

## Crystals and Life

by **Gustaf O. Arrhenius**

Scripps Institution of Oceanography, University of California, San Diego, La Jolla, CA 92093-0236, USA  
(e-mail: arrhenius@ucsd.edu)

Dedicated to Professor *Jack D. Dunitz* on the occasion of his 80th birthday

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The record of life's emergence on Earth has been thoroughly obliterated by the remelting and turnover of the crust, soggy and pliable from the water, retained by the planet's gravitational field. Provided that life existed on a smaller body such as Mars with an arrested crustal evolution, a protected sedimentary record there may give clues to the decisive events in the first 500 million years in the history of our solar system. Until such records become available, we have in our guesswork to rely on laboratory constructions that need to satisfy the demands both of chemical feasibility and environmental boundary conditions. The combination leaves few survivors among competing hypotheses.

As life entails a decrease in entropy and creation of order, the origin and propagation of crystalline order has become a guiding theoretical concept. Recognizing *Jack Dunitz's* fundamental contribution to this field of knowledge, I wish to dedicate my modest discourse to this great scientist upon his scoring of the fourth significant time mark on the staff of life.

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**Introduction.** – The life of crystals? *Descartes* would consider this a contradiction in his terms, and the definitions are clear – ‘*lapides sunt; animales sunt et agunt*’. But by defining life in modern, less-philosophical terms, crystals could make the claim – they are self-assembling, they reproduce efficiently (*Fig. 1*), and are capable of evolution by mutation (*Fig. 2*). In contrast to the practically unlimited evolutionary possibilities for biomolecular systems, the evolution of crystals is, however, limited to changes in the distribution of defects and diadochic substitutions, and they are condemned forever to stay within a narrow range of preordained space groups.

In contrast, greater opportunities are offered by hybrid systems of organic molecules complexed with minerals. These surface-sorbed, hydrated molecules tend to be ordered on the host lattice but are mobile by diffusion because of the weak electrostatic bonding to the host crystal.

The potential role of minerals in concentrating and catalytically transforming organic molecules toward biofunctionality and conferring on them structural properties such as chirality appears first to have been proposed by *Goldschmidt* [1] and *Bernal* [2]. In this role, crystals were simply considered as passive mediators of limited life properties. A new, expanded concept was introduced and pursued in the imaginative work of *Cairns-Smith* [3]. He visualized the hybrid structures formed between minerals and organic compounds as the most-primitive embryonic forms of life, demonstrably capable of self-assembly and replicative reproduction and, with a stretch of the imagination, predestined for evolution. In this evolutionary process, the organic component would, with increasing complexity, gradually take over the support function

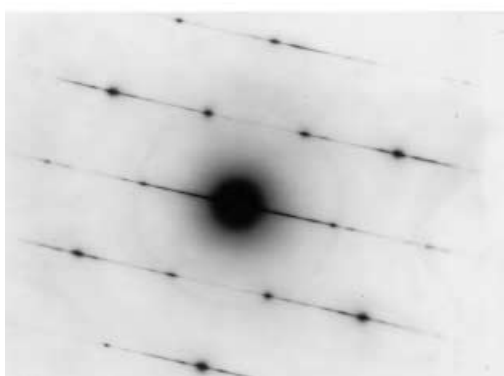
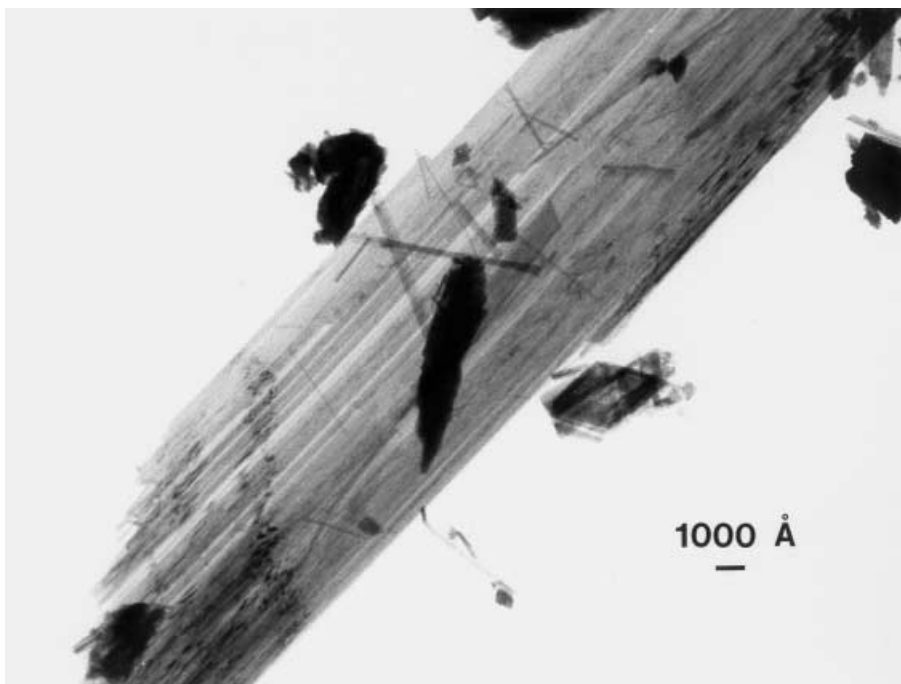


Fig. 1. *Transmission electron micrograph (TEM) of a crystal of todorokite (a marine alkaline earth manganate) in the course of reproduction by cloning.* Under chemical or mechanical stress, the crystal splits off fiber bundles, which serve as nuclei for growth of the new individuals to adult size, demonstrating the ability of crystals to reproduce. A cross-section of the mineral (*Fig. 2*) reveals another interesting property, its aperiodicity, due to varying widths of the unit-cell in the cross-fiber direction, evidenced also by the streaks in the diffraction pattern shown at the bottom of *Fig. 1*.

of the inorganic host crystal structure and eventually emerge from the mineral scaffolding with the flexibility of life as we know it.

