Abiotic synthesis of potential biosignatures on terrestrial planets

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Life away from Earth

The search for signs of life on different planets has been one of our most fascinating endeavors ever since the moon landing. From rovers on the frozen and barren landscape of Mars, Venusian landers gathering data just hours at a time due to the extreme pressure, heat and acidity of the planet, to probes scanning surfaces of Jovian moons or gathering samples of asteroids to bring back home. There has been no shortage of effort in trying to find signs of life directly. Back on Earth however, we have been utilizing telescopes either ground based, or in space like the James Webb Space Telescope to analyze the spectrum of light refracting off planets' atmospheres [1]. By analyzing the data, we can indirectly understand the composition of extra-terrestrial atmospheres, including exoplanets light-years away. By understanding the atmospheric composition, we often find gases otherwise thought to only have biological sources here on earth, thus raising the question of a possible sign of life [2].

What is a biosignature?

Life uses thousands of volatile molecules that could contribute toward a biosphere and its associated atmosphere. Some of these volatiles may accumulate in a planetary atmosphere and be remotely detectable; these are commonly called "biosignature gases." [3] Gases such as methane, phosphine, ammonia, ozone and water vapour itself, could hint at possible signs of life.

Methane (CH_4) could form by carbon dioxide reacting with acidic minerals in Martian regolith. In situ measurements of CH_4 on Mars by the Curiosity rover reported significant variations in its concentration at the Gale Crater, a background of ~0.7 parts per billion (ppb) has been measured, with tenfold spikes detected on four occasions across a period of two months [4].

Recent observations of Venus using ground-based telescopes have detected a spectral feature consistent with phosphine gas (PH_3), which is considered a possible biosignature on terrestrial planets [5]. Currently there is no known abiotic process capable of producing PH_3, which contributes to the biosignature hypothesis. The origin of PH_3 could be from acidic dust reacting in Venus' upper atmosphere with the help of UV solar radiation [6].

Ammonia (NH_3) is an ideal nitrogen source for life on Earth since it can be integrated into various amino acids and other organic molecules without life having to break the strong N_2 triple bond. NH_3 sources on Earth are few and either anthropogenic or biological, with limited abiotic sources. In contrast, it also has many destruction pathways. [7] As such, NH_3 needs to be constantly produced by a reliable source, such as life, in order to have concentrations high enough to be detected remotely.

Methanogenesis

Methanogenesis is an ancient form of anaerobic microbial metabolism that produces CH_4 as a waste product, most commonly by either respiring CO_2 as a terminal electron acceptor or disproportionating acetate to CH_4 and CO_2. These reactions can be written as follows:

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

$$CH_3COOH \rightarrow CH_4 + CO_2$$

where H_2 is hydrogen gas and CH_3COOH is acetic acid—a decay product from fermentation of organic matter. [2]

To explore the possibility of it being a biosignature we must prove it cannot be formed inorganically. Since the detection of CH_4 on Mars in 2012, there have been numerous experiments to discover and prove an abiotic process of CH_4 formation, the most promising of which turned out to be photochemical. The photocatalytic reduction of CO_2 to CH_4 may have strong implications for the origin of CH_4 on Mars. Martian regolith, which covers the surface of Mars, contains approximately 1% titanium dioxide (TiO_2) which is a well-known photocatalyst. [5]

