



Biosignatures Search in Habitable Planets

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Received: 2 August 2019; Accepted: 25 September 2019; Published: 29 September 2019



Abstract: The search for life has had a new enthusiastic restart in the last two decades thanks to the large number of new worlds discovered. The about 4100 exoplanets found so far, show a large diversity of planets, from hot giants to rocky planets orbiting small and cold stars. Most of them are very different from those of the Solar System and one of the striking case is that of the super-Earths, rocky planets with masses ranging between 1 and 10 M_{\oplus} with dimensions up to twice those of Earth. In the right environment, these planets could be the cradle of alien life that could modify the chemical composition of their atmospheres. So, the search for life signatures requires as the first step the knowledge of planet atmospheres, the main objective of future exoplanetary space explorations. Indeed, the quest for the determination of the chemical composition of these planets than that given by the mere directory of the atmospheric compounds. It opens out to the more general speculation on what such detection might tell us about the presence of life on those planets. As, for now, we have only one example of life in the universe, we are bound to study terrestrial organisms to assess possibilities of life on other planets and guide our search for possible extinct or extant life on other planetary bodies. In this review, we try to answer the three questions that also in this special search, mark the beginning of every research: what? where? how?

Keywords: exoplanets; biosignatures; planetary atmospheres; instrumentation

1. Introduction

Since the ancient times, philosophers try to answer to the question "*are we alone*?" Up to now no certain answer has been given due mainly to the huge technological challenge in unveiling extant life (if any) on alien worlds. Giuseppe Conconi and Phillip Morrison in their seminal paper [1] exhorted scientists to be engaged in any case in this quest with their famous sentence: *the probability of success is difficult to estimate, but if never search the chance of success is zero*. Just after, the SETI (Search for Extraterrestrial Intelligence) project started ([2] and see [3] for a review) together with its expectations and eerie silences [4].

The search for life in the Galaxy received a big boost by the bonanza of new worlds discovered so far, also if we are compelled to tackle with the distances at which these worlds are. In fact, it is quite different for searching life in the Solar System bodies where, also if with great technological efforts and challenges, it is possible to explore them on-site and investigate if they are bearing life. Venus and Mars are targets of this wandering of the human beings in the Solar System. In the case of extrasolar planets, the only way to search for life is the remote sensing.

So, one of the big questions on the mat is what we are searching for? A really hard question. Life, as we know it, has been described as a (thermodynamically) open system [5], which exploits gradients in its surroundings to create imperfect copies of itself, makes use of chemistry based on carbon, and exploits liquid water as solvent for the necessary chemical reactions [6,7]. This seems an *a priori* and quite geocentric statement, but considering life as a stochastic process, it has a non–zero

probability of occurring as soon as the environmental conditions for its appearance are met. If this is the case, we have to consider all the circumstances that can maximize this probability. In this framework, the carbon is the only chemical element with which it is possible to form very complex molecules with up to 13 atoms (e.g., $HC_{11}N$). Carbon is also very easy to reduce (CH₂) and oxidize (CO₂).

On the other hand, liquid water has some important characteristics that make it the best solvent for life: a large dipole moment, the capability to form hydrogen bonds, to stabilize macromolecules, to orient hydro–phobic–hydrophilic molecules, etc. Furthermore, water is an abundant compound in our galaxy, that is possible to find in different environments, like cold dense molecular clouds and hot stellar atmospheres, e.g., [8,9]. Water is liquid at a large range of temperatures and pressures and it is a strong polar—non polar solvent. This dichotomy is essential for maintaining stable biomolecular and cellular structures [7]. Furthermore, liquid water has a great heat capacity that makes it able to tolerate a heat shock. The most common solid form of water has a specific weight lighter than that of its liquid form allowing ice to float on a liquid ocean safeguarding the underlying liquid water. All those characteristics let grow the probability that life, once it emerges, could survive and evolve.

For all these reasons, we will base our search for signs of life (biosignatures) on the assumption that alien life shares fundamental characteristics with life on Earth. Life based on a different chemistry is not considered here because such life—forms, should they exist, would have by–products that are so far unknown.

The word "Biosignature" identifies all detectable atmospheric gas species, or a set of species, whose presence at significant abundance strongly suggests a biological origin [7]. Instead the term bioindicators defines all the other gases that are or could be indicative of biological processes but can also be produced abiotically (e.g., on Earth, O_3 is the photochemical by-product of O_2). Their quantity and detection, along with other atmospheric species, all within a certain context (for instance, the properties of the star and the planet) points toward a biological origin. These gases should be ubiquitous by-products of carbon-based biochemistry, even if the details of alien biochemistry are significantly different from the biochemistry on Earth. Besides atmospheric biosignatures, there are also life signatures due to the light reflection characteristics of specific *components* of living being as, for example pigments, that can modify or contribute to the planetray albedo. These are called surface biosignatures and are also detectable by remote sensing, e.g., [10].

The debate about biosignatures and remote sensing search for life is growing livelily in the last years and several reviews tackle the topic [7,10–24] and references therein, where the reader can find precise information on this topic. In this paper the main results of these authors will be summarized.

Atmospheric biosignatures, bioindicators and surface and industrial biosignatures are described from Section 2 to Section 4 while in Section 5 a description of the possible false positives is given. Section 6 introduces the concept of the habitable zone. The detection methods are discussed in Section 7 and the perspective for the future are outlined in Section 8. Finally, in Section 9 we give a summary and outline the conclusions.

2. Atmospheric Biosignatures

The approach to remote detection of signs of life on another planet was set out in the last century by Lederberg [25] and Lovelock [26], which introduced the concept for the search for an atmosphere containing gases severely out of thermochemical redox equilibrium¹ like for example the simultaneous presence of O_2 and CH_4 [27]. The idea that gas by–products from metabolic redox reactions can accumulate in the atmosphere was initially favoured for future sign of life identification, because abiotic processes were thought to be less likely to create a redox disequilibrium.

¹ Redox chemistry adds or removes electrons from an atom or molecule (reduction or oxidation, respectively). Redox chemistry is used by all life on Earth and thought to enable more flexibility than non—redox chemistry.

Lippincot and collaborators [27] found that on Earth other than CH_4 there are also other gases $(H_2, N_2O, \text{and } SO_2)$ out of thermodynamic equilibrium, but they all (with the possible exception of N_2O) are also by-product of geochemical processes and cannot be considered unambiguous signs of life.

In a meeting held in the 1975, Lovelock et al. [28] supported the idea of Lippincott et al. [27] that the O_2 -CH₄ disequilibrium was strong evidence for life, and from then on, CH₄ was established as a biosignature gas [28,29]. This is an appealing concept because the chemical disequilibrium could be considered a generalized biosignature and it is not necessary to have any assumption on particular biogenic and metabolic by–product gas. This concept has been explored also in the recent years [30–32], but no additional, potentially observable disequilibrium redox pair has been identified (but see ahead).

In any case, many reasons suggest to use with prudence the thermodynamic disequilibrium as a life indicator [33]. First of all almost any gas, in Earth's atmosphere, other than N_2 and CO_2 , is out of thermodynamic equilibrium because of the Earth's high O_2 level. So, the argument that Earth's atmosphere is out of thermodynamic equilibrium reduces to a statement about the high levels of Earth's atmospheric O_2 . Even if no or too few O_2 is present, it is possible to have a significant thermodynamic disequilibrium due to geochemical or photochemical processes. On the other hand, Krissansen-Totton and collaborators [19] in their study on the atmosphere-ocean disequilibrium in the precambrian, found that in different era there should be different disequilibrium stages due to the coexistence of O_2 , N_2 and also N_2 , CH_4 , CO_2 and liquid water that could be remotely detected. They concluded that the simultaneous detection of CH_4 and CO_2 in the atmosphere of an habitable planet could be a potential biosignature.

The chemicals produced by life on Earth are hundreds of thousands [16] (estimated from plant natural products, microbial natural products, and marine natural products), but only a subset of hundreds are volatile enough to enter the atmosphere at more than trace concentrations. Among these, only a few handfuls accumulate to high enough levels to be remotely detectable for astronomical purposes and defined as biosignatures. Apart from oxygen, these biosignature (and bioindicator) gases range from highly abundant gases in Earth's atmosphere that are either already existing or predominantly produced by geochemical or photochemical processes (N₂, Ar, CO₂, and H₂O) to those that are relatively abundant and attributed to life (N₂O, CH₄ and H₂S). We have to consider also gases that are weakly present but may play important roles in the atmospheric processes (DMDS and CH₃Cl) and gases that are present only in trace amounts including the hundreds of minutely present volatile organic compounds released by trees in a forest or fungi in the soil [16].

The first remote observation of biosignatures could be considered the UV, visible and NIR spectra of the Earth obtained by the probe Galileo in its fly towards Jupiter in the 1990. Sagan et al. [34] analyzed those spectra searching for signatures of life. In the spectra of the Near–Infrared Mapping Spectrometer (NIMS, [35]) they found a large amount of O_2 and the simultaneous presence of CH₄ traces concluding that this co–presence is strongly suggestive of life (see Figure 1).