**Environmental Constraints.** – Underlying this and any environmentally realistic scheme for biopoesis are certain requirements that would need fulfillment for any reaction to take place. One is the need for concentration. With the demise of the dream of an organically fertile atmosphere producing a concentrated ‘prebiotic soup’ that is still lingering in journalistic jargon, the realization has arisen of the enormous dilution in the planetary hydrosphere that would befall organic source components generated

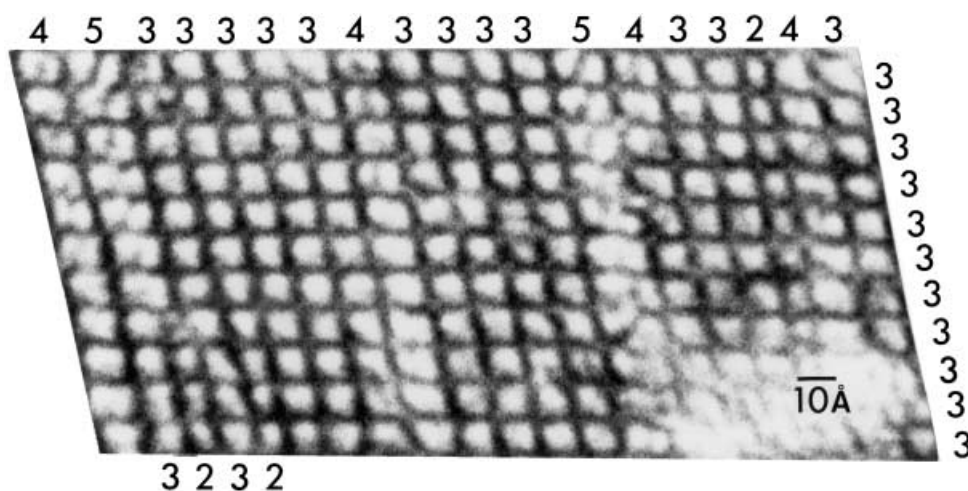


Fig. 2. TEM of a cross-section through a todorokite crystal. The structure consists of ribbons (fibers) of varying widths, consisting of 2–5 linked manganate(IV) octahedra and forming fibrous sheets, stacked in unit heights of 3 octahedra. The varying ribbon widths give rise to tunnels of corresponding variable widths, running along the fiber axis. The interlayer between the fiber sheets accommodates structural cations including (artificially) large organic cations such as dodecylammonium, which freely expand the sheets from the collapsed spacing shown in the figure. If the crystal is considered having grown downward from the top sheet with the tunnel widths 4,5,3,3,3,3, . . . , it can be seen that mutations have been induced during growth, changing the sequence to 4,3,2,3,2,3, conferring upon the crystal yet another one of the main characteristics of life. Todorokite and similar manganates are today among the most-common minerals on the deep sea floor. Although they are highly interactive with organic molecules and are illustrative model structures, they probably lack prebiotic importance, since they form only in an oxidizing environment – manganese in Archean sediments prevails in divalent form, mainly as the carbonate (TEM from [4]).

by ineffective terrestrial processes or introduced as parts-per-million components in accreting cosmic material. To have any value in constructive organic reactions, the reactants have to be raised from their diluted impotence by many orders of magnitude of concentration. The situation is paralleled by the frustration experienced by the patriotic chemist *F. Haber* in his effort to pay Germany's war debt after World War I by extracting some of the large amounts of gold present in enormous dilution in the ocean, and leading to his historical exasperation '*Verdünnung ist der Feind aller Werte*'. Several ways have been sought out of this dilemma. One shown to be highly effective under idealized conditions is freezeout in concentrated eutectic ice-liquid [5]. Difficulties are, however, bound to arise in natural saline solutions and in the presence of high proportions of unwanted interfering coconcentrated organic molecules.

This points to the importance of *selective* rather than indiscriminate concentration and to the potential role of crystals in this process. The most-effective form of selective concentration is by charge; ionic species in dilute solution will be effectively concentrated by adsorption at oppositely charged sites on external (adsorption) or accessible internal crystal surfaces (persorption).

Most molecular ions of importance as sources for biomolecular structures,  $\text{CO}_3^{2-}$ ,  $\text{CN}^-$ ,  $\text{Fe}(\text{CN})_6^{4-}$ ,  $\text{H}(\text{PO}_4)^{2-}$ ,  $\text{COOH}^-$ , etc. are negatively charged. For this reason,

interactive host minerals of potential importance in biopoesis mostly carry excess positive charge in the natural pH range (*ca.* 5 to 9). Furthermore, minerals with accessible internal surfaces have unequaled ion persorption capacity. Those with expanding–contracting sheet structures are capable of accommodating molecules of any size and clamping the layer of sorbed reactant ions, and are found to have particularly high catalytic activity. The most extensively investigated representative group of minerals with these properties comprises the ‘double-layer hydroxides’ (DLH) [6]. Their structure (*Fig. 3*) can be derived from that of brucite ( $\text{Mg}(\text{OH})_2$ ) by replacing one out of three divalent cations with trivalent ions such as  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ , *etc.* This replacement generates excess positive charge on the metal hydroxide sheets and leads to attraction of charge compensating hydrated anions into the interlayer with corresponding expansion or contraction of the adjustable metal hydroxide sheet separation.

Commonly, about four  $\text{H}_2\text{O}$  molecules are associated with the anions sorbed in the interlayer; the hydration varies with the nature of intercalated anion. Because of the weak bonding of the anions to the excess charge sites on the metal hydroxide sheet, diffusion into and within the aqueous interlayer is fairly rapid with a half-life on the order of an hour in micrometer size crystals. The resulting disorder is counteracted by the attractive ordering effect of the cations in the host lattice. The interlayer of the DLH thus forms an unusual medium, a highly concentrated (*ca.* 14M), weakly ordered, viscous solution of monomolecular thickness, clamped between two catalytically active surfaces.

In nature, these minerals are relatively common but inconspicuous. They form as hydration products at ocean weathering of basalts [8], by crystallization from high-salinity solutions [9], at serpentinization, *etc.* Of particular interest is the DLH mineral green rust where the divalent ion is  $\text{Fe}^{2+}$  and the trivalent  $\text{Fe}^{3+}$  (*Fig. 4*). This mineral, discovered by *Bernal et al.* [10], has today a limited occurrence, mainly in reducing soils. However, in the Archean, the earliest period in Earth’s history, the widespread occurrence of sedimentary ferroferric oxide, magnetite, testifies to its precursor, green rust, as one of the most-common components of early ocean sediments. This is due to the lack at that time of free oxygen in the atmosphere, allowing buildup in the hydrosphere of dissolved  $\text{Fe}^{2+}$ . Under the present oxic conditions, this is rapidly oxidized and precipitated as  $\text{Fe}^{\text{III}}\text{OOH}$ . Current experimental work, because of ease of handling, mostly employs the magnesium-aluminum member of the DLH group, the mineral hydrotalcite (*Fig. 5*). Utilizing this DLH system, *Eschenmoser* and co-workers [7] first demonstrated its power in performing the functions of selective concentration and catalytic formation of source molecules for nucleic acids as discussed below. The physical chemistry of formation and exchange in these minerals has been investigated particularly by *Braterman* and co-workers [11].

