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Early Earth

Why on Earth?

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The most troubled period of Earth's history extends from the end of planetary accretion to the onset of plate tectonics: it is certainly the most important for understanding the origin of life but also still the most confusing for its near complete lack of observations. Fundamental uncertainties arise both with the sequence of geodynamic processes that eventually lead to the triumph of plate tectonics and life and with the timing of events. The first issue is the very existence of a terrestrial magma ocean. The upper mantle of the early Earth must have been molten to depths in excess of 500 km by the release of the gravitational energy of planetary accretion, which includes the Moon-forming impact and core segregation. However, this concept has been broadly rejected by geodynamicists for over 15 years on the ground that the major solid silicates (olivine, pyroxenes, and garnet) are denser than the magmas they crystallize from, while the role of buoyant plagioclase remains limited by the strong gravitational field of the Earth. This view holds that barren magma exposed to the surface quickly looses its heat by radiation into space and the Earth freezes in less than a million years. Evidence of ^{142}Nd anomalies created by the extinct radioactivity of ^{146}Sm ($T_{1/2}=103$ My) gathered over the last three years showed this view to be incorrect and that a molten mantle existed until some 30 My after the formation of the nebula, a timing which happens to coincide with core segregation. The crux is likely to be the presence of a hydrosphere, which is unlikely to originate by outgassing of the Earth's magma ocean: terrestrial material lost most of its volatile elements (e.g. 85% of its K) and the interior of the planet certainly emerged bone-dry from the early stages of accretion. Water was therefore introduced from the outer Solar System at a late stage by the perturbing effect of giant planets on the orbits of icy objects. Water reacts with magmas and solid rocks to form hydrous minerals with low densities (serpentine, talc, and amphibole), which accumulated as a protective crust. Such a conductive boundary layer on top of the magma ocean extended the life of the magma ocean by a few tens of millions of years. An additional characteristic of the presence of water is the massive liberation of H_2 upon oxidation of ferrous iron and its ensuing reaction with CO_2 to produce CH_4 and NH_3. A remarkable incidence of these processes on the origin of life is the formation of prebiotic molecules. A second issue is how and when the Earth's dynamic regime morphed into plate tectonics (or at least some early form of it) and why it did not bifurcate into a Mars-type regime of a thick lithospheric lid stagnant over the convective mantle, a situation far less propitious to create a biotic environment. Abundant granites are the hallmark of plate tectonics because they cannot be melts of the mantle and necessitate wet basalts as source rocks. Zircons are ubiquitous in granites but are highly soluble in basaltic melts. The discovery of 4.0–4.4 Gy old zircons in Jack Hills sandstones (Australia) therefore appears as smoking-gun evidence that at least some true granites existed, while their ^{176}Hf isotope compositions indicate that the source of these granites (presumably hydrous basaltic rocks) formed very early in the Earth's history. Continents rising above sea level constitute the major renewable source of nutrients (nitrate, phosphate) essential to maintaining life. This does not necessarily mean that continents were as widespread then as they are today and the case has recently been made that the rise of chlorophyll stepped up the capture of Solar energy, thereby increasing the rate of weathering and indirectly affected the rate of continental crust production. Conservatively, the point can be made that some continental crust existed by 4.3 Gy and that 'a lot' of it had come into existence by the time of the Isua rocks (3.85 Gy ago). Plate tectonics and life share water as a common thread, and water owes its presence on Earth to the strong gravitational field of the planet.

From suns to life: a chronological approach to the history of life on Earth

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We present, in a synthetic chronological frieze, the various events considered by the authors as relevant to the origins of life on Earth. These events have been tentatively ordered chronologically in accordance with actual knowledge within all the scientific disciplines involved in astrobiology. This frieze was originally published in November 2006 in a topical issue of *Earth, Moon and Planets*[1] gathering nine articles written by 25 scientists (astronomers, geologists, biologists, and chemists) who have attempted to share their specialized knowledge concerning a common question: How did life emerge on Earth? Their ultimate goal was to provide an initial answer as a prerequisite to an even more demanding question: Is life universal? By adopting a chronological approach to the question of the emergence of life on Earth (the only place where we know for sure that life exists, even though nobody agrees on the general definition of 'life'), it was possible to break down this question into several sub-questions that can be addressed by different disciplines. After an introduction, the main chapters of this review cover the following: the formation and evolution of the Solar System; the building of an habitable planet; prebiotic chemistry, biochemistry, and the emergence of life; the environmental context of the early Earth; the ancient fossil record and early evolution. The concluding chapter summarizes the highlights of the review and discusses the different points of view concerning the universality of life. Two pedagogical chapters are also included, one on chronometers and another in the form of a 'frieze' summarizing in graphical form the present state of knowledge concerning the chronology of the emergence of life on Earth, before the Cambrian explosion.

[1] Gargaud, M. *et al.* (2006). From the arrow of time to the arrow of life. *Earth, Moon Planets* **98**, 1–4.

Molecular evidence for life on Earth 3.5 billion years ago

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Cherts are amongst the oldest sedimentary rocks on Earth and the origin of Archean cherts contain traces of organic matter is highly debated: are they the result of abiotic formation under hydrothermal conditions or are they organic microfossils?[1,2]. This organic matter occurs both in solvent soluble and insoluble (kerogen) fractions. Assessment of the biological origin of such sediments solely on the basis of the occurrence of organic biomarkers in the soluble fraction is often disputable as this fraction may easily be contaminated through migration of more recent organic matter. In contrast, insoluble molecular structures characterized by covalent bonds are, in all likelihood, of the same age as the host rock. We have therefore investigated the chemical structure of the kerogen from a chert of the lowest metamorphic grade from the Warrawoona Group, using a combination of spectroscopic (FTIR, solid state NMR) and pyrolytic tools. These techniques reveal the occurrence of long aliphatic chains covalently linked to the highly aromatic macromolecular network. As hydrocarbons can be physically trapped in the mineral matrix, we checked that these chains do not to correspond to compounds that might not have formed contemporaneously with the host rock. Interestingly, these chains show a specific distribution with a significant odd-over-even carbon number predominance. Such predominance is a unique characteristic of organic matter formed biologically since it reflects biosynthesis using the addition of C2 units. As a result, the distribution of the aliphatic chains in the kerogen of the Warrawoona chert provides evidence for the involvement of a biosynthetic pathway in their formation. Additional results on other pyrolysis products support the presence of life in this 3.5 billion year old kerogen, possibly related to sulphate-reducing activity.

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Siliceous 'stalactites' of Archaean age, Pilbara Craton, Australia: A biosignature?

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Vertically oriented growth forms of minerals occur at numerous localities and are typically explained as stalactites without a critical evaluation of their origin. Mineralization of microbial filaments in the saturated or unsaturated zone results in stalactite-like structures. Vertically oriented stalactite-like fabrics preserved as quartz are not uncommon in the Archean volcanosedimentary sequences of the Pilbara Craton. Their origin has traditionally been explained as stalactites[1], implying formation from dripping water in the vadose zone. Here we report investigations on banded quartz 'stalactites' from palaeocavities in the ~3400 Ma Strelley Pool Chert and the 3467 Ma Duffer Formation in the Pilbara Craton. 'Stalactites' postdate the deposition of the host strata by an unknown time, but they are of Archaean age because their orientation vertical to bedding demonstrates that they were formed before the tilting of the host strata that occurred between 3300–2760 Ma. An innermost diameter of the 'stalactite' structures of ~2 μm is inconsistent with a stalactitic origin. Fluid inclusion studies by microthermometry and Raman spectroscopy demonstrate the presence of hydrothermal fluids involved in quartz growth, and of later fluids in cracks. Salinities are low (0.4–0.5 wt% equNaCl) and most fluids contain CO_2 and CH_4. Formation temperatures are estimated at 120–200 °C from fluid inclusions, and the calculated water $\delta^{18}O$ is 0 to +5‰ (VSMOW). Late stage $\delta^{18}O$ values are in the range of Archaean cherts. Based on numerous similarities, an analogy is made of the pseudostalactitic fabrics with similar microbially induced pseudostalactitic fabrics in younger rocks, for example the Cenozoic Monaro volcanics, New South Wales, and the oxidation zone of the Broken Hill orebody, New South Wales. For most occurrences, an origin by mineralization of vertically draped microbial filaments is preferred[2], but alternative modes of origin need to be evaluated. 'Stalactites' of the Pilbara Craton are a potential signature of Archaean subsurface life.

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Geochemical profiling of an Early Archaean, littoral environment, photosynthetic microbial mat from the Barberton greenstone belt, South Africa

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The superb state of preservation of an anoxygenic photosynthetic microbial mat formed at the surface of exposed littoral sediments from the Onverwacht Group[1] (3.47–3.33 Ga) allows detailed geochemical profiling in a manner that is similar to vertical profiling of modern microbial mats using microprobes. *In situ* geochemical and morphological studies using HR-SEM + light element EDX, MET + EDX, Raman spectrometry and X-ray mapping of organic sulphur and sulphates on FIB sections through the mat permit detailed vertical profiling on a submicrometre scale. Structurally, although the mat morphology is superbly preserved at the surface by a silica coat, all the organic matter beneath the surface has degraded, resulting in an amorphous to reticulate texture that is reminiscent of kopara[2]. Small detrital particles are embedded particles within the mat. Whereas the lower part of the mat has been micritized (the reticulate, polymer-like texture still preserved), the upper layer immediately below the silicified surface is pure kerogen, although the whole thickness of the mat has also been impregnated by silica. Micritization of modern photosynthesising microbial mats in association with SRBs is a well-known phenomenon[3]. X-ray mapping of reduced sulphur shows that it coincides with the filamentous mat whereas inorganic SO_4 is concentrated in the evaporite crystals (gypsum). This is the first submicrometre-scale profiling of an Early Archaean microbial mat. It demonstrates that the mineralization processes on the early Earth were similar to those in modern photosynthesising mats.

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Tracing life using Mg isotopes

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Like Ca, Mg is a major element in both microbial cells and minerals and, contrary to other commonly used tracers, is immune to redox conditions and atmospheric interactions. In contrast with the negligible Mg isotope fractionation associated with igneous processes and high-temperature water–rock interaction, the broad range of Mg isotopes in low-temperature processes may help identify the specific effects of biological activity. Experimental olivine dissolution in the presence of *E. coli* leads to an enrichment of the solution in ^{24}Mg with respect to abiotic experiments. At low cellular concentrations, ($OD_{600\ \mathrm{nm}}=0.1$), the magnitude of Mg isotopic shift in δ^{26}Mg between the biotic versus the abiotic filtered solutions is -0.52 ± 0.20‰ and increases to -1.88 ± 0.40‰ at higher cellular concentrations ($OD_{600\ \mathrm{nm}}=1$). Both actual analyses and mass balance constraints support that bacteria act as reservoirs of isotopically light Mg ($\delta^{26}Mg_{bact} < -9$‰). δ^{26}Mg of samples with a bacterial origin are systematically lower than δ^{26}Mg of silicate rocks, featuring Mg isotopes as a potential tracer of fossilized microbial activity.

Solar System

Sedimentological evidence for lacustrine activity in Southern Melas Chasma, Valles Marineris, Mars

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The distribution in space and time of liquid water on Mars is a haunting question because of its relevance to astrobiology. To date, all orbital observations which attest to past flow and aqueous sedimentation on Mars have been dedicated to surficial landforms (i.e. drainage networks and depositional fans) so that we cannot know how persistent such aqueous episodes were. Here we report an unprecedented identification of typical stratigraphic architectures made in MGS MOC images of layered material in southern Melas Chasma. The depositional system developed about 3.5 Gyr ago, i.e. Hesperian-aged. A particular set of strata is arranged in three depositional sequences bounded by stratigraphic unconformities. Insights into depositional geometries are used to isolate specific depositional processes. Evidence of progradation of steeply inclined delta foresets and aggradation of giant levees flanking a channel (i.e. channel-levee system) are indicative of gravity-driven, subaqueous sedimentary processes in a deep, long-lived lacustrine environment. The special relevance of the site stems from the persistence of water so that any organic compound could have been shielded from Solar radiation and an oxidizing atmosphere for a while. The significant depth of the water body constitutes an extra favourable context in that any high-amplitude variation of temperature, pH, gas composition and concentration at the surface must have been attenuated at depth by the thick water column. In addition, the channel-levee system affords potential confining and sorting mechanisms for the different grain-sizes of clastic sediments and organics.

A new approach in Terrestrial Exploration Rover Design

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The Multi-Tasking Rover[1] (MTR) is a highly mobile robotic vehicle that integrates functionality to accommodate many different space exploration needs. It employs a hybrid suspension system to achieve rough-terrain stability. The rover is equipped with two gripping mechanisms that allow it to safely hold and carry two containers, each encapsulating different scientific instruments (Science Pack (SP)) or tools (Tool Pack (TP)). In this way the vehicle can offer mobility and also use the smaller subsystems in order to transform its functionality and perform a range of different tasks. The appropriate selection of Science and/or Tool packs enables the robot to perform a great variety of tasks either alone or in cooperation with other robots. The key design goal for the MTR system is to demonstrate varying functionality such that, once deployed, it can satisfy the requirements of not only current but, by sending new Packs, also future Space Exploration. The MTR approach assumes that the Packs have in-built control systems and can operate independently from the rover once deployed. Communication links between the Packs and the MTR will be established when required. The advantage of this approach is that instead of sending a large number of different rovers to perform a variety of tasks, a smaller number of MTRs could be deployed with a large number of different SPs and TPs, offering greater functionality at a reduced payload. Overall, the MTR offers a valuable new platform for Astrobiology.

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Astrobiology, habitability and the Moon

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Lunar exploration provides a high potential to foster the objectives of astrobiology. The Moon played a key role in early Earth evolution. Results from recent Lunar missions have changed our view of the Moon. ESA SMART1 was launched in 2003 and will orbit the Moon until impact in September 2006. Lunar orbiters are readying for launch in 2007 and 2008 (the Chinese Chang'E1, Japanese SELENE, Indian Chandrayaan-1 orbiter as well as the US Lunar Reconnaissance Orbiter and LCROSS impactor). From 2010, a series of soft-landing missions to the Moon could emplace a global robotic presence with precursor life science experiments. The results of these missions will continue to answer open questions concerning the origin of the Earth–Moon system, the early evolution of life, and the planetary environment and habitability. Lunar geo-science studies help us to understand the origin and evolution of our unique Earth–Moon system and other rocky planets. Lunar or cis-Lunar telescopes on the Moon can detect and characterize if life exists elsewhere in the Universe. We can search for samples of the early Earth on the Moon. We can use *in situ* resources necessary to support future life and human presence (e.g. water, oxygen). The Moon will be used for geosciences, life sciences, astrobiology laboratories, human bases and biospheres that will play a key role in the future of life beyond Earth. This talk will also include a summary of a half-day mini symposium on Astrobiology on the Moon, held at AbsSCiCon2006.

Electron lamp and cathodoluminescence instrumentation for analysis of Martian sediments

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An old technique, cathodoluminescence (CL) is a newcomer to space exploration. On Mars, it is expected to contribute to the mineralogical characterization of sedimentary rocks, to the search for bio-markers and also to identify past geochemical conditions. Sample irradiation with an electron beam yields geochemical information, using the spectral analysis of the luminescence in the visible range, and also allows interpretation of the growing process and the diagenesis of minerals. The concept of an 'electron lamp' was developed to get around the presence of the rather high atmospheric pressure of CO_2 in the Martian environment. The electron production will not be disturbed when made under vacuum, since it is separated from the sample kept in atmospheric pressure by an electron-transparent window. The prototype of such a lamp, presently in operation with a common electron source, validates the concept, since CL pictures were achieved and their related spectra do not exhibit any meaningful loss of quality. Two kinds of membrane were tested against the electron transparency and the mechanical reliability: the polycarbonate which appears too fragile, and Si_3N_4 which fits better the space constraints. Two points need improvements: the membrane lifetime and the electron angular diffusion, owing to both the membrane crossing and, mainly, to the atmospheric path. In addition, a trade off has to be done for the electron source itself in view of a space mission.

No more sniffing, but hitting: LIBS/ Raman – GENTNER – for comprehensive *in situ* analysis of the Martian surface

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We propose GENTNER, a novel instrument to determine rapidly and with high sensitivity many element concentrations – including H, C, N, O, P, S, Fe – as well as organics and minerals in Martian rocks, coarse fines and soils. GENTNER combines laser induced breakdown spectroscopy (LIBS) with Raman spectroscopy. GENTNER is distinguished by rapid measurements, high sensitivity, fast repetition, low mass, size and resource needs, high flexibility with respect to sample type, shape and size, and no need for sample preparation. Its basic concept consists of lightweight sensor head(s) mounted on arms, and an instrument module (pump lasers, spectrometer, electronics, etc.) inside a rover, both connected by optical fibres. GENTNER will perform individual analyses of all sample types within reach, including drill core samples. Dust coverage is removed by depth profiling up to 2 mm. GENTNER also pre-characterizes samples prior to GC-MS and isotopic studies. However, varying environmental Martian conditions and varying physico-chemical characteristics of the expected samples require extensive LIBS and Raman studies prior to the final instrument design. To obtain reliable quantitative LIBS results and to optimize the LIBS system performance we first studied the influence of the physical status – rock or powder – and of the temperature of samples.