Other observations of Earth as an exoplanet have performed in the last years observing the earthshine, the faint light seen on the dark side of crescent moon [36–40]. Earthshine is the Sun's light reflected by the day-side of the Earth towards the dark side of the Moon and reflected again onto the night side of the Earth where it is caught by ground-based telescopes. In the earthshine spectra it is possible to observe prominent oxygen absorption feature at 0.76 μ m, instead methane has only extremely weak spectral features (at present day the levels is 1.6 ppm). Furthermore, on Earth, some atmospheric species that show observable spectral features come directly or indirectly from biological activity. The main molecules are O₂, O₃, CH₄, and N₂O. Both CO₂ and H₂O are important greenhouse gases and also potential sources for high O concentration from photosynthesis. Furthermore, the earthshine has been analyzed by a polarimetric point of view. When light passes through the atmosphere, it is linearly polarized by air molecules, aerosol and cloud particles scattering. Reflection by ocean and land can also contribute to the linear polarization of light [41]. Sterzik et al. [42],

using FORS (Focal Reducer Low-dispersion Spectrograph [43]) at VLT, measured the linear polarization spectra of the earthshine, determining the fractional contribution of clouds and ocean surface.



Figure 1. The original Visible, NIR and IR Earth spectrum taken by NIMS instrument during the Galileo fly–by on Earth [34].

In order to describe the possible biosignature gases that are possible to detect by remote sensing, we have to take into account the by–products of the following processes: (i) the metabolic chemical reactions; (ii) the chemical reaction for the construction of organic matter, (iii) the secondary metabolic chemical reactions.

2.1. Metabolic Biosignatures

This biosignatures category contents all those by–product gases due to metabolic reactions that capture energy from environmental redox chemical potential energy gradients [12,13]. Such gases (see Table 1 for aerobic chemotrophy and Table 2 for anaerobic chemotrophy) are abundant due to the presence of large quantity of reactants in the environment, but they could not be considered as produced exclusively by life. In fact, geology for example, works on the same molecules as life does. Moreover, in one environment, a given redox reaction will be kinetically inhibited and it is only started by life's enzymes, while in another environment with the right conditions (temperature, pressure, concentration and acidity), the same reaction might proceed spontaneously.

Reductant	Oxidant	Output	Comment
Oxidati	on of Organi	c Matter	
CH ₂ O	O ₂	CO_2 , H_2O	
Нус	łrogen Oxida	tion	
H ₂	O ₂	H ₂ O	
H ₂	H_2O_2	H_2O	
Sulfur (Compound O	xidation	
H ₂ S	O ₂	SO_4^{2-}	
HS^{-}	O2	S	
S	O2	SO_4^{2-}	
$S_2 O_4^{2-}$	O ₂	$\mathrm{SO}_4^{{ar 2}-}$	
1	ron Oxidatio	п	
Fe ²⁺	O ₂	Fe ³⁺ , OH ⁻	
Am	monia Oxida	tion	
NH ₃	O ₂	NO_2^- , H_2O	Acqueous (Nitrite)
NH_4^+	O ₂	NO_2^{-} , H ₂ O	Acqueous (Nitrite)
NO_2^{\pm}	O ₂	\bar{NO}_3^-	Biological/Abiological

Table 1. Aerobic Chemotrophy: summary of redox reaction by-products. Modified by [12].

An interesting biosignature of this category is Nitrous oxide (N_2O [24,34,44–48]). It is produced in abundance by life (denitrifying bacteria) but only in negligible amounts by abiotic processes. Most of the reaction that produce N_2O are listed in Table 2, a simple scheme of the denitrification reaction is the following:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO + N_2O \rightarrow N_2$$

It is difficult to be detected, especially in a humid atmosphere where the molecular band of water vapour, CO_2 and CH_4 are generally overimposed to the N₂O features. It would become more apparent in atmospheres with more N₂O or less H₂O vapor, or a combination of the two [49]. Segura et al. [50] calculated the level of N₂O for different O₂ levels and found that, though N₂O is a reduced species compared to N₂, its level decreases with O₂. This is due to the fact that a decrease in O₂ produces an increase in H₂O photolysis, which results in the production of more hydroxyl radicals (OH) responsible for the destruction of N₂O. In the near–UV and blue optical region, N₂O and NO₂ have molecular transition bands, but their strength is smaller, in a significant way, than those of other molecules, like O₂ and O₃, that are in the same spectral region. Other features of N₂O are present in the IR wavelength range (4.5 µm and 7.8 µm), but also in this case they are pretty weak features and difficult to be detected [24,45].

Abiotic sources of N₂O are small and are due mainly to the chemodenitrification process, like that occurs in the hypersaline ponds in Antartica [22,51] and, depending by the redox state of the environment, to the high temperature reduction and oxidation reactions of N₂. These reactions occur for combustion or lightings transforming the resulting molecules from N₂ redox reactions (NH_X, HCN and NO_x) in water soluble molecules (e.g., HNO₃, [24]).

 N_2 is another metabolic product of denitrification, released when, under anaerobic environments, bacteria use oxygen by NO_3^- to convert carbon in CO₂. Anammox (anaerobic ammonium oxidation) is another anaerobic biological process that is the oxidation of NH_4^+ with NO_2^- that produce N_2 and H_2O (see Table 2 for other examples). This process can produce about 50% of the N_2 produced in the ocean and that then is released in the atmosphere ([24], and references therein).

Reductant	Oxidant	Output	Comment
Denitrification			
H_2	NO_3^-	NO_3^- , H_2O	Biological/Abiological
H_2	NO_2^{-}	NO, H_2O	Weak spectral feature
H ₂	NŌ	N ₂ O, H ₂ O	Weak spectral feature
H_2	N_2O	N ₂ , H ₂ O	Metabolic product
Fe ²⁺	NO_3^-	NO ₂ , Fe ³⁺	Weak spectral feature
Fe ²⁺	NO_2^{-}	NO, Fe ³⁺	Weak spectral feature
Fe ²⁺	NŌ	N ₂ O, Fe ³⁺	Weak spectral feature
Fe ²⁺	N ₂ O	N ₂ , Fe ³⁺	Metabolic product
	Iron Red	luction	
Organics	Fe ³⁺	Fe ²⁺	Anaerobic bacteria, precipitating minerals
H ₂	Fe ³⁺	Fe ²⁺ , Fe ³⁺	Precipitating minerals
	Sulfur Re	eduction	
Organics	SO_4^{2-}	SO_3^{2-} , SO_2 , H^+ , CO_2	
H ₂	SO_4^{2-}	SO_3^{2-} , SO_2 , H^+	
H_2	SO_3^{2-}	$\ddot{S}_{2}O_{3}$, H ⁺	
H_2	SO_3^-	S ⁰ , H ⁺	
H_2	SO	H_2S , H^+	
CH_4	SO_4^{2-}	H_2S , CO_2	
	Methano	genesis	
Organics	CO ₂	CH ₄ , H ₂ O	
H ₂	CO ₂	CH_4 , H_2O	Abiotic Pathway
	Anam	mox	
NH ₃	NO_2^-	N ₂ , H ₂ O	
$\rm NH_4^+$	NO_2^{-}	N ₂ , H ₂ O	
NH ₃	NO_3^{-}	N ₂ , H ₂ O	
NH_4^+	NO_3^{-}	N ₂ , H ₂ O	

Table 2. Anaerobic chemotrophy: summary of redox reaction by-products. Modified by [12].

The production of methane by methanogen bacteria (methanogenesis) is a typical reaction of this category:

$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$

It is generated by bacteria at the sea floor which reduce the CO_2 available in the sea water due to the mixing with the atmosphere using the H₂ released by hot water coming from rocks (serpentinization). Most of the methane found in the present atmosphere of Earth has this biological origin, but methane is also produced abiotically in hydrothermal systems where hydrogen is released by the oxidation of Fe by H₂O and reacts with CO₂ to form CH₄. The amount of CH₄ produced in this process depends by the oxidation degree of the planetary crust. Therefore, the detection of CH₄ alone cannot be considered as a sign of life, though its detection in an oxygen–rich atmosphere could be an indication of the presence of a biosphere.

On early Earth, CH₄ might have been produced by widespread methanogen bacteria [52] at much higher levels (1000 ppm or even 1%). Such high CH₄ concentrations would be easier to detect. On the other hand, at that time the contents of oxygen in the early Earth's atmosphere was very small or even insignificant, the O_2 -CH₄ redox pairs would be difficult to be detected at present concurrently [7,53], unless perhaps in the case of a planet in a lower-UV (200–300 nm) radiation environment (possible with some M host stars [44]). The recent confirmation of methane in the atmosphere of Mars [54,55], that contains 0.1% of O_2 and some O_3 , is a good example for both the consideration of CH₄ as a biosignature gas, since it is photochemically unstable and must be actively produced, but it is also an example for a false positive because CH₄ could be produced geologically.

 NH_3 (a very similar case to the one of CH_4) is produced on Earth quite only by biological processes (anammox), apart from the one industrially manufactured. Both (NH_3 and CH_4) are released into the Earth's atmosphere by the biosphere with similar rates, but the atmospheric level of NH_3 is orders of magnitude lower due to its very short lifetime under UV irradiation. The detection of NH_3 in the atmosphere of a habitable planet would thus be extremely interesting, especially if found with oxidized species [49].

