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Origin of Prebiotic Organics and Oxygen on Earth. A case for the Pre-Photosynthetic and Carbonyl Sulfide Catalyzed Reduction of Carbon Dioxide by Water, Methane, Ammonia and Hydrogen sulfide.

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Abstract:

It is estimated that the earth is about 4.5 billion years old and it is now believed that by 4.3 billion years ago, earth may have developed physico-chemical conditions suitable to support life, when its atmosphere consisted largely of water (H2O) vapor, nitrogen (N2), and carbon dioxide (CO2) with much smaller amounts of methane (CH4), carbon monoxide (CO), ammonia (NH3), hydrogen (H2), hydrogen sulfide (H2S) and other sulfur compounds like carbonyl sulfide (COS), and the earth had a reducing atmosphere without any free oxygen. The oldest known fossil records show that life came into being about 3.7 billion years ago. It is also believed that life proliferated and evolved in largest scale only after first aoxygenic photosynthesis by viruses and then oxygenic photosynthesis by plants produced large scale biochemocules and molecular oxygen (O2). But this necessitated a period of the evolution of primitive life forms like reprocing cells, which required enormous carbon-based prebiotic chemicals mediated by dialectical chance and necessity as is the case with later biological evolution. This had to involve the production within about a billion years, of specific prebiotic ingradients in enough quantities, in sufficient concentration in a limited, dynamic and physicochemically suitable localized evironment. But only the few primitive chemical compounds mentioned above, most abundent being H2O and CO2 , laready existing on earth, potentially could be source of enormous amount and variety of prebiotic chemicals necessary for the formation the first reproducing cell. Based on the SET (Selective Energy Transfer Theory) developed by one of us (RL), we have reason to speculate for the first time that the carbonyl sulphide (COS) catalyzed reduction of CO2 by H2O and by other less abundant molecules like CH4, NH3 and H2S was the decisive prerequisite for the formation of prebiotic chemical ingredients and for the chemical evolution of the first reproducing cell on Earth.

Keywords: Origin of Life, Prebiotic Chemicals, CO2 Reduction,

Introduction

How the first living and reproducing cells, the most complex but the most vulnerable and delicate system in the universe could arise on Earth, is still an enigma, even after impressive scientific and technological development of the last few thousand years and after the considerable extension of human knowledge from the macrocosm of the galaxies to the microcosm of the quantum world. In this work we will focus mainly on the prebiotic chemical evolution proceeding and on the way to cell formation.

Life is an on-going and enormously complex process on Earth. This fact teaches us the objective truth that life (including consciousness) is an intrinsic property of matter in motion, change, evolution, development etc., in this universe - *"an obligatory manifestation of the combinatorial property of matter"* as Christian de Duve [1] put it. This process can function within the tangible limits of catalytic, kinetic and thermodynamic parameters of chemistry and within a favourable environment that can sustain such a process. This means that the primitive processes that gave rise to the "first life" form may still be on going even now; to sustain

the chain of innumerable qualitative leaps that gave rise to the thinking brain of man, as the highest product of this process.

The traditional concept of the origin of life on earth was based on theological and some philosophical contention that all forms of life was created by God, perfect in themselves. In the 1930s Aleksandr Oparin [2] in his seminal book "Origin of Life" gave a summary of the historically developed concepts on this issue and at the same time laid the foundation for a scientific approach to the question of the origin of life, for the first time in history. Oparin described how even in the eighteenth and the nineteenth centuries the tenuously held mystical views of "vital force' or "spontaneous generation' of living being (at least of lower life forms) was refuted only after Louis Pasteur in 1862 through some brilliantly performed experiment demonstrated the utter impossibility of "spontaneous generation" of life forms. Toward the end of the 19th century, the famous. Swedish chemist Savente A. Arrhenius suggested that life on Earth arose from "panspermia," of microscopic spores that came from elsewhere in outer space. This idea, of course, avoids rather than solves the problem of the origin of life and is still pursued by some, even though it is an impossibility from the perspective of modern astrophysics.

