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BIOSIGNATURES OF EXTRATERRESTRIAL LIFE FROM CHEMICAL VARIATIONS IN THE ATMOSPHERE OF EXOPLANETS

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ABSTRACT

This thesis is an overview on the possibilities of detection through different available techniques to date of any molecules present in the atmospheres of extrasolar planets, which can give us some indication on the presence or not of sources of life beyond our planet and solar system.

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1. Introduction

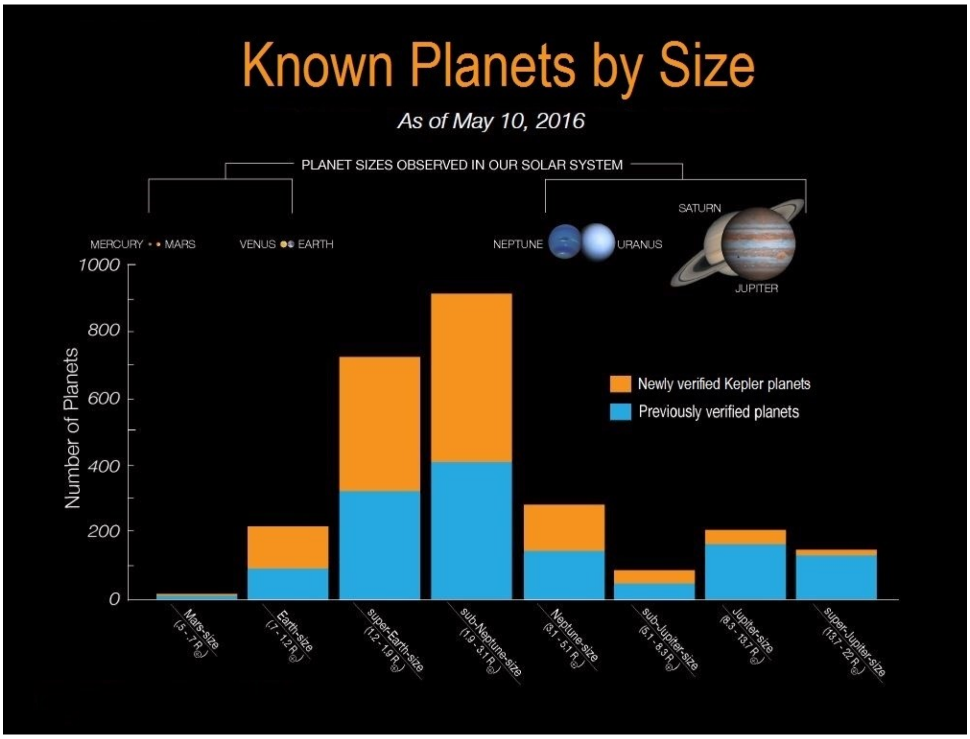
One of the fundamental questions that humanity has debated for centuries concerns its uniqueness in the Universe. Many philosophers and scientists since the earliest times, like Democritus and Anaximander, until the most recent times, from Copernicus to Fontenelle, have investigated this issue, but maybe the finest intuition has been the one of the philosopher Giordano Bruno. In 1584, in the philosophical dialogue *De l'infinito, universo e mondi*, he advanced with some certainty the existence of countless worlds, all revolving around their suns, also countless: we only see the suns because they are the largest and brightest bodies, and their planets remain invisible to us by being smaller and not bright. According to Bruno, these countless worlds are neither worse nor less inhabited than our Earth. Recently, thanks to the increase of technologically advanced observational tools at our disposal, scientists have been able to confirm the existence of a great number of these planets — the first one only in 1992 — some of them having dimensions similar to our planet, thus starting to rise our hopes of no longer being alone. Prior to this date, in 1961, the radio astronomer Frank Drake proposed his famous equation, estimating the number of existing extra-terrestrial civilizations able to communicate in our galaxy, while about ten years before the physicist Enrico Fermi proposed his paradox in which he wondered why no alien civilization has yet come into contact with us. The debate is still quite open: maybe is too early to have any certainties, maybe life as we know it has been a pure coincidence, but as long as there is even the slightest chance it is worth trying as much as possible to get some confirmations. In this thesis I will review the various types of exoplanets detectable with techniques known to date, going to analyze their atmospheres and focusing on those that are most likely to host life; from here I will address the search for atmospheric signals that may have a biological origin and the possible nature of these signals, always keeping in mind our planet Earth as a model of comparison and then looking at future prospects about exoplanets detection and characterization.

2. Exoplanets

For a better understanding of the research field of this thesis, I have to describe first what exoplanets are. We define them as all planets that are outside our solar system and that orbit around a host star. Currently NASA (National Aeronautics and Space Administration) has confirmed as many as 5,071 exoplanets, observed with the use of multiple telescopes and various techniques that I will investigate later. Their masses range from 0.02 times Earth to about 63 times the mass of Jupiter and according to this parameter and their atmospheric composition can be divided into:

- gas giants, planets the size of Saturn or Jupiter that orbit very close to their star — for this reason also called "hot Jupiters"— mainly composed of helium and/or hydrogen; they are quite different from our own Jupiter and, because of the fact that they orbit at such small orbital distances, they are much hotter and therefore have different chemical species present in their atmospheres. The other group, often called the 'very hot Jupiters', is characterized by planets that orbit much closer to their parent stars (with orbital periods less than 2.5 days) and are more massive than Jupiter.
- Neptune-like planets, similar to Neptune or Uranus, with an atmosphere composed predominantly of hydrogen and helium with rocky or heavy metal nuclei. There is a population of exoplanets called sub-Neptunians, smaller than Neptune and often larger than Earth, and are currently seen in relatively close orbits (∼ 200 days or less). The sub-Neptunes are a type of planet that has no analogue in our Solar System, and they are extremely common, currently comprising the largest fraction of the known population of exoplanets. These appear to consist of two sub-groups divided by composition, and potentially formation mechanisms: mini Neptunes that are ice-dominated, and super-Earths that have densities more consistent with rock. Astronomers have also found hot, Jupiter-sized planets and sizzling super-Earths in a close embrace of their stars. But so-called "hot Neptunes", whose atmospheres are heated to more than 900 °C, have been much harder to find;
- super-Earths, a class of exoplanets unlike any in our solar system, more massive than Earth — they can be twice the mass of Earth and have a mass ten times greater — but lighter than the ice giants such as Neptune or Uranus, composed of gas, rock, or a combination of both;
- terrestrial, similar in size to the Earth or smaller, composed mainly of rock, silicate, water and/or carbon. These include Warm Earths, rocky planets that receive much more sunlight than Mercury, and Lava Worlds, with extremely high temperatures. One example is known as Kepler-78b, which orbits its star at only 1% of the distance from Earth to our Sun, with a surface temperature higher than 2,000 °C.

