THE SULPHUR DILEMMA:
Are there biosignatures on Europa’s icy and patchy surface?

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Abstract: We discuss whether sulphur traces on Jupiter's moon Europa could be of biogenic origin. The compounds detected by the Galileo mission have been conjectured to be endogenic, most likely of cryovolcanic origin, due to their non-uniform distribution in patches. The Galileo space probe first detected the sulphur compounds, as well as revealing that this moon almost certainly has a volcanically heated and potentially habitable ocean hiding beneath a surface layer of ice. In planning future exploration of Europa there are options for sorting out the source of the surficial sulphur. For instance, one possibility is searching for the sulphur source in the context of the study of the “Europa Microprobe In Situ Explorer” (EMPIE), which has been framed within the Jovian Minisat Explorer Technology Reference Study (ESA). It is conceivable that sulphur may have come from the nearby moon Io, where sulphur and other volcanic elements are abundant. Secondly, volcanic eruptions in Europa’s seafloor may have brought sulphur to the surface. Can waste products rising from bacterial colonies beneath the icy surface be a third alternative significant factor in the sulphur patches on the Europan surface? Provided that microorganisms on Europa have the same biochemical pathways as those on Earth, over geologic time it is possible that autochthonous microbes can add substantially to the sulphur deposits on the surface of Europa. We discuss possible interpretations of the non-water ice elements (especially the sulphur compound mercaptan) in the context of the studies for future missions. To achieve reliable biosignatures it seems essential to go back to Europa. Our work highlights the type of biogenic signatures that can be searched for when probing Europa’s icy and patchy surface.

Key words: Jupiter's moon Europa, biogenic signatures, sulphur patches on the Europan surface, missions to Europa, biogeochemistry.
Introduction: the patchiness of the icy surface of Europa

The two Voyager spacecrafts crossed the orbit of Jupiter in 1979. The images that were retrieved from the icy surface of Europa were significant: they presented a young terrain with very few craters. Io was a surprise due to its volcanic activity. Sixteen years later the Galilean satellites revealed more physical, chemical and geophysical data. The Galileo mission showed evidence of internal liquid water oceans in Europa and Callisto (Showman and Malhotra, 1999). Unlike the ocean on Europa, Callisto has presented planetary science with an unusual internal structure, since data from the Galileo mission suggests a lower than expected moment of inertia. The internal structure consists of a nucleus of ice and rock with the outermost 200 kilometres of water ice, or liquid water (compatible with the presence of an ocean) with an outer layer of dust accumulated throughout its history by impacting bodies. In spite of this significant discovery, in the present paper we focus on Europa’s ocean, since its internal structure suggests that this satellite provides an environment more favourable to the presence of life. Indeed, its structure is compatible with an outermost water layer of about 1 gm/cm$^3$ density and from 80 to 200-kilometre thickness, an intermediate silicate rock mantle, and perhaps a metallic core (Fe-FeS).