The UREY: Mars organic and oxidant detector for the ESA ExoMars rover mission

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The search for extinct or extant life on Mars is the major objective of several future Mars missions. Looking for key organic compounds that are essential for biochemistry as we know it or that are indicative of extraterrestrial organic influx is the primary goal of the UREY instrument suite, selected for the ESA ExoMars rover mission. The experiment is designed to address in a robust and comprehensive manner one of the primary goals of the ExoMars mission, which is 'to search for traces of past and present life on Mars'. It achieves this goal by isolating and identifying key organic compounds, amino acids/amines and PAHs, directly on the surface of Mars. UREY consists of four separate major components: a subcritical water extractor (SCWE); the Mars Organic Detector (MOD): a novel lab-on-a-chip micro-capillary electrophoresis (μCE) system; and a chemometric sensor array, the Mars Oxidant Instrument (MOI). UREY will target several key organic molecules at very low concentration levels (1000 times better than Viking). Using the μCE system to separate the organic molecules, UREY will have the capability to provide the necessary information to determine the origin of these compounds, for example whether they are extraterrestrial (delivered to Mars by meteorites and interplanetary dust particles), were formed abiotically on Mars, or were potentially biogenic. It will also utilize sensors to detect and characterize oxidants present in the same samples. These complimentary analyses will examine the hypothesis that oxidants and organic matter on the surface of Mars are inversely correlated. The performance of the UREY instrument suite has been demonstrated in a series of comprehensive field tests conducted in the Panoche Desert Valley and in the Atacama Desert. UREY plays a fundamental role in the Pasteur strategy to detect organic molecules on Mars.

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Search for oil reservoirs on Mars

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This paper is focussed on the search for hydrocarbon oil on Mars, with reference to terrestrial oil and to oil as a reservoir of organic material for potential life. The existence of the ideal conditions for sedimentary basins formation, i.e. tectonic processes providing sediments trapping, in Martian history is recognized and is used as the basis for the hypothesis presented here. Plate tectonics were the origin of a specific magnetic signature in the Earth's crust. It is also worth noting that a high-resolution map of the Martian magnetic field, based on measurements of NASA's Mars Global Surveyor (MGS) spacecraft, providing proof for Earth-like plate tectonics, was recently published[1]. Thus the magnetic stripes found on the Martian surface may point to ancient movements of the crust. These movements may have provided the necessary circumstances for the subsidence of organic material (from a biogenic or abiogenic origin), and posterior hydrocarbon oil generation. The necessary conditions for hydrocarbon oil formation and the possible locations for hydrocarbon oil seepage and reservoirs on Mars are discussed. The presence of numerous dark streaks near the equatorial region of Mars, revealed by Mars Orbital Camera (MOC)

images, are correlated with the possible existence of oil seeps. A variety of dark features have also been found on the Martian South Pole. Analysis and comparison of the above-mentioned features with the known behaviour of oil on ice has led to a hypothesis concerning the presence of hydrocarbon oil seeps on Mars surface. The role of CO_2 as an aid to the hypothetical oil leakage on Martian Poles is also suggested.

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Reinforcing the scenario of an early enrichment in organics by dust particles of cometary origin

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Space missions to comets, from Giotto and Vega to Stardust and Deep Impact, have demonstrated that cometary dust particles are rich in organics. The results also suggest that the dust particles have extremely low densities and can easily fragment. From recent numerical simulations of the light-scattering properties of bright comets, we confirm that numerous dust particles are porous (typically fractal aggregates); the model indicates that the proportion of absorbing material – most likely organic compounds – is in the 35–60 % range of the total mass for the comet Hale–Bopp[1]. The method, applied to the interplanetary dust cloud, suggests that a significant amount of fluffy absorbing particles are also present in it[2]. We have thus adapted the Jones and Kaiser theory of meteoritic ablation to fractal aggregates with sizes below a few hundred micrometers. Calculations show that, for fluffy aggregates compared with compact particles, the temperature reached in the crossing of the atmosphere is divided by $\pi^{0.25}$ and the volume arriving to the surface is up to π^3 larger. During the epoch of early bombardment, such particles would have been more likely to reach terrestrial planets than compact ones, and to deposit significant amounts of the organics needed for life to originate.

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First results from the Stardust PET on bulk chemistry of comet Wild 2

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The Stardust spacecraft, launched in 1999, successfully brought back to Earth in January 2006[1] the first extraterrestrial samples since the Apollo mission and thus offered laboratories the opportunity to work on samples of certain cometary provenance. Great expectations have been founded from these first results to yield insights into the evolution of the Sun and planets, and possibly into the origin of life itself. Currently, the aim of the PET program is to produce a preliminary characterization of the abundance and nature of the organics[2] and inorganics in the returned samples. As X-rays are among the most non-destructive probes and are sensitive, multielemental and penetrating, synchrotron radiation-based microanalysis measurements were scheduled as a first priority on these samples. We have performed measurements on beamlines ID22 and ID21 devoted to high/low energy microspectroscopy and recorded results on a collection of six keystones (slices of aerogel containing the terminal particle and fragmentation track of cometary grains) received from NASA. We have recorded total mass composition for elements of $Z \geqslant 15$ by means of X-ray fluorescence, as well as structural information by X-ray diffraction. This allowed the direct identification of the mineralogy of the grains. Finally, we recorded the charge states of S and Fe as a function of the position in the track by means of micro-Xanes measurements. All these analyses were combined to produce a description of the Stardust grains, but also a history of how they formed and of their thermal interactions[3].

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In situ search for life traces in extraterrestrial samples by synchrotron X-ray fluorescence 2D and 3D imaging

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In the last decade, a growing need has emerged in the Planetary Sciences community for an accurate, fast, non-destructive means for the characterization of rare samples of extraterrestrial origin such as those issued from the Mars return or Stardust missions, available only in small quantities in their original container. The characterization of organic phases, from abiotic or biotic sources, also appears to be a fundamental issue. As a result of their penetrative power, the use of hard X-rays proves to be advantageous as they can be carried out across the sample holder. An analytical procedure, based on 2D and 3D synchrotron X-ray fluorescence imaging techniques of elements with $Z > 14$, was developed on meteorites for an *in situ* and systematic search for traces of life. A combination of X-ray tomographies allows the location of alteration phases, fractures and low-Z volumes where microbial habitats should be primarily searched for[1,2]. A combination of synchrotron X-ray Microscopy with XANES spectroscopy at the sulphur K edge allows the mapping some of the few specific X-ray properties of the biological matter[3]. The way in which such an analytical procedure can be coordinated with other non-destructive or destructive analytical tools will be discussed in the context of both the French Stardust Consortium and the Stardust Bulk Chemistry PET experiments.

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Raman spectroscopy of chondritic and cometary kerogens

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Pristine kerogens in chondrites and cometary grains have an interstellar origin and may provide useful clues as to the carbon chemistry in the Interstellar Medium (ISM). They also might be considered as the carrier of the first prebiotic molecules and the origin of life on Earth. Nevertheless, their chemical structure, particularly in cometary grains, is poorly elucidated. A better understanding of their chemical composition and structure, along with the identification of the carriers of the isotopic enrichments, would help to identify reaction pathways and/or alteration processes experienced either in the Solar nebula and/or the parent body. For this purpose, Raman spectroscopy is a useful tool for investigating organic-rich micro-grains. It provides both structural and chemical information, and it can be implemented as a micro-analysis technique suitable for chemical imaging at the micrometric scale. We present two planetological applications. We first report a study on metamorphosed kerogens, which focused on more than 40 chondrites, and ~ 30 ligno-cellulosic coals. We show that the maturity of such disordered samples is efficiently determined, and that Raman spectra also contain information on the chemical structure of the organic precursor[1]. It is thus possible to distinguish extraterrestrial from terrestrial kerogens using this technique. In pristine chondrites, we demonstrate that the kerogen's maturity is related to the temperature of the metamorphism peak[2,3]. In the second part of the paper we address the question of the applicability of this technique to very disordered kerogens. We focus on the use of a 244 nm excitation, which allows to us to resonantly excite specific chemical functions. We report the identification of new features, among them the first identification of the terminating–CN cyanide function.

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[3] Bonal, L. *et al.* (2007). Organic matter and metamorphic history of CO chondrites. *Geochim. Cosmochim. Acta* (in press).

Comparative Raman studies with different excitation wavelengths performed on Mars meteorite material

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Raman spectroscopy is an extraordinary powerful method for determining the mineral and chemical composition of unprepared surfaces. This method is equally suited and well applicable for the detection of minerals as well as organic substances and water. To single out the best-suited laser excitation wavelength for mineral analysis, we have selected materials that are known to contain 'problematic' compounds (strong fluorescence, poor Raman scattering) and are also of relevance for space missions. Measurements were performed on three Martian meteorites: SAU 008, DAG 735 and Zagami. Raman mapping has been carried out with excitation at 244, 256, 532, 633 and 830 nm. Addressing exactly the same small scanning areas on the samples (200×200 μm) when using different Raman instruments was achieved with an in-house developed technique the fixation and marking of the probes. A comparison of the results for the five different excitation wavelengths is presented. The current technological stand and the desired technology level needed for building a space-qualified Raman instrument based on these different laser excitation wavelengths is also discussed. The experiments show that Raman UV excitation is superior when compared with a VIS/NIR excitation, yet VIS/NIR instrumentation is scientifically and technically compliant having a technological head start on UV-based instruments.

Search for a criterion to identify meteorites from the same parent body

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Astronomical analysis as well as petrographic data indicate that some ordinary chondrites could come from the same parent body. For example, the majority of strongly shocked L chondrites are believed to originate from one parent body, whereas almost unshocked and highly porous L chondrites such as Baszkówka, Mt. Tazerzait and Tjerebon are supposed to be fragments of another parent body. An attempt was made to see whether Mössbauer spectroscopy could find a common feature in spectra of meteorites originating from the same parent body, which can distinguish them from spectra obtained for meteorites from other parent bodies. Mössbauer spectroscopy is applicable to different isotopes but most sensitive for ^{57}Fe. The Mössbauer spectra reflect the properties of the environment of the iron atoms. Each iron-bearing compound gives a characteristic Mössbauer spectrum. A typical Mössbauer spectrum of non-weathered ordinary chondrites is a superposition of two sextets and two doublets. One sextet is connected to metallic iron within an iron–nickel-alloy (kamacite), the other to Fe^{2+} in iron sulphide (troilite) of composition FeS. Doublets correspond to ferrous present in silicate phases such as olivine and orthopiroxene. It has been suggested that perhaps the Mössbauer parameters of troilite could serve as a criterion to identify meteorites from the same parent body. This hypothesis was created because the parameters describing the quadrupole and magnetic interaction in troilite depend on the number of vacancies, the level of impurities in troilite and the rate of cooling of the material. These values are characteristic for the conditions of crystallization of the parent bodies of meteorites. The Mössbauer measurements of 15 samples of ordinary chondrites were performed at room temperature. The Mössbauer parameters of troilite in the investigated samples belong to two different groups, which can suggest that the investigated meteorites could come from two different parent bodies.

Carbon isotopic enrichment in Titan's tholins? Implications for Titan's aerosols

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Since the discovery of the main composition of Titan's atmosphere, many laboratory experiments have been carried out to mimic its chemical evolution and, more specifically, the formation of the organic haze particles widespread in this atmosphere. Indeed, some of these simulation experiments produce a solid phase – named Titan's tholins – that is assumed to have properties analogous to those of Titan's aerosols. We have studied the possible isotopic fractionation of carbon during the processes involved in the formation of Titan's tholins, using tholins obtained from different simulation experiments. It is an important issue because it can provide information on the processes of tholins formation. We present the first results obtained on the $^{12}C/^{13}C$ isotopic ratios measured on Titan's tholins synthesized in the laboratory with cold plasma discharges. Measurements of the isotopic enhancement in ^{13}C ($\delta^{13}C$), performed both on tholins and on the initial gas mixture (N_2:CH_4 (98:2)) used to produce them, do not show any clear deficit or enrichment in ^{13}C relatively to ^{12}C in the synthesized tholins, compared to the initial gas mixture. Preliminary retrieval of the data from the Aerosol Collector and Pyrolyzer (ACP) experiment of the Huygens probe suggests that Titan's aerosols may also not present carbon isotopic enrichment. This observation allows us to go further in the analyses of the ACP experiment data. We also focus on the evolution of Titan's tholins under acid hydrolysis treatment. This strong treatment aims to reproduce the evolution of Titan's aerosols in contact with ice water over a longer time scale. Preliminary results on the analyses of the obtained products could give guidelines for the identification of the still unspecified matter that contributes to Titan's surface reflectivity decrease as observed by the DISR instrument. This study is still in progress.

Synthesis of biologically-important precursors from nitrogen-containing species on Titan

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Nitrogen's versatile inorganic and organic chemistry is afforded by the trivalent nature of the element as well as its electronegativity and size. Even though the atmospheres of both the Earth and Titan are dominated by N_2(g), the fate of N_2(g) may be quite different in these two environments. On Earth, the inert N_2 from the atmosphere is fixed by microorganisms into ammonia, nitrate and other nitrogen-containing species that can be incorporated by organisms as protein components and metabolites. However, on Titan the pathways are different, mainly due to the lack of oxygen. Titan's nitrogen- and carbon-dominated atmosphere is the site of very complex organic chemistry that often leads to the production of a myriad of product species including larger molecules from smaller molecular, ionic and radical precursors. Radiation and lightning-driven photochemical conversion of methane and other precursors produces smog in the middle to upper layers of the atmosphere, and an organic rain of methane, hydrocarbons and nitrogen-containing aerosols falls regularly onto Titan's surface, creating an Earth-like terrain of extended river channels. Here we describe plausible nitrogen chemistry under Titan's conditions and show organic synthetic schemes based on ammonia, cyanamide, hydrocyanic acid and other nitrogen-containing species resulting in the production of biologically significant molecules such as amino acids. The relevance of such chemistry to prebiotic evolution on Titan will also be discussed.

Methane recycling on Titan

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The Cassini–Huygens mission provided a wealth of information concerning the chemical ingredients in Titan's atmosphere and surface. Methane found in the atmosphere is mostly consumed by photochemical smog. When the Huygens probe landed on Titan's surface, the instrument recorded a significant jump in methane levels, leading to the question: 'How does the methane replenish itself after being consumed in the formation of photochemical smog in the atmosphere?' We suggest that there are sources that replenish the concentrations of methane at or near Titan's surface. A plausible source for methane production would be geoprocesses as well as organisms on or near the surface. A proposed methane 'cycle' is described.

Titan ionospheric chemistry, laboratory experiments and uncertainty propagation, tools for improving models

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We describe results of a concerted research effort held in 'Laboratoire de Chimie Physique' where experimentalists as well as theoreticians have developed laboratory tools in order to measure the accurate rates of ion molecule reactions and tools to estimate the uncertainty propagation in the models of Titan Ionospheric Chemistry, which are becoming increasingly complex. Laboratory measurement results are presented for energy-selected (internal and translational energy) ion-molecule reactions and doubly charged molecular ion reactions. We will also present the experimental set-up of a new project, which will be installed in the near future in 'Laboratoire de Planétologie de Grenoble'. A very high-resolution mass spectrometer is proposed to study the chemistry of Titan's ionosphere, in particular the molecular growth paths leading to large molecular ions observed by the INMS instrument aboard Cassini. A parallel modelling effort with uncertainty analysis will be conducted in Orsay and Grenoble.

The first results of Venus-Express seen from an astrobiology point of view

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Since May 2006, the Venus-Express spacecraft has reached its nominal orbit and observations have begun. The already obtained images and spectral information give an extremely rich and complex image of Venus' atmosphere including aerosols and clouds. These results have been shown for the first time at the Venus-Express science conference in the frame of the EUROPLANET science conference of September 2006. The obtained data can be put in relation with previous analyses of the possibilities of present and past life in the Venus environment[1]. The Venus images clearly show heterogeneity in Venus' clouds and above relating to both active dynamical systems and complex chemistry. The spectral instrument SPICAV reaches its target molecules and makes constant discoveries relating to carbon-, hydrogen-, oxygen-, halogen- and sulphur-containing molecules. This extremely rich chemistry is still waiting for the discovery of nitrogen-containing species. Venus-Express has confirmed the presence of a zone allowing liquid droplets in the clouds. The analysis of these clouds and hazes will possibly reveal nutrients for life or perhaps even habitats.

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Biogeoscience from the SCIAMACHY instrument on the ESA ENVISAT satellite

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For the four years, the ENVISAT satellite has been surveying the Earth's surface, ocean and atmosphere with ten advanced sensors. One of them, SCIAMACHY, was designed for atmospheric monitoring but a large amount of its data show the influence of life-related processes. The four-year series of results has been examined in terms of phenomena related to evolutions in biological processes on the Earth. SCIAMACHY is an announcement of opportunity instrument proposed by the space agencies of Germany and the Netherlands and the Belgian Science Policy Office. The obtained data include the survey of the atmospheric ozone and its trends, including seasonal ozone depletion in the polar regions. The multichannel character of the instrument allows the mapping of many more gases such as methane, formaldehyde, carbon monoxide, carbon dioxides and even plankton indexes. In particular, the SCIAMACHY series has shown new biological sources of gases in the tropical forests and the ocean. These different aspects have been reviewed from a biogeosciences perspective. Clearly, the high spectral and spatial resolution of the ENVISAT satellite instruments allows the monitoring of the evolution of life processes on Earth from space. This operation could thus, in theory, be repeated on more distant worlds. The Belgian segment of the SCIAMACHY project is managed by the ESA PRODEX programme through the Belgian Science Policy Office initiative.

Development of a 'one-pot/one-step' sample preparation procedure for the *in situ* analysis by GC/MS of the Martian soil: application to the Sample Analysis at Mars experiment (SAM for MSL 2009)

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In the frame of the 2009 Mars Science Laboratory (MSL) mission a new sample preparation system (SPS) compatible with gas chromatography-mass spectrometry (GC-MS) has been developed for the *in situ* analysis of complex organic molecules in the Martian soil. The goal is to detect, if they exist, some of the key compounds that play an important role in life on Earth including carboxylic acids, amino acids and nucleobases. Before analysis by GC-MS, all the targeted refractory compounds trapped in the soil sample must be extracted and chemically transformed (derivatization). The extraction is carried out in a two-step process which requires the separation and evaporation of the extraction solvent in order to concentrate the organic compounds of interest. To improve the compatibility of the technique for spaceflight a one-step procedure is performed using only a thermal processing for the extraction step. These two extraction methods are followed by a derivatization step which uses MTBSTFA (*N*-methyl-*N*-(*tert*.-butyldimethylsilyl)-trifluoroacetamide). The sample preparation methods have been tested on 'spiked' soil and on Atacama Desert soil coming from the most arid part of the desert located in Chile. All the targeted compounds have been detected by these two procedures, demonstrating the applicability of the technique for *in situ* analysis. The one-step procedure has been successfully tested on Atacama soil samples with a laboratory pilot reactor, developed for this study, within representative space operating conditions.

