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Stochastic Prebiotic Chemistry within Realistic Geological Systems

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Abstract: This review introduces its readers to a ‘stochastic approach’ to origins of life research, from the viewpoints of both prebiotic chemistry and geology. The idea of a “primordial soup” has been subject to extensive criticism from thermodynamic, biochemical and geochemical perspectives, yet recent advancements have made clearer the plausibility of this theory. Herein, we review the theoretical and experimental approaches which have previously been explored, among these modelling, laboratory-confined and geologically motivated experimentation. Of these, we consider organo-mineral interactions, uniting aspects of prebiotic chemistry and geology, to be an especially promising way forward. However, we aim here to advance current approaches by advocating a methodology involving chemical systems and their stochastic reactivity on heterogeneous geological surfaces. This models the origins of life as a continuity of chemical reactions in an analogue to the early Earth (Hadean) environment.

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Keyron Hickman-Lewis read for his degree in Earth Sciences at St Edmund Hall, The University of Oxford, graduating in 2015. Presently a doctoral student at CNRS Centre de Biophysique Moléculaire, Orléans, his research concerns assessing enigmatic chemotrophic biosignatures from the Early Archaean, decoding the surface environments of the early Earth, and using these discoveries to inform on the search for biosignatures in a potential Martian biosphere. He has also conducted research using novel techniques to unveil the three-dimensional character of Archaean microfossils and microbial structures. When not doing science, he performs regular concerts on piano and ‘cello.

Dr André Brack is currently Honorary Director of Research at the Centre de Biophysique Moléculaire, CNRS, in Orléans, France, where he founded and headed the astrobiology group. His field of expertise includes the chemistry of the origins of life and the search for extraterrestrial life. He is Fellow of the International Society for the Study of the Origin of Life, which he chaired for three years, and of the NASA Astrobiology Institute. He is also Honorary President of the European Astrobiology Network and of Centre-Science a center for science popularisation, which he founded and chaired.

Following BSc (1985) and PhD (1989) degrees in organometallic chemistry at Durham University, Terence Key spent 18 months as an SERC(NATO) Postdoctoral fellow at the Massachusetts Institute of Technology working with Nobel Laureate Professor Richard Schrock. He was appointed lecturer at the University of Leeds in 1990 and subsequently senior lecturer (1997) and reader (2010). TPK has been Visiting Professor at the Université de Cergy-Pontoise, France (1999) and CNRS Centre Biophysique Moléculaire, France (2016) and holds affiliate faculty membership in the Department of Astronomy, University of Florida, Gainesville, USA. He was an STFC-UKSA Aurora Fellow in Astrobiology (2009-12) and since 2010 has been president of the Astrobiology Society of Britain. TPK has authored or co-authored >100 published journal articles, books chapters and reviews. In 2004, TPK discipline hopped from inorganic chemistry to chemical astrobiology, publishing some 17 papers. He received the Research Award from the Astrobiology Society of Britain in 2008.

Frances Westall is a geologist now working in the very broad discipline of astrobiology, the study of the origins of life and its destiny in the Universe. After a PhD in marine geology at the University of Cape Town in South Africa, she worked in various research institutes around the world: the Alfred Wegener Institute for Polar and Marine Research in Bremerhaven in Germany, the University of Nantes in France, the University of Bologna in Italy, the Johnson Space Center and Lunar and Planetary Institute in Houston, USA and, for the last 15 years, she is Director of Research at the CNRS-Orléans in France where she heads the astrobiology group. Her research interests and activities cover study of the earliest traces of life on Earth and the geological environment in which they lived, the artifical fossilisation of bacteria, the search for life on Mars, especially with the ESA/Russian ExoMars 2020 mission, and prebiotic chemistry and the origin of life.

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1. Introduction

1.1. Rationale

What is our origin? When a graduate student by the name of Stanley Miller published his experimental results in 1953, many believed that mankind was very close to uncovering this mystery. By demonstrating that it was possible to form amino acids from methane, a simple organic molecule containing only one carbon atom, Miller set in motion the ambitious hope that chemists would be able to create life in a test tube, i.e., an organised molecular system capable both of self-replication and of evolving. It is now the year 2016, i.e. 63 years have passed since that famous experiment. Despite tremendous efforts by chemists to tackle the problem, the dream has not yet been accomplished: although there have been many technological breakthroughs and advances in our scientific understanding, we have yet to create life in a test tube. The contemporary approaches have helped us to better understand simple life forms which, when extrapolated backwards, may have been the precursor(s) of extant life. However, the origin of the precursor(s) still remains unexplained. It is pertinent now to review our approaches to the chemical origins of life. This does not imply that we abandon the traditional sciences, but it compels us to reanalyze contemporary approaches and scrutinise our approach to this problem.

Recently, some excellent reviews in prebiotic chemistry have been compiled[1, 2, 3], however, they are generally chemistry centred. Although chemistry in the origins of life (abiogenesis) forms a rich scientific repository, the inclusion of prebiotic reactions pertinent to the early Earth demands adherence to geologically relevant environments. This aspect of experiments in the literature is too often poorly constrained or, indeed, entirely ignored. However, major strides in our understanding of the geological environments of the early Earth have been made, and the discipline of abiogenesis has offered itself to a new audience, with new viewpoints. We have discovered that the Hadean eon (the time period between the accretion of the Earth to *ca.* 4 Ga), in which life arose on Earth, was a considerably different world to the one on which we now live[4, 5, 6]. Atmospheric[7, 8], and oceanic differences[4, 9, 10], primitive planetary dynamics[5, 11], and lithologies unlike those currently able to form on the planet[12, 13] point towards a world that cannot be closely approximated by the modern Earth.

Baross and Hoffman[14] were the first to develop a model for the origins of life at a hydrothermal vent, involving the participation of rock-water interfaces. They proposed that the physical and chemical gradients primarily within hydrothermal fluids, and also on adjacent rock surfaces, may have had the capability to catalyse a diverse array of biological reactions (‘gradient environments’). These reactions were postulated to lead to the formation of ‘precells’, a community containing small fragments of genetic material which, through the endosymbiotic theory (*cf.* Margulis[15]), would have contributed material to the first prokaryotic cells. Russell and Hall[16] furthered this hypothesis to include reaction dynamics on specific mineral surfaces constituting the hydrothermal edifice, thus linking mineralogy to a ‘template’ within which the first (proto)cells could originate.

More recently, a series of studies by Hazen and collaborators have addressed the issue of chemistry at geological interfaces, proposing that crystal surfaces of Hadean eon-relevant minerals provide an effective substrate upon which the concentration of prebiotic molecules could have been achieved [17–24]. These works have demonstrated the pivotal role played by mineral-water interfaces in both concentration and catalysis processes. This approach provides valuable direction for necessary future studies to further elucidate the importance of mineral surfaces at the prebiotic-biotic transition.

Herein, we complement and advance contemporary approaches by not limiting our scope to a single mineral, but by considering the situation inherent within heterogeneous geological substrates i.e., rocks, which was certainly the setting for aqueous chemistry on the primitive Hadean Earth. We therefore promote an approach of stochastic chemistry on the surfaces of diverse mineral faces, within a unified geological-chemical system.

1.2. Ingredients of life

The building blocks of life that we observe today on Earth are mainly composed of organic molecules; *life*, at least as we recognise it, may not have existed without such molecules. Since the aim of this paper is to consider the approaches to the origins of life, it is pertinent to provide a brief introduction to the sources and contexts of organic molecules on the primitive Earth (Fig. 1).

1.2.1. Endogenous organic molecules

Atmospheric

The narrative of the Miller-Urey experiment[25] is important not only from a historical perspective but because this landmark achievement spawned the beginning of experimental prebiotic chemistry and paved the path for further research in understanding the origins of life. The present understanding is that atmospheric conditions on our primitive Earth were unlike the Miller-Urey scenario; instead, the atmosphere was neutral to mildly reducing, e.g., Kasting et al.[26]. Nonetheless, the primitive Earth environment was more or less a primordial soup[27]. The experiment demonstrated the ease of production of several amino acids and other prebiotically relevant organic compounds from small molecules like water (H_2O), methane (CH_4), ammonia (NH_3) and hydrogen (H_2). Recent studies also reveal that more than 40 amino acids and other amines were synthesised with this experiment under varying cosmogeochemical scenarios[27].

Subsurface

Organic molecules in the subsurface are mainly found in the zones around hydrothermal vents. Central to origins of life hypotheses focussed on hydrothermal vents are their associated reactions and products, such as minerals in vent walls and small molecules, such as CO_2, CH_4 and H_2[28], formed in the subsurface by Fischer Tropsch-type (FTT) synthesis. FTT synthesis involves the interaction of hot hydrothermal fluids with (ultra)mafic rocks, i.e., rocks rich in Fe and Mg minerals (olivines, pyroxenes), a process termed serpentinisation. Fischer Tropsch-type synthesis on hydrothermally formed alloys has been demonstrated to catalyse the formation of alkanes (C1-C3) in alkaline hydrothermal conditions[29, 30]; the formation of C2 and C3 alkanes apparently depends on the presence of metallic catalysts e.g., Cr, which is an element common in peridotite rocks associated with oceanic crusts[31]. Common serpentinisation reactions [Equations (1-3)] include:

$3Fe_2SiO_4$ (fayalite) + $2H_2O \rightarrow 2Fe_3O_4$ (magnetite) + $3SiO_2 + H_2$ (1)
$3Mg_2SiO_4$ (forsterite) + $SiO_2 + 4H_2O \rightarrow 2Mg_3Si_2O_5(OH)_4$ (serpentine) (2)

$4H_2 + CO_2 \rightarrow CH_4$ (methane) + $2H_2O$, (magnetite-catalysed reaction) (3)

Although the fact that these kinds of molecules could be produced by and in hydrothermal processes initially suggested a potentially substantial source of organics for prebiotic reactions, McCollum and Seewald[32, 33] proposed that the potential for abiogenic methanogenesis, for instance, on the early Earth may have been minimal. Furthermore, a recent observation suggests that methane (CH_4) and higher hydrocarbons are derived from fluid inclusions trapped in plutonic rocks, which are liberated upon cooling at the seawater-hydrothermal fluid interface, thus generating hydrocarbon-rich fluids[34], rather than being formed by subsurface Fischer Tropsch synthesis. In each of these scenarios, however, the subsurface is an endogenous source of organic molecules.

1.2.2. Exogenous organic molecules

Extraterrestrial delivery

There is abundant evidence for the presence of organic molecules in comets, asteroids, interplanetary dust particles, meteorites (specifically carbonaceous chondrites, which contain up to 4% C) and micrometeorites. The wide variety of organic compounds, including macromolecular carbon, amino acids and monocarboxylic acids among many others, in these extraterrestrial bodies is well-documented and beyond the scope of this review, though we direct readers to comprehensive reviews by Sephton[36, 37], and references therein. The Earth has been bombarded by a large variety of impactors ranging from the huge Mars-sized impactor (Theia) that created the Moon to cosmic dust less than 1 µm in size[38]. This impact phenomenon continues even to this day but is not as punishing as it was during the Hadean and Early Archaean eras before life took over the planet. Some of the carbon in meteorites is so primitive that it is speculated to have a pre-solar origin[39].

Estimates of the flux of extraterrestrial material to the present-day Earth are highly variable, ranging from 30,000-60,000 tonnes per year (±15,000 tonnes); ([40], C. Smith, pers. comm., 2016; J. Zipfel, pers. comm., 2016), the error being related to poor understanding of the complete size range of incoming materials, for instance the mass of incoming micrometeorites[41].

$$\begin{aligned}\text{Extraterrestrial flux} &= \text{mass of incoming material / surface area of Earth}\\ &= 60{,}000{,}000\ \text{kg} / 510{,}100{,}000\ \text{km}^2\\ &= \sim 0.1\ \text{kg/km}^2\text{/year} \quad (4)\end{aligned}$$

This value (~0.1 kg/km^2/year) for the modern Earth impactor flux [Equation (4)] is modelled to have been 1,000 times greater during the Late Heavy Bombardment (LHB), ~3.9-3.8 Ga[42–44], therefore roughly 100 kg/km^2/year. This flux represents the absolute maximum for extraterrestrial input to Earth at any point during its history, perhaps equalled solely in the initial stages of planetary accretion[45]. A rough estimation for the amount of extraterrestrial flux during the Hadean between 4.5 and 4.0 Ga indicates that it averaged <11.76 kg/km^2/year over that time period (from the lunar cratering record, cf. Koeberl[45]).

In summary, it is clear that the basic chemical ingredients of life may have originated from a variety of sources, both endogenous and exogenous to the Earth. The relative contributions of these processes remain contentious.

Figure 1. Modes of production and delivery of organic material to the Hadean Earth.

2. Contemporary prebiotic chemistry approaches

2.1. Theoretical models for primitive life

2.1.1 Chemoton model

The chemoton model, proposed by Ganti[46] is an example of a minimal cell model composed of three coupled cycles: an autocatalytic (metabolic) chemical cycle, the matrix replication (genetic system) cycle and a membrane growth cycle (Fig. 2). However, according to Popa[47] "the chemoton model is a virtual chemical network and does not promote any specific chemistry". Van Segbroeck et al.[48] suggest that the updated stochastic chemoton reaches a unique stable division time after a short transient phase. The authors confirm the existence of an optimal template length and show that this is a consequence of monomer concentration, which depends on both the template length and the initiation threshold. The transformation of this virtual-theoretical model into a working model is yet to be witnessed in its entirety. Nevertheless, along with the closely related concept of autopoiesis (described in Section 2.1.2), its experimental viability could open newer avenues in synthetic biology.

2.1.2 Autopoiesis

Autopoiesis (from Greek: auto, self; and poiesis, production), was first proposed by Varela and Maturana[49]. It refers to a system capable of reproducing and maintaining itself. According to these authors, the autopoietic organization is defined as a unit that produces components which (i) participate recursively in the same network by producing similar or complex components, and (ii) build the network of these productions as a unity in space in which the components exist (Fig. 3). In simpler terms, the theory tries to distinguish a living system from a non-living system.

Eigen and Schuster[50, 51, 52] developed a different model of self-organisation of macromolecules based on two important concepts, the quasi-species and the hypercycle models. The quasi-species model refers to a population of genetically related molecules which act as matrices for the next generation of molecules, which then also belong to the quasi-species. It is assumed that natural selection processes favour a replication of the molecules similar to the quasi-species. In the hypercycle model, several replicators – entities capable of self-replication – form a cyclic catalytic network in which the replication is catalysed by the precursor element, such that the catalytic interactions form a closed loop. The hypercycle was proposed as a model of the chemical origin of life but no convincing experiments have been run thus far to support the model. It is possible for these models to be fine-tuned with respect to space (including complexity) versus a relevant time frame, which is a facet yet to be explored in depth. To propose a model is totally different from constructing a complex living system under realistic scenarios, and this point is emphasised through this review.