Among anions that have attracted particular interest as source components for biomolecules, phosphate and cyanide species are prominent. Because of the pervasiveness and antiquity of phosphate-based biochemistry [13], the autocatalytic activity of p-RNA [14] and the remarkable progress in ribozyme chemistry (*e.g.*, 15), the hypothesis of a nucleic acid based world is explored as an early stage in the emergence of life. This concept is now rather generally considered, but has earlier been questioned due to the previous lack of a successful scheme for the spontaneous formation of ribose

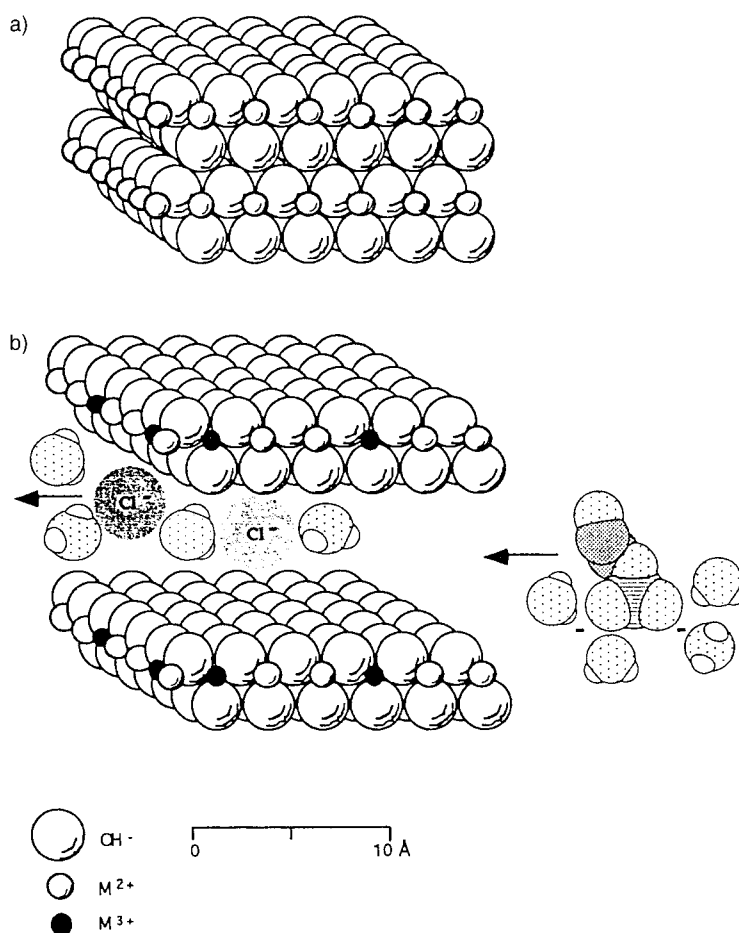


Fig. 3. *a*) Single-layer hydroxide (SLH) structure, exemplified by  $\text{Mg}(\text{OH})_2$  (brucite),  $\text{Fe}(\text{OH})_2$ , and  $\text{Mn}(\text{OH})_2$ . The fairly strongly bound sheets can be separated and intercalated with uncharged polar molecules. *b*) Double-layer hydroxide (DLH) structure arising from replacement of a fraction (1/3) of the divalent cations in the metal hydroxide layer with trivalent ions such as  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ . This substitution induces excess positive charge on the metal hydroxide sheets, which separate and admit an interlayer consisting of anions associated with about four  $\text{H}_2\text{O}$  molecules and weakly bound to the excess positive charge sites. This second layer of the double-layer structure forms a concentrated (ca. 14M) two-dimensional, diffusive, and viscous aqueous solution, clamped between the catalytic metal hydroxide sheets. Monovalent ions such as  $\text{Cl}^-$  are readily replaced by higher-charge-density anions such as phosphate, aldehydephosphate, carbonate, and metal cyanide that are considered as nucleotide source molecules. The figure shows schematically the replacement of two monovalent  $\text{Cl}^-$  ions by the larger, divalent, protonated, and hydrated glycolaldehyde phosphate anion, expanding the interlayer from 3.6 to 6.4 Å (from [7b]).

phosphate, the key backbone molecule in RNA or, lately, of threose phosphate based TNA [16]. This latter, a structurally and geosynthetically simpler nucleic acid analog, is of particular evolutionary interest since it, in contrast to pyranosyl-RNA or hexose based analogs, pairs strongly with the present-day form of RNA.

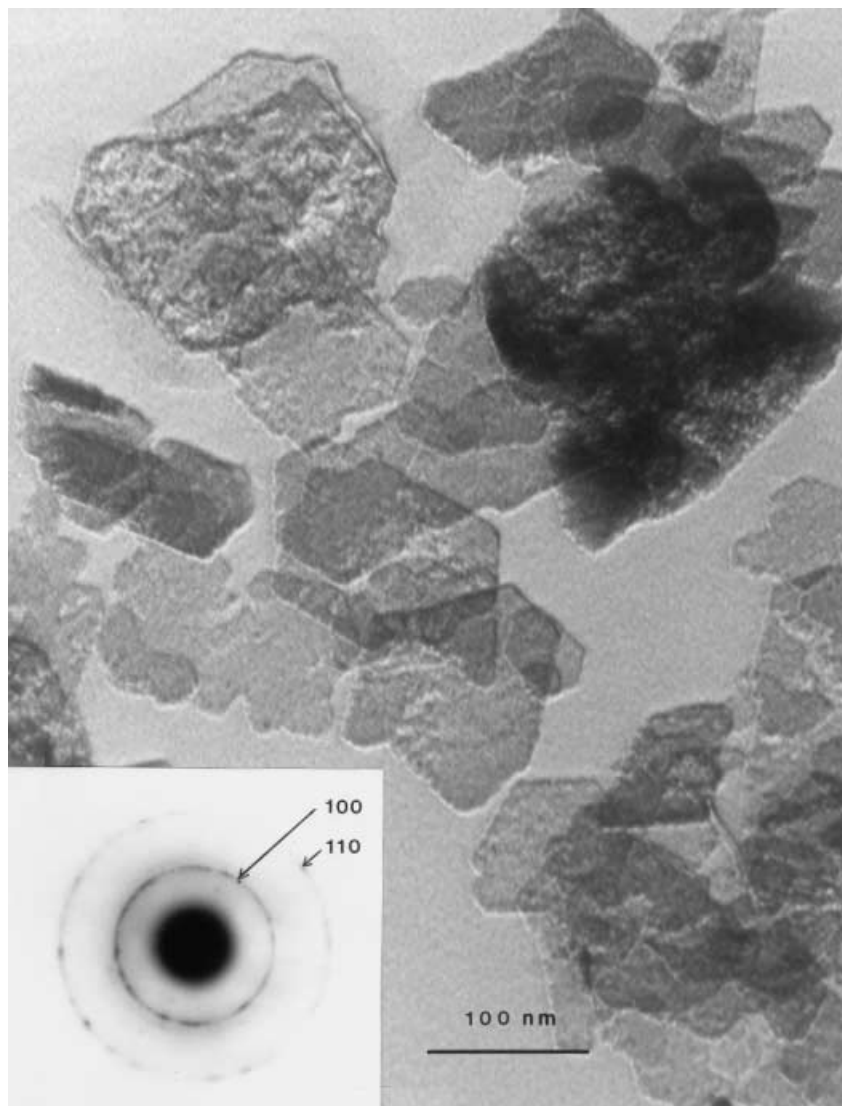


Fig. 4. *Synthetic green rust* (low temperature, rhombohedral modification). The main metal hydroxide layer here has the composition  $\text{Fe}_2^{\text{II}}\text{Fe}^{\text{III}}(\text{OH})_6$ , and the interlayer is populated by  $\text{Cl}^-$  ions and  $\text{H}_2\text{O}$ . The thin, leaf-like crystals rest preferentially on basal faces, exposing almost exclusively vertical planes ( $h00$  and  $hk0$ ) to diffraction of the electron beam (*inset*). Green rust is metastable against conversion to magnetite,  $\text{Fe}^{\text{II}}\text{OFe}_2^{\text{III}}\text{O}_3$ , which does not form directly from aqueous solution; green rust is, therefore, probably a main source of the abundant magnetite in the Archean banded iron sediments. Green rust is an efficient interlayer scavenger of phosphate species, and of cyanide and hexacyanoferroate ion with which it converts to crystalline iron cyanide, a potential reservoir for prebiotic cyanide (*Fig. 7*) (from [12]).