Indeed, the largest population of exoplanets is composed by the Neptunian and Jovian planets, about 80%, with Earths and super-Earths to follow with less than 20% [Galletta, 2021]. These planets are born in the protoplanetary disk, a disk of gas (99% by mass) and dust grains or ice particles (1%), orbiting a newly formed star, from which planets are (hypothesized to be) formed, having a duration of about 10 Myr: the condensation of the granules of which it is composed leads to the birth of large agglomerations up to hundreds of meters — a process called pebble accretion — which accumulate forming planetesimals with dimensions from 10 to 100 km, then collide by generating protoplanets with dimensions of a thousand kilometers, similar to dwarf planets and larger satellites. A further accretion by collisions and captures allows to generate rocky nuclei the size of the Earth: in the outer part of the protoplanetary disk these last ones can increase becoming massive enough at an early stage to retain a thick H/He-dominated atmosphere from the nebular gas. From this can be inferred that the composition of exoplanets is closely related to that of the host star: for example, the probability that a giant planet will form increases with metallicity — defined as the abundance of elements present in an object that are heavier than hydrogen and helium — of the star; the frequency of low-mass planets is in contrast independent of metallicity. The closest discovered exoplanet which could possess life is just 4 light-years away: known as Proxima Centauri b, this Super-Earth is slightly larger than Earth and inhabits the closest planetary system to us. It orbits Proxima Centauri, a red dwarf star that is part of a triple star system called Alpha Centauri. The frequency of the giant planets is lower for lower-mass stars and around 2% for red dwarfs: rocky planets around these will likely be the only potentially habitable planets whose atmospheres could be successfully searched for signs of life in the upcoming exoplanets’ detection missions.



Picture 1 — The histogram shows the number of planets by size for all known exoplanets. The blue bars on the histogram represent all previously verified exoplanets by size. The orange bars on the histogram represent Kepler's 1,284 newly validated planets announcement on May 10, 2016. Credit: NASA Ames/W. Stenzel

2.1 Detection methods

Detecting and characterizing exoplanets techniques have made considerable progresses in the last two decades — mainly thanks to those in the field of Astrophotonics — and can shed light on the limits and possibilities we have for understanding their composition. Earth-like mass planets, despite being abundant, are more difficult to detect than Jupiter-like planets because of their smaller size, so the best-known exoplanets today are gas giants. Different methods of mainly indirect observation have been established, classified according to the planet-star alignment for the amplification or absorption of light, the movement of the star caused by the gravitational pull of the planet and the direct detection of the light emitted or reflected by the planet.

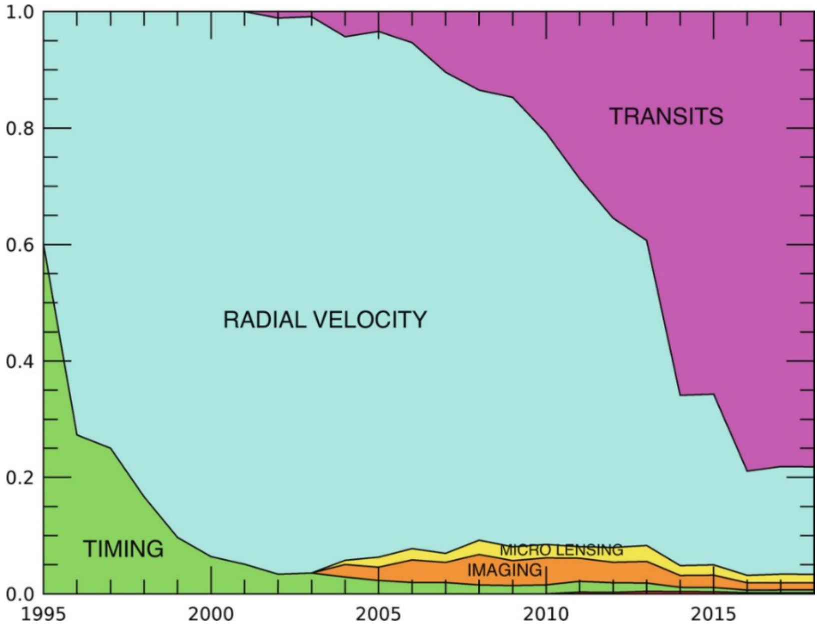
I will list below those techniques that have determined the discovery of the greatest number of exoplanets.

- Transit photometry: this technique, proposed in 1952 by Otto Struve, is based on the principle that if a planet passes in front of the disk of its parent star in line of sight with the observer, then the visual luminosity of the star drops by a small amount, depending on the relative size of the star and planet, much like what happens during an eclipse. This change in brightness can be measured by constructing a light curve, a type of graph that shows the light detected over a given period of time, through which we can derive different information about the size of the exoplanet’s orbit, calculated according to the time it takes to complete its orbit (the orbital period), and the size of the planet itself, depending on how much the star’s brightness drops. We can also learn about average density, which tells us if we are facing a rocky or gaseous planet, and the atmosphere during a transit (also in combination with the radial velocity method): in fact, during this event, a certain amount of light will go through its atmosphere and that light can be analyzed to determine what different atmospheric elements influenced its particular dispersion. According to Kepler’s third law, the orbital period is greater for planets farther from the star, so large planets close to their star are more likely to be discovered. NASA's Kepler mission has hunted for planets using the transit method from 2009 to 2013, founding thousands of possible exoplanet discoveries and giving astronomers valuable information about the distribution of exoplanets in the galaxy. TESS, Kepler’s successor, is currently in space on a two-year mission to discover potentially ten thousand more transiting exoplanets in orbit around bright host stars in our solar neighborhood.
- Radial velocity: this technique considers the gravitational interaction between a planet and a star. Despite the fact that the star prevails by far, the planet also exerts a certain gravitational attraction on the host star, which results in a slight oscillation in its motion and therefore a change in

its radial velocity. This oscillation can be detected by most high-resolution spectrographs as tiny shifts towards the red or blue spectrum in the star's emissions: this phenomenon is referred to as the Doppler-Fizeau Effect. The spectrum of a star that is moving towards the observer appears slightly shifted toward bluer (shorter) wavelengths. If the star is moving away, then its spectrum will be shifted toward redder (longer) wavelengths. From the period, through the Kepler's third law adapted to the mass of the star that depends on the spectral type, we can infer the value of the semi-axis of the planet's orbit: with this value and the mass of the star, from the orbital velocity is calculated the mass of the planet. The most easily detectable planets are those around less massive and hot stars, precisely because these have low rotational speed, giving a cleaner spectral line, and the gravitational attraction exerted by the planet is greater; these planets are the hot Jupiters and the most suitable stars are the red dwarfs. Radial velocity method, as well as one of the first, continues to be one of the most productive methods, often used in combination with others to confirm the presence of a planet. Two important observatories where this work takes place are the Keck telescopes in Hawaii and the La Silla observatory in Chile.

