

Clay Minerals – Blueprints of Early Life

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A. Background

Aside from helium, living and cosmic matter are principally composed of the same chemical elements, hydrogen – oxygen – carbon – nitrogen, reading in order of abundance, as: C – O – H – N vs H – O – C – N. In contrast, the Earth has an entirely different bulk composition iron – oxygen – silicon – magnesium.

In comparing the various patterns one might suggest that living matter sprouts directly out of the ancestral universal matrix, whereas terrestrial matter must be a late derivation product of that matrix. Only oxygen ranks high in all three compartments: cosmos, life, and earth. Thus, it is tempting to look for the roots of life in outer space. Actually, such an attempt is in strong contrast to textbook dogma where the origin of life presupposes a synthesis of vital monomers in a reducing terrestrial atmosphere by means of high energy radiation. A subsequent “raining out” is assumed to have led to a “primordial organic soup” from which physiologically interesting polymers and eventually the first living cell arose (Oparin 1953).

To prime the pump of my antithesis, a few details on the distribution of matter in interstellar space and its fractionation in the course of solar and planetary evolution are needed. Its further assemblage in the direction of a workable cellular system by way of mineral templates and

globular aggregates will represent the essence of my subsequent presentation.

B. On Matter in Dark Molecular Clouds

Our galaxy, the Milky Way, would look if seen from the outside somewhat like a galaxy in Ursa Major, M81, just 9 million light years away from us (Fig. 1). About 100 billion stars are contained in this magnificent spiral about 100 000 light years across, and quite a few may have planets like the Sun. Our solar system would occupy a place close to the medium plain of the spiral about one-third the distance of the total diameter removed from the galactic center. We need roughly 250 million Earth years to circumnavigate the galactic center. Accordingly, this period of time has been defined as 1 cosmic year.

Of the mass we can account for in our galaxy, about 95% resides in stars and the rest is interstellar gas and dust in a ratio of about 99 to 1. However, this interstellar matter is not uniformly distributed throughout the galaxy but is concentrated in the form of clouds in regions close to the galactic plane of symmetry, where new stars are born. To most of us, clouds are seen more in conjunction with weather and climate. Namely, water vapor will condense and form clouds of different sizes and shapes, which are freely moving, can become dispersed or aggregate, and form a cloud cover. Some regions are more cloudy than others. In due course, they will rain out and the meteorological cycle will commence again with the evaporation of water bodies. In analogy, interstellar clouds, a few

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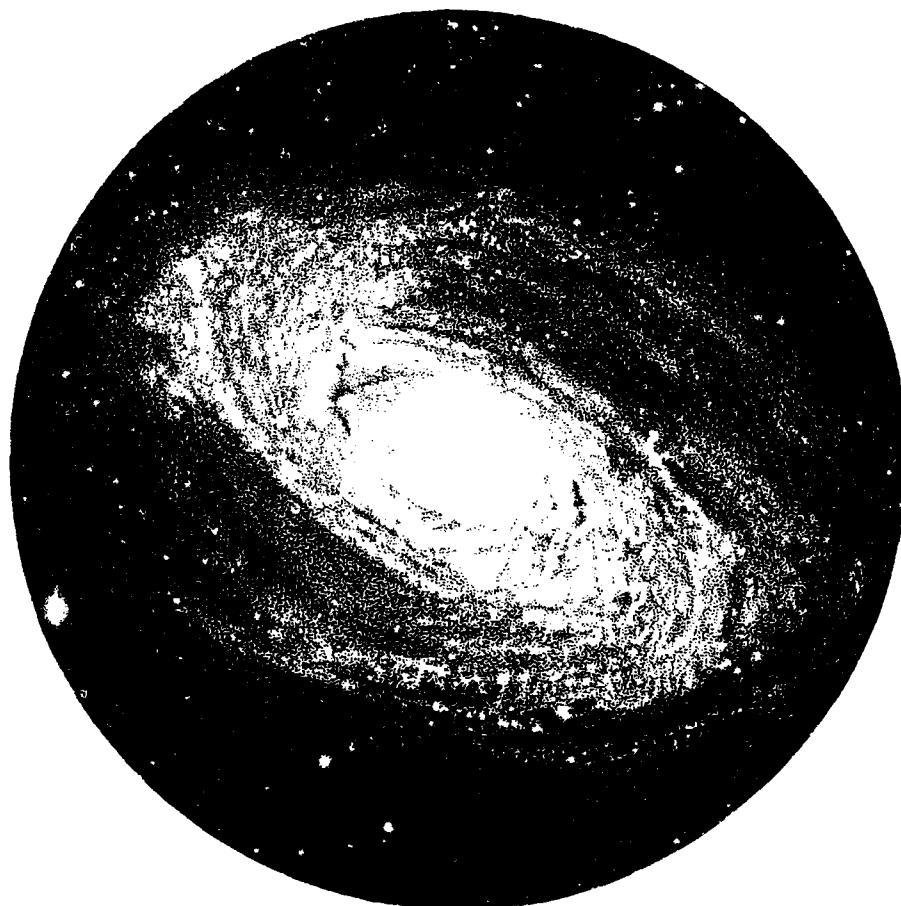


Fig. 1. Galaxy in Ursa Major, M81, about 9 million light years away from us

light years or more in diameter, are in constant slow motion around the galactic center. In their perpetual wandering through galactic space, they may grow in size or collapse. During 1 cosmic year, an average cloud could conceivably double its mass in sweeping up dispersed interstellar gas and dust. Once a critical size is reached or a nearby supernova explosion occurs a cloud can rain out, that is collapse, yielding stars and satellites of various sorts.

Now a word has to be said on the chemistry of cloud complexes. Research on giant interstellar clouds by means of astrospectrographs and radiotelescopes was initiated in 1963 by a team of the Massachusetts Institute of Technology and the Lincoln Laboratory. The most crucial finding was the observation that cloud complexes contained in addition to H_2 a variety of molecules. By including all isotopic species, close to 100 different types of molecules were recognized. A molecule of particular relevance is car-

bon monoxide because its radiation properties at low temperatures make the molecules an excellent signpost for the mapping of cloud complexes. However, the most dominant molecule is hydrogen, in a concentration of about $10^4 H_2$ per cm^3 . This value represents ca. 99% of the mass of a giant molecular cloud. The remainder of the molecules are just "impurities", but considering the size of a cloud, they can pile up to a rather substantial stack of matter. For instance, trace constituents such as carbon monoxide, water, methane, formaldehyde, methyl alcohol, ethyl alcohol, hydrogen cyanide, ammonia, or the hydroxyl radical far exceed all the mass contained in our solar system. Ethyl alcohol by itself could readily fill up the whole Earth with 100-proof "whiskey."

