The role of phosphorus in chemical evolution

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In this *tutorial review* we consider the role of phosphorus and its compounds within the context of chemical evolution in galaxies. Following an interdisciplinary approach we first discuss the position of P among the main biogenic elements by considering its relevance in most essential biochemical functions as well as its peculiar chemistry under different physicochemical conditions. Then we review the phosphorus distribution in different cosmic sites, such as terrestrial planets, interplanetary dust particles, cometary dust, planetary atmospheres and the interstellar medium (ISM). In this way we realize that this element is both scarce and ubiquitous in the universe. These features can be related to the complex nucleosynthesis of P nuclide in the cores of massive stars under explosive conditions favouring a wide distribution of this element through the ISM, where it would be ready to react with other available atoms. A general tendency towards more oxidized phosphorus compounds is clearly appreciated as chemical evolution proceeds from circumstellar and ISM materials to protoplanetary and planetary condensed matter phases. To conclude we discuss some possible routes allowing for the incorporation of phosphorus compounds of prebiotic interest during the earlier stages of solar system formation.

1. Phosphorus as a main biogenic element

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. Almost all coenzymes contain phosphoric acid as an essential component. Adenosine triphosphate (ATP) acts as inorganic phosphate carrier in many important enzymatic reactions implied in chemical energy transfer as well as in specific biosynthetic routes. In addition, some other 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. 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. This properly illustrates the *chemical*

Table 1 Main biochemical roles of different phosphorus compounds in living systems

COMPOUND	BIOCHEMICAL ROLE
Nucleic acids	Storage and transmission of genetic information
Nucleotides	Coenzymes; carriers of P; precursors in DNA and RNA synthesis
Phospholipids	Main characteristic components of cellular membranes
Sugar phosphates	Intermediate molecules in carbohydrates metabolism
HPO_4^{2-}	Intracellular buffer; ionic carrier; bone metabolism

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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. Accordingly, phosphorus belongs to the selected group of **main biogenic elements**, which along with H, C, O, N, and S are present in all known life forms.

1. Elemental abundance of biogenic elements in the universe

Why are certain atoms used frequently in living systems while others are found rarely or never? In the first place, we must consider the *relative abundance* of a given element in those places where life phenomena are supposed to start and develop. Quite interestingly the relative abundance of the main biogenic elements in the universe as a whole compares well with their relative abundance observed in living beings, as illustrated in Fig. 1. Thus, the four most abundant elements in the universe, with exception of the noble gas He, are H, O, C, and N, which are also precisely the four major constituent elements of organic compounds.[1] These abundances are, in turn, determined by the nucleosynthesis processes in stars within the grand scheme of *galactic chemical evolution*, that is to say, the evolution of matter and energy in the galaxies. In fact, galaxies are huge collections of stars, planets, gas, dust and unseen dark matter held together by mutual gravitational attraction. The vast bulk of the volume of a galaxy is filled with the gas and dust which exist between the stars, which is referred to as interstellar medium (ISM). The main activity of a spiral galaxy is the cyclic process in which stars eject gas and dust into the ISM, while at the same time gas and dust clouds in the ISM gravitationally collapse to form stars. The basic idea is then to average several populations of stars that, over the age of the galaxy, will combine their nucleosynthetic products with those coming out of the Big Bang to add up approximately to the observed abundance of the different elements of the periodic table.[5]

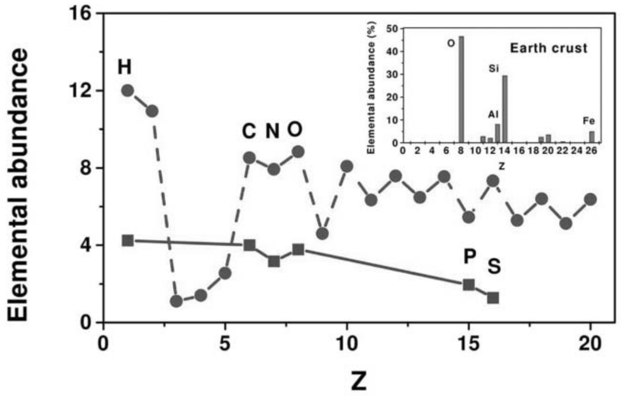

Fig. 1 Elemental abundance comparison between the dry biomass of a representative yeast,[2] and the so-called cosmic reference standard, derived from abundance measurements in meteorites and the sun.[3] The abundances are given on a logarithmic scale with H = 12 for cosmic abundances (●) and C = 4 for biomass abundances (■). The earth's crust elemental abundance,[4] is given in the inset for the sake of completeness. The elements are arranged according to their atomic number *Z*. Main biogenic elements are explicitly labelled.

Atomic and molecular hydrogen are the most abundant species by number and mass in the ISM. The interstellar dust abundance relative to hydrogen varies somewhat both within a given galaxy and from galaxy to galaxy. Nevertheless, as a general rule, the mass of material in dust particles is about 1% of the mass in hydrogen. Dust particles range in size from the molecular domain to sizes of about 0.5 μm and are composed largely of amorphous carbon or graphite, aromatic hydrocarbons, silicates, ices, silicon carbide, and possibly iron particles, metallic oxides and sulfides.[6] In the gas, helium is the next most abundant element after hydrogen, roughly 10% of hydrogen by nucleus. Oxygen and carbon follow, with elemental abundances of 6.8×10^{-4} and 3.3×10^{-4} relative to hydrogen, respectively. It is noteworthy that although phosphorus is an important constituent of living matter, it is relatively scarce in the cosmic scale, with an elemental abundance of 2.8×10^{-7} relative to H in the sun's atmosphere.[3] This suggests that the cosmic abundance of P was not the decisive factor in determining its important role in living beings.