- Gravitational microlensing: in this phenomenon the planet acts as a natural gravitational lens — gravity can bend and focus light like a lens in a magnifying glass or pair of glasses — amplifying the apparent background brightness of a star. While the increase in brightness is large (≈ 2×) the exoplanet and the observer must be aligned for a few milliseconds, making it an extremely rare event (within the Galaxy we are in the order of 10^{-7}); that's why large portions of space must be observed for long periods of time. Einstein himself, who in 1936 introduced the concept of gravitational microlensing, noted in his paper that *"There is no great chance of observing this phenomenon"*. When you record a star that becomes brighter and then fades into the scheme of lens-objects, the data is analyzed to get information about the estimated size of the star. Because of its sensitivity to low-mass planets that orbit at relatively large distances from their stars, microlensing surveys can yield discoveries of Earth-sized (and smaller) worlds orbiting at Earth-like distances from Sun-like and larger stars.
- Direct imaging: astronomers can also take direct pictures of exoplanets. The main problem is that the stars they orbit are millions of times brighter than their planets and as a result any light reflected off of the planet or heat radiation from the planet itself is drowned out by the massive amounts of radiation coming from its host star. The main used techniques are coronography, that uses a device inside a telescope to block light from a star before it reaches the telescope's detector, and the "starshade", a device that is positioned to block light from a star before it even enters a telescope. Once star's glare is reduced, a more optimal view of the objects

around the star is obtained, which may be exoplanets, and their possible composition.



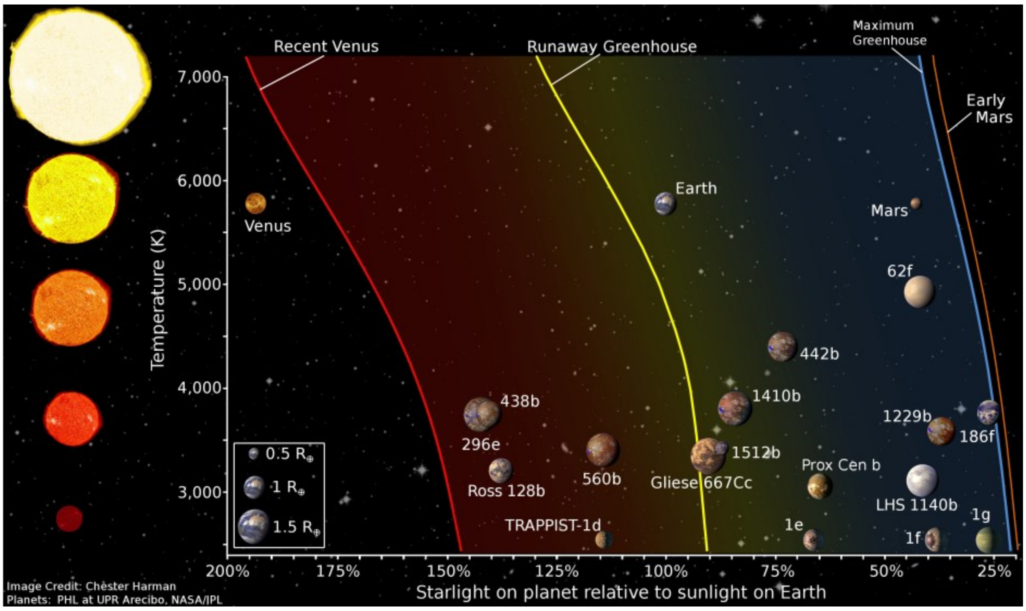
Picture 1 — The fractions by which various detection methods contributed to the accumulated sample of known planets is shown, for years since 1995. [Transit Photometry as an Exoplanet Discovery Method, Hans J. Deeg and Roi Alonso]

2.2 Atmospheric composition

The advent of the above-mentioned detection techniques has been crucial in characterizing a wide diversity of exoplanets, with different dimensions, atmospheric temperatures and compositions. Despite these methods, we must consider the fact that the parameters at our disposal are rather limited and only from these for now we can deduce the atmospheric chemical composition. Atmosphere models assume that the planetary atmosphere is one-dimensional and with plane-parallel geometry, under the constraints of hydrostatic equilibrium, chemical equilibrium, local thermodynamic equilibrium (LTE) and radiative-convective equilibrium — RCE, that describes a balance between the cooling of the atmosphere by radiation and the heating through latent heat release and surface heat fluxes. [Jakob, C., Singh, M. S., & Jungandreas, L. (2019)] The inputs to such a model are typically the system properties such as the planetary bulk properties (e.g., mass, radius, and/or gravity derived from radial velocity and transit methods), orbital properties and the spectrum of the host star irradiating the planet. Such a model also assumes an elemental composition of the planetary atmosphere (e.g., day-night energy redistribution efficiency, presence of clouds/hazes which block most of the spectral signal of the gases, etc.); given these input parameters and the equilibrium assumptions, such a model computes the radiative transfer in the atmosphere with a pressure-temperature (P-T) profile to generate an output spectrum. The General Circulation Models (GCM) instead solves the full three-dimensional structure of the atmosphere given the planetary bulk parameters and irradiation field, capable of simultaneously modelling the dynamics coupled with chemistry, radiative transfer, and clouds. The most important molecules in planetary atmospheres are those containing O, C, and N; high resolution Doppler spectroscopy and direct imaging have led to the detection of various molecules including CO, H_2O, TiO, CH_4 and HCN, present in H_2-rich atmospheres at high temperatures in hot Jupiters, depending on the metallicity, temperature, pressure and C/O ratios. Among these species, H_2O is predicted to be the most abundant oxygen-bearing species, besides CO, in high temperature atmospheres, detected in the dayside of several hot Jupiters and a few exo-Neptunes. Thus gas giant exoplanets are expected to have H/He-dominated atmospheres based on their formation and on the bulk densities inferred from observations. Because of the hydrogen-rich atmosphere, a major species produced by their host star irradiation, which determines the photochemistry, is atomic hydrogen, formed by photolysis and thermal decomposition of H_2 as well as by catalytic photolysis of H_2O: the higher the irradiation of the planet the more abundant becomes H. Another important photochemical product is the radical OH, which results from the photodissociation of water and acts as a key intermediate in the synthesis of other O-bearing molecules such as O_2 and NO. An enhancement of metallicity in H/He-dominated atmospheres of gas giant planets promotes an increase in the abundance of molecules that contain multiple heavy atoms, i.e. CO and N_2 are favored over CH_4 and NH_3 due to greater atmospheric opacity from the heavy molecular constituents. The dominant equilibrium atmospheric constituent on intermediate-sized planets like super-Earths and exo-Neptunes will typically be H_2 at low-enough metallicities but can become H_2O at moderately high metallicities and subsolar C/O ratios, CO_2 at solar-like and subsolar C/O ratios and high metallicities, CO at high metallicities and C/O ratios near unity and can even become O_2 at very low C/O ratios and high metallicities. At high C/O ratios and low metallicities, CH_4 is an important atmospheric component at low temperatures, while HCN and C_2H_2 become more important carbon phases at high temperatures. Indeed, terrestrial-planet atmospheres are expected to be typically dominated by H_2O, CO_2, CO, N_2, Ne, Ar, Kr, SO_2, SiO_2, that were outgassed from the solid planetesimals that formed the planets or that were supplied by later impacts by solid bodies.