In a cloud complex all carbon is molecularly bound, that is, no atomic carbon remains. For oxygen, 30% has entered a complex organic molecule. For nitrogen and sulfur compounds present in the in-

terstellar medium, the data bank is not sufficient to make a tentative assignment as yet.

As far as the "dust" goes which represents about 1% of the total matter, we are essentially dealing with ordinary minerals, <0.5 micron in size, such as Fe-Mg silicates, native iron, and graphite – the same stuff earth is principally made of. The presence of solid particles has numerous consequences for the synthesis and protection of organic molecules in the environment of space. For example, the probability of collision between atoms and molecules is enhanced, and three-body reactions become feasible. Moreover, mineral surfaces may provide not only a convenient "resting place" for certain atoms and molecules, but by virtue of their crystalline order, catalysis and epitaxis may ensue. The generation of more complex molecules such as sug-

ars, amino acids, or the bases of the purines and pyrimidines is conceivable, but their detection requires more sophisticated technologies.

In brief, the chemistry of giant molecular cloud complexes is basically one of hydrogen, oxygen, carbon and nitrogen, judged by the prevalence of molecules containing C-O-H-N. It is noteworthy that in the presence of a mineral catalyst, simple organic molecules such as formaldehyde or hydrogen cyanide are expected to yield biochemically interesting monomers, for instance, sugars, amino acids, purines, and pyrimidines. Laboratory experiments done under low-temperature conditions have indeed shown the feasibility of a rapid synthesis of these compounds. In Fig. 2, the steps involved in the synthesis of common sugars in a formaldehyde-clay system are schematically shown. All of this can be used as

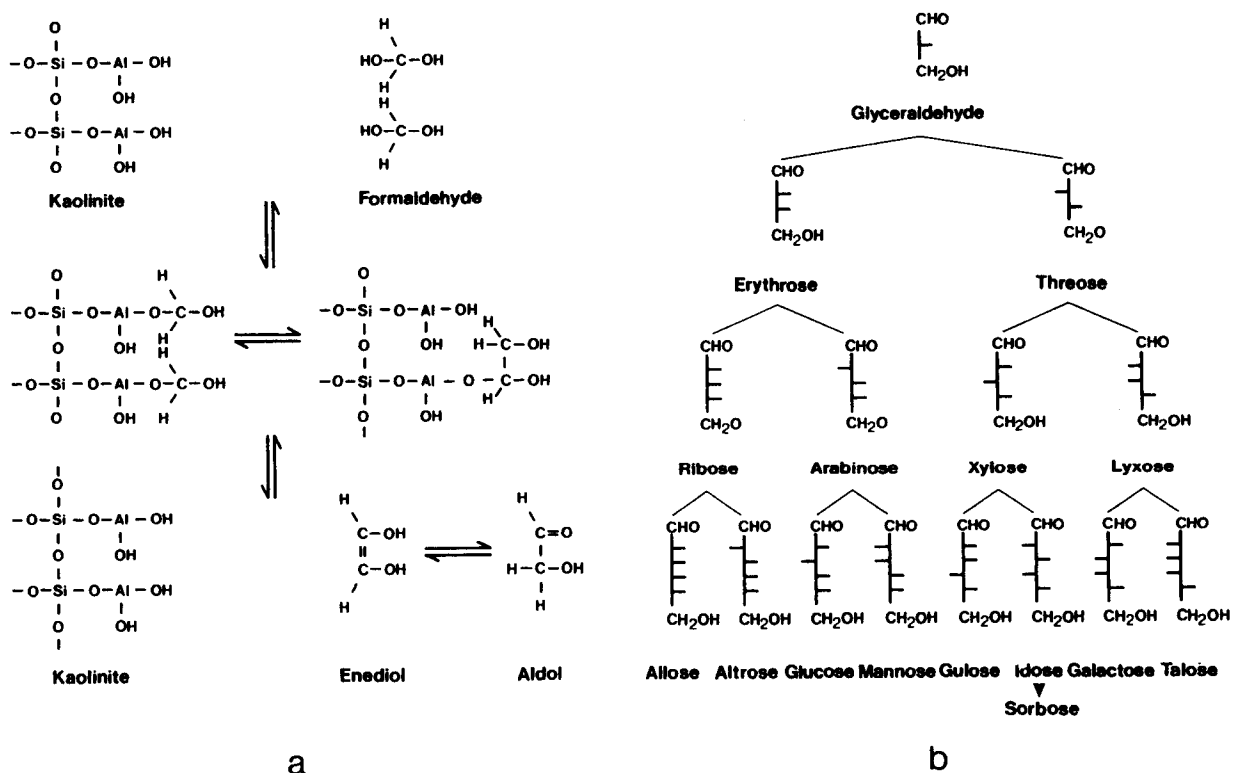
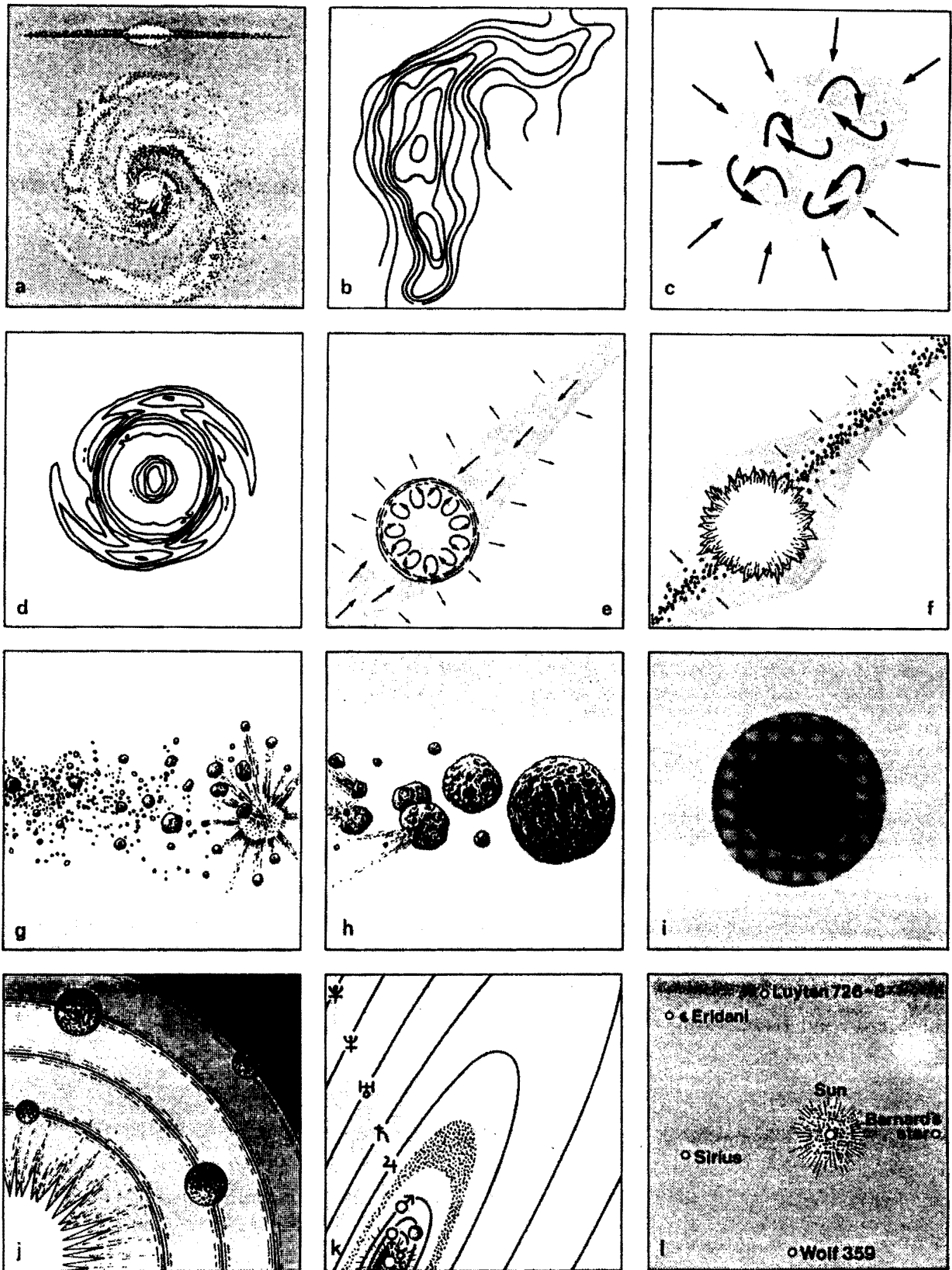
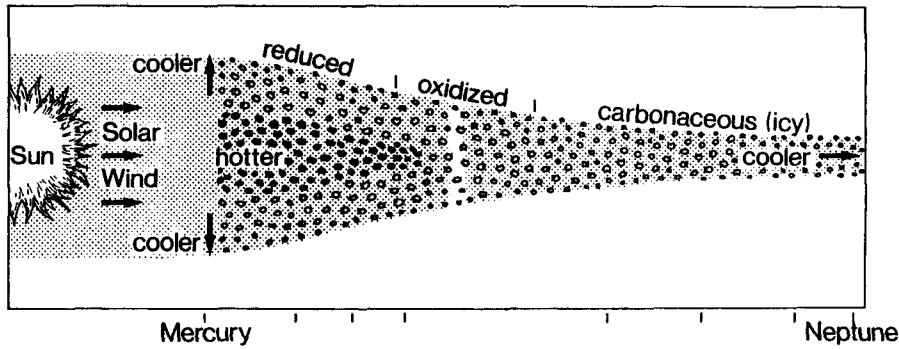