2. Bonding properties of biogenic elements

We should then consider the ability of a given element to bind other atoms as this determines their possible molecular structures and related chemical properties. In turn, this ability is determined by their electronic configuration and electronegativity. In this sense, it is interesting to note that the main biogenic elements provide a minimal set containing a representative of the most common valence states, *i.e.*, H = 1, O,S = 2, N = 3, C = 4 and P = 5. Occasionally, Si has been proposed as a basis for an alternative biochemistry because of its abundance in Earth's crust (silicon is also a relatively abundant element on a cosmic scale, see Fig. 1) and the fact that silicic acid is more abundant in nature than phosphoric acid. However, the chemical properties of C contrast markedly with those of Si, which also has a four valence state. In striking contrast to C, Si combines with O to form insoluble silicates or network polymers of SiO_2 instead of gaseous molecules like CO or CO_2. Accordingly, synthetic processes similar to those producing sugars in photosynthetic organisms are impossible and a metabolic scheme based on Si becomes difficult to conceive. On the other hand, due to the larger size of the Si atom, Si–Si bonds are weaker than C–C bonds, and polymers of Si are unstable in the presence of water. Furthermore, the esters of silicic acid hydrolyze far too rapidly to survive under physiological conditions, so that silicic acid is an unsuitable substitute for phosphoric acid in the backbone of nucleic acids. Similar arguments also apply to other possible alternatives, like sulfuric and arsenic acids or even the O=P(OH)2R acid derivative. In fact, phosphoric acid is specially adapted for its role in nucleic acids because it can simultaneously link two nucleotides and still doubly ionize. The resulting negative charge serves both to stabilize the diesters against hydrolysis and to retain the macromolecules within a lipid membrane.[7]

In biological systems we only find orthophosphoric acid derivatives, which implies that phosphorus appears in tetrahedral coordination with four oxygen atoms. The tetrahedral coordination is indicative of an sp^3 hybrid, which can form if an electron of the fundamental electronic configuration $3s^2p^3$ is promoted to the 3d subshell. The optimal combination of orbitals then leads to four P–O σ bonds in the first place. There remain four electrons, each for one p_π-orbital, at O perpendicular to the bonding axis, and four 3d-orbitals. This allows for two p-d double bonds. In this way, P is the unique element belonging to the main biogenic group whose chemical properties may be significantly influenced by d type orbitals, hence allowing for a richer chemistry.[8] At this point it is worth noticing that the prevailing current view is that both pentacoordinated PX_5 and hexacoordinated PX_6 compounds, traditionally described in terms of sp^3d and sp^3d^2 hybridisation of the central atom, respectively, can be properly understood without requiring the participation of 3d orbitals within the framework of the valence shell electron pair repulsion model.[9]

3. Chemical evolution

Around the middle of the twentieth century a number of findings in several scientific disciplines progressively contributed to the emergence of a broad view of chemical processes in nature. Among the main contributions to this view we can highlight:

•The progressive synthesis of the chemical elements from hydrogen by nuclear transformations in the stars.[10] Thus modern astrophysics has traced the chemical unity of matter in the universe to a common origin of the elements.

•The discovery of abundant molecular species in the ISM and around evolved stars.[11] During the latter stages of their evolution, stars release large quantities of materials enriched with atoms previously formed in their cores to the ISM, where these atoms undergo further chemical processing. From this perspective, stars are open systems that eject to their surrounding medium large amounts of bioelements along with the energy necessary to process them into more complex molecules by means of a peculiar chemistry. More than 75 percent of the molecules detected in the ISM are carbon compounds, indicating that the chemical processes in the ISM favor the synthesis of organics. Moreover, among the detected species are precursors of biological interest, such as water, ammonia, formaldehyde, or cyanhydric acid and the possible presence of the amino acid glycine has been recently claimed.[12]

•The presence of a lot of organic compounds, including aliphatic and aromatic hydrocarbons, carboxylic acids, amino acids, ketones, aldehydes, urea, amides, alcohols, amines and nitrogen has been reported in several chondritic meteorites.[13] The variety of types of compounds found and their molecular structures, exhibiting no preferred chirality, point to origins in nonbiological processes.

•During the past decades of experimental studies, several key compounds, such as amino acids, purines, pyrimidines and other biochemical molecules have been obtained in the laboratory under presumed primitive Earth conditions.[14,15]

Taking into account all these results, the notion of chemical evolution has progressively emerged in order to provide a suitable scenario to explain the progressive tendency of matter to proceed from simple to more complex molecular structures in the course of the evolution of the universe as a whole.[16] Underlying this chemical trend we find the processes determining the evolution of matter and energy in the galaxies which, in turn, determine the *physicochemical conditions* of a given element and its related compounds at different astrophysical scenarios. These processes include stellar winds, planetary nebulae outflows, shock waves, circumstellar envelope formation around evolved stars, supernovae explosions, cosmic ray spallation, gas-phase molecular synthesis within interstellar clouds, absorption, desorption and catalysis phenomena on interstellar grain surfaces, formation of protoplanetary disks around newly born stars, differential condensation of refractory materials in planetesimals, photochemistry in cometary comae and planetary atmospheres, or differential fractionation within planetary cores. In each one of these environments a given element will react with others under specific conditions, giving rise to the formation of characteristic molecular species.

In the light of these considerations, the main aim of this work is to review the role of phosphorus and its compounds within the context of chemical evolution in the galaxies.[17] This evolution proceeds by means of a gradual succession of processes taking place at different sites in the galaxy. In this way, the protagonism of the original atomic species progressively fades as we go from the atomic to the molecular and macromolecular levels as chemical evolution goes on. The chemical nature of the prevailing molecules would be determined by the physicochemical conditions at those places, under the constraints imposed by the well-known energy and entropy optimization requirements. Within this framework the raw materials of which living beings are made may progressively be assembled from a lot of pieces interspersed in several astrophysical environments.

2. Nucleosynthesis of phosphorus

By cosmic standards chlorine and phosphorus are the less abundant species among the third row elements of the periodic table, and P is the least abundant representative in the group of the main biogenic elements. What is the reason for its relatively low cosmic abundance? To answer this question we must consider the synthesis of phosphorus nuclide due to thermonuclear reactions occurring in the core of stars.

