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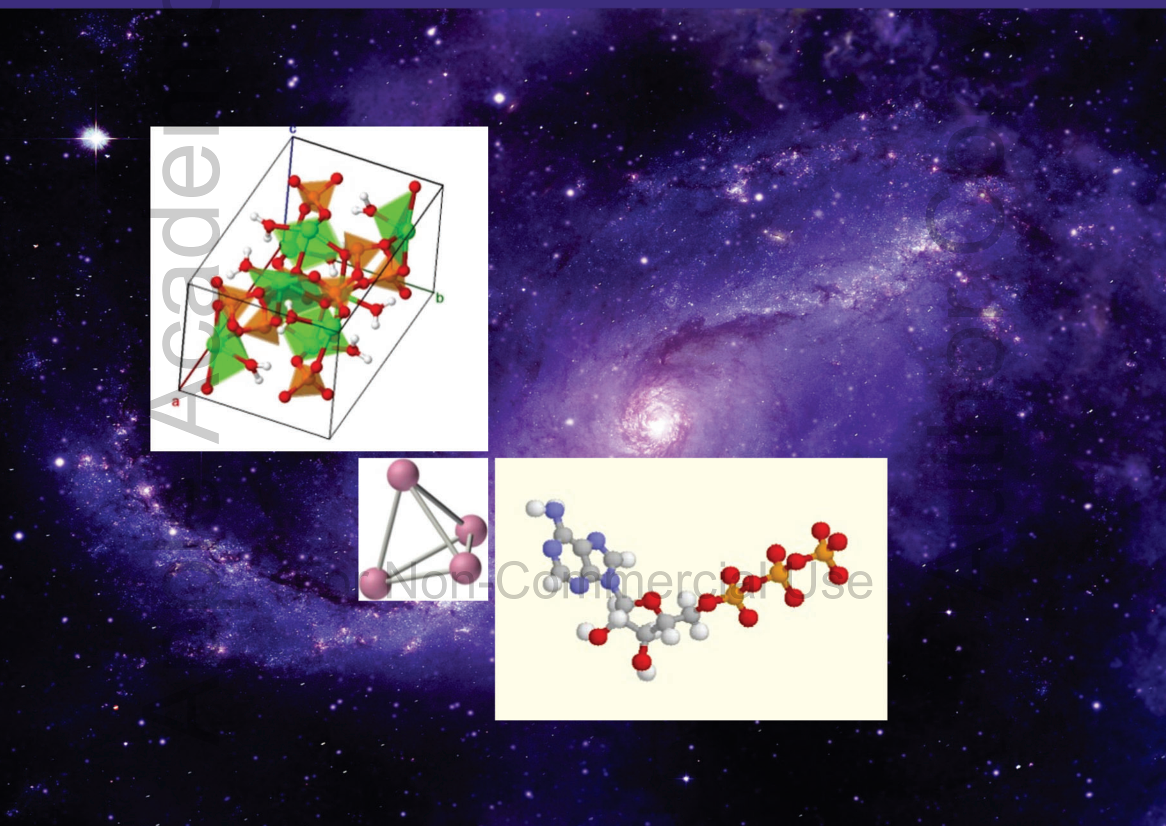
The Chemical Evolution of Phosphorus

An Interdisciplinary Approach to Astrobiology



Enrique Maciá-Barber

APPLE ACADEMIC PRESS

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THE CHEMICAL EVOLUTION OF PHOSPHORUS

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Enrique Maciá-Barber, PhD, is currently a full professor of condensed matter physics at the Universidad Complutense de Madrid. His research interests include the thermoelectric properties of quasicrystals and DNA biophysics. He is also the author of several monographs and the books *Aperiodic Structures in Condensed Matter: Fundamentals and Applications* (CRC Press, Boca-Raton, 2009) and *Thermoelectric Materials: Fundamentals and Applications* (Pan Stanford Publishing, Singapore, 2015). Prof. Maciá-Barber holds a PhD in Physical Sciences from the Complutense University of Madrid (UCM); he was the winner of the Extraordinary Doctorate Award for his thesis on Elementary Excitations in Aperiodics Systems. He received his MSc degree in astrophysics in 1987.

Contents

Abbreviations

AGB	asymptotic giant branch
ATP	adenosine triphosphate
AU	astronomical unit
CH_3CONH_2	acetamide
CO	carbon monoxide
CO_2	carbon dioxide
COOH	carboxylic group
COSAC	cometary sampling and composition
CS	carbon monosulfide
DEPA	diethylphosphorodithioic acid
DIPA	diisopropylphosphorodithioic acid
DMPA	dimethylphosphorodithioic acid
DNA	deoxyribonucleic acid
FAD	flavine-adenine dinucleotide
GCR	galactic cosmic rays
HC_3N	cyanoacetylene
HCN	hydrogen cyanide
HR	Hertzsprung–Russell
HST	Hubble Space Telescope
HZ	habitable zone
IDPs	interplanetary dust particles
IGM	intergalactic medium
IP6	inositol hexaphosphate
IR	infrared
ISM	interstellar medium
KREEP	potassium, rare-earth, and phosphorus
LED	light emission device
LTE	local thermodynamical equilibrium
LUCA	last universal common ancestor
MACHOs	massive compact halo objects
MPO_4	phosphate minerals
NADPH	nicotine-adenine dinucleotide
PAH	polycyclic aromatic hydrocarbon

PN	protoplanetary nebulae
PO	phosphorus monoxide
PO_4^{3-}	phosphate ion
QSO	quasi-stellar object
RNA	ribonucleic acid
ROSINA	Rosetta orbiter spectrometer for ion and neutral analysis
SEP	solar energetic particles
SN	supernova
SNR	supernova remnant
UV	ultraviolet
WHO	World Health Organization
WIMPs	weakly interacting massive particles

Foreword

Since the pioneering work on stellar nucleosynthesis by Fred Hoyle and A.G.W. Cameron in the 1950s, astronomers have been aware that most of the chemical elements in the universe are produced in stars. Chemical elements are made by nuclear reactions deep in the interior of stars, carried up to the surface, ejected into the interstellar medium, and distributed throughout the Milky Way galaxy. The primordial solar nebula, out of which the Sun and the Earth were formed, was enriched by the ejection of the previous generation of stars.

Since living organisms evolved from ingredients of the early Earth, it is therefore not an exaggeration to say that every atom in our body was once inside a star and humans are made of stellar material. The most common elements in our bodies are hydrogen, oxygen, carbon, and nitrogen, which are also among the most common elements found in stars and gaseous nebulae in the galaxy.