Fig. 2. a Possible sequences for kaolinite-catalyzed reactions. b Addition of one unit of formaldehyde at a time to D-glyceraldehyde in the presence of kaolinite would result in the distribution of the sugars illustrated. Thermodynamic factors, such as steric repulsions of hydroxyl groups, play an important role in the distribution of sugars

Fig. 3 a-1. Diagram showing major steps in the evolution of the solar system (from upper left to lower right): a Whirlpool galaxy, similar to Milky Way, about 100 000 light years in diameter; frontal and edge-on views. b Contours of a giant molecular cloud complex, a few light years in



diameter revealed by the radiation of carbon monoxide at 2.7 mm ^{13}CO radio line. **c** Collapse of molecular cloud complex possibly triggered by supernova event. **d** Rotating solar nebula in statu nascendi with the proto-Sun evolving in its center. **e** Formation of accretion disk; *arrows* indicate motion of gas. **f** Aggregation of particles along midplane of accretion disk. **g** and **h** Accretion from dust, to planetesimals, to planets. **i** Retention of primordial atmosphere by a large planet (e.g., Jupiter) **j** T Tauri phase, sweeping off “excess” primordial gases from the solar system leaving atmosphere-free terrestrial planets behind, **k** Spacing of the orbits of the planets (*astrological symbols*) and the asteroids (*dotted area*). **l** Oort’s cloud (comet reservoir) surrounding the Sun with a radius of about 1 light year in relation to the nearest stars



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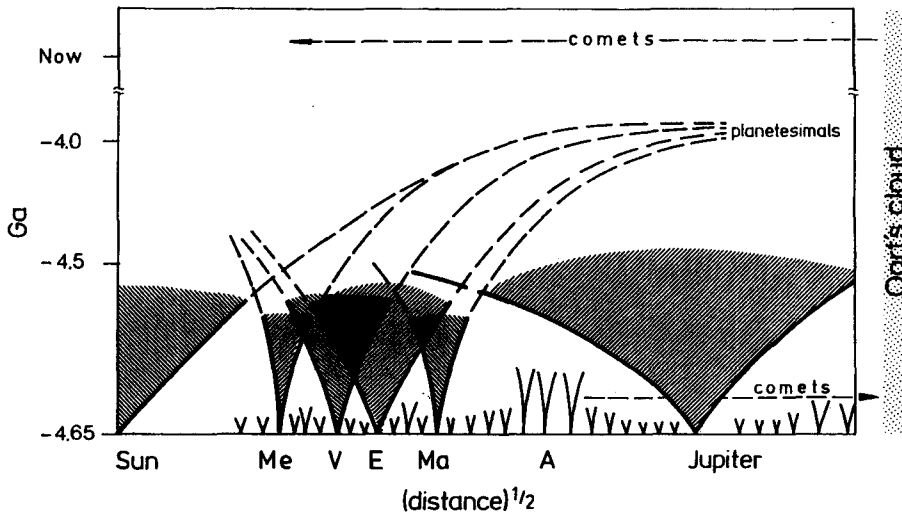


Fig. 5. Diagram showing planetesimals to planets. Feeding zones widen with time in accordance with the growth rate of the protoplanet, eventually yielding overlap of zones. Major surviving feeding zones give rise to planets and asteroids which are displayed at the square root of distance from the Sun. Planetesimals ejected from giant planets yield cometary bodies, which accumulate in the Oort cloud, from where they become episodically ejected and reenter the solar system. Bombardment of the terrestrial planets by comets and asteroids throughout the ages has been omitted for graphical reasons

indication that a dark molecular cloud is a gigantic ice box for all sorts of organic molecules just waiting to become defrosted, processed, and utilized for the construction of a cell, once the environment turns hospitable to the creation of life.

