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THE PROBABLE WAYS  
OF THE SYNTHESIS OF PORPHYRIN COMPOUNDS  
DURING CHEMICAL EVOLUTION

The synthesis of organic compounds in simulated primordial conditions on the Earth have long been the subject of various studies aimed at the testing of hypotheses of the origin of life. These studies were initiated by S. L. Miller in 1953 (17). In his experiment, he used a system enabling the circulation of the mixture of  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , and  $\text{H}_2$  while it was subject to electric discharges, simulating the lightnings during storms in primordial atmospheres. As a result of this experiment, he obtained several amino acids for example,  $\alpha$ - and  $\beta$ -alanine, aspartic acid, and  $\alpha$ -amino-n-butyric acid. Up to now, many experiments of similar nature have been carried out. Apart from electric discharges, the ultraviolet and gamma radiations, thermal energy, and shock waves and other kinds of energy have been applied. Among the chemical compounds obtained by these means, one can find amino acids, polypeptides, simple proteins, purines, pyrimidines, nucleosides, nucleotides, polynucleotides, hydrocarbons, fatty acids, ATP, and porphyrins (cf. review articles 18, 20).

The aim of this article is to review and discuss the results of the synthesis of porphyrin compounds carried out in simulated abiotic conditions. The most recent results not reviewed in the earlier published articles (cf. 19, 36) seem to give support for new possibilities of investigation in the field. Moreover, they may have a significance for paleobiochemistry and paleobiophysics of the protoforms of life.

Although the syntheses of porphyrin compounds in laboratory conditions were carried out much earlier than the first attempts at syntheses of these compounds in conditions simulating the hypothetical atmosphere on primitive Earth, they have been done beyond the context of biogenesis theories. The results of these experiments show that porphyrins are very easy to synthesize from simple precursors. As the experiments from the earlier period simulated the primordial atmosphere, the recent syntheses.

using aluminosilicates may be considered as modelling the surface conditions on the primitive Earth.

Table 1 presents various experimental systems differing in the composition of the mixture of substrates, energy sources, etc. It does not pro-

Tab. 1. Variants of the abiotic synthesis of porphyrin compounds.

Substrates	Kind of energy	Remarks	References
benzaldehyde, pyrrole	gamma radiation	catalyst: zinc acetate	33, 34
benzaldehyde, pyrrole	ultraviolet, visible light		32
benzaldehyde, pyrrole, H <sub>2</sub> O, H <sub>2</sub> , NH <sub>3</sub> , CH <sub>4</sub>	electric discharges		35
formaldehyde, pyrrole	thermal energy: 357 K, 370 K, and 408 K	in the presence of clay, and cations of metals: Ni, Cu, V, Mg, Fe, Ag, Hg	7
CH <sub>4</sub> , NH <sub>3</sub> , H <sub>2</sub> O	electric discharges		8
formaldehyde, pyrrole	thermal energy: room temperature, 276 K, 376 K	catalyst — oxides: Zn, Ca, Ti, Si, and others, silicic acid, parabenzoquinone	12, 13, 14
CO, D <sub>2</sub> , NH <sub>3</sub> , ND <sub>3</sub>	high temperature: 773—973 K, and 373—673 K	catalyst: Al <sub>2</sub> O <sub>3</sub> , Ni-Fe	4
NH <sub>3</sub> , formaldehyde, graphite	plasma		6
CO <sub>2</sub> , NH <sub>3</sub> , graphite			
pyrrole, graphite, formaldehyde	thermal energy: 298—673 K		
hydrazine, formaldehyde, graphite			
hydrazine, formaldehyde, meteorite powder			
CH <sub>4</sub> , NH <sub>3</sub> , H <sub>2</sub> O	electric discharges, plasma		25, 29, 30, 31
benzaldehyde, pyrrole	room temperature	catalyst — montmorillonite	2
formaldehyde, pyrrole	room temperature	in the presence of metal cations, and peridotite rock	28

vide, however, any information on the procedure of experiments, especially the ways to avoid the contamination of the reaction medium with the biogenic porphyrins.

To make the synthesis of porphyrins possible, the probable precursors of them, e.g. pyrrole and benzaldehyde, had to originate in the earlier stages of chemical evolution, and be accessible in sufficient concentrations. Some investigators were able to synthesize these compounds in simulated abiotic conditions.

