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RESEARCH ARTICLE

The Role of Amines, Hydrogen Sulfide and Carbon Dioxide in the Formation of Prebiotic Macromolecules Surrounded by Complex Membranes.

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Abstract

Amphiphilic compounds are known to self-assemble into membranous structures when exposed to alternate dry and wet conditions. This paper presents a model of how such structures could form near hydrothermal vents while containing macromolecules such as amino acids. The formation of amino acids near deep ocean hydrothermal vents as precursors for the origins of life is problematic as amino acids degrade from thermal energy. In the model proposed here, amino acids would degrade into amines (near hydrothermal vents). Amines have an affinity to interact with carbon dioxide (CO2) and hydrogen sulfide (H2S), form weak heat-unstable salts, and then through exposure to thermal energy release the acid gases and regenerate back to amines. Amines carrying and releasing H2S and CO2 would help other macromolecules form along with amino acids within protected cell-like structures; the cyclical release and recapture of acid gases would subsequently help the amino acids form bonds; further thermal action would degrade some of the amines into polymers that provide more strength and rigidity to the membrane walls; and also enable escaping gases to form tubes within the surrounding membranes for inlet and outlet of chemicals. Consider that liquids and gases are undergoing thermal convection inside a porous medium, and the convecting liquids contain some amines. Consider now that an amine weak salt carrying H2S and another carrying CO2 is inside a vesicle that formed through self-assembly. As this vesicle moves around in the thermal convection cell it will come close to the heat source and release the H2S and CO2 inside the vesicle. As the vesicle moves away from the heat source, the gases would be reabsorbed into the amines. This process would create stability and a repeating set of reactions, reactants, and products forming and reforming – cyclical stability is a key criterion for more complex reactions to occur. Some of the amines present would reform into an amino acid (as occurs in industrial amine acid gas treatment systems)– this time within a protected structure. Having reformed within a protected structure an amino acid would survive and combine into peptides as opposed to being formed in free ocean water and being degraded from exposure to direct thermal energy from the hydrothermal vents. This model predicts the size of vesicles that could move about in a likely convection cell formed within typical porous solid structures found near hydrothermal vents – the prediction corresponds extremely well with the sizes of the very early forms of living cells.

Introduction:-

Amphiphilic compounds (containing polar and non-polar groups on the same molecule) are known to self-assemble into membranous structures that contain macromolecules such as amino acids. As pointed out by Deamer et al (2002) - "We cannot be certain about the relative amounts of endogenous synthesis and extraterrestrial delivery of organics, but it is likely that both sources played significant roles in the subsequent emergence of life by providing specific molecular species that were essential ingredients. Critical among these are amphiphilic compounds that have the capacity to self-assemble into more complex structures."

This paper builds on the iron-sulfur world model proposed by Woese and then amplified by several researchers (Woese, 1998, Woese, 2002). Russell and Martin (2007) have proposed that prebiotic chemical reactions involving iron and sulfur could have occurred inside porous mineral formations. Marshall (1994) showed that amino acids can form at conditions such as those at hydrothermal vents. Budin et al (2009) have shown that convection currents in a porous medium would have created vesicles and concentrated reactants. Russell and Hall (1997) and martin and Russell (2007) have also proposed that life emerged from iron monosulfide bubbles at a submarine hydrothermal redox and pH front. The ideas of Russell and Hall involve convection currents moving through a porous iron sulfide formation bringing needed chemicals at needed times. The model proposed here is very similar – except that in this model the iron sulfide bubble is a small fragment of the porous mineral formation that moves around and around in a convection cell made up of gases and liquids. It is not external convection that brings liquids in and out of a monosulfide bubble – the bubble moves with the convection liquids carrying the needed chemicals inside it. Although it may seem at first glance that conceptually whether the liquids move or the solid bubble moves is not very different – there are some key differences that help in the formation of complex macromolecules when the solid bubble moves, chief among which is stability and the formation of a repeating set of reactions.