2.3 Planets of habitable zone

The comparison with the exoplanets detected so far may suggest that a planetary architecture similar to our solar system is not common. For this reason the search for those requirements that allow the development of life as we know it is a useful constraint to discern potentially habitable from non-habitable planets. Life on Earth mainly needs elements such as H, O and C but also N, S, P depending on the types of organisms considered (e.g. extremophiles can survive by only a few elements). Both for the cosmic abundance and for its physicochemical properties, H_2O is the best candidate as solvent of life: the totality of biochemical reactions takes place in an aqueous environment, including the functioning of enzymes, the proper protein folding, the maintenance of the membranes and the formation of the lipid bilayer, to name a few. As for the C, if we consider the living forms as we know them, the only possible substitute could perhaps be represented by silicone-based compounds, in particular silanes, which, although soluble, may exhibit the typical flexibility of carbon-based compounds. This, however, only in very cold environments, such as those of Triton or Titan, being therefore inefficient in warmer environments characterized by the presence of liquid water. That is why is important to go and look for those planets that are in a circumstellar area such as to allow the presence and maintenance of water in the liquid state, what is called the habitable zone HZ (also called Goldilocks zone). One-dimensional atmosphere models analysed in the previous paragraph simulate where surface liquid water is no longer stable, in relation to the proximity of the planet to its host star: if closer leads to an increase of the incident stellar flux (inner HZ, IHZ), if away from it to a decrease of the stellar flux (outer HZ, OHZ), defining the stellar flux as the normalized flux required to maintain a given surface temperature. The IHZ proposes two habitability limits: a moist greenhouse limit, where the stellar radiation warms the atmosphere sufficiently to cause the planet to lose water by photolysis and then subsequent escape of free hydrogen to space; a runaway greenhouse limit, whereby surface water is vaporized and the atmosphere becomes opaque to outgoing thermal radiation due to excess amounts of H_2O in the atmosphere, heating uncontrollably. The OHZ is defined by the maximum greenhouse limit, where the warming provided by the build-up of atmospheric CO_2 is maximum. The enhancement of the greenhouse effect in thick CO_2 atmospheres begins to saturate, while its reflectivity continues to increase, until it wins out over the increases to the greenhouse effect, causing the planet to experience cooling instead of warming and marking indeed the maximum CO_2 greenhouse outer edge limit to the HZ. Alternatively, complementary HZ limits that are not based on models, but rather on empirical observations of our solar system can be derived: for example, the inner edge of this empirical HZ called “recent Venus limit” is based on geological evidence that Venus has not had liquid water on its surface for at least the past 1 billion years [Solomon and Head, 1991]. If we assume Venus was habitable right up until 1 billion years ago, then the recent Venus limit is the equivalent distance from our modern Sun that would have matched the insolation at Venus 1 billion years ago under a fainter Sun. Likewise, a similar empirical limit can be defined for the outer edge: this “early Mars limit” is based on geological evidence that suggests that Mars had liquid water on its surface 3.8 billion years ago.



Picture 3 — This figure shows the HZ limits for an Earth-like planet around stars with different stellar temperatures (vertical axis) in terms of incident stellar flux (horizontal axis) on the planet, from a 1-D climate model.

A practical application of habitable zone is to calculate η_{Earth}, the fraction of stars that have at least one planet in the HZ: this can be used in designing direct imaging missions that can characterize a habitable planet. Current estimates of η_{Earth} for Sunlike stars have been calculated by the data collected from the Kepler mission, and the values range from 2% [Foreman-Mackey et al. 2014] to 22% [Petigura et al. 2013]; for M dwarfs, η_{Earth} is estimated to be ~20% on an average [Dressing and Charbonneau 2015]. Earth-like rocky planets with CO_2, H_2O and N_2 atmospheres and active carbonate-silicate cycles are considered the likely locales for alien life, on the idea that these long-term cycles (i.e. geological time scales) maintain the habitability of Earth, as well as other potentially habitable planets, regulating the transfer of carbon between the atmosphere, surface and interior, and acting as a planetary thermostat that regulates mean surface temperatures. Those processes are favorited by the presence of a volcanic activity that release higher concentrations of greenhouse gases into the atmosphere, including CO_2, that, as we will see below, can promote the accumulation of biosignatures.