The reactions leading to the synthesis of porphyrins can take place in the presence of oxygen and at very low concentrations of reagents. If as catalysts metal ions are used, these ions may be chelated by nitrogen atoms of pyrroles. However, the efficiency of the synthesis taking place in these conditions are very low. For example, if the mixture of pyrrole and formaldehyde was heated during 3 hours in 357 K, the efficiency of synthesis was of the order of 0.001÷0.002%. On the other hand, if the heating lasted for 20 hours, in the presence of some metal ions, the efficiency was 0.003% (for Cu-porphyrin), 0.0008% (for Ni-porphyrin) and less than  $2 \cdot 10^{-5}$  % for the VO-porphyrin (7).

In the experiments, compositions of various kinds of energy, simulating the physical conditions in the primordial environment, were used. These conditions are arranged according to the current theories on the main sources of energy available for the prebiotic syntheses. In the first place the ultraviolet radiation of the Sun is located. Next to the contribution of this radiation, the electrical discharges, the radiation of radioactive nuclides, the heat of volcanic activity, the thermal energy generated during the passing of meteorites through the atmosphere and, finally, cosmic radiation are mentioned (see 20).

Some of the possible ways of the abiotic synthesis of porphyrin compounds, tested in the experiments mentioned above, are presented in the Figure 1.

Experiments simulating the prebiotic atmosphere heighten the plausibility of thesis that porphyrins might have originated in the very early stages of chemical evolution, when the atmosphere still had a reducing character, i.e. 4.5÷3.5 billions year ago. Nevertheless, these results are not to be taken as proving the thesis that these compounds originated in this period of time, and in the ways the experiments reconstructed. Namely, the present biosynthesis starts from completely different compounds, for example from glycine and succinyl-CoA. Moreover, the porphyrins found in precambrian rocks, dated at least 3 billion years (15, 16), might not necessarily have originated prebiotically. They may well be relicts of the metabolism of very old forms of life. This point of view is supported by the presence of isoprenoid alkanes, which may be the products of the

