

# Abiotic synthesis of porphyrins and other oligopyrroles on the early Earth and Earth-like planets

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## Abstract

It is generally accepted that abiotically formed amino acids existed on Earth in the late Hadean and early Archean (four billion years ago). They were mainly dissolved in a salty primordial ocean. At that time, volcanic islands were much more abundant than today. It is therefore reasonable to assume that, at hot volcanic coasts, amino acids could have been thermally transformed into other organic molecules. Based on this scenario, we conducted laboratory experiments that simulated the interaction between amino acid-containing sea water and hot lava. In these experiments, a large number of different volatile products were formed, among them pyrroles. It was also possible to obtain porphyrins and other oligopyrroles from pyrroles under simulated conditions of primordial volcanic islands. All experiments were conducted under plausible prebiotic conditions. Our results reveal an abiotic pathway to possible precursors of oligopyrrole-type biomolecules, such as heme and chlorophylls.

## 1. Introduction

On the early Earth, the first ocean formed when the temperature was low enough for water to condense. From this ocean, volcanic islands protruded which represented the only land masses (possibly together with small non-permanent protocontinents). Primordial volcanic islands provided a wide range of conditions and locations, e. g. (i) eruption clouds in which Miller-type reactions probably proceeded, (ii) hot lava–seawater interactions, and (iii) rock pools with moderate temperatures. On land, molecules could have accumulated. The resulting higher concentrations must have increased the efficiency of chemical reactions. Therefore, primordial volcanic islands are promising places for chemical evolution. When at primordial volcanic coasts amino acid-containing seawater came into contact with hot lava, the water evaporated immediately, and a salt crust

with embedded amino acids remained. Further heating of these crusts by nearby lava could have resulted in new organic molecules. At present-day volcanic coasts, the release of HCl is observed when lava enters the sea (e. g. on the Hawaiian Islands and the island of La Réunion [1, 2]). The HCl originates from the thermal decomposition of solid  $\text{MgCl}_2 \cdot n\text{H}_2\text{O}$ . Hence, it is reasonable to assume that HCl was also formed at primordial volcanic coasts.

## 2. Abiotic Formation of Pyrroles

To simulate the hot lava–seawater interaction, we first prepared an artificial seawater which contained NaCl (705 mmol), KCl (15 mmol),  $\text{CaCl}_2$  (15 mmol),  $\text{MgCl}_2$  (80 mmol), and 10 mmol of an  $\alpha$ -amino acid, for example DL-alanine. After evaporation, the remaining salt crusts were heated to temperatures between 350 and 800 °C. The volatile products formed were analyzed by gas chromatography–mass spectrometry. Among numerous other compounds, several C-alkylated pyrroles could be identified. Also, the formation of HCl was observed.

## 3. Abiotic Pyrrole Oligomerization

In relatively cool primordial rock pools remote from hot lava flows, volatile molecules could have condensed. Thus, the pyrroles and the HCl formed by hot lava–seawater interaction could have accumulated there. Other chemical species such as nitrite, for which an efficient prebiotic formation pathway probably existed [3, 4], reached these rock pools, too. To simulate this scenario, an acidic artificial seawater (10 mM HCl  $\triangleq$  pH 2) was prepared which contained 3,4-dimethylpyrrole, formaldehyde and sodium nitrite as an oxidant (0.5 mM each). Formaldehyde was very probably present on the early Earth [5, 6]. This experiment was conducted in a glove box under inert gas ( $c(\text{O}_2) \leq 5$  ppm). After 5 days, the wine-red solution was analyzed by UV/Vis spectroscopy, which indicated that several products had been formed.

Further analyses by ESI-Orbitrap mass spectrometry confirmed the complexity of the product mixture. This high resolution method allowed the unambiguous identification of 38 oligopyrroles in different oxidation states. The molecular sizes ranged from dimers to hexamers (Figs. 1 and 2, Table. 1). Cyclic tetrapyrroles are of particular interest. The non-oxidized porphyrinogen as well as the completely oxidized porphyrin were found (Fig. 2). Most of the identified oligopyrroles had intermediate oxidation states, that is they were partially oxidized. For detailed information see ref. 7.

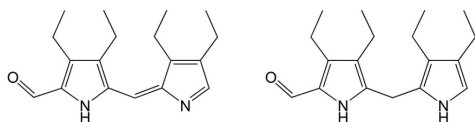


Figure 1: Pyrrole dimers in different oxidation states (left: oxidized, right: non-oxidized form).

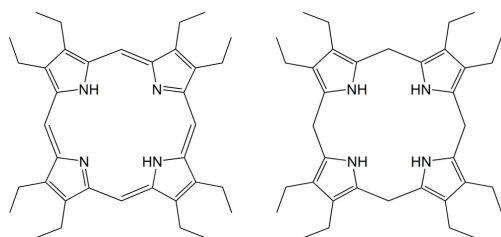


Figure 2: Cyclic pyrrole tetramers: completely oxidized form (porphyrin, left) and non-oxidized form (porphyrinogen, right).

Table 1: Selection of oligopyrroles found in rock pool simulation experiments. The oligomerization degree  $n$ , composition and molecular mass are given.

$n$	chemical formula	$[M + H]^+$ calculated	$[M + H]^+$ found
2	C <sub>18</sub> H <sub>24</sub> N <sub>2</sub> O	285.19614	285.19625
2	C <sub>18</sub> H <sub>26</sub> N <sub>2</sub> O	287.21179	287.21192
3	C <sub>27</sub> H <sub>35</sub> N <sub>3</sub> O	418.28529	418.28540
3	C <sub>27</sub> H <sub>39</sub> N <sub>3</sub> O	422.31659	422.31686
4	C <sub>36</sub> H <sub>46</sub> N <sub>4</sub>	535.37952	535.37936
4	C <sub>36</sub> H <sub>52</sub> N <sub>4</sub>	541.42647	541.42700
4	C <sub>36</sub> H <sub>46</sub> N <sub>4</sub> O	551.37444	551.37444
4	C <sub>36</sub> H <sub>52</sub> N <sub>4</sub> O	557.42139	557.42096
5	C <sub>45</sub> H <sub>57</sub> N <sub>5</sub> O	684.46359	684.46462
5	C <sub>45</sub> H <sub>65</sub> N <sub>5</sub> O	692.52619	692.52679
6	C <sub>54</sub> H <sub>68</sub> N <sub>6</sub> O	817.55274	817.55243

## 4. Summary and Conclusions

Our thermolysis experiments under simulated prebiotic conditions have shown that pyrrole formation from amino acids is possible. It seems plausible that this process occurred on early Earth and, under suitable conditions, can still occur today on Earth-like planets. In experiments that simulated the reactions of a model pyrrole on primordial volcanic islands, oligopyrroles including the porphyrin were found. Abiotically formed porphyrins may have played an important role in the chemical evolution towards the origin of life. In the metabolism of all known organisms, porphyrins are of crucial importance, for example in electron transfer reactions. Simulation experiments that address the behavior of oligopyrroles, especially porphyrins, under prebiotic conditions are currently underway.

## References

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