



Photoelectrons from minerals and microbial world: A perspective on life evolution in the early Earth

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ABSTRACT

Fundamental to the origin and evolution of life are the sources of energy and mechanisms of various energy yielding pathways. Recent investigations revealed that the ternary system of microorganisms, minerals and solar light has played a critical role in the history of life on our planet. Solar energy utilization pathway by nonphototrophic microorganisms mediated by semiconducting mineral photocatalysis provides a new concept to evaluate the origin and evolution of life. Semiconducting minerals are ubiquitous on Earth's surface and widely participate in redox reactions following photoelectron–photohole pairs excited by solar light. As photoholes can be easily scavenged by environmental reductive substances and microorganisms possess multiple strategies to utilize extracellular electrons, the highly reductive photoelectrons serve as potential energy source for microbial life. The discovery of this pathway extends our knowledge on the use of solar energy by nonphototrophic microorganisms, and provides important clues to evaluate life on the early Earth.

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1. Introduction

The dawn of Phanerozoic witnessed the emergence of modern life on our planet, and recent models invoke its initiation of return-flow of seawater into the mantle, emergence of landmass above sea-level, and the distribution of nutrients on a global scale as the main trigger (e.g., Maruyama et al., 2012, 2013; Santosh et al., 2013 and references therein). However, the mode of origin of primitive life during the early Earth history remains enigmatic. One of the mechanisms invoked for appropriate geochemical niches for the origin of early life on Earth is the interaction of the nascent hydrosphere with mantle rocks to form serpentinites and the subsequent reaction of the vent fluids with CO₂-bearing sea water (Sleep et al., 2011). Thus, submarine hydrothermal vents above serpentinite are presumed to have created the chemical potential gradients of aqueous and ionic hydrogen, and provided the appropriate venue for origin of life. The ca. 3465 Ma old Apex chert of northwestern Australia has been in focus for studies related to early life evolution, as these rocks preserve the evidence for diverse assemblages of microbial fossils suggesting the presence of primitive life on the early Earth (Schopf and Kudryavtsev, 2012). The Apex basalts also carry pumice clasts with potential biominerals including sulfides

and phosphates, together with the intimate associations of C, N, P and S. Thus, Brasier et al. (2013) speculated that these clasts, which also contain catalytic minerals such as titanium oxide, and altered clays and zeolites represent a cradle for early life. Fundamental to the formation and survival of life is energy, and understanding the source and mechanisms of various energy yielding pathways are critical to evaluate the origin and evolution of life.

Solar energy is the ultimate energy source on Earth, and almost all life depends on it, either directly or indirectly. It was once believed that all life forms on Earth lived on the energy fixed by photoautotrophy until Winogradsky (1949) first described chemoautotrophy. Now, it is known that the huge diversity of photosynthetic organisms such as purple bacteria, cyanobacteria, green-sulfur bacteria, green algae, plants have all evolved various strategies to capture and store solar energy as chemical fuels, which could be then utilized by other life forms without photosynthetic systems (Fu et al., 2007; Ehleringer and Monson, 1993; Myklestad, 2000; Takahashi and Ichimura, 1968). Chemoautotrophic microorganisms oxidize inorganic substances to acquire electron energy for maintaining metabolism, whereas chemoheterotrophic microorganisms live on organic substances synthesized by chemoautotrophic and photoautotrophic bacteria (Elior, 2006). Due to the deficiency of intracellular photosensitive components, chemotrophic microorganisms could not utilize solar energy directly. Nevertheless, photosensitive components are not necessary for microorganisms to utilize solar energy. In a

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recent study, Lu et al. (2012) presented evidence demonstrating solar energy mediated by semiconducting mineral photocatalysis, acting as energy source, promoted the growth of some non-photosynthetic bacteria and the reconstruction of soil microbial community and this study has important implications in exploring the origin of early life on Earth.

2. Photocatalysis of natural semiconducting minerals

Semiconducting minerals are a unique class that are characterized by distinctive electronic structure composed of a filled valence band (VB) and an empty conduction band (CB) (Schoonen et al., 1998). The valence band electrons can be excited to the conduction band upon absorption of photons with energy equivalents to or higher than the band gap (E_g), which is the energy difference between the top of the VB and the bottom of CB. This process converted solar energy to electron energy in CB and forming negatively charged electrons and positively charged holes in the CB and VB, respectively, which migrate to the semiconductor/solution interface to induce redox reactions (photocatalysis), such as photoelectrons reduction (Li et al., 2008) and photoholes oxidation (Lu et al., 2007) of environmental pollutants. The unique electronic structure gives semiconducting minerals the role as natural solid phase electron sources and sinks, with direct or indirect influences on redox-based geo- or bio-geochemical processes (Schoonen et al., 1998).

There are numerous natural semiconducting minerals in various geological settings on our globe. The most predominant phases among these near the Earth's surface are: Fe and Mn oxides in soils and sediments [e.g., hematite (Fe_2O_3), goethite (FeOOH), pyrolusite (MnO_2)]; sulfides in early Earth's surface [e.g., sphalerite (ZnS), pyrite (FeS_2), chalcopyrite (CuFeS_2)]; oxides in ores [e.g., rutile (TiO_2), ilmenite (FeTiO_3)]. The band structure and other physical characteristics of natural semiconducting minerals were systematically studied in the 1970s (e.g., Shuey, 1975). Xu and Schoonen (2000) summarized the absolute energy positions of conduction band and valence band edges in about 50 semiconducting metal oxide and metal sulfide minerals. Based on their work, natural semiconducting minerals are now known to contain impurities and defects such as substituting ions, interstitial ions or atoms and vacancies which result in major changes in their electronic structure. In most cases, the band gap of a natural semiconducting mineral is narrower than its synthetic "pure" counterpart, which makes it more vulnerable to excitation by photons, thereby generating electron-hole pairs when exposed to visible light.