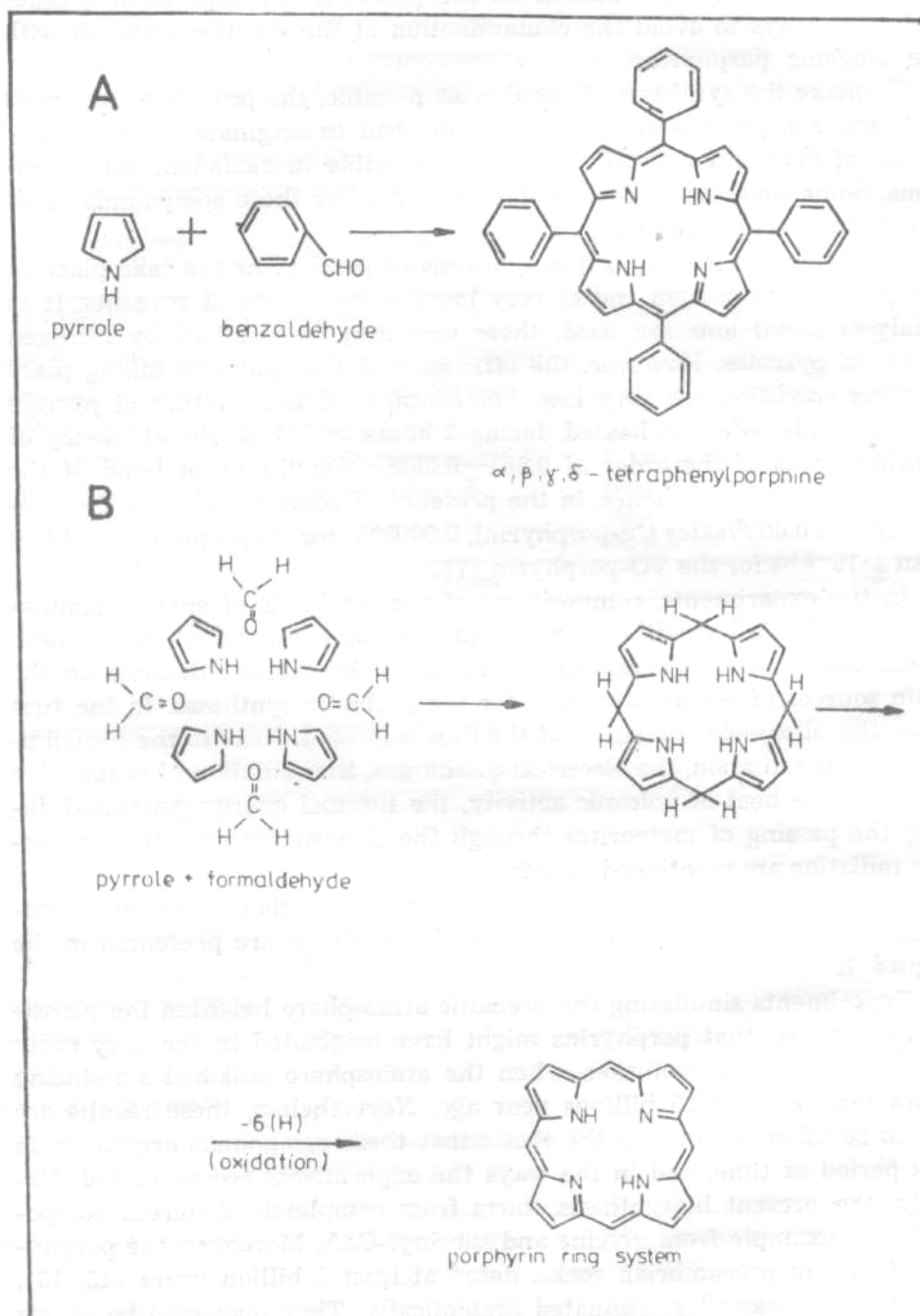


Fig. 1. Some of possible ways of the abiotic synthesis of porphyrin compounds

degradation of chlorophyll, in these rocks. Therefore, the photosynthesis may be thought to take place in this stage of chemical evolution. It is also possible that the presence of porphyrins in these rocks is accidental, they might be present there by diffusion from the geologically younger layers (15).

In recent years, various silicate minerals, such as montmorillonite, kaolinite, zeolites, have been shown to enable the synthesis of such biochemical compounds: amino acids, sugars, lipids, nucleotides, polypeptides, etc. (see for example 1, 21). These successful attempts proved J. Bernal's hypothesis that aluminosilicates took part in the synthesis of biologically important compounds to be reasonable. Aluminosilicates may play the part of adsorbents and catalysts and provide matrices for synthesized organic structures (39). In this connection, it is not surprising that porphyrins were synthesized in this way, as well.

As mentioned above, porphyrins were synthesized using montmorillonite (2). However, not the very fact of synthesis is of interest here, but its extraordinary high efficiency. It reached the value of  $2 \div 12\%$ , what is  $10^3 \div 10^5$  times more than the efficiencies of the abiosyntheses of porphyrins in the gaseous phase, described above. The syntheses on montmorillonite using benzaldehyde and pyrrole as substrates were carried out in water medium and resulted in obtaining meso-tetraphenylporphyrin. If pyrrole and benzaldehyde were added to the water suspension of  $\text{Fe}^{3+}$ ,  $\text{VO}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{H}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ , or  $\text{Na}^+$ -montmorillonite in equimolar concentrations, it resulted in the dark-purple color of the mineral phase. The reaction on the surface of silicates took place if the reagents were mixed either in the presence, or in the absence of atmospheric oxygen. If the most acidic cations were used ( $\text{H}^+$ ,  $\text{VO}^{2+}$ ,  $\text{Fe}^{3+}$ ), the reaction took place in the period of several minutes, and if moderately acidic ions were involved, it lasted about 3 hours. Fig. 2 presents schematically the porphyrin nucleus of the ion  $\text{TPPH}_4^{2+}$  situated between the layers of crystal lattice of montmorillonite, and Fig. 3 gives a scheme of the reaction leading to the synthesis of meso-tetraphenylporphyrin ( $\text{TPPH}_4$ ) from benzaldehyde and pyrrole.

It has been suggested (2) that the rates of the synthesis of porphyrins on aluminosilicates, exceeding by several orders of magnitude those taking place in gaseous phase, have great significance for the investigation of the ways of abiotic syntheses of porphyrins.

In this context, great significance should be ascribed to adsorptive properties of aluminosilicates, only if it is but the possibility of abiotic formation of porphyrin-protein complexes. The ability of clay minerals to adsorb various porphyrins (for example, kaolinite and Ca-montmorillonite adsorbed: hemine, protoporphyrin and hematoporphyrin (11)), is an im-