GC-MS analysis of amino acid enantiomers as their N(O,S)-perfluoroacyl perfluoroalkyl esters: application to space exploration

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The target of the *in-situ* research of optical activity in extraterrestrial samples stimulated an extended investigation of a GC-MS method based on the derivatization of amino acids by using a mixture of perfluorinated alcohols and perfluorinated anhydrides. Amino acids are converted in their N(O,S)-perfluoroacyl perfluoroalkyl esters in a single-step procedure, using different combinations of the derivatization reagents: trifluoroacetic anhydride (TFAA)-2,2,2-trifluoro-1-ethanol (TFE), TFAA-2,2,3,3,4,4,4-heptafluoro-1-butanol (HFB), heptafluorobutyric anhydride (HFBA)-HFB. The obtained derivatives are analysed using two different chiral columns: a Chirasil-L-Val and a $\tilde{\gamma}$ cyclodextrin (Rt-γ-DEXsa) stationary phases which show different and complementary enantiomeric selectivity. The mass spectra of the obtained derivatives are studied and mass fragmentation patterns are proposed: significant fragment ions can be identified to detect amino acid derivatives. The obtained results are compared in terms of the achieved enantiomeric separation and mass spectrometric response. Linearity studies and the measure of the limit of detection (LOD) prove that the proposed method is suitable for a quantitative determination of several amino acids enantiomers[1]. The use of a programmed temperature vaporizer (PTV) technique for the injection of the untreated reactional mixture is a promising method for avoiding the manual treatment of the sample and decreasing the LOD.

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Analogues

Astrobiology quiz: how to recognize extraterrestrial life?

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The search for present or past life on extraterrestrial objects is one of the key goals of the Astrobiology scientific community. This search is based on the detection of biosignatures, which must be an undisputable proof of past or present life. All members of the Astrobiology community agree that there must be a consensus on the type of observations considered as unequivocal proof that life indeed exists or existed on extraterrestrial bodies submitted to an investigation. However, there is presently no consensus on the type of relevant observations considered as biosignatures. It is time to take up this challenge! First, we think that it is necessary to discuss the different clues for life that could be relevant as biosignatures. This is why we propose a virtual scientific experiment to the Astrobiological community. We would like to invite scientists that attend the EANA to participate in the following game. Let us imagine that an unmanned probe was able to bring back to Earth an uncontaminated piece of rock originating from LUGDUNUS, a (virtual) satellite orbiting around a large planet in the Solar System. As an expert you are asked to give your opinion on the interpretation of the results of the LUGDUNUS sample analyses. During the Lyon EANA meeting, we will try to reach some general conclusions based on the answers we will receive.

Hydrogenophilus thermoluteolus DNA in accretion ice in the subglacial Lake Vostok

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The 3561 m Vostok ice core sample originating from the subglacial Lake Vostok accretion ice with sediment inclusions was studied by various means to confirm the earlier reported presence of the thermophile bacterium *Hydrogenophilus thermoluteolus* in the 3607 m accretion ice sample. PCR and molecular-phylogenetic analyses performed in two independent laboratories were made using different 16S rRNA gene (*rrs*) targeted primers and permitted to recover several very closely related clones with a small genetic distance to *Hydrogenophilus thermoluteolus* ($<1\%$). In addition, RubisCO (*rbcL* or *cbb*) and NiFe-Hydrogenase (*hupS* or *hox*) targeted PCR has also allowed the recovery of sequences highly related to *Hydrogenophilus thermoluteolus*. All these results point to the presence of thermophilic chemoautotrophic microorganisms in Lake Vostok accretion ice, presumably originating from deep faults in the bedrock cavity containing the lake.

A survey of UV screens from diverse organisms, with emphasis on plant flavonoids

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UV radiation is likely to endanger life in extraterrestrial environments. We present an overview of known UV screens, comparing absorption spectra (including the VUV) for UV-absorbing substances from pro and eukaryotic organisms. Based on their spectra, we discuss the ability of these natural substances to protect DNA. We single out flavonoids, which are found in plants, because their absorption spectra resemble that of DNA, and we show that plant seeds are uniquely equipped to withstand UVC radiation owing to the accumulation of flavonoid pigments in their seed coats. Using metabolic engineering we have increased the flavonoids in *Arabidopsis* seeds. Since plant seeds have evolved to withstand long periods of dormancy, sometimes under harsh conditions, they provide an alternative model to bacterial spores in the search for terrestrial life forms capable of surviving space travel.

Devonian filamentous microfossils (Hollard Mound, Morocco) as investigated by Focused Ion Beam

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Evaluation of the biogenicity of objects with microbe-morphologies in the rock record is a crucial problem in micropaleontological and astrobiological investigations[1]. The biologic origin of morphologies similar to microbes from the oldest preserved terrestrial sedimentary rocks remains a matter of controversy[2]. Controversies also surround the biogenicity of morphologies interpreted as the first purported evidence of life detected outside of the Earth with the Martian meteorite ALH84001[3,4]. Although minerals with microbe-like morphologies represent ambiguous evidence of life, they are, in a number of conditions, the only achievable information. Methods for distinguishing biotic from abiotic features in microfossil-like objects are especially important in the search for evidence of early life and possible life on other planets, which may include the analysis of samples returned to Earth from Mars and Mars *in situ* investigations[1]. In this study the Focused Ion Beam (FIB) electron microscopy technique was used for nano- and micrometre-scale high-resolution imaging and *in situ* microsectioning of filamentous microfossils. The structural elements of these filaments, their spatial relationships with the host rock, and the artefacts produced by alteration of the original morphology owing to laboratory sample processing have been clearly defined. Improvement in the morphological and compositional evaluation has also enabled an in-depth reconstruction of the metabolic pathways of the filamentous microfossils preserved in the Middle Devonian-aged Hollard Mound deposits, Anti-Atlas, Morocco. The *in situ* sectioning provided a means by which to investigate surface and subsurface microstructures and perform different analytical techniques on the same subject, which minimizes sample destruction and avoids excessive manual handling and exposure of the specimen during analysis. The results of this study demonstrate the potential of the FIB/SEM system for detecting microbial-scale morphologies[5].

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Self-organization of biological systems by environmental noise level signals and modern problems of magnetobiology

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Recently, an idea concerning helio-geomagnetic rhythms as external synchronizers of biological rhythms by analogy with the Solar radiation and temperature variations on the premature Earth forming circadian (diurnal) biorhythms had been proposed[1,2]. These biological rhythms with periods of about the Solar rotation period (28 days) and its harmonics and sub-harmonics (about 14 days; 7 days; 3.5 days) as well as the other very low (micro pulsations of type Pc1 (1–3 Hz)) and very high frequencies (11 years) were likely to reveal themselves on each level of biological systems. The main targets for the helio-geomagnetic factors appear to be the heart and cardiovascular system[1,2] (among 10 diseases for 6 000 000 ambulance calls only myocardial infarctions and sudden deaths correlated with the geomagnetic activity). Biological systems are the most sensitive to the effects of these factors in a state of instability. For this reason there are 'groups of risks' associated with the state of adaptation: undermined (in patients), immature (in children), and burdened by other stresses (e.g. cosmonauts).

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Environmental synchronizer's rhythm frequency capture by biological objects forming by process of evolutionary adaptation and problem of surviving

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Rhythms of weak environmental electromagnetic fields (EMFs) permanently affecting biological objects are creating in a process of interaction between Solar activity and the terrestrial intrinsic magnetic field envelope (magnetosphere). Biological objects on the Earth had to integrate these EMF frequencies into their endogenous rhythm structure for the sake of survival. This paper shows an EMF frequency capture by the important characteristics of humans organisms on the basis of data obtained over three Solar activity cycles. Optimization of spectral analysis reveals, with large significance, the similarity of spectral peaks in both helio-geomagnetic and medico-biological data, make an effective filtration of periodic components and show a frequency capture by biological systems using dynamical point estimations. Resynchronizations of biological rhythms with external drivers can lead to consequences critical for survival, such as arrhythmias or sudden death.

From intraterrestrial to extraterrestrial microorganisms

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In recent years microbial communities were detected, which dwell in rocks, soil and caves deep below the surface of the Earth. This has led to a new view of the diversity of the biosphere and of the environmental boundaries for life. We investigated microorganisms from two types of subterranean environments: (1) Permo-Triassic salt sediments; and (2) thermal radioactive springs and surrounding rocks in the Central Alps. Extremely halophilic archaea were isolated from ancient salt sediments and were shown to represent novel species. Officially classified haloarchaeal species include *Halococcus salifodinae*[1], *Hcc. dombrowskii*[2] and *Halobacterium noricense*[3]. Simulation experiments with artificial halite suggested that these microorganisms possibly survived while enclosed in fluid inclusions. In the alpine thermal springs, evidence for numerous novel microorganisms were found by 16S rDNA sequencing[4]. In addition, scanning electron microscopy of biofilms on the rock surfaces showed a great diversity of morphotypes. These communities appear to be active and growing, although their energy and carbon sources are entirely unknown. The characterization of subsurface inhabitants from both environments is of astrobiological relevance since extraterrestrial salt has been detected in meteorites, on the surface of Mars and in the presumed ocean of the Jovian moon Europa, and since microbial life on Mars, if existent, may have retreated into the subsurface owing to high UV radiation.

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Survivability of hyperthermophilic microorganisms under simulated space conditions

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Space, as far as we know, exhibits some of the harshest conditions which living organisms may encounter during their lifetime. To find possible candidates which could outlast these circumstances, scientists started to look at different extreme environments on Earth. In this study we investigated the ability of several hyperthermophilic Archaea as well as hyperthermophilic Bacteria for their survival under certain simulated space conditions. Resistance to the following parameters was tested: desiccation at different temperatures, vacuum conditions and irradiation. Preliminary results show that some of the tested Archaea do survive under these tested, spaces like, conditions. This makes them interesting model organisms for the study of archaic resistance mechanisms during real space exposure.

Prokaryotic and eukaryotic organisms as model organisms for space research on BIOPAN (FOTON M3, Fotino) and EXPOSE (ISS)

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In the focus of space research are epi- and endolithic organisms. In particular, lichens and endolithic pro- and eukaryotes are chosen as model organisms for future space experiments. The up-coming ESA projects 'Lithopanspermia' related to the BIOPAN 6 experiment on FOTON M3 and STONE as well as LIFE on EXPOSE may lead to important data which may be used to refine the following three stages in the model of Lithopanspermia: (1) escape from the planet of origin; (2) the travel through space; and (3) the capture and landing on another planet. As a result of these planned investigations detailed knowledge on evolutionary aspects, further information for the search of life in extraterrestrial habitats and more information concerning protection strategies of microorganisms against space parameters is expected. Further experiments in planned projects with the previously mentioned organisms will be done by Mars simulation during ground-based studies. In addition, the space missions will provide relevant information concerning Martian substrate-, radiation- and atmosphere-tolerance, the vitality maintenance, the potential for reproduction and DNA protection as well as repair mechanisms of these life forms under these extreme environmental conditions. Interactions between organisms and the Earth or Mars substrates may also lead to detectable bio-traces on the rocks, formed by life forms, which serves for future rover projects to search for present or past life on other planets.

Highly resistant methanogenic archaea from Siberian permafrost as candidates for the possible life on Mars

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The characterizations of the survival potential of microorganisms which are able to thrive in extreme environments are receiving great attention in astrobiological research, driven by the possibility of their existence in extraterrestrial extreme niches. Speculations concerning lithoautotrophic subsurface life on Mars are arising since the ESA mission Mars Express determined the existence of water on Mars, a fundamental requirement for life, and the presence of CH_4 in the Martian atmosphere, which have originated only from active volcanism or from biological sources. Comparable conditions exist in the permafrost regions on Earth. Methanogenic archaea, which colonized Siberian permafrost, are highly specialized organisms which can gain energy by the oxidation of H_2 and use CO_2 as the only carbon source. We present investigations of the resistance of methanogens from the Siberian permafrost complementary to the already well-studied methanogens from non-permafrost habitats to different extreme life conditions of terrestrial or extraterrestrial permafrost: desiccation, temperature extremes, radiation, starvation, high salt concentration and simulated Mars conditions. The methanogenic archaea in pure cultures as well as in their natural environment of the Siberian permafrost represent high survival potential under these extreme conditions. In contrast, these conditions were lethal for the reference organisms from non-permafrost habitats[1,2]. Our data suggest that in the scenario of subsurface lithoautotrophic life on Mars methanogenic archaea from Siberian permafrost could be used as an appropriate candidates for possible life on Mars.

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Halophiles from rock salt – a promising model for the search for extraterrestrial life?

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Halophiles isolated from Permian rock salt might be promising model organisms for the search for extraterrestrial life, owing to the discovery of halite in meteorites, salts on Mars and the fact that several viable microorganisms have been isolated from Permo-Triassic rock salt (age 195 to 250 million years)[1]. In most cases these strains belong to the extremely halophilic Archaea. Two major strategies for the estimation of microbial community composition in ancient rock salt were used. First, diversity was determined by molecular methods such as 16S rRNA gene amplification, clone library construction and phylogenetic analysis[2]. Second, a culture-dependent approach was started in 1999 with rock salt obtained from alpine salt mines. In this work 135 isolates have been examined with restriction fragment length polymorphism (RFLP) analysis of 16S rRNA gene fragments and with pulsed field gel electrophoresis (PFGE), as well as S1 Nuclease-PFGE to identify putative megaplasmids. It was possible to arrange all isolated strains into three groups according to RFLP patterns. Two RFLP groups were closely related to *Halococcus* sp. and one group was related to *Halobacterium* sp. PFGE and S1-PFGE analyses showed, according to whole genome restriction analysis and the presence of putative megaplasmids, that diversity is broader than RFLP analysis showed. Our results show that the diversity of cultivable organisms is, as expected, small, but examination of isolates by molecular methods showed that the closely related strains are more diverse than previously thought.

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Growth of microorganism populations under experimental modelling of Martian and cometary nucleus subsurface conditions

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Modern environmental conditions on Mars and cometary nuclei prohibit the existence of liquid water on the surface layer of Martian soil and cometary mantles because of extremely low atmospheric pressure. However, according to observational data, a large amount of water ice is present in the Martian and cometary subsurface. In both cases the ice is subject to intensive sublimation if the surface is heated by Sunlight. The surface layer which diffusion goes through is a porous material with a poor admixture of organic matter for Mars and high admixuture of organic for comets. In our experiment, we used a special vacuum chamber in order to model the process of ice sublimation and vapour diffusion under heating. In order to model these processes we used a water ice sample covered by several centimetres of sand containing organic matter. Intensive sublimation was provided by radiation heating of the sand's surface. We studied the possibility of the active growth of microorganisms in the vapour diffusion layer. Bacteria *Vibrio sp. X* were added to the sand. We performed several three-day experimental runs of the intensive sublimation of ice. As a result, we have recorded an increase of the bacterial population after each run. These results confirm the possibility of active metabolism and even reproduction of microorganisms under Martian and cometary surfaces.

Application of Solid-Phase Micro-Extraction (SPME) in the analysis of biomarkers in geological samples

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Biomarkers are organic indicator compounds that could be used as tracers for geological and environmental processes[1]. These organic compounds can unambiguously be linked to a known biological precursor and include mainly hydrocarbons (derived from lipids and pigments), fatty acids and long-chain ketones and alcohols. Authors usually use the solid–liquid extraction of the samples as separation step, prior to the analysis of biomarkers by instrumental and chromatographic techniques. The properties of biomarker compounds are appropriate for the use of SPME as preparative step in the analytical process. It is a solvent-free technique that enables extraction and concentration steps simultaneously, using small quantities of the rock or sediment sample and allows the later application of classic extraction techniques in the same sample. SPME, coupled with GC-MS, has a higher efficiency and sensitivity than classic liquid extractions, reduces the process time and increases the cleanness of the technique. We used the SPME technique successfully for the organic analysis of natural samples with different geology and age and we found it applicable in the routine organic speciation of geological samples.

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Light- and electron-microscopic analysis of Haloarchaea embedded in Austrian rock salt

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Subsurface salt mines, such as those in Bad Ischl and Altaussee, Austria, are examples of sites where extremophilic microorganisms can be found. The most recent isolates from these salt mines are *Halococcus dombrowskii*[1] and *Halobacterium noricense*[2]. In order to understand how these microorganisms are able to survive long periods of time embedded within sediments it is necessary to analyse the fine structures and the average chemical composition of the minerals where they were isolated. In this study a JEOL 8200 Electron Microprobe and a JEOL 5800LV SEM equipped with an Oxford Analytical ultrathin-window EDS and an Oxford Isis 300 X-ray analyser were used to analyse the ultrastructure and chemical composition of 250 million year old rock salt. The mineral structures, which occur at grain boundaries and in fluid inclusions, were examined for their significance as possible microbial habitats. In addition, haloarchaeal cells were embedded within salt crystals under laboratory conditions and subsequently analysed by light microscopy. The mineral structures of the ancient rock salt were examined for their significance as possible microbial habitats. Liquid-filled structures such as clay particles, fluid inclusions and grain boundaries are present; the chemical analysis of the liquid composition has been determined. Artificially grown salt crystals containing fluid inclusions were investigated using light-microscopic techniques. Cells were still motile and visible after several days enclosed in salt. Another form of evidence for metabolism would be gas bubbles within the liquid. Physical experiments will reveal more information about the chemical composition of the gas inclusion.

