

## Life in ancient (2.04 Ga) phosphorites

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### Abstract

The period of 2500-2000 Ma is heralded by several other hallmark events, including onset and decline of the greatest positive excursion of  $\delta^{13}\text{C}_{\text{carb}}$  (Lomagundi-Jatuli Paradox), development of a significant seawater sulphate reservoir, abundant deposition of anomalously organic matter (OM)-rich sediments, the oldest known significant petroleum deposits (Shunga Event), and the appearance at 2000 Ma of the first known marine phosphorites. They occur as numerous rounded, soft-deformed, clasts in fine-pebble intra-formational conglomerates, forming two separate c. 200 m-thick turbidite fans within the 1000 m-thick OM- and sulphide-rich turbiditic greywackes of the Pilgajärvi Formation in the Pechenga Greenstone Belt, NW Russia. Carbonate-fluorapatite is the main mineral in the phosphorite clasts and OM, framboidal and micronodular pyrite, as well as inclusions of quartz and chlorite are additional components. Many clasts show micro-layering with a variable degree of soft-deformation, implying that they were derived from non-lithified, bedded phosphorites.

Numerous samples revealed diverse microbial microstructures interpreted as cyanobacterial mats consisting of filamentous (1-3  $\mu\text{m}$  in diameter, 20  $\mu\text{m}$  in length), coccoidal (0.8-1.0  $\mu\text{m}$ ) and ellipsoidal or rod-shaped microfossils (0.8  $\mu\text{m}$  in diameter, around 2  $\mu\text{m}$  in length) (fig. 1) which morphologically resemble modern *Microcoleus* and *Siphonophycus*, *Thiocapsa*, and *Rhabdoderma*, respectively, that have been reported from alkaline or saline environments.

In addition, there are structures that may be treated as biofilms surrounding bacterial cells. Among the latter there are large beanlike or lenticular forms with a relatively thick two-layered wall with pores (canals) (fig. 2).

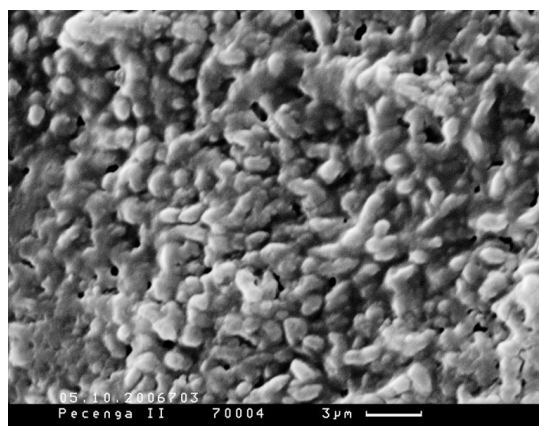


Figure 1: Rod-shaped, oval and filament microstructures and their spectrum.

The voluminous beanlike form of these structures is clearly visible on the 3D reconstructions obtained using the X-ray microtomograph. They are fairly abundant and may occur both singly, being uniformly distributed over the rock, and in aggregations. These forms are embedding in material resembling fossilized bacterial glycocalyx with isolated coccoid forms. Morphologically, fossil biological microstructures may be assigned to eukaryotes based on several characters: (1) structure of cell wall and its ornamentation; (2) convexities (projections) on the surface of the wall; and (3) wall ultrastructure. The character of wall structure in the newly discovered fossilized forms and

their size (up to 130–140  $\mu\text{m}$  in diameter) suggest that these forms belong to eukaryotes and, perhaps, to prasinophyte green algae.

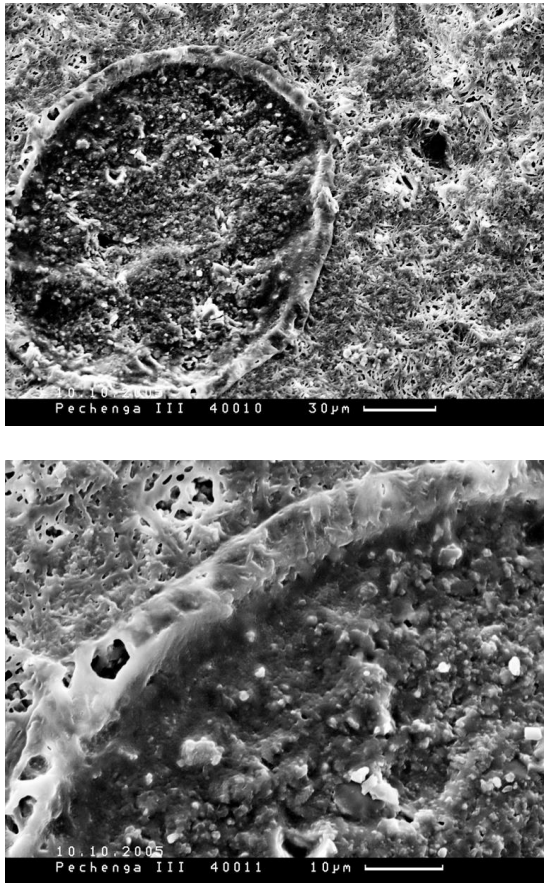


Figure 2: Cam-Scan-4 Scanning Electron Microscope images of: (upper) - Ring-shaped, sack-shaped, or spherical biomorphic microstructure and (lower) - higher magnification image showing detail of edge of ring-shaped microstructure.

No principle differences have been found between microfossils described from Cambrian and Phanerozoic and the 2000 Ma phosphorites.

The sequence of the early Palaeoproterozoic events which point to a significant oxidation of the hydrosphere, now including formation of phosphorites and change in the phosphorous cycle, mimics the sequence

which was repeated once again at the Neoproterozoic-Cambrian transition, implying that oxidation of the terrestrial atmosphere-hydrosphere system experienced an irregular cyclic development.

The Lower Proterozoic phosphorites, as well as younger: Cambrian Khubsugul, Early Cambrian and Sinian phosphorites of Yantzy Region of China and many other phosphorites have biogenic origin, that is either bacterial or is connected with cyanobacterial mats. There are no principle differences in nature of these phosphorites.

It is extremely important to underline that almost all known mineral compounds of phosphorus in the crust of the Earth are salts of orthophosphoric acid ( $\text{H}_3\text{PO}_4$ ) and that the presence of oxygen is a necessary condition for formation of this acid.

Thus it is quite clear that the studied phosphorites were formed in the conditions of a warm shallow-water basin with oxygen-enriched waters.

## Acknowledgements

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## **Spectroscopic study of amino acids adsorption on pyrite surface: From vacuum to solution conditions.**

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### **Abstract**

We characterized the adsorption of cystine molecules among other amino acids on pyrite surface via X-ray photoelectron spectroscopy. A novel comparative analysis revealed remarkable differences with respect to molecular adsorption and surface chemistry induced by environmental conditions. Pyrite is a highly reactive surface and contains two crucial types of surface functional groups that drive molecular chemistry on the surface depending on the surrounding conditions. Therefore, the systems explored in this study hold interesting implications for supporting catalyzed prebiotic chemistry reactions.

### **1. Introduction**

Understanding the interaction between biomolecules, such as amino acids, peptides or proteins, and minerals surfaces is of importance in the fields of surface chemistry, catalysis and prebiotic chemistry. Minerals can be very promising surfaces for studying biomolecule-surface processes; among such minerals is pyrite. Pyrite ( $\text{FeS}_2$ ) is one of the most important and abundant sulfide minerals on earth. Additionally, due to its catalytic activity, pyrite surface plays an important role in heterogeneous catalysis [1]. Furthermore, the study of pyrite's physical properties and reactivity is also crucial to the "iron-sulfur world" [2]. Wächtershäuser proposed that the first reactions that led to the formation of amino acids did not occur in a bulk solution in the oceans (prebiotic soup theory) but on the surface of minerals (such as pyrite) because such surfaces have the potential to facilitate prebiotic polymerization. In fact, minerals may adsorb and concentrate these biomolecules and catalyze reactions. Mineral surfaces could potentially have allowed for almost any type of general catalysis, with low specificity and efficiency. Therefore, the role of mineral surfaces could be relevant to the origin of life [3].

Recent experiments suggest that amino acids are very strongly adsorbed on mineral surfaces and that this adsorption could have facilitated peptide formation by increasing the effective concentration of amino acids and by providing catalytic sites on the surface [4]. In this context, we studied the adsorption of the amino acid cystine on pyrite by evaluating the interaction between the two under different environmental conditions. Therefore, we focused our study on investigating the possible role played by mineral surface reactivity. We report the results of a spectroscopic study, specifically X-ray photoemission spectroscopy (XPS) data, obtained for L-cystine adsorption on a natural pyrite surface and discuss spectroscopic evidence of different molecular adsorption mechanisms on the surface of pyrite constrained by oxidizing or reducing conditions.

