

Pyrrhotite catalyzes the synthesis of uracil under hydrothermal conditions

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Abstract

The hypothesis of a prebiotic origin for metabolic cycles in hydrothermal systems gained interest during last years. The experimental approach to support this hypothesis was oriented mainly to the formation of organic molecules in iron sulfide mineral surfaces from inorganic precursors. In this work, we explore the behavior of previously formed, prebiotically plausible organic molecules in iron sulfide rich, low temperature hydrothermal environments. Using urea as a starting point, we found that uracil and other nitrogen heterocycles could be synthesized using water-urea solution as precursor in a packed pyrrhotite bed reactor, simulating hydrothermal conditions.

1. Introduction

Since the first proposals of a relationship between hydrothermal systems and origin of life [1], the experiments that replicate sulfide rich, hydrothermal chemistry confirmed the potential of these systems for the synthesis of organic molecules through carbon fixation. The main role corresponds to ferrous sulfide minerals [2]. These mineral phases can catalyze the formation of organic compounds from CO and thiols [3] in a hydrothermal environment, leading to the hypothesis of the chemoautotrophic origin of metabolism. About the role of this system in the prebiotic chemistry of nucleic acid components, it has been reported that iron sulfide minerals can catalyze the formation of purines and pyrimidines by formamide condensation [4]. We are interested in the possible role of iron sulfide minerals in hydrothermal environments in the prebiotic chemistry of organic molecules regarded as prebiotic precursors, as urea, amino acids and small organic acid. As an experimental model, we designed a continuous flow reactor with iron sulfide as immobilized phase and, in a first approximation, presented here, we used

aqueous solutions of urea as nitrogen source and tested if urea could be a source of nucleobases in iron sulfide rich hydrothermal systems. Urea was selected after its identification as a good precursor of nucleobases in icy systems [5].

2. Materials and methods

2.1 Pyrrhotite

All pyrrhotite samples used were from the Gualba quarries (Barcelona, Spain), a Fe-Cu (Mo-Pb-Zn) sulfide rich skarn of Hercynian age. The pyrrhotite was characterized by electron microprobe analysis (EMPA-WDS) and X-ray diffraction (XRD). The composition found is Fe_9S_{10} with dominance of hexagonal polytypes. The ore was selected from metamorphic origin in order to minimize the content of organic carbon. The Gualba pyrrhotite is strongly ferromagnetic; this circumstance has been used to the isolation of pyrrhotite from the ore paragenesis.

2.2 Experimental setup

The experiments were conducted using empty HPLC 25x0.25 cm steel columns, filled with pyrrhotite powder. The powder was previously sterilized and extracted using dichloromethane and methanol to remove potential organic contaminants. The column was connected to an HPLC pump using peek tubing and connections. The pyrrhotite column was heated at 120°C and flow adjusted to maintain a constant pressure of 200 bar (aprox. 0.1 ml/min). The aqueous solutions (10 ml total) were previously filtered through 0.22 microns filters and degassed. The effluent of reactor was freeze-dried and organic products were characterized using gas chromatography-mass spectrometry (GC/MS) after formation of trimethylsilyl derivatives.

3. Results

The formation of uracil was identified in a 0.1M solution of urea flowed through pyrrhotite reactor, with a yield of 3.5% of the total urea. The presence of succinic acid, a common prebiotic molecule, increased the uracil yield to 5.8%. The supplementation of the urea solution with glyoxal (0.1M) lead to the expected formation of hydantoin and 2-oxo-4,5-dihydroxyimidazolidine as major compounds, together with uracil, 5-hydroxyhydantoin and succinic and fumaric acids (Fig 1).

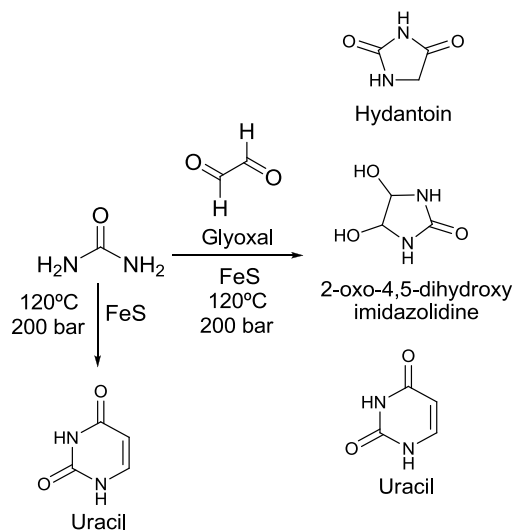


Figure 1: Synthesis of uracil and hydantoin from urea catalyzed by pyrrhotite (FeS) under simulated hydrothermal conditions.

To assess the mineral phase transformation, the worn out pyrrhotite was studied by X-ray diffraction. The new mineral phases identified were mainly pyrite, followed by siderite and minor iron oxides.

4. Summary and Conclusions

This experiment could be added to those that highlight the catalytic properties of iron sulfide minerals in promoting prebiotic chemistry transformations. The ferrous sulfide mineral can catalyze the condensation of urea and/or urea and succinic acid degradation products to form uracil in a mechanism that still needs to be elucidated. The presence of other prebiotic molecules could increase the organic diversity of the products. The presence of glyoxal leads to the formation of hydantoin as the main product, together with uracil. The lack of other pyrimidines or purines could be a consequence of the

extreme conditions of the system, which could degrade other molecules more complex or labile. For example, the potential cytosine could undergo rapid deamination to uracil under these conditions. Uracil remains in the system, as the most stable molecule of the nucleobase-related heterocycles. This is especially highlighted by the use of urea as reactant, which, in cold conditions, leads to the formation of a rich assemblage of nitrogen heterocycles [5].

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