2.1.3 Computer modelling

Through computer models, Kauffman[53] considers that autocatalytic reactions took place during the processes that led to the emergence of life on Earth, as they could evolve by themselves *via* self-amplifying feedback processes up to a critical boundary. Subsequently, a transition from autocatalysis to self-organisation occurred, similar in principle to that seen in the Belousov-Zhabotinsky oscillating chemical reaction[54]. A more recent effort in computer modelling has been shown by the simulation studies carried out on the basis of ideas of Kuhn and Waser[55, 56]. Since this article aims to address the experimental side of this complex subject of origins of life, we must keep discussion of this topic to a minimum, though, interested readers are referred to the works of Kuhn and Waser[55, 56], Shehnev and Lancet[57] and references therein.

A two-dimensional cellular automata model has been also conceived for the emergence of biological cell formation, which incorporated looped membrane and a membrane-bound information system[58]. Within this cellular automata model, three phenomena could be produced: (1) the development of an inner reaction system developed as an information carrier precursor; (2) the emergence of a cell boundary; and (3) the division of these cell structures. The outer loop evolved toward a lipid bilayer membrane, and inner polymeric particles evolved toward precursor information carriers[58].

Figure 2. Simplified iteration of the chemoton model, which is constructed of three cycles, an autocatalytic cycle, matrix replication cycle and membrane growth cycle. Adapted from Ganti (1975)[46].

Figure 3. Schematic representation of the autopoieotic organisation, which is a system comprising membrane boundaries and metabolic networks which are recursive interaction. Adapted from Rudrauf et al. (2003)[59].

2.2. A cellular origin of life

By analogy with contemporary living systems, some believe that primitive life emerged as a protocell-like organised system which could have been a subsequent step in the evolutionary process after prebiotic chemistry[60]. A cell-like system requires, at least, information molecules able to store and to transfer the information needed for reproduction (akin to nucleic acid polymers), catalytic molecules conducting the basic chemical work of the cell (akin to enzymes), and boundary molecules able to isolate the system from the aqueous environment (membrane). The assembly of these various molecular units, with the ultimate aim of building an artificial protocell, has been undertaken more recently. Though the dream has not yet come to realization, several scientific leaps have been achieved in the process, the synthesis of activated pyrimidine ribonucleotides being one amongst them[61]. Although it is an elegant experiment, the situation would be quite different if the chemistry was moved from a controlled, test-tube scenario (Fig. 4) to an actual geological setup. The major implication of this reaction is the utilization of simple prebiotic feedstock molecules: building complex chemical systems starting from two or three carbon molecules would unquestionably be a great asset and a real driving force going forward.

Even though the authors[61] claim the reaction to be under prebiotically plausible conditions, these claims could be argued upon at several levels. For example, the use of inorganic phosphate as a catalytic, efficient buffer system is innovative, but the source of phosphate for this reaction (dihydrogen phosphate) could be replaced by a phosphorylating agent that might be more relevant to the primitive Earth. Furthermore, the reaction was carried out under modern atmospheric conditions i.e., oxygenic, which might not be an accurate representation of early Earth atmospheric conditions [62, 63, 64]. The efficiency of the assembly of pyrimidine ribonucleotide must be demonstrated under such early Earth anaerobic conditions, in a "hands-off", possibly uninterrupted experimental setup. Subsequently, as part of a study on alternative sources of prebiotic phosphorous, field and experimental studies on the mineral schreibersite, (Fe, Ni)P, independently by Pasek et al.[65] and Kee and colleagues[66], provided a possible solution to the P-problem. They demonstrated the corrosion effect on meteoritic schreibersite by hydrothermal fluids and the role of H-phosphite (+3 oxidation state) as an exciting candidate for phosphorylation. Subsequent studies by Pasek and Kee resulted in further recognition that lower oxidation states of phosphorus have considerable potential to make available this key element in both water-soluble and chemically reactive forms[67, 68]. Recently, this has culminated in the demonstration of nucleoside phosphorylation using schreibersite analogues[69]. An interesting feature of schreibersite is the ability of this mineral to phosphorylate in aqueous conditions. Although these experiments provide interesting results, it should be kept in mind that the amount of schreibersite reaching the Earth today is low. Schreibersite occurs only in iron meteorites as macroscopic inclusions, making up 0.5-1.3% of sample volume[70]. Metallic meteorites comprise not more than 7.4% of the total meteorite flux. During maximum meteorite flux [Equation (5)] after the Moon-forming impact and/or the LHB, and assuming a uniform size distribution of all classifications of meteorites, the flux of metallic meteorites (~7.4% of the total) would be 8.7024kg/km^2/year (based on fluxes outlined in Section 1.2.2.).

$$\text{Peak flux of metallic meteorites} = (\text{incoming mass / Earth surface area}) * 7.4\%$$

$$= 60{,}000{,}000{,}000\ \text{kg} / 510{,}100{,}000\ \text{km}^2 * 0.074$$
$$= 8.7024\ \text{kg/km}^2\text{/year} \quad (5)$$

Out of this total, the phosphide component equals a maximum of 1.3%, i.e. 0.1131kg/km^2/year [Equation (6)].

$$\text{Phosphide component flux} = 8.7024\ \text{kg/km}^2\text{/yr} * 1.3\%$$
$$= 0.0131\ \text{kg/km}^2\text{/yr} \quad (6)$$

This represents the maximum flux possible. The typical flux of schreibersite is therefore ~0.0001131kg/km^2/year at non-peak or LHB moments in Earth history (1,000 times less, *cf.* Koeberl[45]). The issue of phosphorus on the early Earth is discussed more fully in Section 4.3.

Figure 4. Powner et al.[61] synthesis of ribonucleotide starting with simple molecules including glycolaldehyde, cyanamide and urea. The successful synthesis herein is indicated by green arrows.

2.3. Hydrothermal vents

The areas around hydrothermal vents are considered to be favourable sites for organic reactions to flourish[14, 16] and one experiment to synthesise organic molecules by Matsuno and colleagues[71] reported peptide oligomerization in an organised flow reactor that mimicked the conditions in a hydrothermal system. The team was able to oligomerise glycine monomers up to six units in the presence of Cu ions. This setup was also able to demonstrate polymerization at temperatures of 200-250°C, contrary to the popular belief that organic molecules are unstable under high temperatures. More recently, Cronin and colleagues[72] mimicked this hydrothermal system and developed an automated method to expose unactivated glycine monomers to prolonged dehydration–hydration cycles and, interestingly, chain lengths of 20 amino acid were observed. In addition to homo-oligomerization, the team was able to observe the hetero-oligomerization to chain lengths involving 8 different amino acids. It will be necessary to determine if the sequence of monomer addition is random or if there is a possibility to define monomer sequence without external human intervention by only manipulating specific parameters.

2.4. A vesicular origin of life

Morowitz[73] postulated that the first step toward the origin of life was the spontaneous condensation of amphiphilic molecules (chemical compounds which are both hydrophilic and lipophilic) to form vesicles. Examples of autocatalytic micelle growth have been noted[74]. These autocatalytic systems alone do not truly store hereditary information and cannot therefore evolve by natural selection. Other studies on membrane self-assembly processes which allow cellular compartmentalisation have been carried out with amphiphiles ([75] and references therein). Hanczyc and colleagues[76] found that the presence of naturally occurring clay minerals, such as montmorillonite, can help in the assemblage of vesicles and, in the process, bring bound RNA into the interior of the vesicles, thus providing information to the vesicular system. Even more ambitious, the “minimal cell project” aims to synthesise a cell model having the minimal number of components to be defined as living. Liposomes are used as cell membranes and attempts are made to introduce a minimal genome[77, 78]. The role of vesicles in the origins of life is unquestionable and is being explored extensively. For a more comprehensive understanding of the topic, we refer the reader to the review by Meierhenrich et al.[79].

2.5. The RNA World Hypothesis

The RNA World Hypothesis is based purely on our understanding of extant life. By that logic, DNA must be given priority over RNA, but RNA is considered as potentially more relevant within the first living entities because it possesses the ability to encode genetic information while performing catalytic reactions, a package of functionality that DNA does not possess. This hypothesis suggests that a series of chemical reactions on the primitive Earth led to the formation of ribonucleotides. Although there are arguments which emphasise that the RNA world hypothesis does not solely credit RNA as the first self-replicating molecule[80], others still advocate the narrative of this hypothesis (e.g. [81]). RNA could have served both as a catalyst and repository of genetic information in the first living cell. Zaug and Cech[82] found that some RNAs, the ribozymes, have catalytic properties, for example, increasing the rate of hydrolysis of oligoribonucleotides. They also act as polymerization templates since chains of up to 30 monomers long can be obtained starting from a pentanucleotide. Since this primary discovery, the catalytic spectrum of these ribozymes has been considerably enlarged by directed test tube molecular evolution experiments[83, 84].

The arguments against the RNA World Hypothesis are significant, but it nonetheless rises above competing hypotheses. The synthesis of nucleotides is a complex issue in itself, in addition to the issues posed by unsatisfactory yields of sugars, and lack of control over the synthesis of any one particular sugar in the formose reaction. For RNA-based nucleotides, ribose is the most important sugar. The poor yield of sugars in the formose reaction[85] has often been cited as the reason that the prebiotic synthesis of nucleotides is unlikely.

The first breakthrough was the observation that glycolaldehyde phosphate reacting with glyceraldehyde phosphate gives ribose-2,4-diphosphate as the principal reaction product[86]. This synthesis was improved by performing the reaction with glycolaldehyde phosphate and glyceraldehyde phosphate on a mixed valence double layer hydroxide mineral surface, where ribose 2,4-diphosphate was the major pentose phosphate formed in overall yield of about 12%[87]. Syntheses by Sutherland and his group showed that activated pyrimidine ribonucleotides can be achieved in a shorter synthetic step that bypasses free ribose and the nucleobases[61]. One should, however, remember that the complete synthesis of RNA under ‘prebiotic conditions’ remains an unsolved challenge. It may be unreasonable to expect a process that probably took place over long geological timescales (e.g., from hundreds of thousands to millions of years) to be demonstrated rapidly in a test tube scenario. Nevertheless, it seems highly unlikely that life started with RNA molecules because these molecules are not simple enough and their synthesis is not simple enough. The half-life of the ribose sugar is so short (73 minutes at 100˚C[88]) that it is hard to imagine that it could have remained stable enough to accumulate over geological timescales.

Experimental evidence suggesting stabilization of pentoses for nearly two months by borate minerals was demonstrated by the team of Benner[89]. Whether borate minerals were present in sufficient quantity to be significant in the development of the RNA world remains a contentious issue, and relies largely on the geological record of such minerals: tourmalines are the only members of the borate family for which there is evidence before 3.5 Ga[90]. Most studies of borate minerals have been conducted on minerals whose direct geological record does not extend beyond the Mesozoic, for instance ulexite, colemanite and kernite (e.g. in [90]).

The RNA world appears to have been an episode in the evolution of life before the appearance of cellular life. Nonetheless, the RNA World Hypothesis is still appealing, partly because it is a derivative of our existence in the present and partly because it definitely serves as a sensible starting point for the origin of primitive life.

2.6. Self-organization and autocatalysis

"All replicating systems are, by definition, autocatalytic and all autocatalytic systems result, in some sense, in replication"[91]. Autocatalysis is observed when the product of the reaction catalyzes its own formation. Different templates have been tested by Terfort and von Kiedrowski[92], and information transfer templates in complex systems by Burmeister[93]. In most cases, the rate of the autocatalytic growth did not vary in a linear sense. The initial rate of autocatalytic synthesis was found to be proportional to the square root of the template concentration, i.e. the reaction order in these autocatalytic self-replicating systems was found to be 1/2 rather than 1, a finding in contrast to most autocatalytic reactions known so far. Two preformed fragments of a peptide have been demonstrated to be autocatalytically ligated by the whole peptide acting as a template[94, 95]. Moreover, the replicated molecules contain only two "letters" and therefore a very low level of information. Autocatalytic reactions are particularly attractive since they might amplify small enantiomeric excesses, possibly extraterrestrial in origin[96]. Some investigations are also focussed on autocatalytic systems adsorbed on mineral surfaces[97, 98]. So far, the replication of a complete peptide sequence fed with a mixture of amino acids has not been yet achieved.

2.7. An autotrophic origin of life

The essentiality of extant life involves replication and metabolism. Metabolic chemical species called “surface metabolists or surface organisms”, later termed as “pioneer organism”, were introduced by Günter Wächtershäuser[99–104], mainly as a challenging perspective to the prebiotic broth theory. The premise of his argument is implicitly based on simplicity preceding complexity, restricted on a two-dimensional layer. In this bottom-up approach, he persuasively describes the formation of complex systems from simpler units, as seen throughout the development of the theory based on simple molecules, simple minerals, simple energy sources and eventually extending this principle to a metabolism that emerges from a two-dimensional surface into a three dimensional one. Originally proposed as the “Theory of Surface Metabolism”, over time it evolved into the “Iron-Sulphur World Theory”[101].

The Iron-Sulphur World Theory proposes a pioneer organism, which is not an organism in the real sense, but rather a chemical set-up where a host surface provides nutrition (starting material) for carbon fixation and allows the synthesis of guest molecules. This chemical set-up is divided into two platforms: an inorganic substructure and an organic superstructure. The substructure comprises transition metals on the surface of the host which function as catalysts and promote the formation of the superstructure. The superstructure is a dynamic entity, i.e., it is capable of lateral growth on the substructure. As the substructure, Wächtershäuser proposes a mineral surface, such as pyrite, at a hydrothermal vent in his model whose surfaces have an inherent positive charge owing to the metal ions on the surface acting as binding sites for negatively charged entities or polyanionic species. The whole set-up takes place under anaerobic, high temperature and high pressure conditions around a hydrothermal vent, and the cascade of chemical reactions occurs at the interface of the pyrite and hot water. This platform enables the chemical set-up to remain efficient by facilitating the inflow of nutrients and preventing loss of constituents by diffusion. The reactions of the pioneer organism occur as a consequence of redox reactions (at least initially), followed by synthesis of low molecular mass organic molecules which, after subsequent metabolic evolution, evolve to a hypothetical tribonucleic acid (TNA), an analogue of present day RNA. However, Wächtershäuser's model has been criticised severely by De Duve and Miller on thermodynamic, mechanistic, kinetic and even philosophical levels[105]. Schoonen et al.[106] specifically criticised that the energetic favourability of the reduction of CO_2 with an FeS-H_2S/FeS_2 redox couple as predicted in the model fails to make it viable. Iron sulphide as a substrate within or upon which protocellular life could arise, however, is met with continuous accolade [16, 107–109], particularly for the prebiotically promising morphologies that it frequently produces. This is addressed in Section 3, wherein we have compared and appraised the ideas of Wächtershäuser and Russell-Hall-Martin.

3. Contemporary geological approaches

The literature abounds also with examples of organic reactions at the surface of minerals, a geological substrate. We here provide a non-exhaustive resumé by mineral group.

Phyllosilicates are considered as having great potential for catalysis and chelation of organic molecules, and are thus common ingredients in origins of life experimentation. Chemical compositions of layered-structure clay minerals are extremely varied, as ion replacement is common. Clays are frequently products of the aqueous alteration of feldspars, micas, volcanic glasses or the ferromagnesian minerals common in (ultra)mafic rocks.