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Deliberations on microbial life in extreme subglacial Antarctic lake environments: Lake Vostok

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The objective of this study was to estimate the microbial content of accretion ice originating from the subglacial Lake Vostok buried beneath a 4 km thick East Antarctic ice sheet with the ultimate goal to discover microbial life in this extreme icy environment. The DNA study constrained by Ancient DNA research criteria was used as a research approach. The flow cytometry was also implemented. As a result, both approaches showed that the accretion ice contains the very low unevenly distributed biomass indicating that the water body should also be hosting a highly sparse life. Up to now, the only accretion ice containing mica-clay sediments allowed the recovery of a few bacterial phylotypes. This unexpectedly included the chemolithoautotrophic thermophile *Hydrogenophilus thermoluteolus* and two more unclassified phylotypes all passing numerous contaminant controls. In contrast, the deeper and cleaner accretion ice with no sediments present and a gas content near to the detection limit gave no reliable signals. The deep glacial ice horizons just above the lake also showed no confident DNA signals, and thus served as a life-barrier between the Lake Vostok ecosystem and surface biota for at least 15 Ma. These findings are discussed in terms of the unusual geobiochemical environment of the lake. Thus, the results obtained testify that the search for life in the Lake Vostok is constrained by a high chance of forward-contamination. Lake Vostok may be viewed as the only extremely clean giant aquatic system on the Earth, providing a unique test area for searching for life on icy planets and moons.

Bacteria in kerosene-based drilling fluid from the deepest ice borehole at Vostok, East Antarctica

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The main objective of this research was to analyse the original Vostok drilling fluid (DF) sampled from the borehole 5G-1 at different depths (up to 3600 m) for bacterial content by 16S ribosomal DNA sequencing and by this to evaluate the DF as an extreme econiche for hydrocarbon degrading bacteria. Additional objectives included gathering the information required for the authentication of ice core findings and the environmental assessment upon exploration of Subglacial Antarctic Lake Environments (SALE). The DNA analysis has led to the identification of six bacterial phylotypes. Two phylotypes recovered from the deepest and relatively warm borehole horizons (greater than 3400 m; -10 °C and higher) were assigned to dominated *Sphingomonas* – well-known degraders of aromatic compounds. Cell enumeration gave about 10^2 cells ml^{-1}. By phylogenetic reconstruction one phylotype, *Sph. natatoria*-related, proved to be conspecific with the isolate shown to degrade mono-aromatic hydrocarbons, while another phylotype, *Sph. sp.*, proved to be conspecific with two isolates degrading poly-aromatic hydrocarbons both found in Vostok DF. The remaining four phylotypes were presumed to be contaminants owing to their human or soil source. Our study showed that Vostok DF sampled from deep borehole horizons features two *Sphingomonas* phylotypes as indigenous DF-originating bacteria which fit the list of bacteria capable of degrading aromatic hydrocarbons and may expect to metabolize them *in situ*. It seems that the new deep ice human-made extreme econiche discovered in Antarctica can pose environmental issues when exploring SALE which may have distinct implications for the search for life in extraterrestrial icy environments where low microbial biomass will be evidently constrained by DF contaminants.

Utilization of minerals from meteorites as energy sources by microorganisms

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Meteorites arriving on the early Earth may have supplied life with minerals and other elements important for their survival and growth. Many meteorites contain minerals that are biologically useful, such as iron and phosphide. It has been shown that some of these meteoritic materials can provide a source of energy for organisms on Earth[1,2]. We have examined the relationship between meteorites and microbe metabolism by assessing the potential for iron-oxidizing microorganisms, including *Thiobacillus ferrooxidans*, to access iron and other minerals from iron meteorites. In acidic conditions, iron from the Casas Grandes meteorite was released into solution and became metabolically accessible for microbial oxidation. This was shown by the formation of goethite crystals in the presence of Casas Grandes fragments as opposed to biologically precipitated jarosite formed in a standard culture medium. In addition, we examined the ability of iron oxidizing microorganisms to utilize phosphide from schreibersite ($(Fe,Ni)_3P$), a mineral found in iron–nickel meteorites. This was done by monitoring the oxidation of Fe(II) to form Fe(III), as well as examining the metabolic conversion of minerals using X-ray diffraction, micro-X-ray diffraction and SEM imagery. This work provides insight into the sources of nutrients and redox couples in early planetary environments.

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Psychrophilic bacteria as possible models of life in Mars or Jovian moons: molecular analysis, a proposal

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Bacteria, algae and also metazoans may live at temperatures below 0 °C and survive ice formation in all body compartments[1,2]. In the Antarctic Dry Valleys[3] microorganisms live at -35 °C. Bacteria in culture metabolize and reproduce[4] at -10 °C. In order to identify and characterize new species we suggest, after having isolated microorganisms in culture from frozen samples, performing a selective cloning of 16S rRNA genes by PCR, electrophoresis to isolate genes, sequence analysis after subcloning and propagation in *E. coli* cells, building a phylogenetic tree of the bacterium. These devices are very common, being used for biomedical purposes in every country in the world. Ecology, evolutionary biology and astrobiology studies, as models of possible life on Mars or Jovian moons, or as microorganisms able to play important roles in terraforming perspectives, will benefit from a greater knowledge of these life forms and, last but not least, their enzymes, because of their low energy requirements, high specific activity at low temperature and thermolability, may provide a real spin-off for biotechnology.

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Bacillus subtilis' ability to adapt to extreme UV stress

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To study the adaptiveness of *Bacillus subtilis* to extreme UV stress we used an experimental evolution system[1] where this environmental stressor acts as the selection force. Previous experiments have shown that vegetative cells of *B. subtilis* are capable of repairing DNA photolesions directly after irradiation. However, no DNA repair is error-free, leading to changes (mutations) in the DNA composition which will be inherited by the following generations. These modifications will be translated into the proteome of the cell and might lead to a higher survivability owing to changes in enzyme activity. We hypothesize that during this (micro-)evolution the newly adapted cells show an increase in UV resistance and most likely also a higher efficiency in their DNA repair capability. Based on this assumption, we periodically irradiate a continuous *B. subtilis* culture with polychromatic UV in a range of 200–400 nm using a defined fluence (15 kJ m^{-2}). Approximately 1000 generations of *B. subtilis* were periodically irradiated by UV and their radiation sensitivity was analysed. It could be shown that the population evolved under UV stress is significantly more resistant (six-fold) to UV irradiation compared with the antecessor population. Further investigations to the adaptation mechanisms will allow us to understand changes to the cellular dynamics on a molecular level. DNA microarray technology will be used to identify changes in the transcriptional profile of different DNA repair pathways.

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Life at the edge: endolithic cyanobacteria in halite rocks from the hyperarid core of the Atacama Desert

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One of the world's driest places – the hyperarid core of the Atacama Desert (northern Chile), bears no visible life forms on soil or rock surfaces. The soil habitat in this region contains minute traces of bacteria and seems to represent a critical threshold for photosynthetic life in the form of hypolithic cyanobacteria. However, a recent study has demonstrated that halite evaporite rocks from the extremely dry core of the Atacama Desert are indeed colonized by endolithic microorganisms[1]. This colonization takes place just a few millimetres beneath the halite rock surface, occupying spaces among salt crystals. These communities are composed of extremeresistant *Chroococcidiopsis* morphospecies of cyanobacteria with heterotrophic bacteria associates. They survive by occupying the endolithic niche among the hygroscopic halite crystals, which is able to condense moisture from occasional fog or dew. This newly discovered endolithic environment is an extremely dry and at the same time saline microbial habitat. This finding of abundant photosynthetic microbial life within 'dry' halite rocks of the Atacama Desert reallocates the absolute limits of life on our planet. Furthermore, halite has been identified in mineral assemblages of SNC meteorites arising from Mars and sulphate and halite evaporite rocks have recently been discovered on Mars. These facts suggest that brine pools might have been relatively common on the surface of Mars. Rapid desiccation of the surface after the loss of its atmosphere may have rendered Mars rich in regions of high salt concentrations in which halophilic microorganisms could have flourished.

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Bacterial signatures in Iron-rich hydrothermal crusts: Tyrrhenian Sea, Italy

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Recent volcanism and associated hydrothermal activity of the Aeolian Arc started 0.2–0.1 Ma ago, and have produced a wide range of iron oxyhydroxide and iron sulphide deposits. Unlike other hydrothermal iron-crusts from the study area our samples contain little or no Mn (394–964 ppm). SEM observations showed a wide range of morphological features that resemble fossilized microbial forms entirely permineralized by iron-oxides, commonly found in association with sulphur- and iron-bearing minerals. Very low TOC levels and fluorescence microscopy did not reveal notable concentrations of organic matter within samples, suggesting that most of the original organic matter was probably lost during early diagenetic oxidation. The $\delta^{13}C$ values (from -14.32 to -17.78) are consistent with a marine microbial origin of the organic matter. The $\delta^{34}S$ values of water (-2.34 to 18.78) and acid soluble sulphate (-2.98 to 16.79), chromium reduced sulphur (-7.53 to 0.14) and Parr Bomb fraction (-2.36 to 0.48) imply two sources of sulphur: magmatic and marine water. In addition, there is no evidence that the observed microorganisms might have significantly controlled sulphur isotope fractionations. Thus, the fossil microbial forms that were detected within the samples probably represent the remains of thermophilic (hyperthermophilic?) iron bacteria. As a microbial habitat predominantly ruled by iron cycling chemistry, Tyrrhenian hot springs represent an excellent analogue model system and a potential tool in the search for life signatures within similar environments on Mars.

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The viability of haloarchaeal microorganisms exposed to environmental stress

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Several strains of haloarchaea have been isolated from Permian rock salt deposits, which were estimated to be about 250 million years old[1]. Therefore, a dormant state of halobacteria, allowing long-term survival as well as the survival of halophilic microorganisms in extraterrestrial salt sediments, seems feasible. A drastic change in morphology was observed upon the embedding of *Halobacterium salinarum* NRC-1 in halite: rod-shaped cells changed to spherical forms with increasing time (up to 10 weeks). Concomitantly, a continuous decrease in viability, determined by cfu's, took place, and inoculation into liquid media resulted in decelerated growth. Nevertheless, green fluorescence following staining with the LIVE/DEAD® kit suggested that the spherically shaped cells of *Hbt. salinarum* NRC-1 were still viable. Whole cell protein patterns of rods compared with those of spheres showed several changes. Some bands of apparently different intensities or sizes were analysed by mass spectrometry. Identification by database search suggested that S-layer proteins, ribosomal proteins, RNA polymerase, transcription factors and others were expressed differently in rods or spheres. Furthermore, following extraction and a photometric scan of pigments, a remarkable depletion of carotinoids during embedding was observed. The data suggested that the halite-induced occurrence of apparently viable spherical cells, which did not grow on usual media and possessed obvious changes in protein expression, pigmentation and polar lipid patterns[2], could signify a dormant state.

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Artificial meteorite materials – protective to fungal spores?

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The experiment 'Spores in artificial meteorites' will be conducted in the EXPOSE facility placed outside the International Space Station (ISS). Its objective is to examine whether fungal and fern spores can survive the harsh environmental conditions in space during a long-term stay. Presently, space simulation experiments (Experiment Verification Tests) are carried out at the Planetary and Space Simulation Facilities (PSI) of the German Aerospace Center (DLR) in Cologne to define the environmental and technical requirements of EXPOSE. Previous experiments showed that bacterial spores may be protected against UV radiation by a thin layer of dust or artificial meterorite material. To investigate a protection effect on fungal spores, spores of *Trichoderma koningii* were mixed with different artificial meteorite materials ('JSCMars-1' and 'MRTE-2 TRE-Ele'). The mixtures were sealed in bags of 'bioFolie'. Two types of lab controls were sealed in bags or stored in reaction tubes, respectively. The samples were treated with different combinations of radiation wavelength, radiation doses and atmospheric conditions. The viability of spores was analysed by ethidium bromide staining and by their ability to germinate on PDA medium. Spores mixed with the Mars soil analogue 'JSCMars-1' showed a considerably lower survival rate than spores without 'JSCMars-1'. Even the lab controls stored in reaction tubes showed a loss in viability. Therefore, a toxic effect of 'JSCMars-1' to the spores of *T. koningii* must be assumed. The mixture of *T. koningii* and 'MRTE-2 TRE-Ele' showed neither a significant toxic nor a protecting effect against UV radiation.

Characterization of Tinto River's (Spain) aqueous solutions by Raman spectroscopy

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The extreme environment of the Tinto River (Huelva, Spain) is widely recognized as a terrestrial analogue for the search of past or present life on Mars. In particular, the study of its water has become crucial to the understanding of life on the Red Planet. The red colour of the Tinto River's water and the average pH of 2 (highly acidic) are due to the natural abundance of iron sulphates. There are chemolitotrophic microorganisms thriving in the water of the Tinto River that turn these sulphates into sulphuric acid, leading to the low pH values[1]. Other bacteria catalyse the oxidation of Fe^{II} into Fe^{III}, giving the river its characteristic red colour. The high acidity and reddish colour of Tinto's water are not solely the result of mine pollution – as was largely thought – but the result of complex interaction processes between extremophile bacteria and the environment rich in sulphides in which they thrive. In order to understand the biogenic processes occurring in the Tinto River ecosystem there is a need for a physical–chemical characterization of the river's acidic aqueous solutions. In this work we present a characterization of the Tinto River's water by Raman spectroscopy. The proposed methodology is based on the identification of the main chemical species and the determination of their concentrations. Raman spectroscopy provides great accuracy since molecular vibrations are determined by specific and unambiguous wavelengths in Raman spectra. Raman spectroscopy also allows the real-time identification of species and a very fast quantification of their abundance through software developed in our group.

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Biosignatures of the *Acidithiobacillus ferrooxidans*/pyrite association?

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Bacteria have colonized most terrestrial environments including 'extreme' ones. The *Acidithiobacillus ferrooxidans*/pyrite system may be considered as an analogue of pristine environments on Earth or on other planets. This study aimed to determine reliable and durable biosignatures of this system through a better understanding of the bio-oxidation process at the mineral surface. A new model of pyrite bio-oxidation has been proposed based on the joint use of various analytical techniques (CLSM, SIMS, Raman spectroscopy, etc.). Two distinct mechanisms related to electron transfers on the mineral lattice have been identified and reflect the effect of both adherent and non-adherent bacteria. Bio-oxidation induces the development at the pyrite surface of deep corrosion pittings and of micrometric and monophased oxidation products (mostly anhydrous sulphates and hematite) with an extremely variable $\delta^{18}O$ (from $\approx -20‰$ to $\approx +25‰$). They result from specific surface mechanisms not in equilibrium with the bulk reactional medium occurring in confined environments. Even if this system is quite simple, a large surface heterogeneity is observed as a result of the non-homogeneous reactivity of the mineral surface and the complexity of the bio-oxidation mechanisms. Consequently, there is no unique biosignature for this system but a succession of clues that betray biological activity at the mineral surface are identifiable when using several complementary techniques.

Preparations for the EXPOSE-ADAPT experiment: studies of the effects of UV radiation on *Halococcus dombrowskii*, an isolate from Austrian rock salt

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Information about the damaging effects of UV radiation on the DNA of halobacteria[1] as well as protection due to bacterioruberin and carotenoids[2] has been published for the extremely halophilic archaeon *Halobacterium salinarum* strain NRC-1. *Halococcus dombrowskii*, a phylogenetically related isolate from Permian alpine sediments[3], has a different envelope structure and will be used for the ADAPT experiment (P.I. Dr. P. Rettberg), which will involve the exposure of cells to the space environment on the International Space Station. Preparations for these studies consist of examining the response of *Hcc. dombrowskii* to UV light from a specially designed Martian radiation simulator[4] and to desiccation. Liquid cultures of washed cells of *Hcc. dombrowskii* were spread on quartz discs (7 mm diameter) and dried. Halobacterial cells accumulated in fluid inclusions of crystals as previously demonstrated[5]. Preliminary results of survival tests using cultivation and flurorescence microscopy showed that *Hcc. dombrowskii*, embedded in salt crystals survived a dose of 10 kJ m^{-2}, which was about 20-fold higher than the dose which was lethal to *Hbt. salinarum* NRC-1 (in a liquid medium). The influence of pigments on protection by UV radiation is being investigated by the inhibition of carotenoid synthesis of *Hcc. dombrowskii* with diphenylamine. For sensitive detection of carotenoids in small samples, Raman spectrometry was established with salt-embedded cells of *Hcc. dombrowskii.*

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Ribozyme under pressure

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The theory of the 'RNA world' suggests that present life based mainly on DNA and proteins was preceded by a simpler form of life based on RNAs which would serve as both informative molecules and catalysts. The discovery of multiple structural and functional potentialities in RNAs and that of catalytically active RNAs (ribozymes) brought substantial support to this theory for the early development of life on Earth. The influence of hydrostatic pressure on the activity of these molecules has not previously been investigated, although there are two general reasons for undertaking such an investigation. One is that this thermodynamic parameter can provide information about structure–function relationships in these molecules[1,2]. The second is that there is increasing evidence that life emerged on Earth under conditions of high pressure and temperature. Such a study was performed here in the case of the hairpin ribozyme in conjunction with osmotic shocks experiments. The results obtained provide valuable information concerning the mechanism of the catalytic cycle of self-cleavage and ligation. The conclusions drawn are in accordance with the structural information coming from crystallographic and NMR studies. This study is currently being extended to an adenine-dependent mutant of this ribozyme.

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Extracellular ATP as a biomarker of stress induced by hypogravity in Arabidopsis thaliana cell suspension culture

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Biomarker profiling has already been proven to be a valuable tool in several areas of life science research. Biomarkers may reflect different stages of a biological process that is, or is likely to be, out of equilibrium. As large amounts of extracellular ATP and its degradation products can accumulate under any kind of energy deficit or as a result of cell death, much interest was focused on the study of the mechanisms of the release and extracellular metabolism of ATP under different environmental conditions. Although recent findings revealed that intact plant tissues release ATP, there is little known about the physiological function of extracellular ATP in plants. Besides its functions inside the cell, extracellular ATP may function as the primary signalling molecule of a diverse range of physiological processes. It seems that it is essential for maintaining plant cell viability. Our studies are focused on the production and the release of ATP influenced by hypogravity. The flexibility of plant bioenergetics helps plants to acclimatize to environmental stresses. Our work is focused on standard free energy changes for PPi and ATP hydrolysis in order to assess the relative importance of PPi versus ATP as an energy donor in the plant cytosol of *Arabidopsis* plants exposed to hipogravity. Our results indicated that PPi would be particularly favoured as a phosphoryl donor, relative to ATP, under cytosolic conditions known to accompany stresses.