Oparin in 1924 and later with J.B.S. Haldane, (prompted by Darwin's speculation of "warm little pond" and the dialectical views of Frederick Engels), in 1929 proposed that the first molecules constituting the earliest cells slowly self-organized from a primodial soup. This involved the prebiotic synthesis of organic molecules, polymer formation, molecular self-replication, self-assembly, the emergence of cell-membrane and above all catalysis which facilitated these processes. Many proposals have been made for different stages of the process; as this theory is called the **Oparin–Haldane hypothesis** [3]. It was only after Stanley L. Miller [4, 5] raised the hopes of understanding the origin of life when on 15 May, 1953, *Science* published his paper on the synthesis of amino acids under conditions that simulated primitive Earth's atmosphere. Miller had applied an electric discharge to a mixture of CH4, NH3, H2O, and H2—believed at the time to be the atmospheric composition of early Earth. Miller's experiments formed many many organic compounds including some primary aminoacids, the most vital component of life. This provided credibility and interest in the idea of "primordial soup" hypothesis.

Miller's success generated lots of interest in simulated and abiotic experiments for the formation of prebiotic chemical components and provided expectation for an understanding of the processes, by which starting from few simple chemical compunds large varieties of progressively complex and directed components could be formed leading to the formation of the first life forms [6]. It was even demonstrated that under laboratory condition the abiotically produced Miller-Urey mixture supports bacterial growth [7]. The "primordial soup" hypothesis believed that the organic molecules necessary for life have been created in the atmosphere of early Earth by such forces as lightning, electric discharges in the atmosphere, heat and ultraviolet energy from the sun, and also materials brought over by the meteorites. These molecules rained from atmosphere into the primitive oceans, where these went through further chemical evolution leading to the first life form. But it is now considered to be a highly unlikely scenario, because these chemicals would be too widely scattered around the surface of the earth and prone to decay to make chemical evolution viable. Also, Miller's experiments contained large excess of methane; which is not very likely to be the case in the primitive earth.

It is now the general concensus among the various researcher on the origin of life that the undersea hydrothermal vents are the locations where life evolved. The discovery of thermophilic organisms, extremophiles [8] in association with deep-sea hydrothermal systems in the late 1970s led to a new idea that life might have originated in hydrothermal vents on the primitive Earth. The advantage offered for such a scenario are many, such as a continuous flow of volcanic gases and mineral in localised environment at high temperature and pressure and in enough concentrations for further chemical reaction, along with potentially

catalytic minerals, the flow of volcanic gases creating a dynamic environment, protection from intense asteroid bombardment and UV radiation on the primitive earth that lacked ozone protection etc. Evidence that supports this scenario has been provided from various research fields since early 2000: a) geological [9]: providing evidence of 3.5-Gyr-old fossil records; b) biological: thermophilic microbial inhabitants of the seafloor populate the deepest branches of the universal phylogenetic tree and c) chemical: intense interest generated by the Miller experiment has led to multitude of claims based both on theoretical and experimental grounds that physical and chemical conditions characteristic of the deep-sea hydrothermal systems are favorable for abiotic synthesis of biochemically significant organic molecules [6]. Most submarine hydrothermal vents studied until the late 1990s are characterized by basalt-hosted Black Smoker sulfide structures that eject mineral-laden fluid and gas either as a warm (5–100°C), diffuse flow from seabed cracks or as plumes of superheated water (250–400°C) from chimney-like structures.

