

Cosmic Symmetry-breaking, Bifurcation, Fractality and Biogenesis

Chris King¹

Mathematics Department, University of Auckland, New Zealand

ABSTRACT: This paper explores the non-linear quantum foundations of biogenesis in interactive bifurcations between the properties of the elements, sourced in the transitions induced by cosmic symmetry-breaking [King 1978]. The key interactions forming the biogenic pathway are modeled in terms of interactive quantum bifurcations explaining why the bioelements play the interactive role they do and why central biomolecules are cosmologically abundant products of the gas clouds forming young stars. RNA and related nucleotide molecules gain a plausible cosmic status, along with major features of the genetic code, and key features of metabolism, including ion and electron transport, the citric acid cycle and glycolysis.

Keywords : cosmology, symmetry-breaking, molecular evolution, chaos, bifurcation, complex system, fractal, biogenesis, astrobiology.

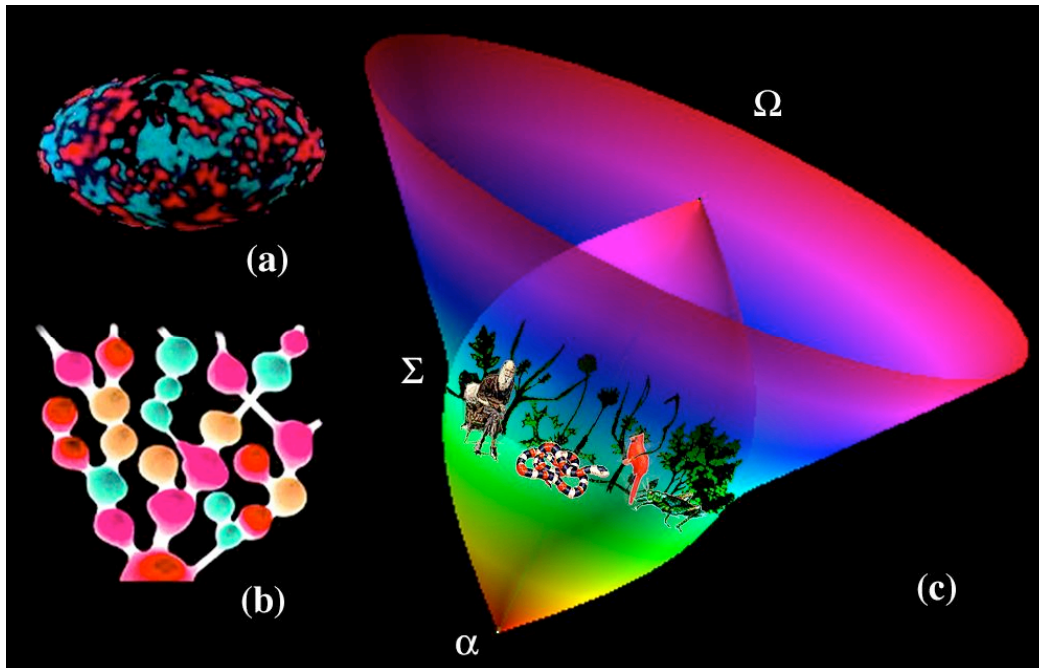


Fig 1: (a) Cosmic background. The inflationary fireball. (c) Paradise on the Cosmic Equator. Biological systems form a central cosmological manifestation of interactive complexity in the universe. The consummative Σ by comparison with the α and Ω of cosmological initial and final 'causes'. Biology's 'equatorial' position in space-time is fundamental in cosmological terms, as interactive culmination, even though biological energetics are too weak to withstand either the big-bang at the origin or the possible final fates, of attrition in an ever-expanding universe, a big crunch, or fractal inflation (b).

¹ © April 2004 E-mail c.king@auckland.ac.nz

1: INTRODUCTION

The thesis of this paper is that biological structures such as tissues, and organisms are cosmological structures, culminating the interactive phase of symmetry-breaking, as fundamental as stars and galaxies to the cosmic design. This process is described in detail in this paper as a fundamental manifestation of non-linear quantum science, elaborating the fractal nature of fundamental force interaction, inevitable from the twisted nature of the forces as they have emerged in our universe. Symmetry-breaking as elucidated firstly in terms of the weak and electromagnetic forces, fig 5(a) results from evolution of the universe from a symmetrical state to one in which the Higgs field has become polarized into a state of lower energy, similar to that of a ferromagnetic substance. It is the transition of this underlying parameter that is responsible for the bifurcations we shall consider.

Although life is of fragile insignificance among the immensity of cosmic energies, its tiny entropy-reducing photosynthetic energy budget and fragile chemical bonds overwhelmed on the cosmic scale, it is nevertheless the interactive consummation of all the forces of nature acting together in sequence. Biological evolution is a stochastic² process combining random mutation and selective advantage, many of whose manifestations are opportunistic, but others the inevitable result of selective forces and environmental bifurcations. Although biological structures are genetically coded in a vast variety of ways by specific nucleic acid sequences, many features of life as we know it on Earth are the product of selective factors which lead inevitably to specific traits. These are founded on the cosmic factors causing the forces of nature to invoke the fractal³ non-linearities which make life possible. Traditional chemistry, despite its quantum foundations, treats molecules as arbitrary building blocks, which can be arranged in almost any combination using suitable reagents and energetic conditions as driving forces. However this view is incorrect when non-linearity and dynamical feedback are taken into account. The origin of life is dependent on dynamical processes of free interaction, not forced reactions and involves fundamental interactive quantum bifurcations and feedback effects characteristic of non-linear dynamical systems.

There is now clear evidence for the optimality of many prebiotic and biological molecules, giving life as we know it a cosmological basis as a culminating interactive structure. This paper explains how the origins of chemical life, major aspects of biological evolution and the elaborate emergent structures of tissues, from biomolecules up to cellular organelles and even to the doors of perception of the conscious brain, are a fractal interactive consequence of the non-linear laws of nature established at the cosmic origin.

In particular, this paper examines major key features of biogenesis, including the selection of the bioelements and the major chemical processes and molecular types contributing to complexifying polymerization and biological metabolism in terms of bifurcations triggered by cosmic symmetry-breaking. The core idea is that the origin of life has occurred as an interactive result of such bifurcations, in the context of the fractal non-linearity of chemical matter, in a transition from far-from-equilibrium dissipative structures to the replicative catalysis we associate with genetic evolution.

² Stochastic - a process mediated partly by random factors, such as the drunkard's walk or Brownian motion.

³ Fractal: Self-similar as in a tree or fern leaf, or having systematically-related structures on changes of scale, or a non-integer power law, as in molecules and the Mandelbrot set (see fig2).

Major features of metabolism, including the role of nucleotides and polypeptides, light-absorbing chromophores, phosphate dehydration energy, RNA, the major features of the genetic code, Fe-S groups, ion and electron transport, phosphorylation and the citric acid cycle are all described as being generic features of a cosmically general bifurcation tree.

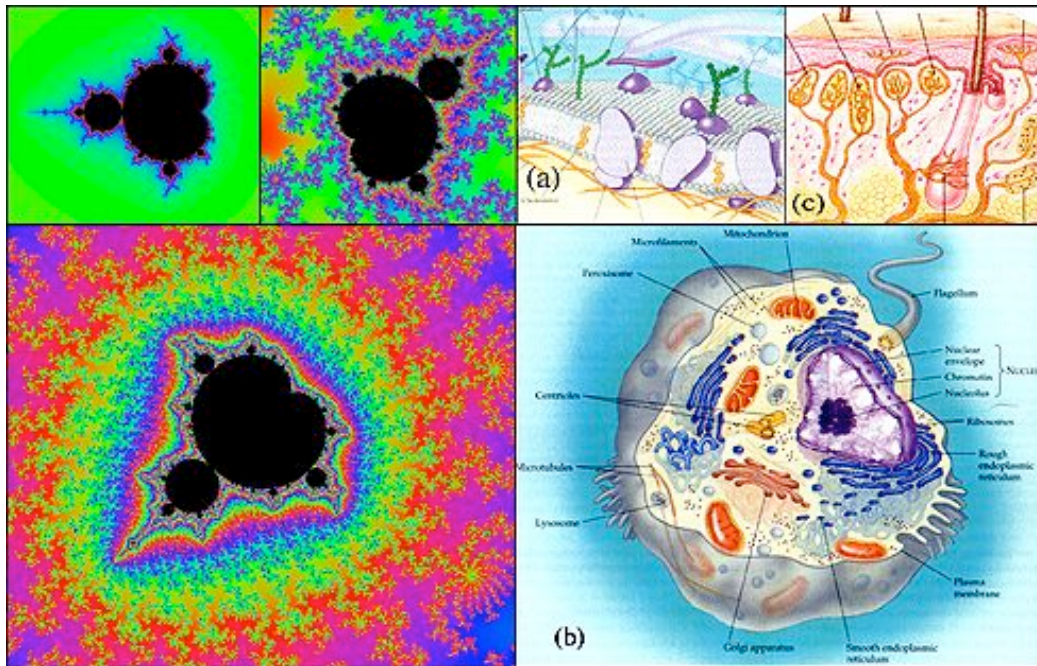


Fig 2: The quadratic iteration of the Mandelbrot set [King] compared with the interactive effects of inverse quadratic charge interaction in tissues [Campbell]. Although their genesis arises from differing non-linear process, iteration on the one hand and interaction on the other, the multi-fractal structures of tissues have features similar to the Mandelbrot set on changes of scale. These fractal effects reach from the molecular (a) in which individual proteins are illustrated embedded in the lipid membrane, through cell organelles (b) to the intercellular structure of whole organs as illustrated by skin (c). Such scale-dependent coherence of structure is possible only because of the highly non-linear nature of the electromagnetic force in quantum charge interactions of fermionic matter.

Biology is a product of the twisted laws of nature derived from cosmic symmetry-breaking. The rich diversity of structure in molecular systems is made possible by the profound asymmetries developing at the cosmic origin, between the nuclear forces, gravity and electromagnetism. The diversity of the elements and their asymmetric charge structure, with clusters of negatively charged electrons orbiting a massive nucleus containing all the positive charges in a concentrated nuclear 'droplet', is made possible only through the divergence of symmetry of the four fundamental forces. Without these asymmetries there would be only one or two simple atoms, consisting of bound particle pairs, without a clear distinction between the nucleus and orbital electrons, and none of the richness of the almost unlimited variety of molecular structures which can be generated by the over one hundred complex atoms occurring in nature as we know it.

Chemical bonding is a consequence of the non-linear inverse square law of electromagnetic charge interaction in space-time. This non-linearity also gives rise to a succession of weak bonding interactions, generating the complex non-periodic secondary and tertiary structures of proteins and nucleic acids and ultimately the fractal structure of tissues and organs as indicated in fig 2. To

appreciate fully the significance of this effect we need to review some of the elementary foundations of force unification, quantum orbital and bonding theory.

2: GENERATING A COMPLEX, TWISTED UNIVERSE

2.1 Quantum:

The four fundamental forces of nature - the strong and weak forces mediating nuclear binding and neutron-proton conversion, along with electromagnetism and gravity are believed to have emerged from a single superforce, perhaps a form of higher-dimensional string, or membrane theory, in twelve, or so dimensions, in cosmic origin, fig 3(a). In supersymmetry, each half-integer spin fermion (e.g. electron, proton, neutrino, fig 4, which form solid matter because only two particles of opposite spin can exist in the same wave function), is matched by a force/radiation-generating integer spin boson (e.g. Higgs, photon, Z_0 , gluon, graviton, fig 4 which can superimpose freely, as in a laser). This enables the negative ground state energy of the former to cancel the positive energy of the latter. However the lack of manifest supersymmetry may mean this cancellation is collective rather than individual. In string theories point particles become resonant loops, strings or membranes in higher dimensional space as distance shrinks, avoiding the infinite singularity of point particles. Strings and membranes attempt to solve the problem of the infinite self energies of point particles by allowing quantum objects to possess excitations as tiny, but finite loops, strings or branes. M-theory appears to unify several of these theories as dual representations of one another [Hawking]. This higher-dimensional space, containing a single generalized superforce is believed to have subsequently compactified most of its dimensions to sub-particulate scales, leaving the four dimensions of space-time, in a symmetry-breaking between the components of the superforce, to form the different forces we see today, in much the way a ferromagnet is polarized at minimum energy, breaking spatial symmetry, so that at the lowest energy, all domains point in one direction. Thus all but four (space-time) of these many dimensions may have curled up on microscopic scales to form inner dimensions like tiny tubes or tori. One or more of these 'hidden' dimensions may be extensive or even hyperbolic, leading to a fifth dimension hidden from most of the forces and particles, which may explain some of the unique properties of gravity.

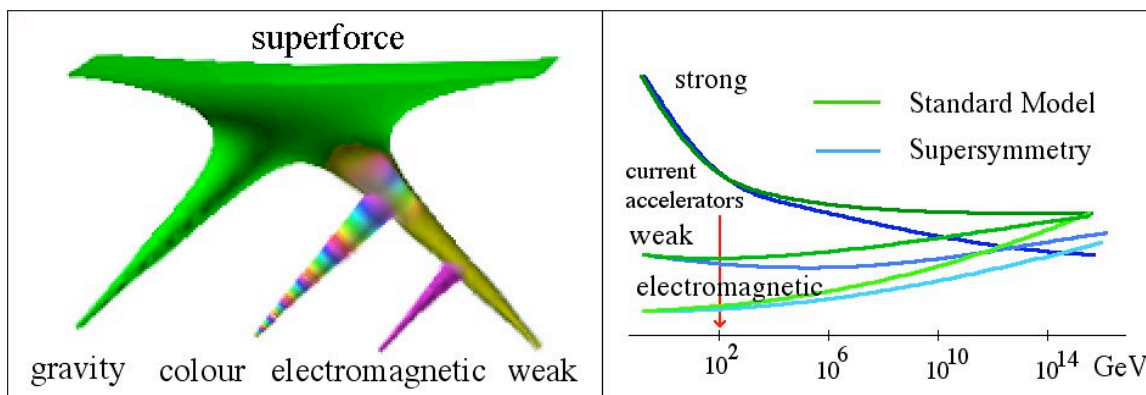


Fig 3 (a) Divergence of the four forces from a single superforce. (b) The three non-gravity forces converge in strength at the unification temperature.

The strong nuclear force is a secondary effect of the colour force between the three red, green and blue quarks comprising a proton or neutron in much the same way that molecular bonding is a secondary consequence of the formation of atoms under electromagnetism. The colour force has three colours and three anti-colours instead of two opposite charges. It also comes in pairs of ground

flavours so that the proton and neutron are a composite of up and down flavours uud and udd. The quarks' charges of $u = +2/3$ and $d = -1/3$ thus generate in threes the integral charges of the proton and neutron. The weak force behaves as a form of electromagnetism which has become very short range because it is mediated by massive particles, two of which also carry charge, which are believed to gain the required extra degree of freedom of non-zero rest mass and hence varying velocity by assimilating a concealed scalar particle, the Higgs boson [Georgi 1981, t'Hooft 1980, Veltman 1986].

The forces do appear to converge at extremely high energies - the unification temperature. The weak and electromagnetic forces have been successfully unified. Unification of these with the nuclear colour force is well described, but unifying gravity with the other quantum forces presents more fundamental contradictions including fine-scale topological disruption of the structure of space-time, leading to potential contradictions between quantum theory and general relativity.