3. Biosignatures

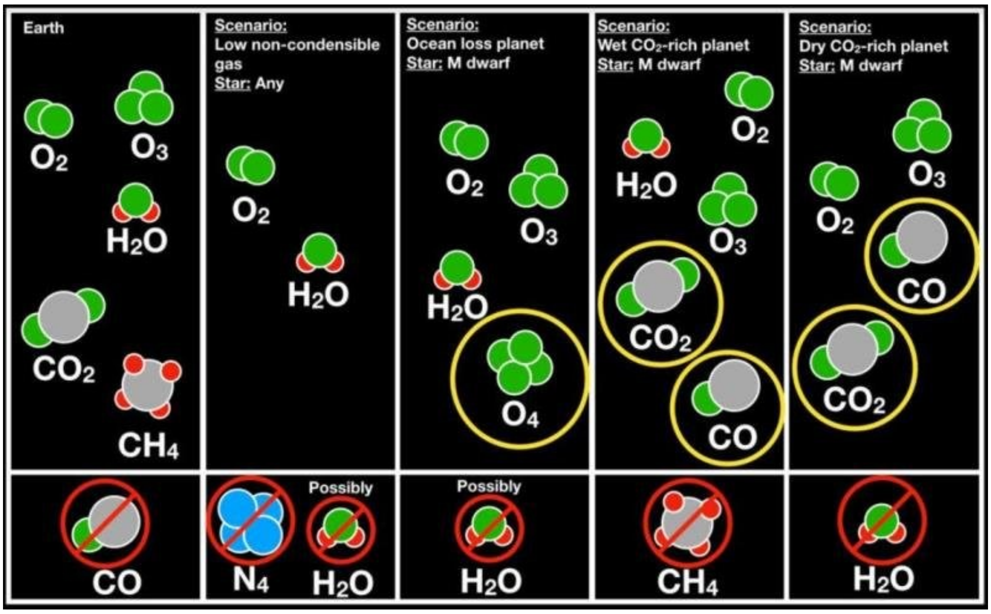
Trying to understand the possible atmospheric composition of the exoplanets is not enough to be able to fuel the search for life outside our solar system. It is also necessary to be certain of the presence of life forms and given the impossibility of making on-site detections due to the astronomical distances, the only way to collect concrete information is to detect the so-called biological signatures. In 1990 the astrobiologist Carl Sagan and colleagues did photometric and spectrophotometric observations of Earth using the Galileo probe, a single-launch Jupiter orbiter built to study the extrasolar planets, to analyse some elements that could have been used as indicators of life on our planet and to see if they could create evidence that could be observed remotely with instruments from space. Considering thermodynamic equilibrium as a life indicator, they measured the presence of water in its different forms, especially gas-phase H_2O over the entire planet, a large amount of O_2, unique among all the worlds in the Solar System, and the simultaneous presence of CH_4 traces. The latter in particular is oxidized quickly to CO_2 and H_2O, and at thermodynamic equilibrium there should not be a single methane molecule in the Earth's atmosphere: however, an extreme disequilibrium abundance occurs of a reduced gas such as CH_4 in a O_2 rich atmosphere, clearly a consequence of natural system activity such as methane bacteria and anthropogenic activity. The presence of disequilibrium abundance nitrous oxide (N_2O) was another indicator of biological processes: the major source of N_2O on the ground-truth Earth is nitrogen-fixing bacteria and algae that convert soil and oceanic nitrate (NO_3^-) to N_2 and N_2O. Therefore all those elements detected were strongly suggestive of life; but what are the constrains that can permit us to evaluate the authenticity of a biosignature? A biosignature is nominally defined as an “object, substance, and/or pattern whose origin specifically requires a biological agent” [Des Marais and Walter, 1999; Des Marais et al., 2008], and is classified according to three criteria: reliability (a feature that is more likely to be produced by life), survivability (the ability of the biosignature to be preserved or otherwise persist in its environment), and detectability (the likelihood that the biosignature can be observed or measured) [NASEM 2017; Meadows 2017; Meadows et al. 2018b]. We must consider that only a few accumulate to high enough levels to be remotely detectable for astronomical purposes and defined as biosignatures; moreover, they can have biological origin as well as being produced by events not necessarily linked to life (false positives), predominantly by geochemical or photochemical processes. Next, I will consider different kinds of biosignatures having different origins, using our planet as a model for their formation and detection.

3.1 O_2 as a biosignature

O_2 has long been considered an excellent biosignature because it is an abundant gas that is stable against photolysis, and so it is evenly mixed throughout the atmosphere. It has risen over time to become the second most abundant gas in Earth's atmosphere, about 20% by volume, and is also one of the very few biogenic gases that absorbs strongly in the visible and near-infrared (NIR), likely wavelength regions to be covered by ground-based telescopes seeking to characterize extrasolar planets. Isotope measurements point to transient low levels of O_2 in the early Earth's environment 3.0–2.65 Ga, which were likely generated by oxygenic photosynthesis, that uses light energy to (indirectly) split H_2O, which serves as an electron donor to produce organic matter from CO_2, generating O_2 as a waste product [Leslie, 2009].

$$CO_2(g) + 2H_2O^{w} + h\nu \rightarrow (CH_2O)_{org} + O_2^{w}(g)$$

where $(CH_2O)_{org}$ represents organic matter and $h\nu$ is the energy of the photon(s) (where h is Planck's constant and ν is the frequency of the photon). Cyanobacteria and plants are responsible for the production of oxygen by using solar photons to extract hydrogen from water and using it to produce organic molecules from CO_2 thanks to photosystems I (PSI) and II (PSII), but phylogenetic analyses examining the origins of oxygenic photosynthesis in cyanobacteria have found that microbes basal to the cyanobacterial lineage (*Melainabacteria* and *Sericytochromatia*) lack photosynthetic machinery: this suggests that photosynthesis arose late in cyanobacteria, and that these genes were acquired by horizontal gene transfer from more primitive anoxygenic phototrophs. They use other reductants like H_2S, H_2 and Fe^{2+} to donate electrons to a single photosystem and can be found in freshwater lakes and ponds, hot and sulphur springs, and some marine waters where the sources of electron donors (e.g., H_2S) can be either geological (in sulphur springs) or biological (produced by sulphate-reducing bacteria). So irreversible, global accumulation of O_2 in the atmosphere evidently occurred somewhat later, between 2.45 and 2.2 billion years ago. Knowledge gained from this delayed rise of O_2 during the history of our own planet helps us identify environmental contexts, stellar and planetary characteristics that are more likely to lead to O_2 false negatives. Whether a planet develops a biogenic O_2-rich atmosphere will depend not only on the evolution of oxygenic photosynthesis but also on the long-term balance between sources and sinks of O_2 at the surface that are favorable for the long-term accumulation of a large atmospheric O_2 inventory. The net release of O_2 in the atmosphere is due to the burial of organics in sediments between the marine and terrestrial photosynthetic biospheres: each reduced carbon buried results in a free O_2 molecule in the atmosphere. This net release rate is also balanced by weathering of fossilised carbon when exposed to the surface and the oxidation of reduced volcanic gases, such as H_2 and H_2S. The detection of significant O_3 in a planetary atmosphere, produced by the photochemical reactions that combines an oxygen atom (O) with an oxygen molecule (O_2) in the presence of UV, has also been proposed as a proxy for photosynthetically generated O_2 [Leger et al., 1993, 2011; Des Marais et al., 2002] with the advantage that O_3 absorbs strongly in complementary wavelength bands to O_2. The possible abiotic O_2 generation mechanism that may produce Earth-like quantities of O_2 on an ocean-bearing world involves photolysis of water and subsequent hydrogen loss from terrestrial atmospheres that are depleted in non-condensable gases such as N_2. With a low inventory of those gases, water is able to rise higher into the atmosphere before it condenses, being more vulnerable to photolysis by incident stellar UV radiation at these higher altitudes. The water's H atoms escape, leaving abiotic O_2 to build up in the atmosphere: this continues until O_2, itself a non-condensable gas, overwhelms surface sinks to reach a sufficiently high atmospheric abundance that it can establish a cold trap, and halt the loss of water vapor. This mechanism is most effective for less massive late-type M dwarfs due to the weak near-UV (NUV) output: this, mixed with the deleterious impacts of the ultraviolet (UV) activity may also drastically limit the rate of prebiotic photo-processes, creating an obstacle for the origin of life on worlds around these stars. Moreover young M dwarfs during their evolution experience an extended contraction phase — in which they become dense until begin to convert hydrogen into helium and give off energy through an exothermic nuclear fusion process — that makes them significantly more luminous than they will be when they enter the main sequence hydrogen burning phase. Consequently, planets that form in what will become the main sequence habitable zone are subjected early on to very high levels of radiation: modelling suggests that this super-luminous phase, that can extend for up to 1 billion years, can drive the loss of up to several Earth ocean equivalents of water for an M dwarf HZ terrestrial planet. The other major class of processes that build up abiotic O_2 relies on the photolysis of CO_2 and circumstances that inhibit CO_2 recombination from CO and O_2: the mechanism that could produce the largest signal from CO_2 photolysis requires a desiccated, cold, H-poor atmosphere. This water-poor atmosphere cannot support photolytic generation of the OH catalyst that accelerates CO_2 recombination. Systems older than a few Gyr may be preferred, to allow time for biologically generated O_2 to overwhelm sinks and rise in the atmosphere, and to increase the probability that abiotic O_2 generated during the star's super-luminous pre-main-sequence phase has been depleted through sequestration in the planetary environment; it would, therefore, be advantageous to select older F, G, K stars, or earlier type M dwarf targets.