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Laboratory simulations of Martian surface parameters and the biological response of terrestrial model organisms to 'extreme' environments

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For *in situ* life detection analysis and for the avoidance of contaminating Mars by terrestrial life forms, it is necessary to understand the limits of life on Earth. Currently no total laboratory Mars simulation has yet performed in a single experiment including temperature cycles, UV radiation, humidity at Martian pressure, with Martian soil/dust analogues, and ionising radiation. However, it is essential to investigate the biological effects of combined environmental parameters, because it is known that biological effects might not necessarily be additive, but synergistic or antagonistic. Up to now, the molecular basis of the oxidizing properties of Martian soil found by Viking landers was attributed to an as-yet-unidentified inorganic superoxides or peroxides in the Martian soil. The determination of the survival of *Deinococcus radiodurans* under the 'extreme' UV climate of Mars in the presence of hematite was investigated. Desiccated *D. radiodurans* cells can survive 7 day Mars-like cycles of temperature and water activity. However, the bacteria are completely inactivated by the exposure to Martian UV radiation equivalent to 7 days on the surface. Haematite could be shown to protect the bacteria against UV radiation. From these first experiments we make the following conclusions. Terrestrial prokaryotic organisms such as *D. radiodurans* could survive on Mars (without UV radiation). The energy-rich UV radiation is the most deleterious of the Martian environmental parameters. Martian dust and/or soil particles such as haematite are able to protect organisms against UV radiation and allow for survival a short distance beneath the surface.

Photochemistry of DNA in bacterial spores

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Spores are dormant forms of bacteria exhibiting increased resistance to UVC and UVB radiation and thereby could possibly survive in space. A major reason for the photoresistance of spores is their specific DNA photochemistry combined with adequate repair mechanisms. Indeed, exposure of spores to far-UV leads to the sole formation of 5-(α-thyminyl)-5,6-dihydrothymine, the spore photoproduct (SP), instead of the cyclobutane dimers (CPD) and (6–4) photoproducts (64PP) generated between adjacent pyrimidines in other cell types. In this work, we quantified all these photoproducts in spores of various strains of *Bacillus subtilis* and in isolated DNA. Identification of the dimeric lesions in dry pure DNA showed that dehydration of the spore only partly explains the novel photochemistry of its DNA. Spores of mutant strains lacking α/β-type small, acid-soluble proteins (SASP), which saturate the DNA in spores, exhibited a lower frequency of SP than those of the wild-type strain, together with an increase in the yield of CPDs and 64PPs. The presence of large amounts of dipicolinic acid (DPA) is another key factor for the formation of SP. The lack of DPA in mutant spores was found to facilitate the formation of all CPDs and 64PPs and to drastically decrease the yield of SP. Therefore, DPA appears to be a photosensitizer as confirmed within isolated DNA. The distribution of DNA photoproduct in the double SASP/DPA mutant was similar to that observed in dry DNA, showing that the combined effects of SASP and DPA are responsible for specific photochemistry of DNA in spores.

Exploration of thermodynamic oscillations in the probable hydrothermal medium for the origin of life (on the example of the Mutnovsky hydrothermal system in Kamchatka)

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According to the original conception, significant oscillations of thermodynamic and physical–chemical parameters (P, T, C_c, pH, Eh) stimulated the origin of life process. The scale of the oscillations in the oceans is very limited owing to the narrow range of values (pH 8.0–8.4, salinity 30–38 g l^{-1}, etc.). In this connection hydrothermal systems and their submarine or terrestrial discharges are considered as probable mediums for the origin of life. We explored long-range and short-range thermodynamic fluctuations in the hydrothermal system associated with the active Mutnovsky volcano in the Kamchatka peninsula (eastern Russia), and compare them with some other databases. The extremes of temperature are 100–240 °C and pressures range from 1 to 40 bars in the 12 explored wells' orifices. We fixed two periods of long-range thermodynamic oscillations: 1.5–2.5 months and 4.3–4.8 months; the amplitudes of the oscillations measure up to 40–50 °C and 2.0–4.5 bars. The correlation between the temperature of the water–steam mixture and the pressure is very high (0.88–0.99). The period of short-range oscillations of pressure, estimated on the basis of measurement on the depth 950 m, is about 20 min; their amplitudes are between 0.4 and 0.8 bar. Similar periods of the short-range oscillations of temperature, pressure and chemical parameters were measured in Mura hydrothermal field in Slovenia[1] (30–70 min) and Pauzhetsky field in Kamchatka (10–60 min). These data could be used in new kinds of experiments in prebiotic chemistry that should be carried out under oscillating conditions in an experimental chamber.

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Cross correlation patterns of some meteorological variables for two extreme terrestrial environments

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As mentioned previously by the authors, the Atacama Desert in Chile is so dry that, in the core region, not even bacteria can survive, a reason why it can be considered in some respects as an analogue of Mars[1]; furthermore, and also mentioned previously, the Pico de Orizaba, a volcano in Mexico, can be considered too, from another perspective, as a terrestrial analogue of some environmental conditions that probably existed in ancient Mars near the equatorial zone[2]. In this report we present some results derived from statistical analyses of some meteorological variables measured in the Yungay area of the Atacama desert over a four year period; in addition we discuss some recent results related to a similar kind of statistical analysis now performed on some meteorological variables measured in the neighbourhood of the treeline area of Pico de Orizaba. In the search of temporal patterns of the corresponding series, the same technique was used for both sets of data. The procedures are of the exploratory type showing real direct data patterns as well as indirect data patterns via cross correlations.

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Hypersaline lake systems in an astrobiological perspective: a case-study of Lake Thetis, Western Australia

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Ecosystems in persistent hypersaline conditions are subjected to severe and stressful conditions (e.g. osmotic shock and/or desiccation) leading to a selection of specialized biota that only survive in these ecosystems[1]. Hypersaline lakes dominated by prokaryotic communities, forming lithified stromatolites and microbial mats, are distributed worldwide and are known to be indicators of environmental change. Stromatolites are indicative of some of the earliest known life on Earth[2]. Mats and stromatolites in hypersaline lakes are significant depositional environments and are potential analogues for early life niches on Earth[3]. Here we present the preliminary results of macro- and micro-scale investigations of fossil and living, lithified stromatolitic communities around the margins of Lake Thetis, a small hypersaline/alkaline coastal lake (~1 km in diameter) located on the Swan Coastal Plain ~250 km north of Perth, Western Australia. Weather, climate, and seasonal variations affect the depth and water chemistry of the lake which is fed by direct rainfall and groundwater influx[4]. The microbial ecosystem of Lake Thetis is dominated by cyanobacteria-forming stromatolites, and flocculant SR-bacteria and diatoms forming mat communities. The stromatolites, with unusual thrombolitic to laminated columnar morphologies, are present at water depths of less than 1 m and form isolated 15–70 cm diameter circular domes to coalesced bioherms (5–6 domes) 10 m in diameter. Relief above the sediment surface ranges between 10 and 30 cm. Submerged walls of these domes have small crenulate protuberances partially generated by microbially precipitates on small cases of aquatic larvae of the arthropod *Trichoptera*. The variety of morphologies, the abundance of mat-forming microorganisms, and their calcification, make Lake Thetis ideal for an investigation from an astrobiological perspective centred on the following factors: (1) the number and type of microbially controlled features; (2) their mineralization (i.e. preservation) processes; and (3) methods for recognition of microbial features through direct (analytical) and remote tools.

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Life's signals preserved in siliceous rock deposits from extreme Earth (Mars?) environments

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With the prospect of a Mars Sample Return mission in the next two decades, attention is now focusing on the types of samples that would be most useful for returning to Earth for laboratory analysis. Recent data on silica deposits reveal that laminated coatings on rocks and in hot-springs are a passive recorder of past and present environments[1]. If coatings exist on Mars then a chronology of the ancient Martian setting may be present, perhaps extending back to a wetter and more biologically active period[2]. To assess the utility of rock coatings as environmental chronologers and recorders of life we have examined samples of siliceous rock deposits from extreme environments in arid and semi-arid areas, Arena Valley, Antarctica, the Negev Desert, Israel, the Mojave Desert, California, the Sonoran Desert, Arizona, and active New Zealand hot-springs and inactive sinter deposits from Opal Mound, Utah and Steamboat Springs, Nevada. Samples examined contain silica phases ranging from opal-A, to opal-A/CT, opal-CT, opal-C, and quartz. Analyses reveal that all the siliceous rocks investigated have similar hardness and morphologies and that their formation and diagenesis occur *via* common processes. Their shared formation mechanism involves amorphous hydrated silica-enriched solutions that polymerize and then undergo transformations to the more thermodynamically stable phase of quartz. The silica matrix is remarkably similar in rock coatings to mineralogically immature hot-spring deposits but whole rock chemical variations are brought about by the addition of exogenous oxides, oxyhydroxides, organic compounds, and detritus in addition to endogenous microbial contributions. The ability of exogenous components to bring about substantial differences in the final constitution of siliceous rock coatings dramatically displays their usefulness as biological and environmental indicators and the incremental nature of their deposition provides temporal information. The most obvious target for Mars Sample Return missions are Martian soil and silica deposits in protected cracks, perhaps even caves or other subterranean environments. Yet, camera images from the Mars Pathfinder landing site exhibit evidence for desert varnish-like coatings that would provide a stable information-rich environmental record. As on Earth, this rock coating may contain ancient microbes or chemical signatures of previous life.

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Prebiotic Chemistry

Synthesis of organic compounds in the circumstellar envelopes of evolved stars

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The last phase of stellar evolution from the asymptotic giant branch (AGB) to proto-planetary nebulae, to planetary nebulae represents the most active period of synthesis of organic compounds in a star's life. Both inorganic and organic molecules and solids are found to form in the circumstellar envelopes created by stellar winds. Over 50 gas-phase molecules, including rings, radicals, and molecular ions have been identified by millimetre-wave and infrared spectroscopic observations through their rotational and vibrational transitions. Infrared spectroscopic observations of emissions from the stretching and bending modes of aliphatic and aromatic compounds have revealed a continuous synthesis of organic material from the end of the AGB to proto-planetary nebulae, to planetary nebulae. These results show that complex carbonaceous compounds can be produced in a circumstellar environment over a period of only a few thousand years[1]. Most interestingly, there are a number of unidentified emission features which are almost certainly carbonaceous in nature but their exact chemical composition is unknown. These include the 21 and 30 μm emission features, and the extended red emission observed in proto-planetary nebulae and planetary nebulae. Recent developments in high-resolution imaging observations in the submillimetre (e.g. SMA) and in the mid-infrared (e.g. Gemini) have made possible the mapping of the distribution of these compounds, making it possible for us to infer the history of circumstellar chemistry. Isotopic analysis of meteorites and interplanetary dust collected in the upper atmospheres have revealed the presence of pre-solar grains similar to those formed in evolved stars. This provides a direct link between star dust and the Solar System and raises the possibility that the early Solar System was chemically enriched by stellar ejecta. In this talk, we summarize some of the recent spectroscopic and imaging observations of the circumstellar envelopes of evolved stars and present a scenario of chemical evolution including the possible role of photochemistry in the late stages of stellar evolution.

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Amino acid formation and enantioselective photolysis under simulated interstellar conditions

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Amino acids, the building blocks of proteins, certainly played a key role in both the emergence of life on Earth and the development of biomolecular asymmetry. We experimentally simulated the abiotic formation of amino acid structures in interstellar ices by the effect of UV irradiation on CO, CO_2, CH_3OH, NH_3, and H_2O. We identified 16 amino acids among the remaining products[1]. We identified diamino acids in the Murchison meteorite verifying the above simulation experiment[2]. The identified amino acids were racemic, since the initial photoreaction was performed with unpolarized light. However, interstellar radiation is circularly polarized. Here we report on the enantioselective photolysis of chiral amino acids under interstellar conditions. First, circular dichroism CD spectra of D-leucine were recorded in the solid state[3]. Second, in order to achieve VUV asymmetric photodecomposition of solid-state D,L-leucine, circularly polarized synchrotron radiation was used to irradiate the samples. After photodecomposition, the e.e. was found to be[3] $+2.6\%$. The results will be verified by the 'chirality-experiment' onboard the Rosetta Lander, which will allow the quantification of chiral organic molecules in a cometary surface[4].

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Experimentally tracing the key steps in the origin of life: the aromatic world

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It is generally believed that the first life to emerge on Earth was at least functionally similar to life as we know it today, and to be much simpler than modern life. On the young Earth, prebiotic molecules must have formed containers, metabolic networks, and informational polymers that cooperatively organized to form a protocell. However, protocells may have been self-assembled from components different to those used in modern biochemistry. The functional integration of these components is a difficult puzzle that requires cooperation among all the aspects of protocell assembly: the starting material, reaction mechanisms, thermodynamics, and the integration of the inheritance, metabolism, and container functionalities. From the astronomical point of view, aromatic compounds (in the form of amorphous carbon and polycyclic aromatic hydrocarbons) are the most abundant carbonaceous material in space. We propose that assemblies based on aromatic hydrocarbons may have been the most abundant, flexible, and stable organic materials on the primitive Earth and discuss their possible integration into a minimal life form. We have elaborated on how aromatic molecules might function as container elements, energy transduction elements, and templating genetic components. We attempt to combine current knowledge of the composition of prebiotic organic material of extraterrestrial and terrestrial origin, and put these in the context of possible prebiotic scenarios. We also describe laboratory experiments that might help clarify the transition from non-living to living matter using aromatic material. This paper presents an interdisciplinary approach to integrate state of the art knowledge in astrochemistry, prebiotic chemistry, and artificial life research[1].

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The first stages of chemical evolution in open space

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Complex chemical processes could take place on the surface of small bodies in any planetary system. Evidently, chemical evolution proceeds under the conditions of open space, which serves as a huge chemical reactor. It is now well known that carbonaceous chondrites contain large quantities of prebiotic molecules, including amino acids, carbohydrates and heterocyclic bases of nucleic acids. A large amount of meteoritic material has undoubtedly showered the Earth over time. The organic compounds which have been delivered to the primordial Earth would have had a very complex structure and reached the second stage of chemical evolution – polymerization. In our experiments, the solid mixtures of biologically significant compounds (nucleosides and amino acids) were exposed to either vacuum UV photons or ionizing radiation. It has been found that both irradiation and photolysis may destroy molecules and may synthesize new and more complex ones. We investigated two types of reactions. (1) The abiogenic synthesis of nucleotides from mixtures of nucleoside and inorganic phosphate. The natural monophosphates of corresponding nucleosides were found. The main product was 5′AMP. (2) The abiogenic synthesis of dipeptides from mixtures of simple amino acids. The films containing a mixture of amino acids yielded various oligopeptides with summary yields of ~2.5 and ~2% after they were exposed to protons and VUV-radiation, respectively. Polymerization is an essential step in prebiological evolution and we have shown that this process probably could take place even at an early stage of Solar System formation, on the surfaces of small bodies.

Quantum molecular modelling of Glycyladenylate

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GlyAMP plays a central part in the activation of Glycine before its fixing to its cognate t-RNA[1]. The adenylation site of Gly is the glycyl-tRNA synthetase, for which the crystal structure is resolved here[2]. On the other hand, aminoacyladenylates can occur in prebiotic evolution as material for the non-enzymatic synthesis of polypeptides using montmorillonite clay[3,4]. Conformational analysis of aminoacyladenylates was initiated previously by Vasilescu *et al.*[5–8] using semi-empirical quantum computations. Here we have performed a quantum molecular modelling of isolated GlyAMP using Hartree Fock *ab initio* computations. Conformation and other properties (electrostatics, electronic chemical potential, electron affinity and electrophilicity) are discussed with regard to the '*in situ*' GlyAMP (GAP 1550) found in the crystal structure of Glycyl-tRNA synthetase (GlyRS) from Thermus thermophilus (code 1GGM at the Protein Data Bank).

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A theoretical study of the stability of molecular structures of interest for the origin of life

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This study was motivated by the fact that some amino acids are currently identified in carbonaceous chondrites but none have yet been observed in the interstellar medium. The more general question of the relative stability of prebiotic compounds with respect to the other possible species of the same chemical formula is addressed by means of quantum chemical simulations based on Density Functional Theory (DFT). A systematic investigation of all the molecules that have been identified under different isomeric forms in the interstellar medium is presented. In addition, it is shown that formamide, acetamide and N-methyl acetamide are the most stable species of their respective families. By contrast, glycine is not the most stable isomer that can be formed, a situation that is reversed when protonated isomers are considered[1].

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Looking for prebiotic phosphorus in the interstellar medium by means of computational experiments

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This contribution reports the results of a computational study that looks at the possibility of astronomical detection of phosphorus containing prebiotic molecules. Attention has been focused on the most stable species that can be formed with one phosphorous atom combined with carbon, oxygen and one, three or five hydrogen atoms. *Ab initio* Coupled Cluster molecular orbital methods and Density Functional Theory (DFT) methods have been used to obtain the relative stability of the various isomers together with the IR spectra and rotational constants[1,2]. It is found that the best candidates for detection are $HP{=}C{=}O$ (corresponding to HNCO), $CH_3\text{-}P{=}O$ and $CH_3\text{-}PH_2{=}O$ when the sets of atoms taken as starting material are [H, P, C, O], [3H, P, C, O] and [5H, P, C, O], respectively.