Reid and Orgel[110] recognised the relevance of clay minerals in the catalysis of the formose reaction. Studies provide evidence for the ability of clay minerals to concentrate and polymerise amino acids, e.g. glycine to the pentamer (e.g., [111, 112]). Hanczyc and colleagues[113] encapsulated RNA in vesicles chelated to clay minerals after mixing RNA with lipids and clays. They demonstrated that clay minerals, including montmorillonite, kaolinite and talc, were especially suited to templating the formation of membranes. Ferris and colleagues demonstrated the use of clay minerals as templates for the oligomerisation of RNA[114, 115].

Zeolites (and feldspathoids) have also come under consideration; these alkaline and alkaline earth metal silicates occur in mafic volcanic rocks and in late-stage hydrothermal environments. They have a framework structure resulting in channels, leading Smith and colleagues to propose the concentration of organics within the pores and channels (see Fig. 9c) which are characteristic of their surfaces[116–118].

Another class of relevant silicate minerals is the feldspar group. With chemical compositions varying between Na, K, and Ca endmembers, this vast group is abundant in igneous rocks. In modern K-Na feldspars, weathering contributes to the production of a sieve-like surface structure[116], although feldspars characteristic of the Hadean were more likely to have been plagioclases (i.e., Na,Ca-silicates). Dealuminated alkali feldspar and zeolite surfaces also have this honeycomb microstructure, which would allow molecular access to fluid inclusions present in the mineral, thereby acting as an organophilic, potentially catalytic surface[117]. The honeycomb structure includes sub-micrometre nanotubes, which further might have acted as precursors to functionally modern cell walls.

Two additional groups of minerals that have excited interest in organo-mineral experiments are oxides of Si (quartz), Al (corundum) and Ti (rutile), and sulphides of Zn (sphalerite) and Cd (greenockite). For example, ornithine, alanine and glycine absorb onto siliceous and aluminous oxides[119, 120, 121]. Rutile (TiO_2) can selectively concentrate ribose from isomeric pentose sugar solutions[122]. Adsorption onto oxides is particularly complex but studies have demonstrated a potential utility in molecular concentration by these minerals (e.g. [2]). Of the oxide and sulphide minerals tested, Fe, Cu and Zn phases are common in hydrothermal systems, but Cd occurs mostly as a minor constituent of chalcopyrite, rather than in a major mineral species. While SiO_2 and TiO_2 are known to be common minerals in early Earth lithologies, Al oxides would have been rare.

Figure 5. Multi-scale approach to the hypothesis of a chemotrophic origin for life. (a) Ocean-scale view, indicating the geological and geodynamic setting of the alkaline smokers atop volcanic oceanic crust. Inset circles depict chemical parameters of the edifice. Note that neither the proposed atmospheric condition nor the water temperature are compatible with current understanding of the Hadean environment. Image from Russell et al.[123]. (b) Edifice-scale view; photograph of a black smoker vent at the Mid-Atlantic Ridge emitting mineral-rich, dense, hot fluid. Image from www.whoi.edu. (c) Microtexture-scale view, secondary electron image showing monosulphide chambers, upon whose compartmentalisation the hypothesis rests. Image from Martin and Russell[109].

Further to the chemistry-based hypothesis of Wächtersäuser, a hydrothermal setting for the chemoautotrophic origin for life from a geological perspective has been proposed in a series of studies by Russell, Hall and Martin[16, 109, 124, 125]. The theory postulates reactions leading to prebiotic syntheses inside mini chambers of FeS (Fig. 5, Fig. 6), a morphology which is naturally arising in this mineral, within the porous structure of hydrothermal vent edifices, which are situated at the interface of hot, sulphide-rich hydrothermal fluids emanating from the vent and the cold Hadean seawater i.e., in a scenario of extreme disequilibrium, where temperature, pH and redox gradients were significant.

The model therefore suggests that the pathways leading to an RNA World, and further to the universal ancestor, began inside small chambers of iron monosulphide, thus implying that a chemically active metabolic network preceded the RNA world (Fig. 6). Within the monosulphidic edifice, crystals of FeS and NiS are proposed to have a catalytic capability for synthesising acetyl-methylsulphide from carbon monoxide and methylsulphide, known molecules in hydrothermal fluids[109]. Martin and Russell support the role of an assemblage of low temperature sulphides, 'mackinawite-smythite-greigite'[126], as a catalyst as opposed to the pyrite surfaces (FeS_2) preferred by Wächtershäuser.

Figure 6. Figurative representation of a monosulphide edifice at an alkaline hydrothermal vent, in which the origin of an inorganic-walled compartmentalised 'cell' predated the first protocell. Going upward, there is an increase in complexification, including the prebiotic-biotic chemistry divide. Note the change in ocean temperature with respect to an earlier version of the hypothesis (Fig. 3). Image from Martin and Russell[109].

Research into monosulphide edifices is ongoing and recent work[127, 128] has demonstrated the formation of chemically distinct precipitates. The seawater chemistry chosen is simple, but with a more heterogeneous complement of ions and molecules, a complete test of the potentials of such edifices as catalysts at the prebiotic-biotic transition could be achieved. The Russell-Hall-Martin model is envisaged as a metabolic network. Wächtershäuser's model views proto-metabolism as a two-dimensional phenomenon which contrasts with the Russell-Hall-Martin three-dimensional network of compartments. Both models are similar in terms of the importance given to sulphide minerals in providing a means for concentrating the prebiotic molecules required for the formation of a life-like entity, the role of surface chemistry and the environment suggested, i.e. submarine hydrothermal vents.

A further geological perspective on the origins of life, involving many of the minerals described above, is given by Brasier and colleagues in the Pumice Hypothesis of protocell generation[129, 130, 131]. This hypothesis is based upon observations of modern pumice rafts which are colonised by biofilms and organic 'slicks'[132]. They suggest that pumice can provide 'natural reaction flasks', in the form of the ovoid vesicles, for the abiogenic-biogenic transition, as it floats in an 'early Earth hydrothermal ocean' (Fig. 7). The mineralogy of pumice is diverse, and is initially feldspar dominated, but evolves by alteration to contain phyllosilicates and zeolites. The drawback of this hypothesis is that acidic volcanics, such as pumice, would have been considerably more minor on the early Earth due to lesser evolution of erupted magmas in the Hadean (as noted by Cleaves et al.[23]).

Figure 7. Rationale for the Pumice Hypothesis. (a) Schematic depiction of a pumice clast. The locations, within the clast, of the properties of pumice and the processes linked to those properties are shown. (b) Life cycle of a pumice clast, from eruption to diagenesis. For each stage, the key alterations to vesicles in pumice are outlined. (c) The final stages of the Pumice Hypothesis, at which point the clast has been witness to a large variety of environmental conditions. At this moment, on a volcanic shore, extensive mineral precipitation can occur over thousands to millions of years, as evaporation, hydrothermal enrichment and alteration, and redox reactions unite. Image adapted from Brasier et al.[129, 130].

4. A new paradigm: stochastic chemistry on mineral surfaces

4.1. Introduction

Parallel efforts by the chemistry and geology communities have worked towards a better understanding of the fundamental question of the origins of life. Unfortunately, there exists a major disconnect between the approaches, analyses and terminologies adopted by these groups. Our paradigm suggests an approach to attempt to minimise this divide by advocating a methodology involving chemical systems and their stochastic reactivity on heterogeneous geological surfaces i.e. on rocks. This models the origins of life as a continuity of chemical reactions in an analogue to the early Earth (Hadean) environment.

As explained above, previous experimentation has not succeeded in creating primitive life in a test tube scenario. This implies that a revised approach to the prebiotic-biotic transition is needed. A pioneering strategy could be to more closely mimic the primordial soup and both geological and environmental conditions, thereupon permitting stochastic chemistry to run without constraint. By doing so, chemists will no longer be able to control each step of the process. Stochastic prebiotic chemistry is conceivable as long as the compounds are relatively small, and as long as we can monitor the complexity within a system. This approach should be principally based on our analytical competences, their confines and our preparedness to spot specific patterns in chaotic chemical systems. The complex ingredients needed for the start of life would not have been obtained just by raising the level of background noise (reaction systems unrelated to the origins of life) but rather by the bias of selective chemical reactions and/or selective resistance to degradative conditions.

Our understanding of primitive life is that to approach a simple biological entity (one characterised with a genotype-phenotype relationship), it is likely to have traversed dynamic, chemical systems (chemical life) which existed in disequilibrium with their local geological environment, the latter itself being examples of dynamic disequilibrium systems in a physicochemical context (geological life[133]). Living systems function through a complex integrated network of chemical reactions and, therefore, if the chemistry of the origin of life is universal under a given set of contingent conditions, then probably life can occur elsewhere in the Universe. An attractive direction in which to develop chemical life systems are those environments where chain polymerization in a self-amplifying series of events via a positive feedback mechanism is favoured. Since life appeared on Earth, we can assume that the presence of several counter-positive feedback mechanisms may have competed on the surface of the primitive Earth. The complex chemical system leading to protocell generation was the result of myriad positive and negative feedback mechanisms. Feedback mechanisms are central requisites for complexity and, using contemporary approaches in prebiotic chemistry, we might have been only encountering negative feedback mechanisms. Such a complex array of feedback mechanisms is analogous to the "primordial soup" of Oparin, in that it represents a complex chemical or reaction consortium. However, a primordial soup in reality may have been a network of competing complex chemical systems, nowhere similar to the "warm, little pond" anticipated by Darwin or the "soup" proposed by Oparin and Haldane.

Primitive life could be defined as, *a minima*, a dynamic entity within an open chemical system capable of self-reproduction, i.e., making more of itself by itself, and also capable of evolving in the face of competing processes or networks that had lower dynamic stability. Primordial living systems were perhaps able to proliferate in a simple way by producing true copies. The autocatalytic growth of specific primer sequences on mineral surfaces followed by chain cleavages would offer such an opportunity. This open chemical system, which exchanges matter and energy, functions as a dissipative dynamic system, thermodynamically far from equilibrium. The continuous interaction of energy from the environment with matter inside the system keeps the overall system from reaching a state of equilibrium. This drives the system to evolve and develop complexity over time by dissipation of energy between the components of the system. It is not possible to define and quantify complexity but, for each system under the process of complexification, complexity can be relatively quantified i.e., the second generation should always be more complex than the preceding one and this process should be irreversible. One might obtain a quantitative perspective on complexity through kinetics. A complex chemical network is presumably one in which there are more and more dynamic kinetic connections between components of the system. The more complex the kinetics, the more complex the dynamic system. We emphasise that complexity, in and of itself, is insufficient justification for defining life. The behaviour of complex systems can be difficult to predict without prior knowledge of the initial conditions. But if we build complexity in a chemical system and track it from the initial conditions with efficiency, this problem of determinism could be overcome. It is not unusual to observe self-organization, generally a characteristic of living matter, in a non-living complex system e.g. ordered crystal growth.

The basic requisite for self-organization is an energy source and a disposal mode which is often termed as a "sink". The energy source could be radiation from a nearby star, the redox change or heat energy in a hydrothermal vent, nuclear energy from a planet's interior, for example. The disposal mode is the absorption followed by dissipation of energy to the nearest acceptor in the surroundings. Molecular systems naturally transduce (convert) energy mutually through molecular interactions, as do most complex interactive systems (such as the interactions of waves on sand dunes, vortices in flowing water on river-beds). They need a set of instructions to govern their actions (laws of physics, chemistry), a set of mutual interactions (the mechanism) and the energy which is transduced (for example a geological source, wind, waves, hydrothermal energy or a life force such as human will, enthusiasm or desire). The interactions can be resonant or discordant and that determines the energy distribution over the available microstates. When energy is distributed thus across more microstates, entropy increases and the second law of thermodynamics holds. The beauty of biological life being based upon macromolecules is that the more atoms a molecule has (the greater the complexity of wave-like interactions when looked at through the optic of wave mechanics), the more energetic degrees of freedom that molecule has, and thus the more microstates that are available over which to re-distribute energy within a given (relatively small) space. An hypothesis on absorption and dissipation thermodynamics (the transduction of energy) is given by Michaelian[134, 135].

4.2. The virtues of mineral surfaces

More than half a century ago, Bernal[136] suggested that surfaces may have played a crucial role in origin of life on Earth. In Wächtershäuser's theory[99], surfaces are considered central due to their role as reactive sites although de Duve and Miller were skeptical about chemical reactivity on surfaces[105]. The idea of polymerization on the rocks was theoretically developed by Leslie Orgel[97] who suggested that long polymers could be synthesised on the surfaces of minerals in a prebiotic process analogous to solid phase synthesis. Surface reactions are of particular interest since atoms at the surface inhabit an environment quite unlike those below the surface, and can attain a more 'relaxed' position in the crystal lattice[137]. This disposition entails that minerals at the surface can provide a large number of crystallographically distinct atomic sites upon which a diverse variety of molecular attachments can occur[18].

4.2.1. The advantages of minerals

The advantages of mineral surfaces for prebiotic chemistry have been elegantly reviewed by Hazen and Sverjensky[22] who also summarise both theoretical and experimental results. Particular 'virtues' of minerals for prebiotic synthesis include the following:

Adsorption: Minerals enforce differential adsorption, and therefore the large diversity of minerals present on the millimetre-scale in a typical rock necessarily enhances the likelihood of hosting a wider range of prebiotic molecules. The position of a molecule in three-dimensional space is defined by three position coordinates and such a system has six degrees of freedom. By adsorption of organic molecules on the surface of these minerals, it is possible to decrease the mobility of molecules from 6 axes (in solution) to 2 axes (on surface) (Fig. 8, Table 1) thereby decreasing the entropy slightly while maintaining a negative ΔG (Gibbs free-energy).

Consider the equation:

$$\Delta G = \Delta H - T\cdot\Delta S \quad (7)$$

Where ΔG is Gibbs free energy, ΔH (internal energy) is enthalpy, T is temperature and ΔS is entropy.

On a solid surface:

$$\Delta G_{adsorbed} = \Delta G_{bound} - \Delta G_{free} \quad (8)$$

The $\Delta G_{adsorbed}$ is the Gibbs free energy in the adsorbed state and can be defined by the difference in free energy between the bound state (ΔG_{bound}) and the free-state (ΔG_{free}), when the interaction between the surface and the molecule is negligible. Since, ΔG, ΔH, ΔS, $\Delta G_{adsorbed}$, ΔG_{bound}, ΔG_{free} are state functions, they can be determined and thus can be integrated from the initial and the final values.

Figure 8. Pictorial representation of the reduction in degrees of freedom in surface and solution chemistry (see Table 1).

Table 1. Comparison of degrees of freedom of molecules between surface versus solution (see Fig. 8)

State of matter	Degrees of freedom	ΔS	ΔH	ΔG
Solution	6	<<<<0	-	Negative
Surface	2	<<0	-	Negative

Minerals also aid selection and concentration of prebiotic molecules from a "soup" in an aqueous environment, thus promoting organic synthesis, e.g. thiols from CO2 and sulphides[138] or amino acids from CO or CO2, NH3 and H2O and sulphides[106, 139]. Adsorption may be influenced by a variety of environmental parameters (pH, ionic strength, salinity, solute concentration, ionic speciation etc.).

