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Planetary Environments: Scientific Issues and Perspectives

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In the frame of the EPOV programme, the exploration of planetary environments is driven by the following question: what are the planetary environments where conditions are best suited for habitability? A first condition is given by the possible presence of liquid water. This condition allows us to define two kinds of media: (1) the atmospheres of solid (exo)planets with a temperature typically ranging between 0°C and 100°C, and (2) the interiors of icy bodies (outer satellites or possibly exosatellites) where the pressure and temperature would fit the liquid phase region of the water phase diagram. In the solar system, targets of interest are Mars and the outer satellites; outside the solar system, we are looking for temperate exoplanets located in the "habitable zone" (not excluding possible icy exosatellites which would remain to be discovered).
In the case of Mars, significant progress has been achieved over the past years about our understanding of the history of water and the presence of liquid water at the surface in the past, thanks to the findings of Mars Express, the Spirit and Opportunity rovers, and Mars Reconnaissance Orbiter; the exploration of Mars goes on with the Curiosity rover, in operation since August 2012. A similar progress is observed in the study of the outer satellites with the on-going operation of the Cassini mission. In the case of the exoplanets, new discoveries are reported almost every week, especially with the Kepler mission, in operation since 2009. With the emergence of transit spectroscopy, which now allows us to probe the atmospheric composition and structure of the exoplanets, a new phase of exoplanets' exploration has started, their characterization, opening the new field of exoplanetology.
In the future, new perspectives appear: following Curiosity, the MAVEN and ExoMars missions to Mars; following Cassini on Saturn, the JUNO and JUICE missions to the Jupiter system; in the case of exoplanets, following CoRoT, Kepler and the HST, new missions are in preparation for detecting exoplanets (Cheops, TESS, PLATO) and characterizing their atmospheres (FINESSE, JWST, EChO).

UV absorption cross section at high temperature

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The evolution of observational techniques paved the way for the study of other planetary systems than our solar system. One of the major advances in recent years is the opportunity to study the composition of their atmospheres thus providing information on their origin and evolution. Hot Jupiters are the first exoplanets of which we can constrain, through the observation, the atmospheric composition. They are gas giant planet with masses of the same order as the one of Jupiter and they transit very close from their star. Their atmospheric temperature is very high (1000-2000 K) and they received a UV flux 10 000 times more intense than the one received by Jupiter.

Understanding the composition and the evolution of their atmospheres requires a time-dependent photochemical model, including photodissociations by the intense UV flux, the chemical kinetics at high temperature and transport processes. We have developed such a model, as well as tools to simulate observations with current and future instruments.

The first step of this work was to construct a chemical scheme adapted to the high temperatures and the high irradiation of these hot exoplanets. Then, thanks to a funding of the PIR-EPOV, we have developed an experiment to determine the absorption cross section of the main molecules of these atmospheres in order to characterize their temperature dependence and to study their impact on thermo-photochemical models.

During the campaigns of measurement performed on a synchrotron, we measured that the UV absorption cross-section increases significantly with the temperature, especially at high wavelength (> 160 nm). For example, for CO2 and at 190 nm, the increase is of two orders of magnitude between room temperature and 750 K. In the future, we plan to continue these studies on other important molecules such as water vapor or ammonia.

The impact of these changes on the model outputs is important to better understand the specific chemistry of the upper atmosphere of these planets so special.

The Grand Tack: A new model for the formation of the inner Solar System and its implications for Earth's growth and water acquisition

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Simulations of planet formation have failed to reproduce Mars' small mass (compared with Earth) for 20 years. Here I will present a solution to the Mars problem that invokes large-scale migration of Jupiter and Saturn while they were still embedded in the gaseous protoplanetary disk. Jupiter first migrated inward, then "tacked" and migrated back outward when Saturn caught up to it and became trapped in resonance. If this tack occurred when Jupiter was at 1.5 AU then the inner disk of rocky planetesimals and embryos is truncated and the masses and orbits of all four terrestrial planet are quantitatively reproduced. As the giant planets migrate back outward they re-populate the asteroid belt from two different source populations, matching the structure of the current belt. C-type material is also scattered inward to the terrestrial planet-forming zone, delivering about the right amount of water to Earth on 10-50 Myr timescales.