One thing that is not well understood so far, is how the vast amount of carbon-based prebiotic ingredients needed to drive the chemical evolutionary process forward, was formed? Such specific ingredients in sufficient quantifies and concentration were necessary before aoxygenic and oxygenic photosynthetic processes could set in; involving sophisticated cell formation. The biosphere is a closed and self-regulating system sustained by grand-scale cycles of energy and of materials—in particular, carbon, oxygen, nitrogen, certain minerals, and water. The fundamental recycling processes are photosynthesis, respiration, and the fixing of nitrogen by certain bacteria. The biosphere is virtually a closed system with regard to matter with minimal inputs from extraterrestrial sources. Regarding energy balance and the interplay of thermodynamic oxidation and reduction processes on earth, which are relevant to life forms, Nealson et al. [8], gave a remarkably exhaustive and detailed account showing that the earth is an open system, with photosynthesis capturing solar energy at a rate of around 130 terawatts per year [8] and still taking place to sustain the process. These authors also point out that for most of its history, the earth has not had an oxygen-rich atmosphere even though it has been teeming with life! Most life lives in the zone 200 meters below sea level and 6000 meters above sea level, which forms the biosphere on earth.

The question arises, how this enormous amount of prebiotic carbon-based coumponds essential for the chemical evolution arose, when most of the elements, (other than oxygen), like hydrogen, carbon, nitrogen sulfur and metals were in their relatively unreactive oxide form on primitve earth with only minor or trace quantities of reducing species like, H2, CH4, NH3, hydrogen cayanide (HCN), hydrogen sulfide (H2S), carbonyl sulfide (COS) etc., spewed out of the vocanoes and still do? Water vapour is consistently the most abundant volcanic gas, normally comprising more than 60% of total emissions. Carbon dioxide typically accounts for 10 to 40% of emissions [10]. Water of course, is the most abundent chemical relevant to life forms.

The prospect naturally arises that if carbon dioxide could somehow be reduced by water, under the condition of the hydrothermal vents, then this could provide huge quantities of prebiotic ingredients is a relatively short time. But so far, apparently not much thought and efforts, both theoretical or experimental was directted towards this issue. This is probably because carbon dioxide is considered to be very inert, like nitrogen and noble gases. Miller's historic experiments used large excess of methane gas – an unlikely natural scenario. From the 1950s, inspired by Miller's experiments, some chemists tried to simulate the synthesis of organic compounds under primitive earth conditions with high-energy radiation sources but had only had limited success. By irradiating CO2 solutions in water with a 60-inch cyclotron led only to formic acid, albeit in fairly high yields [5, 11]. There has been some recent reports about attempted catalytic photo-reduction of CO2 by H2O [13]

In this study, we show that carbonyl sulfide (COS) an ubiquitous minor component of the volcanic gases and also of the earth's atmosphere, could potentially catalyze the reduction of CO2 by H2O – the most abundent ingrdients in primitive earth. Strangely, CO2 and COS seems to be odd companions in the earth's atmosphere.

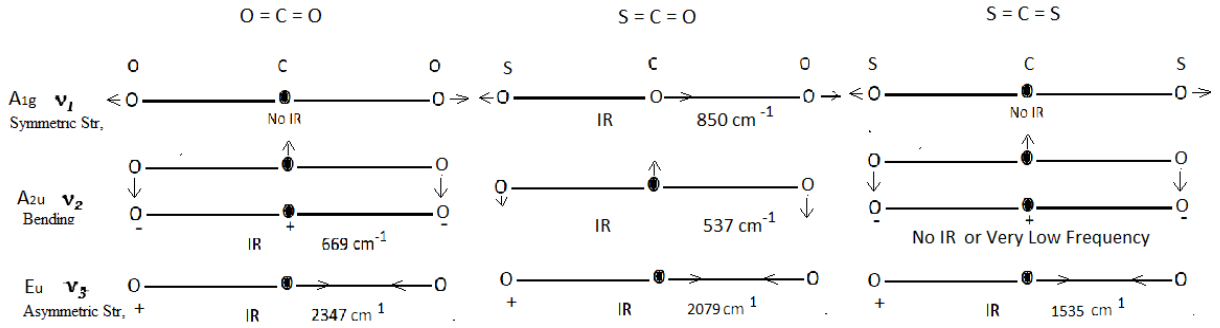
It was reported [12] that the observation-based COS record is most consistent with simulations of climate and the carbon cycle that assume large growth in terrestrial gross primary production (GPP)—the amount of carbon dioxide that is 'fixed' into organic material through the photosynthesis of land plants, during the twentieth century. We show that COS can potentially catalyze the reduction of CO2 by H2O and by the other reducing agents in the volcanic stream like NH3, CH4, H2S to form formaldehyde (CH2O), fomaldimine (CH2NH), ethylene (CH2=CH2) and thioformaldehyde (CH2S) respectively. The futher reactions, such as polymerization of these initial species, hydrolysis, inter-species reaction could lead to the availalibility of the large numbers and amount of prebiotic chemicals necessary for life and could even acts as supplements for nutrition for lower life forms as observed by Xie et al,. [7], even after the photosynthetic processes came into existence. This process may still continue as essential and a supplemenary source of prebiotic chemicals; at the present time!