Picture 4 — Oxygen as a biosignature: False positive mechanisms for oxygen on a variety of planet scenarios. The main contributors to a spectrum of the planet's atmosphere are shown in large rectangles. The yellow and red circles represent molecules that would confirm a false positive biosignature and molecules crossed confirm false positive biosignatures if not detected.

3.2 CH_4 as a biosignature and methane-based life

As said in paragraph 3, biosignatures can be produced by metabolic reactions of living organisms that capture energy, in particular from environmental redox chemical potential energy gradients. The production of methane is generated by methanogen bacteria, anaerobic archaea characterized by their ability to conserve energy for ATP (adenosine triphosphate) synthesis by producing methane gas. Methanogens can be found in extreme environments such as hydrothermal vents or saline lakes but also colonize non-extreme environments such as anoxic soil sediments such as rice fields, peat bogs, marshland or wetlands. Some methanogens can also associate with plants in tree wet wood tissue, animals in the intestinal tract of insects and also in the rumen of herbivorous mammals and could be found in the human body. They produce CH_4 by either respiring CO_2 as a terminal electron acceptor, reducing it with the use of gas hydrogen (H_2), or disproportionation of acetate to CH_4 and CO_2. These reactions can be written as follows:

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

$$CH_3COOH \rightarrow CH_4 + CO_2$$

where CH_3COOH is acetic acid, a decay product from fermentation of organic matter. On early Earth, between 4.11 and 3.78 Ga, widespread methanogen bacteria may have produced CH_4 at much higher levels (1,000 ppm or even 1%), easier to detect; on the other hand the O_2–CH_4 redox pairs would be challenging to detect concurrently unless perhaps in the case of a planet in a lower-UV radiation environment like with some M host stars, where the OH produced by H_2O photolysis is reduced, permitting higher atmospheric CH_4 concentrations. CH_4 is the most thermodynamically stable form of carbon in highly reducing H_2-dominated atmospheres, therefore is often viewed as a companion biosignature that would be most compelling if observed together with O_2/O_3 or other strongly oxidizing gases. The recent confirmation of methane in the atmosphere of Mars, that contains 0.1% of O_2 and some O_3, is also a good example for the consideration of CH_4 as a biosignature gas, since it is photochemically unstable and must be actively produced, but it may be a false positive because CH_4 could be produced geologically. On the basis of both the thermodynamic disequilibrium between the two species and methane's short photochemical lifetime, it may also serve as a biosignature or habitability marker with the presence of CO_2 because would have had to originate from biology or from abiotic water–rock reactions, indirect evidence of liquid water in the planetary environment. Geochemical research has actually demonstrated that abiotic methane occurs on Earth in several specific geologic environments: it can be produced by either high-temperature magmatic processes in volcanic and geothermal areas, or via low-temperature (<100°C) gas-water-rock reactions in continental settings, even at shallow depths [G. Etiope, B. S. Lollar, 2013]. In the rare cases where volcanoes could produce biogenic levels of CH_4 assuming magma production rates larger (>10 times) than those on Earth today, they would also outgas significant amounts of carbon monoxide (CO) gas. Therefore the atmospheric CO/CH_4 ratio could be used to distinguish between abiotic (outgassed) and biotic scenarios, but generally this process is unlikely to produce atmospheric CH_4 fluxes similar to those produced by biology on Earth. Also abiotic CH_4 generation via low-temperature water–rock or metamorphic reactions is unlikely to produce atmospheric CH_4 fluxes comparable to modern biotic fluxes in combination with atmospheric CO_2. Liquid methane is of particular interest because it is the only liquid other than water that forms seas on the surface of a planetary body in our solar system, in particular on Saturn's moon, Titan. Whether it can support any form of cell membrane is not certain, however Titan's surface hosts an unknown process that consumes hydrogen, acetylene, and ethane, all of which continually flow down from the atmosphere but do not accumulate and this makes liquid methane a very interesting solvent to consider for cell membrane alternatives. Sunlight on Titan produces complex hydrocarbons (C_2H_2, C_2H_6, and organic haze) that could be a source of energy when reacted with atmospheric hydrogen: this is in direct analogy with the potential chemical energy in organics on Earth when reacted with atmospheric oxygen. If bacteria are consuming complex hydrocarbons at the surface of Titan, the observable effects might include complete consumption of C_2H_2 at the surface, reduction in C_2H_6 and organic solids at the surface compared to the accumulation expected from photolysis alone, and a sink of hydrogen at the surface creating a gradient in the hydrogen mixing ratio with altitude. There are indeed two issues: the low temperatures that imply very low rates of reaction and the low solubility of organic substances in liquid methane. The use of catalysts can speed up any thermodynamically favorable reaction and is possible that active transport and organisms with large surface to volume ratios could mitigate this problem. As our understanding of conditions that could nurture extra-terrestrial life expands, so does our probability of finding it, perhaps within the liquid methane habitable zone.

