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Editors

Strategies of Life Detection

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Cover illustration: The image shows a vertical profile of a large conical stromatolite with a small column developed on its flank, from the c. 3.4 Ga Strelley Pool Chert, Kelly Group, 'Trendall locality', northeast Pilbara, Western Australia. The small divisions on the scale are each 1 cm. Image courtesy of The Geological Survey of Western Australia, Department of Industry and Resources. © State of Western Australia 2008.

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SUMMARY

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Foreword

**J.L. Bada · J. Gomez-Elvira · E. Javaux · M. Rosing ·
F. Selsis · R. Summons · R.M. Bonnet · O. Botta**

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Two of the overarching questions asked in the pursuit of scientific knowledge are: (1) Is there life outside the Earth? and (2) How did life originate on the Earth? Not coincidentally, these questions are major milestones on the roadmap of the new interdisciplinary science field of Astrobiology. A significant part in the quest for answers to these questions requires the involvement of space exploration, either in the form of the deployment of planetary probes to various target objects in the Solar System or of the construction of large telescopes and spectrometers in various orbits around the Earth or the Sun. It does not come as a surprise that space agencies such as NASA or ESA have established programs in support of these missions as well as the development of instruments. In the case of planetary probes, which in the current epoch are mainly focusing on the exploration of Mars, but also include missions to asteroids and comets, the development of *in-situ* instruments to search for traces of past

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or present life has been established. However, the answer to question of how to recognize traces of past or present life is not straightforward and requires multiple pieces of evidence. This is best illustrated by the difficulties to recognize the first traces of life on Earth, where a combination of morphologic, molecular and isotopic biosignatures is applied, even with the whole arsenal of state-of-the-art laboratory instrumentation available for sample analysis. These difficulties are significantly exaggerated when only limited resources in mass and power are available on a robotic lander or rover operating on another planet. In the case of searching for habitable planets around other stars, the problems are of course the large distances to the object and the immense brightness difference between the host star and the planets surrounding it. The major challenges here are to identify appropriate host stars, to acquire photons from the planets without the interference of the host star, and to identify spectroscopic biosignatures that would provide strong evidence for habitability or even the presence of life on the planet.

This volume is the result of an ISSI Workshop held in April 2006. An international group of 36 chemists, biologists, geoscientists, paleontologists, instrument developers and astronomers was invited to present their data, debate controversies and identify future challenges in an informal setting. The workshop was convened by Jeffrey L. Bada (Scripps Institution of Oceanography, UCSD), Javier Gomez-Elvira (Centro de Astrobiología), Emmanuelle Javaux (University of Liège), Minik Rosing (Geological Museum Copenhagen), Franck Selsis (then at the University of Lyon), Roger Summons (MIT), Roger M. Bonnet and Oliver Botta (both ISSI). It was our aim to foster interdisciplinary collaboration and exchange by combining information about results, interpretations and challenges in terrestrial paleo-biosignature research with the latest developments regarding *in-situ* and remote sensing instrument techniques. The volume is divided into five chapters. The Introduction and Chap. 2 provide an overview about life in general, theoretical concepts of life detection and some important aspects in Solar System exploration. Chapter 3 is subdivided into three sections on morphological, molecular and isotopic biosignatures, respectively, and discusses in great detail the challenges in the recognition of early life on Earth, in particular during the early Archean eon. The *in-situ* instrumentations are presented in Chap. 4, beginning with a look back to the results of the Viking Biology Experiments, followed by an overview of instruments currently under development and construction, as well as a preview of future life detection concepts. Chapter 5 is dedicated to remote sensing of extrasolar planets and discusses the scientific rationale behind the selection of target stars for future searches as well as current and future astronomical techniques to search and characterize terrestrial exoplanets.

With great pleasure we would like to thank all those who have contributed to this volume and to the workshops in general. First of all, we thank the authors for writing up their contributions. All papers were peer-reviewed by referees, and we would also like to thank all the reviewers for their critical reports. We also thank the directorate and staff of ISSI for selecting this topic for a workshop and for their support in making it happen, in particular Roger M. Bonnet, Brigitte Fasler, Andrea Fischer, Vittorio Manno, Saliba F. Saliba, Irmela Schweizer, and Silvia Wenger.



Group photograph (from left to right, nose tip counts): Thierry Fouchet, Jennifer Eigenbrode, Andrew Schuerger, Luc Arnold, Franck Selsis, Margaret Turnbull, Javier Gomez-Elvira, Valentine Wakelam, Paul Mahaffy, Gerhard Kminek, Emmanuelle Javaux, Wladyslaw Altermann, Minik Rosing, Jeffrey Bada, Victor Parro, Christophe Lovis, Peter Gogarten, Antonio Lazcano, Wolfgang Krumbein, Frances Westall, Stephane Udry, Malcolm Fridlund, Roger Bonnet, Francois Raulin, Andreas Quirrenbach, Lynn Rothschild, Beda Hoffmann, David Catling, Jürgen Popp, Sara Seager, Hans Thiele, Shuhei Ono, Oliver Botta, Roger Summons, Alexander Pavlov, and Mark van Zuilen.

Missing: Chris McKay, Francois Forget, Laurence Barron, Nikos Prantzos, and Therese Encrenaz

Introduction

Towards a Definition of Life: The Impossible Quest?

Antonio Lazcano

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Abstract “Life” is an empirical concept whose various definitions and phenomenological characterizations depend on historical frameworks. Although analysis of existing literature suggests that attempts to define life will remain, at best, a work in progress, the history of biology shows that some efforts have been more fruitful than others. There is a major distinction between natural selection—which is clearly a defining trait of biology—and the changes that result from purely physical chemical evolution, which can be observed in non-biological complex systems. Accordingly, it can be concluded that life cannot be understood without considering the presence of genetic material and Darwinian evolution. This shows the usefulness of the suggestion that life can be considered as a self-sustaining chemical system (i.e., one that turns environmental resources into its own building blocks) that is capable of undergoing natural selection.

Keywords Life’s definition · Autopoiesis · Complexity · Natural selection

1 Introduction

Perhaps as never before in the history of science, “life” has been transformed into a value-ridden term that sits in the center of a tense debate, as shown by the (not always well informed) discussions on abortion, euthanasia, transgenic organisms, and synthetic biology, to name just a few. In spite of the spectacular developments in our understanding of the molecular processes that underlie biological phenomena, we still lack a generally agreed definition of life, and not for want of trying (see, e.g., Rizzoti 1996; Pályi et al. 2002). As Nietzsche once wrote, there are concepts that can be defined, whereas others only have a history. This is not surprising: as argued by Immanuel Kant, precise definitions are achievable in mathematics and philosophy, but empirical concepts such as “life” can only be made explicit (cf. Fry 2002) in ways that are strongly dependent on historical circumstances. Eighty years ago, for instance, when the role of nucleic acids was largely

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unknown, proposals on the emergence of life included a wide array of possibilities based on the random emergence of autocatalytic enzymes, on autotrophic “protoplasm,” and on the step-wise evolution of heterotrophic microbes from gene-free coacervates (cf. Lazcano 1995).

It has been argued by many that attempts to define life may be a useless endeavor, bound to fail (Cleland and Chyba 2002). Indeed, attempts to address the definition of living systems have often led to nothing more than phenomenological characterizations of life, which are then reduced to a mere list of observed (or inferred) properties. These inventories are not only unsatisfactory from an epistemological viewpoint, but may also become easily outdated and may fail to provide criteria by which the issue of life (and its traces) can be defined (Oliver and Perry 2006). This can become an unsolved burden for biological sciences, as shown, for instance, by the intense debates on the ultimate nature of the microscopic structures in the Martian meteorite Allan Hills 84001, or those found in early Archean sediments and that not all accept as fossils.

2 Life as a Self-Sustaining System

Since the nineteenth century, metabolism has been recognized as a central trait of life, a conclusion that has led us to consider viruses and other subcellular biological entities as nonliving. The recognition that life’s continuous production of itself is based on networks of anabolic/catabolic reactions and energy flow led Maturana and Varela (1981) to define life as an autopoietic system, i.e., as an entity defined by an internal process of self-maintenance and self-generation. As shown by Bernal’s (1959) statement that “[life is] . . . the embodiment within a certain volume of self-maintaining chemical processes,” the idea of autopoiesis is not without historical precedents. As discussed in the following, however, for Bernal and some of his contemporaries like Oparin, the ultimate nature of living systems could not be understood in the absence of an evolutionary perspective (Lazcano 2007).