The nature of the internal dimensions is at least partially reflected in the internal symmetries of the known particles. If we add to 4-D space time the internal dimensions of colour (3), weak-electromagnetic (2+1), the Higgs field (1) we come close to the 11 or 12 believed to be involved in super-'brane' theories [Green 1985, 1986, Mukerjee 1996, Duff 1998]. However, despite millions of possible compactifications, of this larger space to 4-D space-time, none has so far been defined which completely matches our particles and forces. Whatever the exact features of the ultimate theory resolving the origins of the universe in unification, the form of the forces as we know them is consistently described as a consequence of symmetry-breaking.

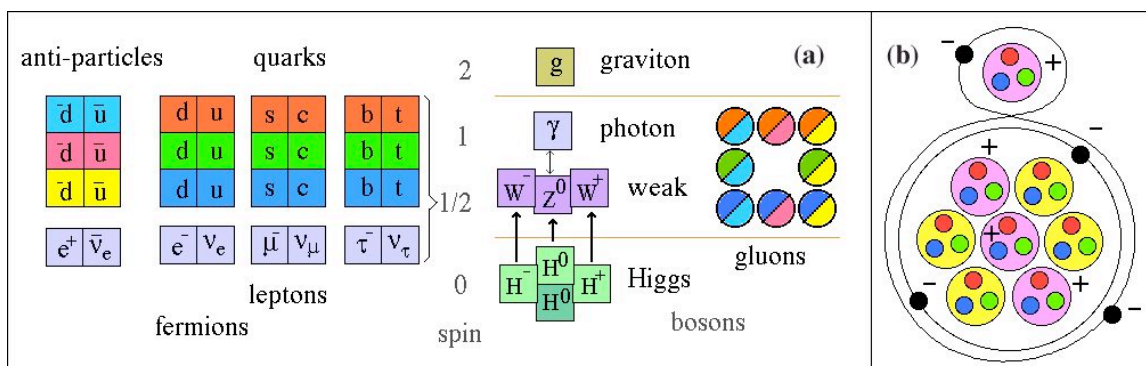


Fig 4: The standard model of particle physics involves half-integer spin fermions which obey the Pauli exclusion principle and form matter; and integer spin bosons which mediate force and radiation.

Right: the composite structure of symmetry-broken fermionic matter is molecular, forming a hierarchy involving the forces in sequence colour, weak and electromagnetic.

2.2 Cosmic:

Complementing the quantum description is a cosmic one in which a central theme is inflation. Although recently questioned by difficulties finding enough dark matter to halt the universe's slide towards hyperbolic expansion [Krauss 1999, Bucher and Spergel 1999], inflation concepts remain central to understanding how symmetry-breaking of the forces may have generated the expanding universe we know. In summary, a seed universe in the symmetrical state, below the unification temperature is in an unstable high-energy false vacuum, like a super-cooled liquid which could freeze to form a polarized magnet. The false vacuum causes a gravitational repulsion representing the negative energy difference between the actual temperature and that required to maintain the Higgs field at the unification temperature. Under this 'antigravity', the empty universe, expands exponentially, smoothing quantum irregularities to structures on the scale of galaxies [Guth & Steinhardt 1984]. The breakdown of the false vacuum (in 10^{-39} sec) halts this inflationary phase,

releasing a shower of high-energy particles as latent heat, forming the hot expanding universe under attractive gravitation we are familiar with. The gravitational potential energy gained almost exactly equals the kinetic energy of the particles, making the generation of the universe possible from a quantum fluctuation. Indications are that the universe will continue to expand, suggesting a hyperbolic inflation or fractal cosmic inflation [Linde 1992], in which the active tips of the universe are permanently inflating, to leave behind non-inflating bubble universes such as ours, or a continuing long-range repulsive quintessence 'dark energy' force [Ostriker and Steinhardt 2001]. This problem combines with the evident lack of sufficient matter to keep spinning galaxies stable, to suggest forms of dark matter may also be required. These may explain galaxy clumping around giant structures such as the 'great wall'.

Cosmology is preoccupied with alpha and omega - initial and final causes - the origin and fate of the universe. But there is another perspective, in which life and its complexity is as central to cosmology, forming the central non-linear interactive processes - the consummative sigma that make the universe the complex one we know and exist within, during the vast epochs of its mature evolution (see fig 1). The anthropic cosmological principle [Barrow and Tipler] rests on just such assumptions.

2.3 Interactive:

The consequences of this symmetry-breaking divergence lead to all the complex structures we see around us today. Although life may be created and annihilated during the formation and demise of the universe, just as the creation and annihilation of virtual particles are essential to quantum field theory, the biological forms and processes can have a cosmic origin as generic structures and a cosmic significance as culminating interactive complexity (fig 1). Although fragile, on the cosmic scale of energies, the complexity of life is the supreme culmination in complexity of the interactive quantum process initiated in the quantum symmetry-breaking. The interaction between the wave-particles emerging from the cosmic origin results in distinct effects on microscopic and cosmic scales. On the cosmic scale we find fractal structures - galaxy clusters, star and planetary formation, mediated by gravity, through contraction, heating and the ignition of the strong nuclear force, producing the energy of stars and the secondary photosynthetic energy of visible light. On the quantum scale we find integration of quarks to protons and neutrons then atomic nuclei in stars, then the formation of chemical elements in supernovae, and finally molecules, in the lower energetics of planets of second generation sun-like stars. Quantum interaction of fermions reaches its full interactive complexity only in the molecular assemblies of biochemistry and finally, in tissues, organs and organisms, the brain being the most complex expression of chemical non-linearities so far known, forming "the three-pound universe" [Hooper and Teresi].

The hierarchical process leading to molecular complexity involves all the forces in sequence, fig 4(b). Quarks are bound by colour force gluons into composite particles, such as the proton p^+ and neutron n . These interact by the strong force, via the nucleosynthesis pathway, to form the elementary nuclei. The nucleosynthesis pathway generates over a hundred atomic nuclei from the already composite proton and neutron. Exchange of identity between protons and neutrons is mediated by weak force decay. The parity between these is slightly broken to balance equally filling lowest energy nuclear quantum levels with increasing electromagnetic repulsion of the positive protons, fig 5(c). Nucleosynthesis is a complex process, catalytically moderated by several of the isotopes of lighter elements, such as carbon and oxygen. Subsequently the weaker electromagnetic force interacts, firstly by formation of atoms through aggregation of electrons around nuclei and then by secondary interaction of complete atoms to form molecules. Molecular bonding is a non-linear quantum interaction, which is never fully resolved and thus perpetuates in a sequence of stages

through successive strong and weak bonding interactions, making possible the complex tertiary structures of biomolecules.

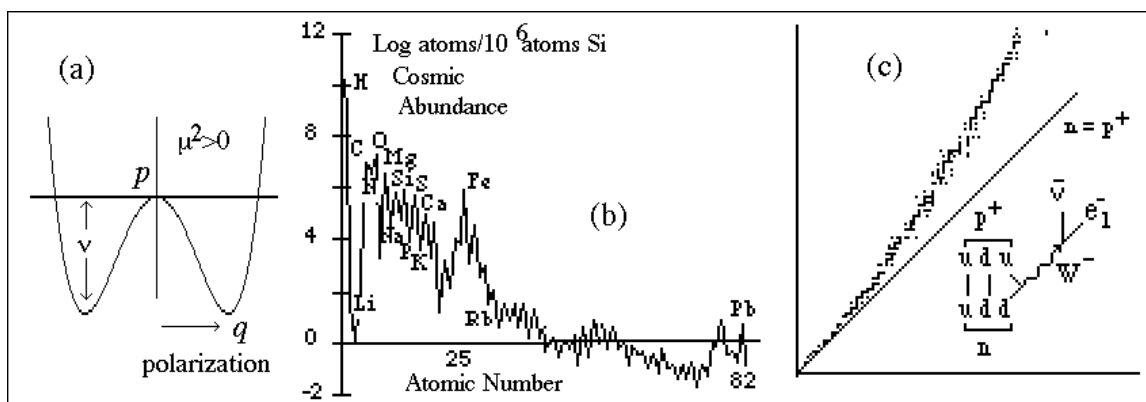


Fig 5: (a) Symmetry-breaking between the weak and electromagnetic forces is modeled as a shift of the Higgs field from zero polarization p to a lower energy polarized state q . It is this shift of the Higgs field as underlying parameter that is at the source of our symmetry-broken non-linear interactions in chemistry, the elementary bifurcation tree. (b) Cosmic abundances of the bioelements. (c) The neutron excess of the stable nuclei reflects the interaction between the strong and electromagnetic forces via the weak force

Generation of the chemical elements requires a cosmic cycle through the supernova explosion of a short-lived hot star, generation of heavier elements like gold possibly involving the collapse of twin neutron stars after supernova formation [Rosswog 2001]. In the second phase, these elements are drawn into a lower energy long-lived sun-like star, the lighter elements associated with terrestrial biology occur in relatively high abundance as a result of nucleosynthesis dynamics, fig 5(b), and can become concentrated on mid-range planets.

The culminating interaction of the differentiated forces representing the final re-interaction of the residual lower energy electromagnetic bosons with their fermionic counterparts in the electromagnetic orbitals of molecules occurs as a result of irradiation of molecular systems by photons emitted as stellar thermal radiation. The typical coupling of the 5000oC surface temperature of sun-like stars provides photonic energy suitable for energizing weak-bonded molecular structures, without destroying them. A pivotal environment in which this final negentropic low-energy reentry occurs in abundance are the surfaces of rocky planets in the temperature belt where water is liquid. The variety of planetary systems so-far discovered demonstrates the capacity of the universe to explore, through the chaotic non-linearities of gravitational orbits, a diverse array of planetary surfaces, ensuring the phase space of potential molecular environments is well explored on a cosmic scale.

3: THE ABUNDANTLY FECUND UNIVERSE AND BIFURCATIONAL ORIGINS

As time passes, more and more evidence is accumulating that, the universe and its galactic gas clouds are abundant in organic chemicals, from the simplest molecules to sugars, amino acids and nucleic acid bases. Since Fred Hoyle coined the term “wooden universe” based on infra-red spectral data indicative of carbohydrate emission, there has been an awareness of the potential of galactic gas clouds to be cosmically abundant sources of prebiotic molecules.

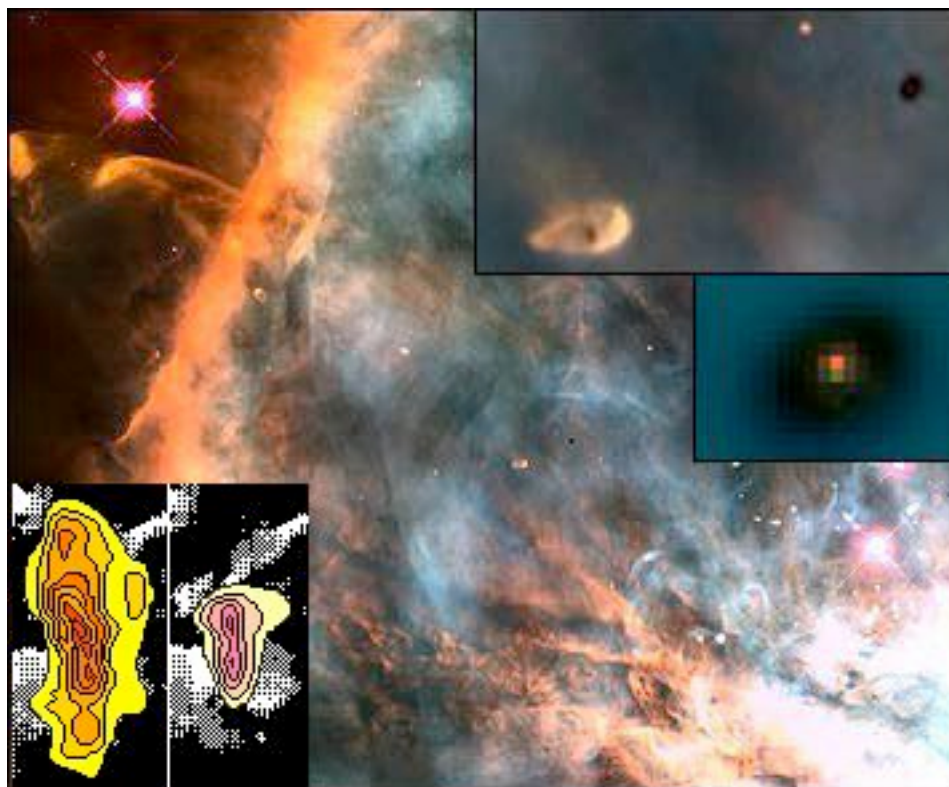


Fig 6: The Orion nebula contains newly forming stellar systems possibly including the propylid (tiny black dot centre) with a dark 'planetary' disc (top and centre right) [Buhl]. Some of these newly forming stars are also surrounded by clouds of HCN and HCHO (inset bottom-left) [Hubble telescope image].

Radio-telescope data as early as 1974, [Buhl] demonstrated clouds of multiple-bonded $\text{HC}\equiv\text{N}$ and $\text{H}_2\text{C}=\text{O}$ spanning the region in the Orion nebula where several new stars are forming, fig 6. These are key precursors of complex polymerization pathways discussed below. Glycine has also been found in interstellar gas and adenine is an abundant product in simulations of collapsing interstellar gas clouds containing a dozen elements including hydrogen, carbon, oxygen and nitrogen [Chakrabarti 2000]. Along with amino-acids, all of A, U, G, and C have been detected in carbonaceous chondrites [Hua et. al. 1986], such as the Murchison meteorite. These also contain amphophilic membrane forming products [Deamer and Pashley 1989]. Cometary impacts are believed to have coated the Earth in a rich endowment of organics from the earliest stages of solar system evolution when impact rates were high.

Glycoaldehyde has recently been detected by Jan Hollis [2000] in a cloud of gas and dust 2 light years across of a type from which new stars are formed. He notes “Interstellar clouds are spread throughout the galaxy and you often find the same molecule in many different clouds. Since these organic molecules are so widespread, it may mean that pre-biotic chemical evolution is an ongoing process.” Glycoaldehyde can combine with other carbohydrate molecules to produce ribose.

A team led by Jason Dworkin [Dworkin et. al. 2001] has also formed complex organic molecules under the harsh conditions of outer space. The main ingredients of interstellar ices are simple chemicals frozen together. Mostly water, some ammonia, carbon monoxide, carbon dioxide and methanol. The team froze a mixture of these chemicals into a thin solid ice at temperatures close to absolute zero ($-441^\circ\text{F}/-263^\circ\text{C}$) under extreme vacuum and exposed this to harsh ultraviolet radiation

that mimics the radiation in space produced by neighbouring stars. Instead of finding a handful of molecules only slightly more complicated than the starting compounds, hundreds of new compounds were produced in every mixed ice studied. The types of compounds produced are strikingly similar to many infalling meteorites and interplanetary dust particles. “Thus much of the organic material found on the Earth in its earliest years probably had an interstellar heritage”.

