

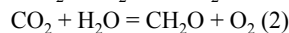
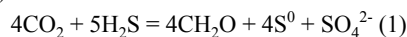
# Possible emergences of cyanobacteria and sulfate-reducing bacteria before the emergence of anoxygenic photoautotrophs

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The conventional view by earth scientists and biologists on the evolution of life on early Earth is that anoxygenic photoautotrophs that utilize H<sub>2</sub>S (and/or native sulfur) as an electron donor in biosynthesis (Reaction 1), preceded oxygenic photoautotrophs that utilize H<sub>2</sub>O as an electron donor (Reaction 2):



This view was developed mostly because of the belief that molecular O<sub>2</sub> was virtually absent in the atmosphere and oceans prior to ~2.5 Ga ago, except for the minor amounts of O<sub>2</sub> that were produced by abiotic photodissociation of H<sub>2</sub>O.

Thermodynamic analyses of the stability relationships among aqueous/gaseous/solid species in the H-C-O-S-Fe system suggest that Reaction (1) may become important only in environments where native sulfur and SO<sub>4</sub><sup>2-</sup>, as well as H<sub>2</sub>S<sub>(aq)</sub>, become stable at  $m\sigma\text{SO}_4^{2-} \geq m\text{H}_2\text{S}_{(\text{aq})}$ . Fe-bearing minerals that are in equilibrium with native sulfur are marcasite/pyrite (FeS<sub>2</sub>), rather than pyrrhotite (FeS) or iron (hydr)oxides (e.g., Fe(OH)<sub>2</sub>, FeOOH, Fe(OH)<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>). Such conditions are typically created in local basins where H<sub>2</sub>S<sub>(aq)</sub> is produced by sulfate-reducing bacteria utilizing SO<sub>4</sub><sup>2-</sup> in seawater; SO<sub>4</sub><sup>2-</sup>-rich seawater is generated from the oxidation of pyrite in igneous and sedimentary rocks during soil formation on land. Therefore, the emergence of H<sub>2</sub>S-utilizing anoxygenic photoautotrophs likely occurred after the emergences of cyanobacteria and sulfate-reducing bacteria.