

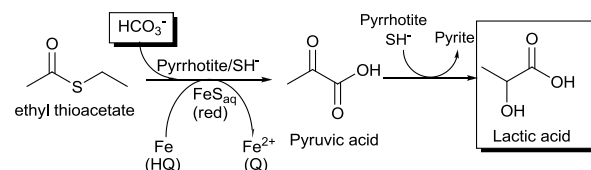
**IRON SULFIDE MINERALS AND THE REDUCTIVE CARBOXYLATION OF THIOESTERS.** C. Menor-Salván<sup>1,2</sup> and A. L. Ibañez de Aldecoa<sup>2</sup>, <sup>1</sup>Department of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA, 30332-0400, USA, <sup>2</sup>Centro de Astrobiología (CSIC-INTA), Ctra. Torrejón-Ajalvir km 4, Torrejón de Ardoz, 28850, Spain.

**Introduction:** One approach to the study of abiogenesis is the hypothesis of a protometabolic, complex chemical system that precedes the first living beings. The first metabolic systems could emerged from the interaction between sulphide minerals and/or soluble iron-sulphide complexes and fluids rich in inorganic precursors, which are reduced and derived from crustal or mantle activity. The role of iron sulphur proteins (which contain Fe-S clusters as active centers in the electron transfer reactions) and their occurrence in what are possibly the most primitive steps of oxidation of organic substrates, the carbon fixation by reductive carboxylation, and in the cell energy transduction machinery, have been an evidence used to connect the geochemical roots of the origin of life to the origin of biochemistry [1]. The structural similarity between the biological iron-sulphur clusters and the crystal structure of iron sulphide minerals [2], the biomimetic activity of synthetic soluble Fe-S clusters [3] and the highly preserved biochemical reactions involved could explain why Fe-S clusters are found in all biological systems. In this sense, Fe-S clusters could trace the origin of life to the iron sulphide minerals as the roots of biochemistry [4]. In this work, we studied the possible connection between the biochemical reductive carboxylation of thioesters and the geochemistry of the iron-sulphide system, by application of a new experimental approach: using an electrochemical cell to simulate how gradients between inorganic species could promote the biomimetic carbon fixation.

**Results:** An electrochemical cell has been constructed using a cylindrical graphite reactor filled with granulated iron metal, a microporous clay barrier and pyrrhotite wet paste formed by pyrrhotite powder, containing 1 mmol of sodium sulphide (pH 9) and, optionally, 1 mmol of hydroquinone. Previously, 1 mmol of ethyl thioacetate was adsorbed by the pyrrhotite powder. A graphite electrode inserted in the pyrrhotite constitutes the cathode. The system was connected to a power supply at 1.1 V under a nitrogen atmosphere. The organic solutes were analysed after three days of standing in anoxic conditions at room temperature; the analysis shows a significant quantity of lactic acid with an estimated yield of 6.5% of the added ethyl thioacetate. Pyruvic acid was also detected, as well as glycolic acid and glycine.

The control experiment without an external voltage source shows a significantly lower yield in the for-

mation of lactic acid, suggesting that a low potential electron donor could be necessary for the process. To test this possibility, we performed an experiment using the same electrochemical cell design but without using an external voltage source and adding 1 mmol of hydroquinone ( $E^\circ = -0.699\text{V}$ ). Hydroquinone can act as analog of the biological ubiquinol and can perform electron transfer reactions on the surface of minerals [6]. The model biochemical reaction that motivates the selection of hydroquinone as an electron donor is the formation of pyruvate by direct carboxylation of acetic acid, promoted by (quinone) pyruvate dehydrogenase.



**Figure 1.** Reductive carboxylation of a simple thioester, Q: oxidized quinone; HQ: reduced quinone.

The presence of hydroquinone promotes the synthesis of lactic acid, increasing the yield to 10.5% and suggesting that electrons can be transferred through iron sulfur clusters or surfaces, similar to the ubiquinol/iron-sulfur system in biochemistry. The experiments performed suggest a model for the reductive carboxylation of thioesters in abiotic and non-enzymatic conditions (Figure 1). Also, an electrochemical cell could be an approach to the experimental study of Origin of Life, as are ideal for the creation of electrochemical gradients and simulate an electrochemically active geochemical interface. Our work is the first experimental use of electrochemical cells within the sphere of abiogenesis and offers a potentially powerful model through which to explore emergent biochemical systems [5].

#### References:

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