2.2. Organic Matter Building By–Products

This class of biomass building by-products records few biosignature gases (see Table 3) among its elements. These reactions require mainly energy from the environment and capture environmental carbon (and to a lesser extent other elements). The main example on Earth is O_2 produced by oxygenic photosynthesis, which gains energy from sunlight. In more detail, photosynthesis captures the carbon in CO_2 into biomass, releasing oxygen that, nowadays, is the 20% by volume of the Earth's atmosphere. Less than 1 ppm of atmospheric O_2 comes from abiotic processes [56]. This high quantity of such a reactive gas like O_2 with a short atmospheric lifetime allows to consider oxygen a robust biosignature [57]. Owen [6] suggested searching for O_2 as a tracer of life. In fact, without continual replenishment by photosynthesis in plants and bacteria, O_2 would be ten orders of magnitude less than present today in the Earth's atmosphere [58]. Any observer seeing oxygen in Earth's spectrum would know that some non-geological chemistry must be producing it. At this point a warning should be raised. In fact, an important pathway for the formation of abiotic oxygen in an observable quantity is through the H₂O photodissociation by the EUV flux of the host star (see Section 5), followed by the Hydrogen escape from the gravitational pull of the planet [59–61].

Input	Radiation	Output	Comment
Oxi	genic Photosyr	ıthesis	
H ₂ O	hv	O ₂	Solid biosignature
Anox	ygenic Photos	Inthesis	
H_2S	hν	S	
$S_2O_3^-$	$h\nu$	H_2SO_4	
S	$h\nu$	H_2SO_4	
H_2	$h\nu$	H ₂ O	
Fe ²⁺	$h\nu$	Fe ³⁺	
NO_2^-	$h\nu$	NO_3^-	

Table 3. Phototrophy: summary of photosynthetic reaction by-products.

Photosynthesis converts light energy to electrochemical energy by redox reactions. Light, exciting pigments, causes a transfer of electrons along bio–chemical pathways having as result the CO_2 reduction. The electron is replaced by one extracted from the reductant. The basic stoichiometry of photosynthesis is [62]:

$$CO_2 + 2H_2X + h\nu \rightarrow (CH_2O) + H_2O + 2X$$

This is a general way to show the reaction for both oxygenic and anoxygenic photosynthesis. H_2X represents the reductant that could be H_2O (oxygenic photosynthesis) or H_2S (an-oxygenic photosynthesis), $h\nu$ is the photon energy (h is the Planck's constant). In the case of oxygenic photosynthesis the reductant is water and we have the following reactions:

$$2H_2O + h\nu \rightarrow 4H^+ + 4e^- + O_2$$
$$CO_2 + 4e^- + 4H^+ \rightarrow CH_2O + H_2O$$

Because the two processes, light capture and biomass building, are mechanistically distinct, the complete reaction is split in two parts. The former reaction generates the electrons, while the latter synthesises carbohydrate (CH₂O). For each O_2 molecule four photons are required (one photon for each bond in two water molecules) while other four photons are necessary to reduce CO₂. Thus, a minimum of eight photons is required both to evolve one O_2 and to fix carbon from one CO₂.

Cyanobacteria, plants and algae are responsible for the production of oxygen by using solar photons to extract hydrogen from water (that is abundant on Earth) and using it to produce organic molecules from CO_2 . The reverse reaction, using O_2 to oxidize the organics produced by photosynthesis, can occur abiotically when they are exposed to free oxygen or biotically by eukaryotes breathing O_2 and consuming organics. Because of this balance, the net release of O_2 in the atmosphere is due to the burial of organics in sediments. Each reduced carbon buried results in a free O_2 molecule in the atmosphere [63]. This net release rate is also balanced by weathering of fossilised carbon when exposed to the surface. The oxidation of reduced volcanic gases, such as H_2 and H_2S , is also responsible for a significant fraction of the oxygen losses. The atmospheric oxygen is recycled through respiration and photosynthesis in less than 10,000 years [11]). In the case of a total extinction of Earth's biosphere, the atmospheric O_2 would disappear in a few million years.

The oxygenic phothosynthesis on Earth is a successful method to transform radiative energy in chemical energy an store it in organic matter. This happens on a planetary scale impacting on the host environment leading to a global transformation.

Anoxygenic photosynthesis uses instead other reductants, like for example H_2S , H_2 and Fe^{2+} . When the reductant is H_2S , elemental sulfur is produced instead of oxygen ([62]):

$$CO_2 + 2H_2S + h\nu \rightarrow (CH_2O) + H_2O + 2S$$
$$3CO_2 + 2S + 5H_2O + h\nu \rightarrow 3(CH_2O) + 2H_2SO_4$$

where H_2S is split by photons to yield an electron donor, CH_2O represents the carbohydrates incorporated into the microbe, and S and H_2O are the metabolic by–products. Eventually, sulfur may be oxidized to sulfate which is not a gas and cannot enter the atmosphere as a biosignature. Also in this case the quantum requirement is 8 to 12 photons per carbon fixed. In summary, the inputs to photosynthesis are light energy, a carbon source and a reductant (see Table 3). The outputs are carbohydrates, elemental sulfur, water and other oxidised forms of the reductant in the reaction.

The best habitats for anoxygenic photosynthetic organisms are illuminated environments but with no free oxygen. Actually, for these organisms oxygen is a poison. Anoxygenic bacteria can be found in freshwater lakes and ponds, hot and sulfur springs, and some marine waters where the sources of electron donors (e.g., H₂S) can be either geological (in sulfur springs) or biological (produced by sulfate-reducing bacteria). From an evolutionary point of view, anoxygenic photosynthesis is believed to have preceded oxygenic photosynthesis and to have appeared on Earth more than 3 billion years ago [12,64].

2.3. Secondary Metabolic Biosignatures

A lot of chemical substances are synthetized by living organisms in order to answer to very different stimuli of the environment. These substances are highly specialized chemicals and are produced for different reasons than energy capture or the construction of the basic components of life. These substances are produced by organisms for defense against the environment or other organisms, for signaling or for internal physiological control. For these reasons, secondary metabolic biosignatures have much more chemical variety if compared with the other type of biosignatures [12,13].

Some of molecules produced as by–products to primary metabolism, including CH₄, NO, H₂S, and CO, are also produced by secondary metabolism but through different chemical routes. On the other hand, most of the secondary metabolic are inorganic compounds like sulfur and nitrogen compounds or organic molecules like isoprene and terpenoids (VOC or volatile organic carbon) and

halogenated organics and all are potentially considered biosignatures (for a complete description see [12]). These gases are produced generally in small quantities, but the wider variety with respect to the other two types of biosignatures should make them to be less prone to false positives. Furthermore, due to the specific catalysis to be produced, it is difficult to find geological impostors, so they are unlikely to be present in the absence of life.

Some sulfur compounds released in atmosphere are very promising in unveiling life as biosignature. The gases to be considered are hydrogen sulfide (H_2S , that is also produced by primary methabolism), carbon disulfide (CS_2), carbonyl sulfide (OCS, sometimes written as COS). All these but the last two are products of the breakdown of organic material, usually bacteria or fungi, although plants can also release these volatiles.

Dimethyl sulfide (DMS), dimethyl sulfoxide (DMSO: $CH_3 \cdot SO_2 \cdot CH_3$) and CH_3SH , called also organosulfur gases are produced by bacteria and higher order life-forms. The dominant chemical path producing DMS follow the breakdown product of the DMSP (dimethylsulfoniopropionate) generated by marine plankton perhaps for stress resistance. This is the largest source of organosulfur gas in the to-day atmosphere of Earth [22,65]. Much of the DMS generated is consumed by other organisms but part is released in the atmosphere and, under the right conditions of excess production or favorable ultraviolet (UV) flux conditions, could accumulate to potentially detectable levels. There is a second chemical path that produce DMS that starts from the decomposition product CH_3SH . The main source of CH_3SH , DMS are cyanobacteria and anoxigenic phototrophs that can produce measurable quantities of these gases [22].

At the end of the description of this kind of biosignature it is necessary to rise a caveat. Unlike the products of primary metabolism, we cannot predict the circumstances in which secondary metabolism by–products might be produced on other worlds. The strength of this kind of biosignature is in the lack, almost complete, of false positive which plagues the primary metabolic biosignatures.

3. Bioindicators

The word *bioindicator* indicates atmospheric signatures that can be produced by life as well as by abiotic processes (e.g., CO_2) or signatures produced by the modification of a biosignature gas by abiotic process (e.g., O_3).

Water (H₂O) doesn't appear as a biosignature also if it is a by–product of many reactions generating biosignatures. This is because water, as well as CO_2 , could not be considered as sign of life by itself, but it is raw material for life and an important molecule for planetary habitability as a greenhouse gas [58]. For example, on an Earth-like planet where the carbonate-silicate cycle is at work, the level of CO_2 in the atmosphere depends on the orbital distance. Close to the inner limit of HZ, CO_2 is a trace gas but it is a major compound at the orbital distance of the outer edge of the HZ [66,67].

Other gases that could be considered bioindicators are, for example, SO_2 and H_2S . This is a gas mixture produced by volcanism and out of thermodynamic equilibrium at terrestrial surface conditions. The reactions between the two will form water and elemental sulfur. Detecting both H_2S and SO_2 in an exoplanet atmosphere could therefore be either a sign of life or just a sign of volcanism [9]. Other bioindicators reported by several authors include ethane (a hydrocarbon compound) from biogenic sulfur gases [68] and hazes generated from CH₄ [52].

