

Oxidoreductase mimic activity of natural pyrrhotite

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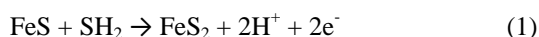
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Abstract

The theory of the chemo-autotrophic origin of life, also called the “iron-sulfur world hypothesis”, proposes that the system FeS/FeS₂ present in the primitive Earth crust gave the reductive power necessary to conduct the first protometabolic redox reactions. Some experimental studies demonstrated the redox activity of the FeS/SH₂ system, but none of them used natural FeS. Here, we show that the iron sulfide mineral pyrrhotite is able to mimic the redox activity of the enzyme lactate dehydrogenase, which reversibly reduces the pyruvate in lactate, under prebiotic conditions with pyrite formation.

1. Introduction

According to the Wächtershäuser’s model of the “iron-sulfur world” the origin of life started with the synthesis of low-molecular-weight organic molecules from inorganic starting materials, in an ore surface, through autocatalytic carbon fixation and redox pathways [6], [7]. The model postulates that these redox reactions were carried out using the reduced power obtained from the oxidation of ferrous sulfide (FeS) to form pyrite (FeS₂) in the presence of hydrogen sulfide (SH₂) (1) [3], [5].



The FeS/SH₂ system is able to drive different redox reactions as the reduction of NO into ammonia [4], the reduction of cyclohexanone [1] and the pyruvate-lactate system under prebiotic conditions [8].

In these experiments the source of FeS was synthesized by precipitation in the laboratory or directly bought. In this work, we checked if natural ore consisting in FeS and without any chemical treatment was able to mimic the oxidoreductase activity. The pyrrhotite is a widespread ore in basic igneous rocks (usually associated with other Fe(Ni) sulfides), hydrothermal systems and metamorphic

rocks with the chemical formulae Fe_(1-x)S_(x=0 to 0.2) [2]. Hence, the target redox reaction is:



2. Materials and methods

2.1 Pyrrhotite characterization

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 Fe₉S₁₀ with dominance of hexagonal polytypes. The ore is ferromagnetic; this circumstance has been used to the isolation of pyrrhotite from the chalcopyrite and silicates that constitutes the Gualba ore paragenesis.

2.2 Experimental model

All experiments were conducted in sealed 22 mL headspace vials and in a glove box with a nitrogen atmosphere. Each vial was filled with crushed pyrrhotite (FeS) 1mmol, elemental sulfur (S) 1mmol and buffer phosphate 5 mM (with different pH: 2, 5 and 8). Then, pyruvic acid (Pir) 100 μmol or lactic acid (Lact) 200 μmol were added, together with sodium sulfide 0.5 mmol and sulfuric acid 0.5 mmol when relevant, which served to provide the SH₂. The reactions were carried out at 130°C during 5 hours. Finally, the aqueous phase was separated and analyzed by GC-MS, after liofilization and BSTFA derivatization of the present acids, and the solid phase with XRD to determine the mineral phase transformations.

3. Results

In figure 1.A it can be seen that the pyruvic acid can be reduced to lactic acid by the SH₂ at pH 5. The presence of the pyrrhotite/sulfur system leads to the strong reduction of pyruvic acid at both acid and

basic pH. The formation of lactate was enhanced in the presence of additional SH_2 at basic pH.

Pyrrhotite and elemental S could oxidize lactic acid into pyruvic acid in a coupled reaction with formation of pyrite (identified by XRD analysis of the solid after reaction) (fig 1.B). Again, the additional presence of SH_2 enhances a higher synthesis of the product, however in this case it happened at acid pH (pH=2).

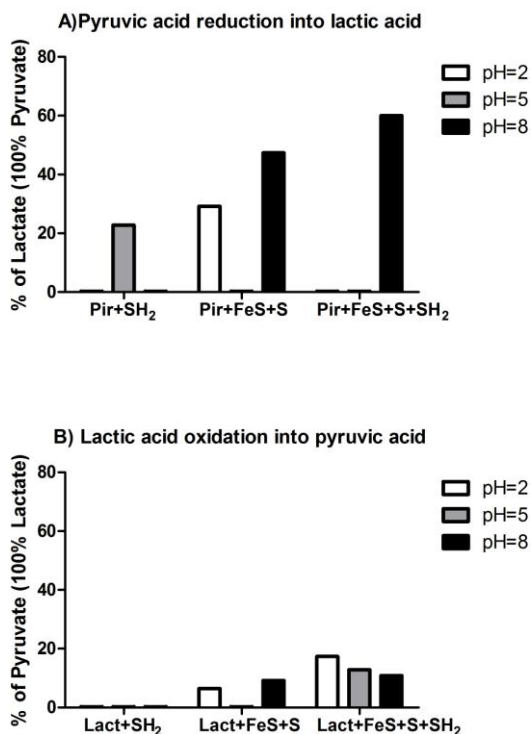


Figure 1: Synthesis of pyruvate and lactate under different conditions. The data show the % of the synthesized product related to the 100% of substrate.

3. Conclusions

Overall, our results demonstrate that the pyrrhotite-sulfur-pyrite system can show oxidoreductase mimic activity, driving the lactate-pyruvate redox chemistry at low temperature hydrothermal systems. The process is pH dependent and is enhanced by the presence of hydrogen sulfide. Our results, the first using iron sulfide mineral, support the hypothesis that the first biochemical pathways evolved from prebiotic chemomimetic pathways and that the extant

Fe-S clusters, present in the active centers of oxidoreductases, could be relicts of those protometabolic systems.

Acknowledgements

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References

- [1] Kaschke, M., Russell, M.: [FeS/FeS₂], a redox system for the origin of life, *Origins of life and evolution of the biosphere*, Vol. 24, pp. 43-56, 1994.
- [2] Klein, C., Hurlbut, C. S.: *Manual de mineralogía*, 4ª ed., Editorial Reverté S. A., 2003.
- [3] Rickard, D., Luther, G.: *Chemistry of iron sulfides*, American Chemical Society, Vol. 107, pp. 514-562, 2007.
- [4] Summers, D., Basa, R., Khare, B., Rodoni, D.: Abiotic nitrogen fixation on terrestrial planets: reduction of NO to ammonia by FeS, *Astrobiology*, Vol. 12, pp. 107-114, 2012.
- [5] Taylor, P., Rummery, T. E., Owen, D. G.: Reactions of iron monosulfide solids with aqueous hydrogen sulfide up to 160°C, *Journal of inorganic and nuclear chemistry*, Vol. 41, pp. 1683-1687, 1979.
- [6] Wächtershäuser, G.: Evolution of the first metabolic cycles, *Proceedings of the National Academy of Sciences of USA*, Vol. 87, pp. 200-204, 1990.
- [7] Wächtershäuser, G.: On the chemistry and evolution of the pioneer organism, *Chemistry and Biodiversity*, Vol. 4, pp. 584-602, 2007.
- [8] Wang, W., Yang, B., Qu, Y., Liu, X., Su, W.: FeS/S/FeS₂ redox system and its oxidoreductase-like chemistry in the iron-sulfur world, *Astrobiology*, Vol. 11, pp. 471-476, 2011.