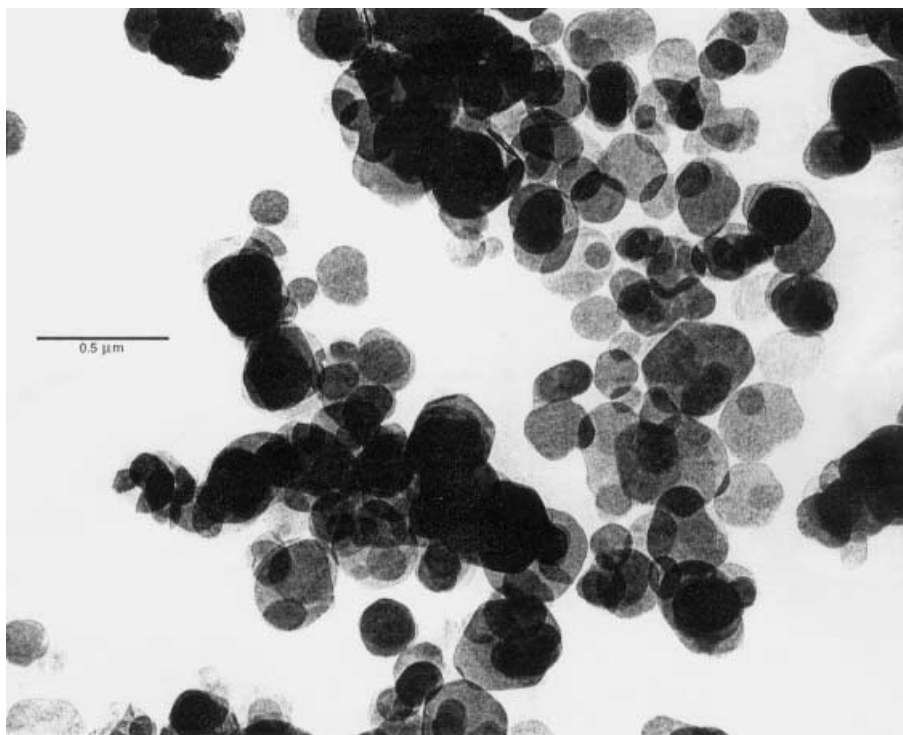
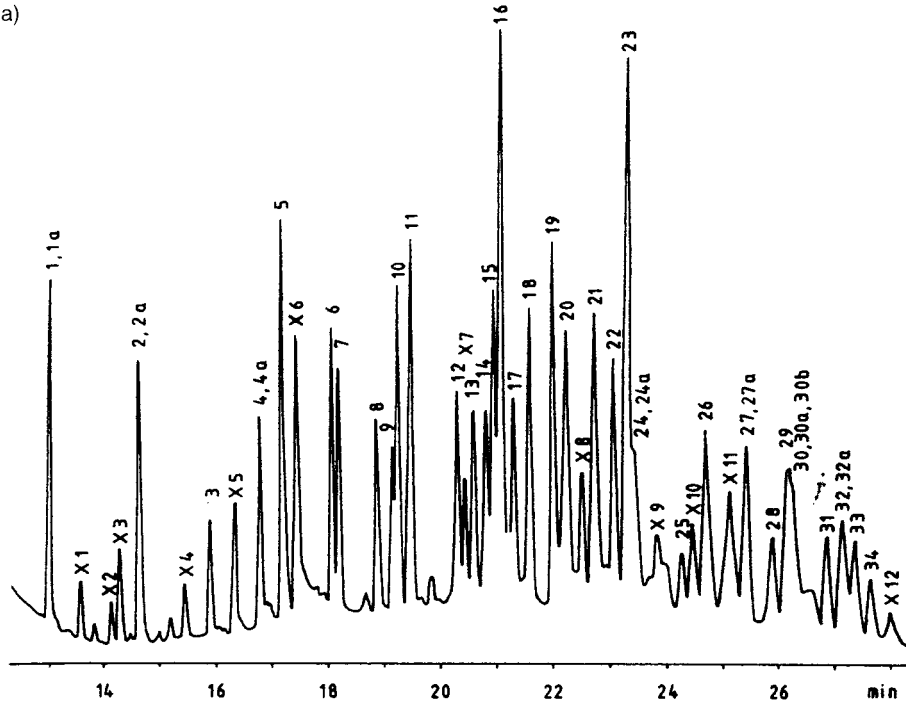


Fig. 5. Thin, platy crystals of the mineral hydrotalcite with main metal hydroxide layer composition  $Mg_2Al(OH)_6$ , together with green rust (Fig. 4), a common representative of the double-layer hydroxide (DLH) mineral family. The interlayer in this synthetic sample consists of an aqueous solution of  $Cl^-$  ion. The round, coin-like habit of the rhombohedral crystals is due to turbostratic growth. Hydrotalcite has proven to be an efficient catalyst for the selective aldol phosphate condensation reaction, a step toward natural formation of nucleic acids (from [7b]).