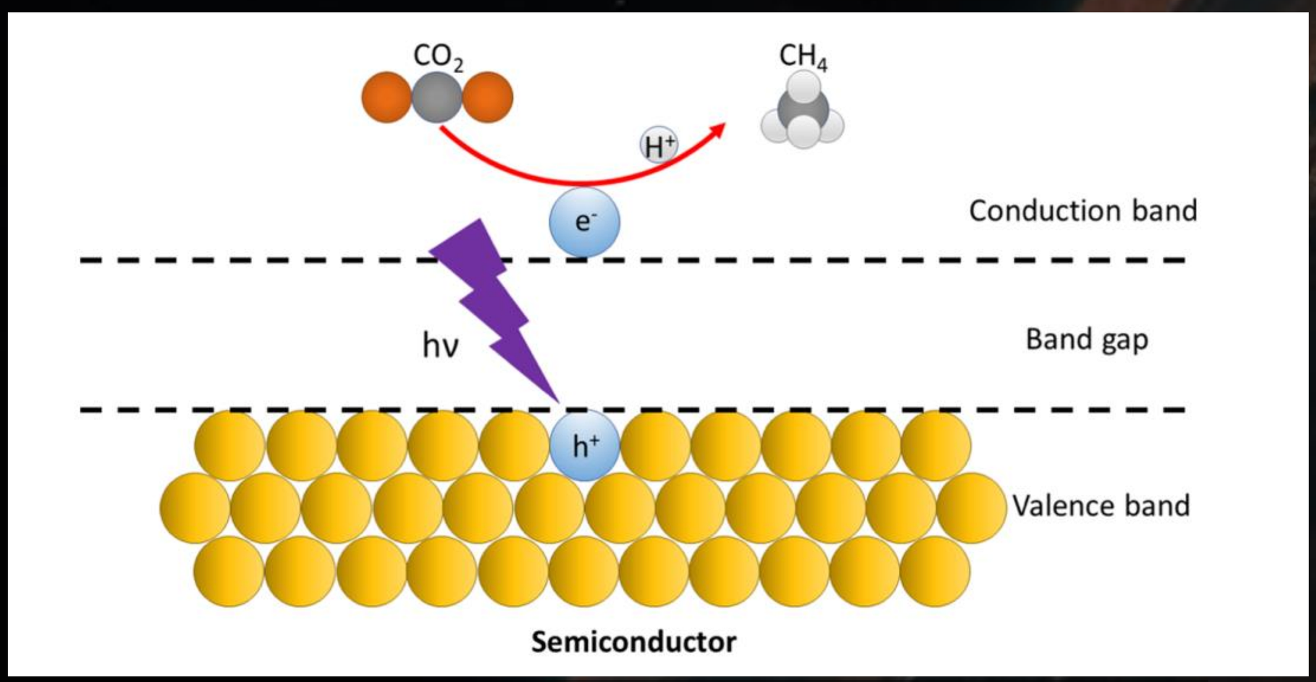

Fig.1: Schematic representation of several processes related to photocatalytic CO_2 reduction. [8]

Methods

Our methods are a continuation of the experimental process created by Civiš and Knížek [4]. Thanks to research published by the Venera team [11], and more recently by M. Gilmore and her team [12], we have created a list of minerals that could be on the surface of Venus and Mars. It included pyrite (FeS_2), anatase (TiO_2), iron oxide (FeO), hydroxyapatite ($Ca_5(PO_4)_3(OH)$) and others. Sample preparation [9]:

- Custom made, glass cuvette [Fig.2]
- Filling cuvette with 0.5 grams of mineral catalyst
- Vacuum dry sample
- Saturation with 30 Torr of HCl vapour and 30 Torr of CO_2 Gas
- Cuvette is sealed to prevent external contamination [Fig.3]

Before irradiating the samples with UV light, we measured the gas composition using a Bruker IFS 125 HR spectrometer (Bruker Optics) equipped with a KBr beam splitter and a nitrogen-cooled InSb detector over the spectral range of 1,800 to 6,000 cm^{-1} at regular intervals , after which we inserted the cuvettes into a UV reactor chamber using a narrow band 365 nm lamp (Hönle UV Technology), and we continued to measure the composition at regular intervals (days/weeks). [4]

