CHEMICAL ABIOGENESIS: ARTISTIC CONCEPT TURNED INTO SCIENTIFIC REALITY

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Contents

- 1. Introduction
- 2. Panels
- 3. Circles
- 4. Conclusions

1. Introduction

The origin of life is an enigma fascinating philosophers and scientists for centuries. Surprisingly, one of the most prolific figures of these histories is an artist, Hieronymus Bosch, Dutch draughtsman and painter from the 15th century. His most prominent works are the triptych 'Garden of Earthly delights' and the painting 'The Seven deadly sins and the four last things.' This masterpiece of art touches the philosophical aspect of the origin of life. Therefore, in our paper, we describe this connection of Bosch's masterpiece with the scientific question of the origin of life and being inspired with this triptych, we also explain a unified picture of chemical evolution reconstructed based on our results published in world leading scientific journals.

The central motif of this study is a picture, which is a variation of the triptych 'Garden of Earthly delights' and the painting 'The Seven deadly sins and the four last things' by Hieronymus Bosch, both displayed in Museo del Prado in Madrid, Spain. For centuries, the triptych 'Garden of Earthly delights' has been firmly connected to the Christian narrative of the Creation of the world. The picture was created solely for the purpose of this work to show the connection of Bosch's work to the origin of life.

The key to understanding the triptych 'Garden of

Earthly delights' by Hieronymus Bosch are its outer wings. If the wings are shut, a magical azure globe is formed. The globe represents the moment and the scene of the Creation. The central motif of the whole triptych is the third day of the Creation of the world by God. On the third day, or rather on the third level of the creation, God created Earth. In the left corner of the left wing one can observe a small painting of God wearing a crown (similar to a papal tiara) and above the globe, which represents the new born Earth, are placed two inscriptions:

"Ipse dixit, et facta sunt: ipse mandāvit, et creāta sunt" which loosely translates as "For he spoke and it was done; he commanded, and it was created."

God from his 'void' issued a command – read the corresponding command line from the Testament – and immediately 'it' was done. Or else the God bid from above and 'it' was created (by itself) without the need for his further intervention, supervision or presence.

The speech of the triptych is clear – It suffices for God to issue a command for the creation to arise, begin and be as we see it. The iconography of the exterior speaks to us: 'God issued the first command and the power of creation was transferred to Earth.'

The Earth in its turn uses its newly acquired power to its full extent, as may be seen from the divisive shapes which arise from the grey shapeless primordial substance. From this moment onwards, the world is gifted with the power of self-evolution and development. This natural order of things, of change, self-creation, reshaping, creation and destruction, this order of Nature, is the main and only message of the triptych as well as the spiritual aspect of our contribution.

Just as Bosch with his awe-inspiring scenery of the world on the third day of its existence, our interest lies in the creation of this world at the time of the formation of the Solar system. This time was the time of the arising of the Sun, of the formation of planets and the beginnings of their evolution. This time is nowadays to some extent relived in the laboratory studies of the primordial conditions and experiments with the creation of our world as we know it. As a model for such laboratory studies, another work by Bosch, is used here. The said painting is The Seven Deadly Sins and the Four Last Things. In our allegory, each panel of the Seven sins central tableau does not depict our sins but is dedicated to a certain aspect of the laboratory process of the re-creation of the chemical evolution. The cycle represents the periodic transformations of the early Earth's atmosphere, composed of various ratios of CO₂, H₂O, N₂ and other gases. During the cycle, this primeval atmosphere is transformed to a mixture of reducing gases such as CH₄ or CO and as the cycle completes, it is again restored to its original state. Each cycle generates

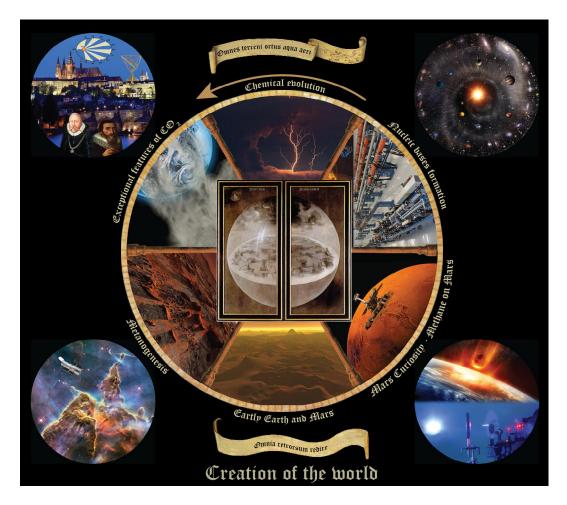


Fig. 1. A central figure inspired by the works 'Garden of Earthly delights' and 'Seven deadly sins and the four last things' by Hieronymus Bosch. The six panels show different steps in the proposed carbon cycle on the early Earth