There are some serious problems associated with the stability of amino acids at elevated temperatures and near hydrothermal vents. Miller and Lazcano (1995), for instance, have pointed out that for such reasons life may not have originated at elevated temperatures. The model proposed here overcomes the problems associated with the degradation of amino acids at elevated temperatures. The model is built on the fact that amino acids form near hydrothermal vents and then degrade to amines. Methyl amines will also form spontaneously and are known to be present inside archaeobaceria with higher concentrations found in organisms at greater depths Amines can withstand higher temperatures for much longer than amino acids. Amino acids would degrade at high temperatures within a few hours. Amines could last for hundreds of days at elevated temperatures. Eventually amines would degrade into polymers. If this degradation to polymers happens inside a vesicle, the polymers could form a skin that then would protect the amines inside the vesicle, and any amino acids that subsequently reform.

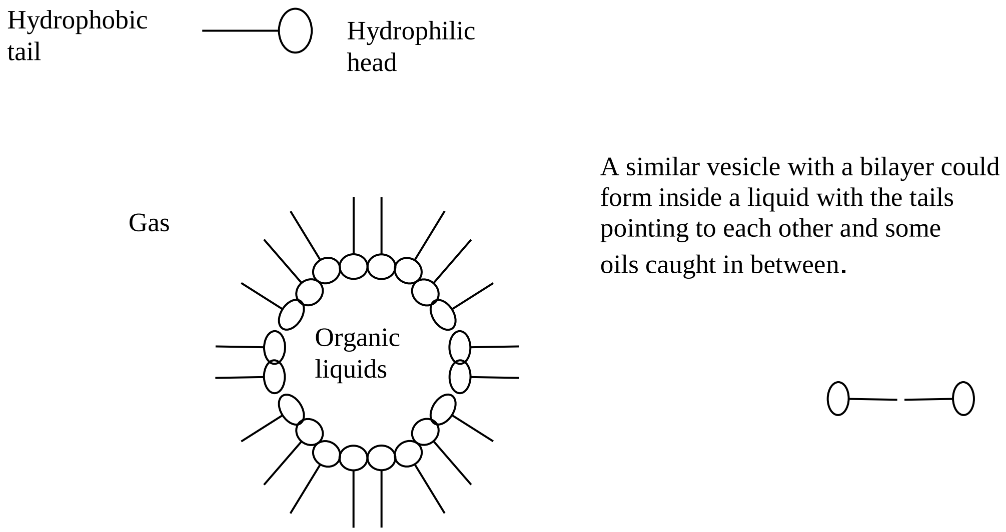
As described by Christian de Duve in "Life Evolving", stability is a key criterion for the growth of complexity in hydrocarbon molecules, leading to amino acids and the first basic chains of amino acids (De Duve, 2002). We seek the origins of life in prebiotic sets of chemical reactions that must also have evolved through natural selection – that is, there were natural advantages that led to certain reactions and structural forms occurring, leading to the stability and growth of certain chemical compositions and forms, and their replication.

The model presented here proposes that multiphase thermal convection cells (gas and liquid phases moving through a solid matrix) provided through recirculation the stability needed for certain chemical species to be continually brought into contact with needed catalysts and thermal energy sources. Alternating gas and liquid phase contact (wetting and drying) then created liquid-filled membrane sacs containing amino acids. The sacs continued to circulate and internally form more complex chains using a variety of bonds. These sacs then grew and divided into duplicate sacs. In the early stages of the formation of such sacs, macromolecules may have formed inside inorganic bubbles, such as iron sulfide bubbles small fragments of which were moving with the fluids – as in the ideas of Russell, Martin and Hall discussed earlier.

The model presented here also proposes that hydrogen sulfide (H2S), carbon dioxide (CO2) and amines interactions played a key role in this process. H2S and CO2 are readily absorbed into an amines and water solution in which weak salts are formed with the amines. These salts are heat regenerable. The salts will break down and release the absorbed H2S and CO2 gases when the solution comes into contact with a heat source. The model proposes that long-lived thermal convection cells formed within a porous and fissured media and continually carried H2S and CO2 in various forms around with the recirculating fluids through the absorption and thermal stripping of the gases. This allowed certain chemical compounds moving in liquid-filled sacs to take advantage of oxidized sulfur and the hydrogen ions available to reduce the sulfur and to gain the energy needed to form additional bonds, such as hydrocarbon and disulfide bonds.