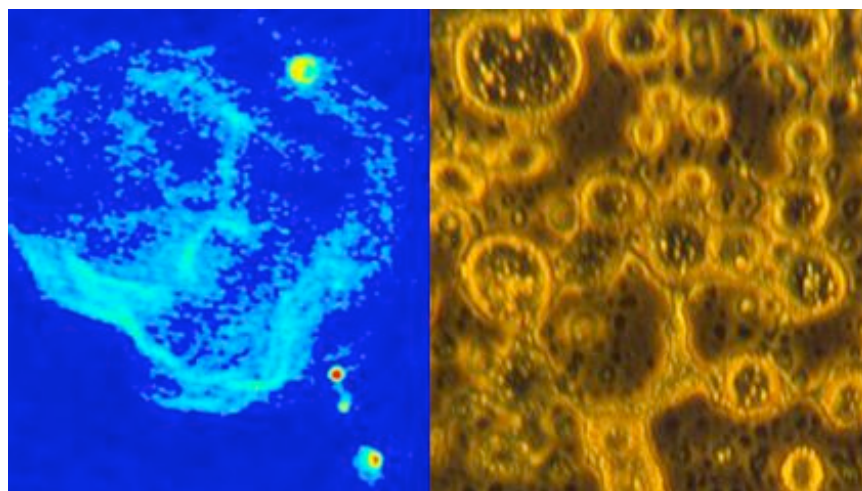


Fig 7: Left: The cloud from which glycoaldehyde has been detected [Hollis]. Right Droplets made by harsh radiation under interstellar conditions [Dworkin et. al.]

The Kuiper belt contains most of the solar system’s water and organic molecules. Infra-red studies have confirmed water-ice and hydrocarbons on some objects [Couper and Henbest]. The capacity of complex organic molecules generated in space to enter Earth's atmosphere intact has been confirmed. Jeffrey Bada has found evidence from a site in Ontario that “mother lodes” of buckyballs, (football-shaped complexes of carbon atoms), have fallen intact to Earth from outside the Solar System when a meteoroid the size of Mount Everest crashed 2 billion years ago. The impact site contained about 1 million tons of extraterrestrial buckyballs loaded with helium, an element rare on Earth, but abundant in interstellar space. If buckyballs could fall on earth without burning up, so could complex organic molecules [Cohen 1996]. Amorphous ice from comets can also protect organic molecules [Blake and Jenniskens 2001].

Although these fecund origins give rise to suggestions of panspermia by researchers such as Francis Crick [1981] and Fred Hoyle [1979], following on Svante Arrhenius’ [1907] idea of migratory spores, there are a host of proposed mechanisms for a planetary origin. Many planets have already been discovered orbiting nearby stars, although these tend to be gas giants. Habitable planets are also believed to be relatively commonplace in our galaxy [Frank et. al. 2001], although some problems remain [e.g. Muir 2003]. Origins of life from cometary material, through energetic discharge from lightning, solar radiation, volcanism, hydrothermal vents have all been proposed as well as shock energy from asteroid impacts [Osinski 2003]. Seeding of life from Mars [Davies 2003] as well as the reverse process [Ball 2004] have all been proposed.

Given galactic clouds of organic molecules and rich depositions of cometary material containing the bioelements, the Gordian knot of the origin of life becomes how to explain the known fractal structures of tissues, cells, organelles and molecules and how key molecular processes, from replication, through translation, to the excitable membrane come about. Given the position an Earth-like planet occupies, with a solar input of free energy from stellar nuclear reaction, the planetary

surface becomes a classic far-from equilibrium thermodynamic system. Solving the problem of the origin of life is equivalent to asking a fundamental question in non-linear science - “Are there genera of fractal structures in the dynamical space of interactions which can ‘evolve’ as ‘dissipative structures’ to support the onset of replicative, or excitable life.” The ‘evolution’ of such structures has moved from predominantly bifurcation-based chemical processes to the manipulation of these through the advent of catalytic replication.

This may have also involved a sequence of specialized boundary conditions, which varied over time to include many of the proposed biogenesis scenarios, from energization of molecules through electrical discharge, and irradiation, through phosphate-rich drying shorelines, high temperature iron-sulphur interactions around hydrothermal vents, and mineral processes involving clays. The non-linear bifurcation model places these all in relation to one another as contributory processes rather than stressing one aspect of the bifurcation scheme’s features as key over others. The key to understanding this riddle is how the dynamics of catalytic replicators like RNA first get bootstrapped into complexity.

In the bifurcational model, the planetary interface is one which, given its free input and fractal bonding is not unlike cellular automata, such as Conway’s game of life, which operating under conditions close to the edge of chaos and which become computationally unpredictable as to whether the process will ever complete. Under these conditions the automaton becomes a universal computer which gains this uncertainty through being able to initiate any computational process.

RNA along with its putated homologues has been proposed as the molecular gateway for the replicative-catalytic process which occupies our central theatre of biological computational unpredictability as a pregenitor and continuing facilitator of DNA- and protein-based life. RNA also presents some of the most serious thermodynamic complexity problems, given its relative difficulty of polymerization, but high capacity to catalyze its own oligomerization and self assembly in ribozyme-mediated interactions. Again RNA possesses generic characteristics which give it a natural place in the bifurcation scheme.

4: QUANTUM CHEMISTRY AS NON-LINEAR SCIENCE OF EMERGENT COMPLEXITY

The basis of orbital energetics, and hence chemical bonds, derives from the solutions of the Schrödinger wave equation. Put in its simplest form, in one spatial dimension, we have a standard

wave equation: $\frac{\partial^2 \psi}{\partial x^2} = \frac{1}{w^2} \frac{\partial^2 \psi}{\partial t^2}$ (1) which we separate into a harmonic time frequency component and a spatial ‘orbital’ wave: $\psi(x, t) = \cos(2\pi vt)\phi(x)$ (2)

The solutions of this time-independent system, $\frac{d^2 \phi}{dx^2} = -\frac{4\pi^2 v^2}{w^2} \phi(x)$ (3), when the particle’s

Newtonian kinetic energy $p^2 = 2m(E - V)$ (4) is interpolated, $-\frac{4\pi^2 v^2}{w^2} = -\frac{4\pi^2 p^2}{h^2} = \frac{8\pi^2 m(E - V)}{h^2}$

(5), gives the standard representation of the Schrödinger equation in one spatial variable:

$$\frac{h^2}{8\pi^2 m} \frac{d^2 \phi}{dx^2} + (E - V)\phi = 0 \quad (6).$$

The power of this derivation and the fact that it was generated from wave equations, which are deterministic, and subject to linear wave superposition, has led chemists to conceive of quantum

chemistry as linear in basis, however the charge interactions, are manifestly non-linear⁴ (inverse quadratic) and both those between the many electrons and the nucleus, and the many body problems of electron-electron interaction, within the quantum wave functions of the orbitals make exact calculations for all but the simplest atoms, let alone molecules, or such notoriously complex issues as the ‘protein folding problem’, fig 9, computationally intractable. In fact what we are seeing here is the manifestation of a non-linear fractal complexity, which is first manifest in the resonance integral of the covalent bond, but ramifies all the way to the structure of molecular complexes, organelles, and tissues.

The complex expressions of chemistry, particularly in biology, are manifest as a final non-linear interactive consequence of cosmological quantum symmetry-breaking. The stability of the nucleus with increasing nuclear mass number and charge, fig 5(b), permits an unparalleled richness and complexity of quantum bonding structures in the nucleus and consequently in the electron orbitals around the diverse chemical elements. Electron-electron repulsions, hydrogen bonds utilizing lone-pair orbitals, polar and hydrophobic interactions, van-der-Waal’s forces involving unoccupied orbitals, spin-orbit coupling, delocalized orbitals, and other effects, perturb the periodicity of orbital properties and lead to the development of higher-order molecular structures.

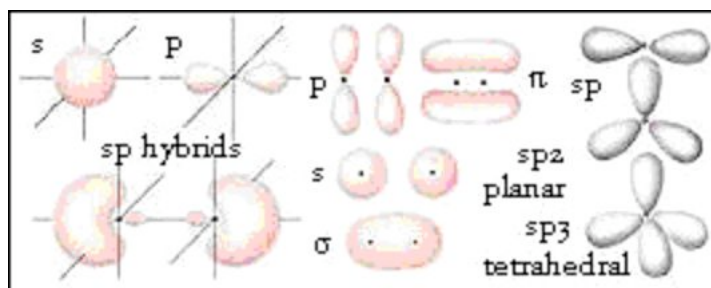


Fig 8: Although all wave functions obey quantum superposition, the non-linear nature of electronic charge distribution and its resulting occupancy energetics, the Pauli exclusion principle and additional electromagnetic effects results in the non-linear energetics of chemical bonding. This non-linear interaction is never fully resolved by any single bonding step and gives rise through subsidiary weak-bonding interactions to the global interactivity of complex biomolecules and cellular organelles.

Although quanta obey linear wave amplitude superposition, chemistry inherits an inverse quadratic non-linearity in the form of the attractive and repulsive charge interactions caused by redistributing electrons between orbital systems. Such non-linear interaction, combined with Pauli exclusion, is responsible for the diversity of chemical interaction, from the covalent bond to the secondary and tertiary effects manifest in the complex structures of proteins and nucleic acids. The quadratic nature of charge interaction, leads to a situation in polymeric chemistry akin to the Mandelbrot set, fig 2(a), and which is central in making complex molecules, fig 10, and the scale-dependent structures of tissues possible, fig 2(b).

The source of this non-linear interaction is the foundation of all chemical bonding, the inverse square law of electric charge interaction. Although the state vector of a quantum-mechanical system is a

⁴ Traditionally quantum mechanics is described as a linear theory (e.g. in Hilbert space) because amplitudes are linear with respect to superposition of states. Here we are however discussing the non-linear interaction of the electromagnetic force due to altered charge attraction and repulsion in covalent and other forms of bonding orbital.

linear combination of base states, exemplified by the formation of linear combinations of s and p wave functions to form the four sp_3 hybrid orbitals, fig 8, the electrostatic charge of the electron causes orbital interaction to have fundamentally non-linear energetics. The total energy is represented by the resonance integral of the Hamiltonian composed with the wave function, divided by the normalizing overlap integral S.

$$E = \frac{\int \phi^* H \phi d\tau}{\int \phi^* \phi d\tau} \quad (7)$$

In the case of the one-electron Hydrogen molecule ion, with $S_{aa} = S_{bb}$ normalized to 1, we have 2 non-linear solutions

$$E_u = \frac{H_{aa} - H_{ab}}{1 - S}$$

$$E_g = \frac{H_{aa} + H_{ab}}{1 + S}$$

(8)

The capacity of orbitals, including unoccupied orbitals, to cause successive perturbations of bonding energetics results in an interaction bonding sequence, from strong covalent and ionic bond types, through to their residual effects in the variety of weaker H-bonding, polar, hydrophobic, and van der Waal interactions, merging into the average kinetic energies at biological temperatures [Watson et. al. 1988]. These are responsible for secondary structures such as the α -helix of proteins and base-pairing and stacking of nucleic acids, and result in the tertiary and quaternary structures determining the global form of large biomolecules and the globally-induced active-site effects central to enzyme action.

By contrast with the periodic crystalline or random amorphous structures of most minerals, the non-periodic scale-dependent primary, secondary and tertiary structures in proteins and RNA are critical to establishing the richness of their forms and their bio-activity, fig 9. The almost unlimited variety of monomeric primary sequences induce higher-order secondary and tertiary structures through subsequent folding of the polymer. These are possible only because the non-linearity of charge interaction which causes chemical bonding also gives rise to further residual interactions at lower energies which are resolved by cooperative weak bonding.

Proteins are powerful catalysts partly because, as well having active foci, which can invoke effects such as quantum tunnelling, enzymes bring to bear a global coherence of action, arising from cooperative weak bonding, which makes for both very powerful and responsive active sites. The ‘protein folding problem’ [Richards 1991] has remained a notorious issue of complexity [Frauenfelder and Wolynes 1994] and computational intractability with initial estimates of the time for molecular random search to be of the order of 10^{27} years [Winkler and Gray 1998]. Modeling in terms of a ‘funnel-like’ potential energy landscape, given parallel and potentially quantum computation by the molecular orbitals themselves is a plausible explanation for the rapidity of such processes.

Despite being genetically coded, such molecules form fractal structures both in the geometry of their primary, secondary, tertiary and quaternary structures and their active dynamics, as illustrated by the fractal dynamics of myoglobin [Ansari et. al. 1985] and ion channels [Liebovitch et. al. 1987, 1991].

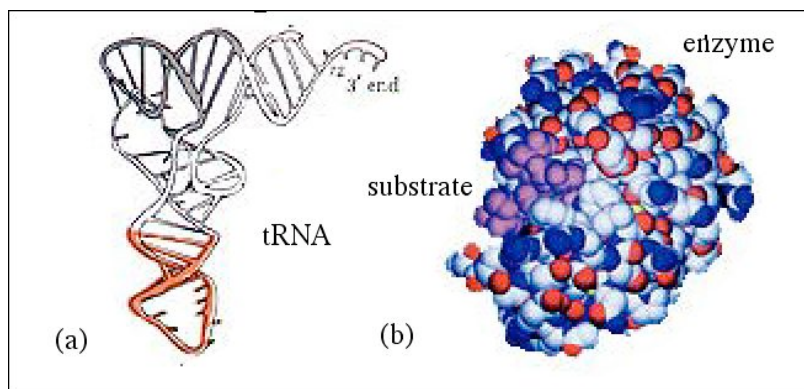


Fig 9: Global t-RNA and protein (enzyme) tertiary structures are the result of hierarchy of strong and weaker chemical bonding interactions operating on a non-periodic secondary structure. These structures are reflected in a fractal hierarchy of primary sequence, secondary structures such as the double and alpha helices, and global tertiary structures capped off by quaternary super-molecular associations. Both nucleotides and proteins derive their structures through polar and non-polar interactions in association with water. The ‘protein folding’ problem remains a non-trivial issue in computational intractability.

The prebiotic polymerizations leading to the chemical origins of life share an informational paradox, in which a small number of simple reactants lead to a large array of complex interacting products with many potential catalytic interactions, fig 13. The initial conditions are thus insufficient to causally determine any but a few of the products, except for a few predominant, thermodynamically favoured products, such as adenine, leading to a huge variety of possible end states with increasing complexity. This is illustrated in fig 13 in the formation of polypeptides. This process allows for a high degree of polymeric variability which can be influenced both by autocatalytic feedback and stochastic effects capped by quantum interference [Ball 2003, Arndt 1999, Hackermüller et. al. 2003]. This extreme tendency to non-linear complexity and unpredictability is offset only by the compensating effect of quantum bifurcations between the elements resulting from cosmic symmetry-breaking itself.

5: THE QUASI-PERIODIC TABLE AND THE ELEMENTARY BIFURCATION TREE

Although the discrete quantum aspects of orbital occupancy are periodic, fig 10 b, c, the properties of successive atoms in the same periods in the table are not exactly, or even approximately, periodic. Successive members of the same group differ significantly in nuclear charge, atomic radius and electron repulsion, resulting in trends, which permit interactive bifurcations⁵ between their properties. For example the properties of sulphur are significantly different from oxygen, although they are a period apart. The same goes for sodium and potassium through to fluorine and chlorine. When this non-linear non-periodicity complicating the underlying periodicity of the s, p, d and f orbitals is further extended to molecular systems, the parameter space of possible interactions resembles a quantum Mandelbrot set, fig 2, forming an atlas of configurations in which the atomic interactions fig 10(a) and resulting molecular species supporting biogenesis, figs 13, 14, play a pivotal generic role.

