isotope (^{32}S) and the next in abundance (^{34}S). In the present work we discuss in terms of the available instrumentation what would be the ideal modifications that would make it feasible to reach the accuracy required for testing biogenicity.

Testing sulfur isotopic fractionation imprinted by a microbial ecosystem

Determining the S abundance required for detecting up to the order of $\boldsymbol{\delta^{34}} \approx -70$ ‰ is a challenge. A Monte Carlo calculation (Cassidy et al., 2009) estimates the neutral density at an altitude of 100 km is 100 - 1000 /cm^3, while at a much lower orbit of 40 km the expected density would be 10.000 to 100.000 /cm^3. The questions that we would like to raise are firstly, whether such abundances are sufficient to test for the isotopic fractionation that an oceanic potential microbial ecosystem would have imprinted on the icy surfaces of Ganymede and Europa. Secondly, whether such effects would in turn also be imprinted on their exospheres. (We pay special attention to the Europa ionosphere). Finally, we enquire about what would be the feasibility of probing the exosphere at low orbits, whether during the time of the JUICE mission, or subsequently.

Sulfur 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 that contains ions. The most plausible candidate for this role is a large subsurface ocean of liquid saltwater (Kivelson, 2000). But some constraints on the composition of Europa's ocean have been discussed concerning the nature of the ocean saltwater (Zolotov and Shock, 2001; 2004). The icy surficial patches were investigated by Galileo near-infrared spectrometry: the sulfate group (SO^{2-}_4) was detected (McCord et al., 1999; Carlson et al., 1999). The source of hydrated sulfate salts detected on low albedo regions are likely from the ocean beneath (Fanale et al. 2000). Magnesium sulfate, for instance epsomite $MgSO_4.7H_2O$ that is highly soluble in water at low temperatures suggesting 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).

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

The young surface age of Europa has been estimated to be 30-70 Myr (Zahnle et al., 2003). One implication of this remark is that possibly there are geological processes in the ocean underneath the icy surface of Europa that are maintaining chemical disequilibrium. 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 form these small bodies of 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 take into account the carbonaceous hypothesis to 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 favor of estimates of Europa's ocean composition that is independent of Galileo orbital remote sensing. Together with this significant experimental work, some theory (Zolotov and Shock, 2001) has supported the predominance of magnesium and sodium sulfates formed from freezing oceanic water. This scenario is in agreement with the Galileo near infrared spectral region.

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 $Na_2Mg(SO_4)_2.4H_2O$	0-27%
Marabilite: hydrated $NaSO_4.10H_2O$	7-20%
Hexahydrate: hydrated $MgSO_4.6H_2O$	5-20%

Table1. The albedo of the icy surface of Europa. The suggested abundances of sulfur compounds on Europa based on analogous terrestrial systems (Shirley et al., 2001).

The biogenic hypothesis

Against the observations from Galileo's orbit, the experimental work of Fanale and co-workers and 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 sulfate reducers and disproportionators, the latter being microbes capable of harnessing energy from reduction-oxidation ("redox") reactions in the environment. In such reactions a species is simultaneously reduced and oxidized to form two different products. The microbes that can derive energy from these processes have evolved means of synthesizing the all-important molecule ATP, by taking advantage physically from the exchange of electrons between the reacting molecules. This hypothesis is subject to experimental refutation (cf., below "Testing the biogenic hypothesis").

Our proposed Europan microbial ecosystem would have the effect of fractionating the sulfate that reaches the low albedo regions whose spectra was observed by the IR Galileo spectrometer. We recall that sulfur isotope fractionation by sulfate-reducing bacteria is the result of a sequence of reactions leading to the reduction of sulfate to sulfide. A conceptual model of sulfate reduction (Rees, 1973) now incorporates the less abundant isotope ^{33}S (Farquhar et al., 2003). Advances in the understanding of the metabolism of sulfate-reducing bacteria lead to the conclusion that the maximum possible sulfur isotope fractionation induced by bacterial sulfate reduction can be in the order of - 70 ‰ (Wortmann et al., 2001; Brunner and Bernasconi, 2005). This is well in excess of the value - 46 ‰ that previously was considered to be the theoretical maximum that has been confirmed in the laboratory with pure cultures of sulfate-reducing bacteria (Kaplan and Rittenberg, 1964).