On the other hand, even before the Voyager and Galileo missions, it was evident that the surface of Europa is dominated by water ice (Johnson and McCord, 1971). It has also been equally clear that there is much spectroscopic evidence for the presence of non-ice substances on the surface (Delitsky and Lane, 1998). In particular, Galileo Near-Infrared Mapping Spectrometer (NIMS) evidence for the presence of sulphur compounds has been discussed in detail (Carlson et al. 2002). It had been suggested earlier that the sulphur contamination was due to the implantation of sulphur from the Jovian magnetosphere (Lane et al. 1981). However, based on combined spectral reflectance data from the Solid State Imaging (SSI) experiment, the NIMS and the Ultraviolet Spectrometer (UVS), it has been argued that the non-water ice materials are endogenous in three diverse, but significant terrains (Fanale et al. 1999). Effusive cryovolcanism is clearly one possible endogenous source of the non-water-ice constituents of the surface materials (Fagents, 2003). The most striking feature of the non-water surficial elements is their distribution in patches. Indeed, implantation would
be expected to produce a more uniform surface distribution if the source were ions from the Jovian plasma. We refer to this phenomenon as ‘the patchiness of the icy surface of Europa’. It may be argued that if the plasma from the magnetosphere were responsible for the sulphur distribution, some geologic process has to be invoked to allow for a non-uniform distribution. Such possibilities have been discussed (Carlson et al. 1999). Alternatively, the sulphurous material on the surface may be endogenous. Some mechanisms for the contamination of the surficial water ice come to mind, based on fluid-dynamic arguments (Thomson and Delaney, 2001): it is possible to interpret the non-water elements on the icy surface as the product of eruptions on the seafloor that were subsequently raised to the icy surface. This assumption is especially reasonable in the chaos-type features, such as melt-through structures that are formed by rotationally confined oceanic plumes that have risen from heated regions on the seafloor. In other words, the cryovolcanism on Europa would not be from its core, but rather from the bottom of the global ocean. It might be more like the "black smokers" that are found on the Earth seafloor. The compounds produced at the bottom of the ocean would make their way up to the surface. In the next section we use models of Europa to support the view that there is sufficient sulphur to be raised from the bottom of the ocean. These models suggest that chondrites are capable of carrying a sufficient amount of sulphur (3.25%). This property renders the chondrite as an appropriate model of a planetesimal that contributed to the formation of Europa (Oro et al. 1992).

Can waste products rising from bacterial colonies beneath the icy surface be a significant factor in the sulphur patches on the Europan surface? (Singer, 2003). The implications of biogenicity on Europa have intrigued science for some time (Chela-Flores, 2003). In fact, the above-mentioned patchiness of the icy surface of Europa presents us with the following dilemma: In forthcoming missions we could test the endogenicity of the non-water ice contaminants. The search would help us to decide whether sulphur contamination of the water ice is due to either cryovolcanism, or alternatively whether the water-ice contamination is due to endogenic factors, including biogenicity. In the rest of the present paper we shall explore some possibilities that could be made available in the foreseeable future for solving this ‘sulphur dilemma’.
Biogeochemistry of the Europa icy surface

Of all the biogenic elements, sulphur has the most relevant isotopic fractionation for the detection of traces of biogenic activity (Kaplan, 1975): Once the primordial planetary mantle material (for example, on the Earth), or satellite internal silicate nucleus (for example, on Europa) had entered their corresponding geochemical cycles, their initial isotope mixtures began to be redistributed. The Earth upper mantle and crust are believed to reflect broadly the isotopic distribution patterns of chondritic meteorites (Libby, 1971). In this context we should stress that carbon, through its \( \delta^{13}C \) \([^{0/00}, \text{PDB}]\) parameter, can be used as a good biosignature. On the Earth biota, for instance, there is ample evidence that photosynthetic bacteria, eukaryotic algae and plants have typical significant deviations that yield values of up to -30 and beyond, due to biological processes (Schidlowski et al. 1983a). These results are analogous to the deviations shown by fractionation due to bacterial sulfate reduction. The point we make here is that for an extraterrestrial test of biogenicity, as for instance, in lunar fines, where we know that life is absent, significant negative deviations in \( \delta^{13}C \) do in fact occur, but are absent in the corresponding sulphur parameter (cf., Figure 11 in Kaplan, 1975). Thus, without prior knowledge whether we are in the presence of life in a given environment, negative values of \( \delta^{13}C \) do not arise exclusively from biogenic sources. For this reason we have mentioned above that sulphur is more relevant for studying possible biosignatures.