### **2. Results**

The adsorption of organic compounds on pyrite has been studied here under different selected and well-controlled conditions. This strategy is designed to be able to evaluate how diverse environments favour or inhibit molecular adsorption on the surface. The interaction of some functional groups may drive molecular interaction with the iron and sulphur chemical groups from pyrite surface.

A comparative study of molecular adsorption in the presence and in the absence of oxidant conditions demonstrated that, in contrast to the behavior observed for metal surfaces, molecular adsorption on pyrite surface is favored under UHV conditions rather than in solution (Figure 1). Furthermore, longer exposure times in solution inhibit molecular adsorption on the surface. Our spectroscopic study revealed the presence of surface oxidation species and a low nitrogen signal as evidence of the oxidation process on pyrite, which inhibited molecular adsorption under solution conditions. Anoxic conditions facilitate molecular adsorption and the formation of a diversity of chemical species,

whereas cystine adsorbs on the pyrite surface only in its anionic form when adsorbed from solution. Surface vacancies on pyrite could affect the chemical form in which cystine is adsorbed, determining the molecular chemistry on the surface.

### 3. Figures

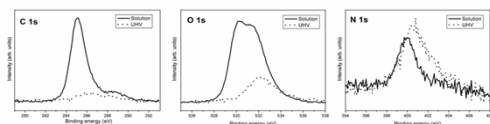


Figure 1: A comparison XPS photoemission spectra of C 1s, O 1s and N 1s core level peaks of L-cystine adsorbed from solution (-) and under UHV(...) conditions on the pyrite surface.

### 4. Summary and Conclusions

We have performed the first spectroscopic characterization of cystine adsorption on a pyrite surface. XPS analysis is employed to efficiently explore the molecular adsorption, to understand surface chemistry, and finally to describe critical influence of the presence of oxygen in cystine-pyrite systems. Successful interaction of cystine on a pyrite surface confirms the high reactivity of this surface, which could operate as a batch-reactor for prebiotic molecules. These studies could therefore shed light into prebiotic chemistry reactions.

### Acknowledgements

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# Adsorption selectivity: a way to homochirality? Computational experiments

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## Abstract

Life, as we know it today, is inseparable from homochirality; standing within the panspermia hypothesis, we investigate computationally the still unknown origin of the enantiomeric excess present in the organic matter of well-defined families of meteorites [1,2,3] through the possibilities open by a selective adsorption of the enantiomers.

## 1. Introduction

Two enantiomers have identical internal energies. When adsorbed on a same chiral surface, the complexes obtained are no longer enantiomers, but diastereoisomers. These diastereoisomers do not have the same energy. Assuming that we have a chiral interstellar surface at hand, we can consider the possibility to adsorb selectively one of the two enantiomers and thus engage a process of enantiomeric enhancement.

## 2. Selective adsorption

### 2.1 Modeling: Periodic model of the $\alpha$ -quartz surface { 1010 }

Quantitative results for adsorption energies are hard to get, experimentally as well as theoretically [4], taking into account that both, the nature of the surface and the nature of the molecule intervene in their own way. To address this problem, we rely on numerical simulations based on the methods of quantum chemistry, namely Density Functional Theory (DFT) that proved efficient in the periodic approach to this category of phenomena.

The periodic code used is VASP [5].

The active surface of infinite dimension is directly obtained by an appropriate cut of the crystal structure, and fully hydroxylated, to account for the nature of the interstellar grains. The dimensions of the unit cell, namely the horizontal interacting surface and the thickness of the slab, as well as the vertical separation between two successive slabs (vacuum), are determined in order to avoid spurious interactions between adsorbates due to the periodic treatment.

### 2.2 Example: Adsorption of lactic acid enantiomers on active surface of silica

Exploratory studies of the adsorption of simple molecules have shown different adsorption energies for different adsorption points on the same surface. In our case, aiming at rather small differences, we consider that the complexity of the  $\alpha$ -quartz surface could potentially generate different adsorption sites with a different selectivity for chiral molecules.

In such conditions, a local adsorption is not representative and may lead to erroneous conclusions. We propose that *the selectivity of the surface is considered as a global property* and should be determined by a *statistical approach* illustrated on the case of lactic acid.

The following steps of such an approach are:

Extensive search on the surface for all adsorption sites optimized using the semi-empirical DFTB+ method (Tight Binding approximation) [6].

Determination of the different representative adsorption sites by means of geometric criteria and affectation of statistical weights to each of them.

Full treatment of each representative in the periodic “first principle model” to get reliable adsorption energies.

Calculation of the average adsorption energy characteristic of the couple adsorbate/surface as the sum of the adsorption energies of the most significant sites weighted by their occurrence numbers normalized to 100%.

For lactic acid, the results are illustrated in Figure 1 and the final difference so-obtained between the R and S enantiomers is [7]:

$$\Delta E_{abs} = 0.7 \text{ kcal/mol} = 0.03 \text{ eV}.$$

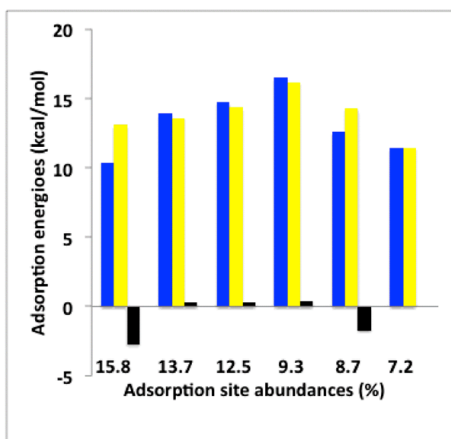


Figure 1: Statistical budget for lactic acid adsorption. Colour code: Blue:R-enantiomer; Yellow:S-enantiomer; Black: R vs S adsorption selectivity.

### 3. Conclusions

For a given chiral molecule, *the adsorption is specific of the enantiomer* though the energy differences are found small, mostly around 1Kcal/mole (which corresponds to 0.04 eV or 500K).

The adsorption depends strongly of the site for complex surfaces and complex molecules. The question of the suitability of a statistic treatment could arise according the degree of complexity, the coverage of the surface and the precision needed.

For a *low* coverage, the energetically most favored position could be the only one to consider if the radiation flux to which the surface is submitted, is sufficient to induce non-destructive photo-desorption allowing re-adsorption on opportune positions.

For a coverage *close to a monolayer*, all sites will most probably be occupied and a statistical behavior should be observed.

If the complexity of the molecule allows a *reorganization of the topology of the adsorption site*, the larger will be the differences between sites and the more a statistics treatment will be necessary to get the global behavior of the surface.

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# Crystallography of magnetite plaquettes and their significance as asymmetric catalysts for the synthesis of chiral organics in carbonaceous chondrites

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## Abstract

We have previously observed the magnetite plaquettes in carbonaceous chondrites using scanning electron microscope (SEM) imaging, examined the crystal orientation of the polished surfaces of magnetite plaquettes in CI Orgueil using electron backscattered diffraction (EBSD) analysis, and concluded that these magnetite plaquettes are likely naturally asymmetric materials [1]. In this study, we expanded our EBSD observation to other magnetite plaquettes in Orgueil, and further examined the internal structure of these remarkable crystals with the use of X-ray computed microtomography.

## 1. Introduction

Magnetite ( $\text{Fe}_3\text{O}_4$ ), a common mineral in some carbonaceous chondrites (CCs), has been shown to be an effective catalyst for the formation of amino acids that are commonly found in these meteorites [4]. Magnetite sometimes takes the form of plaquettes that consist of barrel-shaped stacks of magnetite disks that resemble a spiral [3] (Figure 1). However, a widely accepted description of the internal morphology of this particular magnetite form is still lacking, which is necessary in order to confirm or disprove the spiral configuration.

The spiral configuration of the magnetite plaquettes is worth attention due to their possible role in the synthesis of meteoritic amino acids with enantiomeric excesses (*ee*). *L-ee* is a crucial criterion for life, as extant life has developed a strict chiral homogeneity so that terrestrial proteins are made of exclusively L-amino acids. *L-ee* has also been observed for  $\alpha$ -methyl amino acids (amino acids with limited terrestrial occurrence) in meteorites [2]. If magnetite plaquettes are naturally asymmetric materials, the asymmetric configuration can possibly be transferred to the prebiotic organic molecules that

can result in the chiral preferences we observe today for extant life.

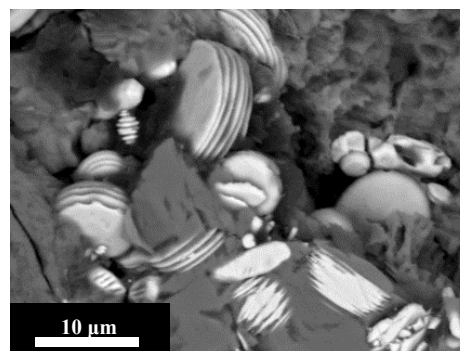


Figure 1: BSE image of the magnetite plaquettes observed in Orgueil.