There are six reported isotopes of phosphorus nuclide, of which the only stable one is ^{31}P, consisting of 15 protons and 16 neutrons. The binding energy of the stable phosphorus nucleus is 8.4 MeV, a figure close to the maximum binding energy per nucleon (8.7 MeV) exhibited by iron nuclides. This indicates that the nuclear structure of phosphorus is very stable. On the other hand, the electrostatic repulsion barrier associated to the nuclear charge ($Z = 15$) of the colliding nuclei implies the existence of significant activation energies, and consequently, high kinetic energies, corresponding to temperatures above 10^9 K, are required for its formation throughout nuclear reactions. This figure places a severe constraint on the mass of the star where thermonuclear reactions leading to the synthesis of ^{31}P nuclides are taking place. In fact, such a high temperature can only be attained in the cores of very massive stars, in the range of 15–100 times the solar mass. In these stars several burning stages follow in succession and each is named after its principal fuel as hydrogen, helium, carbon, neon, oxygen and silicon burning. Each fuel ignites at a progressively increasing temperature, as shown in Fig. 2. Stars spend most of their lifetime burning H and producing He. When most of their H is burned, stars undergo a gravitational collapse, further compressing the core, which reaches temperature and pressure conditions so high that they allow for the combination of three He nuclei into one C nucleus. A reaction requiring the simultaneous collision of three atoms is highly improbable in most environments, so red giant stars, where these reactions occur, provide a unique place to yield substantial amounts of carbon.

Oxygen nuclide begins to burn at about $T = 2 \times 10^9$ K. The oxygen fusion produces excited nuclear states of ^{32}S that may decay through the channel $^{16}O + ^{16}O \rightarrow ^{31}P + p$. However, this promising initiating reaction is followed by a host of secondary ones. When all reactions are considered ^{28}Si and ^{32}S constitute the bulk ($\sim$90%) of the final composition.[10] Consequently, O-burning is not an adequate path for obtaining ^{31}P nuclide, not only due to the consumption of the initially formed phosphorus nuclides, but also since the products of central hydrostatic O-burning are probably never ejected into the interstellar medium, but are trapped inside the degenerate core which will emerge as a neutron star or a black hole after the supernova explosion which massive stars eventually undergo.[18]

In fact, the central regions of a massive star are capable of undergoing static nuclear reactions all the way up to the iron-peak elements. Beyond that, no further nuclear reactions can be exothermic. A dense, inner iron core gradually builds up until it becomes unstable and rapidly collapses liberating large amounts of gravitational potential energy in the form of a shock wave. This wave gives rise to a sudden heating, followed by a rapid expansion and cooling of the outer layers in a process referred to as *explosive burning*. These explosive conditions allow then to surmount the energy barrier separating the nucleosynthesis of P from that of Ne and S nuclides, respectively (see Fig. 2).

Accordingly the primary origin of natural ^{31}P nuclide takes place in the inner zone of stars massive enough (say, above 15 solar masses) to undergo hydrostatic C-burning followed by explosive Ne-burning at roughly $T = 2–3 \times 10^9$ K.[18] The overall network of nuclear reactions leading to the ultimate nucleosynthesis of ^{31}P nuclide is summarized in Fig. 3. From the given branching ratios the final ^{31}P yield is below 2.5%.

In comparison with the nucleosynthesis of the remaining biogenic elements, the case of phosphorus is remarkable. In the first place, the nucleosynthesis of the nuclide ^{31}P can only take place in the minor subset of stars which are massive enough to explosively ignite the C and Ne fuels. This represents less than 10% of the star population in a typical galaxy. In the second place, many nuclear processes are involved in its formation, implying a very low overall yield. These facts properly explain

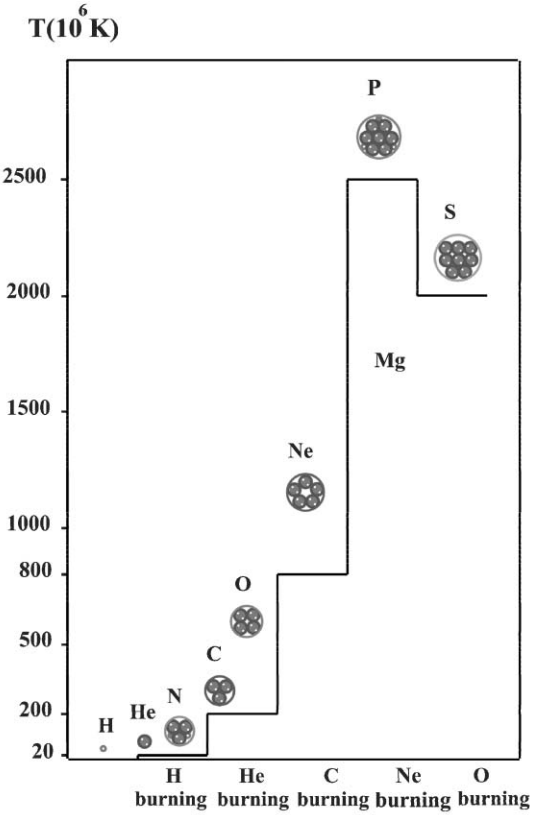

Fig. 2 Nucleosynthesis of the main biogenic elements takes place in stars' cores. In this figure we show the main nuclides produced in each burning stage. Most common, less massive solar-like stars, are able to ignite H and He fuels in the course of their evolution. This explains the high relative abundance of their main nuclear products O, C, and N. On the contrary the nucleosynthesis of P and S requires very high core temperatures, which can only be attained in the minor group of very massive stars able to ignite Ne and O fuels. (More details in the text).

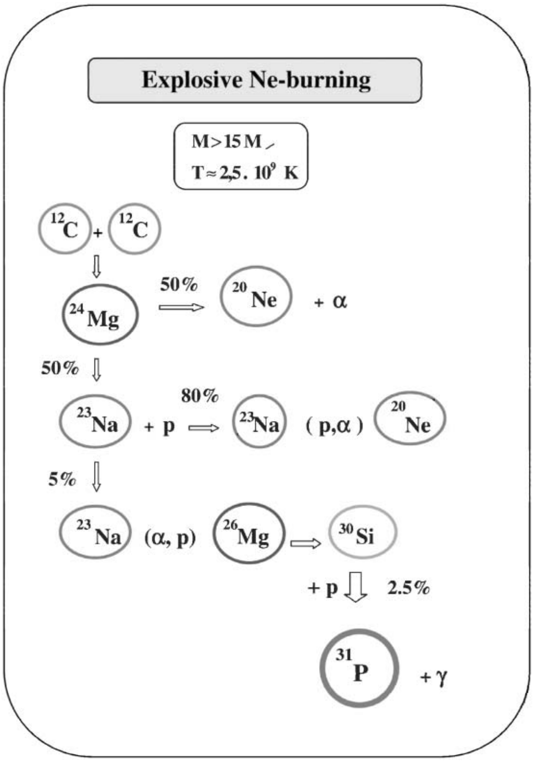

Fig. 3 Nuclear reaction network leading to the synthesis of natural phosphorus nuclide during the explosive neon burning phase in the core of massive stars (more details in the text).

why phosphorus is so scarce as compared with the other main biogenic elements. On the other hand, the explosive conditions leading to its formation guarantee that this element will be readily liberated to the ISM, where it would be ready to react with other available atoms.