Figure 1 shows the types of membranes that amphiphilic compounds could form. Within a gas, a monolayer could curl up on itself and form a vesicle containing organic liquids. Inside a liquid, a bilayer could also form a vesicle and enclose organic liquids. Both of these forms would in effect create a proto-cell structure. As mentioned previously, a solid iron sulfide porous fragment could also play such a role

This paper proposes a model in which such membranous structures could help amino acids form within the structures, then form bonds and turn into more complex compounds. Further, the model also shows how simpler membranous structures could become increasingly more complex with the formation of polymers and other compounds that could provide more strength and rigidity to the membranes, and also enable the formation of tubes within the membranes for inlet and outlet of chemicals.



A similar vesicle with a bilayer could form inside a liquid with the tails pointing to each other and some oils caught in between.

Fig. 1: Amphiphilic compounds forming vesicles in a gas or liquid phase (from Deamer et al (2002)

Thermal convection in porous and fissured media near a hydrothermal vent:-

Thermal convection in porous and fissured media is a well-studied subject. (Rajen, 1990) In the rock surrounding a deep ocean hydrothermal vent, it is possible that a system of fissures could be bounded by a less permeable porous matrix. The inside materials of a solid column formed by precipitation of gases and reactants at a hydrothermal vent will be of lower permeability than the outer edges of the column which will experience thermal stresses imposed by the ambient water around the vent and contain fissures. If such a column becomes unstable and falls onto its side, the situation shown in Figure 2 will result. The sediment on which the column lies will be of low permeability (by virtue of being packed by the water column above). Over this a solid column will lay with a zone containing fissures. Above this zone will be a layer of lower permeability. Even though the zones of lower permeability will allow some leakage of gases and liquids, they will bound a zone of higher permeability within which a recirculating cell of thermal convection will form. In this zone of recirculation, two phase thermal convection will occur, with gases moving in the center of the fissures, and liquids moving along the rock walls (see Figure 3). There will be alternate wetting and drying in these fissures and the spontaneous generation of membranous structures will occur as described in Figure 1.

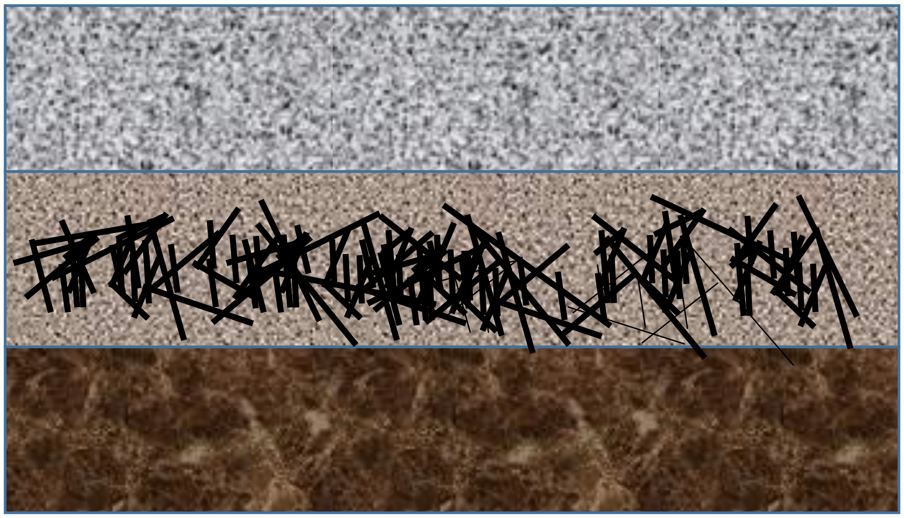


Figure 2: A chimney laying on its side after growing to an unstable size and falling would create layers of varying permeability - a loose fractured zone bounded by tighter low permeability zones

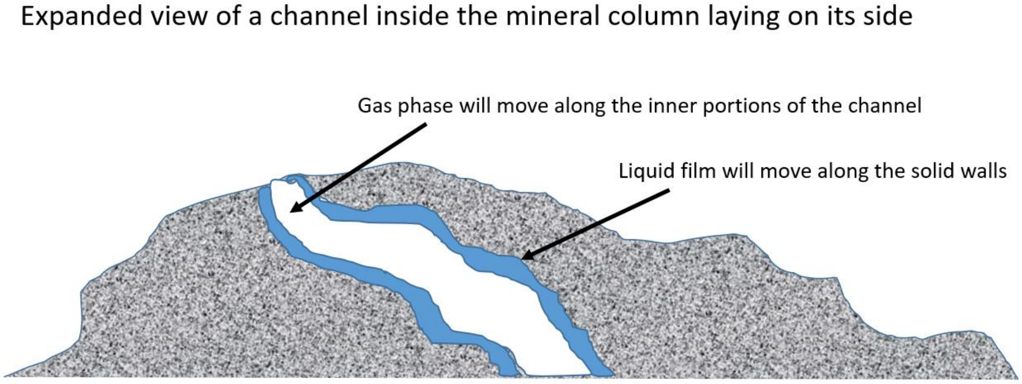


Figure 3: Two-phase (gas and liquid) convection inside a fissured rock creating alternate wetting and drying conditions