In a previous study, we analyzed polished thin sections of fifteen CCs spanning different classes, and found that magnetite plaquettes are commonly associated with meteorites that have experienced aqueous alteration [1]. SEM imaging indicated that the surfaces of the terminating plates of protected plaquettes are smooth and clearly devoid of a spiral feature, which suggested that the plaquettes are stack of individual magnetite discs.

## 2. Methods

We analyzed magnetite plaquettes in a polished thin section of the CI1 Orgueil provided by the Field Museum. Imaging and mineral elemental compositions were obtained using the JEOL 7600F Field Emission SEM at NASA Johnson Space Center (JSC). EBSD patterns were obtained using a Zeiss SUPRA 55VP Field Emission SEM with a Bruker Quantax CrystAlign 400i EBSD system coupled with a Bruker *e*-Flash EBSD detector at JSC.



We removed focused ion beam (FIB) sections from each of the preselected magnetite crystals from Orgueil at Kyoto University. The FIB slices ( $\sim 20 \times 20 \mu\text{m}$ ) of magnetite were then imaged by X-ray computed microtomography (XRCT) at SPring-8 Beam Line (2015A).

### 3. Results and Discussion

We studied the misorientation profiles of >10 magnetite stacks in Orgueil. The EBSD data show that the crystal orientation is fairly consistent within a single magnetite, however, this does not rule out the spiral configuration, as spiral dislocation induced crystal growth can result in constant crystal orientation within a single plaquette and is preserved from layer to layer [5]. Nevertheless, notable misorientations ( $30\text{--}40^\circ$ ) were found between adjacent magnetite discs. The plaquettes appear to be comprised of discs with consistent rotation direction, which indicates a possible rotational feature.

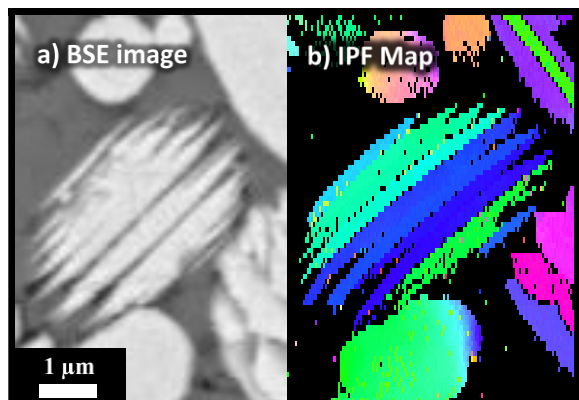


Figure 2: BSE image and inverse pole figure (IPF) map of a selected magnetite stack showing doublet feature in Orgueil.

Although the rotation direction is almost uniform within a given magnetite plaquettes, it is not consistent among different magnetite plaquettes. In order to gain a thorough understanding of the magnetite rotational feature, we studied the misorientation profiles of more magnetite plaquettes using EBSD. In addition, we investigated the internal structure of the magnetite plaquettes using XRCT to support our SEM observations.

We have observed that magnetite sometimes form plate-doublets, where the spacing between the plate-doublet is significantly smaller than the spacing to

the adjacent discs, likely formed by arrangement of discs with alternating aligned and anti-aligned magnetization (Figure 2a). The EBSD data indicate that the plate-doublets are of different crystal orientations, whereas the adjacent discs of the two neighboring plate-doublets share the same crystal orientation (Figure 2b). If magnetic orientation corresponds to the magnetite's crystal structure, the two magnetite discs in a plate-doublet would have their magnetization orientation anti-aligned. The misorientation in the crystal lattices and magnetic alignment between the magnetite plates possibly provide crystallographic control of asymmetric amplification of organics.

### 4. Conclusions

The remarkable morphology of magnetite plaquettes not only fascinates us by their striking appearance, but also their possible rotational feature that is now confirmed with EBSD analysis. These magnetite plaquettes are naturally asymmetric materials, effective catalyst of amino acid synthesis, and are associated with aqueous processing that is commonly involved in many amino acid formation mechanisms. Their possible involvement in the origin of homochirality which might have endowed the prebiotic world with an initial feedstock of asymmetric molecules for subsequent molecular evolution deserves further understandings.

### Acknowledgements

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# Coherent-fields, their responsive colloids, and life's origins.

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## Abstract

In living systems, evolvable sequence-encoded constraints control the incoming energy-matter flows, and are also sustained by their embedded flows/processes. What's more, in such dynamic-organized liquid-state media, the flows can also produce novel materials/mechanisms. Thus, embedded processes of such media enable its spatiotemporal resilience via turnovers, as well as functional 'takeovers'. Further, the responsiveness of such constrained media to their environment enables adaptations, as they can mediate feedback between the changing environment & their embedded flows/processes. Now, the complexity of the constituent functional materials, make it very likely that they themselves emerged/got selected thanks to the creative properties of such dynamically constrained media. We have asked if such Maxwell-demon-like scenario could not be mimicked using other plausible ingredients to achieve similar ways of dissipative sustenance and coherent functioning. In particular, the potential of organizing coherent fields and their responsive anisotropic colloids to enhance the probability of life's emergence—akin to an adaptive transition—to a new way of evolving, seems promising. Note that pattern-sustenance in liquid state requires presence of the specific source that enabled it (c.f. spontaneously formed patterns). For example, external coherent heterogeneous fields (e.g. magnetic rocks) can act as sources both of 1) aperiodic information, and 2) useful energy, for inducing and sustaining (specific) structures of superparamagnetic mineral colloids (via their Brownian-rotation) away-from-equilibrium, to access 3-way coupling between energy-information-matter in liquid-medium. Such dynamic functioning structures seem ideal for stable containment of bottom-up chemical systems; and similar scenario in the nanoscience engineering area can help in design/tests.

## 1. Introduction

Iterations of random variation of genotype-- with judgement/selection of the resulting phenotype's

fitness in its environment context, -- underlies Darwinian evolution. But, what could be the *raison d'être* of such magical evolving liquid-state organizations that can change their environment and be shaped by it? One possibility (supposed by the conventional synthetic bottom-up approach) —albeit discontinuous with life's evolution -- is that they emerged via independent disparate stages, and with somehow selected specific anisotropic building blocks, plus inexplicably harnessed disequilibrium sources producing some useful form of energy (to do work), all from passive host-media. For example, use of non-reconfigurable rock/crystal surfaces, thermal gels, and/or uncontrolled entrapped aqueous-spaces already sets bounds on their potential for controllable kinetics. The picture improves with viscous media, but these lack controlled order needed for functioning. It appears more life-like via mineral/lipid soft-matter aggregates, as dipolar anisotropic components can achieve liquid-crystal-like patterned states, with feedback-enabling response effects; however, patterns formed spontaneously (such as via lowering of temperature) lack the capacity to resist Brownian forces in the long run. A more interesting possibility comes about if one imagines the starting liquid-state host-medium—comprising dispersed mineral/organic soft-matter-- to be a robust field-controlled spatiotemporally-patterned one with a capacity to slowly build-up/integrate information, received over time [1]. In that case, like living media, it could transmit any tiny/major changes caused via environmental interactions to its embedded reactions, or vice-versa.

## 2. Discussion

What could be the anatomy of such an informational liquid medium coupled to a thermal bath? Firstly, being 'rich in information' requires a *subjective* outcome, in place of any one of many alternative possible objective outcomes, e.g. (independent agent-like) components need to have freedom to arrange themselves in maximum possible ways via some non-specific mode of interacting with each other, which is controllable via external influence [1]. To that end,

interplay of randomly orienting Brownian forces and dipolar forces with same order of magnitude (plus some short-range repulsive interaction) is facilitated at the nanoscale. And, thanks to the distributed nature of the controlling H-field, each thermally agitated responsive-particle --via its capacity to couple its magnetic & rotational d.o.f.s-- can act like an ‘agent’, influencing each other and their global interaction pattern. Indeed, feedback between the external and induced internally generated fields in the resulting aggregates (a challenging research subject) is also reminiscent of the feedback between descriptor (DNA) and executor (RNA, protein, etc) levels of constraints, in living systems. Note that diverse asymmetric configurations can be induced depending on the properties of the field (strength, intensity, direction, etc.) and of the particle’s (susceptibility, solid-state properties, etc). Further, these structures are highly sensitive to environment-parameters (ionic strength of the medium, pH, temperature, etc). This suggests that in the same way as field-parameters are tuned to switch between different configurational states (with different network-properties) in the sector of technology, similar tuning/switching could have been realized in such naturally induced-configurations via environmental parameter changes. Again, the influence of H-fields on a membrane’s elastic properties --via magnetic inclusions-- can enable control of shearing/merging of vesicles ([2]; c.f. uncontrolled bottom-up mode). Another scenario for field-control could be the use of liquid crystals (LCs) as host matrices for assembly of nanostructures (see [1] plus references). Organic matter associated with meteorites, despite heterogeneity, may also have propensity to form such phases. And, the findings that mineral colloids can also form liquid crystalline phases seem promising as they can combine the anisotropy and fluid properties of liquid crystals with the electronic and structural properties of minerals. To facilitate the formation and sustenance of such organic/mineral phases, it could be useful to draw from studies on artificial magnetic phases like ferro-nematics (see Brochard and deGennes (1970) cited in [1]). The main point is that the strong orientational coupling between dispersed magnetic particles and their host liquid crystalline matrix helps to enhance the magnetic property of the system; the presence of the dispersed phase helps to assist alignment of the LC phase, plus control the configuration of the whole system, via weak external fields. Indeed, latest liquid crystalline hybrid systems combine the solid-state properties (optical, magnetic, catalytic, etc) of inorganic colloid inclusions with the positional-cum-