3. Chemical properties of phosphorus compounds

Phosphorus compounds can exhibit coordination numbers of 1, 3, 4, 5 and 6, although most of them have coordination numbers 3 and 4. In fact, nearly all naturally occurring P compounds on Earth are orthophosphates based on the PO_4 group.[19,20] Complex, tridimensional networks including chains, rings, cage-like structures and planar arrangements are known for compounds in which P is quadruply connected. None of the compounds with coordination number 1 is stable under normal conditions on Earth, but some representatives can be synthesized under controlled conditions in laboratories. Thus, the HCP molecule was obtained by passing phosphine through an arc between graphite electrodes.[21] The second member of the phosphaalkyne family (CH_3CP) was subsequently identified using microwave spectroscopy along with a broad collection of phosphorus analogs of nitriles given by the general formula $RC{\equiv}P$, with R = {CF_3, NC, HCC, H_2CCH, C_6H_5}.[22] Quite interestingly, some of these species can be found under the extreme conditions prevailing in the ISM. Thus, the CP radical has been detected in circumstellar envelopes around evolved stars (temperatures $\sim 10^3$ K, densities $\sim 10^4$ cm^{-3}).[23]

The most important reaction of elemental phosphorus is oxidation, whose main final products are phosphorus pentoxide $P_4O_{10} = = (P_2O_5)_2$, plus some amount of phosphorus trioxide, $P_4O_6 = = (P_2O_3)_2$, according to the following reaction sequence

$$P_4 + O_2 \rightarrow P_4O + O, P_4O + O_2 \rightarrow \\ P_4O_2 + O, P_4O_2 + O_2 \rightarrow \ldots \rightarrow P_4O_{10} \quad (1)$$

The molecular structure of P_4O_{10}, exhibits the characteristic tetrahedral coordination of the most stable phosphorus compounds, as is illustrated in Fig. 4. It is interesting to mention that the oxidation cycle described by eqn. (1) may take place in the expanded atmospheres of oxygen rich evolved stars. Once formed, P_2O_5 molecules can cluster among them to develop extended networks, which may ultimately grow to form large grains, as sketched in Fig. 4. The structure of the thermodynamically most stable condensed form of phosphorus pentoxide (O'–P_2O_5) consists of infinite layers built from six-membered rings of three corner linked PO_4 tetrahedra.[24] These sheets stack together defining an orthorhombic unit cell. On the other hand, the structure of vitreous P_2O_5 is thought to consist of a three-dimensional network of corner-sharing PO_4 tetrahedra, each of which is decorated with a non-bridging P=O bond.[25] Since phosphorus pentoxide is extremely hygroscopic, the absorption of water molecules may easily lead to the formation of phosphoric acids in such grains of phosphorus oxide. This opens an interesting route to the possible formation of H_3PO_4 in the frozen mantles covering dust particles in the ISM.

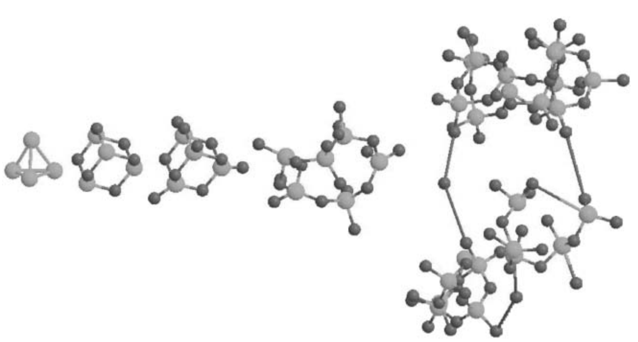

Fig. 4 Sketch illustrating the oxidation sequence of phosphorus which might occur in the extended atmospheres of evolved, oxygen-rich stars. The sequence starts with the P_2 and P_4 molecules, followed by the lower oxides P_4O_6 and P_4O_{10}, whose structures exhibit a characteristic tetrahedral symmetry. The formation of P_6O_{10} rings paves the way to the formation of condensed P_2O_5 sheets, based on linked PO_4 tetrahedra. Depending on the environmental physical conditions these cage-like structures will ultimately crystallise in the orthorhombic system or will acquire a glassy structure instead.

4. Distribution of phosphorus compounds in the galaxy

1. The planet earth

Phosphorus is the eleventh most abundant element in the Earth's crust. Its abundance on the Earth is higher than its cosmic ranking (18th) due to the rocky nature of our planet. On Earth, phosphates occur as ubiquitous although accessory minerals of the apatite group in all important classes of igneous and metamorphic rocks, and also as well-separated crystalline masses formed by differentiation from cooling basic magma. In most rocks, phosphorus is found in small concentrations, usually about 0.15 to 0.2% in weight.[26] The most representative phosphate minerals found in the lithosphere are $Ca_5(PO_4)_3$ (F,Cl,OH) (fluorapatite, chlorapatite and hydroxylapatite), $Ca_3(PO_4)_2$ (whitlockite), $(Fe,Mn,Ca)_3(PO_4)_2$ (graftonite) and $(Fe,Mn,Ca)_7(PO_4)_4F_2$ (sarcopside), the apatite group being by far the most ubiquitous. In igneous and metamorphic rocks, the most common species is fluorapatite. In sedimentary phosphates the typical mineral is carbonate fluorapatite.