Although autopoiesis refers and is limited to minimal life forms (Luisi et al. 1996), it is a concept largely dependent on the existence of metabolism, which is a trait common to all living beings. Cells and organisms made of cells are autopoietic and metabolize continuously, and in doing so continuously affect the chemical composition of their surroundings (Margulis and Sagan 1995). Multicellular organisms, on the other hand, consist of units that are living systems in themselves, and will remain so even if the entire system is destroyed (Szathmáry et al. 2005). This is illustrated, for instance, by the extraordinary success of organ transplants.

There are a number of physical and chemical analogues that have been considered autopoietic and that mimic some of the basic properties of life. One of the most enticing examples is that of the self-replicating micelles and liposomes described by Pier Luigi Luisi and his associates. For instance, synthetic vesicles formed by caprylic acid containing lithium hydroxide and stabilized by an octanoid acid derivative have been shown to catalyze the hydrolysis of ethyl caprylate. The resulting caprylic acid is incorporated into the micelle walls, leading to their growth and, eventually, to their fragmentation, during several “generations” (Bachmann et al. 2002).

However surprising, replicative micelles and liposomes do not exhibit genealogy or phylogeny. Albeit due to different processes, the same is true of prions, whose multiplication involves only the transmission of phenotypes due to self-perpetuating changes in protein conformations. As underlined by Orgel (1992) these systems replicate without transmission of information, i.e., they lack heredity. This is in sharp contrast to living beings. Organisms

may be recognized as the ultimate example of autopoietic systems (Margulis and Sagan 1995). However, the properties that form the basis of the self-sustaining abilities of living beings are the outcome of historical processes, and it is somewhat difficult for biologists to accept a definition of life that lacks a Darwinian framework. Regardless of their complexity, all living beings have been shaped by a lengthy evolutionary history, and since life is neither the outcome of a miracle or of rare chance event, proper understanding of the minimal properties required for a system to be considered alive require the recognition of the evolutionary processes that led to it. The appearance of life was marked by the transition from purely chemical reactions to autonomous, self-replicating molecular entities capable of evolving by natural selection. How did this take place? At what point in time was the difference between a chemical system and the truly primordial, first organisms, established?

3 Life and the RNA World

The lack of an all-embracing, generally agreed definition of life sometimes gives the impression that what is meant by its origin is defined in somewhat imprecise terms, and that several entirely different questions are often confused. For instance, until a few years ago the origin of the genetic code and of protein synthesis was considered synonymous with the appearance of life itself. This is no longer a dominant point of view: four of the central reactions involved in protein biosynthesis are catalyzed by ribozymes, and their complementary nature suggest that they first appeared in an RNA world, i.e., that ribosome-catalyzed, nucleic acid-coded protein synthesis is the outcome of Darwinian selection of RNA-based biological systems, and not of mere physico-chemical interactions that took place in the prebiotic environment.

The discovery and development of the catalytic activity of RNA molecules, i.e., ribozymes, has given considerable support to the idea of the “RNA world,” a hypothetical stage before the development of proteins and DNA genomes. During this stage, alternative life forms based on ribozymes existed. This does not imply that wriggling autocatalytic nucleic acid molecules were floating in the waters of the primitive oceans, ready to be used as primordial genes, or that the RNA world sprung completely assembled from simple precursors present in the prebiotic soup. In other words, the genetic-first approach to life’s emergence does not necessarily imply that the first replicating genetic polymers arose spontaneously from an unorganized prebiotic organic broth due to an extremely improbable accident, or that the precellular evolution was a continuous, unbroken chain of progressive transformations steadily proceeding to the first living beings. Many prebiotic cul-de-sacs and false starts probably took place, with natural selection acting over populations of primordial systems based on genetic polymers simpler than RNA, in which company must have been kept by a large number of additional organic components such as amino acids, lipids and sugars of prebiotic origin, as well as a complex assemblies of clays, metallic ions, etc.

However, it is true that the arguments in favor of an RNA world have led many to argue that the starting point for the history of life on Earth was the *de novo* emergence of the RNA world from a nucleotide-rich prebiotic soup, or in the origin of cryptic and largely unknown pre-RNA worlds. Not all accept these possibilities: there is a group of scientists that favors the possibility that life is a self-maintaining emergent property of complex systems that may have started with the appearance of self-assembled autocatalytic metabolic networks initially lacking genetic polymers (Kauffman 1993).

These different viewpoints reflect a rather sharp division that emerged between those who favor (1) the idea that life is an emergent interactive system endowed with dynamic properties that exist in a state close to chaotic behavior, and (2) those who are reluctant to adhere

to a definition of living systems lacking of a genetic component whose properties reflect the role that Darwinian natural selection and, in general, evolutionary processes, have played in shaping its the central characteristics. From a biologist's viewpoint, however, neither the nature of life nor its origin can be understood in the absence of an evolutionary approach.

4 Complexity and the Nature of Life

In a way, current attempts to explain the nature of life on the basis of complexity theory and self-assembly phenomena can be understood as part of the deeply rooted intellectual tradition that led physicists to search for all-encompassing laws that can be part of a grand theory, one that encompasses many, if not all, complex systems (Fox Keller 2002). Unfortunately, in some cases invocations of spontaneous generation appear to be lurking behind appeals to undefined "emergent properties" or "self-organizing principles" that are used as the basis for what many life scientists see as grand, sweeping generalizations with little, if any, relationship to actual biological phenomena (Fenchel 2002).

Self-assembly is not unique to biology, and may indeed be found in a wide variety of systems, including cellular automata, the complex flow patterns of many different fluids such as tornadoes, cyclic chemical phenomena (such as the Belousov–Zhabotinsky reaction, and the formose reaction, for instance), and in the autoorganization of lipidic molecules in bilayers, micelles, and liposomes. There are indeed some common features among these different self-organized systems, and it has been claimed by a number of theoreticians that they follow general principles that are in fact equivalent to universal laws of nature. Perhaps this is true. The problem is that such all-encompassing principles, if they exist at all, have so far remained undiscovered (Farmer 2005). This has not stopped a number of researchers from attempting to explain life as a continuously renewing, complex interactive system that emerged as self-organizing metabolic cycles that did not require genetic polymers. It is unfortunate that many proposals on an autotrophic origin of life and of living systems as complex systems on the verge of chaos have turned out to be creative guesswork or empty speculation.

However, complexity models have promised much but delivered little. Evidence for the spontaneous origin of catalytic system and of metabolic replication would indeed be exciting (Kauffman 1993) if it could be established. It is true that under given conditions the self-organization of lipidic molecules into liposomes, for instance, can lead to the spontaneous formation of microenvironments which may have had significant roles in the emergence of life. But they are not alive, even if they replicate.

Prebiotic organic compounds very likely underwent many complex transformations, but there is no evidence that metabolic cycles could spontaneously self-organize, much less replicate, mutate, and evolve. Theories that advocate the emergence of complex, self-organized biochemical cycles in the absence of genetic material are hindered not only by the lack of empirical evidence, but also by a number of unrealistic assumptions about the properties of minerals and other catalysts required to spontaneously organize such sets of chemical reactions (Orgel 2000). However complex, systems of chemical reactions such as the formose reaction are not adapted to ensure their own survival and reproduction; they just exist. Life cannot be reduced to one single molecule such as DNA or a population of replicating ribozymes, but current biology indicates that it could not have evolved in the absence of a genetic replicating mechanism ensuring the stability and diversification of its basic components.

5 The (Evolutionary) Emergence of Life

Following his 1946 conversations with Einstein on the underlying biochemical unity of the biosphere, John D. Bernal wrote that "... life involved another element, logically different from those occurring in physics at that time, by no means a mystical one, but an element of *history*. The phenomena of biology must be ... contingent on events. In consequence, the unity of life is part of the history of life and, consequently, is involved in its origin" (cf. Brown 2005). History, in biology, implies genealogy and, in the long term, phylogeny. This requires an intracellular genetic apparatus able to store, express and, upon reproduction, transmit to its progeny information capable of undergoing evolutionary change. The most likely candidates for this appear to be genetic polymers.

A good case can thus be made that Darwinian evolution is essential for understanding the nature of life itself. Accordingly, life could be defined as a self-sustaining chemical system (i.e., one that turns resources into its own building blocks) that is capable of undergoing Darwinian evolution (cf. Joyce 1994). Such tentative definition, which was the outcome of a discussion group convened by NASA in the early 1990s, has been rejected by a number of authors who argue on different grounds that a single definition is impossible (Luisi 1998; Cleland and Chyba 2002). Life cannot be defined on the basis of a single trait, but since natural selection is indeed a unique feature of living systems, the basic nature of living systems cannot be understood without it.