The system of fissures in the layer under consideration (see Figure 4) would behave in the aggregate as a porous medium with a larger permeability. With the flows of liquids and gases being somewhat bounded in this more permeable layer, and thermal instability created by the heat provided by the hydrothermal vent by heating from the side, there would be a series of counter-rotating convection cells that would form. Whether a single convection cell forms or a series of such counter-rotating cells is a function of the aspect ratio (height to width) of the medium in which the convection occurs. A low aspect ratio creates many cells. A high aspect ratio (such as equal to one) might create just one cell. Generally, thermal convection occurs from heating from below. However, a similar type of convection also occurs when heat is provided from the side of a layer. Once such a series of convection cells has formed, it will be a stable system as long as heat continues to be provided, that is, the hydrothermal vent continues to flow.

O'Day et al (1999) have studied the pore structures of hydrothermal sulfide chimneys at the micro-scale using synchrotron x-ray computed tomography. They found that the interior of the chimneys has a different pore structure than the exterior portions. The interior portions had no small pores. Visible channels had sizes ranging from 300-500 micrometers in diameter. The exterior portions had pores ranging from 200-500 micrometers, and larger channels flow channels of 1-2 mm. Thus, we see that if an iron sulfide chimney fell over onto its side, onto less permeable sediment, it would very easily create the kind of system depicted in Figures 2, 3 and 4. Below the chimney that was now on its side would be a less permeable medium. This medium could still allow liquids and gases to enter into the chimney where they would find a set of the larger flow channels of 1-2 mm in diameter to move within. Above this set of flow channels would be the less permeable inner portion of the chimney. The more permeable set of flow channels would thus be bounded above and below by less permeable barriers. Gases and liquids could start to move around in the high permeability zones, with some leakage out and into this zone through the less permeable zones bounding the zone of movement – exactly the mode described in Figure 4.

For both gases and liquids to exist inside the porous medium, we assume that the depth of the hydrothermal vent is of the order of tens of meters –not thousands of meters as is the case today. In the early Hadean Ocean, there is every reason to expect that hydrothermal vents would have existed close to newly rising land masses and at shallow depths. Thus, gases and liquids could have both existed in the convection cell.

As we are hypothesizing that a series of life-like chemical reactions would occur through the structures of these convection cells, it is not difficult to estimate the temperatures that might have existed at such locations. We can then estimate whether these required temperatures might have existed near ancient hydrothermal vents.

Amines will begin to break down or become ineffective as sulfide carriers at around 120 C. Therefore, we assume that the hot side of these cells is at 120 C, and the cold side around 80 C. These are temperatures quite likely to have existed in the oceans in the 3.8 billion years ago time frame. The hydrothermal vents themselves are expected to have been around 350 C. If the ocean was 80 C itself some distance away from the hydrothermal vents the temperatures hypothesized would easily have been available.

Thermal convection in a porous medium occurs at a Rayleigh-Darcy number, Ra-Da, greater than 40. This number is defined as –

Ra-Da = ρ_f g K b (Th-Tc) L/ (m (k_m/ ρ_f C)
where,
ρ_f = density of ocean water = 1063 kg/ m^3
g = acceleration of gravity = 9.81 m/s
K = permeability of porous medium = 10^{-11} m^2 (assumed)
Th = hot side temperature = 120 C
Tc = cold side temperature = 80 C
β = coefficient of linear expansion of ocean water = 0.0003 K^{-1}
μ = dynamic viscosity of ocean water = 0.0002 Pa-s
(k_m / ρ_f C) = 2.7 x10-7 m^2/s, (typical value, where k_m is the effective thermal conductivity of porous media, based on the thermal conductivity of fluid, solid matrix and porosity for ocean rocks, and C = 3993 (J/Kg-K) is the heat capacity at constant pressure of the ocean fluid
L = 2 m