⁵ Bifurcation is a discrete forking, or change. Dynamical bifurcations are discrete changes occurring at a critical value of a continuous parameter. In this context we are describing parametric effects arising from cosmic symmetry-breaking, which subsequently result in interactive forkings between the properties of the quantum objects involved, in chemical reactions.

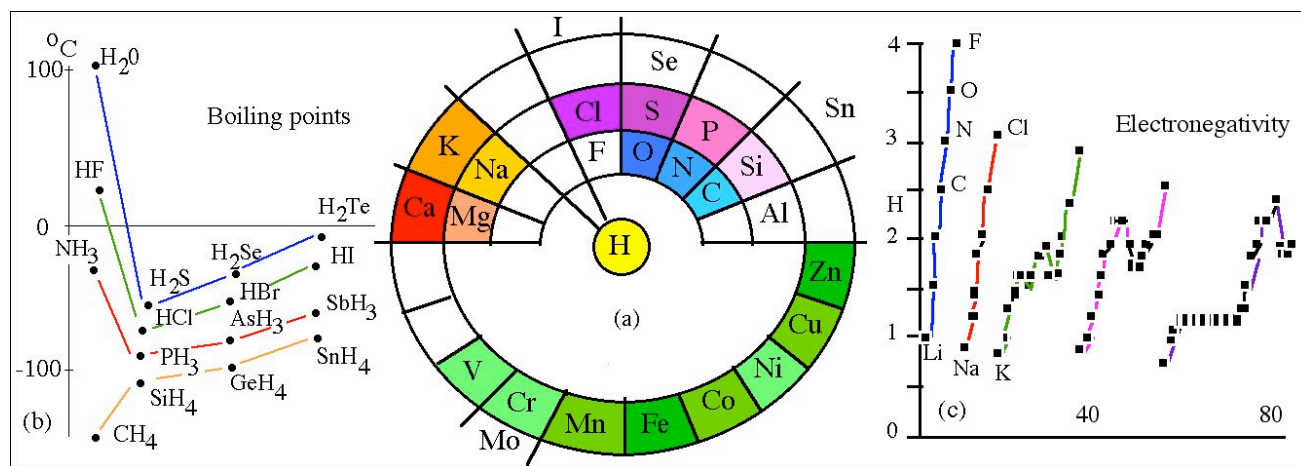


Fig 10: (a) Symmetry-breaking model of selection of bioelements, as an interference interaction between H and CNO, followed by secondary ionic, covalent and catalytic interactions. (b) Boiling points of hydrides illustrate the optimality of H₂O as a polar H-bonding medium. (c) Electronegativities illustrate optimality of O and water as a hydride and emphasize the unique role of first row covalent elements C, N, O. Atomic and ionic radii also result in a two-way bifurcation of the properties of K, Na, Ca and Mg. Transition elements introduce unique catalytic activities partly through bringing the d-orbital into play.

Such trends are illustrated in polar and H-bonding properties of hydrides for which H₂O is optimal, fig 10(b), atomic and ionic radii in which the properties of elements like Na and K differ sufficiently to induce distinct H₂O bonding structures, and electronegativity, fig 10(c) in which O is even more electronegative than Cl. Such partial, or quasi-periodicity is also illustrated by the intrusion of the transition element d-orbital series between the subsequent s and p series [Moeller et. al.]. The stable aspects of quantum orbital interaction in biochemical evolution can be classified into a tree of fundamental bifurcations, which distinguish the elements structurally and cause divisions between their properties in interaction. This forms a generative sequence in which the bioelements have key roles, fig 10(a). Each bifurcation gives rise to a reaction phase with added degrees of freedom and consequently greater interactive complexity. Describing the evolution of interactive chemical quantum structures in terms of fundamental force bifurcations sheds constructive light on the broad categories into which molecular free interaction differentiates, and determines both the degrees of freedom and the constraints for development of interactive complexity in bio-molecules. Successive bifurcations are as follows :

5.1 Principal Bifurcation : The Covalent Interaction of H with C, N, O.

The central covalent quantum interaction in the table of the elements is between the two-electron 1s orbital and the eight-electron $2sp^3$ hybrid. This is the fundamental covalent 1-2 shell quantum interaction and the bifurcation through which biocosmology comes into existence. All the members of the CNO group have tetrahedral sp^3 bonding geometry and form a graded sequence in electronegativity, from carbon in rough parity with hydrogen to electronegative oxygen, with one and two lone pair orbitals appearing successively in N and O. The resulting 3-D covalent bonds give C, N and O optimal capacity to form complex, diverse polymeric structures. Symmetry is split, because the 1s has only one binding electron state, while the $2sp^3$ has a series from 4 to 7 with differing energies and varied occupancy, as the nuclear charge increases. The 1s orbital is unique in the generation of the hydrogen bond through the capacity of the bare proton to interact with a lone pair orbital.

Some of the strongest covalent bonds known to chemistry are the multiple-bonds such as $\text{-C}\equiv\text{C-}$, $\text{-C}\equiv\text{N}$, and >C=O . These can be generated by applying any one of several high-energy sources such as u.v. light, high temperatures (900oC), or spark discharge to the respective atoms. Because of the higher energy of the resulting *p*-orbitals, these bonds possess a specific type of structural instability, in which one or two *p*-bonds can open to form lower energy partially *s*-bonded heterocyclic and other oligomeric structures. Most of the prebiotic molecular complexity generated by such energy sources can be derived from mutual polymerizations of $\text{HC}\equiv\text{CH}$, $\text{HC}\equiv\text{N}$, and $\text{H}_2\text{C=O}$, and related hybrids in association with 'sister' molecules such as urea $\text{H}_2\text{N-CO-NH}_2$. These include purines such as nucleic acid bases adenine and guanine, their pyrimidine complements uracil and cytosine, key sugar types such as glucose and ribose, amino acids, polypeptides, porphyrins etc. They form a core pathway from high energy stability to structurally unstable polymerization, and to complexity, which we will elucidate.

The formation of conjugated double and single bonds in these reactions results in delocalized *p*-orbitals [Pullman and Pullman 1962]. Such orbitals in heterocyclic (N-C) rings with conjugated resonance configurations also enable lone pair $n \rightarrow p^*$ and $p \rightarrow p^*$ transitions [Rich and Rajbandry 1976], resulting in photon absorption and electron transfer. These two effects in combination play a key role in many biological processes including photosynthesis, electron transport and bioluminescence.

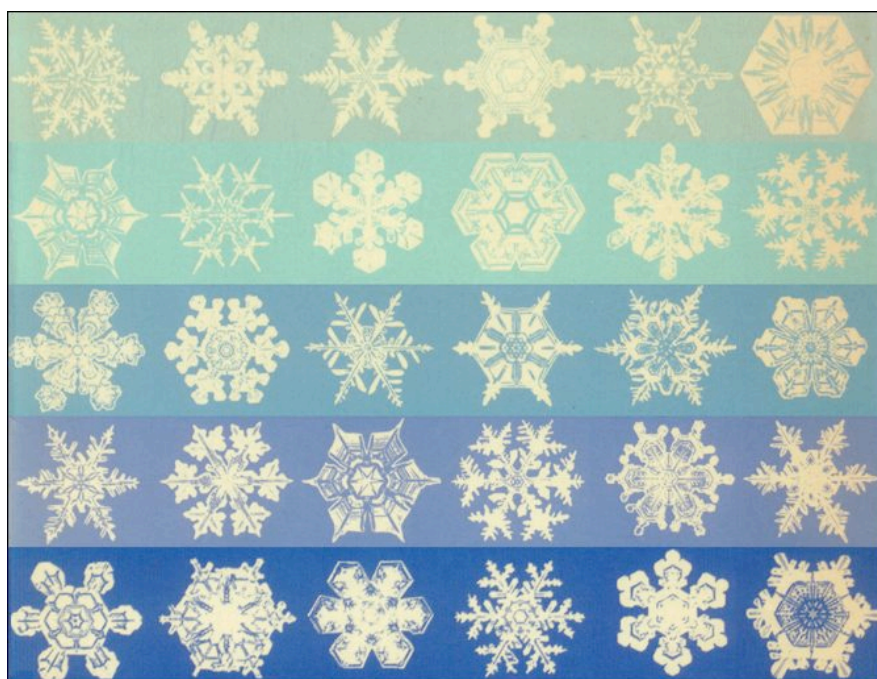


Fig 11: The diversity of ice crystals [Bentley and Humphries] illustrates the complexity of water bonding structures and their diversity under very slight perturbation of initial conditions of vapour condensation.

5.2 Secondary Splitting between C, N, and O : Electronegativity Bifurcation.

In addition to varying covalent valencies, lone pairs etc., the 8-electron $2sp^3$ hybrid generates a sequence of elements with increasing electronegativity, fig 10(c), arising from the increasing nuclear charge. This results in a variety of secondary effects in addition to the oxidation parameter, from the

polarity bifurcation discussed below, to more subtle effects such as the complementation of $\text{-CO}_2\text{H}$ and -NH_2 as generalized organic acidic and basic moieties.

Differential electronegativity results in several coincident bifurcations associated with water structure. A symmetry-breaking occurs between the relatively non-polar C–H bond and the increasingly polar N–H and O–H. This results in phase bifurcation dividing the medium into polar (aqueous) and non-polar phases in association with low-entropy water bonding structures induced around non-polar molecules. This is directly responsible for the development a variety of structures from the membrane in the context of lipid molecules fig 19, to the globular enzyme form and base-stacking of nucleic acids fig 9.

Critical in this process are the optimal properties of water H_2O among all molecules, making possible in turn polarity interactions, aqueous acid-base bifurcation, ionic solubility and hydrogen bonding. The optimal nature of water as a hydride is illustrated in boiling points Fig 10(b). Water provides several other secondary bifurcations besides polarity. The dissociation $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ lays the foundation for the acid-base bifurcation, while ionic solubility generates anion-cation.

Many key properties of proteins and nucleic acids, are derived from water bonding structures in which a counterpoint of H-bonding and phase bifurcation effects, determine the form of the alpha helix and nucleotide base pairing and the energetics of global tertiary folding. Hydrophilic-non-polar bifurcation is central to the tertiary structures of globular proteins as 'micelles' and hairpins of RNAs, fig 9. The solubility or otherwise of a variety of molecules and ions is derived from the energies and entropies of their induced water-bonding structures. The large diversity of quantum modes in water is demonstrated by its very high specific heat, contrasting with that of proteins [Cochran 1971].

Polymerization of nucleotides, amino-acids and sugars all involve dehydration elimination of H_2O , giving water a central role in polymer formation. Gerry Pollack in "Cells, Gels and the Engines of Life" has noted that the reactions of ions and biomolecules such as proteins establish an ordered water phase transition throughout the cellular cytoplasm, confirming the pivotal importance of water structures in the molecular systems supporting life.

5.3 Ionic Bifurcation.

The cations bifurcate in two phases : monovalent-divalent, and series (Na-K, Mg-Ca). Although ions such as K^+ and Na^+ are chemically very similar, their radii of hydration differ significantly enough to result in a bifurcation between their properties in relation to water structures and the membrane (compare Pollack [2001] with any biochemistry text). Smaller Na^+ and H_3O^+ require water structures to resolve their more intense electric fields. Larger K^+ is soluble with less hydration, making it smaller in solution and more permeable to the membrane [King 1978]. Ca^{2+} and Mg^{2+} have a similar divergence, Ca^{2+} also having stronger chelating properties. This causes a crossed bifurcation between the two series in which K^+ and Mg^{2+} tend to be intracellular, with Mg^{2+} having a pivotal role in RNA transesterifications. Cl^- remains the central anion along with organic groups. These bifurcations are the basis of membrane excitability and the maintenance of concentration gradients in the intracellular medium which distinguish the living medium from the environment at large.

5.4 P and S as Lower-energy Covalent Modifiers.

The second-row covalent elements are suboptimal in their mutual covalent interactions and their interaction with H. Their size is more compatible with interaction with O, forming e.g. SiO_3^{2-} , PO_4^{3-}

& SO_4^{2-} ions including crystalline minerals and silicones. In the context of the primary H-CNO interaction, two new generic properties are introduced.

PO_4^{3-} is unique in its capacity to form a series of moderate energy dehydration polymers, both in the form of pyro- and poly-phosphates, and in interaction with other molecules such as sugars. The energy of phosphorylation falls neatly into the weak bond range (30-60 kJ/mole) making it suitable for conformational changes. The universality of dehydration as a polymerization mechanism in polynucleotides, polypeptides, polysaccharides and lipids, the involvement of phosphate in adenosine triphosphate (ATP) energetics, ribonucleic acid (RNA) and membrane structure, and the fact that the dehydration mechanism easily recycles, unlike the organic condensing agents, give phosphate optimality as a dehydrating salt.

The lowered energy of oxidation transitions in S particularly $\text{S-S} \rightleftharpoons \text{S-H}$, by comparison with those of first row element O, gives S a unique role in mediating mild covalent linkage, both in protein tertiary bonding and the redox respiration and photosynthesis pathways, enabling such processes to become established more easily in a sulphur environment before the establishment of oxygen-based two-photon photosynthesis. The role of such reactions in relation to FeS centres has become legendary in prebiotic models, particularly involving reactions at higher temperatures and pressures. Following the ideas of Wächtershäuser [1988], George Cody [2000] established the generation of pyruvate in significant quantities from CO at FeS surfaces under high pressure, confirming a possible role for this as a prebiotic energy-dissipating process in hydrothermal vents. Russel [1999] and Martin suggest a similar hadean scenario.

5.5 Transition Element Catalysis

Transition elements add key d-orbital effects, forming a catalytic group. Almost all of the transition elements e.g. Mn, Fe, Co, Cu, Zn are essential biological trace elements [Frieden 1972], promote prebiotic syntheses [Kobayashi and Ponnampertuma 1985] and are optimal in their catalytic ligand-forming capacity and valency transitions. Zn^{2+} for example, by coupling to the PO_4^{3-} backbone, catalyses RNA polymerization in prebiotic syntheses and occurs both in polymerases and DNA binding proteins. Both the Fe^{2+} - Fe^{3+} transition, and spin-orbit coupling conversion of electrons into the triplet-state in Fe-S complexes occur in electron and oxygen transport [McGlynn et. al. 1964]. Other metal atoms such as Mo, Mn have similar optimal functions, e.g. in N_2 fixation.

5.6 Chirality bifurcation.

There are a variety of explanations for the chirality (handedness) of life into split-symmetry right-handed D-nucleotides and left handed L-amino acids. The most basic manifestation of handedness in nature comes from the weak force. Although the electromagnetic force has chiral symmetry, the electron also interacts via the neutral weak force when close to the nucleus. This causes a perturbation to the electronic orbit causing it to become selectively chiral, fig 12(a) [Bouchiat & Pottier 1984, Hegstrom & Kondputi 1990]. In a polymeric system with competing D and L enantiomer, in which there is negative feedback between the two chiral forms of polymerization, making the system unstable, the chiral weak force may provide a symmetry-breaking perturbation. In a simulation, fig 12(bi) high concentrations of S and T causes autocatalytic bifurcation of system (ii), resulting in random symmetry-breaking into products D or L. Chiral weak perturbation (iii) results in one form only. The selection of D-nucleotides could have resulted in L-amino acids by a stereochemical association [Lacey et. al. 1988, 1990].