The suggestion that life can be understood as a self-sustaining chemical process capable of undergoing Darwinian evolution is consistent with the well-known fact that cyanobacteria, plants, and other autotrophs are not only self-sustaining, but also very much alive. But what about the first life forms? Clearly, if at its very beginning life was already a self-sustaining entity capable of turning external resources into its own building blocks, then it must have been endowed with primordial metabolic routes that allowed it to use as precursors environmental raw materials (such as CO₂ and N₂, for instance). This appears unlikely to many biologists. An alternative possibility is that the first living entities were systems capable of undergoing Darwinian evolution (i.e., endowed with genetic material capable of replication, change, and heredity) whose self-sustaining properties depended on the availability of organic molecules already present in the primitive environment. Although this can be read as an update of the hypothesis of the prebiotic soup and the heterotrophic origin of life, those involved in the study of emergence of living systems have to ponder not just on how replicative systems appeared, but also how they became encapsulated and how metabolic pathways evolved (Lazcano 2007).

6 Conclusions

Research into the origin and nature of life is doomed to remain, at best, a work in progress. It is difficult to find a definition of life accepted by all, but the history of biology has shown that some efforts are much more fruitful than others. As Gould (1995) once wrote, to understand the nature of life, we must recognize both the limits imposed by the laws of physics and chemistry, as well as history's contingency. It is easy to understand the appeal of autopoiesis and complexity theory when attempting to understand the basic nature of living systems. However, there is no evidence indicating how a system of large or small molecules can spontaneously arise and evolve into nongenetic catalytic networks. It is true that many properties associated with cells are observed in nonbiological systems, such as catalysis, template-directed polymerization reactions, and self-assembly of lipidic molecules

or tornadoes. Like fire, life can multiply and exchange matter and energy with its surroundings. It is true that living systems are endowed with properties of autopoietic, self-organized replicative systems. However, there is a major distinction between purely physical–chemical evolution and natural selection, which is one of the hallmarks of biology. In spite of many published speculations, life cannot be understood in the absence of genetic material and Darwinian evolution.

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The Solar System

Infrared Spectroscopy of Solar-System Planets

Thérèse Encrenaz

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Abstract Most of our knowledge regarding planetary atmospheric composition and structure has been achieved by remote sensing spectroscopy. Planetary spectra strongly differ from one planet to another. CO₂ signatures dominate on Mars, and even more on Venus (where the thermal component is detectable down to 1 μm on the dark side). Spectroscopic monitoring of Venus, Earth and Mars allows us to map temperature fields, wind fields, clouds, aerosols, surface mineralogy (in the case of the Earth and Mars), and to study the planets' seasonal cycles. Spectra of giant planets are dominated by H₂, CH₄ and other hydrocarbons, NH₃, PH₃ and traces of other minor compounds like CO, H₂O and CO₂. Measurements of the atmospheric composition of giant planets have been used to constrain their formation scenario.

Keywords Planetary atmospheres · Infrared spectroscopy

1 Introduction

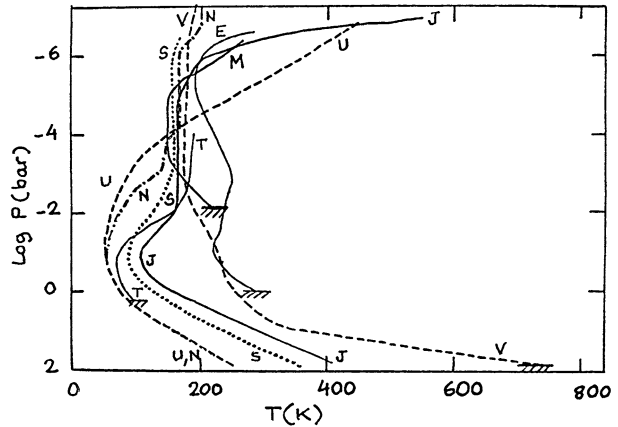
Remote sensing spectroscopy is a powerful tool for investigating the atmospheres and surfaces of solar-system planets. Spectroscopic signatures of gaseous atmospheric components can be found over the whole range of the electromagnetic spectrum. In the UV, visible, and near-IR range—typically below 4 μm—the planetary spectrum corresponds to the reflected solar blackbody, peaking at 0.5 μm, over which planetary absorption features can be observed. These signatures allow us to determine the nature and the column density (the number of molecules integrated along the line of sight) of the different atmospheric constituents—the clouds, the aerosol particles and the characteristics of the surface, if there is any.

At longer wavelengths, the planetary spectrum corresponds to its thermal emission; its maximum depends upon the effective temperature of the planet, and is thus, to first order,

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Fig. 1 The thermal structure of planetary atmospheres



a function of its heliocentric distance. It should be noted that the real temperature also depends strongly on the planetary atmosphere and on internal heat source, and is not a clear function of distance. The Earth, with an effective temperature T_e of 288 K, shows a maximum blackbody emission around $10 \mu\text{m}$, while Uranus and Neptune, for which $T_e = 58 \text{ K}$, have a peak of about $60 \mu\text{m}$. Unlike its reflected solar spectrum, the thermal spectrum of a planet depends a great deal on its temperature structure. Its analysis provides information on the nature and the vertical distribution of the atmospheric constituents, but can also be used in some cases for a retrieval of its temperature structure. Depending upon the temperature lapse rate (Fig. 1), infrared lines can appear either in absorption (in the tropospheres, where the gradient is negative) or in emission (in the stratospheres of the giant planets and Titan, where the gradient is positive). In some cases, gaseous atmospheric species can also be observed in fluorescence (usually resonant fluorescence by the solar flux). Finally, planetary spectra can also be diagnostic of solid or liquid signatures, either due to clouds and aerosols, suspended in the atmosphere, or to the surface itself.

Remote sensing spectroscopy, from the ground and/or from space (in particular with the Voyager 1 and 2 spacecrafts), has provided most of the information we have about the atmospheric composition and structure of the giant planets and Titan. Only recently have we gained access to in situ measurements, in the case of Jupiter with the Galileo probe, and in the case of Titan with the Huygens probe. Mars and Venus, in contrast, have been extensively explored with in situ spacecraft. In the case of Mars these spacecraft were Viking, Mars Pathfinder, and the rovers Spirit and Opportunity; in the case of Venus, Pioneer Venus and the Venera probes. Still, important information regarding their atmospheres and Mars' surface has been obtained by remote sensing spectroscopy, from the ground and from aboard orbiters (in particular the Venera spacecraft, Pioneer Venus Orbiter, Mariner 9, Viking, Mars Global Surveyor, Mars Odyssey, Mars Express, and, more recently, Mars Reconnaissance Orbiter and Venus Express).

This paper discusses the main questions dealing with the formation and evolution of planetary atmospheres, with special emphasis on those which have been addressed by remote sensing spectroscopy, either from the ground or from space. We will focus on infrared spectroscopy which has been the prime tool for investigating the physical and chemical properties of neutral atmospheres.

2 Terrestrial Planets and Giant Planets

This section briefly reviews the main properties of the solar-system planets. These planets fall naturally into two main categories (Table 1): the terrestrial planets (Mercury, Venus, Earth and Mars), and the giant planets (Jupiter, Saturn, Uranus and Neptune). The former “planet” Pluto, is now recognized as one of the biggest representatives of a new, recently discovered category, the trans-neptunian objects, which populate the Kuiper belt beyond the orbit of Neptune. The terrestrial planets, relatively close to the Sun ($R_h < 2$ AU), are characterized by a small size, a large density, and a small number of satellites. Their atmosphere, if present, is only a negligible fraction of their total mass. Beyond 5 AU, the giant planets are characterized by a large volume, a small density, and a large number of satellites; their atmosphere, by mass, is a significant fraction of their total mass. It is possible to understand these basic properties in the light of the formation model of the solar system, widely accepted today. This scenario, initiated by two pioneers, Kant and Laplace, is based on the observations of the planetary orbits, all almost coplanar and quasi-circular around the Sun, with planets orbiting counter-clockwise, as the Sun does.