The only exception is phosphorus. Phosphorus is the fifth most common element in human bodies but only ranks 18th among the most abundant chemical elements in our parent star, the Sun, and in the interstellar medium of our galaxy. Phosphorus is a major constituent of nucleic acids and cell membranes and plays a major role in storage and transmission of genetic information as well as metabolism. Why is phosphorus so heavily concentrated and utilized in our bodies is one of the most interesting unanswered questions in the origin of life. Among the primordial ingredients available, why did terrestrial biochemistry preferentially select phosphorus to create the prebiotic molecules that eventually led to life?

These are the questions that Enrique Maciá-Barber tries to answer in this book. Prof. Maciá-Barber is a world-renowned expert in the astrobiological study of phosphorus. This book beautifully traces the stellar origin of the element phosphorus, its chemical properties, and the observations of phosphorus-based molecules and minerals in the interstellar medium and in the solar system. He then connects the astronomical studies with the role that phosphorus plays in living organisms, presenting the biochemistry of biomolecules that incorporates phosphorus, and the roles that these molecules play in the origin of life on Earth.

This book presents a comprehensive summary of our current understanding of the astrochemical and astrobiological significance of phosphorus. It is invaluable for researchers and students who are interested in the question of the origin of life and the search for extraterrestrial life.

Is the importance of phosphorus in life only confined to terrestrial biochemistry? Can we imagine other biochemical pathways and structures in an unknown alien life where phosphorus plays a different role? These are fascinating questions for future researchers to explore.

— Sun Kwok
President, International Astronomical Union Commission on Astrobiology (2015–2018), University of British Columbia, Vancouver, Canada

Acknowledgments

This book is dedicated to the memory of Professor John Oró with my heartfelt gratitude for the deep interest, valuable advice, and motivating support he provided me during the time I had the fortune to share with him. I warmly thank Marcelino Agúndez, Lou Allamandola, Martin Asplund, Sun Kwok, and Lucy Ziurys for their interest in this research, as well as for fruitful correspondence and useful comments during the last two decades. I am also indebted to Rafael Bachiller, Gabriele Cescutti, Fred Goesmann, Chiaki Kobayashi, Terence Kee, Katharina Lodders, Daniel Murphy, Matthew Pasek, Ilka Peterman, Cameron Pritekel, Víctor M. Rivilla, Caleb A. Scharf, Xiaoping Sun, Josep María Trigo-Rodríguez, Takashi Tsuji, Channon Visscher, and Ian P. Wright, for sharing useful materials and relevant information. Last, but not least, I thank the Apple Academic Press Vice President, Sandra Sickels, for making this book possible, and to Victoria Hernández for her continued interest in my long-standing research project, and for her collaboration and assistance with the manuscript.

Preface

Phosphorus (light-bearer in Greek) was discovered in 1669 by German physician and alchemist Hennig Brand by distilling human urine, a biological waste product. Indeed, phosphorus belongs to the exclusive set of those chemical elements, namely, H, O, C, N, S, and P, which are present in large enough amounts in all living beings, and for that reason, they are referred to as main biogenic elements. Nevertheless, at variance with the remaining bioelements, which are also among the most abundant atoms in the universe, phosphorus is remarkably scarce on a cosmic scale, occupying the eighteenth position in the cosmic elemental abundance ranking.

The scarcity of phosphorus atoms in the universe sharply contrasts with the high abundance of this species in the elemental composition of living cells and tissues as well as in vertebrates' bones and teeth. This feature is quite intriguing, especially when one realizes that phosphorus compounds exist in a great variety in living systems, where they perform many fundamental biochemical tasks. Thus, the esters of phosphoric acid, including sugar phosphates and nucleotides, play a leading role in most biochemical processes, such as glycolysis and nucleic acid metabolism. These esters also determine the structural stability of DNA and RNA nucleic acids. Adenosine triphosphate (ATP) is the best-known conveyer of chemical energy in most metabolic routes, and this molecule also acts as an inorganic phosphate carrier in many important enzymatic reactions. In addition, some cyclic nucleotide derivatives play a significant role in the biochemical activity of diverse hormones, in the synaptic transmission of the nervous system, in cellular division regulation, and even in immune and inflammation responses. Definitively, phosphorus is everywhere in the living world!

Therefore, how did phosphorus atoms, which are produced inside the inner cores of a handful of huge stars, concentrate in relatively high proportions, mainly in the form of PO_4 phosphate groups, in the organisms composing Earth's biosphere to rise up from its 18^{th} cosmic abundance place to the fifth or sixth position in the elemental abundance ranking of biomass representatives so diverse as ancient archeobacteria and modern human beings?

And, closely related to the question above, how did these phosphate derivatives manage to be included in such a great variety of organic molecules playing essential biochemical roles in all known life forms?

These two questions define the essence of what I refer to as the phosphorus enigma, and this book is devoted to describe the very nature of this puzzle, and to provide some hints towards suitable answers to both queries. To this end, within the grand panorama of cosmos evolution, we will grab the limelight onto this chemical element as the main character of our story, and will follow its evolutionary path from massive stars inner cores, where it is formed ruled by the strong nuclear forces, all the way long until its incorporation in the minerals dispersed all over the solar system, ending up with the macromolecular biopolymers encoding the genetic information and the metabolic molecules setting the rhythms of life inside the living beings that populate the planet we inhabit.

We will start this scientific exploration journey by first considering thermonuclear reactions involving atomic nuclei which interact at a subatomic domain, to progressively zoom out the spatial scale by considering simple phosphorus-bearing molecules flowing through circumstellar shells around aged stars to dilute in the cold interstellar medium, and then we will further increase the magnifying-glass power up to the size of schreibersite or apatite mineral crystals readily visible to the naked eye. During this bottom-up voyage across our hierarchically structured cosmos, we will also pay attention to the different energy intervals where these phosphorus-containing structures can exist, ranging in temperature from the thousand million Kelvin degrees required to ignite the nuclear fuels leading to the synthesis of ^{31}P nuclei, to the much lower room-temperature values necessary to preserve the structural integrity of the sugar-phosphate backbone of DNA macromolecules and the stability of the fragile organic compounds moving around inside living cells alike.

The contents of this book are arranged according to three main conceptual stages, which are explicitly distributed in 10 chapters. Due to the interdisciplinary nature of the problem to be addressed, the first stage aims to introduce the fundamental concepts and notions of physics, chemistry, and biology within the astronomical framework that one needs to be able to achieve a proper understanding of the topics discussed in the subsequent stages. In this way, Chapter 1 provides a brief introductory overview describing the main goals of the book. Afterward, some fundamentals of astrophysics, chemistry, and biology disciplines are reviewed in the Chapters 2 and 3, closing the first conceptual stage with a detailed description of the main physical and chemical properties of phosphorus compounds of interest, which is given in Chapter 4.