orientational order of the lyotropic matrix in order to gain control on the fluid system’s configuration at both micro- and macroscopic levels [3]. The physical basis of the coupling between the inclusions and the host-mesophase, facilitates the extension of such scenario based on organic phases to mineral ones; to that end, appropriate tests would be desirable. We urge Systems-chemistry initiatives to consider such externally-tunable patterned media (combining the best of ordered solid and fluid liquid worlds), with environment-sensitivity and low water activity; enabling access to oriented confinement of organics sterically-coupled to the components; having affinity-column-like feature, permitting removal of wastes; capacity to transport under disequilibrium conditions (and provide energy in useful form, electrons, spins); enabling complementary molecular interactions, plus interplay of macroscopic control and microscopic randomness; and how such network properties can help select for equivalents [see 1].

### 3. Summary and Conclusions

Coherent fields and their responsive liquid systems could serve as naturally feasible environment-sensitive functional cell-analogs, to their embedded fledgling prebiotic chemical systems, and enhance the *a posteriori* probability of life’s origins. Indeed, the scenario of induced diverse possible cooperative-configurational states, also make for a (analog-like) primitive language (c.f. insights of Howard Pattee) wherein the associated network properties provide the “functional meaning”. Sure enough, a sustained spatiotemporal organization in liquid state is crucial for storage-transmission-processing of each of the three types of environment inputs: matter, energy sources, and information, in any location.

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# Investigation of micrometre-sized fossils by a laser ablation mass spectrometer designed for *in situ* space research

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## Abstract

Detection of extraterrestrial life is an ongoing goal in space exploration. The detection of signatures of life by means of chemical composition, elemental and isotopic, is one of the most important approaches. There is a need for advanced instruments and methods that can accomplish this task. We present the first investigations of chemical composition measurements of putative microfossils in natural samples using a miniature laser ablation/ionisation time-of-flight mass spectrometer (LMS). The primary aim of the study was investigation of the instrument's capabilities for element composition and isotopic abundance analysis of micro-sized samples.

## 1. Introduction

Fossilised microorganisms contain morphological, molecular and geochemical signatures concentrated in a defined micrometre-sized structure. Due to the small size of these features, the relevant information are not easy to obtain and to establish biogenicity is not an easy task, not even in terrestrial samples. Therefore, there is an urgent need for the development of new and more sensitive instrumentation capable of *in-situ* detection of molecular and elemental bio-signatures on other planetary bodies.

Endoliths fossils (microorganisms lived in the past in the rock interior) are interesting samples, because they are easily preserved over geological time due to fossilisation in the interior of rocks being embedded in vein- and vesicle filling mineral phases such as quartz or carbonates and naturally protected against destructive surficial processes such as chemical and physical weathering or radiation. In the present study we investigate micrometre-sized filamentous

structures embedded in carbonate veins by microscopic imaging and laser ablation mass spectrometry. The chemical analysis of the microstructures could be determined with high spatial (lateral and vertical) resolution. We discuss the implications of the *in situ* chemical analysis of microbials on planetary surfaces and its importance in the search of past life.

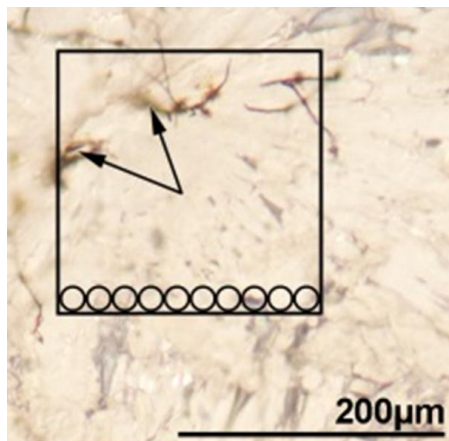
## 2. Experimental

The sample (1271B 4R1 23-26 cm) used in the current study is delivered from the slow-spreading Mid-Atlantic Ridge (MAR) during ODP Leg 209 and was collected from a depth of 26.9 m below seafloor (mbsf) (Bach et al. 2011). The sample contains aragonite veins hosted in serpentinised harzburgite. The age of the aragonite is > 54,900 years since it is radiocarbon-dead but not more than 1 Ma since that is the approximate time when the basement exhumed.

The mass spectrometric investigation was conducted by a miniature laser ablation/ionisation mass spectrometer (LMS) designed for *in situ* space research [2]. The instrument combines laser ablation/ionisation ion source with a reflectron time-of-flight mass analyser. The details of the technical realisation and principles of operation of LMS are described in previous publications [3], [4], [5]. The mass spectrometric analyses were conducted stepwise every 20 µm covering a surface area of 200 x 200 µm<sup>2</sup> (see Figure 1b, right panel). These studies yield chemical surface mapping. The instrument allows also high resolution chemical depth profiling [6]. In the latter studies the sample can be analysed layer by layer with a depth resolution down to sub-nanometre per laser shot.

### 3. Results and Discussion

The measurements were conducted on dark filamentous micrometre-structures at the interface between the aragonite and the harzburgite host rock. The filaments have a uniform diameter of about 2 to 5  $\mu\text{m}$  and range in length from about 20  $\mu\text{m}$  to more than 100  $\mu\text{m}$  (Figure 1). The filaments are anchored to the aragonite vein of size 5–10 mm at the walls of the host rock or occur closely associated with the vein walls embedded in the aragonite.

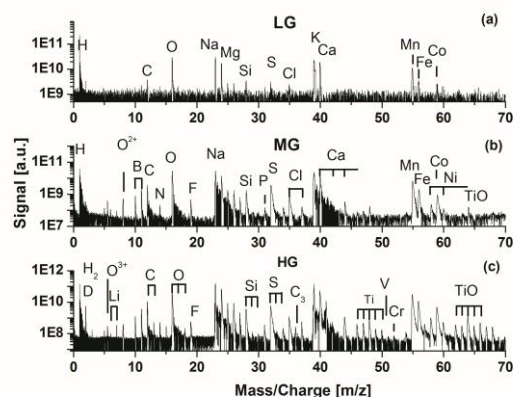


**Figure 1:** Detail of the sample surface used for systematic high resolution chemical mapping by mass spectrometry. The studies are conducted within a rectangular area containing filamentous micro-structures. The circles inserted in the picture are scaled to the laser spot size applied to ablate surface material.

The mass spectrometric measurements of carbonate host deliver composition of major elements: H, K, Na, Ca, C, O and Mg and confirm that the host is nearly pure calcium carbonate ( $\text{CaCO}_3$ ). A typical mass spectrum of the investigated filaments is shown in Figure 2. In addition to major elements (O, Na, Mg, K, Ca, Mn, Fe, and Co) several minor elements (C, Si, S, Cl) and a few trace elements (B, N, F, Al, P, Ti, Cr and Ni) were measured.

### 4. Summary and Conclusions

The studies yield the element composition of the host material and filaments. The investigated filaments contain distinct atomic fractions of non-metallic (B, N, F, P, and S) and metallic (Li, Mn, Fe, Co, Ni, Se) elements in addition to the elements detected also in the aragonite matrix. Substantial differences between



**Figure 2:** Typical mass spectrum measured at a filament location. In the LG spectrum the major and minor elements contained in the filament are identified. The Medium Gain (MG) (middle panel) and HG (bottom panel) spectra yield the detection of minor and trace elements as well as clusters and molecules.

the abundances of these elements in filaments and aragonite matrix were observed. The detection of high atomic fractions of bio-relevant elements including B, S, Mn, Co, Fe and Se is considered to be in favor of a bio-origin of the investigated filaments. Enrichment of the light isotope of S was measured for all investigated filaments but the accuracy of the measurement for isotopic investigations is presently too low. A few other abundant elements including B, F and Cl are observed in filaments. These can be important in metabolic processes but also be remnants of the ocean where the aragonite mineral was formed. The current studies form the basis for further investigations of these putative fossils by other analytical instrumentation.

### Acknowledgements

The Swiss National Science Foundation is kindly acknowledged.