These rotational properties strongly suggest the formation of planets within a disk, product of the gravitational collapse of a rotating nebula; this scenario is now supported by the observation of many protoplanetary disks around nearby stars. At the disk center, matter contracts to form the proto-Sun. Within the disk, solid particles accrete, following instabilities, and grow into aggregates through multiple collisions. The biggest objects grow further as they sweep the nearby material. After a few millions years (or a few tens of millions at

Table 1 Orbital and physical properties of the solar-system planets

Planet	R_h (AU)	Mass (M_E)	Density (g/cm^3)	T_s/P_s (K/bar)	Atmospheric composition
Mercury	0.39	0.055	5.43	90–700/NA	N/A
Venus	0.72	0.815	5.24	730/92	CO ₂ , N ₂ + traces SO ₂ , H ₂ O, Ar, CO, ...
Earth	1.00	1.000	5.52	288/1	N ₂ , O ₂ , + H ₂ O + traces Ar, CO ₂ , ...
Mars	1.52	0.107	3.93	150–300/ 0.006	CO ₂ , N ₂ , Ar + traces O ₂ , CO, H ₂ O, ...
Jupiter	5.20	317.8	1.33	110 @ 0.1	H ₂ , He, CH ₄ , + traces NH ₃ , H ₂ O, PH ₃ , ...
Saturn	9.54	95.2	0.69	90 @ 0.1	H ₂ , He, CH ₄ , + traces PH ₃ , H ₂ O, ...
Uranus	19.19	14.4	1.32	55 @ 0.1	H ₂ , He, CH ₄ , + traces H ₂ O, ...
Neptune	30.07	17.2	1.64	55 @ 0.1	H ₂ , He, CH ₄ , + traces H ₂ O, ...

most), the planets are mostly formed, and the smallest particles of the disk are dissipated by the strong solar wind associated with the T-Tauri phase of the early Sun (so-called in reference to the star where this phenomenon was first observed).

How can we explain the difference between terrestrial and giant planets? As a first approximation, it is linked to the amount of solid material available at a given heliocentric distance to form a planet. The disk is made of primordial interstellar matter, that is, mostly hydrogen (and helium), and all other elements (altogether close to one percent in mass) with their cosmic abundances: first come O, C and N, and the heavier elements are less and less abundant. Near the Sun ($R_h < 2$ AU), where the temperature is several hundred K, only silicates and metals are in solid form; the solid mass available for planetary cores is thus limited. Thus, a few small, rocky planets, can be formed. In contrast, at larger heliocentric distances ($R_h > 4$ AU), the most abundant molecules (after H_2 : H_2O , CH_4 , NH_3 , ...) are no more gaseous, but in condensed form. They are thus available to be incorporated into big nuclei, which can reach about 10 terrestrial masses. Then, theoretical models (Mizuno 1980; Pollack et al. 1996) predict the collapse of the surrounding gas, mostly H_2 and He. This collapse leads to the formation of big planets, of low density, surrounded by a system of satellites and rings formed within their own subnebulae. The limit between the two classes of planets is the “snow line”, at the level of H_2O condensation. It was probably at 4–5 AU at the time of planetary formation, when the disk was warmer than today; it is now at about 2 AU. Following the pioneering work of Mizuno (1980) and Pollack et al. (1996), many new models of giant planet formation have been proposed, some of them suggesting a different formation through disk instabilities which grow into protoplanets (Boss 2000, 2001, 2002), and most of the others still favouring the accretion-collapse model (Hersant et al. 2004; Owen and Encrenaz 2006) and including migration processes (Alibert et al. 2005).

The core-accretion formation scenario described earlier explains well why terrestrial planets are found in the vicinity of the Sun, while giant planets are found at greater heliocentric distances. It was thus a major surprise when, over the past decade, a large number of giant exoplanets were discovered in the immediate vicinity of their star. This strongly suggests that the formation scenario of the solar system is not ubiquitous in the Universe. Which mechanisms could explain how giant exoplanets are so close to their star? Most scientists now favor a formation at large astrocentric distance, in a cold environment, followed by a migration mechanism induced by interactions between the planet and the disk. This question is currently a subject of very active research.

The formation scenario of solar-system planets allows us to understand, to first order, the basic chemical composition of planetary atmospheres. In the protoplanetary disk, carbon and nitrogen can either be in the form of CO and N_2 (at high temperature and/or low pressure) or in the form of CH_4 and NH_3 (at low temperature and/or high pressure) (Fegley et al. 1991). CH_4 and NH_3 probably formed preferentially in the sub-nebulae of the giant planets, which explains why these components are observed in their atmospheres. In contrast, CO and N_2 were dominant in the environments of the terrestrial planets. In both cases, H_2O must have been present. CO in turn reacted with H_2O to form CO_2 , which explains the main atmospheric composition of the terrestrial planets. There are still many unsolved questions, however. The origin of water in terrestrial planets is still unclear. A major question is the diverging evolution of the atmospheres of the terrestrial planets, with the disappearance of most of H_2O on Mars and Venus, and the very tiny and dry present atmosphere of Mars.

An important parameter for the study of planet formation and evolution is the D/H ratio, which can be measured spectroscopically from the analysis of deuterated atmospheric species. In the case of terrestrial planets, D/H is retrieved from the HDO/ H_2O abundance ratio, and provides key information on the history of water in these planets (see Sect. 3.1).

In the case of the giant planets, D/H is inferred from the HD/H₂ and CH₃D/CH₄ abundance ratios, and provides information about the relative mass fraction of their icy core (see Sect. 4.3).

A special mention has to be made about Titan, Saturn's largest moon. Titan is the only satellite with a dense atmosphere; its surface pressure is 1.5 bar and its atmospheric composition is dominated by nitrogen. These similarities with the terrestrial atmosphere have raised considerable interest in this object, which has been explored in situ by the Cassini-Huygens space mission. The spectrum of Titan is discussed in Sect. 4.

3 The Terrestrial Planets

Mercury, the smallest terrestrial planet, is too small and too close to the Sun to retain a permanent atmosphere: indeed, the escape velocity is small because of its small gravity field, and the thermal velocity of molecules is large because of its high temperature. The three other terrestrial planets, Venus, the Earth and Mars, show a striking similarity in their primordial chemical composition (mostly CO₂ with a few percent of N₂), and probably in all cases a large fraction of H₂O. The current atmospheric composition of Venus and Mars is dominated by CO₂, with a few percent of N₂. There are important differences in the case of the Earth: water has been kept in the oceans where CO₂ was trapped, and oxygen has appeared as a result of the development of life. The physical properties of the atmospheres (Table 1) are very different, with a surface pressure ranging from about 90 bars (Venus) to 6 mbars (Mars), and a surface temperature ranging from 730 K (Venus) to about 210 K (Mars). In between, the Earth appears to have the best conditions ($P_S = 1$ bar, $T_S = 288$ K) to keep its water reservoir in the liquid form, a decisive condition for the development of life.

The high surface temperature of Venus is significantly above its effective temperature, that is, its expected equilibrium temperature in view of its heliocentric distance. Indeed, the surface and the lower atmosphere of Venus have been heated by a runaway greenhouse effect, initiated by the large amounts of gaseous CO₂ and H₂O which were most likely present in the primordial atmosphere (see Sect. 3.1). In the case of Earth, water was trapped in the oceans and CO₂ was dissolved in the form of calcium carbonate (CaCO₃), so that the greenhouse effect remained moderate. With about 0.1 terrestrial mass, Mars probably had a primordial atmosphere which was less dense than the two others, although probably denser than today, as measured by D/H (see Sect. 3.1). A moderate greenhouse effect may have taken place in the first billion years, but strongly decreased afterward.

As a result, the three planets appear very different today. Venus is covered by a thick cloud deck of sulfuric acid H₂SO₄, at an altitude of 40–60 km, which prevents the visible observation of the surface. The Earth is the only planet to host water in its three phases, gaseous, solid and liquid; it is the only atmospheric condensable species. On Mars, H₂O and CO₂ are present in the solid and gaseous form (with very tenuous traces of water vapor). Most of the ices are trapped in the polar caps, but clouds of H₂O (and occasionally CO₂) are also present.

3.1 The Reflected Solar Spectrum

Reflected solar spectra provide information on atmospheric composition, but also on aerosol and surface properties. In the visible and the near-IR range, the reflected spectrum exhibits signatures of CO₂, H₂O and CO, and traces of CH₄, N₂O and O₃ in the case of Earth. In the