Molecular organisation: Minerals favour the organisation of molecules, since mineral structures are inherently regular and repetitive. Adsorbed molecules forming periodic two-dimensional structures on mineral surfaces have been imaged[140, 141]. Indeed, the same molecule may attach to a mineral surface simultaneously in different ways (Fig. 10).

The chirality of crystal surfaces may also influence the organisation of molecules. Chirality is an important property of biomolecules. A certain enantiomeric excess of organic molecules has been detected in extraterrestrial carbon[142] that could have been amplified on the surfaces of certain crystals, such as quartz, calcite and metals such as Cu, Ag, Au and Pt. However, of these quartz and copper would have been of limited relevance to the Hadean Earth, becoming common only in later-developed granitic terranes[23]. The importance of minerals in the origin of biological homochirality has already been presented to some extent in section 4.3. However, chirality is a subject that is so complex in itself that it deserves a dedicated review; which is well beyond the scope of the subject at hand.

Stabilisation: Minerals favour molecular stabilization, for example preventing their degradation[143].

Figure 9. Crystal surface textures and defects which might provide a preferred location for surface interactions between prebiotic molecules and the mineral substrate. (a) Plagioclase feldspar crystal, showing well-developed multiple twinning (black and white bands), embedded in the matrix of tachylitic volcanic glass from a Réunion Island lava. (b) Three-dimensional representation of the surface of twinned crystals. The topographic 'seams' between twins could form a locus for organic attachment. (c) Secondary electron image of channel-like voids on the surface of an alkali feldspar crystal; such features have been proposed as compartment-like precursors to cell membranes. Image from Parsons et al.[117]. (d) Strained quartz-rich Greenland rock from Isua (~3.85 billion years old). A solid yellow line outlines a quartz grain, in which zones of extinction indicate that the surface is kinked; dotted lines indicate these kinks. (e) Representation of the 'zoning' seen in (d): arrows indicate kinks, which are migrated concentrations of defects, which could promote the attachment of molecules. (f) Secondary electron image of sub-µm textures that characterise the surface of tachylitic volcanic glass in Réunion Island lava.

Figure 10. Examples of the four ways in which the molecule glutamate can attach to the mineral rutile. These affixations are either through bidentate bridging or chelation, as indicated by the graphs below each scenario. Mode of attachment is pH-dependent, though in all scenarios, there are conditions under which a diversity of modes of attachment can occur. Images from Hazen and Sverjensky[22], based upon Jonsson et al.[20].

4.2.2. Mineral surface specificities

The topology of the surface is of importance; it may be almost completely planar (as in certain metals, graphite, or the phyllosilicates) but more generally there are irregularities either naturally characteristic of certain crystal faces (intrinsic irregularities, Fig. 9b, Fig. 11) or due to defects in crystal growth (Fig. 9, Fig. 10). Irregularities are also caused by the alteration of the surfaces in aqueous solutions, appearing as vacancies and interstitial fillings (e.g. Fig. 11), kinks (inter-grain boundary defects, Fig. 9d) and line or plane defects[144, 145]. Such defects encourage adhesion of organic molecules[146, 147]. Undoubtedly, metal ions participated in prebiotic chemistry until the Last Universal Common Ancestor (LUCA), and further through evolution, by providing cofactors as illustrated by Goldman et al.[148].

Figure 11. Simple defects in an imagined horizontal (i.e., plan view) crystal lattice at the atomic level. To the upper right, the lattice is unaffected. To the upper left is a vacancy, the result of the removal or non-inclusion of a blue sphere; this increases surface area and the lengths of vertices in the void. To the lower left is an impurity, the consequence of inclusion of an unexpected orange sphere. Although no major structural deformation has occurred, the surface ionic variety promoted by the inclusion of this sphere could foster a locus of molecular attachment. To the lower right is a large interstitial red sphere, whose inclusion causes extensive deformation to the surrounding atoms; this alteration of the lattice presumably affects similarly the layers of blue spheres both above and below the layer represented, which are not shown here. Interstitial spheres could reasonably be of lesser size than the blue spheres.

4.3 Realistic scenarios

The above overview serves to underline previous experiments related to organo-mineral interactions in water. However, as previously noted, past experiments have concentrated on very restricted scenarios involving the interaction of a single mineral with organic molecules. The parameters of these experiments frequently do not mimic the conditions of the early Earth in which complex prebiotic reactions took place with “numerous competing species…and numerous competing mineral phases and surfaces, all present over a range of temperature, pressure, pH, and solute concentrations”[22]. Of critical importance is the restricted range of minerals available on the anoxic Hadean Earth compared to the modern day. Minerals that have been used in experiments, but which would not have existed on the Hadean Earth, include uraninite, colemanite, ulexite and kernite (the latter three are borates), or the diversity of minerals associated purely with “modern”, i.e. post Hadean-Early Archaean, granitic continental terranes, such as abundant potassium feldspars[23, 90]. Other minerals for which experimentation has been conducted would have been present only in very small amounts e.g. corundum and schreibersite (see Section 2.2.)

Cleaves et al.[23] propose a three-stage model of mineral evolution on the early Earth, which elucidates the availability of certain minerals through time. Stage 1 occurs during the formation of chondritic bodies in the nascent solar system. At least 60 minerals, spanning the ur-minerals, silicates, oxides, sulphides and phosphides, alongside metal alloys, formed during this period. The ensuing Stage 2, corresponding to the Hadean, is the most relevant to the origins of life, since planetesimal processing occured in this stage, and up to 250 further minerals, including the feldspars, phosphates and clay minerals, formed. This diversity of mineralogy opens new windows for mineral surface reactions. Stage 3 comprises mineral formation after the oxidation of the Earth’s surface. Thus, the Hadean minerals would have been essentially inherited from the volcanic (extrusive and intrusive) and plutonic rocks forming the early crust. The former include peridotites, mafic and ultramafic basalts comprising olivine, pyroxene and plagioclase feldspar that have naturally reactive surfaces of interest for organic interactions in aqueous environments; and komatiitic basalts, particularly rich in Mg and formed from the particularly high temperature magmas characteristic of the early Earth[11, 12, 13 149]. In addition, basaltic glass, an amorphous Fe-Mg-rich phase formed on the surfaces of subaqueous lavas, is also highly reactive[150, 151].

Other minerals associated with the environment of the early Earth would have included phases related to hydrothermal deposits, such as metal sulphides and silica (also found in igneous rocks). All these extrusive, intrusive and plutonic rocks and minerals would have been relatively rapidly altered in the warm ([152, 153, 154], compare to [9] for a discussion of similarly high temperatures in the early Archaean), slightly acidic[155, 156, 157] Hadean seawaters to produce secondary mineral phases.

There was also a vast flux of extraterrestrial minerals raining down on the Earth during accretion, late accretion and the hypothesised Late Heavy Bombardment (LHB) ~3.9 Ga ago. Aqueous alteration of these minerals often took place on differential parent asteroids (e.g., [158]), as well as in the terrestrial ocean.

Phosphorus remains the critically challenging and potentially limiting among the ingredients required for primitive life to flourish. Apatite, $Ca_5(PO_4)_3(F,Cl,OH)$, was the only major phosphorus-bearing phase for the Hadean, however it has been considered challenging to build a chemical evolutionary pathway from this geological source of phosphorus to biological phosphorus, principally on the grounds of its poor water solubility, in addition to the low inherent reactivity of orthophosphate salts[159]. Present innovational mineralogy ascribes P therefore to a wider range of minor minerals, of both endogenous (whitlockite, newberyite and chlorapatite) and exogenous (schreibersite, perryite and merrillite) geneses. Exogenous delivery was addressed in Section 1.2.2. Minerals such as whitlockite and newberyite may have precipitated as secondary mineral phases in oceanic crust, specifically from alkaline volcanic glasses[160], thereby producing a reservoir of reduced and reactive phosphate. Nitschke and Russell[161] propose that the alteration of basaltic glasses to palagonite, for example, can release phosphates in the presence of acidic smoker systems[154], or at milder (165-180°C) hydrothermal systems[161]. Phosphate can be released from chlorapatite, whitlockite and merrillite in the presence of acetic and succinic acids, i.e., in acidic conditions[162]. The concentration of usable phosphorus available in prebiotically plausible Hadean environments remains a major drawback and a necessary research focus.

Hydroxylapatite, a mineral of composition $Ca_5(OH)(PO_4)_3$, binds aspartic and glutamic acids to its Ca^{2+} cations[163]. Water-soluble carbodiimides, R-N=C=N-R', power the ligation of both glutamic and aspartic acids on hydroxylapatite. Oligomers of glutamic acid greater than 45 mers in length were formed on hydroxylapatite and illite after 50 feedings with glutamic acid and the condensing agent N,N’-carbonyldiimidazole, Im-CO-Im[114]. The formation of long polypeptide chains from neutral amino acids has not yet been accomplished. The presence of NaCl was found to significantly enhance the formation of longer peptides[164].

Figure 12. a-b) Alternating polypeptide of poly(Glu-Leu) randomly coiled in water adopting: a) a beta-sheet structure in the presence of CaCl2; b) an

alpha-helix in the presence of FeCl3. c) comparison of resistance to hydrolysis for alpha-helices and beta-sheets over time; beta-sheets are evidently the more stable conformation.

From a strictly chemical standpoint, the role of biopolymers is central to the Origins of Life, as explained throughout Section 2. Even though the biopolymer RNA has been at the centre of the stage as the most favoured informational biopolymer because of its ability to catalyse and self-replicate, one must be wary of the fact that its synthesis under realistic Hadean prebiotic conditions has not been achieved. As pointed out in Section 2.2., the synthetic route used is too ‘controlled’ to be plausible under realistic conditions and the synthesis of sugars generally gives rise to inevitably complex mixtures. In addition to this, as shown by Joyce and colleagues[165], the template-directed self-replication of activated guanosine mononucleotide is terminated by enantiomeric cross-inhibition in the presence of monomers of different handedness (chirality) to the poly(c) template. These observations compel us to look for ‘resilient’ molecules that could be unaffected by the harsh early Earth conditions and still serve as informational biopolymers. Brack and Spach[166], Brack[167] and Maury[168] suggested the role of conformational peptides as potential early Earth informational biopolymers.

The most interesting among them is the beta-sheet (β-sheet) conformation of peptides (Fig. 12). As a rule of thumb, alternating hydrophilic and hydrophobic amino acids are a requirement for formation of a β-sheet structure, whereas a random distribution of amino acids induces an α-helix conformation[169, 170]. The addition of salts, for instance 0.1 M NaCl, spontaneously produces an asymmetrical β-sheet bilayer (with a hydrophobic interior and a hydrophilic exterior) because of hydrophobic side-chain clustering[171]. Fig. 12c depicts the relationship between temperature and the degradation by hydrolysis of these polypeptides; ß-sheets are patently the more ‘resilient’. Resilience is a necessary attribute for the natural selection of molecules on the early Earth. Even insoluble minerals, such as crystalline CdS, catalyse the formation of ß-sheets[172]. The experimental studies of Brack and colleagues support the idea that ß-sheets could have played an important role in the Origins of Life. ß-sheets are more resistant to hydrolysis than the random coil or the ß-helix conformation of peptide chains. This further encourages the idea that polypeptides in ß-sheet conformations have a long lifetime and may be relevant as informational biopolymers on the early Earth. This may have resulted in the selection of only those amino acids capable of ß-sheet propensity and selectivity. This would have limited the number of types of amino acids in the first life on Earth from the wide array of structures formed in simulation experiments and/or from meteoritic sources[173].

Another approach was developed recently by Patel et al.[174], wherein the precursors of ribonucleotides, amino acids and lipids are shown to be derived by the reductive homologation of hydrogen cyanide and some of its derivatives, thus indicating that all the cellular subsystems could have arisen simultaneously through common chemistry (Fig. 13). This is a step towards the congruence advocated by de Duve[175]. We agree that a complex chemical system was available on the early Earth and such a system likely played a part in the rise of life. We strongly encourage the relationship between complex chemical systems and surfaces to be investigated, because any chemical reaction on the early Earth was significantly influenced by the geological conditions of that time. The approach that we should undertake for any further research must very closely resemble these primitive conditions and must include minimal intervention.

Finally, we wish to draw attention to a new experimental approach based on ideas expounded within the biology community some years ago which have yet to make significant in-roads within abiogenesis. We feel they are ideas with significant potential to influence the origins debate and complement the stochastic approach that we propound here. Whilst most prebiotic-related experiments are conducted within an aqueous solvent matrix composed of dissolved salts and contiguous mineral surfaces, Trevors and Pollack have pointed out that contemporary biochemistry does not function within such a matrix but one (the cellular cytosol) that more closely resembles a heterogeneous hydrogel[176]. They propose that experimental prebiotic studies should benefit from being performed in such a medium[177]. To the best of our knowledge there has been, to date, only one such experimental study of prebiotic processes within mineralogically plausible hydrogel environments[178] involving transcription processes. We have also begun a programme studying processes of prebiotic relevance within silica-based hydrogels upon heterogeneous Hadean basalts which includes: chemical transformations, peptide folding and ion diffusivity. Mineral hydrogels are, we believe, a geologically plausible mechanism to maintain concentration gradients, manipulate water structure and influence ion-macromolecule interactions[176]. They thus have significant value as proto-cytosolic media wherein the need for a continuous amphiphilic cell membrane is obviated.

5. Conclusion

In this review, we have presented a rationale to a ‘stochastic approach’ to prebiotic chemistry, which is not radical, but emphasises the fact that early Earth was never a perfect chemical laboratory for organic reactions, and thus prebiotic chemistry must embrace realistic geological scenarios, that were lacking to a great extent in much previous research. We have justified the idea of a stochastic approach based on examples in the literature and presented a relationship between prebiotic chemistry and the geological conditions of the Hadean earth. A comprehensive evaluation of the Hadean mineralogy has been undertaken here, upon which future experimental models can be pursued. The interaction of stochastic prebiotic chemistry with compositionally heterogeneous rocks brings along a higher level of complexity in addition to the inherent heterogeneity of chemical systems. Dealing with such systems is inevitable in order to understand the origins of life and it opens up fresh avenues for origins of life scientists to explore.