The relative importance of different reservoirs of phosphorus on the surface of the Earth can be estimated by considering the biogeochemical cycles of the elements C, P, O and Fe.[27] Two interesting facts are obtained from this study. One is the similarity in the amount of phosphorus on land (4.3×10^{20} g) and on the ocean floor (3.9×10^{20} g), and the other is the low abundance of P in the oceans (6.3×10^{16} g) as compared to the former reservoirs. Quite remarkably, by assuming the average ratio $P/C \simeq 0.02$ in living beings and a total carbon mass of about 10^{18} in the biosphere the amount of P trapped in the biosphere results 2.0×10^{16} g, a figure which compares well with the oceanic phosphorus content.[17]

2. The moon

The phosphates apatite and whitlockite are common accessory minerals in many lunar rocks, and in fact analyses of returned lunar samples indicate that phosphorus is present as a minor element in each of the studied specimens.[28] For most lunar basalts, the range of phosphorus content is quite limited, ranging from 200 to 900 ppm. On the other hand, lunar highland samples may contain the so-called KREEP glass (for potassium, rare Earth elements, and phosphorus), which shows a P abundance of about 0.33 wt%.[29] In these samples the major P-bearing phase is apatite, although whitlockite is also present, along with traces of schreibersite, $(Fe,Ni)_3P$. The presence of reduced forms of phosphorus in lunar rocks is probably the consequence of meteoritic impacts in the production of the lunar regolith.

3. Mars

A direct elemental analysis of the presence of phosphorus compounds on Mars surface was not possible during the Viking mission, due to the fact that P could not be accurately detected by the instruments because of interference from major S and Si peaks.[30] Indirect sources like those provided by the analysis of several martian meteorites indicate a relatively high phosphorus content, within the range 0.1–1.3 wt%.[31] More recent mineralogical studies performed by Mars Pathfinder lander have confirmed the presence of P compounds in five samples, giving large abundance values ranging from 0.9 to 1.5 wt%.[32] These data are in line with those previously obtained from the study of martian meteorites, strongly suggesting that P is more abundant on Mars surface than in the Earth's crust, probably as a consequence of the high P abundance in the Martian mantle as compared to the terrestrial mantle.

4. Meteorites

The analysis of meteorites shows that phosphorus is a minor but ubiquitous element found in many types of meteorites (chondrites, 0.1–0.4%; achondrites, 0.01–1.3%; mesosiderites, 0.03–1.4%; and irons, 0.1–0.6% wt).[33] On the average, phosphorus is the 13th most abundant element in meteoritic material. Chlorapatite, whitlockite and other Ca and Mg phosphate minerals are the dominant phosphorus reservoirs in stony meteorites, whereas in iron-rich meteorites the phosphide minerals $(Fe,Ni,Co)_3P$ and $(Ni,Fe)_5(Si,P)_2$ (perryitite) are dominant.[34]

A homologous series of alkyl phosphonic acids (from methyl to butyl) along with inorganic orthophosphate ($\sim$25 μmol g^{-1}) were identified in water extracts of the Murchison meteorite by mass spectroscopy.[35] The presence of orthophosphates in both Murchison (18 ± 1 μmol g^{-1}) and NWA502 (20 ± 0.1 μmol g^{-1}) carbonaceous chondrites has been confirmed by quantitative NMR analysis.[36] Phosphorous acid can be produced by hydrolysis of schreibersite: interaction of this mineral with water on a meteorite parent body (in the near-surface region) or in ablating comets or meteorites could produce hypophosphorous and orthophosphorous acids. This orthophosphorous acid could serve as a source for photochemical production of phosphite radicals, which in turn could be used in the synthesis of phosphonic acids.[36]

5. Interplanetary dust particles

Interplanetary dust particles (IDPs) come from two main sources: comets and main-belt asteroids. All near-Earth dust collections are highly biased towards the main-belt asteroidal component, due to its lower geocentric velocity as compared to that of comets.[37] The average phosphorus content of dust particles of probable cometary origin collected in the stratosphere is of the order of 0.3% in weight, with extreme values within the range 0.1 to 0.7% depending on the considered sample.[38] These values compare well with those reported for carbonaceous chondrites and iron-rich meteorites.[39] In addition, mass spectral evidence of PO_2 and PO_3 anions in two fluffy IDPs of probable cometary origin has been reported.[40]

6. Comets

The dust impact analyzers carried by the spacecrafts Vega 1, Vega 2, and Giotto probes indicated that most of the Halley comet analyzed particles are rich in the biogenic elements H, C, N and O, suggesting the validity of models that describe cometary dust as a source of organic rich material.[41] The analysis of the obtained mass spectra indicated the presence of a minor feature corresponding to the charge-mass ratio $m/z = 31$, which may correspond to elemental phosphorus. Nevertheless, this assignment remains uncertain due to the difficulty in resolving phosphorus from other organic ions of equal mass ratio, like CH_2OH^+ for instance.[42] The new generation analyzer on board the Stardust probe allowed for studying the mass spectra of negative ions of cometary particles for the first time. The positive-ion spectra obtained during the comet Wild-2 flyby exhibit a high signal at $m/z = 31$, whereas the negative-ion spectra are almost featureless $m/z = 60–80$, where the possible presence of PO_2 and PO_3 anions should be expected.[43] On the other hand, no specific P-bearing chemical species have been spectroscopically detected in comets to date.[12] Consequently, the possible existence of phosphorus compounds in comets has not yet been confirmed, although it is reasonable to expect that this element may be trapped in the refractory component of cometary nuclei.

7. Giant planets

Voyager data confirmed the presence of phosphine (PH_3) with a volume mixing ratio of 0.6 and 2 ppm in Jupiter and Saturn respectively, implying a P/H ratio in good agreement with the solar value. The presence of phosphine in the atmospheres of Jupiter and Saturn and its absence in the atmospheres of both Uranus and Neptune,[44] suggests that the formation of these planets took place from accretion of planetesimals rather than by condensation from a homogeneous nebula.[45]

To the best of our knowledge no organophosphorus compounds have been reported to date in Jupiter's atmosphere,[46] although potentially observable amounts of the HCP and CH_3PH_2 molecules were predicted on the basis of methane and phosphine photochemistry reactions.[47] Keeping in mind these results, it would be interesting to further analyze the materials flowing up to the jovian outer atmosphere after the Shoemaker-Levy comet impact in order to check for the possible presence of some P related compounds, which may be originally trapped inside the comet nucleus.[48]

8. Phosphorus in stellar atmospheres

The presence of elemental phosphorus has been spectroscopically confirmed in most stars observed to date, where it exhibits a similar abundance, although a few cases of stars showing a significant phosphorus enhancement in their atmospheres has been also reported.[49] The presence of P in the external atmospheres of main sequence stars does not imply this element is actually formed in those stars at the observing time. Rather it indicates this element was formed in a previous generation of stars, expelled to the ISM and subsequently incorporated in the gas out of which a new star generation was born.