Extreme life forms: from molecules to cells: Molecular Dynamics Adaptation to Extreme Environments

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Dynamics pertains to forces. Through dynamics, biological molecules adopt a three dimensional fold and motions that are well-adapted to function and activity in their specific environment. Dynamics defines structure and motions through weak forces, including hydrogen bonding, screened electrostatics, those arising from the hydrophobic effect and the Van der Waals interaction, in which the solvent plays a major role. Many organisms have now been discovered that live and thrive in extreme conditions of heat, pressure, salinity that would normally be strongly denaturing for biological macromolecules. Neutron scattering results suggested that macromolecules from the extremophiles display adaptation through molecular dynamics, i.e. residue substitutions that modify internal stabilisation forces and motions.

Organic material in meteorites and the link to the origin of life

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Life requires specific conditions that have been, so far, only proven to meet on Earth. Though the chemical elements required to form living organism (C, H, N, O, S, etc) are widespread in the universe, the molecules that are crucial for Life, like nucleobases or amino acids, may not be so ubiquitous. Carbonaceous chondrites are a class of meteorites rich in organic compounds and host potential precursors for the emergence of Life (organic matter and water). This presentation will describe the main properties of the organic matter recovered from carbonaceous chondrites. However, the isotopic and molecular record in organic compounds is faded by secondary processes that occurred on the parent body of these meteorites. This results in complex signatures that raise multiple questions about the origin of organic compounds in the Solar System.

MICMOC/MICMOS: Photo/Thermo-chemistry of interstellar van der Waals solids and the rise of molecular complexity

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Ices, of well known compositions, are the major carriers of the molecular content of the dense interstellar medium in molecular clouds where planetary systems do ultimately form. In the laboratory, templates of these ices can be tested, thanks to infrared spectroscopy that allows a direct comparison with the spectra of ices in molecular clouds. The natural evolution of these ices (photochemistry and ion driven chemistry) can be simulated. In such simulations, part of these ices is transformed into organic matter, a complex mixture of (macro)-molecules. These organic residues, recovered at room temperature, remain mostly soluble in water, anessentialpoint for possible further prebiotic chemistry.
The MICMOC/MOS experiment allows the building-up of these materials and then, through classical chemical techniques (GC-MS, HPLC, LC-MS), innovative in the sense that they pertain to minute amounts of samples, leads to the analysis of these organic residues. Similarities with organic materials in meteorites are one of the targets of the research presented here. However, the second goal of this experimental approach goes one step further: the presence of large macromolecules that makes them an essential step toward complex chemical systems that may allow, in correct (but still unknown) physical and chemical conditions, the development of auto-catalytic reactions that are a pre-requisite for an efficient prebiotic chemistry. This is the long term goal of MICMOC/MOS. Together with the chemical analysis of primitive meteorites to ensure the astrophysical scenario, this experiment aims answering the challenge «from the inanimate to the animate world», following the ideas recently popularized by A.Pross (2012)
Pross, A. (2012) inWhat is Life? How chemistry becomes biology, Oxford University Press, ISBN 978-019-964101-7

Key steps from the ?RNA World? to the ?DNA World?

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In the « RNA World » hypothesis of the origin of life, RNAs are assumed to be the central macromolecules able to self-replicate by base pairing, conserve information and catalyse the reactions necessary for a primitive metabolism.1-6
Many arguments lead to the idea that RNA predated DNA in Evolution and suggest that DNA is an RNA which has been modified to fit it efficient storage and repair of genetic information.1-6
In the key steps involved in the transition between the RNA World to the DNA World, we can point out two key steps:
(i) the synthesis of 2'-deoxyribonucleotides from ribonucleotides catalysed today by the enzyme ribonucleotide reductase and
(ii) the synthesis of thymine, a base specific for DNA, from uracil which is a base specific for RNA, catalysed today by the enzyme thymidylate synthetase at the 5'-mononucleotide level.