Equipped with this basic knowledge, the second stage of the trip focuses on the presence and distribution of phosphorus, and its compounds as the universe evolves following the arrow of time. To this end, through the Chapters 5–8, we will discuss the relevance of phosphorus among the main biogenic elements by considering its crucial role in most essential biochemical functions as well as its peculiar chemistry under different physicochemical conditions. In doing so, we will review the phosphorus compounds which have been found in different astrophysical objects, such as planets and moons, interplanetary dust particles, asteroids and comets, stars of different sorts, and the interstellar medium. In this way, we realize that this main biogenic element is both scarce and ubiquitous in the universe. These features can be related to the complex nucleosynthesis of phosphorus nuclei in the cores of massive stars under explosive conditions favoring a wide distribution of P atoms throughout the interstellar medium, where they would be ready to react with other available atoms. The tendency towards oxidized or reduced phosphorus compounds will be scrutinized as chemical evolution proceeds from circumstellar and interstellar grains covered with icy mantles to full-fledged minerals resulting from condensation and aggregation into planetesimal bodies within protoplanetary disks ultimately leading to the formation of planetary systems. In the light of these results, we also will discuss some possible routes allowing for the incorporation of phosphorus compounds of prebiotic interest during the earlier stages of solar system formation and the emergence of life on Earth.

Then, in Chapter 9, we will narrow down our perspective from the workings of Nature all over the universe to focus on the workshops of men laboring on the Earth, and its close planetary neighborhood, by considering industrial applications of manmade phosphorus compounds in current areas of research of solid-state physics, materials engineering, nanotechnology or medicine. Finally, some preliminary answers regarding the three main queries related to the phosphorus enigma, namely, the phosphorus nucleosynthesis problem, the phosphorus chemistry puzzle, and the prebiotic phosphate conundrum, will be given in Chapter 10, along with some suggestions for future research work which could be carried out in order to further clarify the cosmic history of phosphorus in the years to come.

Previous books covering the broad topic of chemical evolution have paid little attention to two main aspects which are considered in detail in this book, namely: the significant role of energy fluxes as a parallel development to the increasing structural complexity in the physicochemical processes eventually leading to the possible emergence of life, and the fundamental importance of entropy as a driving force in cosmic evolution, which complements the broadly considered role of minimum energy principle in the appearance of complex enough stable structures as time goes on.

The book contains 16 proposed exercises accompanied by their detailed solutions, along with an Appendix including the values of some important physical constants, astronomical quantities, and conversion factors. I have prepared the exercises mainly from results published and discussed in regular research papers during the last decade, in order to provide a glimpse into the main current trends in the field. Although the exercises and their solutions are given at the end of the book for convenience, it must be understood that they are an integral part of the presentation, either motivating or illustrating the different concepts and notions introduced in the main text. Accordingly, it is highly recommended to the reader that he/she tries to solve the exercises in the sequence they appear in the text, then check his/her obtained result with those provided at the end of the book, and only then to resume the reading of the corresponding chapter. In this way, the readers (who are intended to be both graduate students as well as senior scientists approaching this topic from other research fields) will be able to extract the maximum benefit from the materials contained in this book in the shortest time. For the sake of completeness, the most relevant technical terms introduced through the book are compiled in a detailed Glossary, which is included in the front matter of the book.

The book can be used as a reader-friendly textbook for undergraduate, graduate, or postgraduate students, senior scientists and researchers coming from diverse related fields of physics, chemistry, astrophysics, biology or geology and approaching this topic from other research fields. Indeed, most of the contents covered in this book are included in the curricula of different science courses. Accordingly, I confidently hope this book may provide a motivating unifying topic, the chemical evolution of phosphorus compounds, within a transversal framework which could be fruitfully used by both students and teachers in order to gain a broader perspective on the intertwined workings of Nature as the universe unfolds.

—***Enrique Maciá Barber, PhD***
Madrid, September 2019

CHAPTER 1

The Phosphorus Enigma: An Overview

"*Phosphorus is of interest because little is known about its gas-phase chemistry, although it plays a fundamental role in biological systems.*"

(Lucy Ziurys, 1987)

"The relative abundance of phosphorus in the human body is several orders of magnitude greater than in Solar System, where it is only the seventeenth most common element. So, how did phosphorus concentrate on earth, ultimately becoming part of us?"

(Sun Kwok, 2006)

1.1 THE ORIGIN OF CHEMICAL ELEMENTS

By the late 1960s, astrophysicists already knew that hydrogen, a significant fraction of helium and some traces of lithium atomic nuclei, were made during the primordial nucleosynthesis episode, which took place under the extremely high temperature and density conditions prevailing in the first few minutes of our early expanding universe. Most of the remaining heavier chemical elements present in the periodic table were made a long time after this stage, through an ordered sequence of nuclear reactions occurring in the cores of stars (Burbidge et al., 1957; Fowler, 1984). Astronomers had also discovered that not all stars equally contribute to the final inventory of chemical elements in the galaxy they inhabit, but less massive stars yield relatively lighter atoms, while more massive stars produce heavier elements. Since less massive stars significantly outnumber more massive ones in typical galaxies, the resulting averaged elemental abundance distribution systematically decreases as the atomic number (Z) increases, according to a nearly exponential decline until $Z \sim 42$, thereafter decreasing more gradually, as can be seen in Figure 1.1. Along with this general main trend, we can also appreciate some remarkable dips and peaks in the elemental distribution curve, namely, the beryllium, fluorine, and scandium relative dips, on the one hand, and the oxygen, iron, and lead relative peaks, on the other hand.