The physical conditions of stellar atmospheres change during the evolution of the star, eventually allowing for the formation of some stable molecules during the late stages of their lives, when the atmosphere temperature falls below 3000 K. Chemical equilibrium models indicate that chemistry of P is very different from that of N under the physical conditions prevailing in these stars. Earlier calculations indicated that nitrogen would be mostly locked in the form N_2, while little P_2 is formed and thus phosphorus atoms are available for the formation of molecules like PN, PS, PH, PO, and PC.[50] Recent work on the thermodynamic data of P gases suggests, however, that there was a vast overcalculation of the stability of PN gas.[51] Accordingly, thermodynamic calculations in low oxygen environment indicate the actual dominant species are probably P and P_2 gases.[52]

5. The chemistry of phosphorus in the interstellar medium

Once formed in the stellar cores, the main biogenic elements are then liberated to the ISM by means of stellar winds, the formation of planetary nebulae (low mass stars) and supernovae explosions (high mass stars). In the ISM these elements undergo chemical reactions triggered by ion–molecule reaction networks in the gas phase as well as heterogeneous catalytic processes on grain surfaces.[53]

One way to study the ISM composition is to perform very high resolution spectroscopy on the absorption lines in starlight caused by the intervening clouds of gas and dust. One can thus determine column abundances which can be expressed as ratios relative to the column density of atomic hydrogen, the most abundant element in the ISM. These ratios can then be compared to the corresponding solar-system abundances. Elements not observed or underobserved in interstellar gas must be trapped in a non atomic/ionic phase, namely as molecular species or dust grains. Depletion on grains depends on condensation temperature and chemical reactivity of a given element. The condensation temperature is defined as the temperature at which 50% of the element is depleted by capture on the solid or liquid phase and fits the general picture that grains come, in part, from atmospheres of red giant stars and are injected into the interstellar medium by slow mass outflow. Therefore we must consider two complementary environments as possible repository places of phosphorus in the ISM: the gas-phase and the solid grains.

High-quality UV observations have confirmed that phosphorus is depleted by approximately a factor of 3 relative to its solar-system abundance in sightlines containing both warm, diffuse clouds and denser cold clouds.[54,55] Therefore, a significant fraction of interstellar phosphorus must be trapped in the grain phase. The chemical form in which P is present in these grains is quite uncertain, although some hints can be obtained from the study of the gas-phase component of the ISM.

At the extreme conditions prevailing in the ISM (low temperatures and very low densities) the formation of interstellar molecules is mainly driven by ion–molecule reactions. In fact, neutral–neutral reactions are often endothermic and/or possess appreciable activation energies. Thus, in the ISM, reactions of molecular hydrogen (the most abundant molecule in the ISM) with C, O, N and S ions are particularly important in initiating the chemistry. For the sake of illustration, in Fig. 5 we show the most important reactions involved in the ISM chemistry of nitrogen compounds.

Earlier laboratory studies on the gas-phase chemistry of P indicated, however, that the ion-molecule chemistry of P is

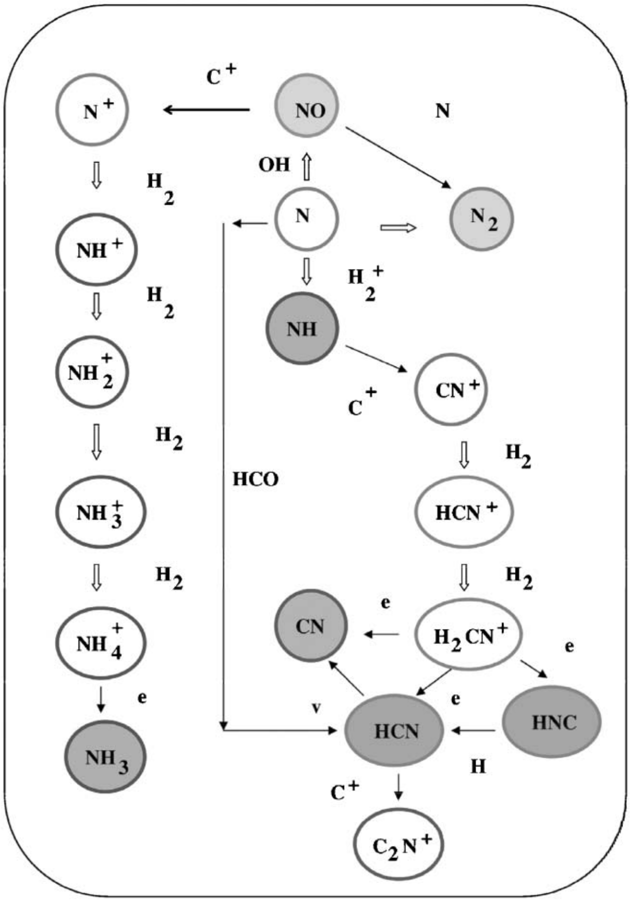

Fig. 5 ISM chemistry of nitrogen. The initiating N^+ and C^+ ions are produced by the intense UV radiation field of nearby stars and cosmic rays ionizing radiation. The presence of highlighted neutral molecules has been spectroscopically confirmed in the ISM. (Adapted from Ref. 6.)

significantly different from that of the closely related N atom under the low temperature conditions of the ISM. In fact, unlike NHn^+ ions, PNn^+ ions react endothermically with H_2, so that PH, PH_2, PH_3 compounds are expected to be very scarce.[56,57] Accordingly, the channel hydrogenation reaction, leading to the ubiquitous presence of ammonia and its derivatives in the ISM, shown in Fig. 5, does not work in the case of P. Alternatively, initial models predicted that species containing P–O bonds would be the most abundant interstellar P compounds. Contrarily to these theoretical predictions the first phosphorus bearing species found in the ISM diffuse clouds was the P≡N molecule.[58,59] Since PN is observed only in highly energetic star-forming regions one should consider the possibility that this molecule was produced by processes like high temperature gas phase reactions or grain disruption. In this sense the fact that both P and Si are depleted by a similar amount in these regions (SiO/Si $\sim$ PN/P $\simeq 10^{-4}$ supports the view of a similar trapping of both elements in the grains.[60]

On the other hand, it would also be possible that the PN molecule was originally synthesized in the expanding atmospheres of evolving stars, then diluting in the surrounding ISM. In line with this scenario the second phosphorus compound detected in the ISM was the $C{\equiv}P^{\bullet}$ radical, found in the circumstellar region around IRC 10216, a late type, evolved star.[23] According to detailed photochemical models its most probable parent molecule is HCP which, in turn, almost completely condenses onto grains, with perhaps 4% remaining free to form CP. In this sense, P behaves like a highly refractory element in circumstellar envelopes.[60] These results clearly indicate that both PN and CP (the only P molecules detected so far) are only minor repositories of phosphorus, which remains mainly locked in some condensed form in the ISM.