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# The potential of Methanogenic Life in the Solar System

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## Abstract

Methanogens from the domain Archaea are obligate anaerobic chemolithoautotrophs or chemolithoheterotrophs producing methane ( $\text{CH}_4$ ). For the  $\text{CH}_4$ -production they primarily use various C1 type-compounds (like carbon monoxide ( $\text{CO}$ ), carbon dioxide ( $\text{CO}_2$ ), formate ( $\text{HCO}_2^-$ )), but some strains are also able to utilize methanol ( $\text{CH}_3\text{OH}$ ), acetate, or even methylsulfides for energy production. The capability of methanogens thriving under various extreme environments on Earth is astonishing. Their enormous diversity and the similarity between their growth conditions and the environmental conditions on extraterrestrial bodies throughout the Solar System make methanogens to an ideal test object for astrobiological experiments.

## 1. Introduction

Methane ( $\text{CH}_4$ ), the smallest hydrocarbon molecule, is found on all planets in the Solar System and its presence has also been verified on other Solar System bodies, e.g. on Saturn's icy moons Titan [8] and Enceladus [13] or on Mars [2, 7, 14]. On Earth, most of the  $\text{CH}_4$  available is of biogenic origin whereby only methanogens are known to produce  $\text{CH}_4$  [5]. Therefore, the detection of extraterrestrial  $\text{CH}_4$  could serve as an indirect indication for (methanogenic) life on another Solar System body.

## 2. Eco-Physiological Characteristics of Methanogens

On Earth, methanogens can be found from hot vents in the deep oceans to icecold permafrost soils. The temperature range lies between below 0 and 122 °C. They are also capable to thrive under both extremely high and low amount of pressure, at a broad pH-range and are able to withstand UV radiation up to  $4 \text{ Wm}^{-2}$

(see Table 1). Their energy metabolism is independent of oxygen and it is likely that it developed early on Earth [6]. Due to the fact that most of the methanogens found so far are prototrophs, they seem to be ideal candidates for inhabiting or surviving on planetary bodies other than Earth.

Table 1: Non-strain specific minima and maxima of methanogens [11].

|             | Ranges                                 | Ref.    |
|-------------|--|---------|
| Salinity    | 1.71 to $2.57 \text{ mol L}^{-1}$ NaCl | [9]     |
| Pressure    | 0.005 to > 75 MPa                      | [3, 4]  |
| pH          | 4.5 to 10.2                            | [1, 15] |
| Radiation   | $4 \text{ Wm}^{-2}$ (UV)               | [10]    |
| Temperature | < 0 to 122°C                           | [12]    |

## 3. Potential Habitats of Methanogenic Life in the Solar System

### 3.1. Mars

Life on Mars would have to resist strong UV radiation due to the lack of an ozone layer. Furthermore, the low surface temperature, low pressure, and desiccation on Mars' surface may act as an inhibitor for life forms, such that they could rather thrive in the subsurface water reservoirs which would be sheltered from radiation. Since 2012, the Rover Environmental Monitoring Station (REMS) on board of NASA's rover Curiosity has returned a huge amount of data concerning the surface UV radiation as well as humidity, pressure, wind, and temperature.

### 3.2. Moons and Small Icy Bodies

The findings of the last decades, that icy moons may harbour a large amount of liquid water under their ice shells have opened new horizons in the rising field of

Astrobiology. Nevertheless, liquid water alone may be sufficient, but not necessary for icy moons to be habitable. Several aspects – like the possibility of liquid water being in direct contact with the silicate core or seafloor, or the salinity and amount of ammonia in the aquifer – have to be ascertained to determine if the sub-surface liquid aquifer of a certain celestial body may be able to harbour life-as-we-know-it.

## 4. Summary and Conclusions

Methanogens are able to survive under a broad range of environments including those applying multifactorial stress conditions to the organisms. Laboratory induced adaptations could act as a basis for inferring the potential capability of methanogens to be able to inhabit environments other than Earth in the Solar System. We conclude, that prototrophic methanogens of the genus *Methanosarcina* exhibit extraordinary physiological features making them promising organisms for astrobiological research endeavours [11].

## Acknowledgements

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# Methane Formation Catalyzed by Awaruite during Forsterite Serpentinization on Seafloors of Planetary Bodies

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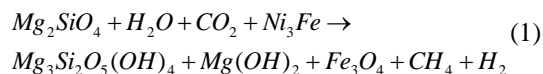
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## Abstract

Olivine is ubiquitous throughout the Solar System. Its presence in such different planetary surfaces that ranges from planets to asteroids makes it a good starting material for the study of the alteration of rocky layers through water activity. The aqueous alteration of olivine is called serpentinization, a process that in reduced environments may release methane, such as the suggested hydrothermal vents beneath Europa's icy shell. The nickel-iron alloy awaruite ( $\text{Ni}_3\text{Fe}$ ), is usually connected to the serpentinization of ultramafic/mafic rocks. During this geologic process, awaruite acts as a surface catalyst promoting methane generation during Fischer-Tropsch Type (FTT) reactions, increasing the energy potentially available for metabolic processes. We carry out two different experiments to infer whether awaruite would catalyze the serpentinization process and if pressure is an important parameter that can influence the efficiency of the FTT reactions. One is performed under relatively low pressure and the other under the expected pressure on Europa's seafloor.

## 1. Introduction

The presence of olivine is confirmed on rocky planetary bodies, asteroids, meteorites and interstellar dust. Its widespread presence makes it a good starting material for the study of the evolution of silicate-rich layers of planetary bodies throughout our Solar System's history. The aqueous alteration of olivine in the presence of carbon dioxide, called serpentinization, may lead to the production of methane. In the case of Mg-olivine (forsterite,  $\text{Mg}_2\text{SiO}_4$ ):



The Nickel-Iron alloy awaruite ( $\text{Ni}_3\text{Fe}$ ) commonly associated with serpentinized ultramafic/mafic rocks, may be originated by the reduction of the nickel-bearing silicates or sulfides during the serpentinization of peridotites [1]. In this process, awaruite is an important catalyst of methane synthesis [2]. The presence of a catalyst, accelerates the process of abiotic formation of methane and may expand the limits for the occurrence of life. Here we show the results of Mg-rich olivine serpentinization simulation experiments in the presence of awaruite. We suggest this process may occur in the rocky layer of Europa, releasing methane into the aqueous ocean.

## 2. Materials and methods

### 2.1. Awaruite Synthesis

The awaruite crystals used throughout our experimental assemblages are synthesized via hydrazine hydrate reduction in an ethanol solution (2:3 ratio) [3].



Our main goal being the production of enough amount of this alloy for the serpentinization simulation experiments, the perfect crystallization became secondary, therefore we increase tenfold the amount of the iron and nickel salts used in the reaction. After collection, the highly magnetic particles are analyzed with XRD and SEM coupled with EDS to confirm the presence of awaruite nanocrystals.

### 2.2 Olivine selection for Serpentinization

Forsterite is chosen for this serpentinization study, first because Galileo's Near Infrared Mapping Spectrometer (NIMS) detected the presence of Mg-



hydrated materials on Europa’s icy shell [4], and second, the forsterite detected in many meteorites is suggested to be a primary condensate of the solar nebula [5].

### 2.2.1 Low Pressure Experiment

The synthesized awaruite is used as a catalyst on a serpentinization simulation experiment under relatively low pressures, together with natural olivine pulverized into a fine grain powder, which composition is determined by XRD to be almost pure forsterite. The experiment is assembled according to Table 1:

| Reactant<br>mass (gr) | Run                              |   |       |       |       |       |
|-----------------------|----------------------------------|---|-------|-------|-------|-------|
|                       | 0                                | 1 | 2     | 3     | 4     | 5     |
| <b>Olivine</b>        | -                                | 1 | 1     | 1     | 2     | -     |
| <b>Awaruite</b>       | -                                | - | 0,005 | 0,010 | 0,005 | 0,005 |
| <b>CO<sub>2</sub></b> | CO <sub>2</sub> pellet [dry ice] |   |       |       |       |       |
| <b>Water</b>          | 5ml [ion chromatography purity]  |   |       |       |       |       |

These vials are heated up to 120°C, hermetically sealed with a vulcanized rubber cork, Teflon and an aluminum cover. The pressure inside each one is caused, firstly by the CO<sub>2</sub> released by the pellets and then by the water vapor as the temperature rose. We select these conditions to simulate planetary surfaces/crusts and also to understand which is the best olivine:awaruite ratio for methane formation catalysis. After 34 days, the solid fractions are analyzed with XRD to verify the alterations suffered by awaruite and olivine.

### 2.2.2 High Pressure Experiment

A mixture of olivine and awaruite, respecting the ratio obtained by the low pressure experiments is loaded into a high pressure chamber. In it, we reproduce the expected conditions of a hydrothermal vent on Europa’s seafloor.

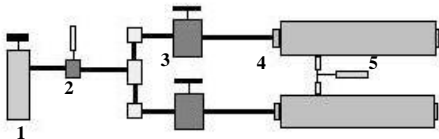


Figure 1: High Pressure Experimental Assembly (1.CO<sub>2</sub> bottle; 2.Pressure Sensor; 3.Valves; 4.Reaction chambers; 5.Temperature sensors)

At 120°C and high pressure, serpentinization is monitored through the analysis of the composition of the solid fraction with XRD.