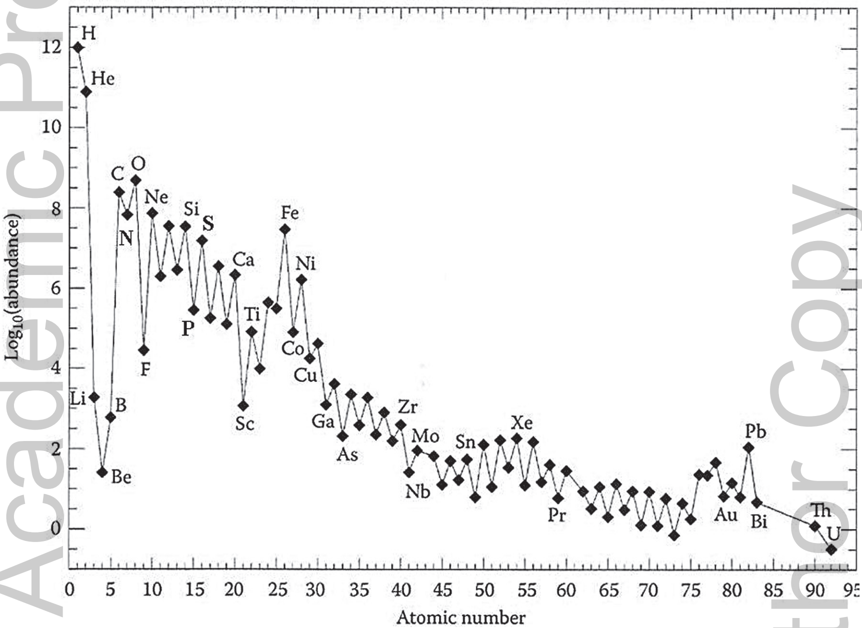

FIGURE 1.1 Plot showing the average cosmic abundance of elements as a function of their atomic number Z. This curve combines data retrieved from spectroscopic observations of the Sun, the Stars, and the interstellar medium (ISM), as well as from cosmic-ray particles and direct chemical analysis of samples collected from Earth, the Moon, Mars, meteorites, asteroids, cometary nuclei and interplanetary dust particles, hence providing the so-called universal (or cosmic) abundances of the elements. Although the obtained chemical distribution curves sometimes differ in detail for particular elements depending on the considered sources, they rarely do so by more than a factor of three on a scale that spans more than 12 orders of magnitude.
Source: Greenwood and Earnshaw, 1986; Asplund et al., 2009; Data taken from Lodders, 2003.

1.2 THE ROLE OF BIOGENIC ELEMENTS IN CHEMICAL EVOLUTION

Living cells consist of a large variety of different biopolymers, namely, proteins, sugars, lipids, ribonucleic acids (RNA), and deoxyribonucleic acids (DNA). Together with smaller molecules, such as water, phosphates, sulfates, and a few metallic ions, these components give the molecular content of the so-called biomass. Elemental analyses of these biochemical compounds have revealed that H, O, C, N, P, and S atoms are needed in large quantities to make living organisms, and for this reason, these elements are referred to as the main biogenic elements. For instance, by properly averaging the main biomass constituents of a typical yeast cell, its elemental composition (normalized to the carbon content) can be expressed by the stoichiometric formula $H_{1.748}CO_{0.596}N_{0.148}P_{0.009}S_{0.0019}M_{0.0018}$, where M stands for metal atoms belonging to the so-called oligo-elements set, including K, Na, Mg, Ca, Fe, Mn, Cu, and Zn, which are required in minor quantities only (Lange and Heijnen, 2001).

By inspecting the elemental abundance curve depicted in Figure 1.1, and comparing it with the elemental composition of living beings, derived from detailed biochemical analysis, some scientists realized that the four most abundant elements in the universe, with the exception of the noble gases helium and neon, are hydrogen, oxygen, carbon, and nitrogen, which are also precisely the four major constituent elements of organic compounds and of living matter (Greenstein, 1961; Oró, 1963). This is illustrated in Figure 1.2, where we can also appreciate that C and P elements are enhanced in biomass as compared to their cosmic abundances. In fact, albeit the cosmic elemental abundance of S is about two orders of magnitude larger than that of P, the latter is more abundant in living beings by a factor of four at least.

Indeed, phosphorus compounds exist in a great variety in living systems, where they perform many fundamental biochemical functions involving storage and transfer of information (nucleic acids), energy transfer (adenine and guanine nucleotides), membrane structure (phospholipids), and signal transduction (cyclic nucleotides). Accordingly, the elemental abundance of phosphorus ranks at the fifth (sixth) position in the chemical inventory of unicellular (pluricellular) organisms, respectively. However, by inspecting Figure 1.1, we realize that phosphorus, occupying the eighteenth position in the cosmic elemental abundance ranking, is the less abundant species among the third-row elements of the periodic table, as well as in the group of the main biogenic elements. Thus, the only biogenic element present in biological tissues at a concentration substantially above its solar abundance is phosphorus (Whittet and Chiar, 1993). This suggests the probable existence of physical and chemical processes favoring a differential enhancement of organic matter in general, and phosphorus bearing compounds in particular, at certain astrophysical environments, stemming from *chemical evolution* in the Galaxy, that is, a progressive and general tendency of matter to go from simpler to more complex atomic and molecular arrangements at certain astrophysical places as times goes by (Mason, 1992; Rauchfuss, 2008; Kwok, 2013).

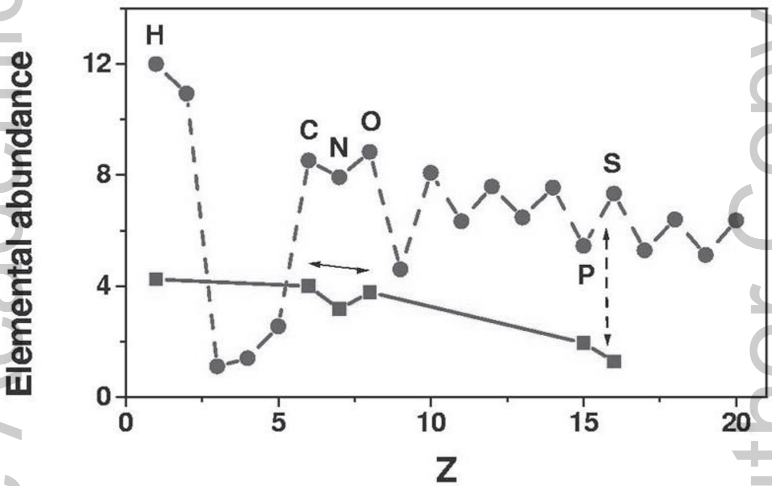

FIGURE 1.2 Elemental abundance comparison between the dry biomass of representative yeast with stoichiometric composition $H_{1.748}CO_{0.596}N_{0.148}P_{0.009}S_{0.0019}M_{0.0018}$ (squares) and the cosmic elemental distribution curve shown in Figure 1.1 (circles). The abundances are given on a logarithmic scale with H = 12 for cosmic abundances and C = 4 for biomass abundances. The elements are arranged according to their atomic number Z, and the main biogenic elements are explicitly labeled. Note that the relative importance of C and O peaks is reversed in biomass and cosmic curves, respectively, and that the P/S ratio in the biomass curve is remarkably enhanced as compared to the observed cosmic ratio.
Source: Maciá, 2005; with permission from the Royal Society of Chemistry.

It should be emphasized, however, that this trend towards a higher chemical complexity is not the result of a continuous process occurring everywhere, but rather the final outcome of a lot of intertwined processes, which take place at different scales of space and time, in such a way that synthesis and destruction events alternate each other along the arrow of time. For instance, as we will describe it detail in Chapter 5, chemical elements heavier than helium must be synthesized by means of thermonuclear reactions requiring very high temperatures, well above those we find in our ever cooling expanding universe once the primeval nucleosynthesis episode ended. The appearance of stars able to reach the required high temperatures in their inner cores then becomes a crucial event for the origin of most of the periodic table elements and their related chemistry. Stellar nucleosynthesis illustrates an important synthesis mechanism which started when the universe was about 200 million years old and will be enduring for a long period in the future universe's history. Now, the elements formed inside stellar cores must be subsequently liberated to the ISM in order to undergo further chemical processing. Such a release takes place through mass loss processes during the life-cycle of stars, first by means of stellar winds, eventually followed by either the formation of planetary nebulae (in the case of low mass stars) or via supernova (SN) explosions (in the case of high mass stars), all of which being essentially disruptive processes by themselves, ultimately leading to the destruction of the original stellar structure (Trimble, 1982, 1983; Kwok, 2000, 2013). Once in the ISM the atoms delivered from stars can undergo chemical reactions among them, promoting the formation of polyatomic molecules, either on the surfaces of minute dust grains (previously condensed in the circumstellar envelopes around aging stars) or in the gas-phase among the stars (Zeng et al., 2018), as it is illustrated in Figure 1.3.