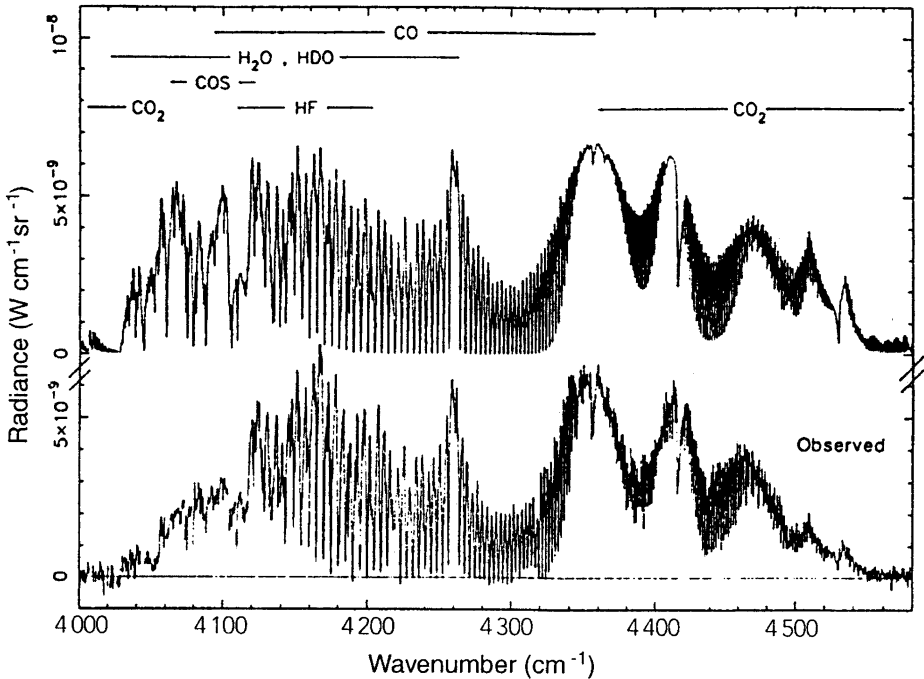


Fig. 2 The 2.3- μm region in the dark side of Venus (Bézard et al. 1990). *Upper curve*: synthetic spectrum; *lower curve*: observed spectrum. Spectral signatures of CO_2 , CO, H_2O , HDO, HF and OCS are detected

latter case, water vapor signatures are by far the strongest ones. Weaker absorptions of CO_2 , CH_4 , O_3 , N_2O and CO are also detected (Drossart et al. 1993), as well as a wide variety of signatures associated with surface mineralogy. With the increasing interest in the search for Earth-like exoplanets, terrestrial spectra have received a lot of attention from scientists (see Arnold, this issue).

The reflected solar spectrum of Venus, observed on the dayside, probes the middle atmosphere above the sulfuric cloud level, at a pressure of about 1 bar. In the case of Mars, the lines are very narrow, because the Lorentz broadening (proportional to the pressure) is very small. Thus, very high spectral resolution is required to search for minor species. For example, measurements of the D/H ratio on Mars (from HDO/ H_2O) have been made by means of high-resolution ground-based spectroscopy (Owen et al. 1988; Krasnopolsky et al. 1997). The results indicated a deuterium enrichment by a factor 5–6, interpreted as the signature of a differential atmospheric escape over the planet's history (with HDO escaping less easily than H_2O), and thus a denser primitive atmosphere. Tentative detections of methane were reported in 2004 (Krasnopolsky et al. 2004; Mumma et al. 2004; Formisano et al. 2004), with two of them using high-resolution spectrographs on ground-based telescopes, and the third using PFS on Mars Express.

3.2 The Thermal Spectrum

Venus presents a very peculiar property: while planetary thermal spectra usually dominate beyond 3–4 μm , the thermal emission of Venus is detected at much smaller wavelengths, down to about 1 μm , because of its very high surface temperature. This emission, detectable

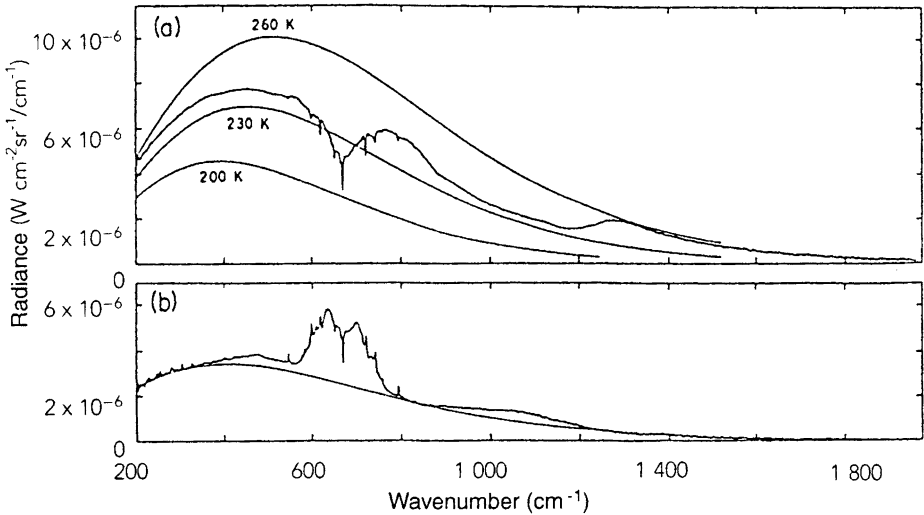


Fig. 3 The thermal spectrum of Mars (Hanel et al. 1992). The main atmospheric feature is the CO_2 band at $15 \mu\text{m}$. *Upper curves*: spectrum at mid-latitude, where the surface temperature is higher than the atmospheric one. *Lower curves*: Spectrum in a polar region, where the surface is colder than the lower atmosphere. The atmospheric temperature decreases with increasing altitude, which explains the absorption core inside the CO_2 band

only on the night side of the planet, provides an excellent tool for probing the chemical composition of the lower venusian atmosphere. This has been done, in particular, from high-resolution ground-based spectroscopy (Bézard et al. 1990) and led to the discovery and/or study of several minor constituents (CO , H_2O , HDO , SO_2 , OCS , HCl , HF ; Fig. 2). A very high value of D/H (see Sect. 2) was inferred from these data (120 times the terrestrial value), indicating the presence of an abundant primordial reservoir of water on Venus, and a very strong outgassing at the early stages of the planet's history. The near-IR thermal emission of Venus has also been observed by the NIMS imaging-spectrometer at the time of the Galileo flyby (Carlson et al. 1991), and is being presently monitored by the VIRTIS (infrared imaging spectrometer) and SPICAV (suite of UV and IR spectrometers) aboard the Venus Express orbiter.

Beyond $5 \mu\text{m}$, the thermal spectra of Venus, the Earth and Mars are dominated by the strong CO_2 band at $15 \mu\text{m}$. The Venus spectrum refers to the atmosphere above the sulfuric clouds. In addition, the terrestrial IR spectrum shows strong signatures of water vapor (very weakly visible on Mars and absent on Venus) and the strong signature of ozone O_3 at $9.7 \mu\text{m}$. The far-IR spectrum of Mars shows an interesting property: the $15\text{-}\mu\text{m}$ band of CO_2 appears either in absorption or in emission, depending upon the temperature contrast between the atmosphere and the surface (Fig. 3). At mid-latitudes, the surface temperature is higher than the atmospheric temperature, and the band thus appears in absorption. The situation is inverted in the polar regions, where the surface (at 145 K) is colder than the atmosphere.

In the case of Mars, ground-based high-resolution spectroscopy in the IR and submillimeter range allowed us to detect two minor constituents: O_3 around $10 \mu\text{m}$, and H_2O_2 , in the submillimeter range (Clancy et al. 2004) and at $8 \mu\text{m}$ (Encrenaz et al. 2004a). At $8 \mu\text{m}$, high-resolution imaging spectroscopy has led to a simultaneous mapping of H_2O_2 and H_2O (Encrenaz et al. 2005).

4 The Giant Planets

A simple look at the total masses of the giant planets allows us to distinguish two categories. We have seen that the giant planets accreted most likely from an initial core of about 10 terrestrial masses. With masses of 318 and 95 terrestrial masses respectively, Jupiter and Saturn are mostly composed of primordial gas; they are called the gaseous giants. In contrast, Uranus and Neptune—with total masses of 14 and 17 terrestrial masses, respectively—are thought to have more than half of their mass made of their initial icy core; they are called the icy giants.

We have seen that the giant planets' outer envelopes are mostly composed of H_2 and He, with CH_4 and NH_3 as minor constituents. Other minor tropospheric constituents include (in the case of Jupiter and Saturn) H_2O , PH_3 , GeH_4 and AsH_3 . These species cannot be detected in the tropospheres of Uranus and Neptune because they condense around the tropopause level, due to its low temperature. Other minor stratospheric species include the products of methane photodissociation (C_2H_2 , C_2H_6 and several other hydrocarbons), and a few oxygen species (H_2O , CO_2 and CO). The origin of the oxygen source is still under debate: it could be either local (from rings and/or satellites) or interplanetary (from comets and/or micrometeoroids); the recent collision of comet Shoemaker-Levy 9 with Jupiter in July 1994, illustrates that such events may feed the stratosphere with external species (Noll et al. 1996). CO is a special case, which may be of both internal and external origin: part of it could come from the deep interior and have been incorporated into the planetesimals, while the external component would come from the oxygen source. In the case of Neptune, both HCN and CO have been detected in the stratosphere, in unexpectedly high abundances; their origin is still under debate.