In case of transformation of a biosignature by abiotic process, the resulting product might also not be naturally occurring in a planet's atmosphere and therefore also a sign of life. The photochemical production of ozone by O_2 is one of the most popular example of this kind of abiotic process. The UV radiation coming from the host star modifies the oxygen reaching the quote between 14 and 30 km in Earth's atmosphere. The photochemical production and destruction of ozone are then only governed by the Chapman cycle [69]:

$$O_2 + h\nu_1 \rightarrow O + O$$

here, hv_1 is the energy of photons in the range between 0.1–0.2 µm, while hv_2 in the range between 0.2–0.3 µm. M indicates any molecule, mostly O₂ and N₂ on Earth. This reaction is not very efficient as it requires at the same time a high enough pressure (because it is a 3 body reaction), and oxygen atoms that are produced at lower pressures where photolysis of O₂ by UV can occur [70].

In the Earth's atmosphere, ozone can be destroyed by a number of reactions dominated by catalytic cycles involving hydrogenous compounds (H , OH, HO), nitrogen oxides (NO_X) and chlorine compounds (ClO_X). These species have various origins and their amount depends on the thermal profile of the atmosphere, the nature and the intensity of the bio–productivity, human pollution, and many other parameters. The presence of these compounds, in an atmosphere made of N₂ and O₂ only reduce the content of O₃ of about one order of magnitude. The column density of O₃ in the atmosphere depends weakly on the abundance of O₂, the mean opacity of the 9.6 µm band remaining >1 for O₂ abundance as low as 10^{-3} present atmospheric level [50,57].

The bottom line is that ozone is a tracer of the O_2 . Legér et al [57] modelled the production of ozone in atmosphere with the presence of O_2 and studied the variation of O_3 column density at the variation of O_2 amount in atmosphere. O_3 is a non–linear tracer of O_2 because its spectral features become rapidly saturated. The depth of the saturated O_3 band is determined by the temperature difference between the surface clouds continuum and the ozone layer. In any case the visible and IR features of O_3 are easier to be observed that O_2 features [57].

4. Surface and Industrial Biosignatures

In order to complete the description of possible biomarkers, we can consider other possible sign of life not included in the previous sections. They can be called surface and industrial biosignatures.

The former class derives by the presence on the planetary surface of vegetables and their pigments that absorb and reflect the incident light coming from the host star with a peculiar reflectance spectrum that shows a rise at about 700 nm. This shoulder is called *Vegetation Red-Edge* (VRE) and it is distinctive of vegetation. Physical explanations of land plant spectral signatures are fairly well understood in some aspects, whereas there is less of such information on other photosynthesizers. Technically, the red–edge is a spectral reflectance feature characterized by darkness in the red portion of the visible spectrum, due to absorption by chlorophyll, strongly contrasting with high reflectance in the NIR, due to light scattering from refraction along interfaces between leaf cells and air spaces inside the leaf [71].

The exact wavelength and the intensity of the VRE depends by the environment and by the species of vegetation. In the Earthshine spectra obtained by several groups (e.g., [36,38]), the VRE feature is tipically of few percent (see Figure 2). On Earth, not only vegetation is able to produce such a surface feature. Many other organisms can generate a wide range of reflective features and colors. Hegde et al. [72] produced a database of spectral characteristics of about 130 different organisms in both the visible and NIR (up to 2.5 μ m) regions. Other absorption and reflectance processes can be taken into account among surface biosignatures. For example the scattering of light by the physical structure of organisms, degradation products of biological molecules, fluorescence and bioluminescence. A description of these phenomena can be find in [22], while [73] made a description of the bioluminescence and fluorescence detectability.



Figure 2. Observed Vis-NIR spectrum of the Earthshine obtained by [38]. The reflectivity of vegetation is dominated by a sharp rise in reflectivity for wavelengths longer than 0.70 μ m, plus some smaller bumps at shorter and longer wavelengths [36,38]). In the spectrum, the rise of the flux due to plants reflection is only about 6% of the nearby continuum. This is because at the time of observation only about 17% of the projected area was land (for details on the observing method see [36]. In the spectrum are also indicated most of the molecules that are addressed in the text.

Lin et al. [74], re-elaborating the idea of Owen [6], pointed out that in addition to these generic indicators, anthropogenic pollution could be used as a novel biosignature for intelligent life. In particular they focused on chlorofluorocarbons (CFCs): tetrafluoromethane (CF₄) and trichlorofluoromethane (CCl₃F), which are the easiest to detect of the molecules produced by anthropogenic activity. The main spectral signatures of these molecules are in the range between $7.76 < \lambda < 7.84 \ \mu\text{m}$ in the case of CF₄ and $11.600 < \lambda < 12.00 \ \mu\text{m}$ for CCl₃F. Their abundances are too low to be spectroscopically observed at low resolution [44]). In any case Lin et al. and Fossati et al. [75] studied the case of an Earth in the HZ of a white dwarf (high transit probability) like Agol and try to foresee the possibility of CFCs detection with James Webb Space Telescope (JWST). They estimated that ~1.2 days (~1.7 days) of total integration time will be sufficient to detect or constrain the concentration of CCl₃F (CF₄) to ~10 times current terrestrial level.

Other kinds of signature that can provides measurable evidences of the use of technology (technosignatures), like for example anthropic settlement or radio and luminous signals, are also suggested in order to recognize the presence of intelligent alien civilization. A review of them is given in Wright [76].

5. False Posivitves

In searching for biosignatures that can unveil the presence of extant or existed life, we are compelled to have clear ideas about all the possible impostors that might mime the true signature of life. A false positive is a by-product of an abiotical process or a signal that could be equal or over-imposed to that produced by life and indistinguishable from the latter.

Most of the features described in the previous sections as biosignatures actually are not unique by–product gases due to the presence of life. There are a lot of atmospheric and geophysical processes that are able to produce the same kind of molecules in detectable quantities.

The most prone to false positives are the metabolic biosignatures (Section 2.1). In this case, in fact, geology uses the same redox gradient in order to produce the same molecules produced by life. In a geologically active planet, hot spots, volcanism, fumaroles and hot springs are the main actors that are able to produce CO, CO₂, CH₄, H₂O, N₂, H₂S. The last one is produced by volcanos in large amount. Moreover there are gases, like N₂ and H₂O that are by–products of life and that are present in considerable amount in the Earth's atmosphere since the beginning. N₂ is the metabolic product of

denitrification (see Section 2.1) and it makes up 80% of the volume of Earth's atmosphere. Its usefulness as a biosignature gas has been debated. Seager et al. [12] consider it not a useful biosignature, due to its stability against the destruction. On the other hand, Lammer et al. [24] assess that an N₂-dominated atmosphere in combination with O_2 and the lack of CO_2 on an Earth-like planet can be considered as a geo-biosignature.

Interesting is the case of N_2O for which there are few abiotic processes that can form it. Lightening is one of them, but it is a very small production [77,78]. Actually, the biotic production of N_2O has a low probability to be a fake. On the other hand, the N_2O features could be hidden by those of CO_2 and CH_4 (see Section 2.1).

The most important false positive is the abiotic production of oxygen coming from photochemical reactions due to the photodissociation of CO_2 and H_2O . The CO_2 photolysis is due to UV radiation coming from the host star with a wavelength of about 140 nm:

$$2(CO_2 + h\nu) \rightarrow 2(CO + O)$$

hv is the photon energy for photons with $\lambda < 175$ nm. This reaction is followed by a recombination of oxygen with the intervention of a third body M:

$$O + O + M \rightarrow O_2 + M$$

with the net result of the loss of two CO₂ molecules and the production of two CO molecules and one O₂. To reach detectable levels of O₂ (in the reflected spectrum), the photolysis of CO₂ has to occur in the absence of outgassing of reduced species and in the absence of liquid water because of the wet deposition of oxydized species. Normally, the detection of the water vapour bands simultaneously with the O₂ band can rule out this abiotic mechanism [79], though one should be careful, as the vapor pressure of H₂O over a high-albedo icy surface might be high enough to produce detectable H₂O bands [49]. In the atmospheres of Venus and Mars, the photolysis of CO₂ is a source of atomic oxygen.

The photodissociation of water, occurs instead when the planet is under a runaway greenhouse effect due to a strong warming of the atmosphere. Liquid water on the surface of the planet is vapourized adding greenhouse gas to the already present gas in the atmosphere. The atmosphere becomes warm and moist and the temperature inversion layer reaches a higher altitude in the atmosphere, causing water vapour to fall prey of the UV radiation. Around 140 nm, H₂O absorbs UV photons in the same wavelength range as CO_2 (see Figure 3), and it is photo–dissociated by the following reactions:

$$4(H_2O + hv) \rightarrow 4(OH + H)$$
$$2(OH + OH) \rightarrow 2(H_2O + O)$$

the oxygen reacts with itself in order to reproduce one molecular oxygen

$$O + O \rightarrow O_2$$

while the light hydrogen escapes form the gravitational pull of the planet. The net result of this photochemical process is the destruction of four water molecules with the production of one molecule of oxygen and the loss of four hydrogen atoms to space. This situation could lead to detectable O_2 levels [80].

In any case, the two processes are strongly coupled: in fact the efficiency of O_2 production from H_2O photodissociation decreases with increasing CO_2 abundances, as CO_2 absorbs UV photons in the same wavelength range as H_2O . Moreover the photochemical production of oxygen is quite self-regulating, because O_2 could be also dissociated by the same photon that splits H_2O and CO_2 [81]. A deeper analisys on O_2 as biosignature and the possible chemical and photochemical routes for the abiotic production are described in Meadows [82].