Both enzymes use the sulphur chemistry for achieving their respective catalysis. Probably, the chemistry of sulphide and disulphide ions has played a major role in the chemical evolution at the origins of life. G. Wächtershaüser proposed a surface-based primordial autotrophic catalysis on the negatively charged pyrite surface7 that could have emerged in the «black smokers » environment. In this regard, iron-sulfur redox proteins containing cage-like clusters formed by sulfides and iron ions linked to cysteine residues of the peptidic chain are widely involved in our contemporary metabolism.
In our recent works, we were interested in the possible prebiotic sulphur chemistry able to catalyse the conversion of uracil to thymine, first from models at the nucleoside level and in aqueous solution.
Many enzymatic cofactors may be regarded as molecular fossils of the «RNA World».
We also developed first experiments in order to obtain under prebiotic conditions pyridoxal (vitamin B6) that leads to the key coenzyme pyridoxal phosphate (PLP) able to catalyse seven different enzymatic reactions.
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En quoi la linguistique peut contribuer à la stabilisation d'une néo-discipline comme l'exobiologie

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La linguistique dispose de méthodes et d'outils lui permettant de construire des définitions à partir des usages attestés dans les corpus de textes. La comparaison des usages des quatre principales disciplines impliquées dans l'exobiologie (astronomie, biologie, chimie, géologie) a permis de dégager une catégorisation des fonctionnements sémantiques qui peuvent être conscients ou non-conscients, conflictuels ou non-conflictuel.
On peut penser que ce travail de circonscription du sens pourrait contribuer à la stabilisation de l'exobiologie en tant que nouvelle discipline.

Formation de clathrates hydrates de CO2-SO2 sur Mars primitif

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Nous montrons que la formation de clathrates hydrates mixtes de CO2 et de SO2 sur Mars au Noachien a maintenu la pression de CO2 à une valeur inférieure à 2 bar, et la temperature globale aux alentours de 230 K. Les clathrates piégeant SO2 plus efficacement que CO2, avec un enrichissement de SO2 de deux ordres de grandeur dans la phase solide par rapport à la phase gazeuse, la plus grande partie du soufre rejeté par les volcans au Noachien a du être piégée dans la cryosphère martienne sous forme de clathrates, inhibant la formation de minéraux sulfatés durant toute cette période et empêchant les carbonates de se former en surface, dû à l'acidité des eaux de fonte de la cryosphère riche en SO2. Ce mécanisme pourrait expliquer l'absence de dépôts sulfatés au Noachien. La formation de tels depôts à l'Hespérien, ainsi qu'observés par OMEGA et CRISM, pourrait être la consequence d'une chute de la pression de CO2 au dessous de 2 bars à la transition Noachien tardif- Hespérien, résultant en un rejet massif du soufre volcanique piégé au Noachien vers l'atmosphère, suivie de la precipitation et de la mineralisation du soufre. Ce scenario, dans lequel la formation de particules de sulfate dans l'atmosphère maintient par effet d'albedo une température basse à la surface, renforce l'hypothèse d'un Mars primitif froid et humide.

Chemical pathways to form peptides on the Primitive Earth, and their implication for the emergence of homochirality.