The first step to achieve this goal is the collapse of a molecular cloud and to illustrate this I have drawn three diagrams. The first (Fig. 3) shows critical events – one by one – that have led to the formation of our solar system. The second (Fig. 4) illustrates the wide range in temperature and oxidation states that prevailed during the formative years of the planets. The third (Fig. 5) elucidates the logic behind the enormous variations in the size of the planets. The situation

revealed in Fig. 5 somehow reminds me of a little boy throwing small rocks horizontally across a water surface, from where the flat pebbles bounce off numerous times – high and low – till their momentum runs out.

Earth has received a tiny share of all types of incoming debris: first the hot and highly reduced irons, then the stones, and finally the icy and oxidized material containing gases, water, organic molecules, and clay minerals. The last dowry may be viewed as frosting on top of a cake which in due course led to air, sea, and life.

The tripartition of Earth into core, mantle, and crust is a reflection of the stepwise accretion of the proto-Earth.

Since the last incoming material – our “frosting” – is assumed to have formed a layer about 700 km thick around the globe, there certainly were organic molecules galore available to trigger life.

C. Crystalline Blueprints

Rock-forming minerals are principally composed of oxygen ions which have as their main coordination partners silicon, aluminum, iron, calcium, magnesium, sodium, and potassium ions. Crust and upper mantle may thus be viewed as an ionic oxysphere. Crystals may contain charge deficiencies, structural irregularities, lattice defects, and, in hydrated varieties such as clays, may even develop hydrogen bonds.

To structure our discussion, I will begin with a process commonly described under the heading “epitaxis,” a term derived from the Greek *tassein*, meaning to arrange or to organize.

The growth of crystalline material on other crystal surfaces is a well-studied subject in the field of crystallography. Epitaxis can also proceed on organic templates with the resultant formation of biominerals in teeth, bones, or shells. Furthermore, organic polymers can promote the synthesis of other organic polymers, and the living cell is vivid proof of that. Finally, mineral surfaces may provide sites for activation and protection of functional groups displayed by organic molecules, and may accordingly serve as polymerization matrix. Thus, one can distinguish between four systems in which one partner represents the template and the other partner the epitaxial product (Table 1).

Epitaxis on solid-state surfaces should be viewed in relation to catalysis because both processes follow a similar reaction path. Catalysis represents a process in which a solid-state surface “tries” to establish a thermodynamically favorable phase transition structure with the adsorbent. Phase-transition structures emerge which, when chemically stable, lead to

Table 1. Four systems of templates and epitaxial products

Template	Product
Mineral	Mineral
Biopolymer	Mineral
Biopolymer	Biopolymer
Mineral	Biopolymer

oriented intergrowth. In contrast, should transition structures introduce a chemical change of the adsorbent such as polymerization, hydrogenation, dehydrogenation, etc., we are dealing with catalysis. Principles of cellular catalysis, as, for example, executed by enzymes, are identical to those observed in mineral systems. Catalysis constitutes a flow of epitaxial associations, whereas epitaxis involves a “frozen in” transition structure provided by a morphological catalyst.

With the help of clay minerals, chemical synthesis of a number of physiologically interesting polymers has been successful; this particularly concerns the formation of peptides. The mechanism involves carboxyl activation and the inactivation of functional groups not participating in the formation of the amide bond by so-called protective groups displayed along mineral surfaces. The relationships for a kaolinite-amino acid system are schematically illustrated in Fig. 6. In the presence of kaolinite, amino acids will be picked up from an aqueous solvent and brought into solid solution. Amino groups become hydrogen bonded to structural oxygen, or in the case of basic amino acids, occur as positive ions. They are tightly fixed to the silicate surface, and thus rendered inactive. Carboxyl groups associated with charged Al-oxy-hydroxy groups by means of ionic bridges become directly attached to the aluminum.

In water, amino acids cannot polymerize because of dipole-dipole interactions. In solid solution, however, amino acids will polymerize, because the solvent medium does not interfere, and because