CH2O and its analogs CH2NH, CH2=CH2 and CH2S are unstable as monomers, but are stabilized by polymerization and other chemical reactions to form possible precursors of biomolecules . All these monomers have also been detected in the interstellar and intergalactic space. It is interesting to note that formaldehyde and its trimeric version heterocyclic 1,3,5- Trioxane were the first polyatomic molecules to be detected in intergalactic space. Its sulfur anolog, the heterocyclic trimer of CH2S; 1,3,5- Trithiane was also detected in intergalactic space.

Results and Discussion

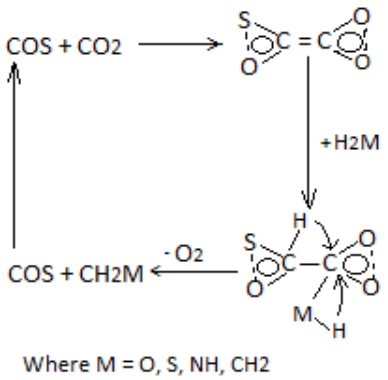
A Comparison of the Vibrational Spectra of CO2, COS and CS2 and the Peculiarity of Fermi Resonance in CO2 Vibrational Frequencies and their implications for its reduction.

CO2 and CS2 are linear and symmetric triatomic molecules. The symmetry group of both molecules is $D_{\infty h}$. COS is an asymetric intermediate between CO2 and CS2 with approximately similar symmetry properties and also similar vibrational modes. Fig. 1 shows the fundamental vibrational modes, in CO2, COS abd CS2. A group-theoretical analysis based on the approximation D_{4h} symmetry of CO2 and CS2 have been reported [17]. These authors have shown that CO2 and CS2 are similar in that they are linear and are symmetric about the carbon atom. Both molecules have three vibrational modes: (1) symmetric stretching, (2) bending, which is two-fold degenerate, and (3) asymmetric stretching. Mode 1 is Raman-active, modes 2 and 3 are IR-active. The sulfur-bearing molecule is expected to have lower vibrational frequencies and longer bonds. COS being similar and intermediate in chemical formula, is expected to have similar vibrational frequencies, with the only difference that, due to its polarity the symmetric stretch v_1 vibrational mode of COS is likely to be IR active.



The peculiarity of the CO2 vibrational modes, as shown in Ref. [17] is that the symmetric stretching mode and the second excited state of the bending mode of CO2 are nearly degenerate and hence shows Fermi resonance due to mixing of vibrational states. This shows the possibility that the bending mode of CO2 can be enhanced through resonance energy transfer by the SET mechanism to make the two oxygen atoms come

close together to form a pseudo-bond in an activated complex with COS, stabilzed through delocalization as shown in the following Scheme 1



Scheme 1

As shown in the Scheme 1 above, the addition of two hydrgen atoms-bearing molecules such as H2O across the >C=C< bond and the transfer of the two H atoms to the two-oxygen bearing C atom can lead to the elimination of O2 , the reduced carbon moiety CH2M (M = O, S, NH, CH2) and the release of COS for further possible catalytic action.