Figure 3. Cross section for photodissociation of H₂O, CO₂, O₂. Taken by Selsis et al. [81].

Thus, abiotic O_2 production will be more efficient either in a CO_2 dominated atmosphere with very little or no water or in a humid atmosphere poor in CO_2 and the loss of hydrogen from the atmosphere into space can result in huge leftover of oxygen. As matter of fact, Venus shows us that this huge quantity of oxygen due to the photolysis of water experienced by the planet in the past has a limited lifetime in the atmosphere due, for example, to the oxidation of crust and to the oxygen loss into space. The loss of hydrogen and the photochemical induced production of oxygen is driven by the distance from the host star and from the gravitational pull of the planet itself [66,67,83]. Less massive planets close to their star experiencing runaway greenhouse effect can lose water easier than heavier and farther planets. To a less extent, this process could work also in Earth–like planets warning us that life is not the only process able to enrich an atmosphere with these compounds.

On Earth, serpentinisation, the hydration of basaltic seafloor, release large amount of H_2 that, in presence of CO_2 can produce abiotic CH_4 [77]. Also in the case of the surface biosignatures, and VRE in particular, there is the possibility to have minerals that can mime the red edge [84].

6. Where to Find a Habitable World?

Presently, the remote search for life has based on life as we know it (based on carbon chemistry and using water as solvent) that induces measurable modification on the composition of the host planet atmosphere. Because it is still to be demonstrated that subsurface life can modify, in a detectable way, the atmosphere of the host planet, we are limited to search for life on planets, or moons, that can maintain a reservoir of water on their surface. The importance of super-Earth, either they are similar to Earth or not, is that they are rocky planets with a rigid interface between the interior and the atmosphere and if they stay at the right distance from their host star, they could retain liquid water on their surface. This condition generally defines a planet as habitable (because all life on Earth requires liquid water). Surface liquid water requires a suitable surface temperature. The surface temperature of planets with thin atmospheres is determined by the fraction of flux reaching the surface of the planet from the host star.

According to the last definitions (e.g., [66,67,85]), the habitable zone (HZ) is an annulus around the star where a geologically active rocky planet with a water reservoir and a suitable atmosphere (e.g., $CO_2/H_2O/N_2$) can maintain liquid water on its surface. The two boundary limits of the HZ (the inner and the outer ones) are defined by a H_2O (the former) or CO_2 dominated (the latter) atmosphere. The location of two limits is defined by the chemical composition of the planetary atmosphere and the presence or not of clouds. Clouds can modify the planetary albedo and perform additional cooling or warming of the atmosphere itself. The 3-D atmospheric models are effective in assessing how clouds can affect the planet's climate and, correspondingly, the width of the HZ or the position of both the inner and outer limits. The debate is sparkly in the literature about the interpretation of 3-D model outputs on how H_2O , CO_2 as well as planetary rotation or the presence of other greenhouse gasses can modify the HZ limits [83,86–102]. Some of those models indicate that slow rotating planets and tidally locked planets could maintain habitability more than fast-rotating planets under high insolation due to the cloud coverage on the dayside (e.g., [100,103]). Another important case is the habitability around binary and higher-order planetary systems around which planets are also discovered (for a review see [10,104]).

The study of the habitability of a planet hosted by a double or multiple star system arose very soon, just after the seminal works of Huang [105,106] about the star habitability. The discovery of several planets in binary systems in the last two decades has highlighted that the formation of planetary companions around a star of a binary system, or also around both the components of the system, is robust. These systems, like the single stars, can host very different types of planets, from the hot Jupiters to the super–Earths [104,107,108].

Binary hosted planets are defined as "S–type" or "P–type" depending on their orbital configuration. S-Type planets, or Satellite type, are planets with an orbital axis a_P less than the binary separation a_{bin} . They could be circum-primary or circum-secondary planets. Instead, planets with $a_P > a_{bin}$, i.e., orbiting both the components of the binary, are called P-Type or Planet type [109].

A catalog of planets in binary and multi-star systems is maintained by (Schwarz et al. [110], http: //www.univie.ac.at/adg/schwarz/multiple.html) (Table 4). So far (2019 July), there are 147 planets in 97 binary systems with also additional 35 planets in 25 multiple systems (triple and higher-order systems). It is worth to consider that the closer planet found, Proxima Cen b, belongs to a triple system [111]. Proxima Cen b is also a super-Earth with minimum mass of about 1.3 M_{\oplus} orbiting an M5.5 V star with a T_{eff} ~3000 K on a circular orbit with semi–major axis equal to about 0.5 au. This placed the Proxima b in the temperate zone where water could be liquid on its surface [67]. It is possible to consider Proxima b as an S–type planet not affected by the other components because Proxima Cen is about 8.7 kau far away from α Cen AB system [112].

System	\mathbf{S}_P	D [pc]	Orb. Type	a _{bin} [au]	a _p [au]	$M_1/M_2~M_{\odot}$	$\mathfrak{m}_{P} \mathbb{M}_{\oplus}$	Method
Binary star systems								
OGLE-2013-BLG-0341 b	?/?	_	_	0.702	_	_	1.57	µ-Lens
Kepler 68 c	G/?	135.0	S	1450	0.0906	1.08/0.175	2.20	Transit
Kepler 68 b					0.0617		5.98	Transit
K2-288 b	M2V/M3V	69.3	S	54.8	0.164	0.52/0.33	2.83	Transit
GJ 676 d	M0V/M3.5V	16.45	S	800	0.0413	0.71/0.17	4.40	RV
Gliese 15 b	M2V/M3.5	3.6	S	93	0.072	0.38/0.15	5.35	RV
55 Cnc e	G8V/M3.5-4V	1302	S	1050	0.0156	0.95/0.13	8.20	Transit
Kepler-453 AB b	?/?		Р	0.1848	0.790	0.94/0.19	9.43	Transit
	Multiple star systems							
System	\mathbf{S}_P	D [pc]	Orb. Type	a _{sys} [au]	a _p [au]	$M_{star} \; M_{\odot}$	$\mathbf{m}_P \mathbf{M}_\oplus$	Method
α Cen AB/Prox Cen b System								
Alpha Cen A	G2V /					1.1		
Alpha Cen B	K1V /					0.934		
Prox Cen b	M5.5V	1.30		8700	0.0485	0.12	1.26	RV
Gliese 667 ABC System								
Gliese 667 A	K5V/					0.73		
Gliese 667 B	K3V/					0.69		
Gliese 667 C b	M1.5V	43.03		230	0.0505	0.33	5.54	RV
Gliese 667 C c					0.125		3.74	RV
Gliese 667 C d					0.276		5.03	RV
Gliese 667 C e					0.213		2.67	RV
Gliese 667 C f					0.156		2.67	RV
Gliese 667 Cg					0.549		4.56	RV

Table 4. Main characteristics of super Earths orbiting binary and multiple star systems. Data are taken by (Schwarz et al. [110], http://www.univie.ac.at/adg/schwarz/multiple.html).

Unlike around single stars where the HZ is a spherical shell with a distance determined by the host star alone, in binary star systems, the radiation from the stellar companion can influence the extent and location of the HZ of the system. Especially for planet-hosting binaries with small stellar separations and/or in binaries where the planet orbits the less luminous star, the amount of the flux received by the planet from the secondary star may become non-negligible [113]. The Kaltenegger &

Haghighipour [113] results show that for S–Type systems, the effect of the secondary star on the position of both the inner and outer limits of the binary HZ is generally small or negligible. Instead, in close eccentric binaries, if the secondary star is luminous (but a little fainter than the primary, like e.g., in the case of α Cen AB), it can influence the extent of the binary HZ.

The Binary HZ, similar to the HZ around single stars, converting from insolation to equilibrium temperature of the planet depends strongly on the planet's atmospheric composition, cloud fraction, and star's spectral type. A planet's atmosphere responds differently to stars with different spectral distribution of incident energy. Other effects that can be experienced by the planet in the HZ of a binary host system are e.g., gravitational perturbation due to the secondary star that can slightly modify the orbit of the planet and modify also the extent and the location of the HZ.

7. The Long Way to Exoplanet Atmospheres Characterization

We can search for life in other sites than Earth in two different ways: via site exploration and remote sensing. The former is the method used for the Solar System planets, satellites and small bodies (see e.g., [114]). Several NASA, ESA, and Russian Space Agency missions had and will have as goal the exploration of Venus, Mars, Titan, icy moons and other Solar System bodies. This method, quite difficult and expensive also for the closest objects of the Solar System, could not be used for the discovered extrasolar planets, also in the case of Proxima Cen b ([111]) that is "only" at 1.295 pc from the Sun thus the remote sensing seems, so far, the only possible method. It is worth to mention the Breakthrough Starshot² project aimed to send a fleet of light solar sail spacecrafts (*StarChip*) (see for example [115]), for a fly–by mission to Proxima Cen b in order to gather images and other measurements of the planet.

Since the first discovered planet, there was a lot of efforts in building instruments more and more sensitive, able to record the very small radial velocity variations due to the reflex motion induced on the host star by the presence of planetary bodies (e.g., [116,117]). In the meantime, the same efforts were done to improve the possibility of directly observing the planet. In both cases, these improvements allowed to probe, in a limited number of cases, the atmosphere of planets.