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Role of cosmic dust analogues in prebiotic chemistry

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Dust grains could have played an important role in driving the formation of complex molecular compounds relevant for the prebiotic chemistry that occurred in the early Earth. Dust and molecular compounds present in space experienced very different environments, with temperatures ranging from a few to thousands of Kelvins, and with very harsh conditions due to particle and UV irradiation. Astronomical observations of the interstellar medium, coupled with direct *in-situ* investigations of Solar System bodies performed by space missions and laboratory analyses of extraterrestrial material have shown the presence of a large amount of organic molecules. The detection of more than 100 molecules demonstrates that chemical reactions can proceed successfully in space. However, owing to low efficiency, the formation of complex molecules in the gas phase is not feasible, and an active chemistry has been suggested to take place at cryogenic temperatures ($\sim$10 K) on cosmic dust grains acting as catalysts. We present laboratory results on the catalytic effects of cosmic dust analogues (CDAs) with olivine composition, on synthesis of organic molecules under different physical conditions by using formamide (NH_2COH). We show the important role of CDAs in prebiotic chemistry experiments simulating processes occurring in astronomical environments relevant for the origin of life in the Solar System.

Cosmic matter as a cradle of ancestral genetic molecules

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DNA/RNA genomes and proteins represent the basic biological program of all life forms on Earth. The nucleotide sequences of nucleic acid molecules contain the genetic information that is transferred through different generations, and thus ensuring the perpetuation and evolution of life. The appearance in a primordial era of a nucleic acid-like polymer able to undergo Darwinian evolution marked the beginning of life on our planet and perhaps any other[1]. The building of primordial genetic molecules, whatever they were, required the presence of a protected environment, allowing the synthesis/concentration/protection of constituents and their correspondent polymers. This ensured the persistence of the genetic material, and the expression of its 'biological' potential, in a changing environment characterized by the presence of various degrading agents (i.e. cosmic and UV radiation). Determining how these steps occurred and how the primordial informational molecules originated on Earth is an open question. Recent observations in different fields, from astrophysical chemistry to molecular biology, have reinforced the hypothesis of the involvement of mineral surfaces in the prebiotic formation of molecules basic to life[2]. In this work, we present the results of our investigations on the interaction between nucleic acids (DNA, RNA), or their constituents (i.e. N-bases, nucleosides, nucleotides), and different minerals, including the Murchison meteorite.

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Contribution of cosmic high-energy impacts in prebiotic synthesis of polypeptides associated with icy matrix

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In the interstellar medium (ISM), the most probable source of organic molecules could be non-equilibrium processes driven by photons, cosmic rays, shock waves and solid body collisions. Cosmic galaxy radiation possesses the important constituent of 12% alpha particles (helium nuclei), 1.3% heavy ions, and 1% electrons. The dense cold phase of the ISM hosts icy dust grains – important chemical catalyst during its life cycle. Such particles consist of mineral core composed of silicate or olivine admixed with metal sulphides and oxides, with the water–ice envelope containing organic molecules. The formation of polypeptides from single aminoacids was traced in simulation experiments representing the inner structure of icy dust grains. An experimental chamber was irradiated at subzero temperatures at the dosage of 2.54 kRad min^{-1}. Solid frozen solutions of Gly and Phe were taken as the experimental samples inserted into the metal tube at subzero temperatures. The formation of di- and tri-peptides was demonstrated after applying mass-spectrometry and HPLC techniques. Having polypeptides within the icy matrix, dust grains with ice mantles are transported to warm, dense, and active protostellar regions, where ultraviolet (UV) irradiation may become important and alter the grain composition. Furthermore UVC radiation may contribute to the formation of additional amounts of polypeptides, since short-wave photons are totally adsorbed by a thin outer layer. This presumption coincides with our previous investigations concerning the UV impact on the prebiotic formation of biomolecules. Combining two irradiation types in different stages of interstellar flight could compensate for the effects of the low concentration and temperature of reagents.

Dissociative recombination – a feasible final step for the formation of biomolecule precursors in the interstellar medium?

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One of the crucial questions in astrobiology concerns the possibility of an interstellar or circumstellar formation of biomolecule precursors. Alcohols and nitriles deserve special attention in this context: nitriles with an α amino group can hydrolyse to yield amino acids; alcohols and other hydroxy compounds are suspected to form simple carbohydrates in the ISM by reaction with HCO[1]. Mostly, one of the proposed interstellar generation pathways for these species involves an ion-neutral reaction leading to the protonated form of the compound, followed by DR leading to the final product under ejection of an H-atom[2,3]. However, usually a multitude of other pathways are feasible for the DR reaction and to determine the feasibility of such a process as a final formation step of biomolecule precursors it is necessary to assess to what extent this process leads to the desired product under the retention of the C—O or C—N bond. Using the CRYRING ion storage ring at Stockholm University we measured the DR of $CH_3OH_2^+$, CH_3OH^+, CH_2OH^+, HCO^+ and CH_3CNH^+ in order to, by using these comparatively simple model ions, obtain an idea as to what extent alcohols, aldehydes and nitriles, can be formed involving DR, and also to establish how the degree of saturation affects the product branching ratios. An interesting pattern emerged: whereas in the case of $CH_3OH_2^+$ pathways involving a fraction of the C—O bond by far dominate (which very probably rules out a gas-phase formation of interstellar methanol), the C—O bond is left intact in the DR of CH_2OH^+ and HCO^+. CH_3OH^+ occupies an interim position in this respect, since the DR of this ion leads to C—O bond rupture with a probability of 43%. Therefore, it seems likely that a higher degree of saturation leads to a preferential break-up of the C—O bond, which would render the sequence of an ion-neutral reaction followed by DR a more feasible synthesis pathway for aldehydes and other unsaturated oxygen-containing carbon compounds than for alcohols. For protonated acetonitrile, a slight preference for the retention of the C—N chain (branching ratio 65%) has been observed. In addition, thermal DR rates of all the ions have been measured. They were found to be $8.9 \pm 0.9 \times 10^{-7}$ $(T/300)^{-0.74}$, $1.7 \pm 0.2 \times 10^{-6}$ $(T/300)^{-0.65}$, $6.8 \pm 0.7 \times 10^{-7}$ $(T/300)^{-0.63}$, $3.0 \pm 0.9 \times 10^{-7}$ $(T/300)^{-0.74}$ and $9.0 \pm 1.0 \times (T/300)^{-0.65}$ $cm^3 s^{-1}$ for $CH_3OH_2^+$, CH_3OH^+, CH_2OH^+, HCO^+ and CH_3CNH^+, respectively.

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Variations of the total-to-selective extinction ratio in interstellar clouds

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Although interstellar (IS) dust represents only ~0.1% of the galactic mass it is still important in order to understand galactic evolution, the formation of stars and planetary systems, and possibly the origin of life. Since the dust grains play a fundamental role in synthesizing molecular species, progress in studying the dust characteristics are clearly important in order to understand how these molecules are physically and chemically processed to give the chemical precursor of life[1]. A convenient indicator of local properties of dust particles is the total-to-selective extinction ratio $R_V = A_V / E_{B-V}$. It is well established that this parameter has an almost uniform value $R_V \sim 3.1$ in the diffuse IS medium, increasing toward more dense regions. This observed behaviour is generally taken as evidence of grain growth[2]. To ascertain how the dust component in the IS clouds is distributed and how its properties change from the boundary to the inner regions, we carried out an observational study of three different dark globules: CB107, CB52, and DC267.4–07.5. By exploiting the wavelength-dependent extinction of the stellar light due to the dust component, we obtained information about the clouds structure and the variation of the mean grain size toward lines of sight crossing these objects[3–5]. In all these objects we found that the R_V map follows quite closely the optical shape of the clouds, with values ranging from those typical of the IS medium, at the cloud boundary, to values $R_V \sim 5$–6 in the innermost regions.

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A study of the heating of micrometeoroids during the atmospheric entry

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Organic molecules capable of triggering the prebiotic synthesis of biochemical compounds may have been deposited on Earth by extraterrestrial bodies within the first 0.8 Gyr after the Earth's formation. Micrometeoroids (MMs) are especially interesting because they now represent the largest mass flux of extraterrestrial matter and their flux was probably even larger during the heavy bombardment period. So, as major carriers of organic carbon, nitrogen and neon to the early Earth they may have been essential for the evolution of the atmosphere[1]. Instead, the possible role of MMs as conveyors of amino acids and nucleo bases is less clear. Thus far only one amino acid, α-amino isobutyric acid, has been found in one of the Antarctic micrometeorites samples[2]. The absence of amino acids may be due to the heating experienced during atmospheric entry: most amino acids should be destroyed at temperatures greater than or equal to 800 K. However, they could avoid this fate if they sublimate before the MMs melt[3,4]. We have developed a new comprehensive model for the atmospheric entry of MMs that computes their velocity, temperature and mass as functions of time, and, as a benchmark, we first used the present-day terrestrial atmosphere. We then extended this to two early Earth-like atmospheric models. The heating depends critically on entry velocity, entry angle and particle size. For example, a 100 μm radius MM survives the atmospheric passage if its initial speed is less than 15 km s^{-1} (for a 45° entry angle). Detailed results are presented and compared in the light of simulation data reported in the literature.

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Comparison of terrestrial and extraterrestrial D/H-ratios of organic matter

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It is assumed that extraterrestrial matter is involved in the formation of the first protocells. We compare D/H-ratios of terrestrial organic matter with the values of related organic compounds in the early Solar nebula. These compounds are hydrogen cyanide and formaldehyde, acting as precursors of complex biochemical substances. In order to estimate the D/H-ratios of these two molecules in the early Solar nebula we have modelled a collapsing envelope around a young protostar. Then, a network of chemical reactions is combined with the dynamic model of this envelope. In the inner nebula our calculations show significant deuterium enrichment ($\delta_D > 1000‰$) for the selected molecules compared to Standard Mean Ocean Water (SMOW) in agreement with cometary data. However, the D/H-ratios measured in oil sources[1], indicate a deuterium depletion ($\delta_D < -100‰$) for terrestrial organic matter relative to SMOW. Hence, we draw the conclusion that this depletion is caused by two interacting, chemical processes: (1) a continuous hydrogen replacement in the course of evolution of organic molecules whereas the main source of this hydrogen was terrestrial water with its low D/H-ratio; and (2) an isotopic fractionation in the biochemical processes responsible for the self-organization of organic matter into protocells. Further investigations are necessary to cross-check our conclusions with future measurements and theoretical studies.

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Ultraviolet irradiation of CO_2 ices

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We have performed a number of preliminary experiments using the capabilities of our astrolaboratory[1]. In these experiments, different samples of CO_2 ice were irradiated with a microwave-powered hydrogen lamp in order to study the formation of new molecules using a quadrupole mass spectrometer. The experiments have been performed in a vacuum chamber operating at a pressure of 10^{-7} mbar and our system was able to vary the temperature from 10 to 300 K. The proportions of a particular mixture are controlled by their partial pressures. Our sample holder is a Quartz Crystal Microbalance and the frequency is measured precisely by a frequencymeter. The deposited samples are chemically processed by UV photons to form new molecules and their composition is monitored by mass spectroscopy. UV photons are provided by a microwave-powered hydrogen lamp similar to that used by other groups[2,3] mounted directly onto the sample chamber separated by an UV-transmitting MgF_2 window. Its spectrum is dominated by 1220, 1360, 1450 and 2800 Å bands and we obtain a flux $\sim 10^{15}$ photons cm^{-2} s^{-1} with an energy up to 6 eV. The objective of these experiments has been to verify qualitatively the production of new molecules. We found that the initial proportions in mixtures, the irradiation time and the method of deposition (mixed or in layers) are determinant to form new molecules. In all our experiments, the most important chemical species detected have been carbon monoxide and oxygen. In addition, other compounds have been detected as traces. The quantitative analysis will be possible when our IR spectrometer will be operative.

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Origin of nucleic acids: the concurrent roles of formamide and minerals

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Formamide chemistry provides a unitary system gathering in a single milieu the precursors needed to synthesize ur-informational polymers[1]. With widely diffused minerals and metal oxides as catalysts, formamide affords all the precursor nucleic bases: purine, adenine, hypoxanthine (bioisomer of guanine), cytosine, uracil and thymine. The selectivity of the reaction being correlated to physical and chemical properties of the catalyst. Appropriate thermodynamics and the simultaneous presence of precursors might have facilitated ur-polymerization processes. Formamide also determines a set of physico-chemical conditions thermodynamically favouring the polymeric state of nucleotides over monomers[2]. It is worth noting that formamide photochemically condenses into acyclonucleosides, favours (trans)-phosphorylations and enhances the micellar aggregation of surfactants providing protective niches to polymers. Thus, in the origin-of-informational-polymers scenario formamide acts on every synthetic step. In this presentation we focus on the synthesis of nucleobases and nucleotides catalysed by soluble (Na_3PO_4, $Na_4P_2O_7$ and $Na_5P_3O_9$) and mineral phosphates ($Al_2PO_4(H_2O)_3$, $Al_3(OH)_3(PO_4)_2(H_2O)_5$, $Mn_5H_2(PO_4)(H_2O)_4$, $Fe_3{}^{2+}(PO_4)_2(H_2O)_8$, $Cu_2{}^{2+}(PO_4)(H_2O)$, $Mg[Al(PO_4)(OH)]_2$ and others) and on their role in the protection of ribo and 2′-deoxyribo phosphoester bonds.

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Cyanate and urea as non-conventional activating agents for amino acids

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Although it has been the first organic molecule to be prepared from minerals, urea is generally considered as organic waste. Nevertheless, at moderate *pH* urea decomposition proceeds through elimination[1], thereby making it a synthetic equivalent of cyanate. Indeed, urea behaves as a cyanate transfer agent converting α-amino acid into *N*-carbamoylamino acid (CAA). As a dissymmetric urea, CAA can undergo two elimination pathways, one of them yielding an isocyanate intermediate derived from the amino acid; the latter is predicted to easily cyclize into an amino acid *N*-carboxyanhydride (NCA, known as efficient peptide monomer). Peptide formation in neutral aqueous medium by reaction of urea with amino acids – or more directly from CAA – has been demonstrated[2] through a mechanism most likely involving an NCA intermediate. This provides a new pathway for the prebiotic formation of NCA intermediates possibly responsible for the already reported peptide bond formation mediated by cyanate[3]. Such process may have occurred anywhere on Earth owing to the abundance of cyanate and urea.

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Chemical evolution: pyrroles and pyridines from the amino acid alanine

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Different possible sources of alanine on the young Earth ($\sim 4 \times 10^9$ years ago) are known. They are exogenous[1] as well as endogenous (e.g. black smokers[2] and Urey–Miller reactions[3]). Dissolved in the primordial ocean, alanine became associated with metal ions (Ca^{2+}, Mg^{2+}) present in the seawater. Geothermal heat (e.g. at lava coasts) could then have transformed the metal-bonded alanine into other organic compounds of prebiotic importance. According to these considerations, we prepared aqueous solutions of calcium chloride containing low concentrations of *rac*-alanine (Hala). Evaporation led to the formation of the previously unknown compound $Ca_3Cl_6(Hala)_2 \cdot n\ H_2O$. In order to simulate thermal effects on the early Earth, preparative-scale thermolyses of this compound were performed. For example, samples were heated to 350 °C in a quartz tube. A constant flow of nitrogen gas served to transport volatile compounds out of the reaction tube to a drip-tip condenser. A number of N-heterocycles were identified by GC-MS. The simplest were methyl-1*H*-pyrrole and methylpyridine isomers. These thermolysis products of alanine are of potential interest as prebiotic molecules. For example, pyrroles are building blocks of porphyrins.

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Thermal behaviour of glycine and alanine intercalated in Ca-montmorillonite

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Amino acids are generally accepted as important molecules in chemical evolution. They could have been readily formed on the primitive Earth or delivered by meteorites. Inorganic surfaces could have played an important role in thermal or catalytic transformations of amino acids[1]. The uptake of polar molecules into the interlayer spaces of some clay minerals is known as 'intercalation'. We have prepared intercalates of glycine and α-alanine with the Ca-montmorillonite SAz-1 (Clay Minerals Society; cation exchange capacity: 120 meq/100 g) by treatment of the ⩽2 μm fraction of the clay with 0.5 mol l^{-1} amino acid solutions. The amino acid content in the intercalate was found to be 7.0% and 6.8% for glycine and *rac*-alanine, respectively. We have conducted preparative thermolyses of the intercalates and free amino acids at 200 and 350 °C in a stream of pure nitrogen gas. Heating of glycine at 200 °C gave a black, probably polymeric substance. In contrast, after thermolysis of the glycine intercalate under the same conditions the cyclic dipeptide (piperazine-2,5-dione) and unreacted glycine were found. Thermolysis of the *rac*-alanine intercalate at 350 °C led to a complex mixture of products. A number of polyalkylated pyrroles, indoles and naphthalenes were identified by GC/MS. The heterocycles formed are of potential prebiotic interest because they are related to important biomolecules such as porphyrines, serotonin and tryptophan.

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On the potential of abiotic ribose formation during serpentinization

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Serpentinization of olivine and pyroxene in ultramafic mantle rocks (rocks low in silica) is a process that has attracted much attention during recent years. This is a complex series of reactions that occurs at temperatures below 500 °C in several active tectonic settings. Biogeochemically, the process is important because it leads to reduction of H_2O to H_2. At the same time, catalytically active compounds such as magnetite are formed. H_2 may be used together with CO_2 and magnetite as a catalyst in Fischer–Tropsch Type (FTT) reactions. FTT processes may lead to the formation of CH_4 as well as heavier hydrocarbons and other abiotic organic compounds. Serpentinization at temperatures below 300 °C is associated with high pH (pH 10–12). It is possible that the high pH may promote the formose reaction in natural environments and the abiotic formation of pentoses such as ribose, the carbohydrate constituent of RNA. Pentoses, and ribose in particular, are stabilized by borate that is scavenged from seawater by brucite – magnesium hydroxide that is yet another product of serpentinization reactions.