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Keywords:
Hadean • mineral surfaces • Origins of life • prebiotic chemistry • stochastic chemistry • systems chemistry

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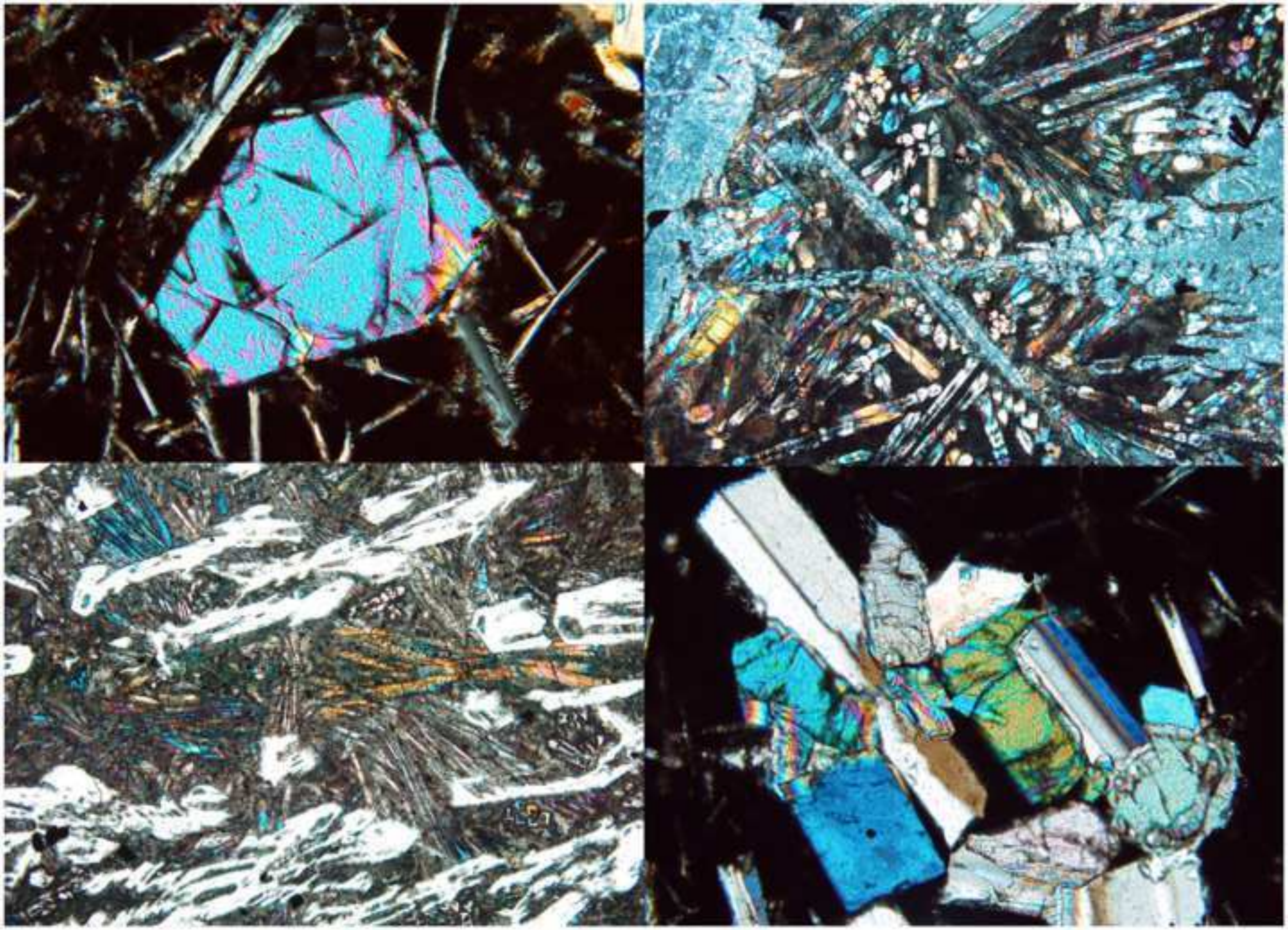
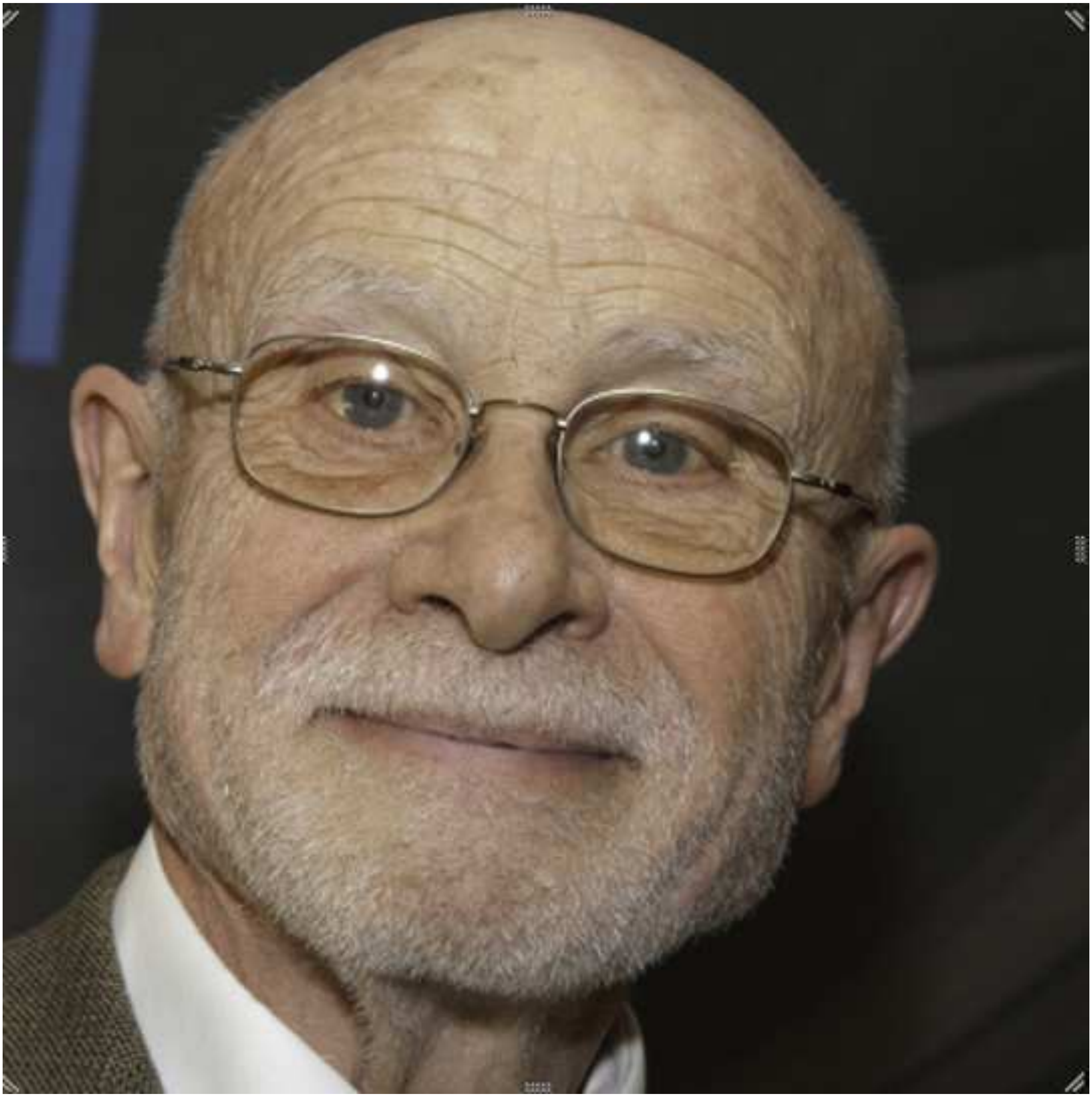
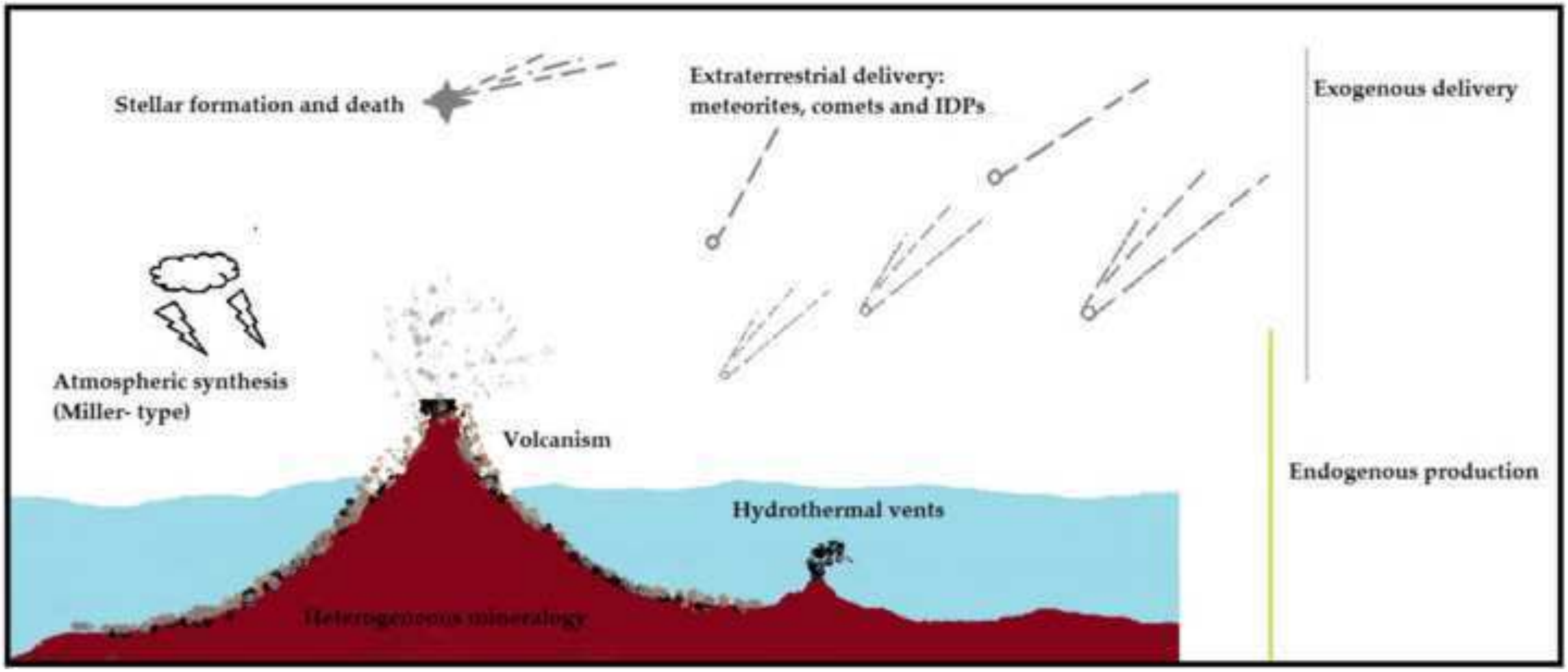
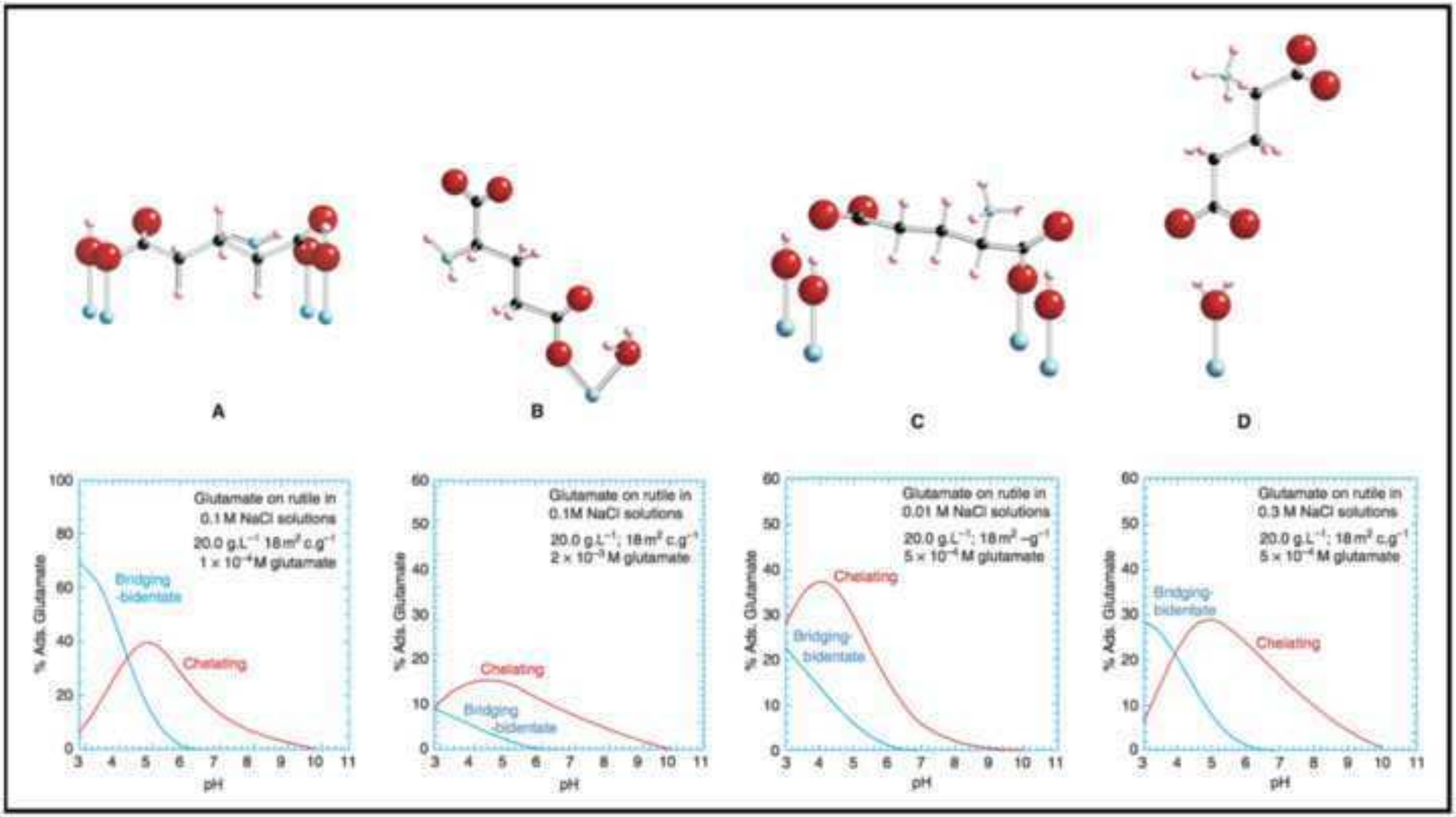