It is well known that natural semiconducting minerals, such as metal oxides and metal sulfides, widely distribute and coexist with various chemical species such as humic acid, ascorbic acid, etc. (Smirnov et al., 2004) in the near-surface geochemical environments (Vaughan, 2006; Wigginton et al., 2007). When sunlight falls on the Earth surface, photons with proper wavelengths excite the semiconducting minerals to generate photoelectron-hole pairs. Based on the data reported by Schoonen et al. (1998), at weakly acidic environment, the reduction potentials of photoelectrons in conduction band are -0.36V and -1.58V (vs. NHE, NHE: normal hydrogen electrons, all the electric potentials in this paper are vs. NHE) for rutile (TiO_2) and sphalerite (ZnS), respectively; whereas the potentials of photoholes in their valence bands are $+2.64\text{V}$ and $+2.32\text{V}$, respectively. The potentials of surrounding species such as humic acid ($+0.32\text{V}$ to $+0.38\text{V}$ (Visser, 1964)), ascorbic acid (-0.28V ; Borsook and Keighley, 1933), as well as other reductive chemicals commonly existing in the early Earth, such as H_2S , ammonia, organic compounds, among others, are negative enough to scavenge photoholes, leaving photoelectrons as potential electron sources (Peral and Mills, 1993; Bems et al., 1999; Yanagida et al., 1990).

Schoonen et al. (1998) proposed that the reducing power of a photoelectron in the conduction band of natural sphalerite could be calculated as the fugacity of hydrogen (f_{H_2}) according to Eq. (1):

$$\log f_{\text{H}_2} = -2\text{pH} - \left(\frac{-2E_{\text{h}}F}{2.303RT} \right) \quad (F \text{ is the Faraday constant}) \quad (1)$$

Considering the pH value (~ 6.8) (Morse and Mackenzie, 1998) and the temperature ($70\text{--}100^\circ\text{C}$) (Sleep, 2010) of the surface of early Earth at about 3.8 Ga ago, the reducing power of sphalerite photoelectron would be equal to $10^{28.8}$ (100°C) to $10^{32.5}$ (70°C) bar hydrogen (corresponding to -1.58V reduction potential vs. NHE). This suggests that photoelectrons were highly reductive and should be thermodynamically acceptable by microorganisms to support their metabolism as the potentials of most important biological chemicals are more positive than photoelectrons (Nelson and Cox, 2004). Chemical potential gradients involving ionic or aqueous hydrogen have been identified to be important aspects of viable energy sources for early life. The marked pH gradient between vent waters and ocean water has been inferred as one of the first energy sources of life (Lane et al., 2010).

Mulkiidjanian et al. (2012) concluded that in primordial geothermal fields, ammonia, sulfide, phosphate and phosphate ions would react with carbonaceous compounds catalyzed by minerals (such as sphalerite and manganese sulfide) to synthesize aminated, sulfated and phosphorylated molecules, which provided energy and nutrition for early forms of life on Earth. Although these authors did not describe the catalysis process, mineral photocatalysis must be an important one as the presence of highly reductive photoelectrons and also semiconducting mineral photocatalysis might directly provide photoelectrons for early life on Earth.

3. Bacterial growth and microbial community formation influenced by photoelectrons

In a recent investigation, Lu et al. (2012) presented evidence demonstrating that non-phototrophic bacteria could indirectly use solar energy in the form of photoelectrons via the photocatalysis of natural semiconducting minerals (Fig. 1).

In Lu et al.'s study, a simulated experiment was conducted, applying a dual-chambered equipment to separate chemoautotrophic bacteria – *Acidithiobacillus ferrooxidans* (*A. ferrooxidans*) or chemoheterotrophic bacteria – *Alcaligenes faecalis* (*A. faecalis*) and semiconducting minerals with a proton exchange membrane (PEM) which only permitted the proton exchange. To form a close electric circuit, two chambers are connected with electric wires.

Lu et al. (2012) performed experiments using this setup in rutile – *A. ferrooxidans* simulated system, where the cell concentration of *A. ferrooxidans* with semiconducting mineral photocatalysis was found to be notably higher as compared with the system without semiconducting mineral photocatalysis which employed an open circuit. The results indicated that mineral photocatalysis promoted the bacterial growth (Fig. 2a). In their experiments, $\text{Fe}^{2+}/\text{Fe}^{3+}$ acted as the electron shuttle for *A. ferrooxidans* growth. Fe^{2+} here was recycled and provided the energy originating from photoelectrons to *A. ferrooxidans*. Moreover, the net *A. ferrooxidans* concentration yield shows a positive correlation with electrons from photocatalysis (Fig. 2b). These results provide robust evidence for the close relationship between bacterial growth and photoelectrons. A similar growth pattern was also observed in sphalerite – *A. ferrooxidans* and goethite – *A. ferrooxidans* simulated systems.

The main factors that influenced the bacterial growth were photon energy and photon quantity. With an increase in the light wavelength, the photon absorption efficiency decreased resulting in less photoelectrons and lower photocurrent density, leading to

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