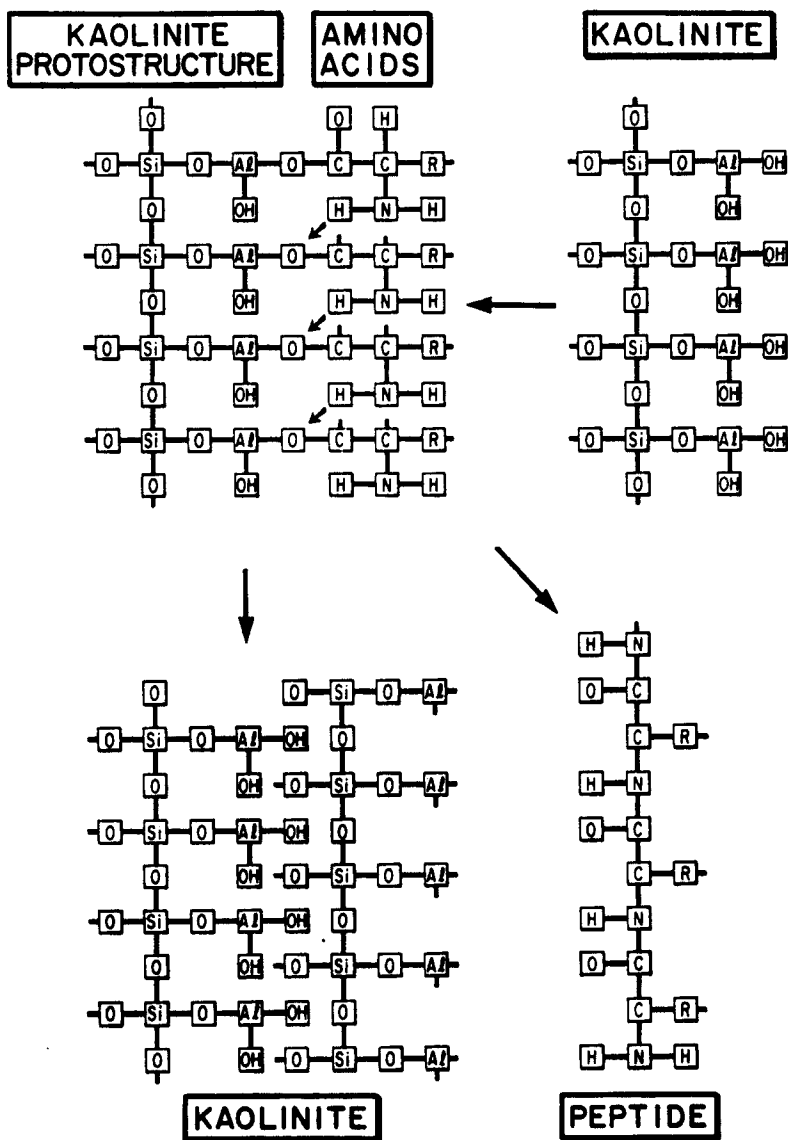


Fig. 6. Polymerization of amino acids along clay templates

this reaction step is favored energetically. In the kaolinite experiment, about 1000 times more amino acids were polymerized to peptides than could conceivably become adsorbed to the clay surface. In consequence, a flow of freshly polymerized molecules across the catalytically effective mineral surface has to be postulated. Kaolinite is also instrumental in preferentially synthesizing pentoses and hexoses from formaldehyde and transforming them into polysaccharides. Kaolinite can also generate fatty acids and entertain esterification reactions leading to glycerides. Furthermore, addition of calcium phosphate to an aqueous mixture of kaolinite, glycerol, and palmitic acids may yield phospholipid monolayers which are deposited in epitaxial order with a 40 Å periodicity on

the crystal surface of kaolinite as ascertained by transmission electron microscopy. In essence, all principal building blocks of life have been synthesized by employing a variety of crystalline blueprints.

A remarkable characteristic of life is that all peptides and proteins are exclusively composed of the L-optical isomers of amino acids. Preferential polymerization of L-amino acids on kaolinite can be attributed to the inherent enantiomorphism of the edges of the octahedral layer of kaolinite (Fig. 7), and to the fact that kaolinite crystals are either entirely right-handed or entirely left-handed. Quite a number of ordinary minerals exhibit chirality. The fact that common carbohydrates such as cellulose, starch, or cane and beet sugars (sacrose) are composed

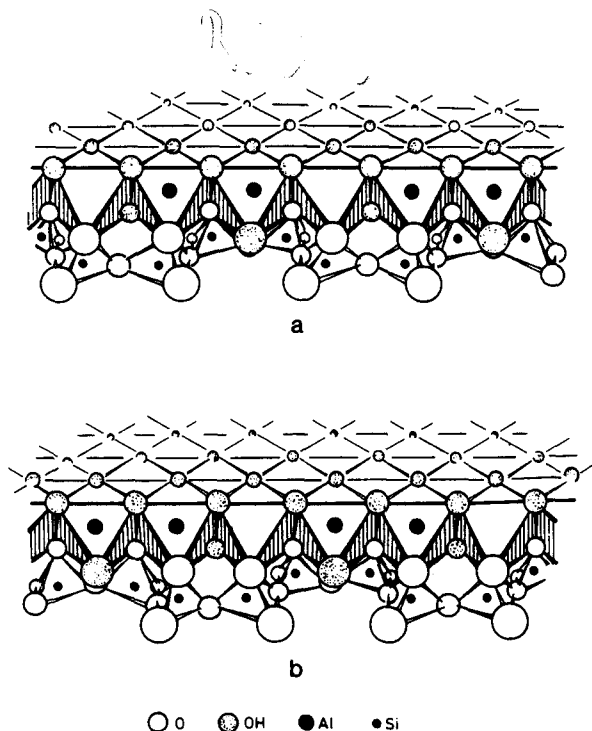


Fig. 7 a, b. Schematic representation of the edge of a kaolinite crystal of ideal composition (a), and its mirror image (b) viewed along the *a*-axis

of D-configured monomers can also be related to the optical activity of the archaic mineral matrix.

The structural shape of biomolecules, which is a key element of cellular function, is asymmetric. It is conceivable that on the prebiotic Earth left- and right-handed polymers were generated by mineral printing machines having either D or L block letters. Once the first organism had chosen the L-configured amino acid polymer, or the D-configured sugar polymer, their mirror images had no chance to evolve further.

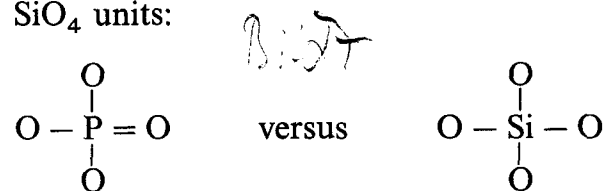
Summing up, crystalline blueprints are effective devices for generating leading biomolecules and for promoting chirality. Clays are outstanding in this respect, but they only deliver semifinished products, not life itself.

D. Towards the First Living Cell

Considering the complexity of life it may come as a surprise that only about 300 monomeric building blocks, lots of water, and some salt are needed to generate all the vital stuff in the genetic and meta-

bolic apparatus. However, this stuff has to become neatly packaged into a cellular envelope in a manner able to fire the engine of life. So it seems that the most critical question has to do with the way membranes arise and of how that system is energized and autocatalytically maintained (evolution is hereby of no relevance because thermodynamically it constitutes just a disorder phenomenon). The answer is simple, life has adopted biophosphates for various structural and functional assignments.

