

**Prebiotic synthesis at hydrothermal vents on the ocean floor: the coupling of mineral growth and CO<sub>2</sub> reduction.** R. L. Jaffe,<sup>1</sup> Z. Zhang<sup>2</sup> and M. Philpott<sup>3</sup>. <sup>1</sup>NASA Ames Research Center, Mail Stop 230-3, Moffett Field, CA 94035, [Richard.l.jaffe@nasa.gov](mailto:Richard.l.jaffe@nasa.gov), <sup>2</sup>Eloret, Inc. 465 S Mathilda Ave, Sunnyvale, CA 94086, <sup>3</sup>Visiting Scholar, Department of Chemistry, University of California, Berkeley, CA 94720.

The “Iron-Sulfur World” hypothesis of the origin of life was proposed by Wachtershauser [1,2] about 20 years ago. He suggested that, on the primordial ocean floor in the vicinity of hydrothermal vents, pyrite formation was coupled to the catalytic formation of small inorganic and organic molecules ejected from those vents and that these small molecules were precursors for the synthesis of larger prebiotic molecules.

In order to evaluate some of the key points in the Iron-Sulfur World hypothesis, we have carried out extensive density functional theory calculations (DFT) to elucidate possible mechanisms for pyrite formation under conditions found at hydrothermal vents on the ocean floors and for pyrite-catalyzed reduction of CO<sub>2</sub>. We have studied the pyrite growth mechanism and the energetics through uptake of FeSH<sup>+</sup> and SH<sup>-</sup> species and the release of H<sub>2</sub>. We have found that at low coverage of FeSH<sup>+</sup> and SH<sup>-</sup>, hydrogenated Fe-S clusters are energetically stable, but at higher coverage dehydrogenation occurs with incorporation of Fe and S into the pyrite lattice. We have also determined reaction pathways for CO<sub>2</sub> reduction catalyzed by stable FeSH<sup>+</sup> and SH<sup>-</sup> clusters on pyrite surfaces. We have found that CO<sub>2</sub> reduction to CO adsorbed at Fe surface sites (Figure 1) occurs either through (1) hydrogenation with adsorbed water as a hydrogen source and with both CO and OH products adsorbed onto Fe species; or (2) hydrogenation with H from the FeSH<sup>+</sup> and SH<sup>-</sup> clusters as the hydrogen sources, with CO adsorbed to the Fe species and incorporation of Fe and S onto the surface of pyrite (intermediate step shown in Figure 2).

In the calculations, the pyrite surface is modeled as a 2x2x2 unit cell with periodic boundary conditions. The DFT algorithm used a plane wave expansion method and the calculations were carried out using the VASP computer code [3,4]. For this work, the computational cell included the iron pyrite surface model, adsorbed species (FeSH<sup>+</sup>, SH<sup>-</sup> and CO<sub>2</sub>) and two layers of water molecules for solvation.

The results of these calculations indicate that redox coupling between the growth of pyrite surfaces and reduction of adsorbed CO<sub>2</sub> to CO allows both reactions to proceed with modest activation energy.

#### References:

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[3] Kresse G. and Hafner, J. (1993) *Phys. Rev. B*, 47, 558.

[4] Kresse, G. and Furthmüller, J. (1996) *Phys. Rev. B*, 54, 11169(1996).

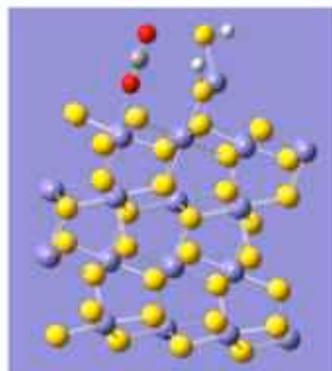


Figure 1. Pyrite surface model with adsorbed FeSH<sup>+</sup>, SH<sup>-</sup> and CO<sub>2</sub> (S = yellow, Fe = blue, O = red, C = gray and H = white). Water molecules are not shown.

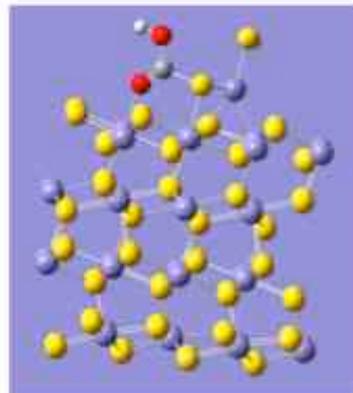


Figure 2. Model in Figure 1 after transfer of hydrogen from SH<sup>-</sup> to CO<sub>2</sub>, forming CO<sub>2</sub>H. Same color code as Figure 1.