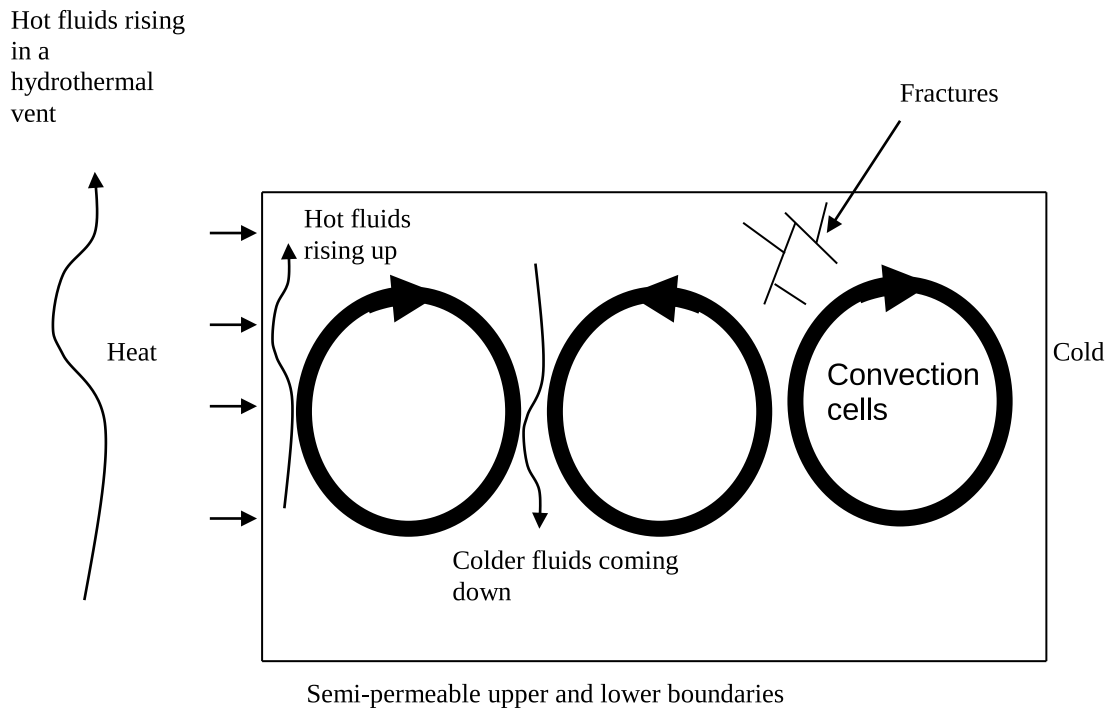


Figure 4: Multiphase (liquid and gas) thermal convection in a porous system with heating from the side – this system could be an iron sulfide chimney that fell over onto its side

For the values assumed above, we see that the Ra-Da > 40 if the length-scale of the convection layer is about 2 m and the permeability of the fractured matrix is about 10^{-11} m^2. Also, generally, convective overturning occurs in a non-dimensional Fourier number of about 0.3 (= k_m*t/L^2, where t = time). Therefore, in this case, we would have convective over-turning in about 50 days.

The point of this discussion is to show that for a temperature difference of about 40 C between the hot and cold side, there are easily possible a range of length scales and permeabilities in which thermal convection could have occurred.

Once such a recirculation system has been established, we have a situation in which the location of certain chemical species with respect to the heat source and the direction of the movement of the gas and liquid phases in the convection cell gives them a certain advantage or disadvantage in terms of being able to access certain catalysts and needed chemicals for given reactions. A form of natural selection is occurring in a prebiotic environment.

Figure 5 illustrates this situation where the model hypothesizes that around the convection cell there are zones of amines that interact with hydrogen sulfide (a hot zone and a cold zone), zones in which oxidative catalysts (such as iron and nickel) oxidize the sulfur in the hydrogen sulfide to elemental sulfur and zones in which the sulfur is reduced releasing energy and enabling certain carbon, disulfide and hydrogen bonds to be formed – that is, complex hydrocarbons to be formed. As soon as the sulfur in the hydrogen sulfide is oxidized to elemental sulfur, there also become available two H+ ions. Carbon dioxide gas is also being released and recaptured by the amines in the vesicles. The CO2 would react with the H+ ions in the presence of metal catalysts to make more complex hydrocarbons.