3.3 Other relevant biosignatures

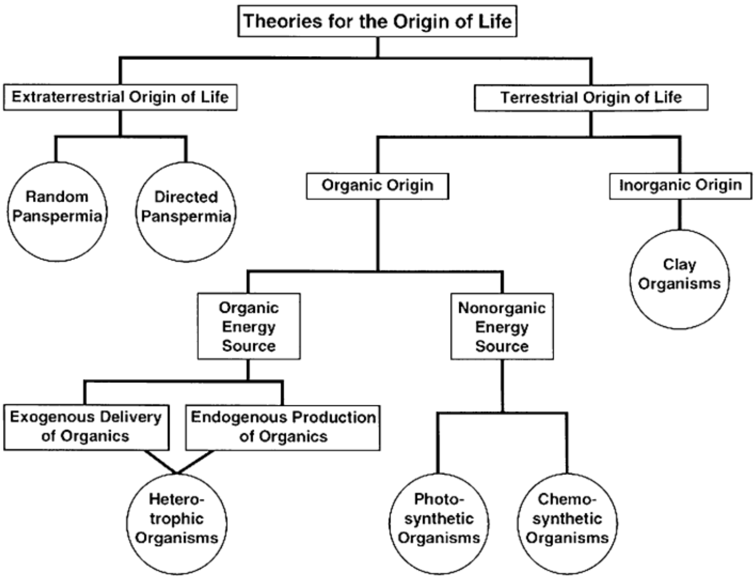
On Earth there are some other gases released in atmosphere very promising in unveiling life as biosignature. N_2O has been proposed as a strong biosignature, in part because its abiotic sources are small on modern Earth and because it has potentially detectable spectral features [Sagan et al., 1993; Segura et al., 2005; Rauer et al., 2011; Rugheimer et al., 2013, 2015a]. Nitrous oxide could have been a major greenhouse gas on the Early Earth, emitted from the strongly reducing, so-called "Canfield ocean" in the middle and late Proterozoic: in this scenario the sulphur-rich early ocean impacted the availability of trace metals in the ocean affecting the nitrogen cycle and allowing biogenic N_2O to build up in the atmosphere as a greenhouse gas. On modern Earth the main production of nitrous oxide, besides the anthropogenic one, is caused by the activity of denitrifying bacteria like *Thiobacillus denitrificans*, *Micrococcus denitrificans*, and some species of *Serratia*, *Pseudomonas*, and *Achromobacter*, microorganisms whose action results in the conversion of nitrates in soil to free atmospheric nitrogen (60–86% of total nitrogen removal). Without denitrification, however, the Earth's supply of nitrogen would eventually accumulate in the oceans since nitrates are highly soluble and are continuously leached from the soil into nearby bodies of water. A small abiotic source of N_2O on Earth is known from "chemodenitrification" (nitrite reduction by Fe(II)) of dissolved nitrates accumulated by the biotic production of reactive nitrogen species during denitrification in hypersaline ponds and brines in Antarctica and marine coastal sediments. Around young or more magnetically active stars, N_2O may build up abiotically due to enhanced production of NO and NH from extreme ultraviolet (EUV-XUV) and particle flux-induced photodissociation and ionization, driving the reaction

$$NO + NH \rightarrow N_2O + H$$

For Earth-like planets orbiting in the HZ of cooler stars like M dwarfs, the low UV output from the star weakens N_2O sinks and build it up to higher concentrations than on an Earth-Sun analogue given the same source fluxes. Sulfur compounds like hydrogen sulfide H_2S, carbon disulfide (CS_2), carbonyl sulfide (OCS), dimethyl sulfide (DMS), and dimethyl sulfoxide (DMSO: $CH_3 \cdot SO_2 \cdot CH_3$) may be another good signature of biotic activity. 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, but can be also produced in abundance by abiotic volcanic and hydrothermal processes and thus are not strong biosignature gas candidates. DMS is the largest source of organosulfur gas in the modern atmosphere and the main source of this compound is the biological degradation of dimethyl sulfoniopropionate (DMSP), which is found primarily in organisms such as certain types of marine algae, corals, plants, and heterotrophic bacteria. DMS and also DMSP can ultimately result from the production of CH_3SH, itself a decomposition product of the essential amino acid methionine; microbial mats containing cyanobacteria and anoxygenic phototrophs produce measurable amounts of CH_3SH, DMS, and DMDS. Although organic sulfur-containing gases may not build up to levels which are detectable for next generation missions, also due to photochemical destruction, their presence could nevertheless be indirectly elucidated since they led to an increase in the C_2H_6/CH_4 ratio: the study conducted by Domagal-Goldman et al. (2011) found that the cleaving of methyl (CH_3) radicals from DMS and DMDS by UV radiation catalyzed the photochemical build-up of C_2H_6 far beyond the level expected for the abundance of CH_4 in the atmosphere, which is otherwise the primary precursor to C_2H_6. Consequently, it was proposed that this anomalously high C_2H_6 signature would be suggestive of a sulfur biosphere [Domagal-Goldman et al., 2011].

4. Final thoughts on extra-terrestrial life

Taking once again our planet Earth as a comparison model, we have seen that the requirements for life formation depend on the composition of the planet — e.g. it is widely accepted that our planet's chemistry was enriched because, early in the history of the Solar system, the Earth collided with another planetary body with the result that our planet acquired extra core material (iron and other heavy metals) which have been crucial for the evolution of life — on the host star's characteristics like metallicity and its lifetime — it takes billions of years for simple life-forms to achieve the oxygenation of a planet's atmosphere and thereby to allow large animals to arise. When we take a closer look, we have also to consider not only the atmospheric composition with its possible gaseous biosignatures, widely discussed before, but also the deep terrestrial subsurface, which hosts large microbial communities not yet fully explored: geological findings suggest that certain prokaryotes may have remained viable in sediments and subterranean water for thousands and perhaps millions of years [Helga Stan-Lotter et al., 2009]. Considering the harsh environments on other planets and moons as well as in interplanetary space, the chances for finding extra-terrestrial life in apparently lifeless exoplanets should be greater when drilling into the subsurface and searching with highly sensitive instrumentation for organic molecules and perhaps living fossils — and the impossibility to do that is one of the greatest limits in our research. Regarding life formation on Earth, what we do know about is what it is made of, its ecological requirements and limits. We do not have consensus theory for the origin of life nor we have knowledge about the timing or location: our earliest evidence dates between 4.1 and 3.5 Gya [Bell et al., 2015; Awramik, 1992] thanks to the preserved microbial mats of the stromatolites, while the earliest evidence of eukaryotic life has been dated between 1.6 Gya and almost 1.9 Gya [Parfrey et al., 2011; Betts et al., 2018]. Eukaryotic life took over a billion years to emerge from prokaryotic precursors and multicellular life itself appeared late in the history of Earth, after three billion years of apparent unicellular monotony. Brandon Carter in his 1983 paper noticed that intelligent life emerged on a timescale within an order of magnitude of our star's lifetime: it took 4 Gya for intelligent life to emerge, and in perhaps less than 1 Gya, the increasing luminosity of the Sun will likely destroy Earth's ability to support complex life, due to increased surface temperatures [Franck et al., 2006] and an eventual breakdown in the carbon cycle [Lenton and Bloh, 2001]. This would mean that most stars will never support intelligent life, as the star will burn out before such life emerges (except for the case of M dwarf stars that last 1 trillion years), leading therefore to the conclusion that it is a far less probable event than the development of multicellular life and simple life must be fairly more common throughout the Universe. About the theories of origin of life, *Picture 5* shows a good schematic exemplification, depending on whether life originated independently on a world or was carried to that world. As we can see, the organic terrestrial origin leads for now to a more complete vision about the development of life — and could apply to suitable exoplanets as well — but also possible panspermia schemes may be relevant to exoplanets.