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In this contribution, starting from a set of molecules that could have been available on the early earth, we will present a chemical reactor capable of promoting amino acid activation and condensation, allowing their elongation into oligopeptides that could accumulate in environments considered as favorable to the emergence of life.
This chemical reactor encompasses a diversity of possible pathways leading to peptide formation either under oxidizing conditions (with the assistance of nitrogen oxides) [1] or under reductive ones [2], with cyanic acid and cyanate (or its precursor, urea) and amino acids as the only required starting materials. Through these reaction path, amino acids could be activated and condensed into oligopeptides which once formed, can be elongated at theirN-terminal residue [1]. We have subsequently shown that under certain conditions the amino terminus can react with cyanic acid which limits peptide elongation to short peptide chains [2]. To overcome these limitations to peptide elongations, reagents could be available to enable an elongation that no longer takes place at theN-terminal residues, but atC-terminal residues through aC-terminal activation [3].
Furthermore, because our scenario is formed of a cyclic sequence of reactions with continuous flow of energy and matter [4], we investigate its possible implications in the prebiotic emergence of homochirality. The ability of this scenario to drive the prebiotic pool towards homochirality (e.g. through the amplification of small enantiomeric excess) relies on the combined stereoselectivity at different stages such as the stereoslectivities of polymerizations, epimerizations and depolymerisations [4]. Computer-simulated kinetics [5] showed that for some sets of the above stereoselectivity factors, the racemic state is unstable, the system being irreversibly driven towards homochirality though it does not involve direct autocatalysis but network autocatalysis. Experimental investigation in order to better understand the phenomenon are in progress [6].

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Analyses des composés organiques volatiles et des résidus organiques réfractaires provenant du réchauffement d'analogues de glace cométaire/interstellaire

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Comprendre l'évolution chimique de la matière organique au sein des environnements astrophysiques nous donne des indices sur la composition chimique de la matière organique qui peut avoir ensemencé les planètes telluriques, et plus loin l'origine des systèmes biochimiques sur Terre. La matière organique présente dans les nuages moléculaires denses sous forme de manteaux de glace à la surface des grains interstellaires va évoluer et pouvoir se retrouver au sein de systèmes planétaires. Tout au long de cette évolution, de nouvelles et plus complexes molécules sont formées grâce à divers processus énergétiques, notamment par irradiation UV et effets thermiques. Les petits corps du système planétaire (astéroïdes et comètes) vont éventuellement servir de réservoir pour cette matière organique, et être des vecteurs pour délivrer celle-ci à la surface de planètes telluriques comme la Terre primitive. Par conséquent, il y a probablement un lien entre les molécules contenues dans les grains cométaires ou météoritiques, et les molécules présentes dans les grains interstellaires du nuage moléculaire dense primitif, et ce sont ces relations que nos expériences en laboratoire essayent d'établir, en simulant les processus d'évolution de ces glaces ou grains interstellaires. Cette contribution se concentre sur deux aspects de nos travaux, qui concernent pour l'un l'analyse des résidus réfractaires formés à partir de l'irradiation UV d'analogues de glaces, le projet RAHIIA ; et pour l'autre un nouveau projet qui sera développé courant 2013 et qui a pour objectif l'analyse des composés organiques volatiles provenant du réchauffement de ces mêmes analogues, le projet VAHIIA (ANR 2013-2016). La compréhension de la formation et de la constitution des résidus réfractaires, généralement appelés "Yellow Stuff", est une étape importante pour établir quelle sorte de matière organique pourrait être disponible au sein d'objets interplanétaires tels que les comètes ou astéroïdes, et donc disponible pour le développement d'une chimie prébiotique à la surface de planètes telluriques. Nous présenterons ici les premiers résultats obtenus par analyse en spectrométrie de haute résolution spectrométrie (LTQ-Orbitrap) de ces résidus. Ces analyses montrent que ces résidus sont composés de molécules de hauts poids moléculaires ($m / z > 4000$), et de compositions élémentaires moyennes H/C=1.6 ;N/C=0.4 ; O/C=0.4. En outre, ce type d'analyse permet la recherche de molécules spécifiques. Nous avons ainsi identifié différents dérivés de l'hexaméthylènetétramine (HMT) qui confirment les observations antérieures. Dans une seconde partie, nous présenterons le concept du projet VAHIIA qui permettra d'apporter de plus amples informations sur les molécules susceptibles de sublimer lors du réchauffement des glaces interstellaires et cométaires, ainsi qu'une meilleure compréhension des processus chimiques à l'origine de la formation des résidus réfractaires.

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