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Pyrite-induced uv-photocatalytic abiotic nitrogen fixation: implications for early atmospheres and Life

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Nitrogen is an essential element for life, a prerequisite for the origin and evolution of life on Earth, or in any other potentially habitable planet. The molecular form of nitrogen, N_2, is universally available but is biochemically inaccessible for life due to the strength of its triple bond. Prior to the emergence of life, there must have been an abiotic process that could fix nitrogen in a biochemically usable form. The UV photo-catalytic effects of minerals such as pyrite on nitrogen fixation have to date been overlooked. Here we show experimentally, using X-ray photoemission and infrared spectroscopies that, under a standard earth atmosphere containing nitrogen and water vapour at Earth or Martian pressures, nitrogen is fixed to pyrite as ammonium iron sulfate after merely two hours of exposure to 2,3 W/m2 of ultraviolet irradiance in the 200–400 nm range [1]. Our experiments show that this process exists also in the absence of UV, although about 50 times slower. The experiments also show that carbonates species are fixed on pyrite surface [Figure 1]. We conclude that UV photocatalysis on pyrite may have been a natural mechanism of prebiotic fixation of nitrogen into ammonium sulfates which is then easily released upon contact with liquid water. This property of pyrite may have been incorporated naturally in the prebiotic chemistry evolution, leading to the inclusion of pyrite nano-clusters as reaction centres to generate ammonia from nitrogen, and then from ammonia to generate ammonium sulfates salts in the presence of oxygen. This process has furthermore implication for the abiotic nitrogen fixation on other planetary environments, and it has critical implications for the habitability of planet and the origin of life.

Fig. 1 Picture of the Planetary Atmosphere and Surfaces Chamber and XPS spectra of the presence of ammonium sulfate on pyrite surface (on the left). Schematic representation of the

processes that lead nitrogen fixation on pyrite surface (on the right), (i) by UV photo-catalysis under low pressure conditions (on the top) and, (ii) by the catalytic effect of iron oxide-iron sulfide tandem under visible light conditions and standard earth atmosphere (on the bottom).

[1] E. Mateo-Marti, S. Galvez-Martinez, C. Gil-Lozano and M-P. Zorzano, Scientific Reports, **9,** 15311 (2019)