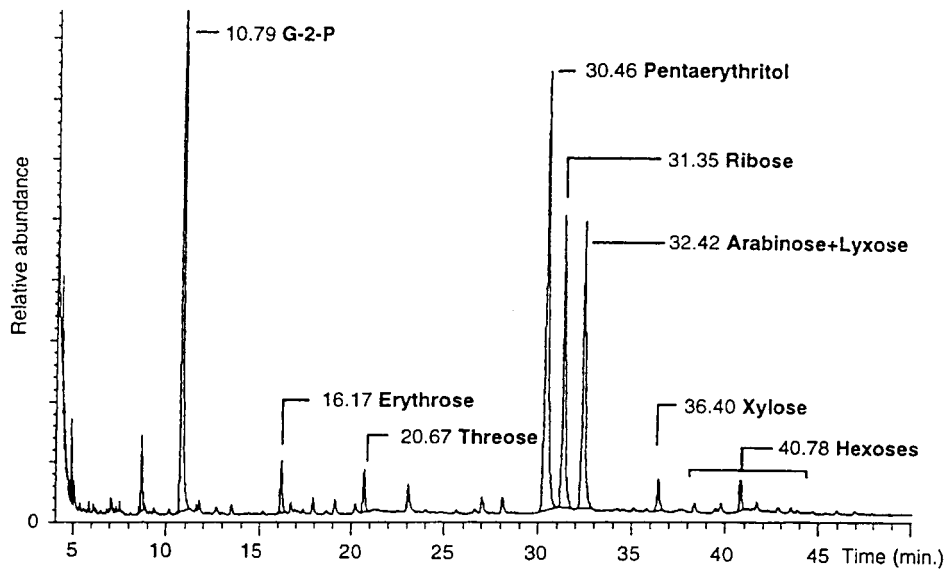
**The Formose Reaction in Prebiotic Chemistry – An Outdated Concept.** – The commonly raised but now obsolete geosynthetic argument against spontaneous natural production of the various forms of nucleoside phosphates has been based on the weakness of an earlier commonly invoked pathway through the formose reaction. This relies on the autocatalytic formation of sugars and sugar derivatives by aldolization, initially of formaldehyde. The biogeochemical improbability of this process has several roots. One derives from the fact that the reaction proceeds at a constructive rate only under naturally improbable conditions [17]. Second, it is nonselective and leads to a large variety of aldoses, ketoses, and sugar alcohols with only small fractions of potentially bioactive compounds such as ribose (Fig. 6). Furthermore, unprotected sugars have a short lifetime against hydrolysis, making them unlikely as participants in biogenic processes [18]. Finally, dilution and lack of plausible selective and effective concentration mechanisms that imperil most prebiotic schemes exclude the formose reaction when invoked in this context.

In attempts to establish geochemically acceptable solutions to these problems, progress has been achieved by demonstrating probable sources in nature of activated

a)



b)





(condensed) highly soluble phosphates [19] that have been shown experimentally to be efficient phosphorylation agents [20]. They are effectively sorbed in surface-active minerals such as DLH and thereby strongly concentrated [21]. Effective phosphorylation mechanisms and rapid mineral-assisted condensation of aldehyde phosphates have been demonstrated to form tetrose and pentose phosphates in high yield [7][22].

Of the simple aldehydes, glycolaldehyde provides a source for condensed aldehyde phosphates. It is produced in the space medium [23] and in geochemically reasonable (neutral, CO<sub>2</sub>–N<sub>2</sub> based) atmospheres, as shown in the classical experiments by L $\ddot{o}$ b [24], modeling planetary electrical-discharge reactions.

A remaining uncertainty has been how highly dilute solutions in the hydrosphere of these uncharged aldehydes (or, for that matter, any of the countless uncharged molecules invoked in prebiotic chemistry) could have been selectively brought to sufficiently high concentration to permit further reaction, including charging by phosphorylation. A potential solution to this problem is offered by recent experimental results [25]. Sulfite ion is an abundant product in volcanic exhalates and is efficiently sorbed in the interlayer of DLH minerals. It attracts aldehydes from dilute solution by complex formation, placing them in contact with reactive phosphate species that may share the sorption sites in the expandable interlayer. The subsequent phosphorylation step has yet to be demonstrated experimentally; it is expected to occur upon removal of the sulfite in equilibrium with the sulfonate ligand.

A plausible mechanism has been found in the facile phosphorylation of aldehydes with amidotriphosphate catalyzed by magnesium ion [22]. The reaction proceeds to completion even in dilute solutions of the reactants. This process may be extended to the micromolar range of reactants by utilizing the aldehyde capture and interlayer concentration effect of the surface active DLH minerals. Other successful phosphorylation mechanisms [26] become geochemically more complex by invoking adjuvants such as urea, which, for its formation, depends on reduced nitrogen compounds as source molecules.

- ← Fig. 6. *The failure of the formose reaction to serve as a selective source of specific sugars and to operate in the Archean hydrosphere.* a) Gas chromatogram of trifluoroacetylated forms of the butyl oximes of the carbohydrates arising in a formose reaction. The peaks 8 and 14 are the ribose derivatives; the numerous other products are ketoses, aldoses, and various sugar derivatives (from [7b]). It is difficult to consider a selective prebiotic synthesis of specific sugars such as ribose or threose from this complex mixture. This explains the frequently made claim that nucleic acids would be highly unlikely natural products in the Archean environment. Also, a concentrated alkaline solution is needed for meaningful yields, and unprotected sugars hydrolyze rapidly in H<sub>2</sub>O. These conditions contribute further to the negative formose-based opinions. b) *The mineral-induced glycolaldehyde phosphate reaction* [7b,c]. Here, advantage is taken of high selectivity due to the exclusion of ketoses and to kinetic effects. Further advantage is offered by the high concentration and catalytic aldolization achieved by sorption in the interlayer of DHL minerals and the protection against hydrolysis offered by phosphorylation and by the crystal interlayer environment. The application of these findings to prebiotic chemistry has opened up a more-credible path to the formation of specific pentose and tetrose sugar phosphates as potential prebiotic components of p-RNA and TNA. The figure shows a gas chromatogram of products from the glycolaldehyde phosphate reaction; in this case, with glyceraldehyde phosphate in the interlayer of mangalite, a DLH mineral with Mn<sup>2+</sup> as the divalent ion in the main hydroxide layer and at pH 7.5, 40° and 6 d. The reaction is highly selective for the formation of pentose phosphates; the proportions of ribose vs. lyxose + arabinose phosphate are influenced by the cation species in the mineral; the highest total yield of pentoses was obtained with Co<sup>2+</sup> as hydroxide layer cation [7c].

**The Nitrogen Problem.** – A geochemically plausible synthesis path and concentration mechanism for nitrogen-containing molecules must eventually be found since nitrogen-based life is evident. Such a model should take into account modern concepts of ancient planetary atmospheric and hydrospheric chemistry. This requirement has yet to be satisfied; in a low-energy, environment,  $N_2$  tends to behave as an inert gas, and concentrated sources of reduced nitrogen are hard to come by on a lifeless Earth. In contrast, nitrogen is reactive in the energetic and strongly-reducing space environment where cyano compounds are abundant. Perhaps the most-promising avenue to this problem is, therefore, reliance on comets as a proven factory of cyanide species and the accretion of cometary matter on Earth. An efficient mechanism exists for extraction of cyanide from the resulting highly dilute solution [25]. In the primordial anoxic hydrosphere,  $Fe^{2+}$  ion is expected to reach steady-state concentrations on the order of several parts per million and would readily form the stable tetravalent hexacyanoferroate complex. This, in turn, has a high affinity for the interlayer in green rust (Fig. 4), a common DLH mineral in the primordial ocean, as evident from the abundance of its decomposition product, magnetite, in Archean banded-iron sediments. The green rust–hexacyanoferroate solid is structurally unstable and slowly (within weeks) decomposes to magnetite and an insoluble cubic iron cyanide (Fig. 7) similar or identical to Prussian Blue, potassium ferriferrocyanide.