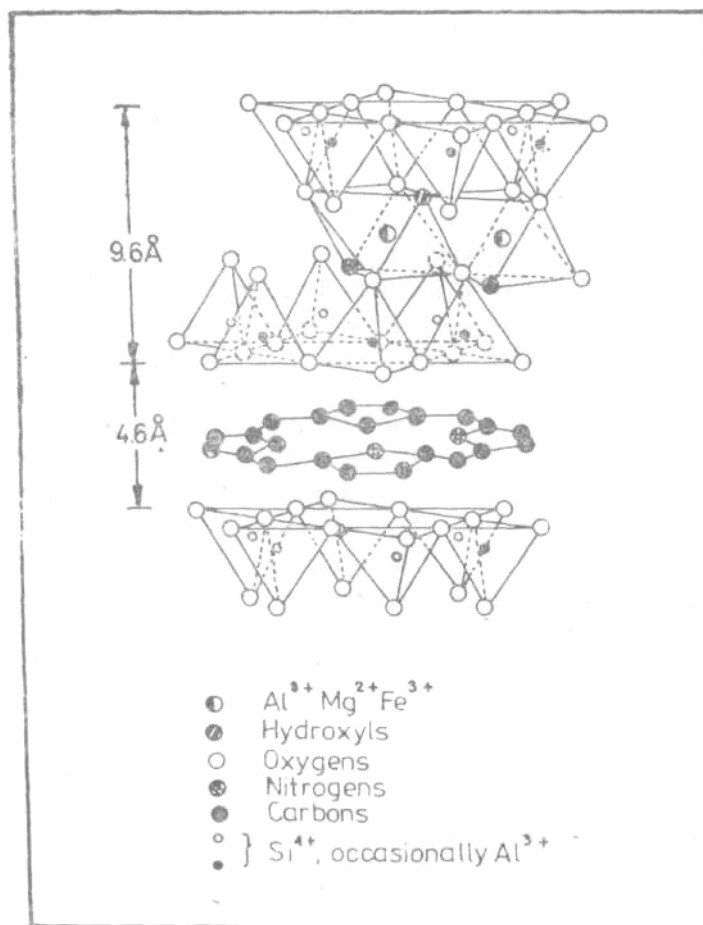


Fig. 2. Schematic illustration of the TPPH<sub>4</sub><sup>2+</sup> porphyrin nucleus oriented in the interlayers of montmorillonite. Protons and phenyl groups are omitted for clarity

portant premise for this point of view. What is more, it has been shown that meso-tetraphenylporphyrin and meso-tetra-4-pyridilporphyrin, adsorbed in intralamellar spaces of montmorillonite, react with metal cations of this aluminosilicate (38). The porphyrins mentioned above react also with Na<sup>+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup> (37).

As far as the amount of metalloporphyrins adsorbed in intralamellar spaces of montmorillonite is concerned, the following array has been given: Co<sup>2+</sup>, Cu<sup>2+</sup> >> Mn<sup>2+</sup>, Ni<sup>2+</sup> > Fe<sup>2+</sup> > Sn<sup>4+</sup> (3). It seems probable that this regularity may be a hint for the research on the reconstruction of the abiotic molecular evolution of porphyrin-protein complexes. An additional argument for this standpoint is the observation that these complexes may form from amino acids and porphyrins adsorbed on volcanic ashes (9, 10).