6. The phosphorus puzzle

The relative abundance of phosphorus in the condensed phase of diverse astronomical samples is summarized in Fig. 6. From this figure we conclude that this element is, at the same time, scarce but ubiquitous in the solar system. P compounds are also minority components present in the gas phase of ISM. In contrast to the apparent scarcity of phosphorus, as suggested by these astrophysical observations, phosphorus compounds exist in higher abundances in living systems, where they perform many fundamental biochemical functions (see Table 1).

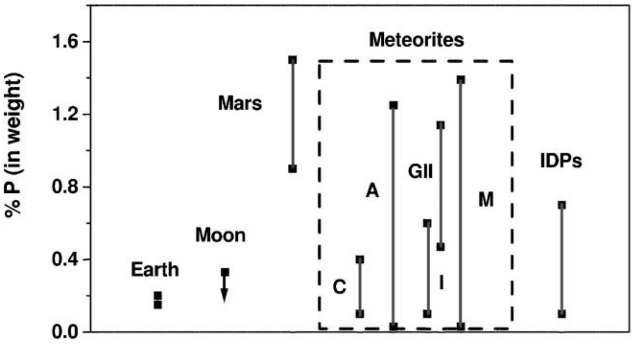

Fig. 6 Relative abundance of phosphorus (in weight%) as derived from elemental analysis of different collected samples (references are given in the main text). The data corresponding to meteorites are given for (C)hondrites, (A)chondrites, (I)rons, and (M)esosiderites, respectively. We have also included data corresponding to the newly established IIG iron meteorites, which exhibit relatively high P contents.

This fact naturally raises the following questions: how would such a scarce element become so relevant for most current biochemical processes? In particular, how can we explain its crucial role in the energetics of present day living forms, and what was the primary source of phosphorus during the initial stages of prebiotic evolution? In order to get some plausible answers we will start by recalling the following facts:

•The nuclide ^{31}P is synthesized by a minor subset of stars ($\sim$5–10% of the galaxy population) which are massive enough to explosively ignite the C and Ne fuels (Fig. 2). In addition the complex nuclear reaction network implied in its formation leads to a very low P yield (Fig. 3). These facts account for the scarcity of phosphorus in the universe.

•Phosphorus compounds are found in many different astrophysical environments. Consequently, phosphorus is a minor but ubiquitous element in the universe. This result is further illustrated in Fig. 7 where we observe the presence of:

–Diverse phosphate minerals (MPO_4) in planets and satellites (Earth, Mars, Moon), stony meteorites, IDPs and possibly also in cometary nuclei.

–reduced phosphorus compounds are present in iron meteorites (M_3P) and the atmospheres of Jupiter and Saturn (phosphine).

–organophosphorus compounds like phosphonic acids have been found in some meteorites and CP radical is present in circumstellar regions

–PN molecule has been detected in several star forming regions.

•These phosphorus compounds exhibit different oxidation degrees in different astrophysical environments. 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

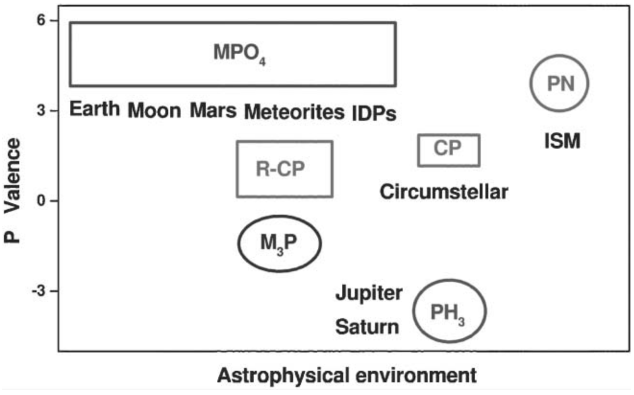

Fig. 7 Distribution of phosphorus compounds in several astrophysical environments arranged according to their oxidation degree (more details in the text).

iron-rich meteorites. Finally, intermediate oxidation states are observed in some chondrites and the ISM.

•The P chemistry of the solar system seems to be determined by thermodynamics, whereas the chemistry outside the solar system is mainly determined by kinetics.

•The basic chemical form of phosphorus in living systems is based on the esters of phosphoric acid.

Once the bioelements are produced in the stars and liberated to the ISM the first stage of chemical evolution happens in the ISM, where two distinct phases must be distinguished: the gas phase and the solid phase. In fact, we have learned that chemical synthesis of complex organic and inorganic compounds can take place over very short timescales (10^3 yr) in the low-density circumstellar environment.[11] By inspecting Figs. 6 and 7 we realize that a general tendency towards more oxidized phosphorus compounds is clearly appreciated as chemical evolution proceeds from circumstellar and ISM materials to protoplanetary and planetary condensed matter phases in the crust of bodies.[61] This chemical trend correlates with a progressive enhancement of the relative abundance of bioelements in condensed matter due to the processing of chemical compounds during their transition from gas phase to condensed phase in both ISM and protoplanetary stages. This point is properly illustrated by comparing the elemental abundances of bioelements in the gas phase of interstellar diffuse clouds with that measured in meteorites. Thus, the logarithm of the abundance of biogenic elements observed toward the diffuse cloud ζ Oph relative to meteoritic abundances amounts $\log\left(\frac{\mathrm{ISM}}{\mathrm{Solar}}\right) \simeq -0.4$ for O and C, and $\log\left(\frac{\mathrm{ISM}}{\mathrm{Solar}}\right) \simeq -0.5$ for P.[55]

From these data we realize that biogenic elements are depleted from the gas phase by different amounts and concentrated in interstellar grains composing the solid phase. At their initial stages these grains are mainly composed by a core of highly refractory materials, and have undergone little processing. As chemical evolution proceeds, the grains are progressively covered by different ices (CO_2, NH_3, CH_4, H_2CO, H_2S) resulting from their interaction with the gas phase which, in turn, has experienced a substantial chemical processing, *via* ion chemistry molecular networks (see Fig. 5).