When there are gas and liquid phases moving through a porous medium, the liquid phase will move along the solid matrix, and the gas phase will fill the remainder of the pore space. This is a situation very much like a trickle-bed reactor used in the processing of hydrocarbons. In such circumstances it is not unusual to have pulsating flows develop, and for there to be times when the pore space is entirely full of either the liquid or gas phase – that is, there would be alternating wetting and drying sequences at given locations.

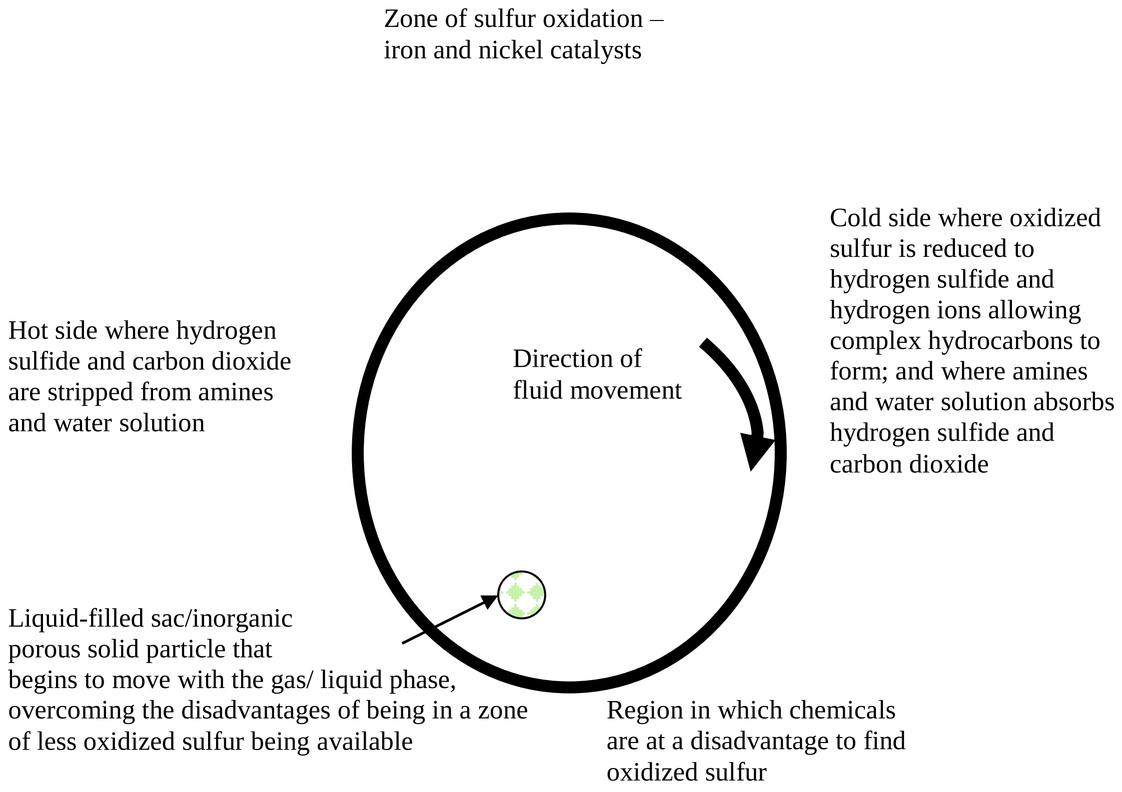


Figure 5: Various zones through which the gas and liquid phases circulate continually

Consider the situation described in Figure 5. At the top of the convection cell is a zone in which iron and nickel catalysts are present and these oxidize the sulfur present in the form of hydrogen sulfide and convert it to elemental sulfur. Further along the cell, this sulfur is reduced by existing compounds to release energy and form complex hydrocarbons – as we hypothesize that ammonia is also present in the form of amino acids and amines, some of these reactions could create amino acids by binding a carboxyl group to an amine, or remove a carboxyl group from an amino acid to make an amine. However, further along the movement of flow, the chemicals which might also have formed new bonds are at a disadvantage in terms of finding oxidized sulfur to reduce. Among the complex hydrocarbon compounds that are forming would be lipids that have hydrophobic and hydrophilic properties. As alternate wetting and drying situations would occur, it is possible that a membrane liquid-filled sac could form, with the lipids' hydrophilic ends facing inward and the hydrophobic ends facing outward. If such a sac forms and begins to move with the gas phase away from the disadvantaged zone, the chemicals in such a sac could overcome their disadvantages in terms of finding oxidized sulfur.