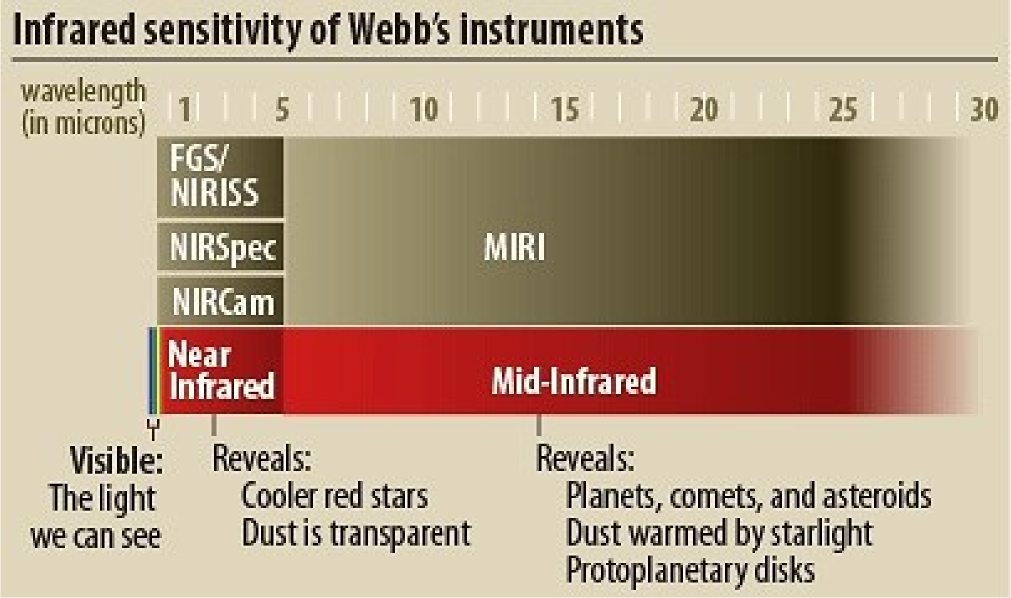


Picture 5 — Theories for the origin of life on Earth as categorized by Davis and McKay intended for Mars but applicable to the origin of life on exoplanets.

Napier WM (2004) has proposed that life could be carried on dust between stars and others have suggested rocks could travel between star systems [Adams FC, Spergel DN, 2005]: if such dust grains or rocks were incorporated into the preplanetary nebula, then every planet and moon that formed would be infected with life. It is evident that external conditions are fundamental in increasing the possibilities for life to develop, due to the fact that living organisms are open systems — they exchange both energy and matter — and as the Bauer principle (1935) tells in its full form "The living and only the living systems are never in equilibrium, and, on the debit of their free energy, they continuously invest work against the realization of the equilibrium which should occur within the given outer conditions on the basis of the physical and chemical laws." If we consider this statement, the origin of extra-terrestrial life, as well as life on Earth, cannot be a totally random event, compared to the roll of the dice: there are few starting conditions or constrains, given precisely by the physical and chemical laws, that result in different probabilities and rates for a given event to happen. The exact outcome is not predictable, but, as Darwin did when he predicted the existence of a moth knowing only the pollinator and plant co-evolutionary relationship, we can predict to a certain length doing what is called an "inference to the best explanation", without going from examples already examined to examples not examined, but from clues to plausible conclusions. A helpful clue in our prediction can be, for example, the existence of terrestrial organisms which live in extreme conditions: extremophiles can be perhaps a good study model of extra-terrestrial life forms because of the extreme biological niches they occupy; even the peculiar microscopic eight-legged animals called *Tardigrades*, observed in all kinds of environments, from the deep sea to sand dunes, may help us thanks to their resiliency — they can go up to 30 years without food or water, live in temperatures from −272.8 °C [Becquerel, 1950] to about 150 °C (up to 15 min) [Rahm, 1923, 1924, 1926], at pressures six times that of the ocean's deepest trenches, and in the vacuum of space — being good candidates for exoplanets' environments. It looks like we live in a Universe characterized by all the conditions to possibly support life as we know it: maybe the latter is the result of a contingency event and if we replay the "tape of life" from a different or the same starting point, the result would be an evolutionary menagerie bearing biological forms markedly different from the present ones or even no living organisms at all. At the moment questions are definitely prevailing over the answers, but thanks to the increasingly powerful technological equipment available, as those of which I will speak below, perhaps we will soon have a clearer vision of life and its presence in the Universe.

5. Future prospects

Two of the promising projects for life research beyond the Solar System are actually the James Webb Space Telescope (JWST) and upcoming extremely large ground-based telescopes (ELTs). Webb is NASA's largest and most powerful space science telescope so far, launched on 25 December 2021 and orbiting the Sun around the second Lagrange point (L2). It is designed primarily for near-infrared astronomy, but can also see orange and red visible light, as well as the mid-infrared region, thanks to its four science instruments: Near-Infrared Camera (NIRCam), Near-Infrared Spectrograph (NIRSpec), Mid-Infrared Instrument (MIRI), and Near-Infrared Imager and Slitless Spectrograph (NIRISS) with the Fine Guidance Sensor (FGS). It can detect objects up to 100 times fainter than its predecessor Hubble can and visible light emitted by the very first luminous objects that has been stretched or "redshifted" by the universe's continual expansion and arrives today as infrared light. Scientists will use Webb to study planets and other bodies in our solar system to determine their origin and evolution and compare them with exoplanets through transit studies; it will also observe exoplanets located in their stars’ habitable zones, trying to characterize for example the habitable zone of M dwarf planets and their atmospheric composition.



Picture 6 — Overview of JWST’s instruments wavelength coverage. The MIRI is both a spectrometer and an imager: it contains two apertures that can be pointed at an object in space to record both its image and spectrum. An aperture is an opening through which light travels. The MIRI is basically two instruments in one, so it has "two faces." MIRI records light with wavelength in the range of 5 to 28 microns. ***Credit:*** *NASA*

The ELTs are ground-based astronomical observatories featuring an optical telescope, capable of detecting through the Earth’s atmosphere optical wavelengths including ultraviolet (UV), visible, and near infrared wavelength, planned to increase the chance of finding Earth-like planets around other stars. One example is the upcoming ESO’s (European Southern Observatory) Extremely Large Telescope, or ELT for short, a revolutionary telescope that will have a 39-metre main mirror and will be the largest visible and infrared light telescope in the world. In addition it will be equipped with a line-up of advanced instruments, designed to cover a wide range of scientific possibilities and it will be controlled in real time by a system of high-precision sensors that provide constant optical alignment. Thanks to this, the observatory will be able to collect 15 times more light than the largest operating optical telescopes, tracking down Earth-like planets around other stars, and could become the first telescope to find evidence of life outside of our Solar System.

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