organic molecules of varied composition and abundance and as the cycles go by, the organic matter accumulates. These organic molecules may have been destroyed many times during many such cycles. Eventually, however, some of them prevailed, hidden in some sheltered refuge, and evolved by chemical pathways into more complex systems, of the top of which, nowadays, stands the current fauna and flora on Earth, not excluding man.

It is an astounding idea to imagine, that such simple conditions may give rise to something as complex as the multicellular, self-standing, thinking and feeling creature, which is a human being. What is even more spectacular is the fact that such conditions can be found in many places in the Solar system and beyond, in the empty, vast and unexplored universe. The rise of a living structure is, in this context, only a matter of the sheer luck of the tiny and unimportant organic molecule in the never-ending cycles of creation and destruction.

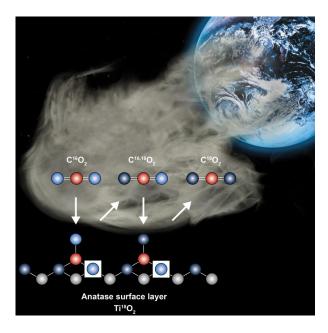
2. Panels

The following six sections contain a thorough description of the panels depicted in the main figure of the article.

2.1. Panel I: Exceptional features of CO2

In a series of our previous papers^{1–8},we report a wide range of experiments and theoretical studies devoted to the interaction of carbon dioxide with the anatase titania (TiO₂) surface. In previous publications, we have discovered that the solid anatase surface spontaneously exchanges oxygen atoms (labelled ¹⁶O, ¹⁷O and ¹⁸O) with gas phase CO₂. The reaction rate of this exchange strongly depends on the character and structure of the solid sample.

The amorphous non-crystalline nanoparticles of titania exhibit a much faster isotope exchange activity even at room temperature and without the presence of any visible or UV light. This is but one exceptional feature.

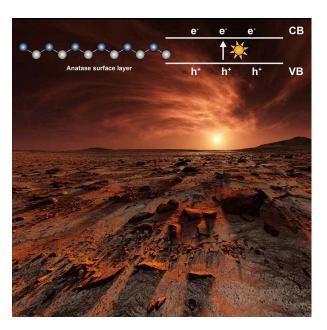


Panel 1. Oxygen atom exchange between gaseous carbon dioxide and oxygen containing minerals (here an example of the isotopic exchange between surface of ${\rm Ti}^{18}{\rm O}_2$ anatase and ${\rm C}^{16}{\rm O}_2)^{8.9}$

We have also detected gaseous products from the reaction of CO2 with the surfaces of natural minerals and synthetic samples containing TiO2: Natural anatase from the region Hordaland in Norway, natural rutile from the locality of Golčův Jeníkov in the Czech Republic, synthetic anatase (prepared by the hydrolysis of TiCl₄, see ref²), synthetic rutile, and clay containing a small amount of anatase (4-6%) deposited in the Sokolov Coal Basin in the Czech Republic. Due to the high reactivity (oxygen exchange) between such minerals and CO2, we decided also to study the surface activity of selected parent minerals, i.e., crushed basalt (Rožňava, Slovak Republic), montmorillonite (Sigma-Aldrich), natural calcite, siderite, and silica^{9,10}. Contrary to several studies that build on the idea that isotopic fractionation occurs between CO₂ vapour and CO₂ adsorbed on an oxygen substrate, our experiments confirmed the direct interaction of solid surface with CO2 gas and fast oxygen exchange activity.