Problems with stability of amino acids at hydrothermal vents:-

Deep ocean hydrothermal vents have been recognized as likely having played a formative role in the origins of life (Hennet, Holm and Engel, 1992, Marshall, 1994). Bada, Miller and Zhao (1995) have also shown that amino acids although known to form at conditions like those of hydrothermal vents will quickly undergo decarboxylation and form amines at temperatures near such vents. A similar conclusion has been found by Sato et al (2004).

The decomposition reaction of many amino acids at elevated temperatures is decarboxylation yielding amines:

RR' (NH2) COOH → RR'NH2 + CO2,

where R and R' are the substituents on the a-carbon.

The half-life of common amino acids is measured in minutes to days; while that of the amines could be hundreds of days.

In this paper, I propose that the amines would help in the formation of complex membrane-surrounded cell-like structures within which amino acids could reform, as well as other complex hydrocarbons, such as fatty acids, and the amino acids within these concentrated, protected environments could begin to form bonds and more complex chains.

Amines and formation of heat regenerable salts with acid gases inside vesicles:-

Consider that liquids and gases are undergoing thermal convection inside a porous medium. Figure 4 describes this situation. Such a condition could easily occur in the sediments and rocks near an ocean hydrothermal vent.

Amino acids are known to form in such environments. (Baross and Hoffman, 1985) If amino acids were present inside the porous medium, they could also have been converted into amines.

Amines have a very significant role in gas purification for the removal of carbon dioxide and hydrogen sulfide, and are widely used in the petroleum and natural gas industry for this purpose. (Kohl and Nielson, 1997) A common amine used for this purpose is methanolamine (MEA), denoted here as RNH2. In conjunction with hydrogen sulfide (H2S), we get the following reaction –

RNH2 + H2S <=> RNH3HS

Essentially, the MEA forms a weak salt with the acid gas, H2S. When brought into contact with a heat source, the H2S will get released. The weak salt regenerates back into MEA, allowing the MEA to reabsorb H2S in a colder zone. A similar set of reactions occurs between MEA and carbon dioxide (CO2). What this means is that amines like MEA in a thermal convection cell can continually transport H2S and CO2 from colder regions into hotter regions and back.

Consider now that an amine weak salt carrying H2S and CO2 is inside the vesicle that formed through self-assembly, or that was a fragment of an inorganic porous solid. As this vesicle moves around in the thermal convection cell it will come close to the heat source and release the H2S and CO2 inside the vesicle. If an iron particle were present in the outer layers of the membrane, the H2S gas in trying to find a way out from inside the vesicle could come into contact with the iron, and get oxidized to elemental sulfur – the iron would get reduced from Fe (III) to Fe (II). This is a role that many metals can play – many of which would be found in the hydrothermal environment.

What we must understand about the situation shown in Figure 4 is that it is extremely stable – and occurs in a continuous cycle. If the H2S does not find a way out of the vesicle and/or meet an iron particle on the way – it would get reabsorbed into the amine and again form a weak heat regenerable salt. Once we have a continually repeating and stable cycle, there is every reason to expect that some H2S would find a way out of a weaker part of the vesicle's membranous wall and also an iron particle that could oxidize it to elemental sulfur. Once oxidized sulfur is available it could be used by other compounds to form more complex bonds and ever more complex structures.

As CO2 would also be available inside the vesicle, there is every reason to expect that it could also be getting reduced by the H+ ions available when H2S was oxidized to form complex organic compounds in a series of multiple reactions. Some of these could have reconstituted amino acids from the amines.

We could, therefore, have a situation in which the escaping H2S and CO2 gases could form a tunnel within the membranous wall of the vesicle. Here, the H2S could come into contact with iron or other metals, and then be oxidized to elemental sulfur. This sulfur would be available as a source of electrons and help form more complex bonds. If peptides began to form these could fold over and provide structural stability to the tunnels made by the escaping gases. The tunnels formed within the membranous wall of the vesicle would provide for the inflow and outflow of chemicals.