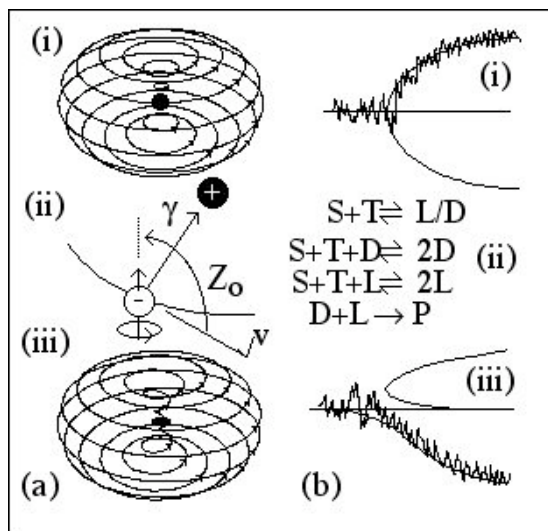


Fig 12: (a) Perturbing effect of the neutral weak force results in violation of chiral symmetry in electron orbits. Without perturbation (i) the orbits are non-chiral, but the action of Z_0 results in a perturbing chiral rotation. (b) Autocatalytic symmetry-breaking causes random chiral bifurcation (i). Weak perturbation breaks stability to one chiral form (iii)

Circularly polarized light has been reported [Bailey 1998] from a region of star formation in the constellation Orion with as much as 17% circular polarization. Such dusty regions probably contain organic molecules, including amino acids, a supposition based in part on the discovery of extraterrestrial amino acids within the Murchison meteorite that fell on Australia in 1969. The handedness of life could be explained if circularly polarized ultraviolet light bathed the dusty cloud that condensed into our own solar system and preferentially destroyed the right-handed amino acids. The astronomers observed only circularly polarized infrared light (a wavelength that can pierce dusty regions), whereas ultraviolet light is needed to weed out chiral molecules, but computations showed that the scattering could also affect u.v. frequencies. Last year's discovery that even the non-biological amino acids in the Murchison meteorite tend to be left-handed argues that some extraterrestrial mechanism must have operated to create this imbalance.

Kenso Soai [1998] and his team have demonstrated the autocatalytic bifurcation framework as well. They took a mixture of compounds containing a small excess of one enantiomer of the amino acid leucine. In the presence of this imbalance, the components of the solution reacted to form a compound called a pyrimidyl alkanol, also with a small excess of one enantiomer. But this molecule then acted as a catalyst in its own formation, becoming the dominant molecular species.

5.7 Phase Transitions, Interfaces and Tertiary Interaction at the Mineral Interface.

Both silicates such as kaolinite clays [Strigunkova et. al. 1986] and volcanic magmas [Lavrentiev et. al. 1984] have been the subject of intensive interest as catalytic or information organizing adjuncts to prebiotic evolution. Clays have been proposed as a primitive genetic system and both include adsorbent and catalytic sites [Cairns-Smith 1982, Weiss 1981]. Clays also appear to play a key role in stabilizing ribonucleotide polymerization [Ferris et. al. 1996, Ferris 2001]. The mineral interface involves crucial processes of selective adsorption, chromatographic migration, and fractional concentration. In addition a compact metabolic phase may be reinforced by a phase transition to K^+ ion - polypeptide water gel formation. Such process may be essential to explain how rich concentrations of molecules such as polypeptides and oligonucleotides could have occurred over

geologic time scales. Interface interactions are characteristic of the diversity micro-environments brought about by non-linear interaction on the planetary surface. They include redox and electron transport processes such as the FeS catalyzed reactions suggested by Wächtershäuser and others. A key interface is likely to have been a four-way interaction over time between phosphate-nucleotide dehydration processes (see RNA section), negatively charged polynucleotides and positively charged silicate mineral surfaces, the redox potential of FeS systems, and polypeptide-induced water structures interacting with positive ions to undergo phase transition to compact gels [Pollack 2001]. The above processes between them constitute the major quantum bifurcations in the free interaction of the elements. They are also the central processes operating in biogenesis. Put together this says the following: The central biogenesis pathways are themselves results of the central interactive quantum bifurcations of symmetry-breaking and its resulting non-linear interactions. While life may be possible from other combinations of elements and other temperatures and pressures, life as we know it has taken the optimal 'sang raal' or blood-royal route of quantum cosmology.

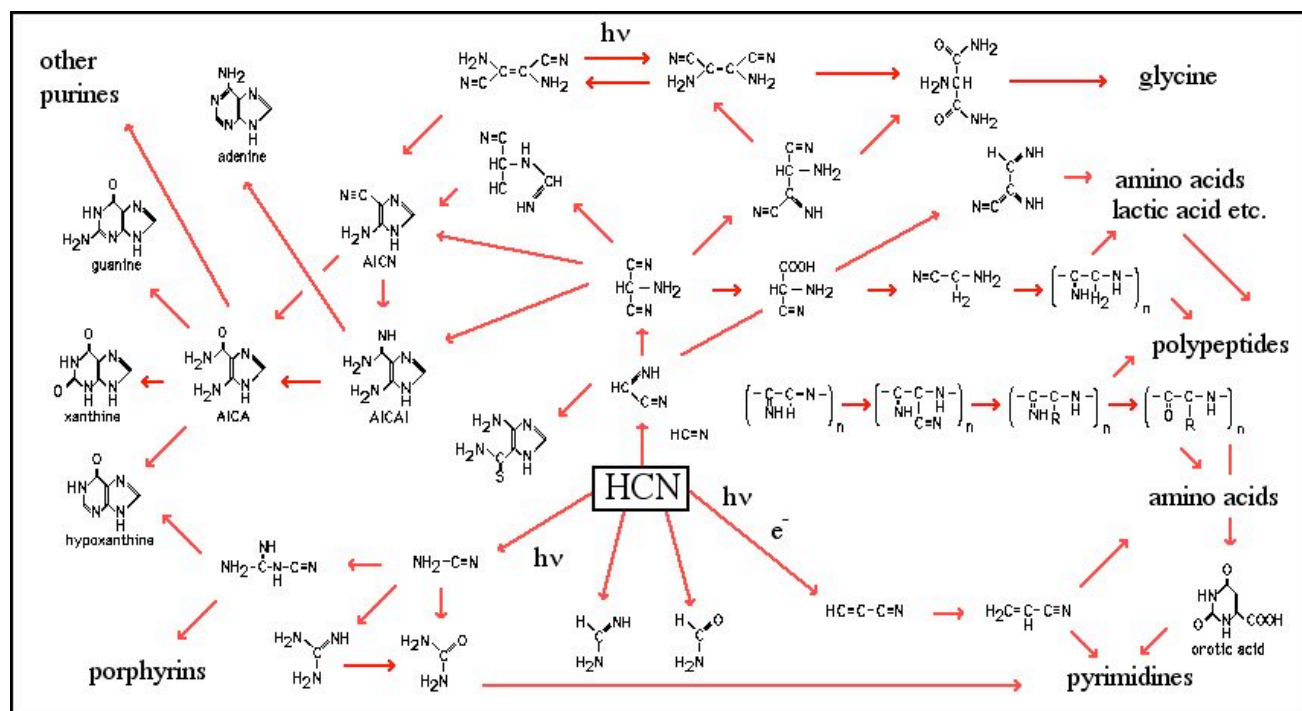


Fig 13: Known product structures and pathways in HCN polymerization [ex. Mizutani et. al.].

6: STRUCTURAL DYNAMICS OF THE CORE POLYMERIZATION PATHWAYS

The initial polymerizations of energetic multiple-bonded monomers in the reactions in figs 13 and 14 form a paradoxical information puzzle from a quantum-chemical point of view, because they provide some of the richest examples of growth in quantum-mechanical complexity, in which a relatively small number of simpler precursors give rise to increasingly complex product structures whose properties cannot be fully predicted from the simpler initial conditions.

$\text{H}_2\text{C}=\text{O}$ in aqueous solution gives rise to 4 to 7 carbon sugars, including ribose, as well as branched polysaccharides. $\text{HC}\equiv\text{N}$ gives rise to heterocyclic purine and pyrimidine nucleic acid bases, and in addition several amino acids, polypeptides, porphyrins, and many other types of biomolecule [Lowe et. al. 1963, Calvin 1969, Mizutani et. al. 1975]. A similar array of products arises from hybrids such as cyanogen $\text{N}\equiv\text{C}-\text{C}\equiv\text{N}$ [Schwartz et. al. 1975] and cyanoacetaldehyde $\text{N}\equiv\text{C}-\text{CH}_2-\text{H}_2\text{C}=\text{O}$.

Although several of these products, such as the ring polymers adenine $(\text{HCN})_5$ and ribose $(\text{H}_2\text{CO})_5$

are stable product structures, many of the more complex products, such as particular oligopeptides are metastable or stochastic products of the reaction. These conditions differ markedly from the current biochemical regime in which structurally-stable metabolic pathways are maintained through genetically-coded enzyme catalysis except where recombinational stochasticity is specifically initiated as in generation of antibody immuno-diversity.

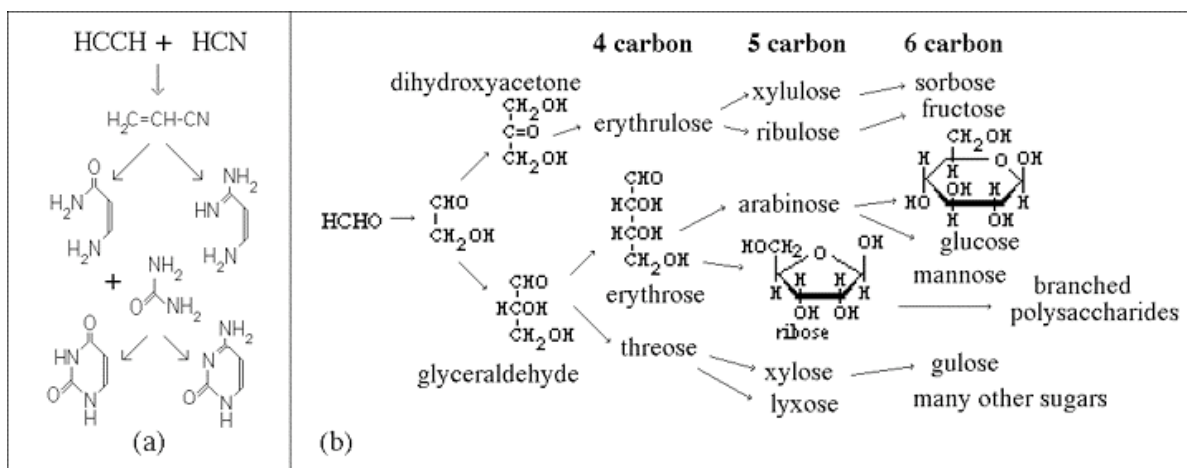


Fig 14: (a) One of several synthesis pathways for pyrimidines.
(b) Sample HCHO polymerization routes.

Phosphorylation of the oligo-aldehydes causes the reaction to favour ribose. [Eschenmoser 1992]. Since the initial conditions do not contain sufficient information to determine the final products, the system contains many potential outcomes. The lower energy configuration of key products, such as adenine's resonance stabilization, leads to some stable conformations based on free energy. Stochastic indeterminacies in the interaction of simpler molecules can lead to multiple branching pathways. Products of increasing complexity such as polypeptides possess increasingly active catalytic potential, which may alter the structural-stability of polymerization to favour certain types of product. The dynamics may trigger a sequence of autocatalytic bifurcations, forming catalytically attracting molecular products. These reaction pathways are capable of producing a vast variety of complex molecules with generic relationships to key biomolecules, including amino acids, polypeptides, HCN polymers, purines, pyrimidines and porphyrins.

Both HCN and HCHO polymerizations have prominent cyclic products which act as spontaneous end points of polymerization, because cyclization mutually neutralizes reactive moieties. The purines, pyrimidines, ribose and porphyrins all display structure consistent with being cyclic terminators. The capacity of polymers for non-periodic primary sequencing gives rise to complex tertiary structures, which are fractal as a result of structure on several overlapping scales from the atom, through local groups, to structures such as α -helices through to global conformation changes. This fractal nature is reflected both in the geometry and the quantum energetics of molecular transformations [Ansari et. al. 1985, Liebovitch & Toth 1991]. Substrate form is dependent firstly on local active sites, and in turn on the global tertiary structure of catalytic molecules.

Although the first syntheses produced the purines adenine and guanine readily, cytosine and uracil, the complementary pyrimidine bases making up the other half of the pair A-U and G-C, however Stanley Miller, forty three years after his original pioneering experiment in spark synthesis, with Michael Robertson, discovered a way for the primordial pond to make them in high yield. Although urea is produced in Miller's original experimental setup, it never reaches a high enough

concentration. When he added more urea, it reacted with cyanoacetaldehyde, another by-product of the spark synthesis, churning out vast amounts of the two bases. Urea would have been able to reach high enough concentrations as shallow pools of water on the Earth's surface evaporated. [Cohen 1996, Horgan 1996].

Eschenmoser [1992] has found that glyceraldehyde phosphate in the presence of HCHO will produce 5-carbon sugars with up to 33% ribose. In the absence of HCHO the reaction tends to produce 6-carbon sugars. The phosphate-induced reaction is key here because RNA, ATP and glycolysis all involve phosphate dehydration energy. This indicates a specific link to phosphate energy primordial to the formation of oligonucleotides and even ribose.

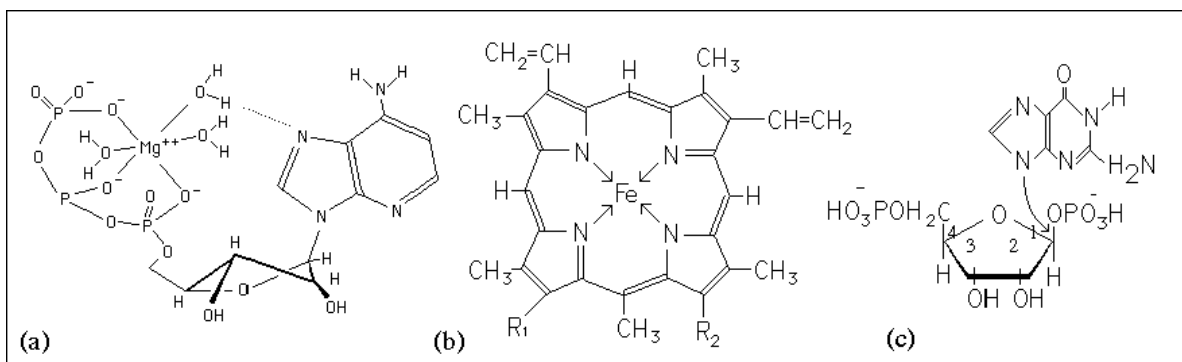


Fig 15: (a) MgATP-complex illustrates linkage between primal stability structures. Cyclic pentamers of HCN (adenine) and HCHO (ribose) are linked by phosphate dehydration, stabilized by cation and water structures. (b) Heterocyclic form of heme. Porphyrins have also been detected in primal syntheses. (c) Nucleophilic attack of adenine N₉ on ribose.