2.2. Panel II: Early Earth and Mars

Several papers report on laboratory studies of carbon dioxide adsorption on oxygen-containing minerals, ¹¹ soil and carbonate minerals^{12,13}, different types of oxides^{14–16}, titanium dioxide, magnesium vanadate, ¹⁷ magnesium oxide, ¹⁸ aluminium oxide, ¹⁹ clays, ²⁰ nontronite, palagonite and basalts including different types of mineral substrates, which all to some extent mimic the planetary soil surface of Mars (Martian regolith simulations)^{21–24}. Laboratory measurements of CO₂ and H₂O adsorption indicate that



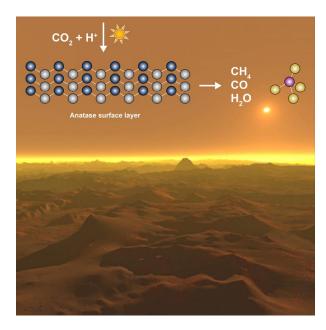
Panel 2. The surface of Mars is made primarily of regolith, which is composed mostly of iron oxides, but contains TiO_2 as well. Our laboratory experiments reveal the presence of the methanogenesis process, i.e. carbon dioxide conversion to CH_4 in the presence of a catalyst (TiO_2) in acidic environment [H^+ and H_2O] and driven by UV. TiO_2 acts as a semiconductor. Soft UV radiation is able to excite an electron from the valence band to the conduction band. The electron then migrates to the surface of the catalyst, where it reacts with the CO_2 , thus initiating a reaction cascade leading to methane, CO and additional hydrocarbon molecules $^{25-28}$

such minerals or rocks exhibit a high efficiency for storing large amounts of adsorbed gas.

2.3. Panel III: Mars Curiosity - Methane on Mars

The environmental conditions that once prevailed on Mars may have been suitable to host prebiotic activity and the emergence of life before the planet lost the intrinsic magnetic field that shielded it from energetic solar particles and cosmic rays, ca. 3.5 billion years ago. Mineralogical or organic evidence of these evolutions could be preserved at present in the Martian regolith and subsurface because of the limited tectonic activity of the planet through geological time.

The Curiosity rover recently detected a background of 0.7 ppb and spikes of 7 ppb of methane on Mars. This in situ measurement reorients our understanding of the Martian environment and its potential for life, as the current theories do not entail any geological source or sink of methane that varies sub-annually. In particular, the 10-fold elevation during the southern winter indicates episodic sources of methane that are yet to be discovered. More recently Curiosity rover of the MSL mission confirmed the



Panel 3. Both Mars and the early Earth could have at the beginning of our Solar formation sustained similar chemical compositions in which photochemistry and catalysis on minerals with various compositions could lead to the formation of simple hydrocarbons ^{14,20–24,29–31}

presence of oxychlorine compounds in the regolith of Mars and detected traces of indigenous organic molecules. Good knowledge of the reactivity of the Martian regolith is essential to understand the possible transformations and ultimately the origin of organic molecules.

2.4. Panel IV: Methanogenesis

The presence of methane on Mars was recently supposedly explained²⁹ by the following three testable hypotheses. The first scenario is that the regolith in Gale Crater adsorbs methane when dry and releases this methane upon deliquescence. The second scenario is that microorganisms convert organic matter in the soil to methane when they are in liquid solutions. This scenario entails extant life on Mars. The third scenario is that deep subsurface aquifers produce bursts of methane. Here we add a fourth hypothesis for the methane presence.

In 1979, Inoue et al.³⁰ first succeeded in direct photocatalytic reduction of CO₂ to methane on semiconductor surface upon illumination with UV light. Although this was done in aqueous solution, it launched a whole myriad of experiments concerning the photocatalytic reduction of CO₂ in various environments. The aim of most of those studies was to discover a way to harvest solar power.

The primary role of the semiconductor in photocatalysis is to absorb an incident photon, generate an electronhole pair, and facilitate its separation and transport.

The transfer of an electron to the adsorbed molecule initiates a cascade of chemical reactions which eventually determine the outcome and the efficiency of the photocatalytic process.

Recently published studies^{32,33} related to application of semiconductors (anatase TiO₂ or In-doped TiO₂ and montmorillonite modified TiO₂ nanocomposites) indicate considerable improvement in CO₂ reduction and the enhancement of the photocatalytic process. The photochemical reaction pathway from CO₂ to methane involves several reaction steps producing both stable and unstable molecular intermediates.