In the biological sciences a quiet revolution is presently going on, namely the recognition that the architectural principles observed in biophosphates are identical to those established in the inorganic phosphates. The early adoption of the name phosphorus, the carrier of light, has not lost its true meaning over the centuries. Phosphorus, in the form of phosphate bonds, is the carrier of energy in the living system. It is the "energy currency" as George Wald so nicely put it, which becomes printed, exchanged, and converted at various rates in the perpetuating cycle of life. It is phosphorus which controls the structure and shape of cellular material and which thus selects the energy transfer sites. Thus, in the element phosphorus lies the answer to the question of what distinguishes life from an ordinary mineral. Life is based on PO_4 units, and rock-forming minerals on SiO_4 units:



It is essentially the π electron – the high energy bond – in PO_4 which maintains the animated world. Since the π bond can lie "parallel" to any of the four sigma bonds, giving rise to a variety of differently shaped tetrahedra, a flexible and dynamic tetrahedra network can be created. It is principally the type of metal ion adopted by PO_4 that shapes the tetrahedron. In contrast, the SiO_4 unit has "just" four sigma bonds which only per-

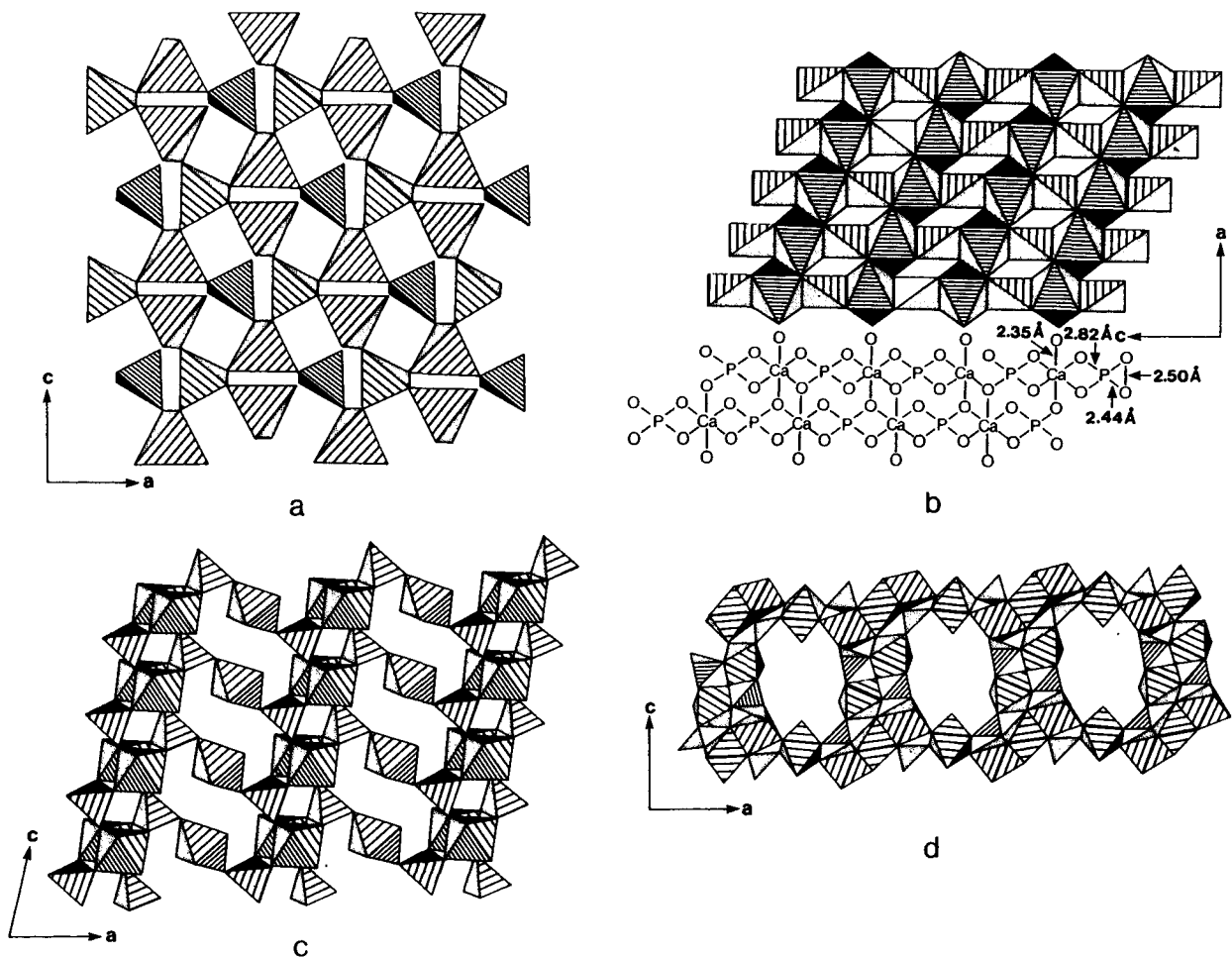


Fig. 8a. Gallium phosphate, GaPO_4 . Each PO_4 tetrahedron is joined to four GaO_4 tetrahedra. **b** Molecular structure of a sheet composed of phosphate-calcium chains developed in dicalcium phosphates: $\text{CaHPO}_4 \times 2 \text{H}_2\text{O}$, $\text{CaHPO}_4 \times \text{H}_2\text{O}$; water is not shown for graphical reasons. **c** Iron phosphate: $\text{Fe}_3(\text{PO}_4)_2 \times 8 \text{H}_2\text{O}$. The PO_4 groups are shown as tetrahedra. **d** Molecular structure of beraunite: $\text{Fe}_{0.5}^{\text{II}}\text{Fe}_{2.5}^{\text{III}}(\text{OH})_{2.5}(\text{PO}_4)_2 \times 3 \text{H}_2\text{O}$

mit the establishment of rigid networks. How can we possibly imagine such networks to look alike? To overcome difficulties in visualizing order phenomena, for instance, in biological membranes, examples of known layered phosphate structures in ordinary minerals are presented for illustration (Fig. 8). Phosphate tetrahedra and metal ion oxygen polyhedra can combine to a variety of geometries including undulating surfaces or concave/convex perforated surfaces. These loosely arranged space fabrics exhibit selective molecular sieve properties and ion exchange characteristics.

Phospholipid membranes are expected to exhibit identical properties and structures as they exist in inorganic phosphate

crystals, even including holes and surface granularities. It is proposed that the interchangeable nature of metal ions causes membranes to act as *dynamic molecular sieves*. Their pore size and shape must be quite variable as a function of type and availability of metal ions which in the last instances are enzyme controlled. Assuming adenosine triphosphate (ATP) is capable of trapping metal ions but adenosine diphosphate (ADP) is not, a periodic pulsation of the membrane lattice is the consequence.