This cyanide separation process would also provide an escape from the ‘Miller paradox’ [27], which recognizes that cyanide, in the presence of ubiquitous formaldehyde in the environment, forms highly stable cyanohydrin and thereby eliminates cyanide as a useful prebiotic downstream reactant. In its extracted, solid form, iron cyanide may provide a concentrated potential reservoir from which free HCN may be released upon local elevation of pH.

In contrast to its strong bonding in green rust, hexacyanoferroate ion is more weakly bound in the interlayer of DLH minerals that lack transition-element ions in the main hydroxide sheet; however, other interesting aspects of DLH–cyanide complex reactions can be studied in this environment [28].

**Proto-crystalline Solids.** – Recently, experiments relying on mineral-induced catalysis for the spontaneous formation of bioorganic source molecules have been expanded to include the amorphous precursors of hydrous minerals forming by precipitation in the hydrosphere of  $[HMgCa][A^-]$ -type minerals, where  $A^-$  represents anions such as  $OH^-$ ,  $H(PO)_4^{2-}$ ,  $SO_3^{2-}$ , etc. In the ordered structures formed by Ostwald ripening of the initially amorphous precipitates, catalytically active cations such as  $Mg^{2+}$  occur at precise, and catalytically not necessarily optimal, distances in the ordered crystal structure. In contrast, in the amorphous precursor precipitates, cation–cation distances vary over a range of ca. 1 Å, potentially offering access to optimal cation distances for the catalysis of specific reactions. Attention has been drawn by G. Zubay to the potential importance of specific Mg–Mg distances in mineral-induced catalysis, based on the observation by Steitz and Steitz [29] that all known nucleic acid polymerases employ two strategically positioned divalent cations in the polymerization step with an invariant interionic distance of 3.9 Å.

Experiments with amorphous precursors in the hydrotalcite–whitlockite compositional systems show that the presence of sugar phosphates or nTP in the source solution

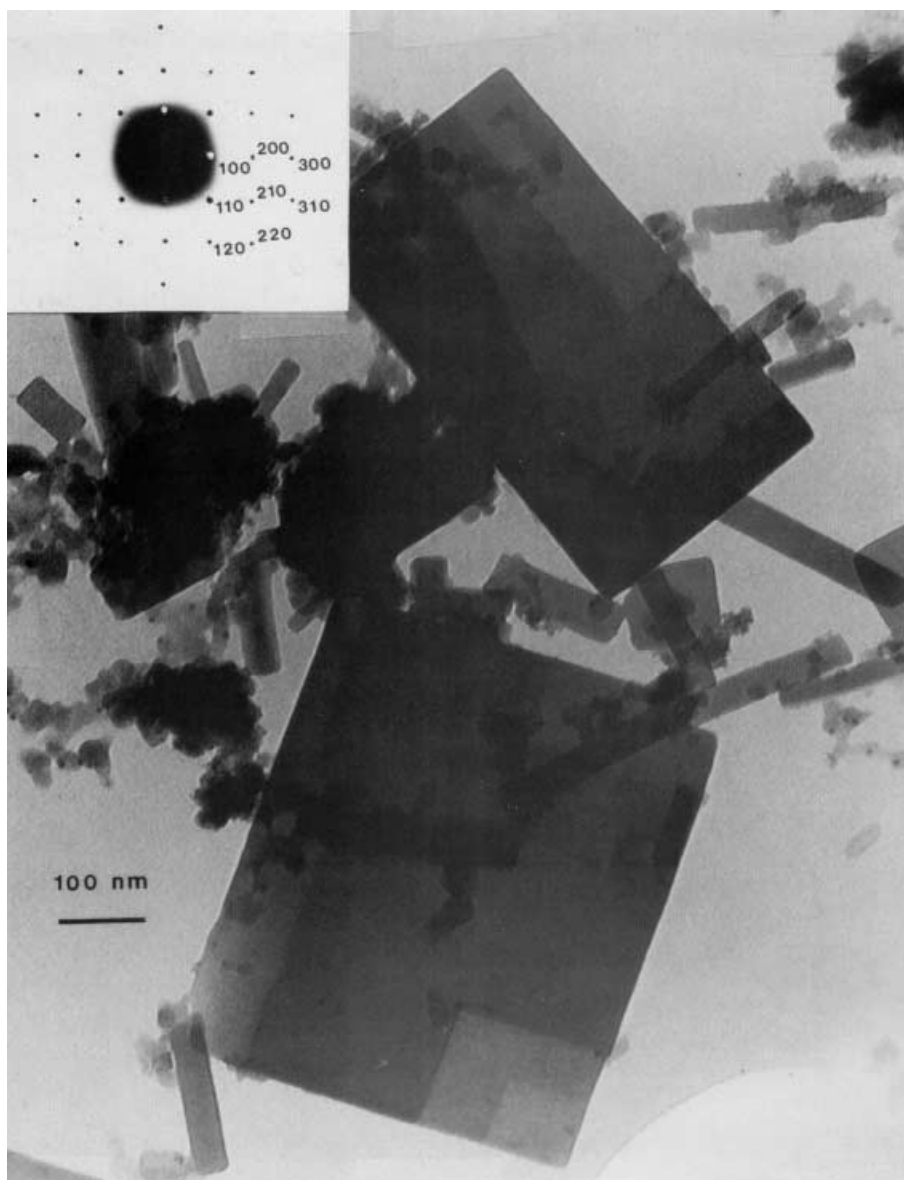


Fig. 7. Thin, platy crystals with the structure of ferroferricyanide (Prussian Blue) formed by epitactic growth from green rust (Fig. 4) intercalated with hexacyanoferrate ion sorbed from dilute solution. The electron-diffraction pattern (*inset*) indicates a high degree of crystalline perfection in this solid, which is thought to have provided a reservoir of concentrated cyanide in the Archean hydrosphere, available for prebiotic reactions requiring reduced nitrogen (from [12]).

leads to initially amorphous, stoichiometric compounds with these anions, and with a range of Mg–Mg distances, comprising the *Steitz* value and supporting the potential of the *Zubay* proposition.

**Compartmentalization of Life.** – Collectively, the mineral-catalysis experiments are placing the TNA–pRNA world concept on a somewhat safer geochemical footing. Photochemical energy can be transduced into motion in DNA, and surface-active DLH minerals expand freely to accommodate molecular complexes of any size. These structures, thus, also serve as compartmental systems with flexible membranes and what may be called primitive cellular metabolic function. Like cells, they retain phosphate-charged reactants against high concentration gradients and exchange matter with the surroundings by controlled diffusion through the ‘pores’ provided by the opening of the interlayers at the crystal edges. Here, the exposed negative charge on the interrupted metal hydroxide ‘membrane’ leads to sorption of cations as ‘gatekeepers’.

Current prebiotic-model experiments represent oversimplifications that, in many cases, ignore competing side reactions with the other compounds expected to be present, a dilute state of the reactants and geochemical–cosmochemical improbabilities. However, the choice of experimental conditions, emphasizing selective concentration and reaction, and simulating geophysically and geochemically plausible conditions have contributed to narrowing the credibility gap.