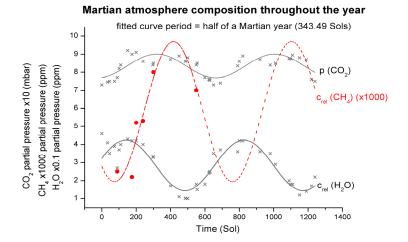


Fig. 2. Seasonal variation of atmospheric pressure: CO_2 content (red), H_2O content (black) and CH_4 content (blue). Data points have been scaled to allow for visual comparison of their fits. The data were obtained by the NASA Mars Curiosity Rover (2013/2014) and the OMEGA instrument aboard the Mars Express. Sinusoid curves in the plot represent only trends in the data^{50,52}

The creation of methane from carbon dioxide has been shown to work to a certain extent in solid-gas, liquid-gas, and solid-gas interfaces³⁴. As the source of energy for the process, for it is and endergonic process, ultraviolet light or visible light has been used.

So far, three plausible reaction mechanisms have been proposed though none have been definitely proven yet. They are called the formaldehyde pathway³⁵, carbine pathway²⁵, and glyoxal pathway³⁶. All three of them yield various product mixtures, but all of them yield methane as the main product. All those pathways require for their proper work a catalyst in the form of a semiconductor.

Mars could be a planetary "photoreactor", which decomposes carboxylated feedstock molecules producing methane (Shkrob et al.²⁶), or rather, it could be a "photosynthetic" planet, where methane is photosynthesized from carbon dioxide over catalytic surfaces (Civiš, Ferus et al.²⁸ Shkrob et al.³⁶).

The Mars atmosphere represents a carbon dioxide rich environment similar to the early Earth's. The methane production is influenced by the amount of adsorbed water and adsorbed carbon dioxide on photocatalytic surfaces of mineral catalysts in combination with sufficient insolation. Mars is not currently shielded against UV radiation from the Sun. Such a planet can be used as a model for the study of the pure photochemistry in planetary atmospheres in contact with large, mineral rich surfaces. The abiotic synthesis of methane as a reducing gas in a natural carbon dioxide rich atmosphere is also highly relevant to studies

of Earth and Mars for early stages of atmospheric evolution. Both planets contained water as a source of hydrogen, and they were exposed to a significant UV flux³⁷. Even though their levels are debated, according to a comprehensive study by Chyba and Sagan³⁸, energy dissipation from UV irradiation on the early Earth might have been two orders of magnitude more powerful as an energy source than impact shock waves and four orders of magnitude more powerful than electric discharges.

Methane on Mars shows seasonal variation. The effect has been observed by the Curiosity rover. We propose that this variation can be explained by the UV-induced photocatalytic reduction of CO₂ to methane.

2.5. Panel V: Nucleic acid bases formation

A two-step scenario of methane synthesis and the subsequent origin of simple biomolecules on terrestrial planets (e.g. Mars, early Earth) has been proposed. The whole mechanism involves continuous photocatalytic (UV-induced), mineral-mediated abiotic formation of CH₄ followed by an extra-terrestrial body-induced impact formation of simple organic molecules, later transformed into biomolecules. In our experiments, an equimolar mixture of reducing gases CH₄ and CO was produced from CO₂ over acidic mineral surfaces upon 365 nm UV irradiation. In order to sum up the plausibility and relevance of the mechanism, we determined its overall effective rate constants, external quantum efficiencies and effectiveness. This first



Panel 4. At the moment, the Curiosity Rover roams the plains of the Gale Crater of Mars. So far, the rover has detected all our reaction participants: methane, water and carbon dioxide^{39–41}



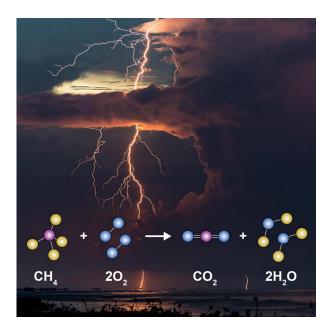
Panel 5. Prague Asterix Laser Systém (PALS) is a terrawatt iodine laser, which was used to simulate high-energy density processes. The laser shots simulated impacts of extra-terrestrial bodies into the early Earth's atmosphere simulant (Late Heavy Bombardment period). During this process, the formation of organic molecules (as complex as nucleic acid bases) from simple precursors (H₂O, CO₂, CH₄, CO, N₂) was discovered^{38,42-45}