Only experiment can sort either confirm of reject our biogenic hypothesis of an anaerobic oceanic population of sulfate reducers and disproportionators. Such fractionations shed new light on the issue of sulfur isotope effects by sulfate-reducing bacteria, which by their matabolism trigger a clear biosignal detectable with instruments that are capable of an accuracy of up to 2 ‰. This, in fact, is not beyond the current available miniaturized instruments that have a significant heritage in solar system exploration, as we shall discuss in detail in the following sections.

Testing the biogenic hypothesis: Instrument issues

The Galileo Mission heritage for the Europan tenuous exoatmosphere

Sulfuric acid hydrate abundance is linked to the magnetospheric charged particle energy flux, and could result from radiolytic processing of implanted sulfur from Io, or of sulfur emplaced as part of the surface deposits that came from the interior (Grassett et al., 2013b). Destruction of large molecules by the same radiation, however, suggests that there may be equilibrium between creation and destruction that varies based on sulfur 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., 1998; Fanale et al., 1999; Carlson et al., 1999a; Johnson et al., 2003; Hand et al., 2007). If oxidants can be delivered to the internal liquid water reservoirs, they can be a source of free energy available for biology. JUICE will provide information on the contamination processes acting on the surface of Europa. At medium spatial resolution in the range 5–10 km/px, it will map large areas to reveal leading/trailing asymmetries due to contamination by exogenic material. These data should be complemented by a study of the exospheric composition. 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, sulfate salts and their decomposition products, including potential organic compounds (Miljkovic et al., 2012). However, one of the most remarkable heritage from the Galileo Mission was the careful probing form orbit of Castalia Macula, a prominent ~30-km-diameter dark patch near 0°N, 225°W. It is one of the likely patches that can be from endogenous source, giving us a hint to the nature of the ocean below (Prokter and Shenk, 2005), and hence which chemical elements to expect in Europa's tenuous exoatmosphere. A careful discussion of what we learnt from Galileo about the Europan icy surface has been reviewed earlier (Carlson et al., 2009).

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. The masses of dust particles that the DDS could detect go from 10^{-16} to 10^{-7} grams. The speed of these small particles could be measured over the range of 1 to 70 kilometers per second. The instrument could measure impact rates from 1 particle per 115 days (10 megaseconds) to 100 particles per second. Such data was used to help determine dust origin and dynamics within the magnetosphere. The DDS weighed 4.2 kilograms and used an average of 5.4 watts of power. Detection of the dust around Europa can provide information about its surface and in turn about its ocean (Milkovic, 2011). Assuming that the internal material circulates inside the moon and could reach very close to the surface, it could be assumed that 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.

The JUpiter ICy Moon Explorer

The JUpiter ICy Moon Explorer (JUICE) is an ESA mission that will probe the Jovian system, especially the three moons: Ganymede, Callisto, and Europa, a Large-class mission in ESA's Cosmic Vision 2015-2025 program (Grasset et al., 2013b). Planned for launch in 2022. 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. Our special interest in this instrument is summarized in 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).

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, cf., also Table 2, "Instruments").

If this option is realized then the well tested miniature laser ablation time-of-flight mass spectrometers would be ideal instruments to take into consideration for the payloads to be decided upon (Riedo et al., 2012, 2013a and 2013b). In this context the laser-ionization mass spectrometry (LIMS) are especially relevant. They are capable of detecting almost all elements, including sulfur. 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 sulfur are of the same order of magnitude (Riedo et al., 2013a, Figs. 13, 15 and Table 3).

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

Since at present there is no certainty of a possible landing on the icy surface of the Galilean satellites, 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, sulfur 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).