What we learned in this brief discussion on the structural and functional relationship between inorganic and biotic phosphate "membranes" may now permit us to understand better the mecha-

nisms behind the origin of cellular structures at the dawn of time. It all has to do with the ability of phospholipids to jointly with metal ions construct stable fabrics and become separated from the aqueous medium. Experimental data on emulsions and foams show that micelles equipped with anisotropic membranes are able to grow at the expense of other micelles by consuming them through surface attachment (lowering in surface energy) in a process called emulsification. These globules, soaps, or emulsions as they are termed exhibit an optimal critical diameter in the order of 10^3 to 10^4 Å. The main feature of this water-organic system is an anisotropic and charged phase boundary layer. The newly generated macromicelles created in a process termed *coacervation*, will envelop water droplets, whereby the original micelle content is exchanged but according to laws different from those established in aqueous systems. That is, condensation of lipid membranes towards a rigid membrane is achieved by the uptake, for instance, of cholesterol or metal ions. The expulsion of water proceeds during intercellular attachment by means of oxygen-coordinated metal bridges. Due to the ionic fabric closely attached to the coacervate, dissolved organic molecules such as peptides or carbohydrates are bonded and precipitated on the membrane surface. In the course of coacervate development structures will arise which are enclosed by a double phospholipid skin (bilayer membrane). Phosphate groups become oriented towards the aqueous phase and double layers may combine to multilayered stacks. Membrane pouches come into existence, resulting in the formation of multichambered coacervates bearing striking resemblance to mitochondria. Judged by the conservative nature of mitochondria, it appears that, as a system, it still carries relics of its abiotic origin. The development of such a self-controlled reaction agrees with the thermodynamics of system behavior. A stable cyclic process can exist in the vicinity of a stationary phase and may operate

repeatedly an infinite number of times without ever passing through the stationary phase itself.

In conclusion, the primordial metabolism of the coacervate was in all probability maintained by means of a reversible phosphorylation cycle. In consequence, the origin of metabolism is in no way linked to the development of the genetic transcription apparatus. It must be considered an independent formation process. For this reason the abiotic origin of phosphorylation must be regarded as an equally important step towards the creation of the primordial cell. The problem, therefore, centers around the question of how to polymerize the common monophosphates into di-, tri-, or tetraphosphates, since polyphosphates are unstable in natural environments. The only reasonable choice left is to place the polymerization event within the coacervates. It is conceivable that phospholipid solid-state surfaces served in this capacity, because inorganic mineral surfaces too act as templates and furthermore may catalyze phosphorylation as has been demonstrated for apatite crystals.

The establishment of an interconnected and chemical reaction pattern for the coacervate system as a whole exists when phosphorylation can be maintained. This requires a constant supply of organic molecules and metal ions that are consumed, or utilized during this development. In this manner, a certain *modus vivendi* is established. Sources of energy were oxidizable organic compounds in the ambience. Molecules such as amino acids or sugars must have been present in huge quantities in the environment in view of their mineral fabricated origin.

So far, however, no vital power was involved. It is postulated that a primitive heterotrophic metabolism improved progressively. Its development took shape independently of the evolution of the nucleic acids and the genetic code. By superimposing the two separately developed entities, (a) the genetic apparatus, and (b) the heterotrophic metabolism, the primordial cell came into existence.

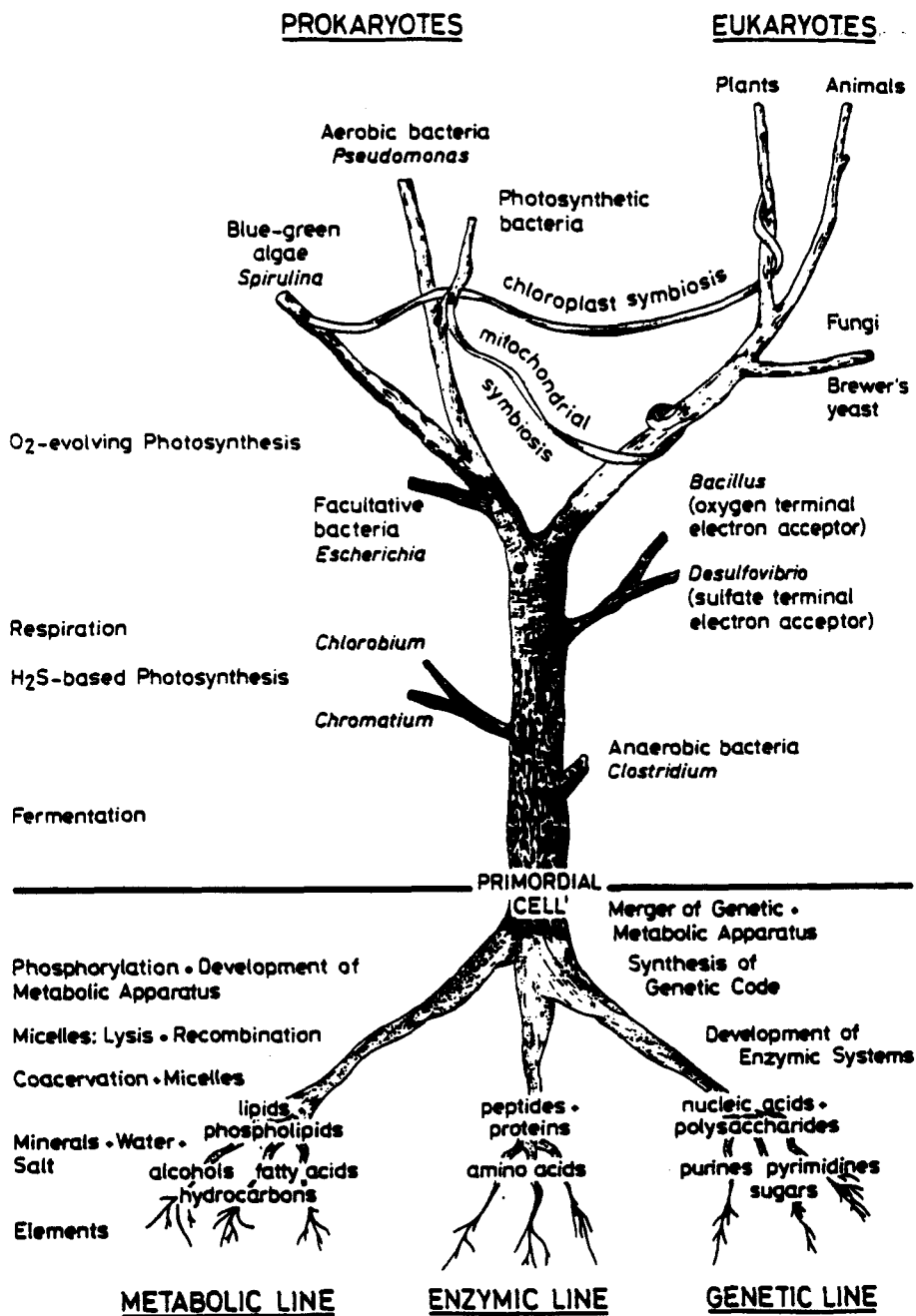


Fig. 9. Composite evolutionary tree (schematic) summarizing the principal steps in chemical and biological evolution. The sequence of events depicted for chemical evolution follows from the discussion in the text. The upward progression from anaerobic to facultative to aerobic forms is indicated in the shading pattern. Mitochondrial and chloroplast invasions are roughly drawn between points of suggested origin and uptake, respectively

The primitive metabolism of coacervates was kept "alive" via phosphorylation processes and became embodied by the self-reproducing cycles. It is likely that the nucleic acids were able to encode polypeptides utilizing certain metal ions. Alternately, nucleic acids succeeded in adopting the available metalloproteins in their environs – among which must have been enzymes in the billions – for their own reproduction. In any event, the link between the two independently developed events, (a) the primitive metabolism, and (b) the genetic reproduction apparatus is represented by the peptides.