step, photocatalytic reduction of carbon dioxide on the ubiquitous montmorillonite and TiO2, possibly explains the continual formation of reduced gases in neutral atmospheres. Such process balances various sinks of reducing gases in planetary atmospheres and possibly explains the presence, origin and dynamical variation, of methane in the atmosphere of Mars. The formation of reduced gases is also assumed to have occurred on early Earth, Mars, possibly Titan (Saturn's moon) and also has implications for Mars now. The second part of this study is focused on the transformation of planetary atmospheres by impact events during early stages of orbital trajectories evolution. Shock waves produced in the atmosphere of CH₄ and CO resulting from photochemical transformation have been simulated using terawatt high power hall laser PALS. In the reprocessed mixtures, glycine and RNA canonical nucleobases were found^{42–45}. Therefore these processes provide an explanation for the creation of reduced gases and the subsequent formation of simple biomolecules from neutral CO₂containing atmospheres of e.g. early Earth, possibly Mars and other terrestrial planets. The proposed mechanism is, as a source of organics, complementary to meteoritic flux on planets or the potential hydrothermal formation on Earth. The mechanism also suggests an explanation of the CH₄ cycle currently occurring on Mars.

2.6. Panel VI: Chemical evolution

This following section is also part of the main text and is here repeated to keep the logical flow in the supplementary information.

The chemical evolution of the early Earth and other terrestrial planets is a longstanding enigma which, among others, involves the uncertainty of the early chemical atmospheric composition and the origin of biomolecules. Many questions are still being raised regarding the sources of energy³⁸, the starting compounds^{46–48} and the physical³¹ and chemical conditions⁴⁹ of the processes related to the formation of the first biomolecules and their polymers (likely a molecule of RNA⁵⁰ ca. 4.1 Myr ago)⁵¹. The primordial atmosphere consisted primarily of carbon dioxide, nitrogen, methane, water vapour, hydrogen sulphide, hydrogen cyanide, ammonia, and carbon monoxide. Although its precise composition is unknown, in 1953, Harold Urey and Stanley Miller at the University of Chicago chose a plausible mixture of molecular hydrogen, water vapour, methane and ammonia as the basis for their classical experiments on the Earth's prebiotic chemistry. As energy sources they used electric discharges to simulate lightning and UV light as a proxy for solar radiation. After circulating the mixture for several days in a closed system equipped with a cooling trap, they detected many of the amino acids found in the proteins of all living organisms. However, Miller and Urey found no signs of the basic subunits of RNA (ribonucleic acid), which is now thought to have predated the hereditary material DNA as a repository and propagator of genetic information. We have now repeated and extended the classical Miller-Urey strategy



Panel 6. Earth, as well as other bodies, experience frequent lightnings and extraplanetary objects impacts. At these conditions, the majority of impacted organic matter is burned to H₂O and CO₂. At the early stages on Earth, when the atmosphere was oxygen-free, the burning was not possible and hydrocarbons had higher chances of survival after each impact

by adding a further source of energy to the set-up. Their results show that, under these conditions, all four of the canonical nucleobases can be found after irradiation by a high power Prague Asterix Laser System.

The new experiments thus take into account the socalled Late heavy bombardment (LHB) between 4.0 and 3.8 billion years ago. During this period, the Earth experienced a marked increase in the rate of asteroid and cometary impacts, which could have contributed to the synthesis of the building blocks of life. The results obtained by Civiš et al.⁵² indeed point to a critical role of high energy inputs in prebiotic chemistry. For only the combination of highenergy laser light and electrical discharges leads to the formation of hydrogen cyanide (HCN) and formamide (HCONH₂), whose dissociation by the shock wave promotes the synthesis of nucleobases.

The last panel is the way for synthesis of large molecules as well as their destruction by the high energy density events such as an asteroid impact, lightning, volcano eruptions, etc.

Thus our scenario regards endogenous synthesis, which begins with the evolution of an atmosphere plausible for the synthesis of biomolecules and ends with their production in shock wave chemistry, as a highly possible chain of events at the beginning of life on Earth and elsewhere.

Earth supports the idea that photocatalytic reduction has probably occurred both on early Earth, occurs on present-day Mars and possibly other terrestrial exoplanets throughout space.

Previous analyses considered only that methane and ammonia would be rapidly photolysed by solar UV on prebiotic Earth and therefore the atmosphere would be at least neutral if not oxidized. It can be expected that any carbon dioxide rich atmosphere can be at least partially and locally converted to a mixture of methane upon UV light irradiation in the presence of catalytic minerals.