As we have seen above, in 1995 Galileo revealed that Europa has a tenuous atmosphere composed mostly of molecular oxygen (O_2) (Hall et al., 1995). The surface pressure of Europa's atmosphere is 10^{-12} bar. The Galileo spacecraft performed six radio occultation observations of Jupiter’s Galilean satellite Europa during its tour of the Jovian system, which revealed the presence of a tenuous ionosphere on Europa, with a average maximum electron density of nearly 10^4 per cubic centimeter near the surface (Kliore et al., 1997). In addition, chemical elements that are known to be in the atmosphere include SO_2 (Volwerk et al, 2001). Modeling of the atmospheric spatial resolution has been done with a Monte Carlo collisionless model (Cassidy et al., 2009). In this manner the atmospheric density as a function of altitude has been obtained. With this estimate it is likely that the atmospheric sulfur content can be mapped by a neutral gas mass spectrometer, NGMS. A successful new generation of NGMS based on time-of-flight principle has been discussed − the Polar Balloon Atmospheric Composition Experiment, P-BACE (Abplanalp et al., 2009). It was tested at an atmospheric altitude of 35-40 Km that would be a model for the measurements that ought to be made on the Europan tenuous atmosphere. The extrapolation for a Galilean satellite environment seems likely due to the tested performance of P-BACE with its excellent mass range from 0 to 1000 amu/q as well as with a mass resolution $m/\Delta m > 1000$, confirming that the instrument is capable of performing adequately in planetary missions provided it is placed on an orbiter, such as the Jupiter Ganymede orbiter (JGO).

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 (sulfur and oxygen) that eject H_2O molecules. Other molecules representative of non-ice elements from the icy surface, such as the sulfur that is on the surficial icy patches, will be carried off with the ejecta at levels detectable using an ion mass spectrometer on an orbiting spacecraft (Cassidy et al., 2009), just like JUICE's PEP that includes an orbital spacecraft with an ion MS, 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). Consequently, the possibility arises to measure anomalous S isotope ratios that would test the biogenicity, or not of the surficial icy patches.

Miniaturized mass spectrometers

There is a wide possible selection of miniaturized instruments as listed in our earlier paper (Gowen et al., 2010). They employ heritage from, for instance, the Ptolemy and COSAC GC/MS instruments (Wright et al., 2006; Todd et al., 2007; Goesmann et al., 2007) on-board the ROSETTA lander package, and Beagle-2 Gas Analysis Package (Wright et al., 2003), and could cover a large mass range of species including some isotopic differentiation. Of particular importance would be the S^{32} /S^{34} ratio for the common sulfur stains on the Europan surface which are expected to be quite different between a biological and a geological origin.

There is a new generation of instruments that have been developed at the University of Bern: A neutral gas mass spectrometer (NGMS) is a time-of-flight mass spectrometer (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 Ion Mass spectrometer (NIM, a component of the PEP instrument) is the isotopic analysis of the Galilean satellites' atmospheres when the signal levels are sufficiently high, whic is based on the heritage of instruments that were intended to measure the chemical composition of the terrestrial stratosphere (Abplanalp, 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). A LIBS instrument is a part of the scientific payload of

• The Mars Science Laboratory (MSL) of NASA (Maurice et al., 2012, Wiens et al., 2012) and LIMS was a part of the scientific payload of the Phobos-Grunt lander. Sadly, the Phobos-Grunt mission did not succeed, but the related instrumentation was of utmost importance for subsequent planning. It will be a part of the Luna-Glob lander by Roskosmos (Galimov, 2010; Zelenyi et al., 2010, Marov et al., 2004).

Mass spectrometric analysis of elemental and isotopic compositions can be performed by a miniature laser ablation/ionization reflectron-type time-of-flight mass spectrometer (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 mill level and at the per cent level for isotope concentrations higher and lower than 100 ppm, respectively. Also 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

In Tables 2 and 3 we summarize the main problems that we have raised in the paper.

Instruments	Implications	Challenges
• NASA's lander for measurements on the icy surface of Europa. • ESA's PEP orbital instrument in the JUICE orbiter (JGO) for measurements in the atmosphere.	• With the lander we can probe the surficial biogenic S. • With JGO we can probe the atmospheric and ionospheric S for biogenicity.	• At the scale of a lander very little is currently known about the surface of Europa. • Choosing a landing site requires additional mapping of Europa (better resolution than with Galileo).

Table 2. Instruments and challenges in the Europan search for habitability in the Galilean moons. For the NASA lander (Pappalardo et al., 2013). For the miniature laser ablation TOF MS measurements (Riedo et al., 2013). For the ESA PEP instrument (Barabash et al., 2013).