Models of Europa suggest that a type of chondrites carry sufficient amount of water (13.35%), carbon compounds (2.46%) and sulphur (3.25%) to stand as good models of the planetesimals that gave rise to the proto-Europa (Oro et al. 1992). The meteorite in question is petrographic type-2 carbonaceous chondrite of chemical class CM, i.e., similar to the prototypical Mighei meteorite (Cronin and Chang, 1993). This shows that in an ice-ocean model of Europa, collisions with the proto-satellite planetesimals of this composition would have carried with them sufficient amounts of water to account for an ocean on Europa (up to 7 % of the mass of the satellite). Other models have been discussed during the last decade independently (Kargel et al. 1999). There would have been also sufficient carbon input for eventually inducing a substantial biota. The redistribution of the primordial isotopic mixtures can be followed up in terms of the appropriate parameter, namely the parameter:
For simplicity this function will be referred to as the delta-34 parameter, or simply as the delta parameter. Its value is close to zero when the sample coincides with the corresponding value of the Canyon Diablo meteorite (CDM), a trilite (FeS) that was found in a crater north of Phoenix, Arizona. This parameter allows a comparison of a sample (sa) with the standard (st) CDM. The relevant terms are the dominant sulphur isotope ($^{32}\text{S}$) and the next in abundance ($^{34}\text{S}$). In fact, $(^{34}\text{S}/^{32}\text{S})_{st}$ coincides with the average terrestrial fraction of the two most abundant isotopes of sulphur. We obtain positive values of the delta-parameter when by comparison we have a larger quantity of the less abundant isotope $^{34}\text{S}$. Nevertheless, the advantage of having defined such a parameter is that negative values will indicate an abundance of the most abundant isotope $^{32}\text{S}$. Besides, we remark that in non-terrestrial solar system materials (such as lunar dust, or meteorites), the values of the delta parameter are close to the CDM average. This, in turn, signifies that biological processes will be more easily recognizable when sulphur, rather than the other biogenic elements (hydrogen, carbon or nitrogen) will be considered. There is an overwhelming amount of data supporting the view that metabolic pathways of sulphur bacteria have enzymes that preferentially select the isotope $^{32}\text{S}$ over $^{34}\text{S}$. As pointed out above, this will be reflected in habitats that are depleted of $^{34}\text{S}$. In other words, in lakes, seas or oceans, where the sulphur microbes are present, the value of the delta-$^{34}\text{S}$ parameter will have characteristic large negative values.

This suggests that focusing on sulphur might be more reliable means for estimating biological effects (if any) on Europa. In contrast, to the isotopes of hydrogen, carbon or nitrogen, sulphur shows fractionation with a relatively narrow distribution range in meteorites, as well as the Moon fines, breccias and fine-grained basalts retrieved by the Apollo missions. In the case of meteorites these values are about $2^\circ/\text{oo}$ relative to the standard CDM average (Kaplan, 1975, Farquhar and Wing, 2005). The measurements of isotopic ratios of the biogenic elements were not considered during the Galileo Mission. Fortunately, they are in principle measurable in future missions to Europa.
The Galileo results and the interpretation of the NIMS data

Some arguments militate in favour of focusing on spectrometry measurements of Europa in situ. There are very clear signals associated with sulphate-reducing bacteria living in reducing environments. Dissimilatory sulphate reduction releases hydrogen sulphide with associated turnover rates of sulphur unlike the significantly much smaller assimilation processes. The consequence of this biochemical cycle is that the dissimilatory sulphur reducers are responsible for the well-observed large-scale interconversion of sulphur between oxidized and reduced reservoirs in lacustrian, marine, or oceanic environments. For instance, seawater sulphate has a delta$^{34}$S parameter value of $+20 \permil$, in sharp contrast with, for instance, biogenic insoluble sulphide in marine environments. (We find mostly biogenic pyrite, since sulphate-reducing bacteria unite H with S atoms from dissolved sulphate of seawater to form hydrogen sulphide; the H$_2$S then combines with Fe in sediments to form grains of pyrite). In these biogenic cases the delta$^{34}$S parameter can have values of even less than $-40 \permil$ (Schidlowski et al. 1983b).