The cycle repeats, methane is transferred into parent molecules or burned into carbon dioxide. The whole cycle is thus complete and begins anew.

3. Circles

The original work of Hieronymus Bosch contains four circles in the corners. Adhering to this fact, we created four circles and set them to the respective corners of our collage. The circles are shown and described in detail below

Mystic Mountain is a turbulent star-forming region of three light-years tall inside the Carina Nebula (NGC 3372), located in the Carina–Sagittarius Arm of our Milky Way, roughly 7,500 light-years from Earth in the southern constellation of Carina. From the outside of this pillar of thick gas and dust, material is being eroded by fierce winds of energetic particles and intense radiation from

super-hot newborn stars. From the inside the pillar is also being pushed apart, as infant stars buried inside it fire off jets of hot ionized gas that can be seen streaming from towering peaks. The denser parts of the pillar are resisting being eroded by radiation (Image Credit: NASA, ESA, M. Livio and the Hubble 20th Anniversary Team (STScI).

4. Conclusion

The main message hidden in the work of Hieronymus Bosch is that God may not have created the world as is presented by the church, but that He created a primordial soup and gave the nature the power to evolve itself. We took this message and transformed it into a scientific theory which states that there existed a carbon cycle in nature which may significantly govern the creation of biomolecules under early terrestrial planets and exoplanets conditions, even on the early Earth. This cycle proposes a photocatalytic reduction of CO2 to CH4, its subsequent reprocessing by high energy chemistry, the creation of biomolecules and last, their destruction back to CO2. This cycle may have stood at the rise of life on our planet and contains the latest scientific results. The idea of a set of initial conditions and spontaneous evolution of the living, however, is more than 400 years old.



Circle 1. Tycho de Brahe and Johannes Kepler, two stargazers and astronomers spent parts of their careers at the court of Rudolph II in the 17th century in Prague. Tycho Brahe performed precise astronomic measurements and Johannes Kepler, using Brahe's data, derived his law of planetary motion



Circle 2. A giant breakthrough in astronomic observation capacities and our understanding of the Universe was achieved with the launch of the Hubble Space Telescope, named after the American astronomer, Edwin Hubble



Circle 3. Late heavy bombardment was an important era on the life of the Earth. This era coincides with the first evidence of the existence of life as well. Craters formed during this era can be observed on the surface of the Moon to this day. Nowadays, we try to simulate such processes in the laboratory using high-power laser facilities⁵³

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http://www.booktryst.com/2011/12/tycho-brahes-sculpture-garden-of.html

Image courtesy of Bruun Rasmussen Auctions of Denmark.



Circle 4. A contemporary view of the Universe and its expansion. We look inside into an expanding Universe at whose beginning, 13.8 Gya, lies the Big Bang. A visual history of the expanding Universe includes the hot, dense state known as the Big Bang and the growth and formation of structure subsequently. But quantitatively knowing what the expansion rate is (and was) in the present (and past) is vital to understanding our cosmic history and future

http://www.polaris.iastate.edu/EveningStar/Unit2/unit2 sub3.htm

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S. Civiš^a, A. Knížek^{a,b}, and P. Civiš^c (^a J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, Prague, ^b Charles University in Prague, Faculty of Science, Department of Physical and Macromolecular Chemistry, Prague, ^c Laboratory Imaging s.r.o., Prague, Czech Republic): Chemical Abiogenesis: Artistic Concept Turned into Scientific Reality

Scientists have been striving to find a theory which would describe the origin of life on Earth for centuries, so far without success. To succeed in solving these problems, one has to broaden their view, to approach the scientific subject from a philosophical standpoint, to set firmly a framework of the research and to define its borders. In order to asses the philosophical contribution of the work, one need not resort to new ideas only, because many ideas have already been expressed in the past. Such concepts are nowadays often remembered only in History of arts and Philosophy classes. In our recent article published in Nature Astronomy, we have presented a very complex model

for the creation of methane and its reprocessing to more complex organic molecules including nucleic acid bases from simple gaseous precursors. The purpose of this work is to show the repeating cycle of the creation of complex molecules from $\rm CO_2$ and their subsequent destruction back to their basic parent molecules in the light of the 500-year-old idea of the creation of life by Hieronymus Bosch.

Keywords: Hieronymus Bosch, photocatalytic reduction, origin of life, carbon cycle

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