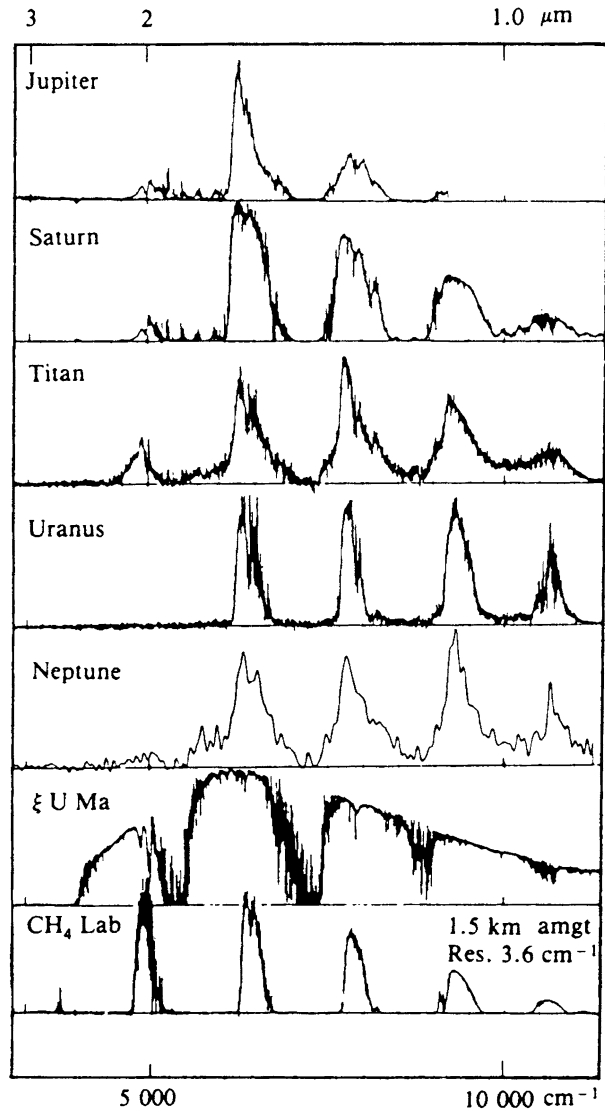
In the case of all giant planets and Titan, the thermal distribution is characterized by a troposphere, driven by convection, where the temperature gradient is close to adiabatic; the spectral lines formed in this region (those of the tropospheric species) are seen in absorption. In all cases, the minimum temperature, at the tropopause, occurs at a pressure level of about 100 mbars, with temperatures ranging from 110 K (Jupiter) to about 50 K (Uranus and Neptune; see Fig. 1). Above this minimum, the temperature increases again in the stratosphere, and the lines formed in this region (in particular the hydrocarbons and the oxygen species) are seen in emission.

What is the cloud structure of the giant planets? In the case of Jupiter and Saturn, an NH_3 cloud is found at about 150 K, and a lower cloud of NH_4SH appears at about 200 K. An H_2O ice cloud is expected at temperatures above 210 K. Note, however, that this main structure applies to the global cloud composition of the planets, and does not take into account local meteorological effects associated to convection (see the following). In the case of Uranus and Neptune, methane condensation takes place at about 80 K, and H_2S could condense at about 120 K (unless some chemistry with H_2O and NH_3 takes place at lower levels).

4.1 The Reflected Spectrum

Methane dominates the reflected spectrum of giant planets (Fig. 4). Signatures of H_2 and NH_3 (on Jupiter and Saturn) were also detected several decades ago. These early ground-based measurements were used to infer the first abundance ratios (C/H , N/H) and it was soon realized that the C/H ratio in Uranus and Neptune was far above its solar abundance; this was the first argument in support of the nucleation model of the giant planets. Further evidence came later, as will be discussed in the following. In addition to CH_4 , its deuterated species CH_3D was also detected on Uranus and Neptune and led to the first estimates of D/H (from CH_3D/CH_4) in these two planets (see the following).

Fig. 4 The near-infrared ground-based spectrum of the giant planets and Titan (Larson 1980). A stellar spectrum is shown to indicate the terrestrial atmospheric windows, and a CH₄ laboratory spectrum is shown for comparison. It can be seen that the planetary spectra are dominated by CH₄



4.2 The Thermal Spectrum

The thermal spectrum of the giant planets (and also Saturn's major satellite Titan) has been extensively observed by the Voyager spacecraft, and later by the Infrared Space Observatory (ISO-SWS, Fig. 5). Between 7 and 12 μm , thermal spectra show a mixture of emission (stratospheric) and absorption (tropospheric) lines. All emission lines are due to hydrocarbons: C₂H₂, C₂H₆, and several less-abundant species. Many of them have been detected by ISO-SWS, and more recently by Spitzer in the case of Uranus and Neptune (Burgdorf et al. 2006). Ground-based observations have been performed in the 4–5 μm and 7–13 μm windows (Bézar et al. 2002; Encrenaz et al. 2004b).

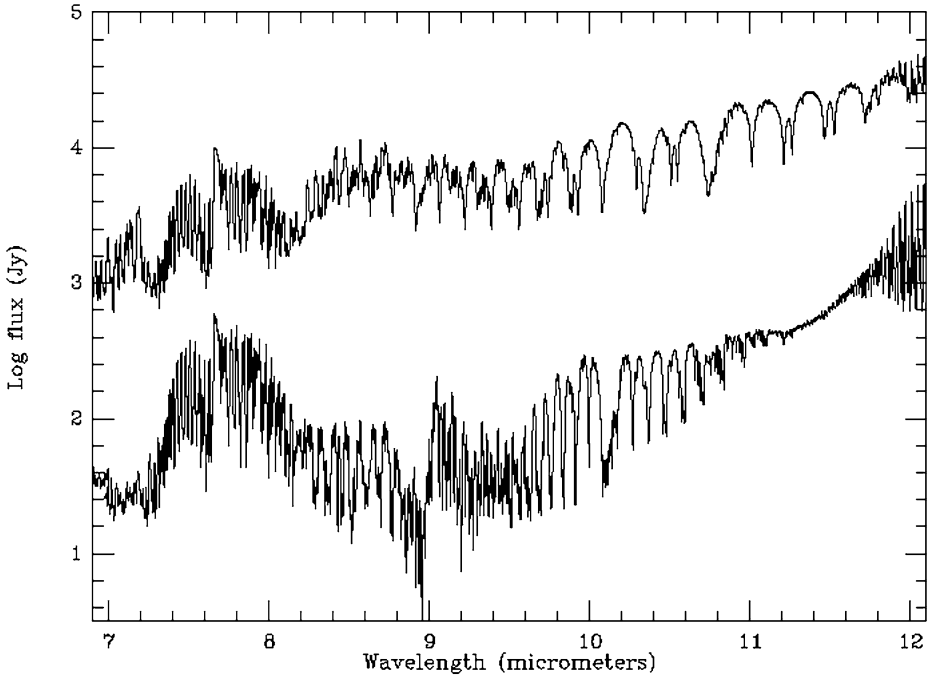


Fig. 5 The ISO spectrum of Jupiter (*top*) and Saturn (*bottom*) between 7 and 12 μm . This region exhibits a mixture of absorption (tropospheric) features and emission (stratospheric) signatures. CH_3D at 8 μm , PH_3 (at 9 μm) and NH_3 (around 10–11 μm) are in absorption in Jupiter; in Saturn, PH_3 is in absorption (at 9 μm and 10 μm). CH_4 (at 7.7 μm) and C_2H_6 (at 12 μm) are in emission on both planets. The figure is taken from Encrenaz (2003)

The 5- μm window is of special interest, as it allows us to probe the troposphere of Jupiter and Saturn below the clouds of ammonia (NH_3) and ammonia hydrosulfide (NH_4SH) (Uranus and Neptune are too cold for thermal emission to be detectable at 5 μm). Ground-based observations at 5 μm have shown that the IR radiation comes from localized regions, called “hot spots”, where the cloud coverage is much thinner than elsewhere. The 5- μm window is the range where tropospheric H_2O was detected, as well as germane (GeH_4) and arsine (AsH_3). An interesting result was the strong depletion of tropospheric water, as compared to its expected cosmic abundance (Drossart et al. 1982). The answer to this puzzling question was given by the Galileo probe which entered the jovian atmosphere in 1995. The probe entered one of the hot spots mentioned above, that is, a dry region of subsidence, almost free of clouds (Atreya et al. 1999). As a result, the oxygen content was found to be very low. The explanation of the oxygen depletion is thus linked to meteorological phenomena, driven by convection; in wet regions of upward motion, the water content was actually found to be higher. A similar depletion of oxygen in the hot spots was observed on Saturn with the Short Wavelength Spectrometer (SWS) of ISO (de Graauw et al. 1997).