Direct imaging [118,119], is specialized on young giant planets orbiting far away from the host star. This method is limited by the available angular resolution (due to the telescope diameter and adaptive optics) and by the necessity to eliminate the glare of the star using coronagraphs. Coronagraphs limit physically the possibility to observe regions very close to the star and, also if the new generation of these optical devices is able to work with very small IWAs (Inner Working Angle³), the HZ of stars distant more than 10 pc are out of reach. In fact, the smallest IWA possible is about $2 \lambda/D$ [120] that means 0.8 au at 10 pc. Note that the inner border of HZ of the solar system is at about 0.9 au [66,67]). Other important difficulties affect the possibility of getting directly the spectrum of a planet: first of all, there is the capacity to observe the smaller planets at the high contrast of flux of 10^{-10} , required for an Earth–like planet (e.g., [121–123]).

SPHERE@VLT [124,125] and GPI@GEMINI [126,127] that have scores on detection of young giant planets (e.g., [128–131]) in the outer regions of host stars are the forerunners for similar instruments to be mounted on the new generation of extremely large telescope in construction: E–ELT (European–Extremely Large Telescope), Thirty Meter Telescope (TMT) and Giant Magellanic Telescope (GMT). The contrast reachable by these instruments as a function of the angular separation of the planetary systems is given in Figure 4, together with that of other instruments mentioned in the next section.

² https://breakthroughinitiatives.org/about

³ IWA is universally defined as the 50% off–axis throughput point of a coronagraphic system, expressed usually in λ/D (resolution element)



Exoplanet Direct Imaging in the Optical and Near-infrared

Figure 4. The planet-star contrast as a function of the planetary system separation. In the plot are shown the performances of current high contrast imagers together with future ground and space-based instrumentation (see Section 8). This plot, updated to 2018, is taken by the NASA Exoplanet Exploration Program Office page (https://exoplanets.nasa.gov/exep/technology/technology-overview/). The orange points are the young self-luminous planets imaged by ground-based telescope in the NIR. The black points are estimates of contrast for planets detected with the radial velocity method. Solid lines are the performances of ground-based coronagraph (orange lines) and space-based (black lines). For the space-based coronagraph, both HST/ACS (in black) and JWST/NIR Cam (in orange) are reported. SPHERE contrast curve represents the best contrast achieved on Sirius, while the GPI labeled line represents its typical performance. The solid black line shows the predicted contrast curve for WFIRST-CGI (see Section 8). The names of SS planets show the contrast star-planet of the analogous planets placed at 10 pc of distance.

SPHERE has four main parts: a common path system that include coronagraphs and an extreme adaptive optics module, an infrared dual-imager and spectrograph (IRDIS [132]), a NIR integral field spectrograph (IFS [133]) and the Zürich imaging polarimeter (ZIMPOL [134]). SPHERE can also measure the state of the polarization of the light reflected by the planet with ZIMPOL, which is devoted to this aim, and also with IRDIS that has polarimetric capabilities. There are several advantages to exoplanet search and characterization using the polarimetric technique. The starlight, that is typically unpolarized (e.g., [135]), when it is reflected by a planet, it is linearly polarized (e.g., [136–138]). Polarimetry can enhance the contrast between the planet and its host star. Because light from stars is not polarized, if a polarized object is detected close to the star, its planetary nature would at once recognized. Polarization can also unveil if the planetary atmosphere has clouds and hazes.

The first detection of a polarimetric signal from an exoplanet was announced for the hot Jupiter HD189733 b by Wictorowicz et al. and Bott et al. [139,140].

At present, the more productive technique for atmosphere observation takes advantage of the combined light of transiting planets and their stars. The technique could be split in the following: transit transmission spectra [141–143] and secondary eclipse spectra in thermal emission [143,144] and reflected light [145–147]. Transmission spectroscopy, possible only when the planet transits its host star along the line of sight, allows to infer the main opacity sources present in the high atmosphere of the planet [142,148,149]). Complementary, emission spectroscopy [150], observing the day hemisphere of the planet and exploiting its occultation during the secondary transit, gives evidence on the thermal structure of the planetary atmosphere and the emission/reflection properties of the planetary surface.

Ground-based atmospheric characterization of exoplanets advanced through the use of high-resolution spectrographs like High Dispersion Spectrograph (R = 45,000) at the Subaru 8-m telescope, CRIRES (Cryogenic High-Resolution Infrared Echelle Spectrograph) and its new

refurbishment CRIRES + at VLT [151]. Also high resolution spectrograph at smaller diameter telescope but with larger spectral range like GIARPS (GIAno and haRPS) at Telescopio Nazionale Galileo (TNG [152–155]). CARMENES at Calar Alto [156] and SPIRou at Canada–France–Hawaii Telescope (CFHT [157,158]) could be proficient in this business. With these high-resolution spectrographs (50,000 $\leq R \leq 100,000$) it is also possible to use an alternative technique to characterize the planet's atmosphere. In fact, for those planets with short orbital periods and resulting high orbital velocities, a high spectral dispersion cross-correlation technique could be (and actually has been) used to measure atmospheric spectral features, taking advantage of the planet's orbital motion (with the subsequent Doppler shift in the planetary spectrum compared to the stellar spectrum) and a known template of high spectral resolution molecular lines [159]. A detailed review of the high spectral dispersion Doppler correlation technique for characterize the planet atmospheres is given in Birkby [160]. So far, this technique was applied with success to hot Jupiter and other giant planets, transiting or not (e.g., [161–168]) and has provided some upper limits on mini—Neptune and super-Earth atmospheres [169,170].

Another promising path towards the atmospheric characterization is the coupling of high contrast imagers with high-resolution spectrographs (HCHR [171–173]). Snellen et al. [174] used for the first time this technique to study the atmosphere of β Pic b, detecting CO. In this case, the technique used adaptive optics (MACAO) to spatially resolve the companion from the host star. Once the exoplanet has resolved, the light from it has sent to a high-resolution spectrograph (CRIRES). At the same time, a reference star, located away from the system, is also observed with CRIRES. After that, to recognize the spectral features of the planet, the Doppler deconvolution technique has applied. Lovis et al. [175] propose to couple SPHERE@VLT with the high-resolution spectrograph ESPRESSO [176], offered to the community by ESO in 2018, to observe Prox Cen b. In the last year, among projects for the SPHERE improvement, M. Kasper (Priv. Comm.) proposed a project that envisions to couple SPHERE with CRIRES+.

Some results in the past were obtained with space-based observations of hot Jupiters using HST and Spitzer (e.g., [177]) and, on the way, there are several ESA and NASA space missions that are going to be launched in space to find and characterize extrasolar planets. CHEOPS (CHaraterising ExOPlanet Satellite [178,179]) will measure precise radii and bulk densities of known exoplanets by transit photometry and select the best-suited targets for atmospheric characterization with future spectrographs from space or on large ground-based telescopes. The launch of this mission is expected in the last quarter of 2019, probably December, 17th. Another mission, with demographic vocation, is following the pathway initiated by CoRot [180] and in particular, by *Kepler* [181]: TESS (Transiting Exoplanet Survey Satellite) developed by NASA, [182] launched on April 18, 2018. The mission is monitoring photometrically, bright stars and thus find many new transiting planets around bright stars adding a lot of target of which will be possible to characterize the atmosphere.

8. Perspectives

In the next decade, the advent of Extremely large Telescopes, E–ELT (expected to operate in 2025), TMT (first light foreseen in 2027) and GMT (foreseen to be operative in 2027), all of the 30–40 m class, will open new paths to the characterization of the new worlds discovered by the demographic space missions (e.g., Kepler, TESS and PLATO). The expected performances of the future ELTs are shown in Figure 4.

All the three ELT projects will mount extreme Adaptive Optics modules and coronagraphs and contemplate medium/high resolution ultra-stable spectrographs as ancillary instrumentation. In particular the Mid-IR ELT Imager and Spectrograph (METIS [183,184]) will be able to image about 20 RV planets and super earths in the habitable zone of M stars [185]. METIS (see Figure 5) is a mid infrared imager and spectrograph that will cover L, M and N bands. Furthermore, it will offer medium resolution spectroscopy in the range between 3–19 μ m together with integral field spectroscopy in L and M bands (3–5 μ m). METIS foresees an observing mode that will couple the high contrast imager with an IFU-fed high-resolution spectrograph in L and M bands performing HCHR spectroscopy. The IFU will have a field of view of 0.5 arcsec² and a resolution of about 100,000. METIS will be able to investigate protoplanetary disks with the possibility to study the chemical composition of planet-forming material, climates and atmospheric properties for a large sample of exoplanets.

For the high resolution spectroscopy at the E-ELT has been proposed HIRES [186]. HIRES will be a high resolution fiber—feed spectrograph (R ~ 100,000) which will have two ultra-stable spectral arms, VIS and NIR, providing a simultaneous spectral range of 0.4–1.8 μ m (see Figure 5). The main science goal of HIRES is the study of the atmospheres in transmission during the transit of an exoplanet in front of its host star in order to detect CO₂ or O₂ in Earth- or super-Earth sized planets. Marconi et al. [186] evaluate to observe the CO₂ in Trappist-1 b with a S/N ~ 6 in four transits or O₂ in 25 transits.