7: RNA AND COSMOLOGY

In 1981 Francis Crick commented that “the origin of life appears to be almost a miracle, so many are the conditions which would have to be satisfied to get it going.” [Horgan 1996] Now, several findings bolster the dominant theory of genesis - that life began in an era in which RNA was both the genetic and catalytic basis - the RNA era [Gilbert 1986, Benner et. al. 1989, 1993] in which simple replication and ‘enzymatic’ processes based on RNA catalysis established evolutionary biochemistry. The general outlines are clear. Ribose as (HCHO)₅, unlike the deoxyribose in DNA, has plausible prebiotic syntheses. RNA's capacity to both form double-helices, like DNA and to also three-dimensional tertiary structures similar to proteins, fig 9(a), through base-backbone bonding to ribose causes RNA to have both genetic and catalytic capacity. Simple biological RNAs have been demonstrated to have autocatalytic self-assembling capacity. The catalytic activity of polynucleotides, hinges on various forms of proton transfer fig 17(a,b,c) [Pace and Marsh 1985], in particular transesterification.

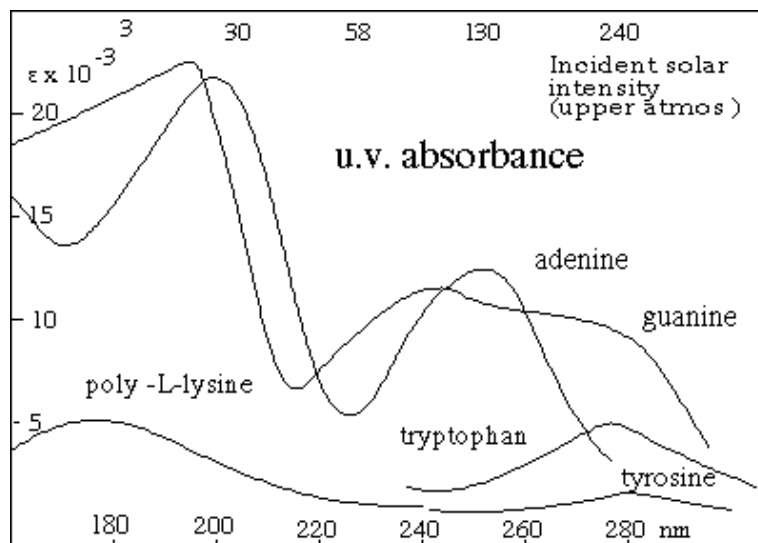


Fig 16: Ultra-violet absorption of the nucleotide bases compared with amino acids and polypeptides.

Recent biophysical simulations [Mulkidjanian et. al. 2003, see also Bhattacharya 2003] also indicate u.v.-radiation could have been a lot less harmful than previously thought, as a result of the strong absorbance of nucleotide bases, supporting their capacity to transfer energization into potentially complexifying oligomer interactions. A regime of cyclic dehydration of a phosphate rich shoreline combined with partial irradiation could thus provide a direct transition to replicative catalysis, consistent with the formation of oligonucleotides by u.v.-irradiating kaolinite clays [Strigunkova et. al. 1986] and that of Ponnamperna et. al. [1963], who first synthesized ATP under primitive earth conditions using u.v. irradiation.

The essential core of the protein-assembling ribosome remains RNA as does the signal recognition particle which shepherds nascent proteins through the membrane. The ancient fossil nucleotide coenzymes including ATP, NAD, coenzyme-A and Vitamin B12 are all ribonucleotides. Eucaryote organisms continue to have a massive commitment to RNA processing within the nucleus, including the use of many small nuclear ribonucleotides or snRps involved in RNA splicing. This suggests eucaryotes have never fully transferred from an RNA-based metabolism. Reverse transcriptases also remain ubiquitous and essential for such basic functions as telomere extension, and have a common evolutionary tree, giving retrotransposons and retroviruses a potentially ancient origin in the commonality of the RNA era.

There is still debate about whether RNA was actually the primordial genetic molecule and other hybrid molecules such as peptide-nucleic acids which use peptide rather than sugar linkages also have genetic potential and plausible prebiotic status [Nelson et. al. 2000], and more recently TNA, based on the 4-carbon sugar threose has also been suggested as a viable replicative nucleotide polymer [Coglan 2003], however it is clear RNA itself has plausible generic status as a cosmological molecular structure on several grounds. Adenine is a principal thermodynamic product of HCN polymerization in industrial yields. All of A, G, U and C now have prebiotic status as favoured products of such reactions. Ribose is an optimal sugar conformationally in terms of permitting complementary double helix formation, and has a synthesis route from glyceraldehyde phosphate. The H-bonding complementations A-U and G-C possess structural optimality by comparison with other bases found in primitive syntheses, such as xanthine. The heterocyclic polymers are restricted in their variety by the positions of N atoms required by the polymerization process. The tautomeric

states of A, U, G and C indicate AU and GC may be optimal for base-pairing among close prebiotic variants.

The nucleotide unit, as exemplified in ATP consists of a direct concatenation of key products of HCN and HCHO polymerizations. Adenine and ribose are the cyclic pentamers of HCN and HCHO linked via dehydration to a dehydrating oligo-phosphate giving it the status of a generic structure, fig 15(a) stabilized by water and Mg^{2+} . Positive ions also play an important role in stabilizing mono- and oligo-nucleotides. Mg^{2+} ions are also bound to transfer RNA and play a critical role in transesterification, balancing the negative phosphates. The fact that the polymerizing phosphodiester bond results from the removal of H₂O from phosphate suggests that phosphate was the active moiety linking of the base-sugar-phosphate complex, fig 15(c) and thus drove the entire formation of nucleic acids.

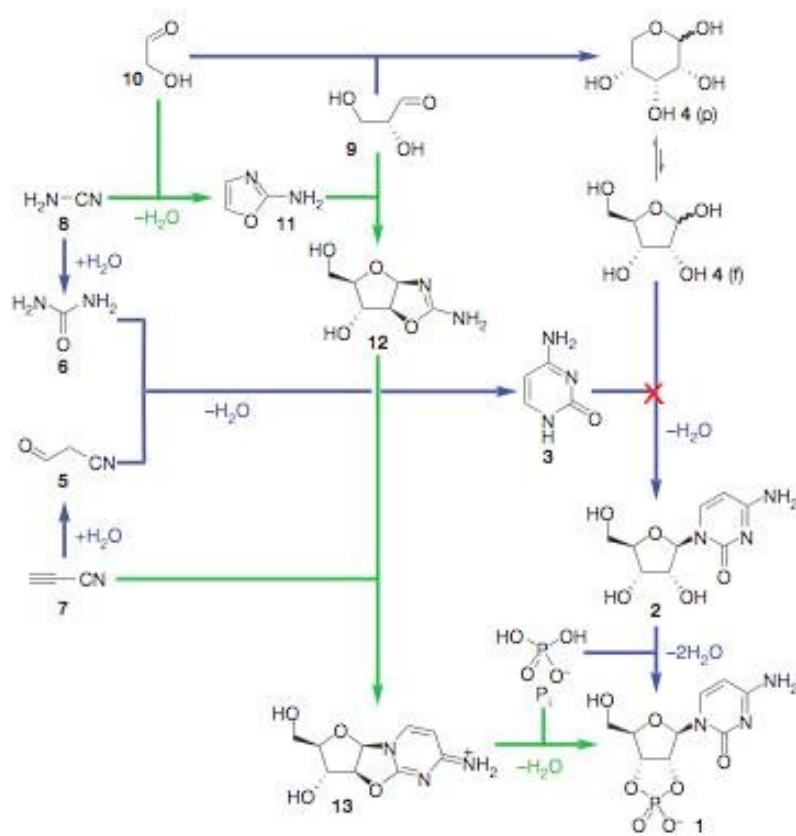


Figure 1 | Pyrimidine ribonucleotide assembly options. Previously assumed synthesis of β -ribocytidine-2',3'-cyclic phosphate **1** (blue; note the failure of the step in which cytosine **3** and ribose **4** are proposed to condense together) and the successful new synthesis described here (green). p, pyranose; f, furanose.

In 2009, John Sutherland's group [Powner, Gerland, & Sutherland 2009] blew the field of the cosmic origin of RNA wide open by reporting the synthesis of pyrimidine nucleotides from prebiotic precursors by a route that did not try to synthesize the ribose, heterocyclic base and phosphate groups separately before rejoining them – a bane of previous synthesis attempts. The key was the catalytic effect of phosphate, which caused the precursors to form composite intermediates capable of subsequently combining to form complete nucleotides along previously undiscovered pathways.

RNA proved difficult for a time to induce into complementary replication in enzyme-free systems, but its relative difficulty of synthesis may be essential to its function. It is necessary that RNA be thermodynamically unstable, or life could not exist dynamically but would 'crystallize' all the way to non-genetic polymers. A variety of partial model systems of complementary replication have been realized by Orgel and his coworkers, however instabilities in polymerization have hindered experimental enzyme-free complementary polymerization of RNAs [Orgel 1992]. It is clear that a regime of polynucleotide chemistry would have to have occurred stably over evolutionary time scales for an RNA-based form of life to evolve to the point where it had established translation and captured metabolic synthetic pathways.

Ferris has reported [Ferris et. al. 1996, Ferris 2001] that he has found a means by which the first large chains could have been forged. When his team added montmorillonite, a positively charged clay believed to be plentiful on the young Earth, to a solution of negatively charged adenine nucleotides, it spawned RNA 10-15 nucleotides long. If these chains, which cling to the surface of the clay, were then repeatedly 'fed' more nucleotides by washing them with the solution, they grew up to 55 nucleotides long. Ferris notes the clay gets RNA off the hook of having to take on the tasks of information storage and catalysis in one fell swoop. It would catalyze RNA synthesis, stocking pools with a large range of RNA strands that, as Szostak and others have shown, would evolve a catalytic capacity of their own. [Horgan 1996]. Thus complementary replication can come into existence after a phase of single-stranded polymerization has given rise to a fractal RNA environment with a diverse array of oligomeric and polymeric structures, which in turn feedback autocatalytically on replication and monomer synthesis.

A central scenario out of many, including volcanic hot pools, and hydrothermal vents, is the three-phase boundary of a phosphate-rich, clay shore line under tidal or weather-related variations in a pool in which the margin is reversibly dehydrated e.g. by sun-drying. Both clays and volcanic basalts have been cited as possible mineral interfaces. Precipitated phosphate at 37°C, leads to pyrophosphate formation and hence phosphate bond energy [Hermes-Lima 1990]. Since the energy for nucleotide polymerization is driven by H₂O removal, reversible dehydration of a medium containing phosphate, bases and sugars provides one of the most direct and simple routes to polynucleotide formation.

8: DIVERSE HORIZONS OF THE RNA EPOCH

A whole new field of RNA research has developed from the discovery of spontaneous splicing of RNAs in living systems by Tom Cech [1986a] and the demonstrated capacity of such RNAs to function as catalysts in transesterifications and the work of Jack Szostack's teams in selective RNA catalysis [Horgan 1996]. This immediately made the idea of the RNA world before proteins a natural hypothesis. This work has grown with artificial selective evolutionary studies, culminating with the development of a ribozyme which is capable of high fidelity complementary replication of short RNA oligomers of arbitrary sequence [Johnston et. al. 2001]. This has become a turning point in the credibility and maturity of the RNA world as a precursor to DNA-based life which can develop as an autonomous molecular system. The model has been extended to others for RNA-based error-correction, synthetases and the ribosome [Bass and Cech 1984, Cech 1986b, Zany and Cech 1986, Garriga et. al. 1986, Weiner and Maizels 1987]. Modified ribozymes are capable of acting as polymerases which can replicate complements to subsections of themselves [Green et. al. 1990, Doudna et. al. 1991].

The discovery that RNA appears to be the agent of peptide-bond synthesis in the modern ribosome [Guthrie 1992, Pace 1992, Noller et. al. 1992] and the capacity of modified ribozymes to act as

amino-acyl esterases [Picarilli et. al. 1992], the first step of ribosomal action in protein synthesis, establish RNA has the potential to act as synthetase as well as transfer, messenger and ribosomal functions. This gives RNA the capacity to act on its own to catalyze both its own replication and the ordered polymerization of proteins. Simpler model systems have also been advanced of the stereospecific capacity of D-nucleotides to act as a catalyst of L-amino acid polymerization [Lacey et. al. 1990]. These results enable RNA to be the key prebiotic molecule generating ordered polynucleotide and polypeptide structures.

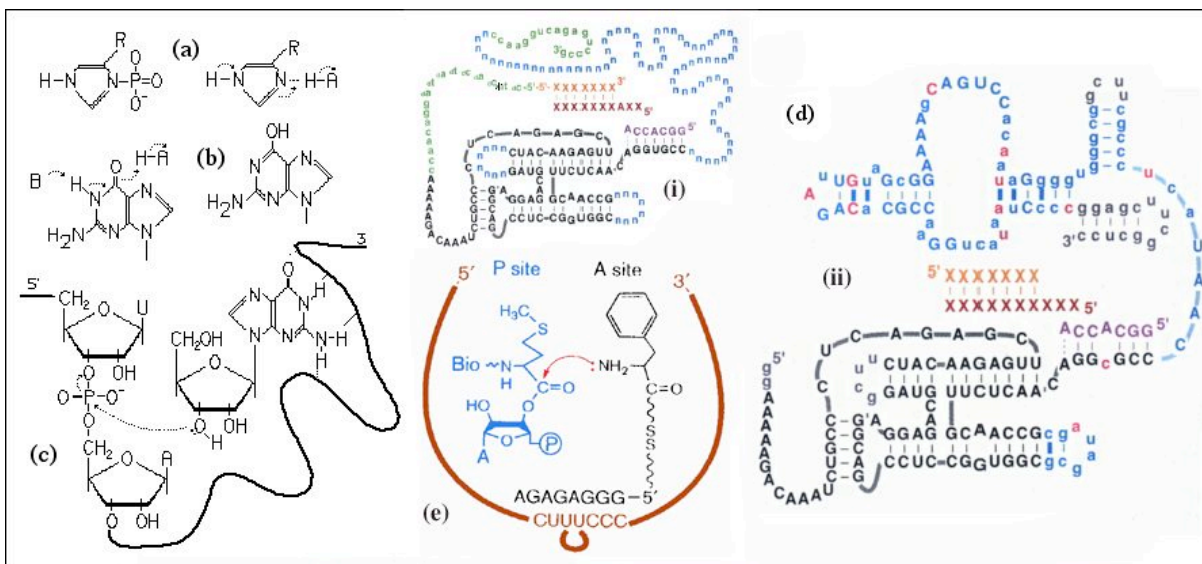


Fig 17: The ribozyme world: (a) Phospho-imidazole. Proton transfers in (a) imidazole, (b) in base tautomerization, (c) in Tetrahymena intron. (d) The first effective ribozyme RNA polymerase (ii) - a 172 unit molecule bred by molecular selection from a ligase ribozyme (i black section) through selective evolution of a pool of other intermediates (i coloured). This ribo-RNA polymerase will faithfully perform complementary replication of oligo-ribonucleotides of arbitrary sequence up to 14 units long with accuracies of up to 98% per base pair [Johnston et. al. 2001]. (e) Trans-acting ribozyme replicates key sequence and structure of the ribosome [Zhang and Cech 1997, 1998].