## 6. Summary and Conclusions

The discovery of serpentine-hosted vent systems on Earth’s seafloor coupled with fossil records to support the sustainability of high-biomass communities by them, indicates the possibility that such systems may have played important roles in the emergence of life on Earth’s primitive oceans. Hydrothermal vents are proposed to exist in the rock layer in contact with the global ocean of Europa [6][7], which was indirectly detected by the Galileo spacecraft. Some of the structures observed on the surface strongly point towards the idea that a liquid subsurface ocean exists and periodically, through different processes exchanges materials to and from Europa’s surface (e.g. cracks on the icy shell or local melting or subduction episodes). These endogenous materials could be measured by future missions, including methane vented from plumes, if they occur.

The understanding of the action of methane catalysts such as the nickel-iron alloy awaruite, during the serpentinization process of the magnesium end-member of the olivine family, forsterite, becomes a priority in order to grasp the complex processes involved in the carbon cycling in Europa.

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# Interaction of tryptophane and phenylalanine with mercury and tungsten ferrocyanides and its implications in chemical evolution and origins of life

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## Abstract

Adsorption of two naturally occurring alpha-amino acids tryptophane and phenylalanine on the surface of mercury and tungsten ferrocyanides was studied at neutral pH ( $7.0 \pm 0.01$ ) and at room temperature  $30 \pm 1^\circ \text{C}$ . The progress of adsorption was followed spectrophotometrically by measuring the absorbance of tryptophane and phenylalanine at their corresponding  $\lambda_{\text{max}}$ . The interaction followed the Langmuir type of adsorption in general. The tryptophane was found to have greater affinity for mercury and tungsten ferrocyanides than the phenylalanine. Present study suggests the significance of metal cyanogens complexes and metal ions in condensation and stabilization of aromatic  $\alpha$ -amino acids during process of chemical evolution and origin of life on primitive earth.

## 1. Introduction

Beck[1] has suggested that  $\text{CN}^-$  could easily have formed some soluble and insoluble complexes with the transition metal ions which were abundant in the primeval sea. The insoluble cyanide complexes such as metal hexacyanoferrate(II) complexes could have settled at the bottom of the sea or sea shore and might have catalyzed number of reactions during the course of chemical evolution. Metal ferrocyanides also acted as adsorbents[2] and photosensitizers[3]. A search of literature indicated very few studies on interaction of amino acids[4] with metal ferrocyanides in view of this present work described as the study of Interaction of Tryptophane and Phenylalanine with Mercury and Tungsten Ferrocyanides.

## 1.1 Experimental Section

All chemicals used were of AnalaR grade. Mercury and tungsten ferrocyanides were prepared according to methods reported by Kourim[5] and Kraus[6] et al. Synthesized metal ferrocyanides were characterized by elemental and spectral studies mercury ferrocyanide percentage (Hg = 54.90; Fe = 10.50; C = 14.0; H = 0.60; N = 14.35) Tungsten ferrocyanide percentage (W = 52.71; Fe = 7.27; C = 9.31; H = 1.67; N = 12.07). The infrared spectral data for mercury and tungsten ferrocyanides are given in the Table. Effects of pH concentration and salts for the adsorption of phenylalanine and tryptophane on mercury and tungsten ferrocyanides were studied.

## 2. Results and discussions

The maximum uptake of phenylalanine and tryptophane was found at neutral pH. The percentage uptake of tryptophane was found to be higher than phenylalanine for both metal ferrocyanides studied.

$$\% \text{ uptake} = \frac{\text{difference in absorbance of amino acids before and after adsorption}}{\text{Absorbance of amino acid before Adsorption}} \times 100$$

The interaction follow general Langmuir equation given in Equation Section. The maximum uptake of amino acids on metal ferrocyanides follow order:  $\text{HgFc} > \text{WFc}$  similar order but higher uptake of amino acids on metal ferrocyanides were observed in the presence of salts.

### 3. Tables

IR data for Mercury and tungsten ferrocyanides.

| MFC  | Adsorption frequency (cm <sup>-1</sup> ) |             |                |      |                                   |
|------|--|-------------|----------------|------|-----------------------------------|
|      | H <sub>2</sub> O molecules / OH group    | HOH bending | C N stretching | Fe-C | Metal -N degree of polymerization |
| WFC  | 3510                                     | 1600        | 2000           | 620  | 490                               |
| HgFc | 3600                                     | 1620        | 2000           | 600  | 490                               |

MFC = Metal ferrocyanide

WFC = Tungsten ferrocyanide

HgFc = Mercury ferrocyanide

### 4. Equations

$$1/q_{eq} = (1/Q_0) + (1/C_{eq}) (1/bQ_0) \quad (1)$$

Where  $Q_0$  and  $b$  are Langmuir constants.  $C_{eq}$  = equilibrium concentration of amino acids;  $Q_{eq}$  = amount (mg) of adsorbate adsorbed per gram of adsorbent. .

### 5. Summary and Conclusions

Interaction of phenylalanine and tryptophane with mercury and tungsten ferrocyanides was studied at room temperature and neutral pH range. The concentration of amino acids was determined spectrophotometrically by measuring their absorbance at tier corresponding  $\lambda_{max}$ . The  $\alpha$ -amino acids interaction with both metal ferrocyanides follow the order tryptophane > phenylalamine. Salts effect studies suggested that the adsorption occurs due to the interaction of amino acids molecules with metal ions present in the outer layer lattice of metal ferrocyanides. During course of chemical evolution insoluble metal cyanogene complexes are thought to have concentrated biomonomers from dilute prebiotic soup and facilitated a class of prebiotic reactions.

### Acknowledgements

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## Microbialites on Mars: a fractal analysis of the Athena microscopic images

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### Abstract

The Mars Exploration Rovers investigated Martian plains where laminated sedimentary rocks are present. The Athena morphological investigation [1] showed microstructures organized in intertwined filaments of microspherules: a texture we have also found on samples of terrestrial (biogenic) stromatolites and other microbialites and not on pseudo-abigenic-stromatolites. We performed a quantitative image analysis in order to compare 50 microbialites images with 50 rovers (Opportunity and Spirit) ones (approximately 30,000/30,000 microstructures). Contours were extracted and morphometric indexes obtained: geometric and algorithmic complexities, entropy, tortuosity, minimum and maximum diameters. Terrestrial and Martian textures resulted multifractals. Mean values and confidence intervals from the Martian images overlapped perfectly with those from terrestrial samples. The probability of this occurring by chance was less than  $1/2^8$ ,  $p < 0.004$ . Our work shows the evidence of a widespread presence of microbialites in the Martian outcroppings: i.e., the presence of unicellular life on the ancient Mars, when without any doubt, liquid water flowed on the Red Planet.

### 1. Introduction

Microbialites/stromatolites are the oldest evidence of life on Earth; they are rocks formed by microbial mats trapping, binding and/or precipitating minerals. Stromatolites/microbialites are an organization of primitive cyanobacteria into large structures, analogous to coral reefs. They grew in vast colonies. Fossil stromatolites, as well as other microbialites, can be identified through their macro- meso- micro-characteristic structures that result from the growth patterns of their constituent bacteria.

Rizzo and Cantasano in 2009 claimed the presence of microstructures that resembled stromatolites/microbialites in the Opportunity Rover microscopic images [2], Wagstaff and Corsetti in 2010 wrote on the absence of stromatolites in the Opportunity images, analyzing 4 Martian photos at macro level [3].

To solve the problem, we have performed a quantitative morphometric approach of the microstructures present in the stromatolites and other microbialites, Earth comparing them with the microstructures present in the outcrops photographed by Opportunity and Spirit, Mars.

### 2. Materials and methods

We have performed a quantitative fractal analysis comparing 50 terrestrial microbialites images with 50 rovers (Opportunity and Spirit) ones, corresponding, approximately to 30,000 terrestrial and 30,000 Martian microstructures. Contours were extracted by a Canny edge filter (fig.1) and fractal indexes were obtained: geometric and algorithmic (LZ) complexities, entropy, at low and high scales, and tortuosity (Dmin). Minimum and maximum diameters were also evaluated.

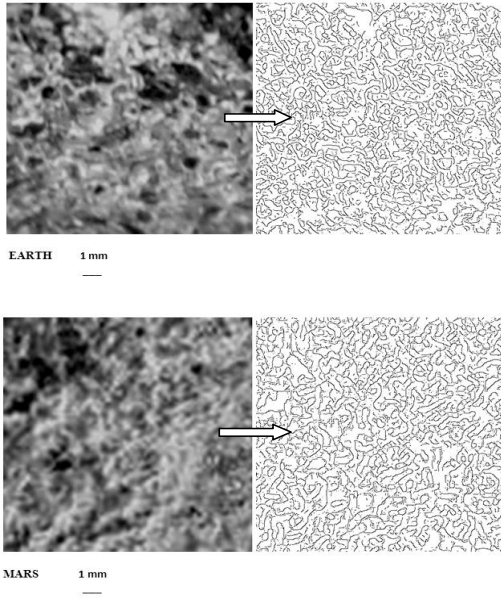


Figure 1: A texture of microspherules and intertwined filaments appears in terrestrial living or fossilized microbialites/stromatolites, as well in Martian sediments, after a canny-edge filter is applied

### 3. Results

The morphometric analysis reveals that both the textures, from biogenic microbialites (Earth) and from selected rover images (Mars), present a multifractal aspect (fig.2).