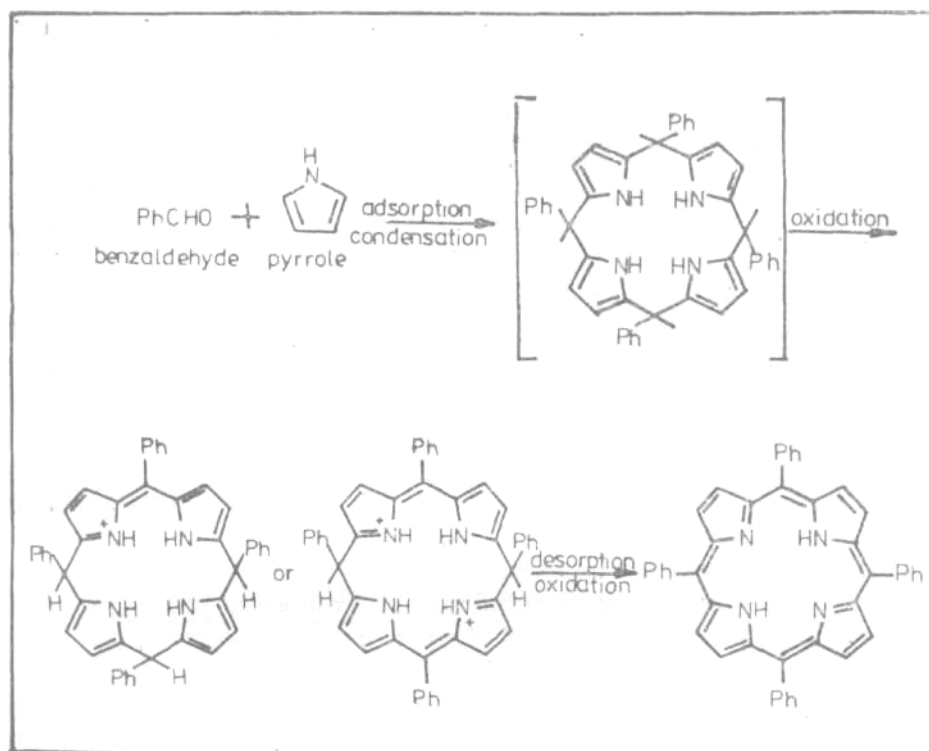


Fig. 3. Benzaldehyde-pyrrole reactions on layered silicate minerals

This process may also take place when polypeptides and metalloporphyrins are adsorbed. The Cu(II) porphyrin-polypeptides and Fe(III) porphyrin-polypeptides revealed the activity characteristic of peroxidase and catalase (10).

There are many problems which remain to be dealt with in the field of abiosynthesis of porphyrin compounds. First of them is that, despite many experiments devoted to abiosynthesis and carried out in the conditions simulating prebiotic physical and chemical conditions, no one succeeded in synthesis of porphyrin compounds playing essential role in present forms of life (chlorophylls, hemes). It seems probable, that not all significant factors occurring in prebiotic environment, had been taken into consideration in experiments modelling the prebiotic synthesis. In this connection, one may suggest that telluric currents as an energy source should be taken into account, because the electrosynthesis of chemical compounds is known to be possible in vitro. Next, the question whether the chlorophylls and hemes mentioned above originated in the course of chemical or only biochemical evolution, remains open. These classes of porphyrin compounds are very ancient and only metabolism of Clostridia

does not porphyrin compounds (except for *Clostridium tetanomorphum*, which is able to synthesize uroporphyrin and vitamin B<sub>12</sub>). It is also plausible that chlorophylls and hemes are the result of long evolution of metalloporphyrin and metalloporphyrin compounds.

Turning to high efficiencies of the syntheses carried out on the interfaces of aluminosilicates, it may be said that new field of investigation have been opened. In this context, one may suggest that in the abiotic synthesis of Al-porphyrin and Si-porphyrin complexes, aluminosilicates were involved. Furthermore, the possible role of Si-porphyrins and Al-porphyrins as precursors of hemes and chlorophylls in the evolution of porphyrin compounds, may be considered. The hypothesis on the role of Si-etio-porphyrins as initial compounds in early phases of the evolution of protoliving systems, was put forward by Sedlak (23) in his approach to paleobiochemistry of silicon. This problem seems to be of importance, because the possible role of silicon in biochemical evolution (22) suggests a different perspective of biogenesis than the widely accepted one.

Finally, the syntheses in plasma conditions are also an interesting possibility. The syntheses of this kind may occur in extra-terrestrial space, as for example, in the atmospheres of stars (5), what bears serious implications for the problem of the existence of life in the outer space. However, a more interesting approach, originating from the theory of bioplasma (i.e. physical plasma in biological systems) (24), is consideration of the necessary conditions for these syntheses in the semiconductor electron plasma of aluminosilicates. Therefore, electrosynthesis on aluminosilicates and synthesis in semiconductor plasma of these minerals, create a promising perspective for abiotic syntheses of the complexes of metallo- and metalloporphyrins with polypeptides.

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## PRAWDOPODOBNE DROGI SYNTEZY ZWIĄZKÓW PORFIRYNOWYCH PODCZAS EWOLUCJI CHEMICZNEJ

### Streszczenie

W artykule przedstawiono przegląd badań nad syntezą związków porfiryńowych w symulowanych warunkach abiotycznych pierwotnego środowiska Ziemi. W dyskusji wyników eksperymentów podkreślono duże znaczenie faktu abiotycznej syntezy porfiryń na glinokrzemianach typu montmorylonitu, której wydajność jest  $10^3$ - $10^5$  razy większa od wydajności syntez w typowych eksperymentach, np. w fazie gazowej z udziałem wyładowań elektrycznych. Wysokowydajne abiosyntezy porfiryń na montmorylonicie otwierają nowe możliwości badawcze. Proponuje się kilka sugestii: a) możliwość abiotycznej syntezy kompleksów Al- i Si-porfiryńowych na glinokrzemianach, b) możliwość roli tych kompleksów jako poprzedników hemów i chlorofili w ewolucji związków porfiryńowych, c) możliwość wykorzystania energii elektrycznej modelującej prądę telluryczne środowiska pierwotnego do elektrosyntezy związków porfiryńowych na glinokrzemianach, d) możliwość realizowania się warunków abiosyntezy w elektronowej plazmie półprzewodnikowej glinokrzemianów.