Szostak and Wilson [1996, Wilson and Szostak 1995] have evolved ribozymes capable of a broad class of catalytic reactions. The catalysis of previous ribozymes tended to involve only the molecules' sugar-phosphate "backbone," but these could also promote the formation of peptide bonds (which link amino acids together to form proteins) and between carbon and nitrogen. [Horgan]. David Bartel a former member of Szostak's team, has evolved RNAs that are as efficient as some modern protein enzymes. The problem with most ribozymes is that they are as likely to snip an RNA molecule apart as stitch one together which makes copying a molecule fifty nucleotides long (the minimum size necessary to catalyze a chemical reaction) difficult or impossible. Bartel's new ribozymes, on the other hand, can stitch small pieces of RNA together without breaking larger molecules apart. These ribozymes use high-energy tri-phosphate bonds similar to ATP as their fuel, speeding the reaction up several million-fold [Cohen 1996].

Zhang and Cech have reported a step towards linking amino-acids. They isolated RNAs that could efficiently link specific amino acids together [Zhang and Cech 1997]. These pseudo-ribosomes were selected from a random pool of 10^{15} synthetic RNAs. They then elicited a trans-acting by coupling one of the amino acids to a short RNA with complementary sequence to the ribozyme achieving a ribozyme which would join a ribosynthetase-amino acid to form a peptide bond with another thus

replicating even more closely ribosomal function. They also found that a small region of many of the RNAs they selected was 70 per cent identical to some regions of the ribosomal RNA. “We not only copied ribosome function, we seemed to have recapitulated its evolution,” says Cech. The two researchers then removed or mutated these sequences in the synthetic RNAs [Zhang and Cech 1998] any change to this region cut the activity of the RNA by a factor of between 20 and 600. This suggests this region in both the modern ribosome and the synthetic RNA may have the same role in the fusion reaction, such as holding the amino acids in the correct position and that they may have converged on the same molecular solution.

The alternative hypothesis is that replication began with a molecular hybrid – PNA, or peptide nucleic acid. PNA has a similar structure to RNA except for having a peptide backbone based on prebiotically abundant glycine and can co-instruct complementary RNA sequences and vice versa [Böhler, Nielsen and Orgel 1995]. The units of PNA are joined together with peptide links like those in proteins which may not present the instabilities which sugars may have faced on the early earth. Matthew Levy and his colleagues [Nelson et. al. 2000] persuaded up to 78 per cent of plausible prebiotic chemicals to transform into PNA backbone subunits amino-ethyl glycine or AEG. The acetic acid derivatives of the bases A, G U and C can likewise be generated from prebiotic reagents including NH_4CN with glycine and cyanoglyceraldehyde. AEG units link up readily at 100°C , which may have been common temperature four billion years ago when our planet was rich in volcanic activity. PNA is an alternative route to establishing the RNA era which also has a good cosmological foundation.

9: UNIVERSAL STABILITY STRUCTURES IN MOLECULAR BIOLOGY

The previous discussion of the RNA era can unravel a double-bind that is central to biogenesis - how did the core biochemical pathways become generated? The traditional viewpoint is that they were successively created starting from a simple chemical-feeding heterotroph, through mutational evolution, building one-by-one the protein components necessary to make a working whole. This however does not explain how integrated systems such as electron transport and the citric acid cycle could have functioned at all with only a vestigial complement of enzymes.

This suggests that many of the major features of molecular biology are generic structures which can come into existence under suitable conditions, through bifurcation, independently of the emergence of genetic RNA, and that these were subsequently captured by genetic takeover as genetic complexity permitted. Such generic structures include the polymeric structure of proteins and nucleic acids, nucleotide coenzymes, bilayer membrane structure and the topological closure of the cell, ion transport and membrane excitability, membrane-bound electron transport, glycolysis and the citric acid cycle.

Such a perspective has far-reaching consequences for molecular biology in cosmological terms, for while the details of mutational evolution will be unique to each environment, the major features underlying biology could be universal.

9.1 Nucleotides and the Nucleotide Coenzymes.

The nucleotide co-enzymes are widely regarded as ancient molecular fossils retained from the RNA-era. In addition to the key role of ADP and ATP as energy currency in the bio-metabolism, GTP is used in protein synthesis, and the nucleotides UDP and CDP are carriers of glucose and choline and other membrane components. Model prebiotic reactions have successfully coupled UDP and CDP to

glucose and choline [Mar et. al. 1986]. Both NAD, and FAD function as carriers of redox energy. Coenzyme A consists of adenosine coupled to pantothenic acid and functions as a carrier of acyl and other groups via the terminal SH bond [Reaney 1977]. Vitamin B₁₂ also illustrates how a dinucleotide can bind a metallic porphyrin ring. Eschenmoser [1988] has also discovered a plausible prebiotic pathway generating the more complex B12 molecule which involves two nucleotides and a Co-porphyrin. Prebiotically such a molecule could have also utilized a lowered Fe²⁺ – Fe³⁺ activation energy as a carrier of electrons.

9.2 Translation.

According to the genetic takeover hypothesis, evolution of RNA captured existing stability structures in the prebiotic medium that are a result of bifurcation. The most central of these and the most complex is the use of proteins as coded enzyme catalysts. Such a process could only have occurred in an environment in which RNAs coexisted with amino-acids and in which a very small additional genetic advantage could capitalize on simple coding of existing structures to good effect.

CCY Pro	CGY N-base	CUY VLIP	n	CAY N-base	p
GCY Ala	GGY Gly	GUY VLIP	o	GAY Acid	a
UCY Ser	UGY Cys	UUY VLIP	p	UAY Stop	l
ACY Thr	AGY Ser	AUY VLIP	a	AAY N-base	r

Diagram annotations: A pink box labeled "OH SH" is between the first two columns. A blue arrow labeled "abundant" points from GGY to GUY. A vertical yellow bar labeled "amides" is between the third and fourth columns. A vertical green bar labeled "polar" is between the fifth and sixth columns.

Fig 18: The genetic code contains evidence for several primal bifurcations [King 1982]. Centre position AU selects polar /non-polar as broad groups. VLIP are Val-Leu-Ileu-Phe.

First position G determines primally abundant amino acids.

Expansion: first codon C and A fix synthesis routes from Glu and Asp.

Subsequent bifurcations include H-bonding block and acid-base.

A variety of amino acids and oligopeptides are common products of prebiotic syntheses. The polymerization of amino acids and the development of peptide backbones with cyanide side chains from the linear HCN oligomer fig 13, provide alternative routes to oligopeptide structure. A natural propensity for -NH₂ and -CO₂H moieties as basic and acidic groups arises directly from the electronegativity bifurcation.

The discovery that ribosomal, synthetase, messenger and transfer functions of protein synthesis can all in principle be carried out by RNAs alone leads to a natural interpretation of the development of the genetic code from a protein-free translation system. The major partitions of the genetic code have structural features consistent with an origin in underlying chemical bifurcations. The fundamental bifurcation sequence, fig 18 is as follows:

(a) Polarity bifurcation: There is a major bifurcation in polarity between amino acids with anticodons having centre bases U and A. Uracil is correspondingly more hydrophilic than adenine, as reflected in their dominant split in hydrophobicity A(3.86)>G(2.3)>C(1.5)>U(1.45) and water solubilities A=1/1086, U=1/280. This leads to the idea that the polarity bifurcation was a principal symmetry-breaking factor in the origin of the nucleic acid code [King 1982].

(b) Abundance and GC: The initial base G also codes the most abundant amino acids, consistent with a GXY code starting with GAY=polar (anticodon U), GUY=non-polar (anticodon A) providing binding strength of GC and frame shift suppression (Y=pyrimidine).

(c) Four-fold code: Extending to include GGY, GCY, provides a fourfold specificity for polar (Asp/Glu), non-polar (Val and larger), along with Gly, and Ala as most abundant.

(d) Eight- and Twelve- fold codes: This could have then doubled to an 8-word code by including CAY, CUY, CGY, and CCY coding for non-polar and basic groups, and then a similar series based on AAY, AUY, AGY, and ACY Wong [1975] originally noted a correspondence between the first codon base and biosynthetic pathways in primitive organisms such as sulphur bacteria with Pro, Arg, Gln Leu, His derived from Glu and having first codon base C and Ser, Thr, Ile, Asn, Met, Lys being derived from Asp having first codon base A [Knight, Freeland and Landweber 1999]. OH- and SH-containing amino acids also form a single additional block (UA)(GC)Y, suggesting a third bifurcation for H-bonding, with UAY reading stop. Notably there is significant stereospecific affinity between certain amino acids such as Ile and Arg and their codons [ibid].

(e) Evolutionary takeover: From this point evolutionary selection begins to optimize the bifurcations caused by stereospecificity and the growth of these interactions into synthesis pathways, based on error minimization and the incorporation of the last of the amino acids. Later assignments such as Trp are consistent with evolutionary adaptations, consistent with the evolutionary emergence of differences in these codons [Cohen 2003].

Freeland and Hurst [1998], have shown that strong selective pressures must have acted on the code during its evolution. Hurst found that single-letter changes to a codon, inserting the wrong amino acid into a protein, tended to specify amino acids that were very similar chemically to the correct ones, minimizing the impact on the protein. Freeland then reasoned that the code should minimize chemical differences most between the correct and incorrect amino acid at the third base in the codon since translation misreads this base 10 times as often as the second. In an analysis that gave extra mathematical weight to the vulnerable sites most likely to be mistranslated, Freeland showed that no more than one in a million random codes was better at reducing the impact of errors than the natural code. The possibility of evolutionary change in the code is affirmed by both mitochondrial and nuclear variants [Knight, Freeland and Landweber 1999].

Ikehara [2002] suggests a 16 member code exemplifying an intermediate stage of this diversification. Freeland et. al. [2000] have analyzed other work showing that more optimal global solutions do exist to propose that stereochemical and synthesis path constraints fixated the code early on into one which was later evolutionarily optimized on error minimization constraints, the modern code being optimal under these constraining conditions. This analysis gives strong weight to the idea that the form of the code is derived from chemical, historical and selective factors rather than being a frozen accident which happened to the predecessors of the last common ancestor of living cell lines.

9.3 The Membrane, Excitability and Ion Transport.

Life as we know it is dependent on maintaining a distinct internal micro-environment as an open far-from-equilibrium thermodynamic system [Glansdorff and Prigogine, Agladze et. al. 1984, Epstein et. al. 1983], through the topological closure of the cell. Viruses, for example, depend on cellular life. The structure of the bilayer membrane is a direct consequence of the polarity bifurcation. The formation of amphophilic lipid-like molecules, joining a linear non-polar hydrocarbon section to an

ionic or H-bonding polar terminal, leaves 2 degrees of freedom for layer formation. Backing of the non-polar moieties to one another, fig 20(b), completes the bilayer. Cell structure can then arise directly from budding of the bilayer, as illustrated in budding in several types of prebiotic reaction medium. Microcellular structures are abundant in many origin of life syntheses, fig 19. The use of CDP associated with choline, inositol & lipids in membrane construction is consistent with membrane formation in the RNA era. The structure of typical biological lipids such as phosphatidyl choline display a modular structure similar to ATP, consisting of fatty acid, glycerol, and substituted amine again linked by dehydration and involving phosphate, fig 20(e).

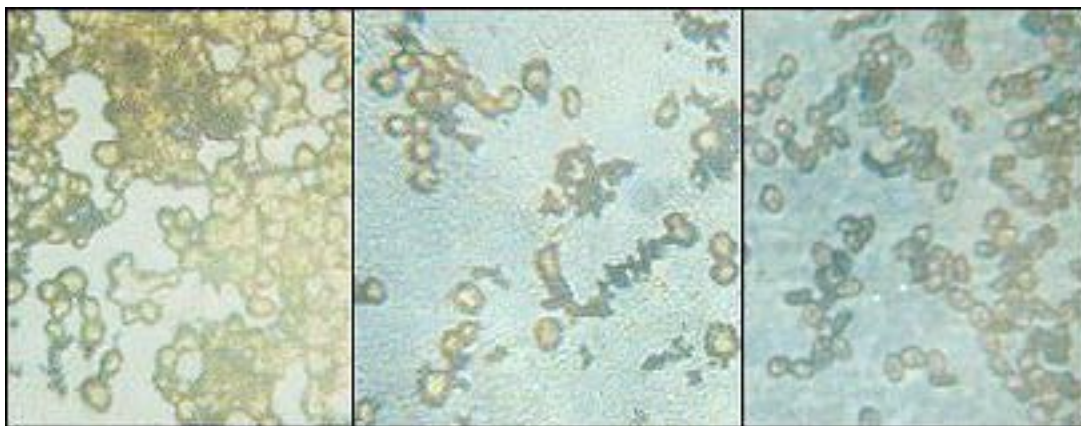


Fig 19: Left and centre: Microcellular formations generated by the author from HCN and HCHO [King]. Right: Spores of a psilocybe species at the same magnification for size comparison.

The existence of the membrane as a non-polar structure leads to segregation into ionic and non-polar reaction phases. Ion transport is essential in maintaining the concentration gradients that distinguish the cytoplasm from the external environment and thus must develop in the earliest cellular systems [MacElroy et. al. 1989]. Ion transport is a source of significant electronic effects, because the membrane under polarization is piezoelectric and is capable of excitation in the presence of suitable ions. Model systems using the simple 19 unit oligopeptide Na-ionopore alamethicin and artificial membranes display action potentials [Mueller and Rudin 1968]. Similar results have been reported for microcells produced by prebiotic techniques containing light irradiated chromophores [Przybylski and Fox 1986], demonstrating that such effects are fundamental to the quantum architecture of lipid membranes [King 1990]. Four groups of non-polypeptide neurotransmitters: acetyl-choline, catecholamines (epinephrine and dopamine), serotonin and histamine are all amines, the latter three being derived from amino acids tyrosine, tryptophan and histidine by decarboxylation. Two others are amino acids and thus also contain amine groups. This may represent a fundamental chemical bifurcation between basic amines and the acidic phosphate groups in the lipid membrane.

Alamethicin also has glutamine amides located in the core of the pore [Fox and Richards 1982]. The catecholamines are linked to indoles such as serotonin by a prebiotic pathway, fig 20(c).

Ion transport, the membrane and excitability appear to have a common progenitor in the phase transition to ordered water gels [Pollack 2001] with negatively-charged proteins, under ion gradients which reject Na^+ and attract K^+ , the latter leading to a compact ordered water phase transition leading to a stable gel phase cytoplasm without the need to impose a structurally unstable membrane and ion transport mechanism at the birth of the first cell to maintain a far from equilibrium thermodynamic limit cycle.