4.3 Elemental and Isotopic Abundance Ratios

According to the nucleation model of the giant planet formation, planets accreted from an ice core made of heavy elements (with “heavy” meaning all elements heavier than helium). Following the gravitational collapse of the surrounding sub-nebula and homogenous mixing

inside the protoplanet, one expects an enrichment of the heavy elements with regard to the solar abundances. Such enrichment has indeed been measured in the case of C/H, with increasing fractions from Jupiter (4) to Neptune (55). On the basis of this enrichment, it is possible to evaluate the mass of the initial core of the giant planets, assuming that all heavy elements are equally trapped (this assumption, however, may be questionable and will be discussed in the following). In all cases, it is found that the mass of the initial core for all four giant planets ranges from 8 to 13 terrestrial masses (Owen and Encrenaz 2006). In the case of Jupiter, in situ measurements from the Galileo probe mass spectrometer have led to the determination of a large number of abundance ratios (C, N, O, S and rare gases). With the exception of O (depleted because of local meteorological phenomena) and He and Ne (depleted by internal condensation processes), all heavy elements are enriched by a factor 4 ± 2 (Owen et al. 1999; Owen and Encrenaz 2003, 2006). The enrichment of N and Ar is surprising, because, according to laboratory measurements, these species are not expected to be trapped in ices (nor in clathrates) at temperatures above 40 K. Their presence in Jupiter seems to indicate that the planetesimals which formed Jupiter were accreted at very low temperature. There is no answer presently to this important question.

As discussed earlier, the D/H ratio in Mars and Venus, measured in water, was an important diagnostic of their atmospheric evolution. The D/H ratio can be measured in giant planets, either in methane or in hydrogen, their major constituent. The interest lies in the fact that deuterated species tend to be enriched in ices, as observed in the interstellar medium, and confirmed by laboratory measurements (Irvine and Knacke 1989). The enrichment is due to ion–molecule and molecule–molecule reactions which, at low temperature, favor the formation of D-bearing species, as compared to H-bearing species. As a result, the D/H ratio is an indicator of the formation temperature of the medium where it is measured. In the protosolar nebula, D/H is about 2×10^{-5} , as derived from solar wind measurements (Geiss and Gloeckler 1998). In the case of the giant planet Jupiter, one expects a small enrichment with respect to this value (since the icy core is only 3% the total mass). It should be moderate for Saturn (whose icy core is 10 percent of its mass) but significant for Uranus and Neptune, which are mostly made of their icy core. Spectroscopic measurements of HD and H₂ with ISO have confirmed these predictions: while Jupiter and Saturn have D/H ratios close to the protosolar value, Uranus and Neptune are enriched by a factor 2–3 (Feuchtgruber et al. 1999). Independent measurements of D/H in methane, obtained from the CH₃D/CH₄ ratio using Voyager and ground-based data, have also confirmed this result (Lellouch et al. 2001).

4.4 The External Oxygen Source

Another important discovery of ISO was the unexpected detection of water vapor emission lines in the thermal spectrum of all giant planets (Feuchtgruber et al. 1997). CO₂ was also detected by ISO on Jupiter, Saturn and Neptune, and also later on Uranus by Spitzer. Because of the low temperature at the tropopause, water has to come from an external source, the origin of which is still an open debate. The origin might be local (from rings and/or satellites), or interplanetary (in the form of comets or micro-meteorites), or a combination of both effects, depending of the planet (Lellouch et al. 2002). In the case of Jupiter, the collision of Shoemaker-Levy 9 with Jupiter in July 1994 fed the jovian stratosphere with minor species, formed by shock chemistry (H₂O, CO, CS, OCS, HCN, . . .), which, in some cases, survived for months or even for years.

A question linked to the oxygen source is the source of CO in the giant planets. In the case of Jupiter and Saturn, CO was first observed at 5 μm, with an abundance consistent with the thermochemical models; it was then believed that CO was of internal origin. However,

large abundances of CO (by a factor a thousand) and HCN were detected in the stratosphere of Neptune (Rosenqvist et al. 1992; Marten et al. 1993). It was again suggested that, on Neptune, CO could be of internal origin, and is indicative of a formation process different from the three other giant planets. However, CO can also come from the external source of oxygen or be a reaction product of these oxygen species in the stratosphere. Recent ground-based observations of CO at high resolution seem to indicate that CO is both external and internal in Jupiter and Saturn (Bézard et al. 2002). Finally, CO was also detected in Uranus at 5 μm , but another emission mechanism is at work: the lines are formed by fluorescence, in the lower stratosphere, which apparently favors the external origin (Encrenaz et al. 2004b).

4.5 H_3^+ in the Giant Planets

H_3^+ is the only ion found so far in the giant planets. It was first detected on Jupiter, at 2 μm (Drossart et al. 1989), and later also on Saturn (Geballe et al. 1993) and Uranus (Trafton et al. 1993), at 2 and/or 4 μm . H_3^+ lines are formed very high in the upper stratospheres, at pressure levels on the order of a microbar. The formation mechanism could be either thermal emission or fluorescence. Thermal emission seems to be the most likely mechanism; at these levels, the temperature is high enough (600–1,000 K) for thermal emission to be detected.

5 Summary and Conclusions

This review illustrates the very large variety of spectra observed in the different solar-system planets, both in the reflected and the thermal regimes. In the latter case, this is partly due to different stratospheric structures, which strongly influence the observed spectrum. This variety of spectra is to be kept in mind when spectra of extrasolar planets become available.

Another conclusion to be drawn is the importance of remote sensing spectroscopy as diagnostic of chemical composition, thermal and cloud structure, elemental and isotopic composition, and even dynamical processes. Even in the case of terrestrial planets, extensively studied by in situ probes, remote sensing spectroscopic monitoring is essential for mapping temperature fields, wind fields, cloud and aerosol properties, and surface mineralogy.

Finally, recent detection of minor species, on both Mars (H_2O_2 , tentatively CH_4) and the giant planets (CO) have illustrated the importance of ground-based high-resolution spectroscopy, in complement with space missions. Indeed, high spectroscopic resolution is essential for detecting and studying narrow lines, like the martian lines and the stratospheric lines of the giant planets. High resolution ($R > 10^6$) is achievable with heterodyne spectroscopy and has been mostly used in the millimeter range; its spectral range is now extended to the sub-millimeter range and the 10- μm region. In addition, imaging spectrometers with resolving powers of 10^4 – 10^5 are available in the near-infrared and thermal ranges. Coupled with large telescopes, they allow us to map planetary disks at high spatial and spectral resolution, and will continue to offer a precious complement to in-orbit planetary remote sensing spectroscopy.

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Extraterrestrial Organic Matter and the Detection of Life

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Abstract A fundamental goal of a number of forthcoming space missions is the detection and characterization of organic matter on planetary surfaces. Successful interpretation of data generated by in situ experiments will require discrimination between abiogenic and biogenic organic compounds. Carbon-rich meteorites provide scientists with examples of authentic extraterrestrial organic matter generated in the absence of life. Outcomes of meteorite studies include clues to protocols that will enable the unequivocal identification of organic matter derived from life. In this chapter we summarize the diagnostic abiogenic features of key compound classes involved in life detection and discuss their implications for analytical instruments destined to fly on future spacecraft missions.

Keywords Astrobiology · Solar system · Meteorites · Organic · Abiotic · Mars · Urey · SAM

1 Introduction

It is generally accepted that the origin of life on Earth was preceded by a period of chemical evolution utilising organic material that may have been generated in situ or inherited from the protoplanetary disk and its presolar starting materials. The relative importance of these sources has been debated for decades. However, a growing awareness that the Earth's early atmosphere contained too small a proportion of reducing gases for large-scale in situ production of organic matter (Kasting 1993) has encouraged many scientists to support theories of life's origins relying on organic matter supplied by extraterrestrial objects to the surface

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of the early Earth (Oró 1961). Although recent reports do suggest that a Titan-like organic haze may have prevailed on the early Earth and aerosol production may have contributed organic material to the surface (e.g. Trainer et al. 2006).

The Earth-based record of pre-biotic chemical evolution has long-since been removed by geological processing. However, remains of the materials that would have been delivered to the early Earth are preserved in ancient asteroids, fragments of which are naturally-delivered to the Earth as meteorites. Carbonaceous chondrites are a particularly primitive class of meteorite that generally contain 2 to 5 wt.% carbon, most of which is present as organic matter. Much of our current understanding of meteoritic organic matter has come from investigations of the Murchison carbonaceous chondrite, approximately 100 kg of which fell in Australia in 1969. Indigenous organic matter in Murchison contains several classes of compounds that are important components in terrestrial organisms, further supporting the role of exogenous delivery for supplying life's starting materials.