**Crystals as Recorders of the Ancient Environment.** – In yet another capacity, crystals serve as indicators of the controlling environment of Earth and Mars, the latter as yet rudimentary. In some cases, they are suggested as actual remnants of the earliest life. When autotrophic organisms in the most-basic life processes draw on inorganic carbon to build up biogenic matter using unique enzymes, the light isotope  $^{12}\text{C}$  is strongly favored over  $^{13}\text{C}$ . In the search for mineral biomarkers that can be used to trace life in the earliest rock record on Earth, preserved in the Isua supracrustal formation in southern West Greenland, graphitic iron carbonate rocks were found, which were, at the time, generally believed to be of sedimentary origin, and some graphite crystals in this rock sample showed a marked enrichment of the light  $^{12}\text{C}$  isotope [30]. This finding was considered unique since it would establish traces of life as far back as 3,800 million years. A detailed follow-up study revealed, however, that this was a false start in the tracing of ancient life. The graphite-bearing iron carbonate rocks, generally thought at the time to be of sedimentary origin proved to be a product of deposition from hot carbonate bearing solutions, infiltrating the deep crustal rocks under high pressure at temperatures in the range of 450–600°.

The misinterpreted iron carbonate rocks proved interesting in themselves by pointing to a geochemical process capable of generating graphite by an inorganic mechanism and possibly fractionating the carbon isotopes in the process. The divalent iron in the carbonate reduces the carbon monoxide in equilibrium with carbon dioxide and carbonate to abundant crystalline graphite. As a result,  $\text{Fe}^{\text{II}}$  is partially oxidized and forms associated masses of magnetite,  $\text{Fe}^{\text{II}}\text{OFe}_2^{\text{III}}\text{O}_3$  (*Fig. 8*). At lower temperatures than those that prevailed in the Greenland rocks, laboratory experiments have later shown [31] that the disproportionation of iron carbonate leads to the formation of a vast array of organic compounds. Unfortunately, from the point of view of prebiotic

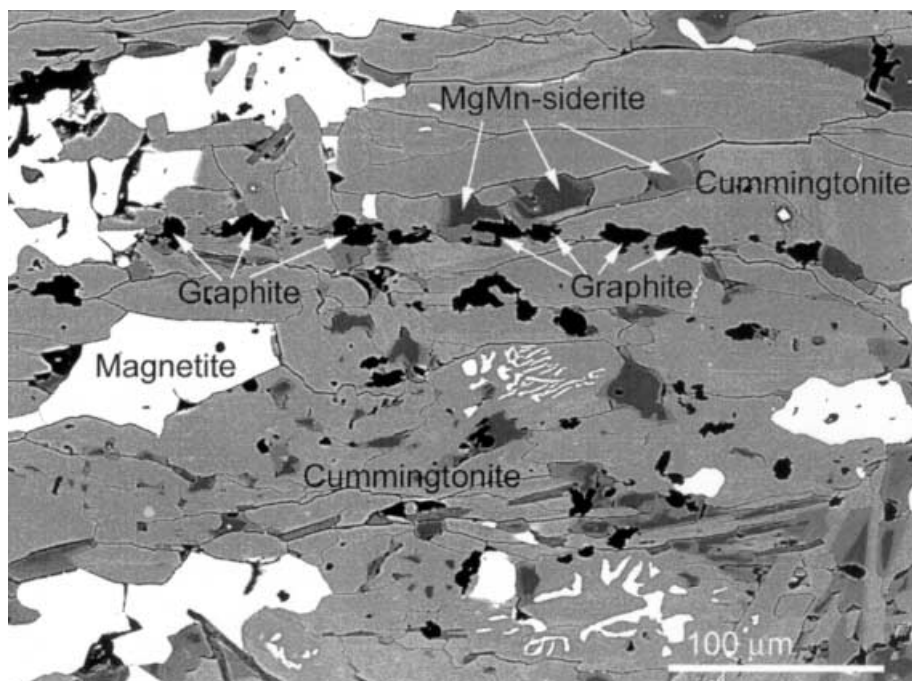


Fig. 8. Backscattered electron image of a polished section through a representative metasomatic carbonate rock from the Isua supracrustal belt (ISB) showing the association of elemental carbon (graphite) with ferrous oxide (magnetite) formed upon disproportionation of ferrous carbonate (siderite). Cummingtonite, also a component of the source rock, is an iron-magnesium silicate. The disproportionation of ferrous carbonate as an alteration process, taking place at high temperature (450–550°) at depth in the crust, has proven to be an important source of carbon, obviously abiogenic, in this type of rock. The metacarbonate is widespread in the ISB and was earlier thought to be of sedimentary origin with the graphite interpreted as a remnant of early life.

chemistry this process appears, under the conditions used, to limit the synthesis to mono- and polycyclic aromatic compound inimical to life.

The relegation of the Isua metacarbonates to the inorganic world was, however, soon followed by the discovery [32] of isotopically fractionated graphite in other, clearly sedimentary rocks from the same ancient 3,8-billion-year-old Isua formation. In this case, the host rocks appear to be of unquestionable sedimentary origin, and furthermore lack iron carbonate and magnetite that would have been indicative of the iron(II) carbonate disproportionation process. The graphite particles here appear to be the end products of alteration of the earliest organisms known. Unfortunately, the temperature/pressure/time-induced changes and graphite crystallization have completely obliterated the shape of the suspected microscopic source organisms and of course also their original molecular composition. However, their ability to enzymatically metabolize and, thus, isotopically fractionate inorganic carbon suggests that life, at this time, already 700 million years after the formation of the Earth, had reached a level of high biochemical sophistication. It is interesting to note that an extrapolation from evolution of tRNA [33] suggests an age of the genome of 4 billion years, 200 million years before the appearance of what seems to be biochemically evolved life.

**The Oldest Crystals.** – The oldest preserved sedimentary rocks on Earth, (3.8-billion-year-old banded-iron formations) are part of the Isua supracrustal belt in southern West Greenland. Movements in the Earth's crust have buried, heated, and recrystallized them almost beyond recognition. Even older intact sedimentary rocks with potential record of the Earth's most-ancient history appear to have been totally worn away – at least none have yet been found. However, datable fragments of such rocks in the form of single crystals of zirconium silicate, the mineral zircon, have been weathered out from their ancient igneous parent rocks and transported into younger-sediments found in Australia. The zircons, datable because of the propensity of this mineral for concentrating uranium at its time of crystallization, extend the range of the geological record from 4.0 to 4.4 billion years, just 150 million years after the formation of the Earth. These crystals would be only geriatric curiosities were it not for the remarkable discovery [34] that their oxygen-isotope record, currently representing ten points in time distributed over this 600 million year time period, without exception testify to the existence of an ocean on Earth. This experimental evidence is placing in question the earlier speculation that the Earth, during this time period, was being bombarded by marauding asteroids, invading the entire inner solar system and held responsible for the well-documented 'late heavy bombardment' on the Moon, culminating *ca.* 3.8 billion years and decaying until 3.5 billion years (*Fig. 9*). With the larger gravitational pull of the Earth, the effects here would have been even more devastating than on the Moon, melting the surface of the Earth's crust and converting it to a magma ocean and vaporizing the hydrosphere.

