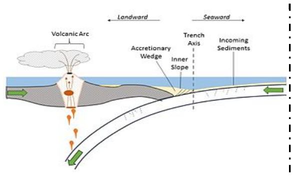
Hydrothermal Vents and Black Smokers

A Bioinorganic Approach to the Importance of Iron Species

Kaylin A. Pickle, Marcetta Y. Darensbourg

Texas A&M University, College Station, TX 77843

Abstract: Hot toxic bursts of fluids and gases are released deep below the ocean's surface at exceedingly hot temperatures. The Earth's tectonic Plates are active, and cause the process of "trench rollback" creating hydrothermal vents and black smokers along the ocean floor. These vents release flux of iron species, as well as sulfur dioxide. X-Ray Fluorescence on plume Particulates confirmed prominent composition of Ferrous sulfide and Ferric hydroxide. The presence of ferrous ions, hydrogen sulfides, and carbon dioxides expelled from hydrothermal vents would appear to create an environment unfavorable to life.

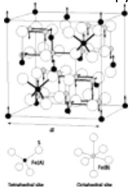


However, the "Iron-Sulfur World" model formed by Gunter Wachtershauser theorized that chemoautotrophic organisms are able to convert Iron sulfides to pyrite by biochemical reduction. His argument that the origin of life began with chemo-autotropic uptake of iron sulfides has been studied and proven by chemists that the process of reduction proposed is viable. Evolution began with these chemoautotrophic species transforming inorganic materials to organic polymers capable of supporting life. Further evidence of this model is given by numerous biological roles that iron and iron-sulfur clusters can perform in a variety of organisms.

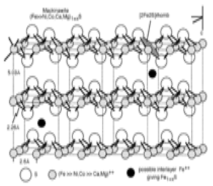
The reliance on hydrothermal vent release of iron sulfur compounds by an underwater empire of archaea, highlights the possibility of nutrients available in this environment. Therefore, the ability to support life indicates that hydrothermal vents and black smokers are an important source of iron to oceans.

Formation of Iron Sulfur Lattices

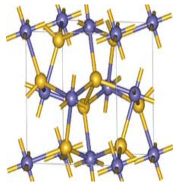
Hydrothermal vents release large amounts of Iron (III) species, that are quickly turned into Fe(III) phosphate species by *Thermococcales* bacteria. These Fe (III) phosphates are secreted by the microorganisms into their surrounding environment. The temperature of the hydrothermal vents rapidly evolve these species into greigite. Greigite, , Fe_3S_4, and mackinawite, Fe_2S, these are key intermediates for the reduction of hydrogen sulfides and ferrous ions to pyrite in excess dihydrogen sulfides.



Greigite



Mackinawite



Pyrite

Pyrite Oxidation by Carbon Dioxide

Pryite Oxidation by Carbon Dioxide was first hypothesized by Gunter Wacthershauser, in his "Iron-Sulfur World Theory", where he states that the environment surrounding hydrothermal vents allows for chemoautotrophs to oxidize pyrite. Temperatures drive the thermodynamics of the reaction, and allow production of succinic acid.

Anaerobic Reduction of Pyrite

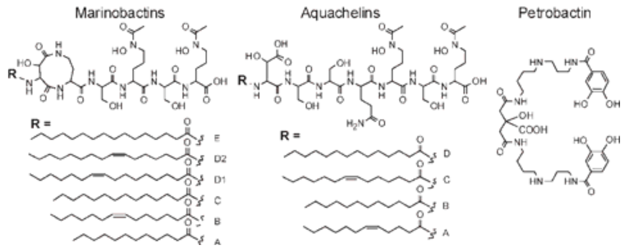
$$4CO_2 + 7FeS + 7H_2S \rightarrow (CH_2COOH)_2 + 7Fe_2S + 4H_2O$$

AG °= -420 kJ/mol

Reduction of Carbon Dioxide is driven by the positive surface charge of transition metals and nucleophilic attack by the thiol group. Ligand binding of –COO- groups to Fe (II) species is favorable. Succinic acid creates sugars that allow anaplerotic reactions in microbials.

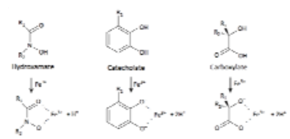
1. Energy Source must be a reducing power
2. Redox Potential must create an irreversible exergonic reaction
3. Metabolism can inhibit electron flow
4. Electron flow can not be coupled
5. Energy source must operate within the organism
6. Energy source is geochemically plausible

Siderophores in Shallower waters

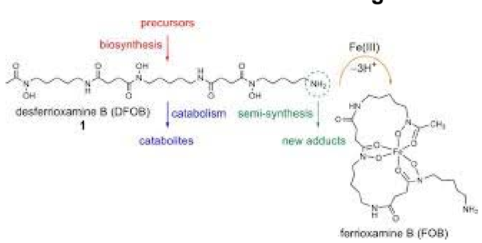


Siderophores are present in pelagic marine organisms. These structures have a high affinity for Iron Sulfide species released by deep water organisms and plumes. However the difference in Iron concentration at this depth of ocean might account for the formation of ligands, instead of tightly packed cyrstals. Fe (III) species bind tightly to the organic ligand

The chemistry behind pyrite oxidation is similar to the binding of siderophores. These have some of the strongest binding affinities to Fe (III) species known and will reduce to Fe(II), partially due to ferromagnetic properties.