Calculations of flux rates reveal that substantial amounts of organic matter could have been delivered to the early Earth by extraterrestrial infall. There are three main types of object that can deliver organic molecules intact to planetary surfaces: asteroids (or their meteoritic fragments), comets and interplanetary dust particles (IDPs) (Chyba and Sagan 1992). Using the very recent history of the Earth as an example, the major mass, by about two orders of magnitude, is estimated to come from the IDP flux. The total flux of 'giant' micrometeorites (particles in the size range of 100 μm to about 1 mm) before atmospheric entry was determined from direct impact crater counts on the metallic plates of the Long Duration Exposure Facility (LDEF) satellite, from which a global value of approximately $(4 \pm 2) \times 10^7 \text{ kg yr}^{-1}$ of extraterrestrial matter was inferred for this source (Love and Brownlee 1993; Maurette et al. 2000). Assuming a carbon content of approximately 2.5 wt% (similar to carbonaceous chondrites), the annual accretion rate of carbon from micrometeorites and meteorites was estimated to be approximately $2.0 \times 10^5 \text{ kg yr}^{-1}$, with meteorite-sized objects contributing a negligible 10^{-5} of that mass. Carbon delivery by comets is also relatively low and is thought to be three orders of magnitude less than for the IDPs both in modern and ancient times (Chyba and Sagan 1992).

2 Carbon in Carbonaceous Chondrites

The carbon in the carbonaceous chondrites is present in a number of forms. Organic matter is, quantitatively, the most important carbon bearing phase but can be subdivided into three phases defined by their physical and chemical responses to laboratory procedures (Sephton et al. 2003). The divisions rely on simple operational characteristics and although each organic fraction may respond to processing in a similar way, they may be composed of molecules from a number of extraterrestrial sources. *Free organic matter* is composed of various compound classes (such as amino acids, carboxylic acids, aromatic hydrocarbons, etc.) but all can be extracted by common organic solvents (Table 1). Macromolecular materials account for over 70% of the total organic matter in CI1 and CM2 meteorites and are structurally complex and relatively intractable. Some macromolecular materials can be broken down using heating techniques and these represent the second operational division, *labile organic matter*. In contrast, the third type of organic matter comprises macromolecular materials termed *refractory organic matter* that must be reacted with oxygen at high temperatures before degradation takes place.

The remaining carbon-bearing phases in carbonaceous meteorites are inorganic. Carbonates form a significant proportion of the carbon inventory in carbonaceous meteorites.

Table 1 Types of mostly abiogenic organic matter in the Murchison (CM2) carbonaceous chondrite and their abundances

Compounds	Abundances		Reference
	%	$\mu\text{g g}^{-1}$ (ppm)	
Macromolecular material	1.45		(Chang et al. 1978)
Carbon dioxide		106	(Yuen et al. 1984)
Carbon monoxide		0.06	(Yuen et al. 1984)
Methane		0.14	(Yuen et al. 1984)
Hydrocarbons:			
aliphatic		12–35	(Kvenvolden et al. 1970)
aromatic		15–28	(Pering and Ponnampereuma 1971)
Acids:			
monocarboxylic		332	(Lawless and Yuen 1979; Yuen et al. 1984)
dicarboxylic		25.7	(Lawless et al. 1974)
α -hydroxycarboxylic		14.6	(Peltzer et al. 1984)
Amino acids		60	(Cronin et al. 1988)
Diamino acids		0.04	(Meierhenrich et al. 2004)
Alcohols		11	(Jungclaus et al. 1976b)
Aldehydes		11	(Jungclaus et al. 1976b)
Ketones		16	(Jungclaus et al. 1976b)
Sugar-related compounds (polyols)		~24	(Cooper et al. 2001)
Ammonia		19	(Pizzarello et al. 1994)
Amines		8	(Jungclaus et al. 1976a)
Urea		25	(Hayatsu et al. 1975)
Basic N-heterocycles (pyridines, quinolines)		0.05–0.5	(Stoks and Schwartz 1982)
Pyrimidines (uracil and thymine)		0.06	(Stoks and Schwartz 1979)
Purines		1.2	(Stoks and Schwartz 1981a)
Benzothiophenes		0.3	(Shimoyama and Katsumata 2001)
Sulphonic acids		67	(Cooper et al. 1997)
Phosphonic acids		1.5	(Cooper et al. 1992)

“Exotic” carbon (diamond, silicon carbide and graphite) is contained within the insoluble carbon but can be isolated by progressive oxidative techniques (e.g. dichromate and perchloric acids). However it is the free organic matter and macromolecular materials that can be solubilized by reactions with heat and water that is relevant for discussions of the Origin of Life.

3 Soluble Organic Compound Classes in Carbonaceous Chondrites

3.1 Amino Acids

The first compound class usually associated with life that was unambiguously identified and quantified in Murchison was the amino acids (Kvenvolden et al. 1970) and to date more than 80 different amino acids have been found in this meteorite. However, of these only eight α -amino acids (glycine, alanine, aspartic acid, glutamic acid, valine, leucine, isoleucine, and

proline) are the same as those used in terrestrial biology as constituents of proteins, e.g. are encoded in DNA and translated in the ribosome. A few others, including β -alanine, α -aminoisobutyric acid (AIB) and sarcosine, have a very restricted biological occurrence on the Earth, e.g. as components of bacterial cell walls. The remainder are found naturally only in meteorites (i.e. they exist on Earth, but have to be synthesized in the laboratory).

Meteoritic amino acids can be mainly divided into two types, monoamino alkanoids (e.g. alanine) and monoamino alkandioic acids (e.g. aspartic acid), each of which can occur as N-alkyl derivatives or cyclic amino acids (Cronin and Chang 1993). One of the molecular characteristics of each type of compound is that they exhibit complete structural diversity, meaning that all isomeric forms of a certain amino acid are present in the meteorite, a fact that was experimentally confirmed for the C₁ to C₇ α -amino acids (Cronin and Pizzarello 1986). Additional characteristics include a decrease in abundance of isomers in the order $\alpha > \gamma > \beta$, the predominance in abundance of branched carbon chain isomers over straight ones, and a smooth exponential decline in concentration with increasing carbon number within homologous series. Recently, diamino acids have also been detected in the Murchison meteorite (Meierhenrich et al. 2004).

In a typical amino acid analysis protocol (Fig. 1), the compounds are extracted with hot water, and a fraction of the extract is acid hydrolyzed and desalted in order to obtain critical information about the concentration ratio between the free and bound amino acids in the meteorite. Individual amino acids are then isolated through separation on a chromatographic column either in the gas phase (gas chromatography, GC) or liquid phase (high performance liquid chromatography, HPLC). Quantification occurs via detection by either a mass spectrometer or a fluorescence detector. In most cases, the amino acids have to be derivatized in order to be volatile enough to pass through the chromatographic system or to allow separation of the enantiomers (Botta and Bada 2002). This relatively straightforward protocol can be applied to biological samples, biogeophysical samples such as endolithic bacterial communities as well as abiotic material in meteorites to allow a direct comparison of the absolute and relative amino acid compositions. The assessment of the putative biogenicity of

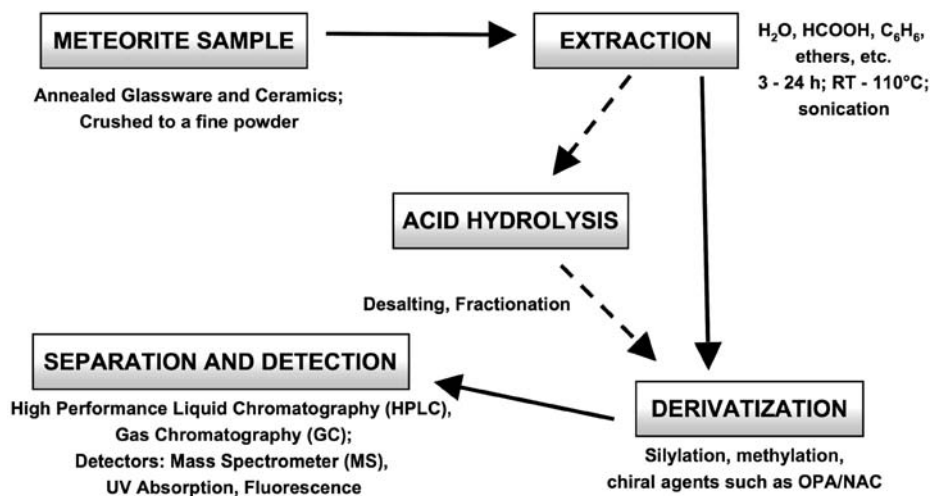


Fig. 1 Flow diagram illustrating an extraction procedure for organic compounds in meteorites. *Solid lines* are mandatory steps; *dashed lines* indicated additional steps (for example acid hydrolysis to liberate bound amino acids). Abbreviations: OPA: o-phthalaldehyde; NAC: N-acetyl-L-cysteine