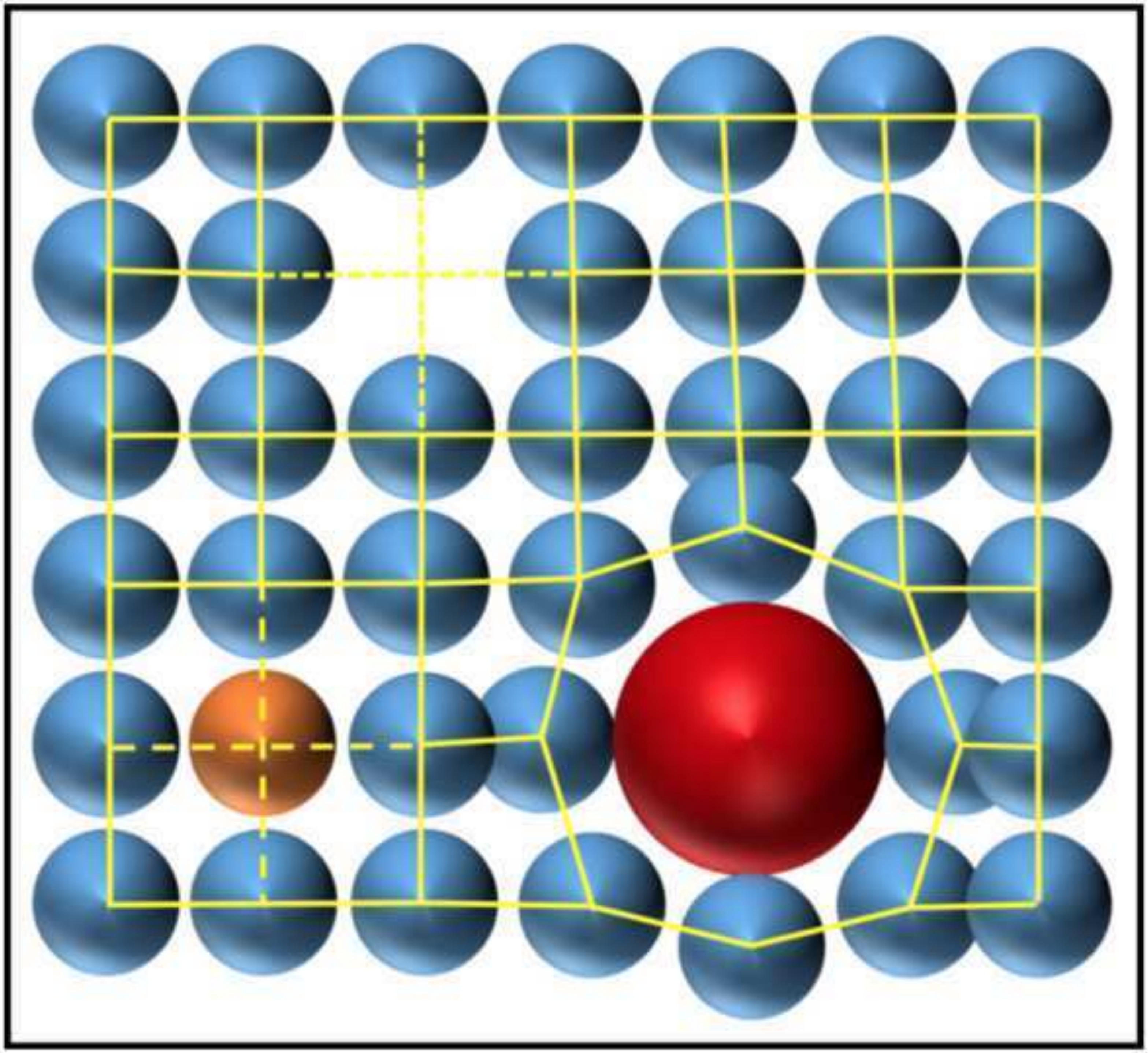
Portrait 1_Avinash Vicholous Dass

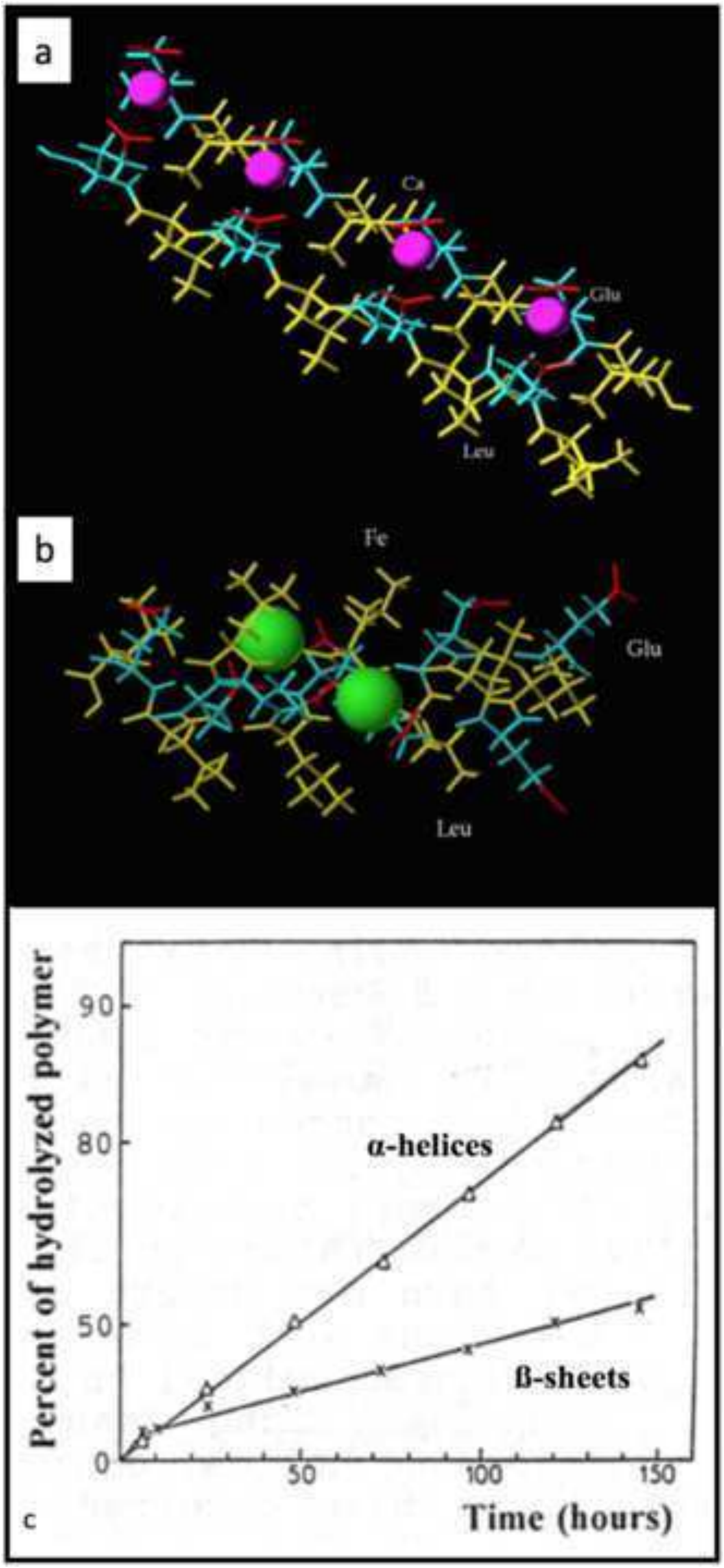
Portrait 3_Andre Brack

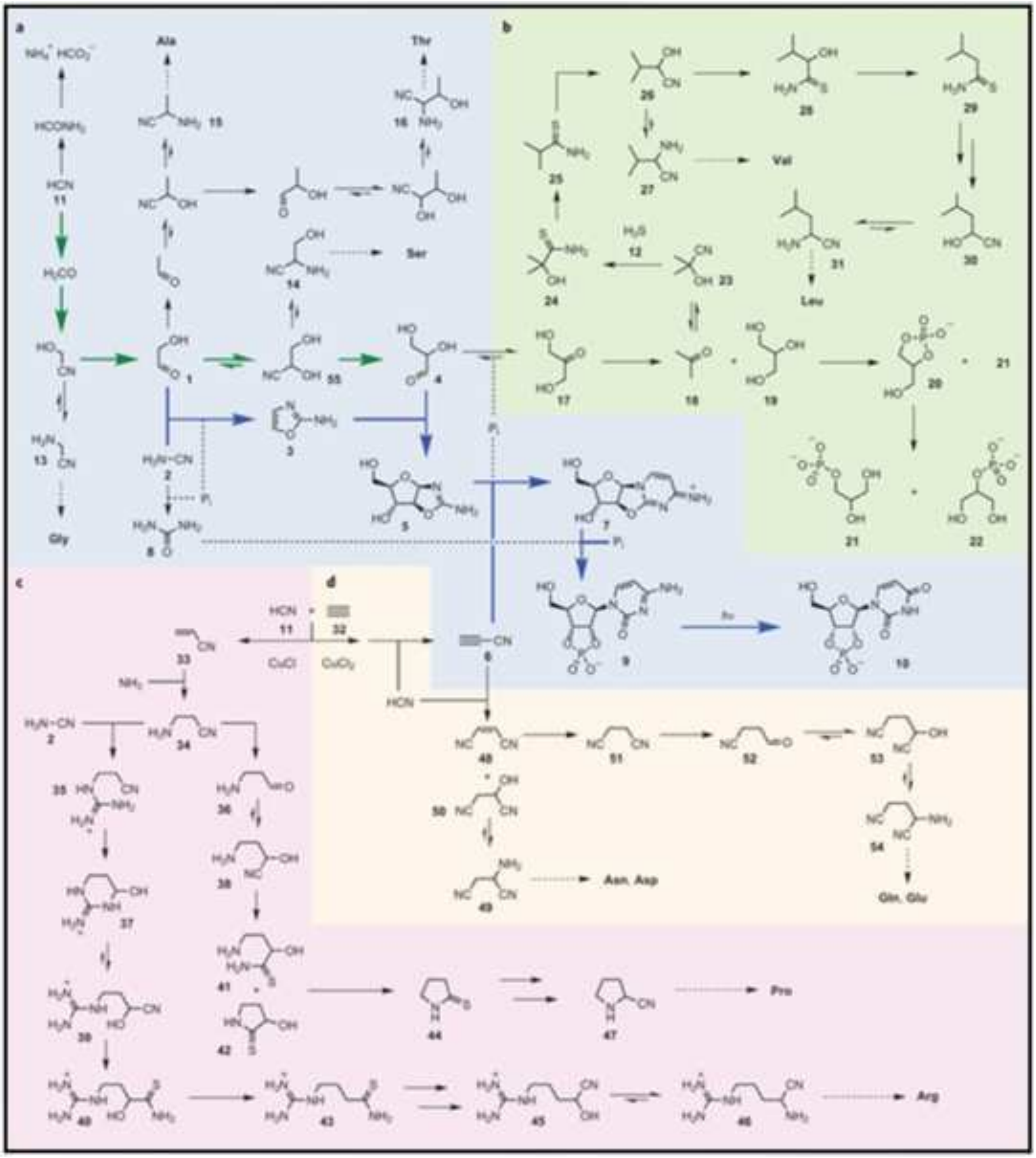


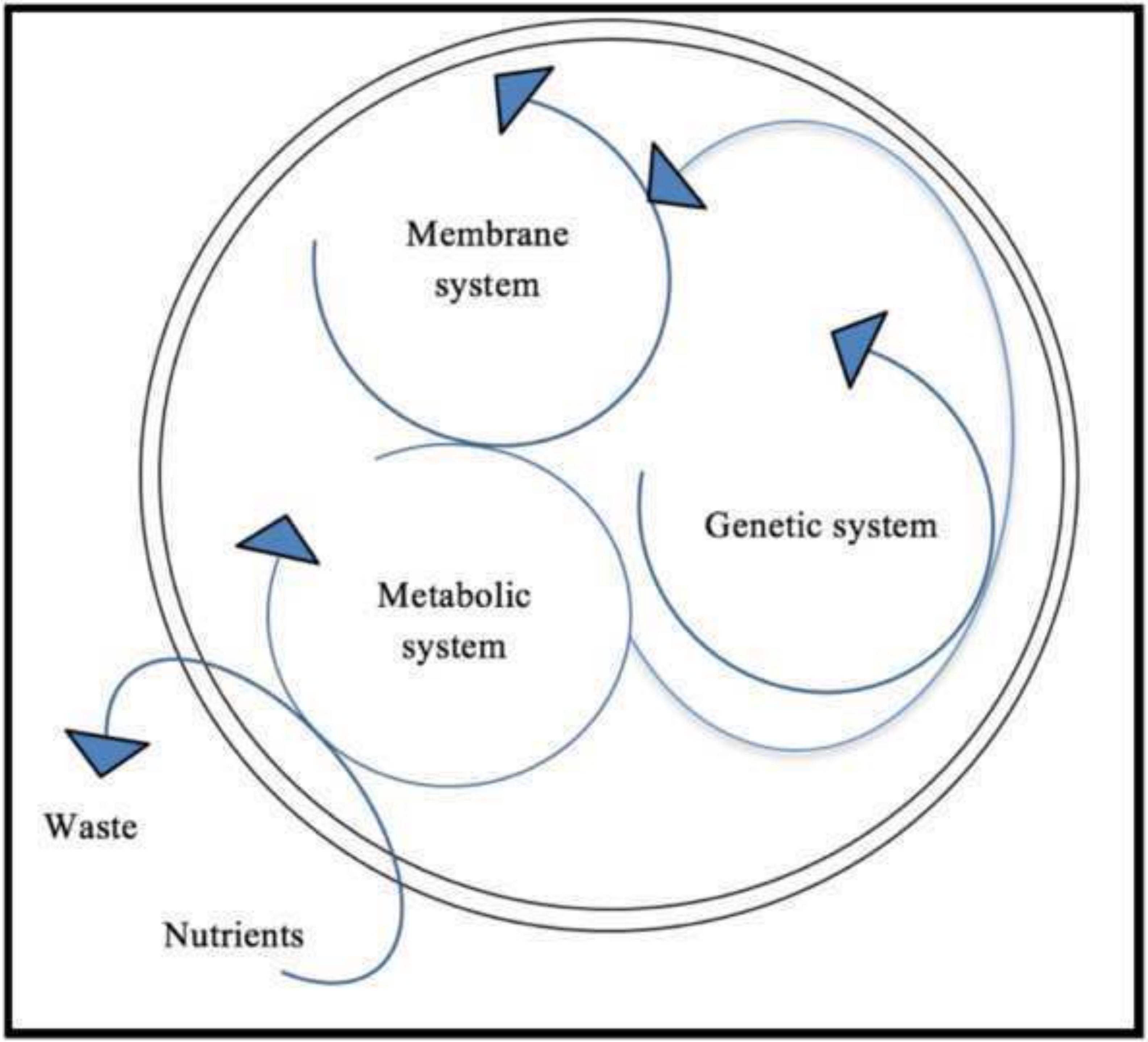

Stellar formation and death
Extraterrestrial delivery: meteorites, comets and IDPs
Exogenous delivery
Atmospheric synthesis (Miller- type)
Volcanism
Endogenous production
Hydrothermal vents
Heterogeneous mineralogy