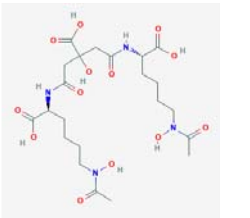


Desferrioxamine B Binding



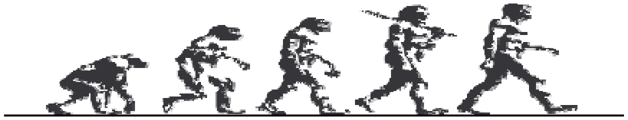
The graphic reveals the binding of Fe (III) species to siderophore, Desferrioxamine B. The ligand created is similar in stability to the crystal iron sulfur species utilized by primitive chemoautotrophs. As evolution continues, the significance of the oxidation of iron shifts to stereospecificity, instead of redox potentials.

Aerobactin in Terrestrial Bacteria



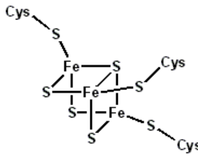
A shift in the importance of transition metal binding to prebiotic peptides is evident as microorganisms continue to evolve. Nitrogen is an essential element in organisms

Aerobactin is a ferrosiderophore present in *Escheria coli*. It allows for a functional iron transport system in the bacterium. It has been proven that E.coli can starve in iron deficient environments, revealing the significance of iron in metabolic pathways of these organisms.



The Importance of Iron in Humans

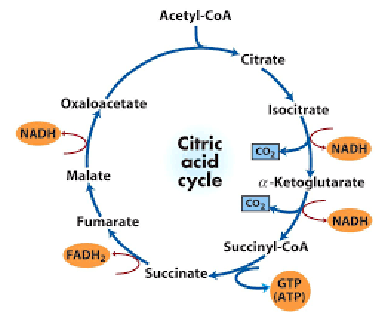
The presence of Iron Sulfur clusters does not stop at bacterium, human metabolism is also heavily reliant on the importance of these clusters. Ferredoxins aid in stereospecificity of both the aconitase and succinate dehydrogenase reactions present in the Krebs Cycle, the main component of oxidative phosphorylation.



Ferredoxin

Comparison of Ferredoxin structure, an important Iron Sulfur cluster in human metabolism, to anaerobic chemoautotrophic pyrite.

The Citric Acid Cycle



Formation of succinic acid is again present in human metabolism. The Krebs cycle is the main producer of metabolic energy in organisms. However, it must occur in aerobic conditions because of the reduction of O2.

Discussion

The Iron-Sulfur World theory proposes the first reduction of a carbon source to biological sugars, that can be utilized by other microorganisms. The chemoautotrophic organisms responsible for pyrite reduction are reliant upon hydrogen sulfides and ferrous ions released from hydrothermal vents. Mineralization of these components creates nanocrystal structures essential to iron oxidation.

The iron species that aid in metabolic processes of primitive aquatic microorganisms are paralleled to terrestrial bacteria and even human metabolism. Supporting the argument for the importance of iron species in metabolic processes, and their importance to the origin of evolution.

References

A. Gorlas et al., Greigite nanocrystals produced by hyperthermophilic archaea of Thermococcales order. Plos One. 13(2018), doi:10.1371/journal.pone.0201549.

A. Roldan et al., Bio-inspired CO2 conversion by iron sulfide catalysts under sustainable conditions. Chemical Communications. 51, 7501–7504 (2015), doi:10.1039/c5cc02078f.

G. Watchershauser, Before Enzymes and Templates: Theory of Surface Metabolism. Before Enzymes and Templates: Theory of Surface Metabolism. 52, 452–484 (1988).

G. Zhang et al., Ferric Stability Constants of Representative Marine Siderophores: Marinobactins, Aquachelins, and Petrobactin. Inorganic Chemistry. 48, 11466–11473 (2009), doi:10.1021/ic901739m.

National Center for Biotechnology Information. PubChem Compound Database; CID=27284, https://pubchem.ncbi.nlm.nih.gov/compound/27284 (accessed Mar. 8, 2019).

National Center for Biotechnology Information. PubChem Compound Database; CID=14828, https://pubchem.ncbi.nlm.nih.gov/compound/14828 (accessed Mar. 8, 2019).

National Geographic Society. "Ocean Vent." National Geographic Society, National Geographic, 9 Oct. 2012, www.nationalgeographic.org/encyclopedia/ocean-vent/.

Toner, B.M., M.A. Marcus, K.J. Edwards, O. Rouxel, and C.R. German. 2012. Measuring the form of iron in hydrothermal plume particles. *Oceanography* 25(1):209-212.

V. D. Lorenzo, S. Wee, M. Herrero, J. B. Neilands, Operator sequences of the aerobactin operon of plasmid ColV-K30 binding the ferric uptake regulation (fur) repressor. Journal of Bacteriology. 169, 2624–2630 (1987), doi:10.1128/jb.169.6.2624-2630.1987.

Wächtershäuser, G. The case for the chemoautotrophic origin of life in an iron-sulfur world. Kluwer Academic Publishers. (1990) 20: 173.

Wang, Wei, et al. "FeS/S/FeS2 Redox System and Its Oxidoreductase-like Chemistry in the Iron-Sulfur World." Astrobiology, vol. 11, no. 5, 2011, pp. 471–476., doi:10.1089/ast.2011.0624.