The early stages of future missions may be initially tested on Earth, in environments that are similar to Europa, namely the dry valley lakes of southern Victoria Land of Antarctica (Doran et al. 1994; Parker et al. 1982; Priscu et al. 1999). One large lake lies underneath the Vostok Station, the Russian Antarctic base about 1,000 km from the South Pole. A lake, the size of Lake Michigan, was discovered beneath this Station in 1996 (Ellis-Evans and Wynn-Williams, 1996), after having drilled in that area since 1974. The lake lies under some 4 kilometres of ice. Lake Vostok, as it is known, may harbour a unique micro flora. The retrieval of biota from Lake Vostok will serve as a test for handling a larger aquatic medium, such as the proposed Europan submerged ocean that may be teeming with life. At the time of writing the lake itself has not been sampled, prevented by the bioethical principles of planetary protection. On the other hand, in the dry valley lakes there is already a well-studied biota that consists of abundant microorganisms living underneath their iced surface. The estimated annual sulphur removal is over one hundred kilograms in the case of the Lake Chad in the dry valleys (Parker et al. 1982). Thus, endogenic sulphur and other chemical elements will be, at any time, found on the icy surface of the dry valley lakes. These environments
will help us to decide on the experiments that should be performed with the help of the forthcoming Europa missions.

**Sulphur is a non-water ice constituent on the surface of the Galilean satellites**

Right from the beginning of the Galileo Mission the icy surface of Europa, and other icy Galilean satellites, were studied by spectroscopic means (Noll et al., 1995). Subsequent measurements with NIMS (Fanale et al. 1999; McCord et al. 1998) have provided some evidence for the presence of various chemical elements on their surfaces (cf., Table 1).

<table>
<thead>
<tr>
<th>New absorption features (µm)</th>
<th>3.50</th>
<th>3.88</th>
<th>4.05</th>
<th>4.25</th>
<th>4.57</th>
</tr>
</thead>
<tbody>
<tr>
<td>Possible non-water ice constituents</td>
<td>H₂O₂</td>
<td>C₂H₅SH mercaptan</td>
<td>SO₂</td>
<td>CO₂</td>
<td>(CN)₂ cyanogen</td>
</tr>
</tbody>
</table>

Although the NIMS data allows various interpretations (a situation that ought to improve during future missions), we should discuss at present the implications of some of these possibilities, in preparation for the planning of what type of biogenic signatures should be searched for, when probing the Europa icy surface for signs of life. We should recall in this context that on Earth there are chemical compounds that are associated with metabolism, or microbial decomposition. Mercaptan, for example, is one of the most intriguing interpretations of the data that is available (Bhattacherjee and Chela-Flores, 2004). We should discuss the possible interpretation, and the equipment that could test biogenicity of such sulphur compounds.
Mercaptans can be the product of the decay of animal, or vegetal matter. (Consequently, it is also found in petroleum.) The term ‘mercaptan’ applies specifically to ethyl mercaptan \( \text{C}_2\text{H}_5\text{SH} \). This is a biogenic, volatile compound of sulphur that is found in bacteria that is eventually obtained from reduced cellular sulphate. Nevertheless, in this context it should also be pointed out that the six-atom interstellar molecule \( \text{CH}_3\text{SH} \) could be present in the Jovian system from the time of its formation, since the molecule has been identified in interstellar dust (Ehrenfreund and Charnley, 2001). Consequently, if a signal at 3.88 micrometers is present on the Europan surface, before it can be attributed to a biogenic constituent, it is necessary to test its source with the appropriate instrumentation. In other words, if the presence of mercaptan is due to a relic of the interstellar medium preserved during the satellite formation, then the biogenic hypothesis could be excluded by appropriate use of the delta-34 S parameter. This enquiry is not beyond the reach of present technology, as we shall illustrate in the following section.