Additional processing would occur in periodic comets, which are formed from low temperature aggregation of these interstellar grains. In fact, although comets remain most of the time far away from stars, they occasionally approach them due to small gravitational perturbations. During their approach to the star their temperature progressively increases, promoting an intense episode of photochemical processing of their originally pristine materials. In the case of periodic orbit comets this processing assumes a cyclic nature, undergoing successive episodes of condensation due to the recurrent loss of most volatile materials forming their comae and tails. In this sense, periodic comets somehow mimic usual handling in chemical labs, leading to the synthesis of complex organics by means of cyclic sublimation/condensation processes along their orbits.

In order to illustrate the relevance of cometary chemistry in Fig. 8 we compare the elementary abundances of bioelements in living matter as referred to the solar system and mean compositions of cometary ices, respectively. As we can see the H content of living matter is very similar to its abundance in comets. In the case of cometary ices, a similar result is obtained for C, O, and to a lesser extent, for S and N as well. Unfortunately, due to the absence of available data, we do not yet know if a similar trend is also valid for P. Conversely, the bioelements are overabundant in living matter by several orders of magnitude as compared to their solar system abundance. Such an enhancement is particularly significant in the case of P. In summary, we conclude that during their transition from stars to protoplanets the bioelements are efficiently incorporated to the raw materials out of which new planetary systems will be formed. In fact, among the molecules observed in the protoplanetary disk surrounding the newborn star DM Tauri the organic species HCN, H_2CO, CS, CN and C_2H exhibit large depletion factors with respect to their gas phase abundances, hence indicating they are being efficiently incorporated into the condensed phase.[63]

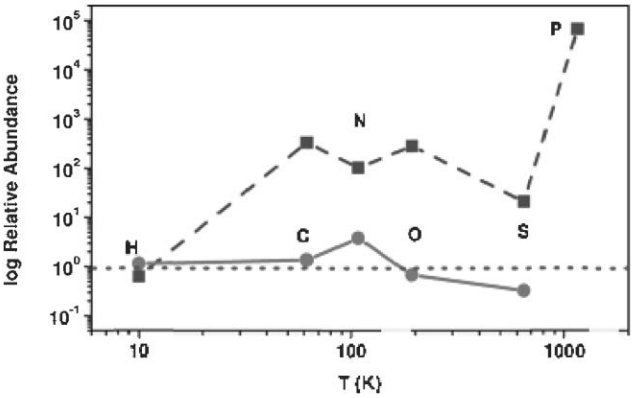

Fig. 8 The logarithm of the abundances of biogenic elements in human body[62] relative to meteoritic (solar)[3] (dashed line) and cometary abundances[63] (solid line) plotted against condensation temperature. For a given element, X, its elemental abundance in human body is normalized to silicon [X] and then divided by its corresponding solar system or cometary abundance [X]′, respectively, to obtain log([X]′/[X], where all [X] is expressed in atomic percent number.

7. Conclusions

The comparison of the elementary abundances of bioelements in different astronomical environments shows a progressive enhancement of elements C, N, O and S in the condensed matter phases out of which protoplanetary nebula are made. A similar enhancement of phosphorus, favouring a progressive tendency towards more oxidized compounds is also observed. The discovery of alkyl phosphonic acids in the Murchison meteorite suggests the possibility of delivery of these water-soluble, phosphorus-containing molecules by meteorites to the early Earth. Since alkyl phosphonic acids are related to orthophosphorous acid, *via* substitution of the P–OH grouping by a P–C bond, this could have provided a supply of organic phosphorus for the earliest stages of prebiotic evolution. In turn, the phosphonic acids observed in meteorites can be related to the compounds containing the extremely stable C–P bond in the ISM. In fact, the CP radical has been observed around evolved stars, where it may be indicating the presence of the HCP molecule adsorbed onto dust particles. Most of the remaining phosphorus may be trapped in the refractory high-temperature condensate form Fe_3P, which along with silicates, diverse oxides and carbon condensates constitute the cores of interstellar grains. These grains, formed in the circumstellar envelope may survive passage through the diffuse ISM, particularly if they are coated with refractory organic mantles before being expelled from the stellar cocoon. Eventually, some of these grains would aggregate to form cometary nuclei, or may be incorporated in the protoplanetary nebulas around newborn stars. In the later case, most of these grains will be incorporated in planetesimals out of which bigger planets are composed. This opens an alternative way to collect reactive P products capable of being incorporated into primitive biomolecules by means of the corrosion of schreibersite minerals present in those parent bodies.[36]

Anyway, many steps within this overall picture are to be confirmed and quantitatively assessed in order to gain a detailed knowledge of the role of phosphorus and its compounds in chemical evolution. With this aim in mind, we would like to conclude by suggesting some possible topics well deserving a closer scrutiny in the years to come:

•Molecules like PO, PO_2 and HC_nP have complicated rotational levels and their lines are expected to be weak. Nonetheless, their systematic search with large single dish radio telescopes would be appealing.[64]

•Since the optical constants of the organic refractory grain mantle material are derived from a combination of astronomical and laboratory spectra of residues of UV photoprocessed ices, it would be worthwhile to consider the possible effects of the inclusion of phosphorus compounds, in reduced or oxidized forms, in the matching between astronomical and laboratory obtained infrared spectra.[65]

•A search for phosphorus oxides and organophosphorus species in future spacecraft missions to comets, within the framework started by the Stardust Mission, would be pertinent.

•Detailed analysis including elemental composition studies, mass spectroscopy, and mineralogical characterization of IDP samples of cometary origin, would be very promising in order to understand the phosphorus chemistry in the earlier stages of solar system.

Finally, the use of phosphorus as a potential guide in the search for extinct or extant life on Mars and other planets should be encouraged. Indeed, the role of the mineral apatite with inclusions of isotopically “light” carbon pointing to possibly the oldest traces of life on Earth, although controversial, has been reported.[66] This interesting result illustrates the wide possibilities that the study of phosphorus compounds in the Solar System and other astrophysical environments can provide to the knowledge of the origins of life.

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