Photocatalysis of Natural Sulfides and Its Implication for the Origin of Life

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Minerals have been suggested to serve as vital sorbents, catalysts and templates for the synthesis of biomolecules and chemical origin of life [1]. Semiconducting mineral, a sort of catalyst converting solar energy into chemical one in nature, has aroused increacing attention [2, 3]. In this work, sphalerite (ZnS) sample with natural dopant of Fe (15.85%), Cu (2.71%) and Cd (0.28%), which should be once widespead in hydrothermal system in early Earth, was used to investigate its photocatalytic activity in ractions with inorganic carbon (CO_2) and a kind of representive microbe. Results show that the formic acid (HCOOH), the essential organic intermediate in the abiotic reduction of CO_2 to other hydrocarbons, was formed in the presence of natural sphalerite and UV light. The photoreduced product could reach 12 mg/L after irradiating UV light for 9 h in weak acidic and anaerobic system, higher than synthetic pure ZnS (9 mg/L). The advantage of natural sphalerite was attributed to its wider range of optical absorption than its synthetic counterpart. Some co-existing reducing agents, such as S^{2-} and $H_2PO_2^-$, could serve as scavenger of photo-generated holes and thus boost the photoreduction of inorganic carbonous species. Moreover, photo-gengerated electrons of natural ZnS could result in the reduction of dissolved Fe^{3+} to Fe^{2+}, and the latter could be bio-oxidized by a chemoautotrophic and acidophilic microbe *Acidithiobacillus ferrooxidans* for metabolism. Though this pathway, bacterial cell density in the light was 3-fold and 6-fold higher than that in the dark and that without photoelectrons, respectively. This work implies redox reactions triggered by photocatalysis of semiconducting minerals (mainly sulfide minerals) could play potential roles in abiogenesis as well as folowing metabolism of living beings.

[1] Goldschmidt (1952) *New Biology* **12**, 97-105. [2] Schoonen *et al.* (2004) *AMBIO* **33**, 539-552. [3] Lu *et al.* (2013) *Precambrian Res.* **231**, 401-408.