Predicting the sizes and wall thicknesses of proposed vesicles:-

The average velocity, U*, of fluid movement in the convection cell is easily estimated based on the permeability, the viscosity and the buoyancy gradient. This velocity is –

$U^* = \rho_f \, g \, K \, \beta \, (Th-Tc)/ \mu = 6.25 \text{ x } 10\text{-}6$ m/s

For this average (or superficial) velocity (assuming that the gas phase is moving at a velocity similar to the liquid phase), we can estimate what size of liquid-filled sac could be lifted off into the gas phase from the settling velocity of the sac.

We have, for the velocity U* to be a lift-off velocity of a liquid-filled sac the equation -

$U^* = ((\rho)p – (\rho)g) \, g \, Dp^*Dp/18 \, (\square)$

$(\rho)p$ = density of the particle = 1063 kg/m3 (assumed that of ocean water)
$(\rho)g$ = density of the fluid (gas) around the particle = 1.5 kg/m3
μ = dynamic viscosity of the fluid = 0.00002 Pa-s
g=acceleration due to gravity = 9.81 m/s2
Dp = sac diameter

Then, for U* = 6.25 x 10-6 m/s, we get a Dp = 0.46 microns.

Once this approximately 0.5 micron sized liquid-filled sac forms and lifts off with the gas phase, it has an advantage in being able to find a richer source of oxidized sulfur than when the chemicals in its liquids were positioned disadvantageously and in a position in which other chemicals had already had a chance to use up oxidized sulfur. It is interesting to note that this size of 0.5 microns is that associated with (still controversial) nanobacteria and quite close to that of the smallest thermophilic bacteria which are of the order of 1 micron.

Let us assume that the vesicle is a small fragment of a solid porous iron sulfide bubble moving inside the liquid phase. Let us further assume that fifty percent of the fragment is pore space filled with ocean water. Then, the density of the fragment will be a function of the density of iron sulfide (4840 kg/m^3) and the density of ocean water (1063 kg/m^3) and could be 2950 kg/m^3. The size of the particle that could be lifted off is estimated as follows:

In this case,

$U^* = ((\rho)p – (\rho)l) \, g \, Dp^*Dp/18 \, (\square)$

$(\rho)p$ = density of the particle = 2950 kg/m^3 (assumed that of ocean water plus a skin of iron sulfide)
$(\rho)l$ = density of the fluid (liquid) around the particle = 1063 kg/m3
μ = dynamic viscosity of the fluid = 0.001 Pa-s
g=acceleration due to gravity = 9.81 m/s2
Dp = sac diameter

Then, for U* = 6.25 x 10-6 m/s, we get a Dp = 2 microns.

This is a size closely associated with bacteria.

Conclusions:-

Amines have an affinity to interact with CO2 and H2S, form weak salts, and then through heat release the acid gases and regenerate back to amines. In the model proposed here, an amine weak salt carrying H2S and another carrying CO2 is inside a vesicle that formed through self-assembly and is moving in a thermal convection cell. As this vesicle moves around in the thermal convection cell (either as an inorganic bubble, a monolayer vesicle in the gas phase, or a bilayer vesicle in the liquid phase) it will come close to the heat source and release the H2S and CO2 inside the vesicle. As the vesicle moves away from the heat source, the gases would be reabsorbed into the amines. This process creates stability and a repeating set of reactions, reactants, and products forming and reforming – a key criterion for complex reactions to occur. Also, as the complex macromolecules form within a vesicle, their concentrations remain high enough for even more complex molecules to form. The vesicle forms with some sub-micron metal particles inside, such as iron. The H2S comes into contact with iron or other metals, and then the H2S gets oxidized to elemental sulfur. This elemental sulfur is available as a source of electrons and helps form more complex bonds. Further, when the H2S is oxidized to elemental sulfur, we also have two H+ ions available to interact with the CO2 in the presence of metal catalysts and form more complex hydrocarbons. The CO2 participates in Fischer-Tropsch type reactions and forms complex hydrocarbons. The amines present can reform into an amino acid – this time within a protected structure. This model predicts the size of vesicles that could move about in a likely convection cell – this prediction corresponds extremely well with spatial dimensions associated with living cells.

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