As we see, in the course of these chemical reactions some molecules are formed, while others are destroyed according to complex entangled networks driven by energetic ultraviolet (UV) photons emitted by young stars or fast cosmic rays: wandering particles spiraling throughout the Galaxy as material echoes of ancient SN blasts.

In this way, we realize that notwithstanding the important role certain astrophysical objects may play in their due time, different material structures are progressively emerging and fading away, as the cosmic clock ticks on, ruled by energy optimization and entropy production criteria. Keeping this in mind we realize that the emergence of life, which requires the existence of very complex and fragile biopolymer systems, continuously exchanging matter and energy with their surroundings under conditions very far from thermodynamical equilibrium, can only take place in a mature and cold enough evolved universe.

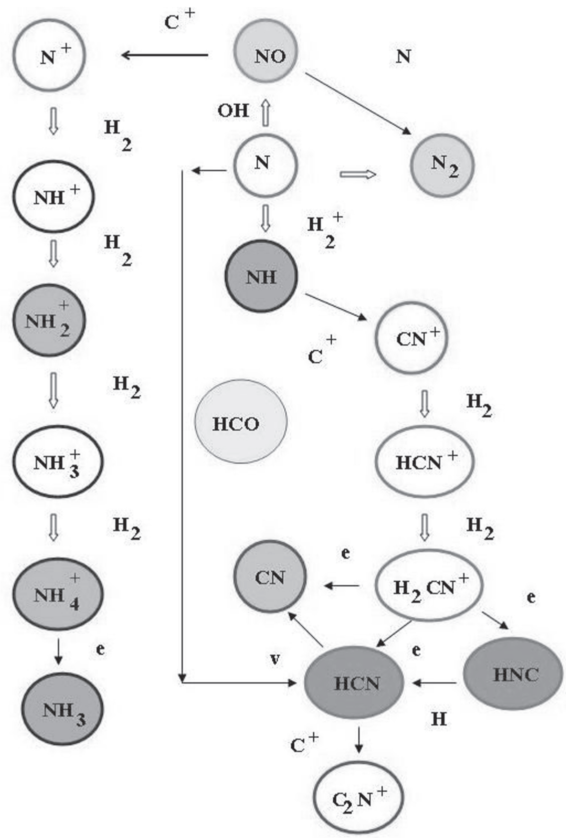

FIGURE 1.3 Some important chemical reactions in the ISM gas-phase nitrogen chemistry. The initiating N^+ and C^+ ions are produced by the intense UV radiation field of nearby stars and cosmic rays ionizing radiation (dissociative processes). The presence of the molecules highlighted in the filled circles has been spectroscopically confirmed in the ISM.
Source: Maciá, 2005; with permission from the Royal Society of Chemistry.

1.3 THE ROLE OF PHOSPHATES IN LIVING SYSTEMS

Phosphorus, mainly in the form of phosphate derivatives, is a universal constituent of cells protoplasm and is required for growth, health, and reproduction in all forms of animals, plants, and bacteria. Accordingly, this element belongs to the selected group of the main biogenic elements, which along with H, C, O, N, and S are present in all known life beings. In fact, phosphorus compounds profusely appear in living systems where they perform many fundamental biochemical functions. Thus, the esters of phosphoric acid, including sugar phosphates and nucleotides, play a leading role in most biochemical processes, such as glycolysis and nucleic acid metabolism, and these esters also determine the structural stability of DNA and RNA nucleic acids. Almost all coenzymes of photosynthesis, fermentation, respiration, and biosynthesis, such as nicotine-adenine dinucleotide (NADPH), flavine-adenine dinucleotide (FAD), or coenzyme A contain phosphoric acid derivatives as an essential component. Adenosine triphosphate (ATP) is the best-known conveyer of chemical energy in most metabolic routes, and this molecule also acts as an inorganic phosphate carrier in many important enzymatic reactions. In addition, some cyclic nucleotide derivatives play a significant role in the biochemical activity of diverse hormones, in the synaptic transmission of the nervous system, in cellular division regulation, and even in immune and inflammation response. On the other hand, the ion HPO_4^{2-} plays a crucial role in tasks ranging from active carrier transport through cellular and mitochondrial membranes to bone metabolism. The $H_2PO_4^-$-HPO_4^{2-} system is also an important intracellular buffer. The main biochemical roles played by phosphorus compounds are summarized in Table 1.1.

By inspecting this table, we realize that different phosphoric acid moieties cover a broad spectrum of biochemical activities involving storage and transfer of information, energy transfer, membrane structure, or signal transduction. Thus, phosphate esters and anhydrides dominate the living world (Westheimer, 1987). This properly illustrates the chemical unity of phosphorus compounds in living matter, expressed by the fact that such diverse and fundamental biological tasks are related to a unique basic chemical motive, namely, the orthophosphoric acid molecule H_3PO_4.

TABLE 1.1 Biochemical Roles of Compounds Containing Phosphorus*

Compound	Biochemical Role
Nucleic acids	Storage and transmission of genetic information
Nucleotides	Coenzymes; carriers of P; precursors in DNA and RNA synthesis
	Chemical energy transfer (ATP)
Phospholipids	Main characteristic components of cellular membranes
Sugar phosphates	Intermediate molecules in carbohydrates metabolism
HPO_4^{2-}	Intracellular buffer; ionic carrier; bone metabolism

*Main biochemical roles of different phosphorus-bearing compounds in living systems.

1.4 THE PHOSPHORUS ENIGMA

So, how did phosphorus atoms produced inside giant stars concentrate as phosphate derivatives in the organisms composing earth's biosphere to rise up from its 18th cosmic abundance place to the fifth or sixth position in the elemental abundance ranking of biomass representatives, going from archeobacteria to human beings? And, closely related to the question above, how did phosphorus atoms belonging to PO_4 phosphate groups manage to be included in such a great variety of molecules playing essential biochemical roles in all currently existing life forms?

The two questions above define the essence of what we refer to as the phosphorus enigma.