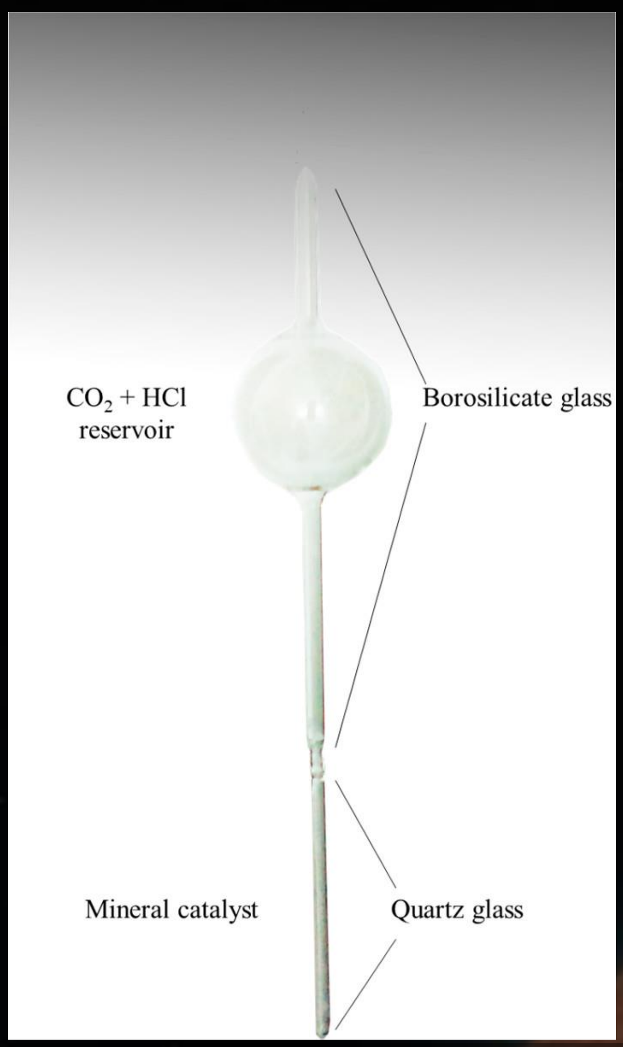

Fig.2: The sample cuvette containing a mineral catalyst. The whole system is sealed and any external contamination or side reaction with the ambient atmosphere after the sealing process is thus prevented. [9]

Fig.3: Finished cuvettes with samples containing hydroxyapatite, apatite, iron chloride, gypsum, halite and hedenbergite.

Results & discussion

Post analysis, we have discovered that anatase (TiO_2) is a viable catalyst for the photocatalytic reduction of CO_2 to CH_4 as seen on Fig.4. [9] Furthermore, we have detected a growing concentration of CH_4 in FeO, and simulated Martian and Lunar soils.

This means that CH_4 can be formed abiotically which would rule out its potential as a biosignature. It is possible there is a photochemical reaction similar to CH_4 formation that could also hint at a possible abiotic origin for PH_3.[6]

Currently PH_3 is a promising biosignature gas, as it has no known abiotic false positives on terrestrial planets from any source that could generate the high concentrations required for detection.[3] In Earth's atmosphere, phosphine is a trace gas. It is possible, however, that biospheres on other planets could accumulate significant detectable phosphine levels. [10]

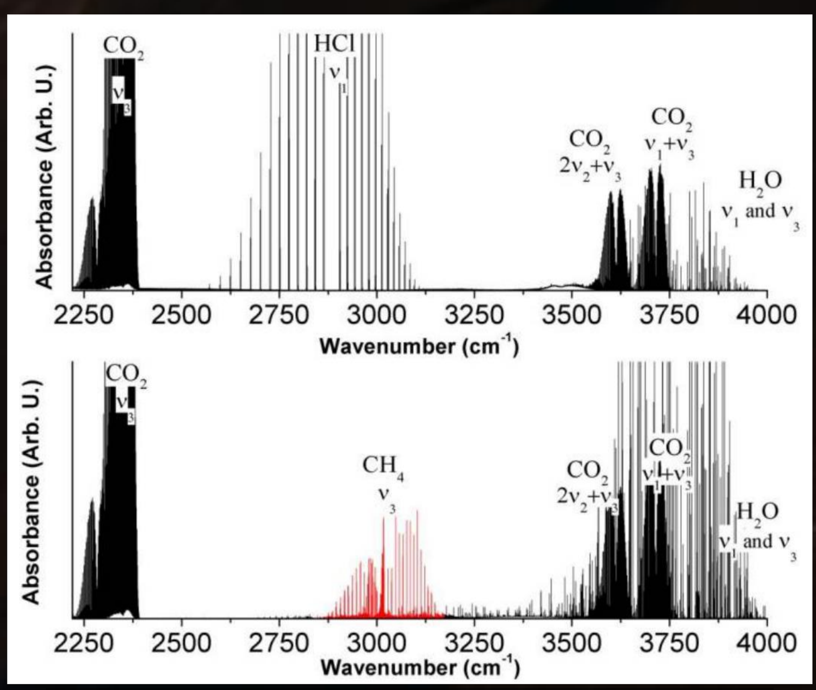

Fig.4: Gas phase results of the methanogenesis monitored by infrared spectroscopy. The spectrum before irradiation (top) shows the bands of CO_2, HCl and residual H_2O. The spectrum after 3500 h of UV irradiation (bottom) shows bands of CH_4, CO_2 and residual H_2O. HCl has been consumed in the reaction and is therefore not observed after irradiation. [9]

Conclusion

Biosignatures are a very important part of our search for extraterrestrial signs of life, and it is also equally important to not hasten our conclusions on whether something is or is not a definitive biosignature. As such we must thoroughly explore all our options to understand possible origins of gaseous biosignatures, to make sure they cannot be produced by some kind of abiotic process. Methane seems to be able to be produced in a laboratory without any organic processes. And so, its status as a biosignature comes into question. Phosphine on the other hand, has still numerous questions behind its status as a biosignature, and if it is possible to form without the help of organic life. Much work remains to be done.

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