Not only ground based project, but also several space missions are in the pipeline. In the next ten years are foreseen the launch of the demographic mission PLATO (Planetary Transits and Oscillations of Stars) by ESA, and the JWST by NASA, a general purpose space telescope with the characterization of exoplanet atmosphere in its goals. Other missions like ARIEL (ESA) and Finesse (NASA) are specific missions for exoplanetary atmospheres characterization.

Beyond 2030 no ESA missions will be dedicated to the exoplanet search and characterization. In particular Darwin type mission will be taken into consideration after 2040. On the contrary, NASA is considering three out four future missions that will explicitly study and characterize extrasolar planet atmospheres also searching for signs of life. Origins space Telescope (OST), LUVOIR (Large UV/Optical/IR Surveyor) and HabEx (Habitable Exoplanet Imaging Mission) are the names of the three NASA Mission. In the following is given a brief description of each mentioned mission.

- **PLATO:** PLAnetary Transit and Oscillations of stars (PLATO, launch expected in 2026) is a ESA transit survey mission devoted to the detection and prime planet parameters characterization for new planets orbiting bright stars [187,188]. The photometric perfomances that PLATO will achieve are light curves that are precise enough to detect and determine the radius of an Earth-sized planet around a G0V star of $m_V = 10$ mag with an accuracy of 3%. On the other hand, it will be able to asteroseismologically measure the age and the radius of the same star with an accuracy of 10% and 1–2%, respectively. The payload concept is a bus containing 26 cameras with a pupil size of 120 mm covering a field of view of 1037 square degrees each. 24 cameras out of 26 are CCD based camera with a reading cadence of 25 s. These cameras are devoted to observe stars fainter than $m_V = 8$ and are arranged in four groups of six cameras each. Each group has the same field of view but is offset by a 9.2 degree angle from the payload module Z axis, allowing for a total field of view of about 2232 square degrees per pointing. This arrangement results in different sensitivities over the field, with four parts monitored by 24, 18, 12, and 6 cameras. The two remaining cameras have a faster cadence (2.5 s) for star with visual magnitude $4 \le m_V \le 8$, acting also as fine guidance of the satellite.
- **JWST:** NASA's and ESA's James Webb Space Telescope (JWST; launch expected in 2021) will enjoy an unprecedented thermal infrared sensitivity and provide powerful capabilities for direct imaging, including coronagraphy (see Figure 4) [189]. It will mount four instruments: a short-wavelength imager NIRCam, NIRISS, a complementary imager that utilise sparse Aperture mask (SAM) in the wavelength range between 1–2.3 µm, MIRI, the spectrograph in the 5–28 µm wavelength range, and finally NIRSPEC (1–5 µm) will be equipped with an integral field spectrograph. Its four instruments will, in addition to direct imaging of planets, attempt transit observations at low–to medium–resolution (100 < R < 1500) in the near- and mid-infrared domain for atmospheric characterisation. The synergy between the discovery possibilities of TESS and the capability of JWST will allow to characterize several super Earths among with some in the HZ and life detection is a possibility if life turns out to be ubiquitous on exoplanets [33].
- **ARIEL:** Atmospheric Remote-Sensing Infrared Exoplanet Large-survey (ARIEL, launch foreseen in 2028), an ESA mission that will conduct a large, unbiased survey of exoplanets in order to

begin to explore the nature of exoplanet atmospheres and interiors and, through this, the key factors affecting the formation and evolution of planetary systems [190,191]. ARIEL, that will be fully dedicated to this aim, will carry a single, passively-cooled, highly capable and stable spectrometer covering 1.95–7.80 μ m with a resolving power of about 200 mounted on a single optical bench with the telescope and a Fine Guidance Sensor (FGS) that provides closed-loop feedback to the high stability pointing of the spacecraft. ARIEL will observe a large number (~500) of warm and hot transiting gas giants, Neptunes and super–Earths around a range of host star types using transit spectroscopy in the ~2–8 μ m spectral range and broad-band photometry in the optical. Observations of these warm/hot exoplanets, and in particular of their elemental composition (especially C/O, N, S, Si), will allow the understanding of the early stages of planetary and atmospheric formation in the protoplanetary disk and the history of their evolution.

- **FINESSE:** Fast Infrared Exoplanet Spectroscopy Survey Explore (FINESSE, launch expected in 2021) is a NASA mission purpose-built for characterizing exoplanet atmospheres [192]. The mission concept is very similar to the ARIEL one, the payload will be constituted by a small aperture Cassegrain telescope (0.75 m), that feeds a spectrometer with a wavelength range between $0.5-5 \mu m$ with a resolution of 80@1.2 μm and 300@3.0 μm . The mission is designed to survey about 500 planets with the main scientific goal of determining the key aspect of the planet formation process studying the exoplanet atmospheres in order to measure their metallicity and the value of the C/O ratio. Furthermore, the mission will be able to have information on the main factor that estabilish planetary climates ⁴.
- **LUVOIR:** Large UltraViolet Optical and InfraRed surveyor (LUVOIR, launch foreseen 2035) is a project of mission at study by NASA. The baseline design of LUVOIR is a large segmented aperture space telescope (9 m) that will mount coronagraphs in order to suppress the star light. It will carry on board three instruments not optimized for exoplanet science but devoted to general astrophysics. An ultra-high contrast coronagraph with an imaging camera and integral field spectrograph spanning 0.20–2.00 μ m (ECLIPS), a near-UV to near-IR imager covering 0.20–2.50 μ m (HDI); a far-UV imager and far-UV + near-UV multi-resolution, multi-object spectrograph covering 0.10 μ m–0.40 μ m (LUMOS). Among these, only ECLIPS will be used to directly observe exoplanets and obtain spectra of their atmospheres [193].
- **HabEx:** Habitable Exoplanet Imaging Mission (HabEx, launch foreseen 2035) is a mission at study by NASA. It will be a space observatory, with a primary mirror of 4 m covering ultraviolet, visible and near infrared and consist by two spacecrafts that will fly in formation. One of the spacecraft will carry the 4 m telescope (off–axis) and four science instruments. The four instruments will be a coronagraph, a star–shade instrument (SSI) working in the range $0.3 \le \lambda \le 1.7 \mu m$, a wide–field camera (HWC) that will work between 0.5 μm and 1.7 μm and a wide field high resolution ultraviolet spectrograph (UVS) covering the wavelength range $0.115 \le \lambda \le 1.7 \mu m$. The second spacecraft is a 72 m star–shade. The star–shade will fly in formation at a separation of about 120,000 km from the telescope and both will form an externally occulting observatory [194–196].
- **WFIRST-CGI:** Wide Field Infrared Survey Telescope (WFIRST, launch expected in 2025) is defined as a technology demonstration mission and is a mission mainly projected for the study of dark matter but in the science case there is also the study and the characterization of extrasolar planets. The concept of the mission is constituited by a small aperture telescope with 2.4 m in diameter, the same size as the Hubble Space Telescope's primary mirror. WFIRST will have two instruments, the Wide Field Instrument, and the Coronagraph Instrument. The former will be able to provide Wide Field imaging and slitless spectroscopy aimed to dark matter and exoplanets microlensing. Its imaging mode has filters covering 0.48–2.0 μm.

⁴ https://www.jpl.nasa.gov/missions/web/FINESSE_factsheet.pdf

slitless spectroscopy modes cover 1.0–1.93 µm with resolving power 450–850, and 0.8–1.8 µm (not yet defined) with resolving power of 70–140. The latter, Coronagraph Instrument (CGI [197]), has three coronagraphic modes: the first is a broadband imaging with a Hybrid Lyot Coronagraph with inner working angle 3 λ/D (150 mas) in a 0.546–0.604 µm bandpass. The second mode is constituted by a Shaped Pupil Coronagraph [198] for spectroscopic imaging with a lenslet-based integral field spectrograph, at spectral resolving power R ~ 50 in a 0.675–0.785 µm bandpass. Finally, a Shaped Pupil Coronagraph for broadband imaging of debris disks at separations ranging 6–20 λ/D in a 0.784–0.866 µm bandpass. CGI will reach a contrast of 5 × 10¹⁰ [199,200]. The exoplanet science that is possible to do with WFIRST-CGI is described in several papers (e.g., [201,202]).

- **OST:** The Origin Space Telescope (OST, launch foreseen in 2035) is a mission studied to be the follow up of JWST [203,204]. The current baseline is a space telescope with a large aperture (segmented off-axis design with a diameter of \sim 9 m) carrying up to five instrument [205–209]: (i) Far-infrared imager and polarimeter (FIP) is a broad band imager able to use two wavebands in parallel at a time, over large angular areas ; (ii) the Mid-infrared Imager, Spectrometer and Coronagraph (MISC), which operates between 5 and 28 µm, has an ultra-stable spectrometer channel built to do exoplanet transits with high precision; (iii) the OST Survey Spectrometer (OSS) can survey the sky over its whole wavelength range of 25 and 590 μ m with low resolution spectroscopy with $R \sim 300$; (iv) the Heterodyne Receiver for OST (HERO)uses an array of 9 coherent detectors over the wavelength range of 111 to 617 μ m to achieve the highest spectral resolutions of $R \sim 10^6 - 10^7$ for measurements of simultaneous spectral lines. The MISC instrument will be devoted to the study of transiting systems in order to gather information on the presence of biosignatures also in weird world in the habitable zone of M stars. Moreover the use of the high resolution of OSS and HERO will make possible to study the water distribution and the gas mass in protoplanetary disks, in order to have hints on the development of habitability conditions during the planets formation phase.
- **DARWIN/TPF-I:** it is a project of space mission based on an infrared spectrometer, working in the range between 6 and 20 μm, that will be used to directly detect and characterize exo-worlds around nearby stars. The idea of the mission has been developed by ESA [210–214] and NASA [215–217] in the end of the last century and the beginning of 2000 s, and was based on the Bracewell's nulling iterferometer [218]. The activities related to both the proposed missions stopped in 2007 due to the hard technological challengers in maintain the distance among the free floating telescope flotilla controlled at level of nanometer. The main scientific aims of these missions were to gather measurements on the composition of rocky planet atmospheres, their habitability, the detection of biosignatures and the frequency of habitable and inhabited planets. Due to the really current scientific goals of these missions, they are discussed yet and, also if with a more simplified concept, still proposed [219–221].