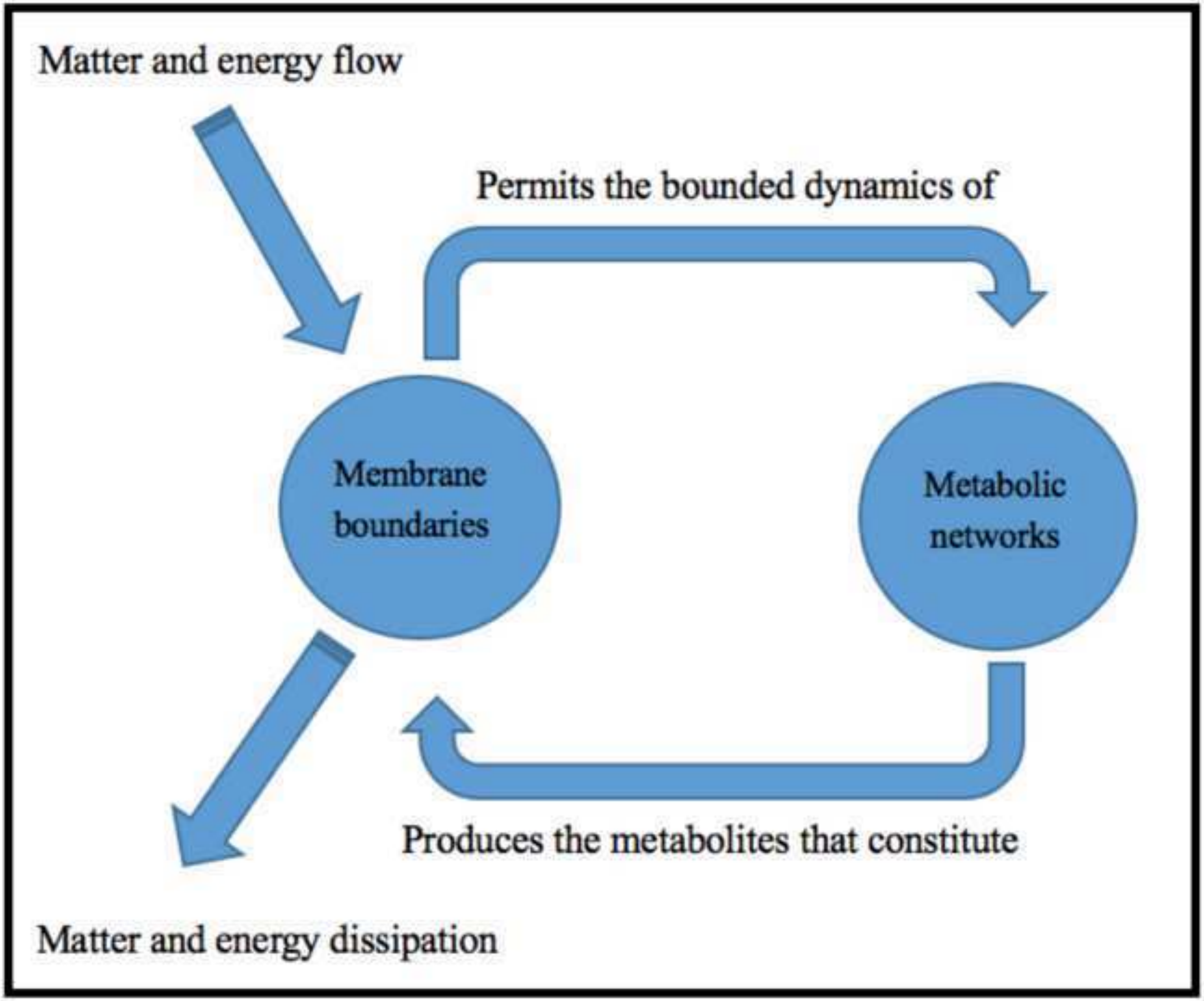

A
B
C
D
100
80
60
40
20
0
% Ads. Glutamate
Glutamate on rutile in
0.1 M NaCl solutions
20.0 g.L⁻¹ 18 m² c.g⁻¹
1 × 10⁻⁴ M glutamate
Bridging
-bidentate
Chelating
3 4 5 6 7 8 9 10 11
pH
60
50
40
30
20
10
0
% Ads. Glutamate
Glutamate on rutile in
0.1M NaCl solutions
20.0 g.L⁻¹; 18 m² c.g⁻¹
2 × 10⁻³ M glutamate
Chelating
Bridging
-bidentate
3 4 5 6 7 8 9 10 11
pH
60
50
40
30
20
10
0
% Ads. Glutamate
Glutamate on rutile in
0.01 M NaCl solutions
20.0 g.L⁻¹; 18 m² –g⁻¹
5 × 10⁻⁴ M glutamate
Chelating
Bridging-
bidentate
3 4 5 6 7 8 9 10 11
pH
60
50
40
30
20
10
0
% Ads. Glutamate
Glutamate on rutile in
0.3 M NaCl solutions
20.0 g.L⁻¹; 18 m² c.g⁻¹
5 × 10⁻⁴ M glutamate
Bridging-
bidentate
Chelating
3 4 5 6 7 8 9 10 11
pH

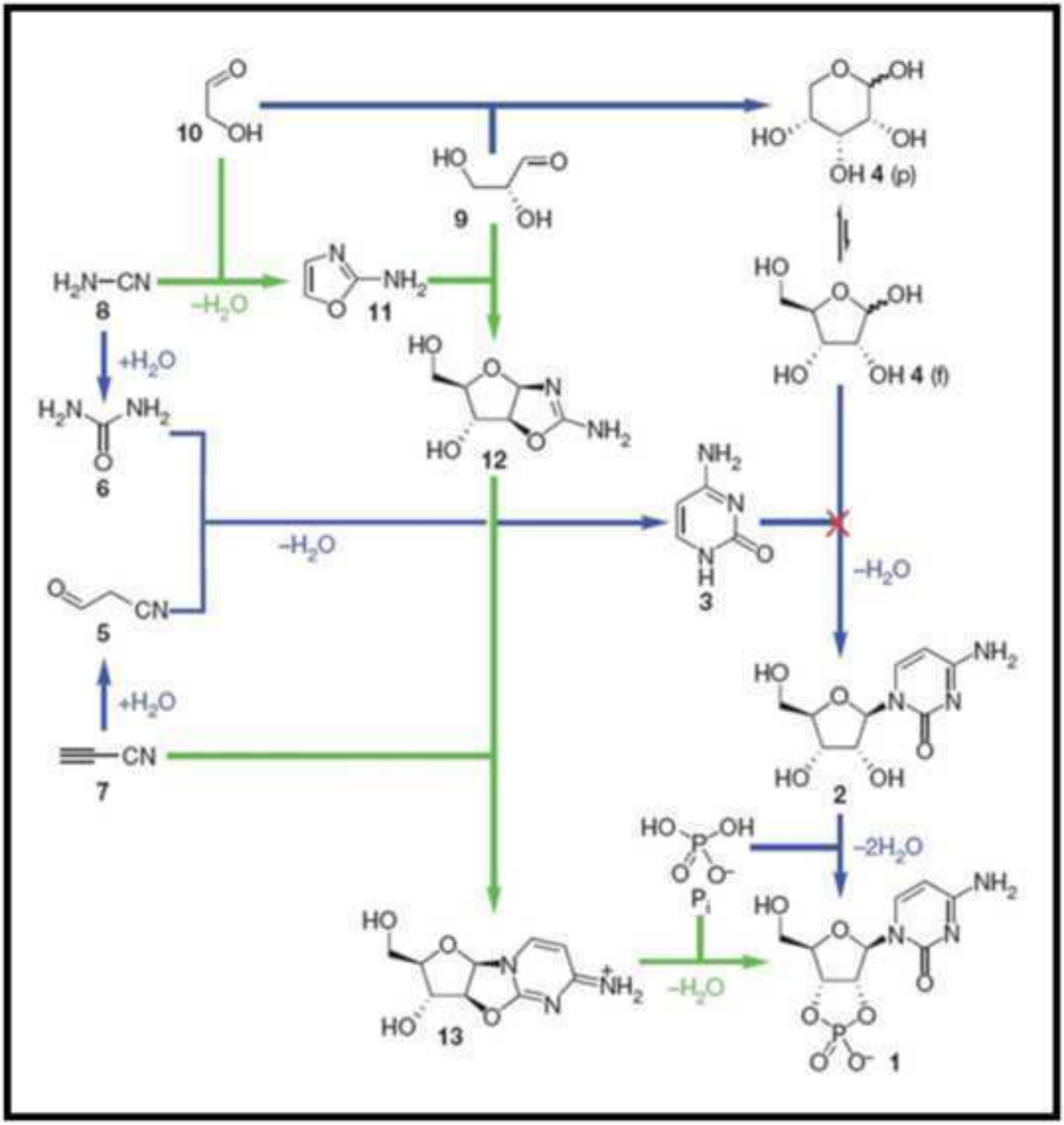


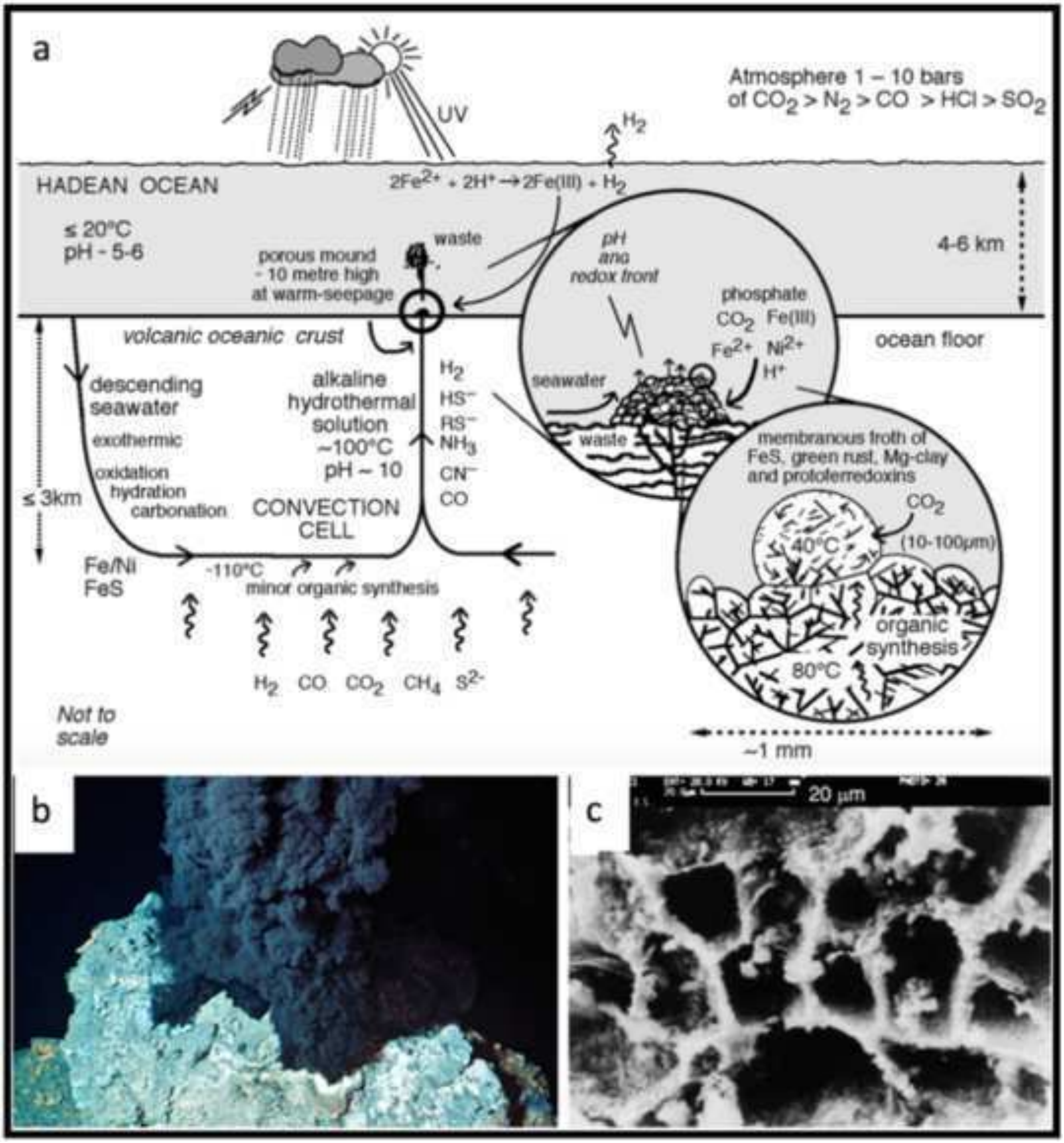

a
Ca
Glu
Leu
b
Fe
Glu
Leu
Percent of hydrolyzed polymer
90
80
50
0
50
100
150
α-helices
ß-sheets
c
Time (hours)

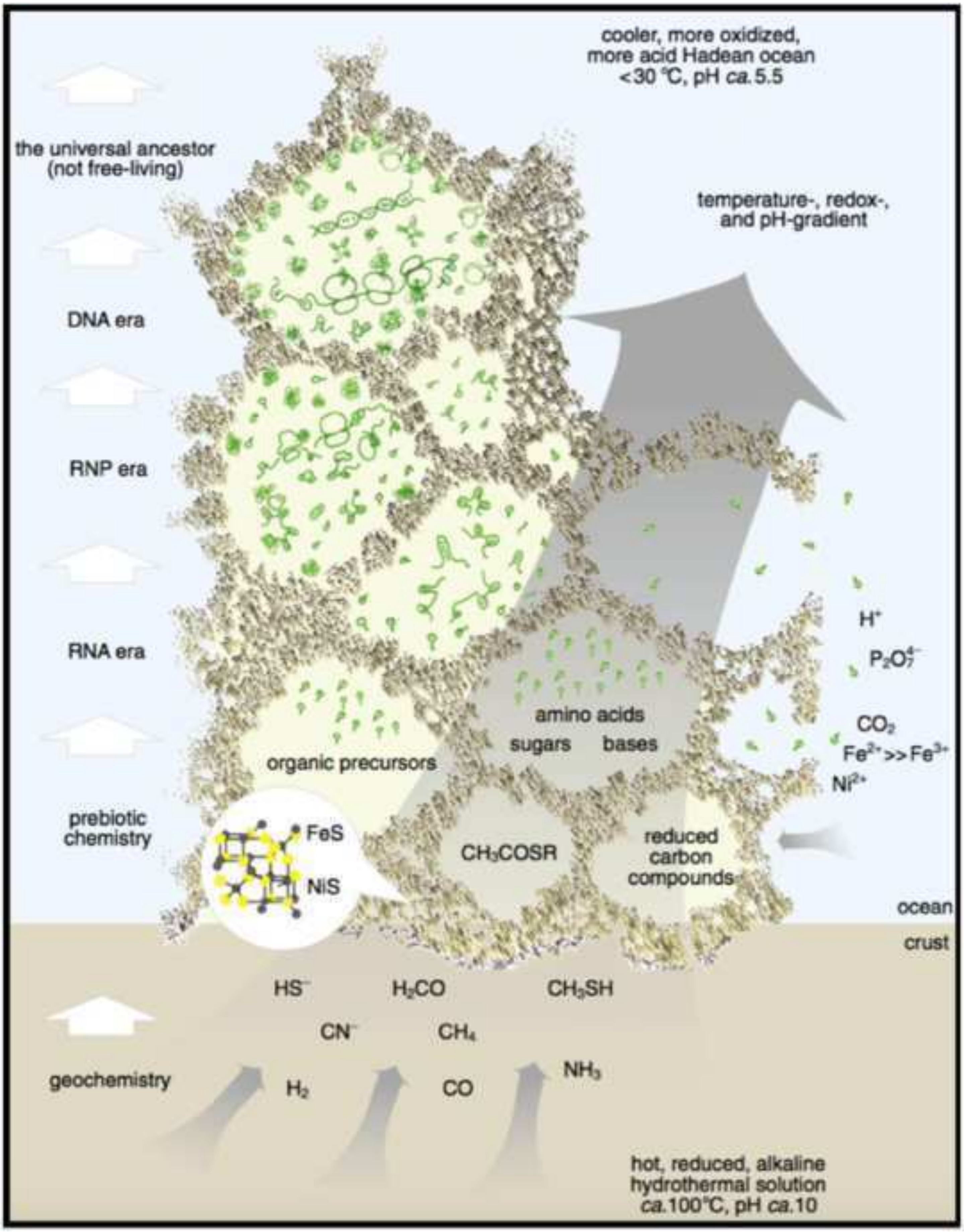

a
b
c
d
NH₄⁺ HCO₂⁻
HCONH₂
HCN
11
H₂CO
13
Gly
Ala
15
1
H₂N–CN
2
3
8
P$_i$
Thr
16
14
Ser
55
4
5
7
9
10
hν
17
18
19
20
21
22
23
24
H₂S
12
25
26
27
Val
28
29
30
31
Leu
HCN
11
32
CuCl
CuCl₂
33
NH₃
6
HCN
34
35
36
37
38
39
40
41
42
43
44
45
46
47
Pro
Arg
48
49
50
51
52
53
54
Asn, Asp
Gln, Glu