The first step towards its elucidation will be presented in Chapter 5, where we compare the different nucleosynthesis routes yielding the main biogenic elements C, O, N, S, and P. In doing so, we will realize that the case of phosphorus is quite remarkable. In the first place, the nucleosynthesis of the ^{31}P nucleus can only take place in the minor subset of stars which are massive enough to ignite the previously synthesized C and Ne fuels under explosive conditions. In the second place, its synthesis proceeds through an involved nuclear reactions network, rendering a very low overall yield of phosphorus. These facts account for the scarcity of this element in the cosmic elemental abundance inventory, hence highlighting the importance of differential abundance enhancement mechanisms occurring during the condensation and aggregation episodes giving rise to the synthesis and degradation of different chemical compounds in the course followed by atoms from dying stars' external atmospheres (Chapter 6) to newborn planetary systems around new generation stars (Chapter 7). Indeed, once the atoms are formed inside the stars, the next step in chemical evolution is the synthesis of molecular compounds joining them. During the past 80 years astronomers have detected many molecules containing biogenic elements in different astrophysical environments beyond our solar system, such as extended stellar atmospheres, circumstellar shells, diffuse nebulae and dense clouds interspersed in our Galaxy, as well as in other galaxies far away, and in the intergalactic medium (IGM) between them. For the sake of illustration, a detailed account of the ISM gas-phase molecular inventory in our Galaxy is given in Figures 1.4 and 1.5.

Quite interestingly, the number of carbon-containing compounds observed in diverse galactic sources amounts to about 75% of the 221

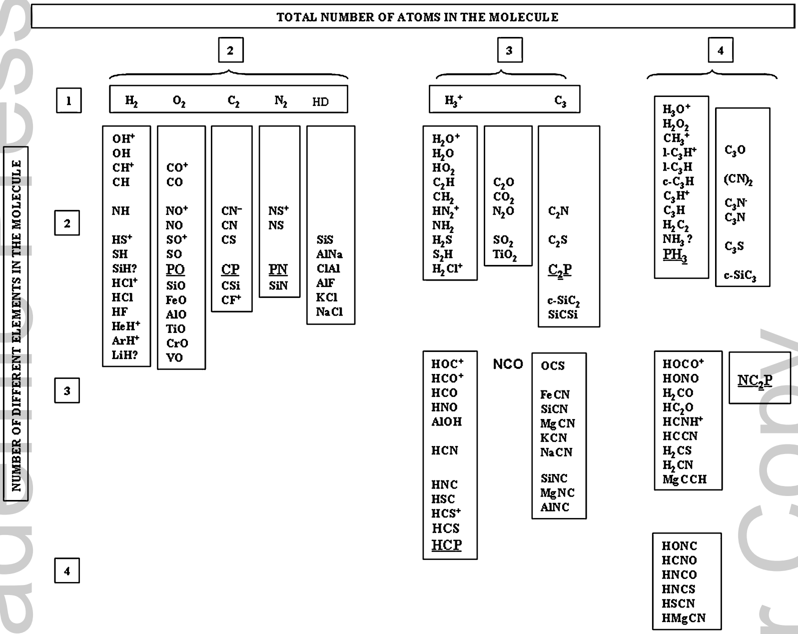

FIGURE 1.4 Molecules containing up to four atoms detected in different astrophysical environments of the ISM (including diffuse and dense clouds, circumstellar envelopes around aged stars, and planetary nebulae) are arranged according to their chemical complexity, measured in terms of the number of different elements present in the considered molecule (in ordinates) and the total number of atoms they contain (in abscissas). In each box, the molecules are listed attending to the elemental abundance rank of the atoms they contain. The seven P-bearing compounds observed to date are highlighted.
Source: Tielens, 2013; Agúndez et al., 2014b, 2018, Ziurys et al., 2015. http://www.astrochymist.org/astrochymist_ism.html; http://www.astro.uni-koeln.de/cdms/molecules/; https://en.wikipedia.org/wiki/List_of_interstellar_and_circumstellar_molecules.

molecules identified up to now (28 August, 2019), so that one may properly state that the chemistry of the universe as a whole is mainly organic chemistry (Oró, 1963). Nitrogen and oxygen-bearing compounds are also profusely found throughout the Galaxy, each one accounting for about 34% of the molecules listed in Figures 1.4 and 1.5, whereas the 21 sulfur-bearing molecules only represent a 10%. The number of molecules containing phosphorus is even smaller, since just seven representatives have been reported to date in the ISM. Suitable information regarding these molecules is provided in Tables 1.2 and 1.3. Most molecules listed in Table 1.2 are notable in that all compounds but PH_3 contain a strong

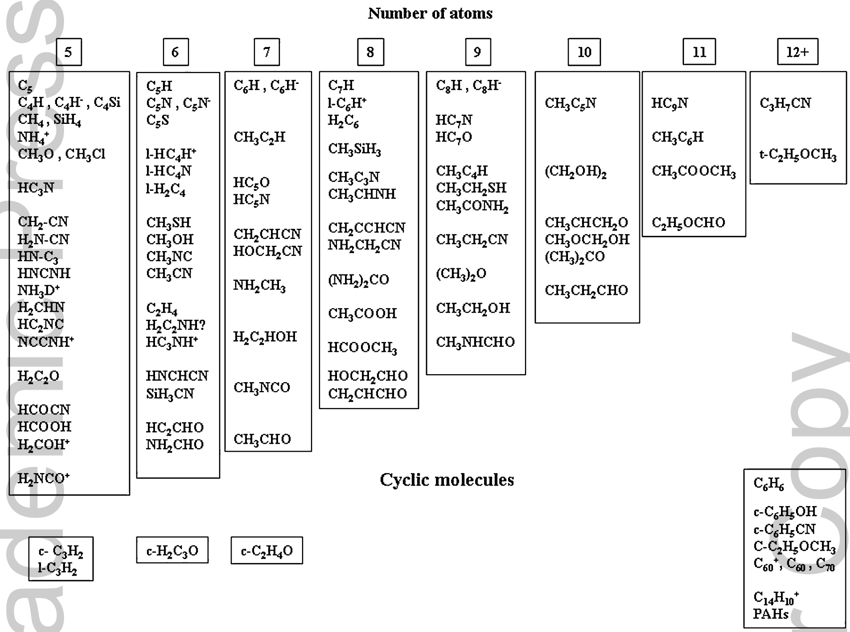

FIGURE 1.5 Molecules containing more than four atoms detected in different astrophysical environments of the ISM (including diffuse and dense clouds, circumstellar envelopes around aged stars, and planetary nebulae) are listed according to their chemical complexity measured in terms of the total number of atoms present in the considered molecule. No P-bearing compounds containing more than four atoms have been detected to date.
Source: Tielens, 2013; Ziurys et al., 2015. http://www.astrochymist.org/astrochymist_ism.html; http://www.astro.uni-koeln.de/cdms/molecules/; https://en.wikipedia.org/wiki/List_of_interstellar_and_circumstellar_molecules.

double or triple bond amounting to energies between 600 and 760 kJ mol^{-1} (6.2–7.8 eV, see Table 4.2). In contrast, phosphine only contains P – H single bonds with a bond energy of just 343 kJ mol^{-1} (3.5 eV). It is also interesting to note that analogs to each of the compounds listed in Table 1.2 have been discovered in the ISM with P substituted by its isovalent element N, namely, N_2, CN, NO, HCN, CCN, and NH_3 (see Figure 1.4).