We are now forced to believe either that all of the zircon crystals so far analyzed, against substantial statistical odds, happen to represent periods of quiescent cool intervals, alternating with undocumented periods of intense bombardment, wholesale melting of the crust, and vaporization of part or all of the hydrosphere. Alternatively, the documented impact sequence on the Moon may have been due to capture of a series of small original co-orbital satellites of the Earth during the tidally induced recession of the Moon [35]. Such a process would be limited to lunar orbital phase space with minimal scattering of debris out of the Moon's gravitational field, explaining the absence of an even more-catastrophic impact record on Earth.

**Conclusions.** – Crystals and life are seen to encounter each other in several different modes in the formative era. In some cases they do, as part of the geological record bear witness to the earliest history of the Earth when life emerged or arrived on the planet. Similar clues are being sought in the, so far fragmentary, record of the evolution of Mars and in interstellar and intergalactic particles that could bear evidence of 'life as a cosmic imperative' [37].

In another context, model experiments highlight the concentrating and catalytic properties of crystals with active external or accessible internal surfaces, and their potential role in generating source compounds for biomolecules [38] and their linking together to form biopolymers [39].

All of these and numerous other model experiments in prebiotic chemistry demonstrate rather suggestively that, at least under unnatural and in some cases more-natural conditions, it is possible to generate the components of RNA and even (albeit with artificial activation) oligomers approaching the length required for biological

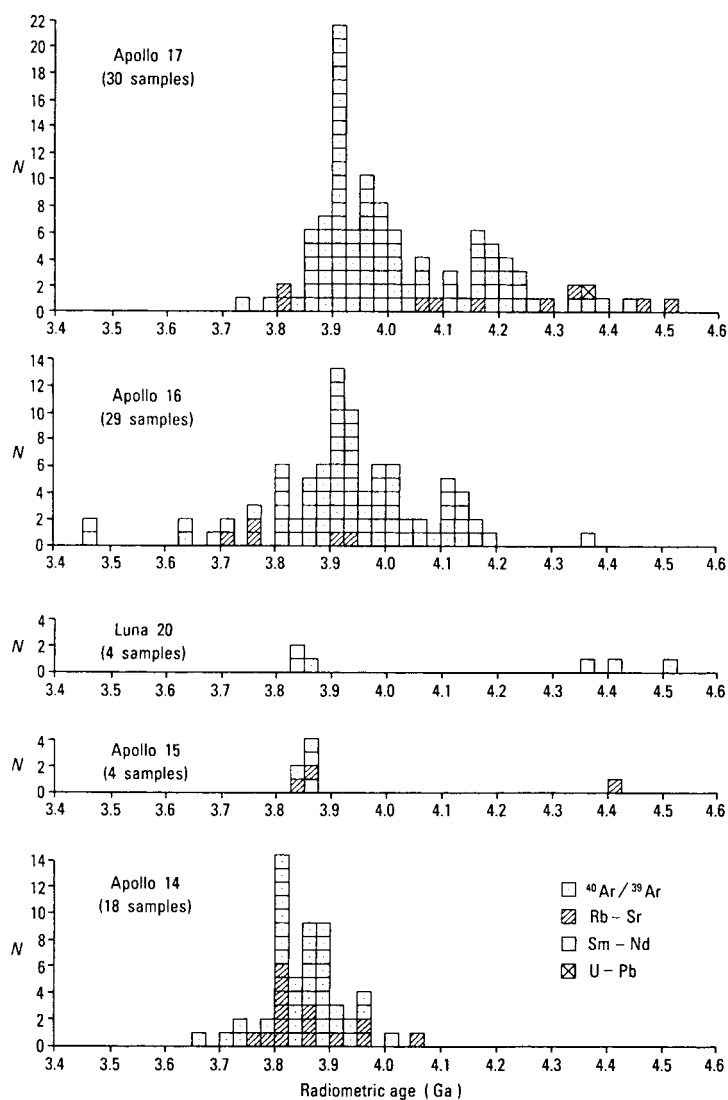


Fig. 9. Age distribution of impact-generated rocks on the Moon, associated with cratering events. The apparent maximum around 3,800 million years followed by impacts with decaying frequency down to *ca.* 3,500 million years is known as ‘the late lunar bombardment’. Before the corresponding rock record on Earth had been investigated, it was speculated that the lunar events were caused by an invasion into the inner solar system of swarms of marauding asteroids, attacking the planets with even more impact energy because of their stronger gravitation. On Earth, the crust would have been molten, forming a ‘magma ocean’ and the boiled-off hydrosphere forming a thick, insulating atmosphere that would prevent rapid cooling. Life would, under these circumstances, have been prevented or eliminated. Smaller, less-devastating impacts could possibly have permitted life to take refuge to the deep ocean or the crust below. The fragmentary record on Earth now emerging shows a conspicuous lack of effects from devastating impact events such as those postulated. Explanations are, therefore, sought for the apparently parochial nature of the lunar bombardment. A possibility that is being further explored [35] involves the relatively low-energy sweep-up of a series of original, small Earth satellites during the gradual recession of the abnormally large Moon after its formation by capture or by, currently most popular, impact on Earth of a Mars-size body (from [36]).

function [39]. At the chemical level, elegant experiments even demonstrate replication and induction of chirality [12], resolving one of the outstanding mysteries in prebiotic chemistry. Making the leap of faith into fully functional, programmed polynucleotides in the form of ribozymes, the field has opened to an understanding of the emergence of Darwinian evolution [15][40] and the beginning of biological chemistry [39].

The progress so far in prebiotic chemistry merely suggests that it may be possible to synthesize the tape on which the information for life could be recorded, if we only knew how. The origin of this information, although it is the subject of much speculation, remains a central unsolved problem awaiting an experimentally demonstrated solution aside from stochastic propositions, which encounter difficulties in probability–time/space, a transfer of the characteristic aperiodic features of crystals has been suggested. More specifically, it was proposed by Cairns-Smith [3] that the irregular distribution of crystal defects such as in Fig. 2 could provide repeatable sequences to be impressed on crystal-surface-generated organic oligomers. Alternatively and with more synthetic control, the variable pattern of cations, conserved within individual crystals, may be speculated to affect the configuration of nucleic acids bound and reacting on their surfaces [40]. The resulting messages would initially be meaningless [41], but a large number of different sets of internally identical, probably short, sequences could possibly be produced, decreasing the enormous improbability that functional polymeric sequence could arise spontaneously from random interaction of single nucleic acids.

If such an animation process ever existed, it would be guided by the subtle electronic forces that metal cations exert on their environment, and by the order induced by covalent forces in organic crystals, both subjects where Jack Dunitz has laid the foundation for our present knowledge.

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