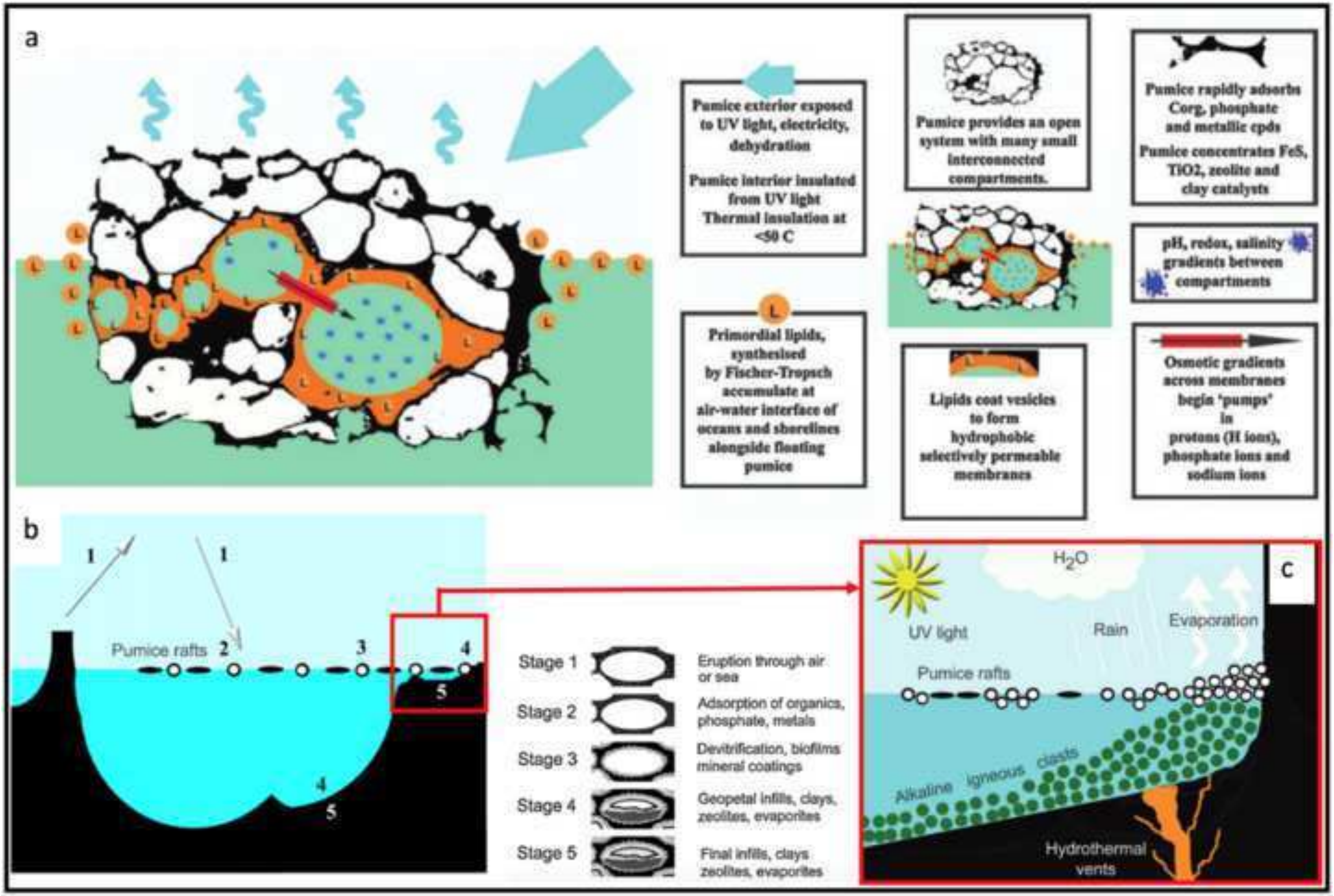

Membrane system
Genetic system
Metabolic system
Waste
Nutrients

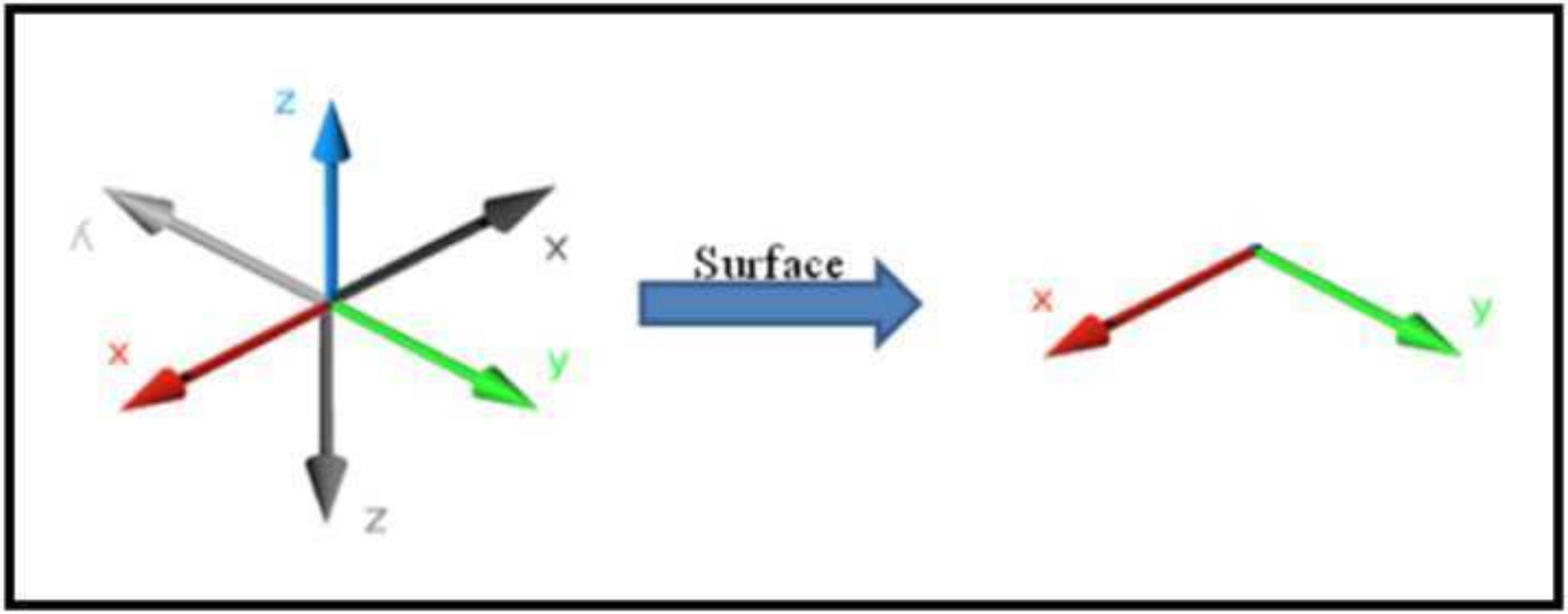

Matter and energy flow
Permits the bounded dynamics of
Membrane boundaries
Metabolic networks
Produces the metabolites that constitute
Matter and energy dissipation

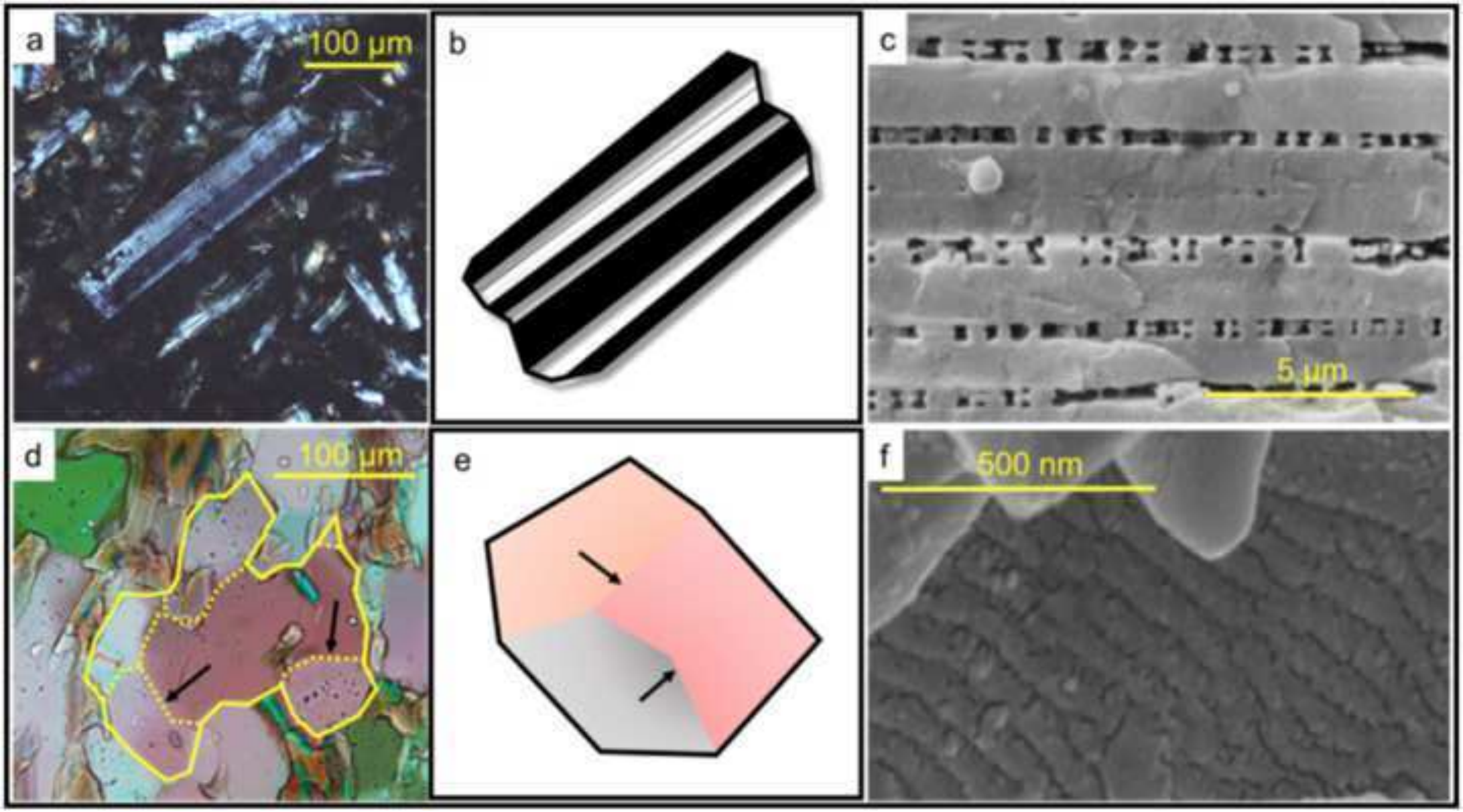

10
9
4 (p)
4 (f)
8
–H₂O
11
+H₂O
12
6
3
–H₂O
–H₂O
5
+H₂O
7
2
–2H₂O
Pᵢ
–H₂O
13
1


a
UV
Atmosphere 1 – 10 bars
of $CO_2 > N_2 > CO > HCl > SO_2$
H_2
HADEAN OCEAN
$2Fe^{2+} + 2H^+ \rightarrow 2Fe(III) + H_2$
≤ 20°C
pH ~ 5-6
waste
porous mound
~ 10 metre high
at warm-seepage
4-6 km
pH
and
redox front
phosphate
CO_2 Fe(III)
Fe^{2+} Ni^{2+}
H^+
volcanic oceanic crust
ocean floor
seawater
waste
descending
seawater
exothermic
oxidation
hydration
carbonation
alkaline
hydrothermal
solution
~100°C
pH ~ 10
H_2
HS^-
RS^-
NH_3
CN^-
CO
≤ 3km
CONVECTION
CELL
membranous froth of
FeS, green rust, Mg-clay
and protoferredoxins
CO_2
40°C
(10-100µm)
Fe/Ni
FeS
~110°C
minor organic synthesis
organic
synthesis
80°C
H_2 CO CO_2 CH_4 S^{2-}
Not to
scale
~1 mm
b
c
20 µm


cooler, more oxidized, more acid Hadean ocean
<30 °C, pH *ca.* 5.5
the universal ancestor (not free-living)
temperature-, redox-, and pH-gradient
DNA era
RNP era
RNA era
H^+
$P_2O_7^{4-}$
amino acids
sugars
bases
CO_2
$Fe^{2+} >> Fe^{3+}$
Ni^{2+}
organic precursors
prebiotic chemistry
FeS
NiS
CH_3COSR
reduced carbon compounds
ocean
crust
HS^-
H_2CO
CH_3SH
CN^-
CH_4
geochemistry
H_2
CO
NH_3
hot, reduced, alkaline hydrothermal solution
ca. 100°C, pH *ca.* 10


a
Pumice exterior exposed to UV light, electricity, dehydration
Pumice interior insulated from UV light
Thermal insulation at <50 C
Pumice provides an open system with many small interconnected compartments.
Pumice rapidly adsorbs Corg, phosphate and metallic cpds
Pumice concentrates FeS, TiO2, zeolite and clay catalysts
pH, redox, salinity gradients between compartments
L
Primordial lipids, synthesised by Fischer-Tropsch accumulate at air-water interface of oceans and shorelines alongside floating pumice
Lipids coat vesicles to form hydrophobic selectively permeable membranes
Osmotic gradients across membranes begin 'pumps' in protons (H ions), phosphate ions and sodium ions
b
1
1
Pumice rafts
2
3
4
5
4
5
Stage 1
Eruption through air or sea
Stage 2
Adsorption of organics, phosphate, metals
Stage 3
Devitrification, biofilms mineral coatings
Stage 4
Geopetal infills, clays, zeolites, evaporites
Stage 5
Final infills, clays zeolites, evaporites
c
H_2O
UV light
Rain
Evaporation
Pumice rafts
Alkaline igneous clasts
Hydrothermal vents


z
y
x
x
y
z
Surface
x
y


a
100 µm
b
c
5 µm
d
100 µm
e
f
500 nm