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., Table 2 and Riedo et al., 2013 a-c). From Table 1 ("Range of weight %"), we appreciated that on Europan surficial icy materials sulfur is expected to be present at less than 1 wt % to even 50 of of weight percent, depending on the species and on the surficial location.

Instruments	Implications	Challenges
• **NASA:** The Sample Analysis at Mars (SAM, Curiosity heritage) for analyzing organics and gases from both atmospheric and solid samples. • **ESA:** Miniature laser ablation TOF MS for isotope composition measurements.	• With geochemistry we can test for microbial life. • It is eventually feasible to be able to measure sulfur isotope fractionations of up to the order of $\delta^{34} \approx -70$ ‰.	• Measurements of isotope ratios at the ‰ level (accuracy ≈ 2 ‰). • The S isotopic concentration must be above ≈ 100 ppm (Castalia Macula seems an appropriate landing site).

Table 3. Instruments and challenges in the Europan search for habitability in the Galilean moons. For TOF instruments (Riedo et al., 2013).

The considerations in this work make it likely that an eventual test for biogenicity proposed earlier should be feasible (cf., Conclusions). 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).

The origin of habitable ecosystems is linked to the seafloor activity of hydrothermal vents, which requires direct contact between the silicate core and a liquid water ocean, as it occurred in early Earth, according to the geochemical evidence that we have retrieved from some South African cratons: firstly, the Pilbara Craton including its microfossil-rich reservoir. Secondly, the Dresser Formation in Western Australia, and finally, the South African Kaapvaal Craton, which contains ancient rocks (> 3.6 billion years, Gyr before the present, BP). From these sites we can safely infer preserved details of ancient hydrothermal vents. Besides, in these sites there is some evidence for sulfate reducing bacteria (Shen and Buick 2004) and methanogens (Ueno et al., 2006). All of these microorganisms were already in existence a mere 1 Ga after the formation of Earth itself with fractionation of the isotopes of sulfur and methane.

Conclusion

The various geophysical insights that are evident from Archean 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 would not be in contact with its silicate core. In the two Galilean satellites that the JUICE mission intends to explore in some detail, mass spectrometry either on a lander or inferred from orbital measurements in the should yield different results for fractionated sulfur according to our hypothesis: The biogenically processed icy patches of Europa should give substantial depletions of ^{34}S, while Ganymede measurements should give significantly lower values for the depletion of ^{34}S.

In other words, a large minus $\delta^{34}S$ for Europa and small minus $\delta^{34}S$ for Ganymede, would test the origin of habitable ecosystems in two of the Galilean moons (Chela-Flores, 2008, 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. Our 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, as recalled earlier(Zahnle et al., 2003).

How can we make some progress in the search for these biomarkers? We recall that the surface of Ganymede is known up to 80 % from the Voyager (low resolution images) and Galileo (middle resolution images ≅10 km/px, exceptionally reaching down to 100 m/px). In contrast to these relatively low resolutions, JUICE is expected to provide some urgently needed high resolution imaging < 5 m/px (cf., Table 2, "Challenges"). Firstly, dark, heavily cratered ancient terrain covers about one-third (Shenk et al., 2001) that can be dated to at least 1 Gyr BP. *Galileo Regio*, is an outstanding example on the leading hemisphere: it is semicircular 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, which is on the average 2 Gyrs BP (with large uncertainties ranging from 1 to 3.6 Gyrs). Bright terrain covers, for example, polar areas.

Following Greely, we expect that bright terrain forms from earlier dark terrain by some internal processes that may have changed its surface; 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 sulfate salts that we have mentioned earlier for the case of Europa (cf., Table 1, "Sulfate-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 $\delta^{34}S$).

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 an 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 (10,000x200 km) 30 days.
• High altitude circular (5,000 km) 90 days.
• Second elliptic (10,000x200 km) 30 days.
• Medium altitude (500 km) circular (102 days)
• Low altitude (200 km) circular (30 days).

At a later date it is possible to discuss what would be required to analyze the isotopic sulfur content of the Ganymede exosphere that would faithfully reflect Ganymede's surface contaminants, following an analogous line of reasoning for the case of Europa as argued in the present work. This future study would go a long way to complete the test of biogenicity on the main Galilean satellites that is a major focus of the JUICE Mission. However, such theoretical enquiry lies beyond the scope of the present work.

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