They are the essential tool by which coacervate metabolism – for the purpose of nucleic acid replication – was utilized.

The structure of phospholipid membranes and the genetic code are archaic elements – biochemists generally use the term "universal elements" – which remained steadfast in the course of evolution. In Fig. 9, the three modes of life leading to the first living cell, the progenote, are schematically depicted. The compost of life started to form in dark molecular clouds. Once on Earth, the metabolic, enzymic, and genetic lines took shape, and progressed independent-

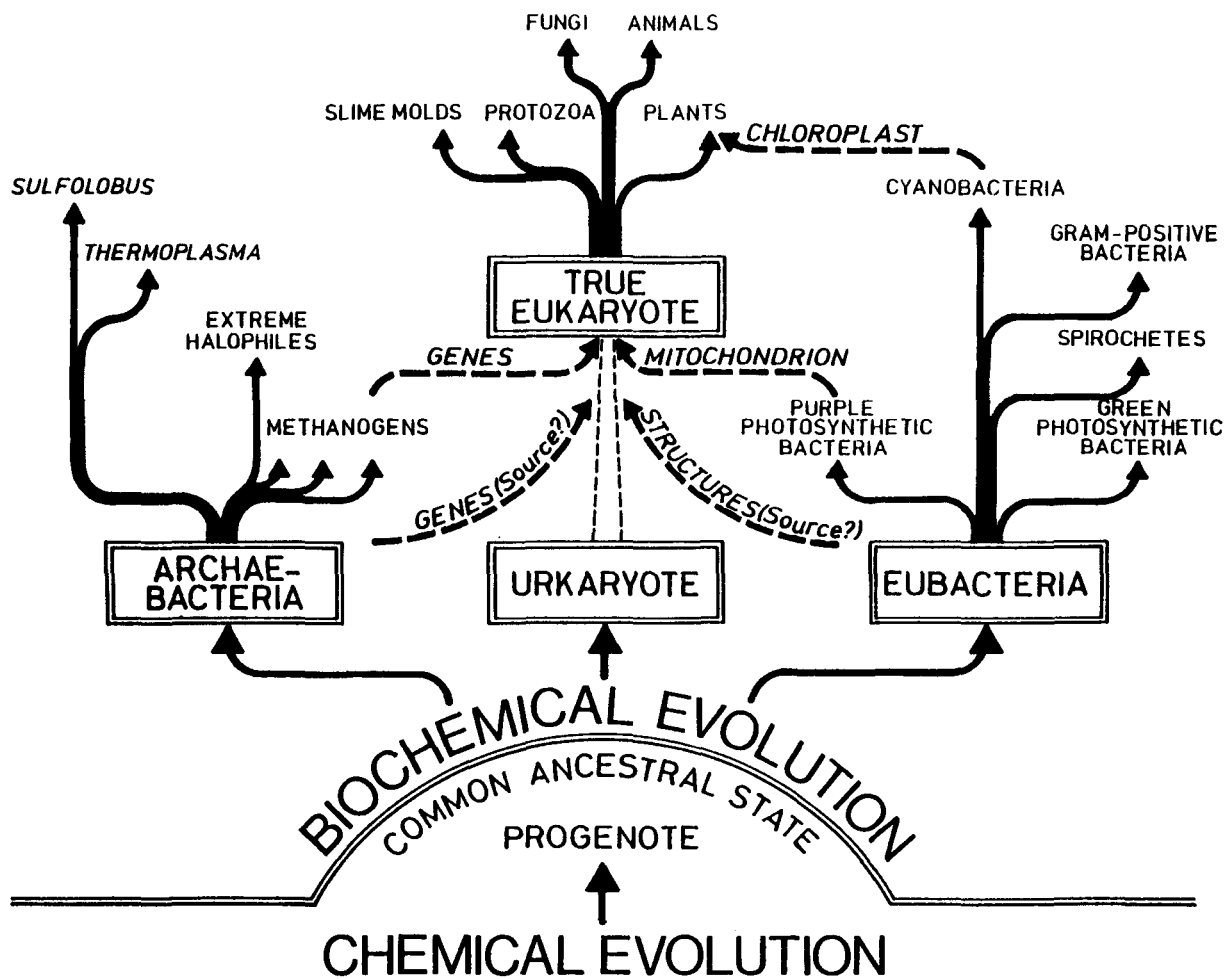


Fig. 10. Biochemical evolution starting from a common ancestral state: the progenote (highly schematic)

ly to eventually merge into the *progenote*. The subsequent evolution based on protein and nucleic acid sequence data, has been constructed in the form of a composite "evolutionary tree" thus linking the eukaryotes directly to one kingdom of the prokaryotes, the true bacteria or eubacteria. Although it is tempting to use such a tree in order to draw conclusions with respect to the sequence of events such as the start of (a) photosystem I, (b) photosystem II, (e) respiration, (d) sulfate reduction, etc., recent work using the 16 S ribosomal RNA sequence suggests a different scenario. Data indicate that three lines of descent diverged before the level of complexity usually associated with the prokaryotic cell was reached, that is: archaeobacteria, eubacteria, and 'ur'eukaryotes. All three lineages were independently derived from a common progenote (Fig. 10).

E. Final Comment

We have come a long way during this presentation. I have "crudely" abstracted from the wealth of data available on the origin of the first living cell, but still hope that my "nutshell" approach has provided at least some idea of the work being done in a field of science involved with unraveling the mysteries of life. A more comprehensive treatise may be consulted (Degens 1989) for special references or to obtain further details on the roots and evolution of the biological cell in the course of more than 4 billion years of Earth's history.

References

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