Table 1 : Fundamental IR Active Frequencies of Some Selected Linear Triatomoc Molecules

Molecule	υ_1	υ_2	υ_3	Remarks
O C O	Raman active	668.8	2347	Raman $\upsilon_{1\ 1295m,\ 1382S,\ Possible\ IR\ at\ 1329}$
S C O	859	527	2079	
S C S	Raman active	undetected	1535	Raman $\upsilon_{1\ 639.5vs,\ 780w}$
Cl C N	729	3987	2201	
Br C N	580	368	2187	
I C N	470	321	2158	
S C N^-	750	398	2066	
N N O	1285	589	2224	
H C N	2089	712	3312	
O C O^-			1665	^{12}C at 25^{O} C
O C O^-			1636	^{13}C at -190^{O} C
O CH O^-			1651	A bond angle of 127^{O} was calculated from ^{13}C isotopes

Data Sources:

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c. Hakura a. et al., "High Pressure Raman Study of Fermi Resionance Spectra in Gaseous Carbon Dioxide", (1990), J. Mol. Structure, 218, 297 – 302.

Table 1 shows the Raman and IR active bands in CO2, COS and CS2 and their corresponding vibrational modes. It is to be noted that the two atoms of the O2 molecule in the above scheme 1 has to come from the original CO2 species.; while in photosynthetic process both the oxygen atoms is known to come from the H2O molecule; as was demostrated [18] by using O^{18} enriched isotope. A similar investigation using O^{18} enriched CO2 can probably distinguish between COS catalyzed reduction of of CO2 from the photocatalytic reduction. Geochemical records of terrestrial oxides indicate that O_2 evolution must have taken place in the precursors to cyanobacteria before *ca.* 2.8 billion years ago and led to the accumulation of O_2 in the atmosphere [19, 20]. The creation of a photosynthetic apparatus capable of splitting water into O_2, protons, and electrons was the pivotal innovation in the evolution of life on Earth. Because aerobic photochemical metabolism generates 18 times more energy (ATP) per metabolic input (hexose sugar) than does anaerobic metabolism. The accumulation of O_2 in the atmosphere led to the biological innovation of aerobic respiration, which harnesses a more powerful metabolic energy source. This sequence of evolutionary steps enabled the emergence of complex, multicellular, energy-efficient, eukaryotic organisms. As the way it happened, by freeing photosynthesis from the availability of reduced chemical substances, the global production of organic carbon could be enormously increased. But never-the-less as Dismukes et al. [18] speculated and we assert, CO2 must have been the source of the O2 in conjuction with the COS catalyzed prebiotic organics formation long before the photocatalytic process came to play the more prominent role.

Conclusions

In conclusion, we can say more or less what Nealson et al., [8] wrote in the introduction of their article; i.e., the ideas expressed in this work *"may seem somewhat non-conformist: they are meant to stimulate thought and draw reactions rather than to be given truths"*. In this work as in the previous three publications [14-16] of the chemical origin of life on earth, we attempted to use indirect IR spectrocopy of the SET theory, unlike the various direct spectroscopiic investigations used by the astronomer to study and to understand remote and inaccessible regions of the world and to speculate about the processes going on there. Whether any insight gained through this investigation would bear fruits, only future can tell. We can only hope that this work might stimulate interest in some capable investigators to perform laboratory scale simulation of the COS catalyzed reduction of of CO2 by H2O under various conditions of high pressure and temperature and in conjuction of some possible solid catalysts. Any potential positive outcome may lead to the development of industrial processes to use the vast and cost free raw materials (CO2 and H2O) to convert them to useful and energy efficient organic products and at the same time greatly and efficiently reduce the atmospheric CO2, which has now become a great global concern for humanity.

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Conflicts of Interest

The authors declare that they have no conflict of interest.

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