**Planned missions can contribute to solve the sulphur dilemma**

New missions for Europa are possible according to preliminary studies. One example is the “Europa Microprobe In Situ Explorer” (EMPIE), which has been framed within the Jovian Minisat Explorer Technology Reference Study of the European Space Agency (Renard *et al.* 2005). In this study a set of four microprobes are intended to land on the icy surface with a mass constraint of 1.7 kg. (Each lander is constrained to some 350 gm.) Their penetration in the ice could be up to just over 70 cm (Velasco *et al.* 2005). These studies could be sufficient to allow adequate instrumentation that is capable of constraining the possibilities of a biota lying beneath the surface.

Gas chromatography-mass spectrometry (GC-MS) is a possible appropriate instrumentation for the detection of such sulphur-related compounds. Indeed, there is a wide variety of miniaturized instruments available, the development of which has been required by other missions of planetary exploration, especially the Mercury-bound Bepi Colombo mission that is due to be launched next decade (Sheridan *et al.* 2003).
Originally the mission intended to have a GC-MS on a lander, but this mission has now been restricted to an orbital probe.

Endogenic, non-living sources (cryovolcanism) can, in principle, be tested with the technology of landers and probes, such as the combined microprobe concept studied by EMPIE (with its intrinsic constrain on the four small payloads that would reach the icy, patchy surface). A more advanced lander concept has been put forward envisaging landers on the icy and patchy surface, such as the JPL study (Gershman et al. 2003).

We have argued above that measuring deviations of the delta-34 S parameter from its mean CDM value can test our biogenic hypothesis. Sufficiently large negative values of the delta-34 S parameter would militate in favour of biogenicity.

Understanding the exogenous contribution of Europa’s surface patchiness

Besides the early Earth, the most likely scenarios for early life are Mars, Europa, and even Titan (Fortes, 2000, Chela-Flores, 2001). A whole fleet of missions are likely to be planned in the foreseeable future in the search life in planetary, or satellite environments. On the other hand, different sets of missions that focus on solar exploration are adding substantially to the knowledge of our nearest star. Ulysses, a solar probe, is one of them. It has made significant measurements of the Sun from a polar orbit, but in spite of not being planned for the exploration of the Jovian system it has also unexpectedly discovered the presence of abundant streams of chemical elements originating form Jupiter and its moon Io. Such a surprising discovery is relevant to the accumulation of exogenous sulphur on the surface of Europa.

From the point of view of identifying the source of the patchiness of Europa’s surface, there is a valid reason for persevering with solar missions of the Ulysses-type (Messerotti and Chela-Flores, 2006). Solar probes such as Ulysses could contribute to testing to what extent the patchy surface of Europa is being influenced by Io’s volcanic activity, but clearly further solar missions alone could not settle the question of reliable biosignatures. In other words, we need to be more certain of the mechanisms that the rotating magnetosphere of Jupiter uses for distributing the chemical elements that it receives from the volcanic activity of Io that is merely some 6 Jovian radii away from
the giant planet. The Jovian system is emitting streams of volcanic particles at passing spacecraft. The discovery of this phenomenon dates back to 1992 when Ulysses was hit by a stream of volcano dust while approaching within 1 AU from Jupiter (Grun et al. 1993). These particle streams were detected not only by Ulysses, a solar mission, but also subsequently by two of the most successful planetary exploration missions: Galileo and Cassini. It is now agreed that Io's volcanoes are the dominant source of the Jovian dust streams (Graps et al. 2000). In September 2004 the impact rate of the stream of dust particles was recorded once again by the instrumentation on Ulysses. However, Cassini's dust detector was more capable than the instrumentation on Ulysses when faced with a similar event (Sarma et al. 2000). In addition to mass, speed, charge and trajectory, Cassini measured elemental composition, finding sulphur and other elements of volcanic origin. Further measurements of the interplanetary distribution of sulphur that is spread by the dust streams of Jupiter’s magnetosphere would help us to understand to what extent the exogenic and non-biogenic sulphur accumulates on the patchy surface of Europa (cf., Discussion).