Origin of homochirality in an early peptide world

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Life on Earth has chosen one of two possible chiral forms: amino acids left handed, and sugars right handed. Life may very well have been the other way around, and maybe it is actually the other way for some alien life forms still to be discovered. In our talk we review various approaches to achieving full homochirality, focusing mainly on the polycondensation of peptides but also addressing the polycondensation of polynucleotides. In the latter, autocatalysis and enantiomeric cross-inhibition play key roles[1,2], whilst in the former activation and epimerization are crucial[3]. The latter possibility may have been more relevant for the prebiotic chemistry on the early Earth, either in the porous structures in hydrothermal vents or in drying and wetting beach scenarios. This scenario may also be more readily amenable to laboratory investigations. The model captures effects similar to autocatalysis and enantiomeric cross-inhibition without, however, producing unreactive 'waste' product[4]. Finally, the spreading of chirality on the early Earth is discussed by solving a set of reaction-diffusion equations based on a polymerization model. It is found that effective mixing of the early oceans is necessary to reach the present homochiral[5].

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Photolysis of mixtures of gases containing cyanoacetylene or cyanubutadiyne

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Nitriles and particularly unsaturated nitriles play a determining role in Astrobiology. Cyanoacetylene **1** (H—C≡C—C≡N) has been observed in the atmosphere of Titan, in comae, in the Interstellar Medium (IM) and in numerous lab simulations of Planetary Atmospheres. The first cyanopolyyne, cyanobutadiyne **2** (H—C≡C—C≡C—C≡N), has been detected in the IM and in lab simulations of the atmospheres of Titan and the Primitive Earth. Several approaches leading to mixtures of products have been reported to detect it and to record its spectra[1–3]. We have recently reported the first preparative synthesis of cyanobutadiyne **2**[4]. The photolysis of compounds **1** and **2** could have played a very important role in the formation of many compounds in the IM, in comae or planetary atmospheres including the Primitive Earth. The photolysis of cyanoacetylene by itself or with various other gases has been reported[5,6]. Tricyanobenzenes and tetracyanocyclooctatetraenes have been obtained as well as the corresponding 1,4-adduct or diadduct with ammonia, phosphine (PH_3), silane (SiH_4), H_2S, alkynes or alkenes. Performing the same photolysis in gaseous phase with cyanobutadiyne **2** instead of cyanoacetylene **1**, we have never been able to detect an adduct except with thiols. Even if the vapour pressure of cyanobutadiyne **2** is low at room temperature, very small quantities of vinylic or aromatic compounds can be easily detected by ^1H NMR spectroscopy. Similarly, the kinetic instability of cyanobutadiyne, which is much more important than the one of cyanoacetylene **1**, cannot be proposed as an explanation, cyanobutadiyne being still easily observed in all the photolyzed samples.

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3-Amino-2-propenenitrile

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Cyanoacetylene has been observed in the Interstellar Medium, in comae, in Titan and in many simulations of planetary atmospheres. The presence of ammonia on the Primitive Earth has been the subject of strong debates. However, many compounds postulated as precursors or building blocks (α-aminonitriles, aminoacids etc.) easily give ammonia on hydrolysis or heating. Cyanoacetylene quickly and easily reacts with ammonia to form 3-amino-2-propenitrile in very good yields. In the area of Exobiologie, studies on 3-amino-2-propenitrile have been dramatically underinvestigated. We have developed a quite general study on the chemistry of 3-amino-2-propenenitrile[1–3]. We demonstrated particular properties on the chemistry, acidity and basicity in gas phase of this compound[2]. On the hypothesis that this compound could be formed in the IM or planetary atmospheres, we recorded its gas-phase infrared[1] and microwave spectra[3] to allow its detection in planetary atmospheres or in the Interstellar Medium.

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Effects of Fe (II) in the formation of biomolecules in simulations experiments using spark discharges and aqueous aerosols

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The emergence of life is one of the most puzzling scientific problems. In this context, it has been proposed that aerosols played a major role on the origin of life on the Archean Earth. On the other hand, it is postulated that ancient sea had a salinity of 1.5 to 2 times the modern value, a pH = 5–10 and the presence of the banded iron formations show that dissolved iron was present in excessive quantities in the early Earth. Our experimental approach to synthesize abiotically organic molecules with biological interest consist in the simulation of an aqueous aerosol in a plausible prebiotic atmosphere (CH_4, N_2 and H_2) and in a plausible ancient sea (pH = 5.8, salinity about 2 times the modern sea and Fe^{+2} 0.01 M) and the simulation of storms using spark discharges. Using different sources of Fe (II) ($FeCl_2$, $FeCO_3$ or FeS) we observed the formation of some amino acids, hydroxy acids, di- and tri-carboxylic acids and heterocycles involved in biological process. Indeed, the presence of dissolved Fe^{+2} in our simulation experiments generates the formation of Prussian Blue, $Fe_4[Fe(CN)_6]$. This inorganic salt could be an important reservoir of HCN in the initial prebiotic conditions of Earth. However, in the experiments carry out in presence of insoluble FeS the formation of Prussian Blue is not observed but amino acids containing S are detected.

Chemical effects of gas–water interface: analysis and structural characterization of complex materials obtained from a $CH_4/N_2/H_2$ atmosphere and an aqueous aerosol

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It has been proposed that aerosols played a major role on the origin of life on the Archean Earth. Our experimental approach consists of the simulation of an aerosol in a plausible prebiotic atmosphere and the simulation of storms using spark discharges. The organic compounds with biological interest (i.e. amino acids, purine bases) are not present *per se* in the raw collected in simulation experiments otherwise as, generally, unknown precursors. Therefore, it is necessary to characterize the structure of these complex materials in order to clarify the nature of precursors and to find a plausible mechanism of synthesis. We used different spectroscopic techniques (IR, UV-vis, XPS, Solid State ^{13}C NMR spectroscopy) and other analytical tools (HPLC, GC-MS) to characterize the structure of our products. In our experiment, we obtained one water-soluble fraction (S) and one insoluble fraction (I). The bulk S fractions are constituted by polar units (containing carboxylic acids, amines, alcohols, and nitriles) with different molecular weights. It yields a relatively high amount of amino acids, purines bases and carboxylic acids. We propose the Strecker synthesis as the most likely mechanism in the formation of amino acids under our prebiotic conditions. However, the I fraction is an apolar solid that seems to be formed by large and rigid hydrocarbon chains. The presence of a punctual unsaturated bond (C=C, C≡C) in the chains could be the reason for the rigidity and the amine and hydroxyl group could allow the hydrogen bond among neighbour chains. The oxidative cleavage shows the presence of structures —C=C—C—C=C—.

Studies on prebiotic synthesis and ionophoric activity of model cyclic peptidomimetics

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Selective transport of ions and small molecules across cell membranes is crucial for the origin of the living cell's homeostasis. Prebiotic synthesis of simple peptides or peptidomimetics must have been essential for formation of ion channels and pores in early cell membranes. We report our attempted synthesis of peptidomimetics with pore-forming activity, performed under prebiotic-like conditions. Synthesis was based on compounds already presented in a prebiotic Earth environment. The key-step of the total synthesis is the Ugi reaction, a four-component condensation reaction between an isocyanide, an amine, a carboxylic acid and an aldehyde, leading to the peptidomimetic structures. These products can be readily cyclized to final ionophoric compound. We suggest that upon proper substrate choice, intramolecular hydrogen bonds can be formed between side chains of amino acid used as substrates for synthesis of peptidomimetic compounds. This hydrogen bond pattern can be responsible for stereoselective course of Ugi reaction. Ionophoric activity of cyclic compounds is confirmed by the standard mitochondria swelling assay and by data obtained by measuring picrate salts trans-phase transport of target compounds.

Oscillating prebiotic model: the theoretical substantiation and the program for experimental proof

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Various explored prebiotic models are able to self-complicate under certain conditions. However, the conducted experiments have not led to their transformation into a kind of simplest living units. According to the theoretically elaborated conception[1], this transformation is possible through the intermediate stage – formation of oscillating (pulsing) prebiotic microsystem. Such a 'bistate' system may originate during non-equilibrium transition of a prebiotic microsystem from the initial into advanced state, in case there appears the balance between the states keeping through the oscillations around the highest 'bifurcate' point of transition. The system acquires the paradoxical way of organization – 'stabilized instability': the principally unstable point of bifurcation is 'incorporated' between two opposite but equal forces. The regular oscillations to the initial and advanced states give the transformed microsystem the following properties, which are at the foundation of life: incessant inner fluctuations and re-arrangement of molecules; integrity through cooperative events; exchange by matter and energy with the outside world; forked structure consisting of two interrelated co-structures; repulsion of the co-structures from the central point of instability and their dichotomy at the end of cycle of the existence, etc. Experimenters are invited to begin experiments in this way. The aim of the experimental research is to obtain oscillating prebiotic microsystems, which are able to evolve to life. During the experiments various prebiotic models should be explored at the state of bifurcate transition and under oscillating conditions in experimental chambers.

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Adsorption and thermal transformation of simple amino acids on oxides

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It has long been proposed that the surfaces of oxide materials may have played an important role in promoting and directing the synthesis of oligopeptides from amino acids, on the prebiotic Earth or in interstellar conditions. Mostly macroscopic level results have been obtained so far; the molecular environment of adsorbed amino acids is unknown. In particular, polymerization selectivities are hard to rationalize, so that one cannot evaluate the likelihood of the synthesis of 'useful' polymers. In this study, simple amino acids were adsorbed on high surface area solid oxides (silica, alumina, saponite clay, Al-pillared saponites, goethite) with well-known surface structures. The adsorbed amounts were quantified as a function of pH. The adsorbed amino acids were characterized at the molecular level by vibrational spectroscopy, ^{13}C NMR and DFT modelling. Thermal activation resulted in the clean formation of cyclic or linear dimers depending on water activity. Some hypotheses have to be reconsidered in view of our data. Even in the case of glycine, no less than four molecular environments are observed for the deposited amino acid: bulk α- and β-glycine, molecularly adsorbed zwitterions, and molecularly adsorbed neutral glycine. The systems studied exhibited a more complicated behaviour than anticipated, and thus a wider range of opportunity for the appearance of complex phenomena. Mixtures of two amino acids were also adsorbed on the same oxide surfaces. In the (lysine+glycine) system, we observed a preference for lysine adsorption that depends on the nature of the surface, the solution pH and the amino acid concentration. Thus, a simple form of molecular selection may have been operative in the prebiotic polymerization of amino acids.

Preparation and use of an iron sulphide–montmorillonite hybrid under prebiotic-like conditions

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The aim of this work is to connect two important hypotheses of prebiotic chemistry: the function of sheet silicates (clays) as potential prebiotic catalysts[1] and the possible influence of iron sulphides according to the iron–sulphur world scenario[2]. Clays and metal sulphides have been proposed as mineral catalysts that could have promoted the first prebiotic chemical reactions. Our main objective was to investigate the thermal reactions of amino acids in the presence of a hybrid material comprising of an iron-sulphide and a clay mineral. The experimental work consisted of the preparation of an iron sulphide containing montmorillonite, then loading it with amino acids, submitting the material obtained to thermolysis, and finally, analysing both the thermolysis residue and the volatile compounds that might have evolved. As a first step, we focused on glycine since it is the most commonly formed amino acid under various potentially prebiotic conditions. In a typical experiment, a glycine-loaded Mont-FeS was submitted to thermolysis for 48 h at moderate temperature (200 °C). Investigation of the thermolysis residue by means of GC-MS, HPLC and NMR led to the identification of short-chain glycine oligomers and 2,5-diketopiperazine.

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On the availability and potential of reduced oxidation state phosphorus to prebiotic chemistry

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Anoxic, photochemical irradiation of a type IIICD iron meteorite fragment, part of the Nantan meteorite fall in China witnessed in 1516, in a deoxygenated ethanol water ice afforded as the major product H-phosphinic acid (H_3PO_2) by ^{31}P-NMR spectroscopy. Subsequently, we find that the same phosphorus oxyacid is produced using Fe_3P as a model of the schreibersite-containing inclusions within iron meteorites. Furthermore, H-phosphinic acid is also observed to be the key P-containing product when Fe_3P reacts with gaseous water vapour under microwave plasma conditions. The volatile species phosphine (PH_3) is also a consistent bi-product of these reactions. In the absence of such forms of energy input, H-phosphonic acid (H_3PO_3) is the major product. The significance of such anaerobic 'corrosion' of meteoritic phosphides lies in the fact that salts of H-phosphinic acid are considerably more soluble than those of H-phosphonic acid whereas orthophosphates are very insoluble. Given the availability of significant UV light flux on the early Earth and an estimated meteoritic in-fall of 103 kg yr^{-1} of phosphide minerals, we feel these results offer a significant contribution to the role of phosphorus in pre-biotic chemistry and may indicate pathways to organophosphorus biomolecules not yet considered.

Gas-phase reactions relevant to prebiotic chemistry: a laboratory investigation by the crossed molecular beam technique

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In the sequence of steps which are believed to have lead from elementary particles to the emergence of life in the Universe, an important one is certainly the formation of prebiotic molecules (simple sugars and amino acids) from very simple parent molecules or atoms abundant in the Universe. The aggregation of H, O, N, C (and other element) atoms into molecules and the subsequent chemical evolution are still occurring in the Universe, if it is true that more than 100 molecules have been identified in the harsh chemical environments of interstellar clouds (ISC) and that a gas-phase organic chemistry is taking place in the atmospheres of Solar objects such as Titan. Simple as they might seem if compared with other processes of relevance in astrobiology, the formation mechanisms of many of the observed molecules and radicals are far from being understood. In our laboratory, we have investigated gas-phase reactions involving atomic (N, C, O)[1–3] and radical (CN, OH, CH_3)[1] species of relevance in prebiotic chemistry by means of the crossed molecular beam technique with mass spectrometric detection. That has been done within the framework of two European Networks (*Europlanet* and *Molecular Universe*). In these studies we have been able to characterize: (a) the nature of primary reaction products; (b) the branching ratios of competing reaction channels; (c) the microscopic reaction mechanisms; and (d) the product energy partitioning, which can strongly influence the destiny of the reaction products.

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Alternatives to nucleotides as the basis of a genetic alphabet

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Information, in the terrestrial genetic alphabet, is encoded both in the purine/pyrimidine nature of a nucleotide (1-bit), and in the hydrogen/lone-pair donor/acceptor (D/A) patterns expressible using up to three positions (3-bits)[1]. Nucleotides, however, are not the only molecular forms capable of expressing information, and alternatives to nucleotides and nucleotide analogues have been independently suggested by both Szathmáry[2] and Zimmerman[3]. In this study, we report the results of simulations on potential alternatives based on the set of hydrogen/lone-pair D/A patterns employing four positions. The molecules we employ, as the basis for an alternative expression of patterns, have a skeleton based on naphthalene, but with appropriate positioning of keto and amino groups, together with substitution of nitrogen or oxygen for carbon, as required, to obtain the desired D/A patterns. Quantum Chemical calculations at both *ab initio* and semi-empirical levels of approximation are employed, and the various interactions between complements and non-complements, among the sixteen possible patterns, are examined. Viable alphabets are considered to be those in which there is a significant repulsive interaction between non-complementary patterns. The results indicate that the potential for viable alphabets based on these alternatives to nucleotides patterns is unexpectedly limited.

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DNA Shuffling: a dynamic model for novel gene synthesis

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Prokaryotes have evolved on our planet over the last 3.8 billion years during which they developed an impressive adaptation capacity, which led to their adaptation to a wide range of ecosystems. This refined adaptation capacity is responsible for microbial response to environmental perturbations. When new genes are required, the molecular mechanisms respond rapidly. In order to evaluate this adaptation capacity, we examined microbial response to highly chlorinated molecules. These synthetic xenobiotic molecules were introduced recently into the environment (50 years ago for the oldest), where they exert selective pressure because they are both a potential source of nutrition and toxicity. Although an extensive bioinformatics study did not identify any ancestor gene (i.e. a gene from which the xenobiotic gene evolved), several DNA fragments, which are similar in a group of xenobiotic genes were discovered. These fragments were amplified from the metagenome of a non-polluted soil (i.e. from the total DNA of soil, which has not undergone selection pressure). Then, these DNA fragments were used to rebuild the xenobiotic genes *in vitro* with an accelerated evolution method. These results suggest that DNA fragments from soil could be reassembled *in vivo*. These results also support the notion that novel genes might have been derived from a diversity of microorganisms. The molecular mechanisms responsible for this type of DNA shuffling might be able to incorporate a wide range of exogenous DNA into the microbial genome.

Astrobiology Networks and Education

ITASEL ongoing activities

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An accurate detection of relevant amounts of water vapour in the atmosphere of extrasolar planets is of primary importance for the knowledge of the planetary chemical composition and, more speculatively, for the study of a possible development of water-based life. The ITASEL project has the aim to detect, using radioastronomical tools, a particular kind of radiation emitted at a frequency of 22 GHz by the planet atmosphere – the radiation amplified by MASER effect – which provides a direct way to register the presence of water with ground-based telescopes. In the frame of the ITASEL project we are monitoring a selection of exoplanetary systems and other potential scenarios where the water MASER line could be found, such as nearby stars when considered interesting from an astrobiological point of view and peculiar bright comets with short perihelion distances. Observations are ongoing together with the development of innovative hardware technologies that should allow the detection of faint lines with more accuracy and reliability. The new hardware system named SPECTRA1 (SPECTRum Analyser 1) is a modular spectrometer for radiotelescopes that provides several analysis capabilities. Compared with other digital backends, SPECTRA1 offers relevant advantages such as reconfigurability, low dimensions and low cost. The high flexibility can potentially make the instrument interesting in numerous application fields, such as biomedical elaboration equipments and telecommunications. Customized data processing procedures are also required to identify possible weak signals drifting in frequency along the spectra sequences – due to the doppler effect which, in the case of still undiscovered exoplanets, is unknown.

The Italian Astrobiology Society

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The international community of astrobiology is continuously growing larger through the settling-up of new associations of scientists. The Italian Astrobiology Society (SIA) was recently born. It is a free, independent and non-profit association of Italian scientists sharing an interest in astrobiology. The SIA has primary objectives to coordinate, encourage, share and protect the astrobiological knowledge among scientists and educators from different backgrounds. The activity of the SIA is strongly interdisciplinary. It favours the exchange of knowledge and know-how among different scientific communities, promoting the development of new technologies for terrestrial and space applications. Our program is placed in an international framework of cooperation and collaboration among institutions and organizations from different countries. The program and objectives of the Italian Astrobiology Society will be here presented.