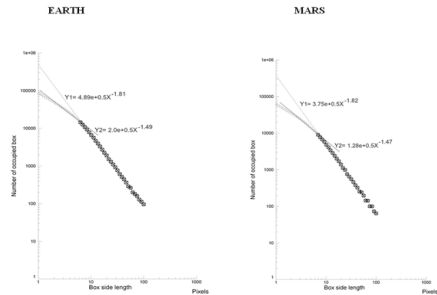


Figure 2: Multifractality in terrestrial microbialites (left) as well in the analysed Martian sediments.

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Table 1: Fractal parameters and diameters of the Martian microscopic microstructures are overlapping the ones of terrestrial biogenic microbialites. The probability of this occurring by chance is less than  $p < 0.004$ .

|               | Earth<br>(mean/SD) | Mars<br>(mean/SD) |
|---------------|--------------------|-------------------|
| Complex, High | 1.82(0.02)         | 1.81(0.02)        |
| Complex, Low  | 1.48(0.05)         | 1.52(0.07)        |
| Entropy, High | 1.88(0.01)         | 1.87(0.02)        |
| Entropy, Low  | 1.41(0.05)         | 1.44(0.05)        |
| LZ index      | 0.46(0.04)         | 0.48(0.04)        |
| Dmin          | 0.79(0.03)         | 0.78(0.03)        |
| Max Dia (mm)  | 0.08(0.001)        | 0.08(0.001)       |
| Min Dia (mm)  | 0.21(0.003)        | 0.21(0.003)       |

### 4. Summary and Conclusions

Microtexture indexes, multifractality and diameter values present in biogenic stromatolites and other microbialites are extremely similar to those present in the Martian images taken by the Opportunity and Spirit Mars Rovers. The probability of this occurring by chance is less than  $1/2^8$  (less than  $p < 0.004$ ). Our work show the evidence of a widespread presence of microbialites in the Martian outcroppings: i.e., the presence of unicellular life on the ancient Mars, when without any doubt, liquid water flowed on the Red Planet.

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## Evidence of Ancient Microbial Activity in the Martian meteorite 'Tissint'

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### Abstract

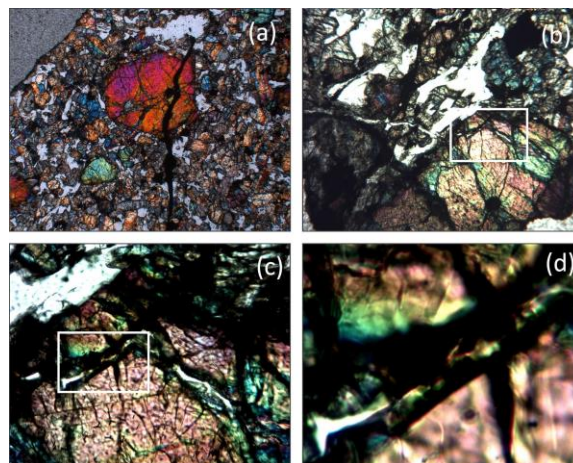
A relatively rare mineral, iron arsenate-sulphate bukovskýite  $\text{Fe}^{3+}_2(\text{As}^{5+}\text{O}_4)(\text{S}^{6+}\text{O}_4)(\text{OH}) \cdot 7(\text{H}_2\text{O})$  was found in a shock melt vein of the Tissint Martian meteorite. We hypothesise it formed within high concentrations of aqueous  $\text{H}^+$ ,  $\text{Fe(III)}$ ,  $\text{SO}_4$  and  $\text{AsO}_4$  in microenvironments created within wet subsurface Martian clays from microbial oxidation of  $\text{FeS}_2$  with concurrent release of sequestered As. This hypothesis is supported by SEM analysis of a  $15\mu\text{m}$  spherical structure comprising a carbonaceous outer coating and an inner pyrite ( $\text{FeS}_2$ ) core. The pyrite surface has morphologically distinct spherical pits and chains of pits. The pits and channels are similar to bio-mediated microstructures created by Fe- and S-oxidising microbes in the laboratory and interpreted as trace fossils resulting from the attachment of bacteria to the pyrite surfaces

### 1. Introduction

Previous studies of the Tissint Martian meteorite have focused on the carbonaceous component, whose interpretations vary from igneous and magmatic to biogenic origin [1,2,3]. In our sample, we found a number of  $5\text{-}50\mu\text{m}$  carbonaceous globules both embedded in the rough pyroxene substrate and others unbound, having been dislodged during the preparation process. SEM and EDS elemental spectra for 11 selected globules confirmed that they comprise a carbonaceous outer coating with an inner core of  $\text{FeS}_2$  (pyrite) and are characterised as immiscible globules with curved boundaries [4]. The petrographic setting of the organic carbon component showed examples of organic carbon completely occupying the cracks and cleavage around pyrite crystals, suggesting that pyrite had acted as an attractive substrate for the collection of organic material in a hydrothermal setting.

In this study we report the results of SEM, optical microscopy and Raman spectroscopy on a relatively rare secondary iron arsenate-sulphate mineral found in a shock melt vein of the meteorite. These results agree with previous interpretations of Tissint's organic carbon being precipitated from fluid [3].

### 2. Experimental Studies

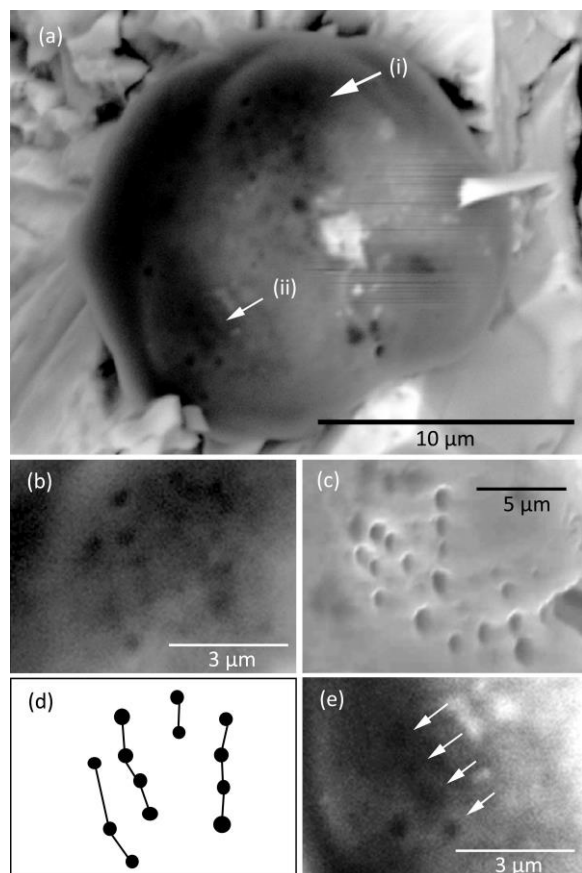


**Figure 1** images of a  $30\mu\text{m}$  thin section of Tissint in cross-polarised transmitted light. Black glass shock veins and pockets show up as black with maskelynite phases in white. (a) typical glass shock vein cutting through the pyroxene groundmass and olivine crystal (b) shock vein containing the arsenic signature with the site of interest highlighted, note also the presence of a typical olivine crystal with a melt inclusion and radiating cracks (c) enlarged image of the vein showing enclosed mineral inclusion and (d) same, in higher magnification. Field of view (a)  $2.5\text{mm}$  (b)  $1\text{mm}$  (c)  $250\mu\text{m}$  (d)  $100\mu\text{m}$

Via scanning electron microscopy, enriched arsenic domains were identified in one polished  $30\mu\text{m}$  thin section (section A) and one polished thick section (Section C) of Tissint, prepared at Cardiff University. Details of these sections are provided in Wallis *et al.*, [4]. Hi-Res Raman spectroscopy of the As-enriched domains constrained the mineral species. An As-enriched

domain was observed in EDAX elemental maps in the vicinity of a ~10 µm wide glass shock vein. Black glass melt pockets and veins are characteristic of Tissint. Figure 1 (a-d) shows an optical light montage of a typical glass shock vein.

### 3. Bacterial etch pits on pyrite



**Figure 3** (a) shows an SEM image of a pyrite grain coated with carbonaceous material. The area marked with arrow (i) in shown in higher resolution (b) where a cluster of etch pits become visible. (d) shows an overlay diagram of their position and spacing, while (e) shows a similar set of four rounded pits equally spaced in a straight line as indicated by the four white arrows. For comparison, figure 3 (c) shows a cluster of spherical etch pits in the surface of pyrite taken from the Strelley Pool Formation (SPF).