In this regard, it is worthy to note that, albeit both N and P atoms belong to the same group in the periodic table, phosphorus chemistry is quite peculiar as compared to that of nitrogen (Cummins, 2014). A significant difference between N and P chemistries is properly illustrated by the fact that, on the grounds of energetic considerations, earlier theoretical calculations predicted that the production of the PO molecule should be highly favored in the extreme conditions (low temperature, very low densities) prevailing in the ISM (Thorne et al., 1984).

However, although the extensive search was performed, the detection of this molecule in the ISM has remained very elusive, and it was first observed in the circumstellar regions around oxygen-rich evolved stars, in agreement with previous suggestions (Maciá et al., 1997). Similarly, while nitrogen hydrides are relatively abundant in the ISM (see Figures 1.4 and 1.5), and phosphine has been long known to be present in the atmospheres of the giant planets Jupiter and Saturn (Sánchez-Lavega, 2011), no hydrides of phosphorus have been detected in the ISM yet, although PH_3 has been observed in both a circumstellar shell and a protoplanetary nebula to date (see Tables 1.2 and 1.3).

TABLE 1.2 Phosphorus Bearing Molecules Detected in the ISM Arranged in Chronological Order

Compound	Chemical Formula		Source		References
Phosphorus mononitride	PN	P≡N	Ori KL	SFR	Ziurys, 1987
					Turner and Bally, 1987
			W51M	SFR	
					Ziurys, 1987
			Sgr B2	SFR	Turner and Bally, 1987
					Ziurys, 1987
			M17SW	SFR	Turner and Bally, 1987
			DR 21OH	SFR	
			NGC 7538	SFR	Turner et al., 1990
			IRC +10216	C-rich CSE	Turner et al., 1990
			IRC +10216	C-rich CSE	Turner et al., 1990
			VY CMa	O-rich CSE	Guélin et al., 2000
			CRL 2688	PPN	Agúndez et al., 2007
			L1157 B1	SFR	Ziurys et al., 2007
			IK Tau	O-rich CSE	Milam et al., 2008
					Yamaguchi et al., 2011
					De Beck et al. 2013

TABLE 1.2 *(Continued)*

Compound	Chemical Formula		Source		References
			W51, W3(OH)	SFR	Fontani et al., 2016
			TX Cam	O-rich CSE	Ziurys et al., 2018
			R Cas	O-rich CSE	Ziurys et al., 2018
			NLM Cyg	O-rich CSE	Ziurys et al., 2018
Carbon monophosphide	CP	•C≡P	IRC +10216	C-rich CSE	Guélin et al., 1990
			VY CMa	O-rich CSE	Milam et al., 2008
Phosphorus monoxide	PO	•P=O	VY CMa	O-rich CSE	Tenenbaum et al., 2007
			IK Tau	O-rich CSE	De Beck et al. 2013
			TX Cam	O-rich CSE	De Beck et al. 2013
			R Cas	O-rich CSE	De Beck et al. 2013
			L1157	SFR	Lefloch et al., 2016
			W51, W3(OH)	SFR	Rivilla et al., 2016
			G+0.693–0.03	DMC	Rivilla et al., 2018
			NLM Cyg	O-rich CSE	Ziurys et al., 2018
Phosphaethyne	HCP	H–C≡P	IRC +10216	C-rich CSE	Agúndez et al., 2007
			CRL 2688	PPN	Milam et al., 2008
Dicarbon phosphide	CCP	•C–C≡P ↕ C=C=P•	IRC +10216	C-rich CSE	Halfen et al., 2008
Phosphine	PH_3	H | H–P–H	CRL 2688	PPN	Tenenbaum and Ziurys, 2008
			IRC +10216	C-rich CSE	Agúndez et al., 2014a
Cyano phosphaethyne	NCCP	N≡C–C≡P	IRC +10216	C-rich CSE	Agúndez et al., 2014b

Keys: DMC (dense molecular cloud), CSE (circumstellar shell envelope), PPN (protoplanetary nebula), SFR (star forming region). Among the detected P-bearing molecules, PN, and PO are the only ones that have been reported in star-forming regions.

TABLE 1.3 Abundances of Phosphorus-Bearing Molecules (Relative to Molecular Hydrogen) Observed in Several Circumstellar Envelopes and the Protoplanetary Nebula CRL 2688*

Source	Molecule	Abundance $f(X/H_2)$	References
VY CMa	PO	$(5 \pm 3) \times 10^{-8}$	Ziurys et al., 2018
	PN	$(7 \pm 3) \times 10^{-9}$	Ziurys et al., 2018
IK Tau	PO	$(4.5 \pm 2.5) \times 10^{-8}$	Ziurys et al., 2018
	PN	$(1.0 \pm 0.2) \times 10^{-8}$	Ziurys et al., 2018
TX Cam	PO	$(5.5 \pm 2.5) \times 10^{-8}$	Ziurys et al., 2018
	PN	$(1.0 \pm 0.3) \times 10^{-8}$	Ziurys et al., 2018
NLM Cyg	PO	$(7 \pm 3) \times 10^{-8}$	Ziurys et al., 2018
	PN	$(3 \pm 1) \times 10^{-9}$	Ziurys et al., 2018
R Cas	PO	$(1.0 \pm 0.3) \times 10^{-7}$	Ziurys et al., 2018
	PN	$(2.0 \pm 0.5) \times 10^{-8}$	Ziurys et al., 2018
CRL 2688	HCP	2×10^{-7}	Milam et al., 2008
	PN	$(3–5) \times 10^{-9}$	Milam et al., 2008
IRC +10216	HCP	3×10^{-8}	Milam et al., 2008
	CP	1×10^{-8}	Milam et al., 2008
	PH_3	1×10^{-8}	Agúndez et al., 2014a
	CCP	1×10^{-9}	Halfen et al., 2008
	PN	3×10^{-10}	Milam et al., 2008
	NCCP	$< 4\times10^{-10}$	Agúndez et al., 2014b

*The model parameters employed in the analysis of the O-rich stars IK Tau, TX Cam, R Cas, and NLM Cyg are given in Tables 6.3 and 6.4 in Section 6.2.2. Those corresponding to IRC +10216 and VY CMa stars are given in Sections 2.4.4 and 2.4.5, respectively, and those of the source CRL 2688 are: stellar radius $R_* \sim 9 \times 10^{12}$ cm, photosphere temperature $T_e \sim 3000$ K, distance of 1,000 pc, and a mass-loss rate of 1.7×10^{-4} $M_\odot$ yr^{-1}.