Astrobiology in France: science, research and development programmes paving the way for the future exobiology

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For more than a decade now, astrobiology is organized in France federating, under the joint auspices of the French space agency (CNES) and the French science and research administration (CNRS), around 50 laboratories and 200 researchers. This highly interdisciplinary domain is now supported not only for the science but also, since 2004, for the research and development activities (R&D) of the CNES. The French scientific community is involved already in European led and international missions which are relevant for astrobiology as well as in ground work. This involvement deals also with laboratory simulations, models and basic science. Considering the different domains of interest of astrobiology and the possibility to use the search for traces of the early life on Earth as a model, scientists and CNES developed a strategy to prepare future missions exploring the Solar System and beyond. This strategy is split into R&D actions on the following two main themes. *In-situ analysis*: to prepare future instruments flying on space mission (for separation of chiral products, identification of molecules of exobiological interest using microchips, etc.). *sample return activities*: to prepare the analysis of samples using electronic paramagnetic resonance or to define a portable planetary protection level 4 container. Some of these R&D activities could, in the future, be partially implemented on Exomars but most of them are aimed at further missions dedicated to searching for traces of life or evidence of prebiotic chemistry in the Solar System.

Planetary biology, evolution and intelligence: the SETI Institute's NAI Team research

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The SETI Institute team studies the co-evolution of life and its planetary environment. We demonstrated that peroxy in rocks can lead to the formation of free O_2, suggesting that the oxygen transition on an Earth-like world could take place independently of the invention of any particular metabolic pathways (e.g. photosynthesis) that have been proposed as driving this transition. Since Earth's oxygen transition ultimately set the stage for oxygen-based metabolism, understanding this transition is crucial to elucidating both Earth's evolution and the evolution of life, especially the evolution of oxidant protective strategies and aerobic metabolism. We demonstrated that nanophase ferric oxide minerals in solution provide a sunscreen against UV while allowing the transmission of visible light. This makes the evolution of photosynthetic organisms possible on early pre-oxygen Earth. Just as global-scale changes in oxygen were critical for the early biosphere, so too were global processes involving nitrogen. In coupled laboratory and field studies we have shown that abiotically produced NO_3^- is stable in liquid and frozen seas, such as on early Earth and frozen ice crystals such as on Mars. We analysed data from missions and created models to examine the geology of Europa and its implications for the free energy sources that would be needed to power a Europan biosphere. We then couple these results with low-temperature laboratory experiments to make predictions concerning the possible abundance and survivability of biomarkers that might reach Europa's surface through active geology. We conclude with a project that has shown that planets orbiting M stars may be suitable for life.

Contribution for the development of the astrobiology education and public outreach in Europe

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The recent breakthroughs and the development of highly advanced technologies have contributed to the rapid expansion of astrobiology. This new science aims at studying biological processes on Earth and beyond, through interdisciplinary research in chemistry, physics, biology, geology, astronomy and planetary sciences[1]. This interconnected scientific network allows us to visualize a new approach concerning life's nature, origins and development on Earth and elsewhere in the Universe. In order to achieve this goal, it is essential for astrobiology to be integrated into the curricular domain, as well as into public and private scientific policies[2]. This communication continues our previous work on astrobiology education and public outreach. In this sense, we present a curricular proposal on astrobiology and strategies for an adequate public outreach[3]. Some of these activities were tested as part of extracurricular projects in several Portuguese high schools and institutions with excellent results[2,4]. We consider that the type of activities presented will contribute to the development of astrobiology education and public outreach in Portugal and in Europe, as a domain for culturally significant dynamism in scientific knowledge. This will enable the development of more holistic and cooperative learning, and we will also expect to contribute to fighting against the scientific illiteracy and to a better understanding of modern science.

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SETI Searches as of 2006

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As of 2006, SETI (the Search for ExtraTerrestrial Intelligence) is being pursued by a small group of countries only: the USA, Australia, Argentina, Italy, Russia, Japan, perhaps a few more. Why is SETI not being 'taken seriously' by the majority of scientists and decision makers? Because it has so far failed to get in touch with aliens. However, the key explanation for this apparent failure seems to us to be rather simple: we just did not explore *far enough* in the Galaxy! Our present SETI range, in fact, cannot exceed a few hundred light-years. Two important on-going SETI programs are the Allen Telescope Array (ATA) and the SETI-Italia Project. ATA is well known and will not be described further here. SETI-Italia is the national Italian SETI Program run by IRA (Istituto di Radio Astronomia) as a part of INAF (Istituto Nazionale di Astrofisica), under the ITASEL PROGRAM (Italian Search for Extraterrestrial Life). Italy is the only European country performing 'listening' SETI searches. SETI-Italia activities started early 1998 with a Serendip IV spectral analyser connected in piggyback mode to the VLBI 32 metre antenna located in the countryside at Medicina, near Bologna, in Italy. In the years 2002–2006, many efforts were devoted to set up a fast computation system to calculate the KLT (Karhunen–Loève Transform), a better algorithm than the FFT for searching for the presence of wideband signals of any kind embedded in the noise. The mathematics of the KLT for SETI is briefly described in this poster paper.

Extrasolar Planets

The many faces of Earth

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If we were to observe the Earth as an extrasolar planet, the portion of the planet reflecting starlight toward us would change depending on the viewpoint of our observatory. Here we have modelled the changes in the Earth's albedo as a function of its phase angle, and in the direction of the observer. The reflectance models used here have been previously validated by simulating the Earth's reflectance as seen from the Moon (the Earthshine). Real cloud data from satellite observations are inputted for each day and this allows us to characterize the hourly, diurnal, and seasonal variability that we might observed in Earth-like extrasolar planets. Among other results, we find that the determination of the rotational period of the Earth is a non-trivial matter, and that deviations from the 24 hour rotation, caused by cloud changes, can be used to infer the presence of tracers in the atmosphere. This could provide a useful technique for the detection of cloudiness in Earth-like exoplanets, and infer the possibility of liquid water in its surface and atmosphere.

Detailed estimation of the vegetation on the Earth integrated spectrum

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The detection of exolife is one of the future goals of very ambitious space missions or extremely large ground-based telescopes. While associations of simple molecules present in the planet's atmosphere have been identified as possible global biomarkers, we analyse here the detectability of vegetation on a global scale on Earth's ground. The vegetation reflectance shows a sharp edge around 700 nm, called the Vegetation Red Edge (VRE). This work, based on observational data of the Earthshine Moon, aims to characterize and to quantify this signature in the disk-averaged Earth's spectrum. To get the Earth integrated spectrum from the Earthshine spectrum, we take particular attention to correct from various effect such as Moon phase, Chappuis band and the Rayleigh and aerosol atmosphere scattering. For all the steps of the process, we make an estimation of the error on the VRE estimation which results in a typically ± 0.5. The Earthshine spectrum obtained for various phases allow us to detect VRE when lands with forests are present (4.0% for Africa and Europe), and is lower when clouds and oceans are mainly visible (1.3% for the Pacific Ocean). We showed that measuring the VRE or an analog on an Earth-like planet remains very difficult (photometric relative accuracy of 1% or better), and remains a small feature compared with atmospheric absorption lines.

Instrumental constraints for the spectral characterization of terrestrial exoplanets: Application to the detection of biosignatures

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The characterization of terrestrial exoplanets through their low-resolution spectra is the purpose of future space observatories: Darwin (ESA) and TPF-I/C (NASA). Darwin/TPF-I will use infrared interferometry to study the thermal emissions of the planet while TPF-C will consist in a visible/near-infrared coronograph looking at the light reflected by the planet. The properties of the planet that can be inferred from the spectra (radius, temperature, albedo, atmospheric composition) are strongly limited by the performance of the instrument, in particular the width of the spectral window, its resolution (R) and signal to noise ratio (SNR). The goal of the present work is to constrain these limitations and to determine the minimum values of R and SNR required to perform the reliable detection of a given spectral signature or to measure a planetary property (for instance the radius) with a given precision. For that purpose, we have developed a new version of the code PHOENIX, dedicated to the modelling of stellar and planetary atmospheres, which now allows us to compute synthetic spectra of terrestrial planets. We have applied this model to the atmosphere of terrestrial planets of various compositions and at different locations in the habitable zone of their stars. After degradation of the synthetic spectra to a realistic observed spectrum, we have performed statistical tests to validate or reject the detection of spectral features. In this particular work, we focus on the detection of spectral signatures with high astrobiological interest: atmospheric species (H_2O, O_2, O_3, CH_4) and the VRE.

The search for ocean-planets with CoRoT, Kepler and HARPS

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Planets less massive than 10 M_{Earth} and formed beyond the snowline of protoplanetary disks, are expected to have a cometary composition (~50% rocks, 50% water), and no massive H-He atmosphere. Owing to migration, such planets should be found at any distance between their formation site and the star. If migration stops within the habitable zone, this will 'ocean-planets'[1]. They typically consist in a silicate core, surrounded by a thick ice mantle, itself covered by a 100 km deep ocean. The existence of ocean-planets raises important astrobiological questions. Can life originate on such body, in the absence of an emerged continent and ocean-silicate interface? What would be the nature of the atmosphere and the geochemical cycles? In this work[2], we address the fate of these planets when migration ends at a much closer distance (orbital period less than 75 days). Although we do not expect these hot planets to harbour life, close-in planets can be detected through their transits and their identification as water-rich planets would confirm the existence of this new type of planets that should also populate circumstellar habitable zones. The water reservoir of these planets seems to be weakly affected by gravitational escape, provided that they are located beyond some distance, for example 0.04 AU for a 5 M_{Earth} planet around a Sun-like star. We have thus studied the possibility of detecting and characterizing these hot ocean-planets by measuring their mean density using transit missions in space – CoRoT (CNES) and Kepler (NASA) – and Doppler velocimetry from the ground: HARPS (ESO) and possible future instruments. We have determined the stellar magnitude versus orbital distance domain where discrimination between ocean- and rocky-planets is possible with these instruments.

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Dynamic habitability for Earth-like planets in extrasolar planetary systems

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The likelihood of finding habitable Earth-like planets on stable orbits has been estimated for 86 selected extrasolar planetary systems, where luminosity, effective temperature and stellar age are known. For determining the habitable zone (HZ) an integrated system approach is used taking into account a variety of climatological, biogeochemical, and geodynamical processes[1]. Habitability is linked to the photosynthetic activity on the planetary surface. We find that habitability strongly depends on the age of the stellar system and the characteristics of the virtual Earth-like planet. We approximated the conditions for orbital stability using a method based on the Hill radius. The likelihood that a virtual Earth-like planet is both on a stable orbit and also within the HZ can be quantitatively estimated from the width of the HZ excluding the interval of orbital instability. Almost 60% of the investigated systems could harbour habitable Earth-like planets on stable orbits. In 18 extrasolar systems we find even better prerequisites for dynamic habitability than in our own Solar System. In general, our results are comparable to those with an HZ determination based only on climatic constraints. However, there are remarkable differences for land worlds and for systems older than about 7 Gyr.

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Influence of giant planets near the 5:2 resonance on the habitable zone of Sun-like stars

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The detection of an 'exo-Earth' in a 'proper distance' to the host-star (called habitable zone (HZ)) does not imply the habitability of the planet. This is an interdisciplinary venture, including astrophysical research, where dynamical stability studies of extrasolar planetary systems provide an important contribution, since the evolution of a biosphere occurs over a very long time. Motivated by the fact that in some of the discovered multi-planet systems the giant planets move in mean motion resonance (MMR), we studied the influence of planet pairs (close to the 5:2 MMR) on the habitable zone of a Sun-like star. Starting with the actual Jupiter–Saturn configuration, one can see how the perturbation changes, when we increase Saturn's mass (up to 13 $M_{Jupiter}$). Moreover, the variation of Saturn's initial position (8–11 AU) clearly shows the appearance of other MMRs between Jupiter and Saturn, for example 2:1 MMR (Saturn at 8.25 AU); 7:3 MMR (Saturn at 9.15 AU); 3:1 MMR (Saturn at 10.82 AU), and how they perturb the HZ depending on Saturn's mass. A detailed paper is in preparation.

Polarization of light reflected from forest canopies on Earth with possible applications to Earth-like planets

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Quasi-specular reflection of Sunlight at the waxy surface of a leaf yields appreciably polarized light, especially near the Brewster angle. Sunlight entering the leaf is either absorbed by photosynthetic pigments or, after reflection at internal interfaces, emerges as a diffuse component with a non-zero but low linear polarization and a yet smaller level of circular polarization[1]. The net polarization varies with the leaf's surface roughness, internal architecture and health and is difficult to model. The polarization of a forest canopy is complex and depends on the leaf orientation distribution. The global polarization and reflectance properties of Planet Earth have been measured by the POLDER satellite[2]: at 43 nm atmospheric Rayleigh scattering dominates, but at 865 nm the surface properties of ocean, vegetation, desert and snow can be estimated. For cloud-free surfaces at 865 nm and 90° phase angle the percentage polarization, p, and reflectance, R, are, respectively [55%,9%](ocean), [7%,23%](vegetation), [6%,40%](desert) and [3%,80%](snow). Allowing for the fractional global areas of each component, and global cloud cover of 55%, yields $p=7.3\%$ for a pale-blue-dot Earth[3]: pR is greatest for oceans and least for vegetation and hence prospects for detecting pR from vegetation on an Earth-like planet are poor unless more than 50% is covered in vegetation. However, the prospects of using the phase and wavelength dependence of polarization of a pale-blue-dot planet to deduce its properties as it rotates and orbits are more encouraging. The possible application of a circular polarization signal that is unique to vegetation remains an intriguing possibility for remote sensing.

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Resonant configurations in planetary systems

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We review the occurrence of mean-motion resonances in planetary systems and discuss their role in our understanding of planetary system formation and evolution. Studies of commensurabilities have already been applied successfully to analyse the motion of gaseous giants and pulsar planets, and they proved to be a powerful tool in deciphering their past evolution[1]. They might be similarly useful in our search for Earth-like planets in other systems.

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Stability of habitable Trojan planets in exoplanetary systems

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Although up to now we have not found any terrestrial planet (we have only evidence of 7 M_{Earth} (Gliese 876d) and larger) but we are convinced that our Galaxy is full of such planets. The size of most planets is too large for the formation of life and only a few of them lie in the 'habitable zone' (HZ)[1]. That is the reason why we study the dynamical stability of possible additional terrestrial planets. The discovery of giant planets in the HZ does not exclude the existence of additional Earth-like planets since we have the possibility of 'habitable moons', or 'habitable Trojan planets'. For the latter configuration, we have a common example of the so-called Jupiter Trojans in our Solar System, which are in a one-to-one mean motion resonance with Jupiter. These asteroids populate two regions, one 60° ahead of Jupiter (L4), and another one 60° behind (L5) with the same semimajor axis. This work investigates the stability of Trojan planets for multi-planetary systems, where one of the two detected giant planets move partly or completely in the HZ. According to our results, only one (HD108874[2]) of the six investigated systems[3] may host habitable Trojan planets.

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3 Schneider, J. *The Extrasolar Planets Encyclopedia.* http://exoplanet.eu/

Habitability and dynamics of counter-rotating planetary systems

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In this work we discuss two types of planetary systems where planets are orbiting the central star in opposite directions. The first one has two massive planets and the second one consists of a terrestrial planet and a giant planet. We consider the dynamical stability of these systems and the possible habitability of the terrestrial body in these cases. This study is based on computer simulations. The work is inspired by observations from a protoplanetary disk in IR-source IRAS 16293-2422 where the disk seems to have counter-rotating regions. Also, the protoplanetary disk around β Pictoris has been observed to consist of two dynamically different components. These observations made us assume that counter-rotating planetary systems may actually exist. We find that perturbations in counter-rotating systems are generally smaller than in an ordinary planetary systems, especially the semi-major axis, a, and eccentricity, e. This stabilizes the shape of the orbit and thus heavily reduces the effects of temperature variations and therefore a terrestrial planet may be more stable to harbour life. Dynamically we find most orbits to be stable over long time scales and typically this happens in a wider parameter area than in co-rotating systems. The problematic part here might be how to form a counter-rotating system dynamically, without having initially inhabitable conditions.

Experimental silicification of extremophilic archaea, *Methanococcus jannaschii*: applications in the search for evidence of life in early Earth and extraterrestrial rocks

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Early life on Earth was anaerobic and apparently thermophilic. It included chemolithotrophs organisms that could have existed on early Mars, as well as photosynthesisers. Since the earliest life forms known to date (older than 3 Gyr) were preserved owing to the precipitation of dissolved silica on cellular structures (silicification), we undertook an experiment to silicify a type of microorganism that could have existed in the environmental conditions of early Earth and early Mars, given the different environmental conditions. We chose the thermophilic species *Methanococcus jannaschii* (methanogenic Archaea) as a representative of an anaerobic, autotrophic, thermophilic microorganism. This is the first time that an Archaea has been used in a simulated fossilization experiment and one of the very first fossilizations of an hyperthermophile microorganism. After having been cultured under Early Achaean conditions (autotrophic and anaerobic medium, $T°C > 60$ °C, $CO_2 + H_2$ atmosphere), the microorganisms were placed in a silica-saturated medium in order to study the evolution of both cells and biofilms exposed to silica. SEM observations showed that the *M. jannaschii* cells themselves are not preserved but that the extracellular polymeric substances (EPS) were silicified. In order to verify and better understand these results, other species, including *Pyrococcus abyssi*, and other hyperthermophilic Archaea, were silicified in the same way. In that case, cells as well as EPS were preserved, although actual silicification of the cells still needs to be confirmed by TEM. These results suggest that differences between species have a strong influence on the potential for different microorganisms to be preserved by fossilization. This experiment provides valuable insight into the silicification and preservation processes of the kind of microorganisms that could have existed on the early Earth. Knowledge of these mechanisms can be helpful for the search and the identification of microfossils in both terrestrial and extraterrestrials rocks, and in the particular case of Mars.