The potentiality in the biosignature detection of all of these future ground based instruments and space missions is summarized in Figure 5. In the figure, the central wavelength of each absorption band of the different molecula, discussed in Section 2, is listed. In the upper part of the plot, the wavelength range of each afore mentioned mission or instrument is plotted. The effective wavelength coverage of each instrument indicates what species of features can be potentially detected by what instrument. The real detection depends on the resolution of the spectroscopic mode of each instrument and by its performances.



Figure 5. The effective wavelength coverage of each instrument indicates what species of features can be potentially detected by what instrument. The colored filled circles identify the central wavelength of the absorption band of the moleculas named on the vertical axis. On the top of the plot, the wavelength range of the considered instruments is indicated by the corresponding horizontal colored solid line. OST and MIRI@JWST the final wavelength of their used spectral range is also indicated. The use of colors has the unique aim to make the plot clearer.

9. Summary and Conclusions

In the previous sections we tried to give some hints about the search for life as we know it. Mainly, we tried to give tentative answer to the three questions that arise when those kind of quests are at the beginning: *what? where? how?*

First of all, rocky planets, named super Earths, seems to be the really putative loci where to search for alien life. While the *where* is today a straightforward answer, not only for single star but also for binary and multiple systems, the answer to the question *what* is complicated and not so clear. In fact, we have considered different classes of spectral features coming from life metabolic reactions working on Earth. We discussed also the possible false positives that can be generated by geo-physical and geo-chemical reactions. In Table 5 the different types of biosignatures are summarised together with the pro and con's for their detection.

Biosignatures	Example	Pros	Cons
Inorganic Gases	O ₂ ; O ₃ ; CH ₄	Detectable	Also abiotic process
Organic Gases	DMS; isoprene etc.	Only bio by–product Many different Compounds	Small Concentration
Photopigments (surface reflectance)	Chlorophyll	Unique	Complex in detecting and dependent on evolution
Industrial	CF ₄ ; CCl ₃ F	complex evolved and polluting life	Small Concentration

Table 5. Summary of biosignature classes with pros and cons.

On Earth, the only sure biosignatures netted off false positives are O_2 and N_2O . The other primary metabolism gas by–products discussed are either short-lived in the atmosphere or also produced in dominant amounts by geophysical processes. For the present day, methane is not readily identified with low resolution due to the low atmospheric abundance. In any case it is worth to mention that at higher abundance, as it was in the primeval Earth [58], the methane IR feature at 7.66 µm will be easily detectable [9].

A promising biosignature could be the DMS, the secondary metabolic by–product discussed in Section 2.3. However, on Earth, we are dealing with small atmospheric concentration. On an extrasolar planet could be also more difficult that this kind of high specialised by–products could be synthesised by organisms that evolved in a different way and under different environment condition of those on Earth.

So far, O_2 has been assumed as the best case for a biosignature gas in the search for life beyond our solar system, and the presence into the atmosphere of its photosinthetized product O_3 is considered as the evidence of the presence of life forms producing oxygen. In any case we have to pay attention to the retrieved spectra in order to unambiguously identify O_2 and other atmospheric gases, which would set the environmental context in which we are confident that the O_2 is not being geochemically or photochemically generated [222]. Actually Ozone is a not a linear indicator of the presence of biotic oxygen. In fact a saturated ozone band appears already at very low levels of O_2 (10^{-4} ppm), while the oxygen line remains unsaturated at values below the present atmospheric level [50]. In addition, the stratospheric warming decreases with the abundance of ozone, which makes the O_3 band deeper for an ozone layer less dense than that in the present atmosphere. The depth of the saturated O_3 band is determined by the temperature difference between the surface-cloud continuum and the ozone layer. The O_2 has a strong UV signature at about 120 nm and a visible signature at 0.76 µm (the Frauenhofer A-band) observable with low/medium resolution and also a faint one at 0.69 µ, visible with high resolution [49,223,224]).

 N_2O is detectable at 7.8, 8.5 and 17.0 µm with high resolution [49,223]. It would be hard to detect in the Earth's atmosphere with low resolution, as its abundance is low at the surface (0.3 ppmv) and falls off rapidly in the stratosphere.

Detection of water vapour in a planetary atmosphere is the first clue indicating that a planet may be habitable. Water absorption can be seen in several bands in the visible and infrared. On the visible-NIR (0.5–1 μ m) it is possible to detect water absorption at 0.7, 0.8 and 0.9 μ m. Other possibilities are the bands at 1.1, 1.7 and 1.9 μ m. As for the mid-IR, water can be detected between 5 and 8 μ m and from around 17 out to 50 μ m. With extremely high resolution, the absence of water can also be deduced from the presence of highly soluble compounds like SO₂ and H₂SO₄. Venus' spectrum, for example, has some weak absorption bands from water but its bulk atmospheric chemistry can only be explained if the planet is dry.

In searching life on other planets it is important to characterise the atmosphere of the planet in order to understand how it works from both chemical and physical point of view. In order to do that we have several useful tools like e.g., the definition of HZ or the understanding of how life as we know works on a planet and what kind of by–product it synthesises. In any case, this is only half of the story. In fact, if we are going to search for life without any constraints on what kind of life we are looking for, we need to tackle this argument with an open mind and, for example, regardless of the possibility that the planet is in the HZ or not, searching for atmospheric components that are in chemical disequilibrium with respect of the bulk of the atmosphere. Once stated this, we have to go deep and investigate the reasons of that.

Also to the question *how*? not a straightforward answer can be given or, better, we can give a partial answer. For the moment we can use the remote sensing techniques that can exploit more and more sophisticated and complex instruments. But, in so far, we were able to study mainly giant planet atmospheres. This is a big step forward in the right direction and it seems that we are on the rim of our goal.

How many years will be necessary to obtain some hints on it? It's difficult to answer to this question. At the moment we have several brand new instruments both ground and space based, that are devoted to the aim to find and characterise extrasolar planets. In the next future, huge ground telescopes, dedicated space missions and space telescopes (JWST, OST) will be able to begin to address such an intriguing astrophysical problem.

Author Contributions: R.C. contributed to the conceptualization, funding acquisition and supervision. R.C. and E.A. contrinuted to the investigation, writing-original draft, writing- review and editing.

Funding: R.C. acknowledges support from INAF trough the "Progetti Premiali" funding scheme (WOW project) of the Italian Ministry of Education, University, and Research.

Acknowledgments: The authors acknowledge Luca Fossati, Serena Benatti and Ilaria Carleo for the useful discussion and suggestion.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

ARIEL	Atmospheric Remote-Sensing Infrared Exoplanet Large-survey		
CARMENES	Calar Alto high-Resolution search for M dwarfs with Exoearths with		
	Near-infrared and optical Echelle Spectrographs		
CFC	Chloro-Fluoro-Carbons		
CFHT	Canada-France-Hawaii Telescope		
CHEOPS	Characterizing Exoplanet Satellite		
CRIRES	Cryogenic high Rsolution Infrared Echelle Spectrograph		
DMS	Dimethyl Sulfide		
E-ELT	European Large Telescope		
FINESSE	Fast Infrared Exoplanet Spectroscopy Survey Explore		
FORS	Focal Reducer Low-dispersion Spectrograph		
GIARPS	GIAno and haRPS		
GMT	Giant Magellanic Telescope		
GPI	Gemini Planets Imager		
HabEx	Habitable Exoplanet Imaging Mission		
HCHR	High Contrast High Resolution		
HZ	Habitable Zone		
IFU	Integral Field Spectrograph		
IWA	Inner Working Angle		
JWST	James Webb Telescope		
LUVOIR	Large UltraViolet Optical and InfraRed surveyor		
METIS	MID-IR ELT Imager and Spectrograph		
NIR	Near Infra Red		
OCS/COS	Carbonyl Sulfide		
OST	Origin Space Telescope		
PLATO	Planetary Transits and Oscillations of Stars		
SPHERE	Spectro-Polarimetric High-contrast Exoplanet REsearch instrument		
TESS	Transiting Exoplanet Survey Satellite		
TMT	Thirty Meter Telescope		
TNG	Telescopio Nazionale Galileo		
VLT	Very Large Telescope		
VOC	Volatile Organic Carbon		
VRE	Vegetation Red Edge		
WFIRST-CGI	Wide Field Infrared Survey Telescope-Coronagraph Instrument		

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