By inspecting the data listed in Table 1.3, we see that the fractional abundances (relative to molecular hydrogen) of the P-bearing compounds given in Table 1.2 fall in the range $f = 10^{-10}–10^{-7}$. The relative abundance of PN molecules observed in dense molecular clouds is even lower, ranging from $f = 10^{-12}$ to 10^{-10}, relative to H_2 (Ziurys, 2008). Keeping in mind the cosmic abundance value [P] = 2.6×10^{-7} relative to hydrogen we conclude that only a minor fraction of the available phosphorus is in the gas phase in the considered sources. For instance, it has been estimated that HCP and PH_3 molecules account for 5% and 2% of the total P budget around

IRC +10216, respectively (Agúndez et al., 2014a). In addition, we see that the fractional abundance of PO is more abundant than PN by a factor of five in the circumstellar envelopes around the evolved O-rich stars TX Cam, IK Tau and R Cas, and by a factor of ~ 20 in the envelope of the supergiant star NLM Cyg. On the other hand, it can be reasonably assumed that the organophosphorus HCP moiety may likely be the precursor species for the two organophosphorus compounds CCP and CP in the envelope around C-rich star IRC +10216. Accordingly, the amount of phosphorus contained in the scarce molecules so far detected in the gas phase is clearly insufficient to account for the quantity of phosphorus-bearing compounds one may expect from its elemental cosmic abundance, strongly suggesting that most phosphorus inventory could be stored in suitable condensed forms in solid dust particles (Guélin et al., 1990; Turner et al., 1990; Maciá, 2005). Indeed, according to recent observations of PN and PO molecules towards seven molecular clouds located at the Galactic Center, these molecules are probably formed in the gas-phase after the shock-induced sputtering of the dust grain mantles, while they are efficiently destroyed in those regions dominated by intense UV, X-ray, and cosmic ray radiation fields. Indeed, PN was detected in five out of seven sources, whose chemistry is thought to be shock dominated. The two sources where PN was not detected, on the other hand, correspond to clouds exposed to intense radiation fields. PO molecule was only detected towards the cloud G+0.693–0.03, with a PO/PN abundance ratio of ~1.5 (Rivilla et al., 2018).

It is interesting to note that phosphorus compounds exhibiting different oxidation states are found in diverse astrophysical environments, as it is depicted in Figure 1.6, where we observe the presence of:

1. Several phosphate minerals (MPO_4) in rocky planets and satellites (Earth, Mars, Moon), stony meteorites, and interplanetary dust particles (IDPs);
2. Phosphorus monoxide (PO) in O-rich circumstellar shells;
3. Organophosphorus compounds such as phosphonic acids in carbonaceous chondrites, and the molecules CP, CCP, HCP, and NCCP found in circumstellar regions;
4. The ubiquitous PN molecule detected in eight star forming regions, six circumstellar envelopes, and a protoplanetary nebula; and

5. Reduced phosphorus compounds like schreibersite (Fe_3P) in iron meteorites, or PH_3 in a carbon-rich circumstellar shell, a protoplanetary nebula, and the atmospheres of Jupiter and Saturn.

As we see, phosphates are the predominant form in terrestrial planets, stony meteorites, and IDPs of possible cometary origin. Reduced moieties predominate in the atmospheres of giant planets and iron-rich meteorites. Finally, intermediate oxidation states are observed in some chondrites and the ISM.

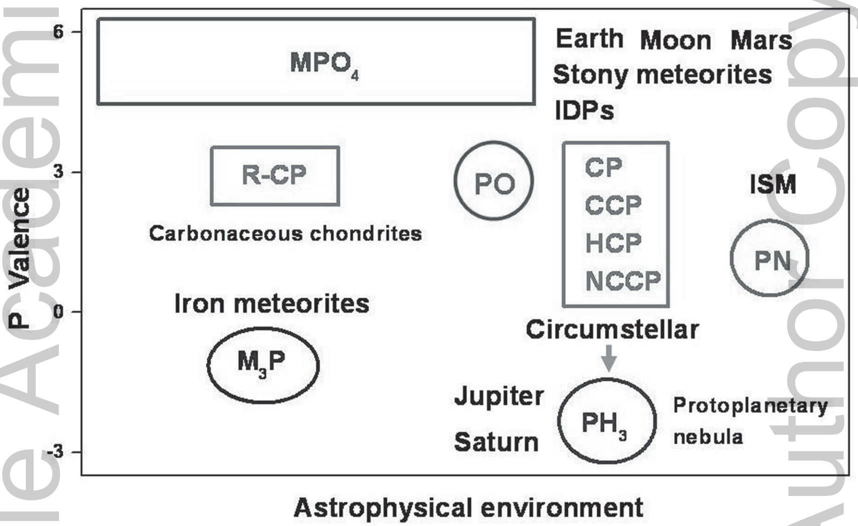

FIGURE 1.6 Distribution of phosphorus compounds in several astrophysical environments arranged according to their oxidation degree.
Source: Maciá, 2005; with permission from the Royal Society of Chemistry.

Quite remarkably, the fact that most phosphorus on earth's surface is in the form of phosphate leads to an important problem in prebiotic chemistry arising from the difficulty of the spontaneous phosphorylation of organic compounds by minerals likely present on the early earth's crust (Pasek, 2015b). In fact, a major open question in evolutionary biochemistry concerns both the role of phosphorus compounds in the chemical evolution which preceded the emergence of life on earth and the primary sources of such phosphorus compounds (Chapter 8).

In summary, keeping in mind the queries we have enumerated in this introductory chapter, the phosphorus enigma can then be briefly posed as follows: Why should such a relatively scanty element be so important for biological systems? In order to provide a plausible answer, in the following chapters we will adopt an interdisciplinary approach by addressing key physical, chemical, and biological aspects of phosphorus atoms journey from their very formation in the cores of massive stars to their incorporation into the early planet earth, or similar exoplanets orbiting around other stars, and then to the possible emergence of the first metabolic pathways inside the first living cell on our planet… and elsewhere in the universe?

KEYWORDS

- **biogenic elements**
- **biomass**
- **biosphere**
- **chemical evolution**
- **circumstellar shell**
- **cosmic rays**
- **galaxies**
- **intergalactic medium**
- **interstellar chemistry**
- **interstellar medium**
- **nucleosynthesis**
- **oligo-elements**
- **organophosphorus compounds**
- **prebiotic chemistry**
- **supernova event**
- **thermodynamical equilibrium**