**Discussion**

As mentioned in the above section on Biogeochemistry, large negative values of the delta-34 S parameter (i.e., in the range from - 20 to beyond - 40 ‰) would be a strong and clear signal of biogenic activity. Studies of extraterrestrial materials (both lunar dust and meteorites) suggest that in the solar system no natural process, other than biological activity, yields such large corresponding depletion of the less abundant isotope $^{34}$S, compared to the more abundant isotope $^{32}$S. In fact, the small deviations from the average CDM value that are known could be due to various physical processes, as in the case of Moon dust. For example, hydrogen stripping due to solar wind proton bombardment of Moon dust can lead to minor deviations from the average CDM value < - 15 ‰. (For the relevant literature the reader is advised to refer to Kaplan, 1975.)

In this work we have addressed several questions: Why should the search for biosignatures focus mainly on the sulphur isotopes? Would a combination of sulphur and carbon isotope anomalies give the best biosignature that would show that biology is
involved? We have argued that sulphur is unique amongst the main biogenic elements in the sense that sulphur, unlike carbon, shows a very narrow range of values about zero per mil in isotopic fractionation in extraterrestrial material (lunar fines and meteorites).

Similarly, an additional question raised by our proposed selection of sulphur isotopic fractionation, rather than the corresponding analysis in term of carbon, is: Can you accept some contribution of sulphur from Io, and still find the biogenic fraction in those sulphur deposits? In this case since we are assuming from the data that only biogenic processes alter the null values of the isotopic sulphur fractionation, the contribution from the exogenous (Io) sulphur would not give the telltale signals for life that would otherwise be produced by the endogenous sulphur, if it were the product of bacterial metabolism.

Thus, indirect tests of sulphur deposition involving the solar missions do not have the same profound significance than the direct biogeochemical results that we have suggested. Clearly, it would not be possible to rule out any exogenous sources. Indeed, such an attempt would be unreasonable and might be asking too much, since we know that the sulphur distribution is patchy on Europa’s icy surface, and hence an exclusive exogenous source of sulphur is not to be expected in the first place. It could even be argued that when Ulysses and Cassini went past the neighbourhood of Jupiter and Io, special episodes of sulphur distribution were occurring that were not representative of the long-term sulphur distribution processes generated by the Jupiter magnetosphere. But in a future sequence of flybys the situation could possibly be more representative of the effect of the Jovian magnetosphere. For these reasons we have suggested that additional solar missions should be supported, but in this paper we have instead focused sharply on the question of sulphur isotope fractionation, arguing that further solar missions could nevertheless still add a small contribution to our understanding of the exogenous source of the non-water ice chemical elements on Europa’s surface.

Surely, the proposed tests for biosignatures can tolerate some exogenous sulphur, and still identify the biogenic sulphur as we have suggested above by searching along vents, or cracks, where sulphur would be concentrated. This approach suggests significant strategies for identifying those places where future landers could search for the biosignatures. The most likely sites would be where the salt deposits, or organics, are concentrated, as suggested by the NIMS data. For instance, the search for
biosignatures could focus on the area north of the equatorial region, between 0° and 30° N and between the longitudes 240° and 270° (cf., McCord et al. 1998, Fig. 2A). But a more intriguing and smaller patch would be the narrow band with high-concentration of non-ice elements that lies east of the Conamara Chaos, between the Belus and Asterius lineae, namely, between 18° - 20° N, and longitudes 198° - 202° (cf., McCord et al. 1998, Fig. 2D).

Definite answers can be searched in situ on the icy surface with GC-MS instrumentation for the corresponding measurements of the delta-34 S parameter. But even before the biogeochemical research we have briefly sketched above can be performed by four miniprobes (EMPIE studies) or by landers (JPL studies), valuable additional information about the distribution of sulphur throughout the solar system (and especially in the neighbourhood of Europa itself) could make a modest contribution to the overall question of settling one of the most significant problems in astrobiology, namely the sulphur dilemma.

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