SEM was also used to identify bacterial etch pits in the surface of pyrite grains present in the meteorite, shown in Fig. 2. The similar size and sphericity of etch pits and their geometric pattern are significant since pitting and channelling of pyrite surfaces can result from the non-biological oxidation of pyrite.

### 4. Discussion

Various processes forming bukovskýite involve biological processes, notably biologically induced mineralisation. Márquez *et al.* [5] studied a two-step oxidation pre-treatment process involving a combination of bacterial and pressure oxidation of ores mined in the São Bento deposits in Brazil. Majzlan *et al.* [6] suggested clay minerals create sealed microenvironments where high concentrations of aqueous  $H^+$ ,  $Fe(III)$ ,  $SO_4$  and  $AsO_4$  are maintained for long periods of time.

Bukovskýite formation is not unambiguously associated with bio-activity. Nonetheless, the initial mobilisation of arsenic from As enriched Fe oxides, the subsequent sequestration of As by precipitating sulphides under anoxic conditions, followed by the oxidation to sulphide of sulphate species and the formation of relatively rare As secondary phases are all processes commonly associated with bacterial activity.

McKay *et al.* (1996) first suggested Fe- and S-oxidising microbes may have etched ‘biomorphs’ on pyrite surfaces in the martian ALH 84001 meteorite. Our etch pits have morphology and patterns distinct from abiotic alteration features, being comparable to biologically mediated microstructures created by Fe- and S-oxidising microbes. At present, these features are interpreted as trace fossils resulting from the attachment of bacteria to the pyrite surfaces

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## **A European Roadmap for Research in Astrobiology – The AstRoMap Roadmap**

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### **Abstract**

AstRoMap (Astrobiology Road Mapping activity—[www.astromap-eu.org](http://www.astromap-eu.org)) is a collaborative project which will provide the European Planetary Science Community with a road map in astrobiology. The goals of the project have been: (i) to pose big questions related to astrobiology; and (ii) the identification of experiments, new technology and/or those space missions to be developed in future programs and which could answer those big questions. This collaborative infrastructure includes the organization of expert panels and international workshops in order to discuss about those big questions and the science objectives by the community to be addressed. The main deliverable will be a Roadmap document. The project is steered by a consortium of six European and national research institutes and associations:

- Centro de Astrobiología (INTA-CSIC), Spain
- European Science Foundation, France
- Association pour un Réseau Européen d'Exo/Astrobiology (EANA), France
- B-USOC, Belgium
- Deutsches Zentrum für Luft- und Raumfahrt (DLR), Germany
- National Institute for Astrophysics (INAF), Italy

### **1. Introduction**

The roadmapping effort is based on a series of four expert workshops organised between October 2013 and November 2014, these events allowed brainstorming on current challenges and future research priorities for astrobiology, specifically considering the following topics (one per workshop):

- Origin of solar system
- Origin of organic compounds - steps to life
- Physico-chemical boundary conditions for habitability
- Biosignatures as facilitating life detection

The outcome of these topical workshop have been integrated into the AstRoMap Roadmap by a panel of European experts in the fields covered by astrobiology. This synthesis effort has been performed in the spring 2015 and involved two workshops and one community consultation. The Roadmap should be finalised by the end of June 2015.

The AstRoMap Roadmap will be a strategic document aimed at supporting the development of scientific programmes across Europe. In line with the project structure, the AstRoMap roadmap will be structured around five key topics:



- Origin and evolution of planetary systems
- Origin of organic compounds in space
- Rock-water-carbon interactions, organic synthesis, and steps to life
- Life and habitability on Earth and in Space
- 
- Biosignatures as facilitating life detection

The key topics will focus on a limited number of strategic scientific objectives to be addressed in the next 20 years by European astrobiologists, and suggest research activities for future development.

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# Transport of Organics through the Europa Icesheet

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## Abstract

We consider the large scale transport of material through the bulk ice sheet on Europa. This occurs on terrestrial Antarctic ice sheets, with material removed by wind ablation on the surface constantly being replaced by water frozen on to the underside of the sheet. This leads to transport of material, including the corpses of fish, through the icesheet, and its deposition on the surface. We propose that a similar mechanism might occur at Europa, with the high radiation levels causing sputtering over the Solar System age which could have the same effect as wind in Antarctica .

## 1. Introduction

The surfaces of icy moons, in a high radiation environment, undergo significant modification and erosion (eg Paranicas et al, 2007). We are recalculating the observed heavy ion fluxes (Lee-Payne et al this meeting) and this may have a significant effect on the calculated erosion rates of icy moon surfaces in a high radiation environment, since these heavy ions are the main agents for the sputtering of the surface. We will further extend our GEANT based model to consider ice sputtering and erosion by the radiation environment, thus obtaining a more sophisticated analysis of the erosion of the dirty ice of Europa. Into this we will feed our revised heavy ion flux measurements. The end result should be a revised, and more robust, estimate for the timescales for ice erosion and turnover. A key further question we can model is the survival of recognisable life signatures in the harsh radiation environment at the surface.

We will compare these sputtering losses, with the losses and gains due to other processes such as impacts, condensation of ejecta, plumes, dew formation and upflow through fissures, derived from observations in the current literature, and applied to Europa and other icy moons. They will be augmented by modelling, and by comparison with temporal imagery of icy moon processes. Surface frosts have

been recorded at high latitudes craters on sun shaded slopes on Callisto and other icy moons (Khurana *et al.*, 2007), and plume activity from Saturn's icy moon Enceladus has been observed off the planetary limb, against the night sky. Similar frosts are observed in Antarctica. Icy moon surface temporal differences can be found using correlation quality, a by-product of automated patch-based stereo matching software (Cook and Robinson, 2000), when applied to temporal image pairs. We can then investigate whether these changes support current models of charged particle bombardment, sputter redistribution, radiation damage, or thermal sublimation and freezing (Khurana *et al.*, 2007), and modify our own model accordingly.

We are to investigating the morphology of the surface ice sheets of Europa. It is attractive to draw comparisons, as illustrated by the images below. We will study: impact morphologies, lenticulae, cryovolcanic features, pull-apart bands, chaos terrain, ridges, surface frosts, topography, and global tectonic structures, all of which can be used to provide evidence of an extant subsurface ocean. These structures bear many similarities to terrestrial, floating Antarctic ice shelves which contain similar rifts, fractures, pull-apart structures, calved blocks and debris-rich folds and fractures (see image below for our analysis). We propose to use Earth's Antarctic ice shelves to provide structural insights into the features on Europa, to understand better their origin and significance.

A significant factor on Earth is the erosion of the ice surface by surface melt and wind, which transports organic and other material to the surface (Glasser *et al* 2006). It may be that erosion in the severe radiation environment at Europa plays a similar role. However, the accurate knowledge of heavy ion populations (sulphur and oxygen) which are the main species producing sputter erosion of ice (Johnson, 1999) is based on Gallileo measurements which were compromised by radiation damage. The results of our reanalysis will also be extended to Ganymede and Calisto, in preparation for JUICE arrival.



### Comparison of Europa and terrestrial ice sheets.

**Left:** Interpretation of part of the surface of Europa showing key geological features including lines and the prominent stained bands that indicate spreading of rifts and healing from within. "Freckles" are also visible. Note that different generations of features can be inferred from the relative movement implied by the different cross-cutting relationships. Image credit: NASA/JPL/University of Arizona/University of Colorado.



**Right:** Rifts on McMurdo Ice Shelf. The rifts clearly show along-rift spreading with the addition of new material in the rift as it spreads. This partly explains how water (and life) from underneath gets to the surface. This Earth example shows the types of structures that form on a thin floating Antarctic ice shelf and demonstrates how geological principles on Earth can be applied to Europa. Could a similar process operate on Europa?

## Conclusion

Connecting ice sheet morphology with radiation environment and survivability of biosignatures is new. It is clear that ablation by hard radiation will take place. Sputtering is momentum dependent, efficiency peaking at velocities where the ion stops in the surface monolayers - the material that escapes. This efficiency peak corresponds to Europa orbital velocity; the most efficient sputtering is by heavy particles, and sulphur fluxes are the most seriously underestimated due to the EPD radiation damage. Sputtering yield in dirty ice requires careful modelling, which the JUICE radiation modelling equips us for, and are far higher than for simple solids. The nature of "dark material" on Europa is a matter of extreme current controversy (eg radiation modified sea-salt *Hand and Carlson, GRL 15 May 2015*). Relating bulk transport to upflow through cracks and differential erosion/modification of material is key. In the Antarctic ablation leads to the appearance on the surface of organics (fish corpses) which have been transported through the bulk ice *Swithinbank et al Science 1961*. Our code can model contrast changes and survival of such material.

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