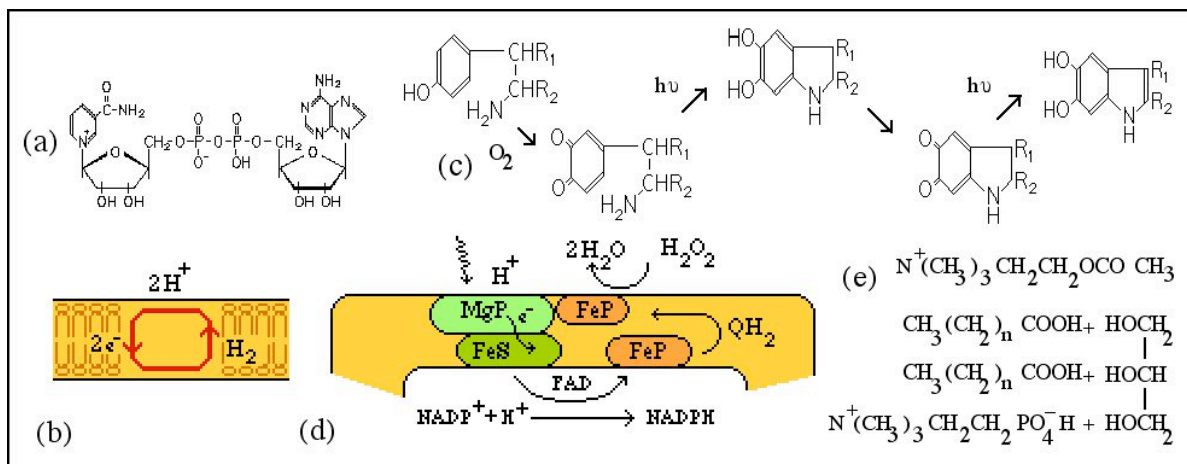


Fig 20: (a) NAD structure permits linkage of other energies to a redox bifurcation. (b) H^+ and e^- transport linked by H_2 in membrane due to insolubility of e^- and solubility of H^+ . (c) Prebiotic link between catecholamines and indole via quinone-type photoreduction. (d) Hypothetical form of primitive electron transport as a non-equilibrium limit cycle. (e) Acetyl-choline and phosphatidyl choline compared. Phosphatidyl choline lipid stacks tail to tail as shown in the clothes pegs (b).

9.4 Electron Transport

The fact that the proton is soluble in water to form the hydrogen ion, but the electron is not, unless attached to another group such as a protein, causes a physical linkage to exist between the polarity bifurcation and the charge bifurcations associated with electron and proton transfer, fig 20(b) mediated by H transport through quinone reduction, (c). Despite the complexity of modern electron transport in photosynthesis and respiration, there is considerable evidence that membrane electrochemistry could have arisen before translation could produce coded enzymes. Firstly there is a consistent basis for the existence of many of the components of electron transport during the RNA era, since the nucleotide coenzymes NAD, FAD, a nucleotide-bound Mg and Fe-porphyrin ring similar to B12, a cysteine-bound FeS group [Hall et. al. 1974], possibly based on glutathione (g-glutamyl-cysteinyl-glycine) and quinones provide all the key components of electron transport in an RNA dependent but protein-free form, fig 20(d) [King 1990]. The Fe-S-centre has also been cited a basis for prebiotic metabolism as discussed in section 5.4. Russel and Martin [1999] in line with Wächtershäuser [2000] suggest a hadean scenario as a basis for a transition from an Fe-S dissipative cycle to peptide nucleic acids, however a similar event could happen as a hydrothermal phase in the RNA era.

Both porphyrins and quinones have obvious prebiotic syntheses and the primal role of nucleotide coenzymes has already been discussed. Secondly, membrane structure and the solubility differences between the electron and proton guarantee a link between electron and hydrogen ion transport fundamental to quantum symmetry-breaking. Electron transfer does not in principle require the complex coded active sites required to catalyze specific molecular transformations. Model systems using Fe-porphyrins and imidazole can couple oxidative electron transport to phosphorylation [Brinigar et. al. 1966] and photo activated Mg-porphyrin to phosphate [Goncharova and Goldfelft 1990, Lozovaya et. al. 1990]. These would initially have used H_2S as a substrate rather than the higher splitting energy of H_2O .

9.5 Glycolysis

Glycolysis forms a bridge between six and three carbon sugars, reversing the synthesis pathway from H_2CO , glycoaldehyde and glyceraldehyde to cyclic sugars, fig 14(b). Glycolysis is made energetically possible by phosphorylation, and releases high energy phosphate capable of driving other phosphorylations [Hermes-Lima and Vieyra 1989], fig 21(a). It is notable that glycolytic di-phosphorylation of fructose is homologous with the route for nucleotide formation of fig 15(c). The high phosphate environment leading to RNAs would then naturally lead to similar phosphorylation of other sugars, and release of the high-energy phosphate bond through cleavage of the sugar. Mineral catalysis associated with phosphate gives the glycolytic pathway a natural basis for lysis of sugars as a dissipative structure. Biological UDP-glucose coupling is consistent with nucleotide-dependent glycolysis in the RNA era.

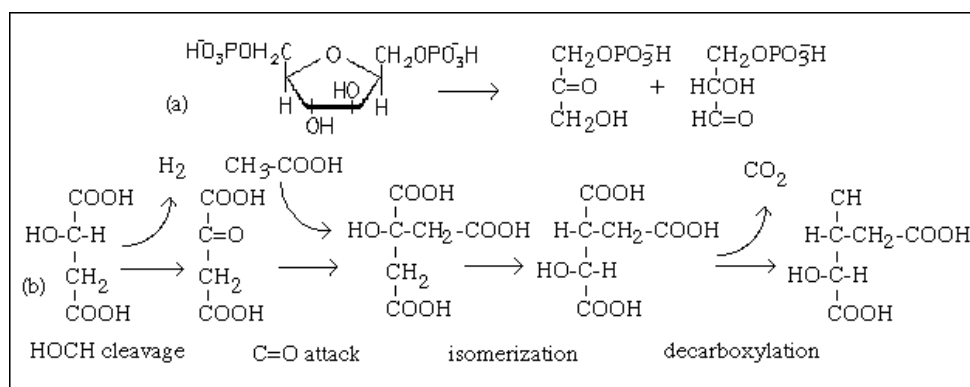


Fig 21: (a) Di-phosphorylation of sugars leads to glycolysis through interaction of charged phosphates. (b) Generic examples of group transfer in the tricarboxylic acid cycle.

9.6 The Tricarboxylic Acid Cycle

The tricarboxylic acid cycle forms a pool of multiply carboxylated molecules which carry CO_2 in various states of energy, and result in reducing energy via nucleotide coenzymes NAD and FAD, which coupled with the use coenzyme A provide a basis for the tricarboxylic acid cycle in the RNA era. This could have existed as a limit cycle of di- and tri-carboxylated molecules acting both as an acceptor of acetate (a carbohydrate-equivalent i.e. $(\text{H}_2\text{CO})_2$) and as an emitter of molecular CO_2 and reducing H, thus bifurcating carbohydrate level redox potential into reduced and oxidized components.

The linkage to nucleotide coenzymes such as NAD would have served to create a bifurcation of redox potential in the molecular milieu contributing to the diversity of reacting species. The cycle may have been hypercyclic [Eigen et. al. 1981] or chaotic, consisting of a population of molecules undergoing various generic transformations with net inflow of carboxylic acids and net emission of CO_2 and transfer of H, due to generic transformations as illustrated in fig 21(b). Isomerization would have been catalyzed by Fe^{2+} . Several steps may have been driven by sunlight photolysis [Waddell et. al. 1989].

The hypothesis that the central structures of molecular biology existed in the RNA era is consistent with their being chemical stability structures utilized by catalytic RNAs. The small genomes during the RNA era and limited catalytic capacity of RNAs by comparison with protein makes it likely that the emerging RNA-based system had to capitalize on existing chemical stability structures because it lacked enzyme-based biosynthetic pathways. Genetic takeover also places these stability structures in

a category determined by the cosmological milieu, thus giving evolutionary biology a cosmological foundation.

Together these systems answer in convergence the potentially diverse definitions of life drawn attention to by Clelland and Chyba [2002]. Eventually each of these systems became sequentially fixed into metabolic relationship by the evolution of genetically coded enzymes through the translation process, fixing nucleotide coenzymes, Fe-S groups, porphyrin-based factors and metal atom catalysis as markers of the original catalytic bifurcation landscape.

10.1 : The Precocious Origins of Life on Earth

Far from being an improbable accident taking billions of years to find the right conditions, life may have become established on Earth as soon as the conditions permitted a liquid water ocean. Either Earth was richly bombarded with complex organic molecules which quickly found within the diversity of microclimates on Earth some which were directly conducive to the processes leading to the genetic epoch, or life had already begun in the gas and dust cloud initially forming the solar system. Gustaf Arrhenius, [Mojzsis et. al.] studying tiny apatite grains in the Isua formation of Greenland, has found carbon 12 to 13 ratios consistent with the grains originating from living matter. The Isua rocks date from 3.85 billion years ago. Although oxygen-18 in zircon crystals indicate a solid crust 4.2 billion years ago, suggesting a cool start with liquid water hospitable to life [Valley et. al. 2002], no intact rocks have been discovered older than 3.96 billion years.



Fig 22: Modern stromatolites (left), generated by cyanobacteria (blue-green algae) Shark Bay, Australia. J. W. Schopf has found remnants of 3.6 billion-year-old stromatolites lying near fossils of 3.5 billion-year-old cells that resemble modern cyanobacteria (right). Life thus arose within the first billion years of earth's formation from the planetary disc [Scientific American Feb 1991]. The moon and probably the Earth likewise was heavily bombarded with meteors up to 3.8 billion years ago, suggesting that life may have evolved on earth as soon as environmental conditions allowed. There is continuing debate about whether these chemical and 'fossil' traces, now further studied with Raman spectroscopy to give carbon isotope evidence, really represent early cyanobacterial life, prebiotic 'soup' or volcanic or meteorite material [Schopf et. al. 2002, Brazier et. al. 2002, Mojzsis 2002]. However some researchers contend on the basis of inorganic simulations that these microfossils are purely mineral [Hogan 2003]. Jacques Touret [2003] has found that methane as well as high salt water trapped in pillow lava from Isua suggesting the involvement of hydrothermal vents beside an undersea volcano. However these findings are questioned by David Vanko [Necht 2003]. John Parnell has also suggested radioactivity trapped in oily grains may have

had a role [Lawton 2003]. In any case there is consensus agreement that life was under way by 3.5 billion years the age of the fossil stromatolite in fig 22, although the nature of these is also debated. These fossils could be the earliest evidence of life on Earth, yet these relics, with names like Chromococceae and Oscillatorioceae, are morphologically identical to modern cyanobacteria that cover the globe from Antarctica to the Sahara [Cohen 1996].

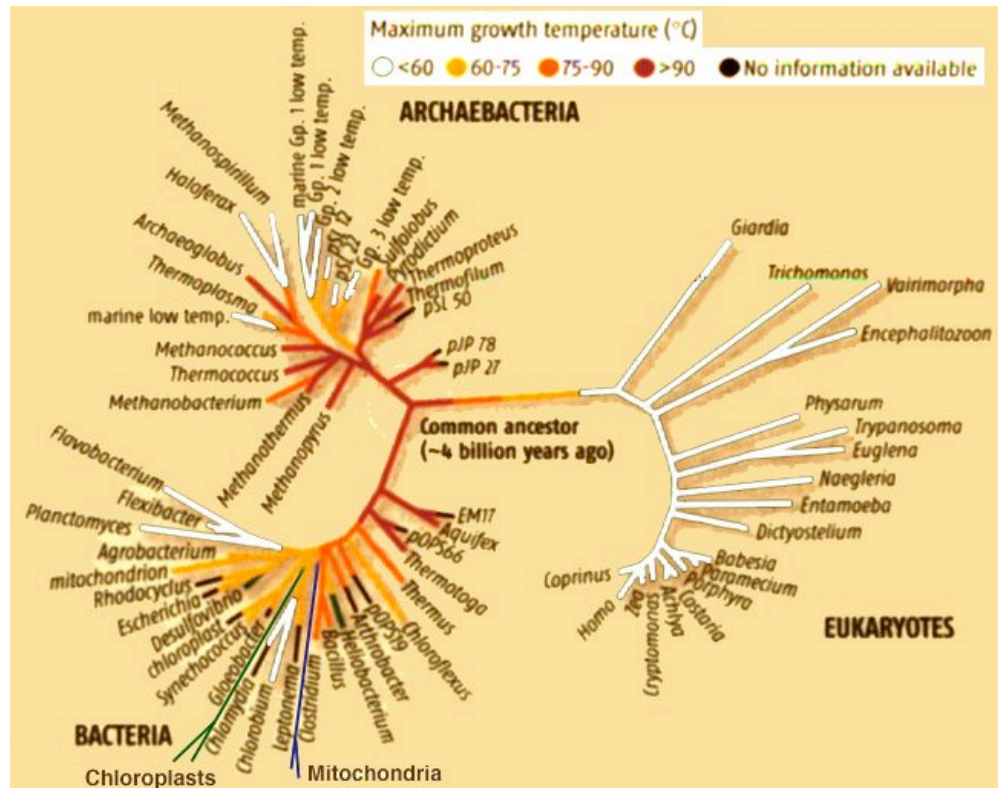


Fig 23: The root of the tree of life [ex Pace Anathswamy]: shows the division into archaea, bacteria and eucaryota, with subsequent divisions of eucaryotes into multicellular plants, animals and fungi (zea, homo and coprinus). Earliest branches of bacteria and archaea are thermophiles (red).

Symbiotic mitochondria and chloroplasts are also shown. Recent adjustments of the tree (inset) suggest a cold start, with the thermophiles peripheral specialized adaption [Brochier and Philippe] and planctomycetes, which share budding and an encapsulated nucleus with the eucaryotes, close to the root. Tertiary analysis is also consistent with a eucaryotic origin [Caetano-Anolles].

The emergence of the eucaryotes that led to the higher organisms is also very ancient. Compounds in traces of oil extracted from Australian shale suggest that eucaryotic cells, which make up all life on Earth except for bacteria, had evolved as early as 2.7 billion years ago. It is not until about 2.1 billion years ago that fossil imprints appear in the geological record that are so large that they can only be eucaryotes. A team of researchers in Australia has found steranes, molecules with 26 to 30 carbon atoms arranged in four rings, in droplets of oil extracted from rock 700 metres below the surface in the Pilbara region of northwestern Australia. These are produced by the decay of cholesterol and other steroids found in the membranes of eucaryotes, but not bacteria [Brocks et. al.].

10.2 Universality Three Realms, Five Kingdoms and the Auto-heterotrophic Bifurcation

The five kingdoms of plants, animals and fungi, protista and prokaryotes, are now known to be completed by the archaea, grouped into three realms with eucarya and bacteria. These divisions reflect major bifurcations of the thermodynamic and metabolic environment. There is a fundamental bifurcation of energy metabolism between photosynthetic fixation of incident solar energy, the principal incident energy source at the planetary surface, and all other forms of heterotrophic energy-pillaging budget, including animals as frank predators, fungi as saprophytic and symbiotic decomposers, the highly catalytic biochemical pathways of prokaryotes subtended by the diverse partially differentiated protista. The biochemical basis of both photosynthesis and respiration is through a common electron transport pathway which utilizes primal molecules such as porphyrins and nucleotide coenzymes as receptors. The major divisions of life are thus clearly universal in nature. Such universality also extends to the formation of excitable cells using amine-based neurotransmitters and ion channels.

Williams and da Silva [2003] note a series of major evolutionary developments as reactions to bifurcations in the environment precipitated in turn by previous evolutionary innovations, establishing the idea that many stages of evolution may be bifurcatory. These include the transfer from a reducing metabolism to oxidized form as a result of generation of O₂ by the biota, the role of Ca⁺⁺ and Na⁺ ions as expelled cytoplasmic poisons becoming cell signallers and mediators of excitation.

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