Evolutionary and geologic consequences of organic carbon fixing in the primitive anoxic ocean

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ABSTRACT
Steps leading to development of the modern photic-based marine food web are postulated as the result of modifications of the environment, enhanced by the activity of Archean sulfur chemosynthesizers. Such organisms (Anoxium) evolved in an anoxic ocean prior to 3.9x10^9 yr ago at Archean analogs of modern oceanic hydrothermal vents. At this time geothermal energy was more readily available to organisms than photic energy, given atmospheric conditions at the surface similar to Venus, where intensity is low and only middle and red visible wavelengths penetrate the cloudy CO_2-rich atmosphere. Competition for the reduced sulfur developed due to oxidation and loss of sulfur to sediments. Consequently, evolutionary advantage shifted to Anoxium isolates that could use alternate energy sources such as light to supplement the diminished supplies of reduced sulfur. Initially, photo-sulfur organisms evolved similar to modern purple bacteria that absorb in the red visible spectra. Subsequent carbon fixing and oxidation improved both the quantity and range of light reaching the ocean surface. This permitted absorption in the blue visible range so that water splitting was now feasible, releasing free oxygen and accelerating oxidation. Eventually, reducing environments became restricted, completing the shift in the principal marine carbon-fixing activity from anoxic chemosynthesizers to aerobic photosynthetic organisms.

INTRODUCTION
Modern marine food webs are based on photosynthetic organisms functioning in a well-aerated near-surface ocean (Strickland, 1965). However, abundant metazoan and microbial life is found about the Galapagos and other deep-ocean thermal springs (Corliss and Ballard, 1977; Corliss et al., 1979; Spiess et al., 1980), apparently trophically isolated from the main oceanic food web (Jannasch, 1980; Jannasch and Wirsen, 1980; Karl et al., 1980). Analyses of the biological interrelationships around these springs suggest that geothermally produced hydrogen sulfide is the basic energy source used by chemosynthetic bacteria to fix carbon. Karl et al. (1980) noted that these bacteria compose the basic food resource about the springs. The uniqueness of the vents and their potential as an analog of primitive conditions has led Corliss et al. (1981) to propose a model for the origin of life there. The discussion here is concerned not with the origin of life but with the use of the vents as a uniformitarian analog of primitive conditions. Specifically, we propose a sequence of geologic and ecologic steps that developed as a result of biomass production by sulfur organisms at Archean oceanic vents prior to, but leading to, significant photosynthesis. Early carbon fixing by these organisms and their descendents could have reduced the available CO_2 and the greenhouse effect in an early terrestrial atmosphere similar to that of Venus. This would enhance both the quantity and quality of light reaching the surface. During the clearing of the atmosphere, photodissociation (Towe, 1978), accompanied by the differential escape of reducing gasses (Miller, 1963), could increase P_2O_5 with time. This is required to use a Sillen-type model (Garrels and Perry, 1974), as reactions of carbon-fixing sulfur bacteria involve no oxygen release. Eventually, due to the decline of available reduced sulfur and the increase in availability of blue light, nonsulfur photosynthesis, splitting water to produce free oxygen, became the optimal carbon-fixing system.

GEOLOGIC EVIDENCE
Probable Archean analogs of the deep ocean thermal vents exist in Canada, South Africa, Greenland, and Australia (Corliss et al., 1981, p. 63). Cameron and Garrels (1980, p. 193) described Archean greenstone belts in the Canadian Shield in which graphic sequences occur "within or near" organic sequences. Anhaeusser et al. (1968) recorded the presence of carbonaceous layers interbedded with sedimentary and volcanic rocks in the older Archean Onverwacht and Fig Tree Series in southern Africa. These rock sequences formed near deep-ocean volcanic activity. Cameron and Garrels (1980, p. 193) pointed out that graphitic sediments in the Canadian Shield Archean greenstone belts "are frequently related stratigraphically to the sites of volcanic exhalations." They noted the association of relatively high amounts of carbon and sulfur in Archean greenstone belt samples and suggested that this association "may be because the sites where volcanic exhalations entered the sea were particularly suitable for organic growth." Cameron and Garrels (1980, p. 193, 192) also suggested that "bacteria that utilize the oxidation of S compounds" could have flourished in such an environment, and that "hot sulfur springs of Archean time may have been the equivalent of today's tropical rain forest."

ISOTOPIC EVIDENCE
Schidlowski et al. (1979, p. 196) analyzed carbon isotopes for the Isua carbonates and iron formations (the oldest known sedimentary rocks) and concluded that "the terrestrial carbon cycle was virtually stabilized at least as early as 3.7x10^9 years.
ago.” This conclusion supports the Garrels and Perry (1974) estimate that at least one-third of the organic carbon reservoir was in place prior to development of iron formations or in pre-Iusa time. Accordingly, appreciable carbon fixing must have occurred before $3.7 \times 10^9$ yr ago (Iusa time).

Sulfur isotope studies by Monster et al. (1979), including Iusa rocks, indicate no sulfate reduction (that is, no oxidized sulfur as sulfate available) until $3.2 \times 2.8 \times 10^9$ yr ago (post-Iusa). The combination of the oxygen demand required for the deposition of iron formations with insufficient sulfate available for sulfate reduction implies low PO$_2$ in the ocean before about $3.2 \times 10^9$ yr ago until both cyclic iron and sulfur were oxidized (see Garrels and Perry, 1974, p. 326). Cloud (1976) and Schidlowski et al. (1979) concurred that the magnitude of the iron formations requires cyanophytic photosynthesis. Oxidation of sulfur to sulfate would follow iron oxidation with increasing PO$_2$. Monster et al. (1979, p. 412) suggested that photosulfur bacteria could provide sulfate at low PO$_2$. Skyring and Donnelly (1982) believed that the sulfur isotope data show that sulfate (SO$_4^{2-}$), not sulfate, reduction was indicated before about $2 \times 10^9$ yr ago. After then, true sulfate reduction began. Accordingly, complete sulfur oxidation to sulfate would occur after iron oxidation and deposition of the iron formations.

**OCEANOGRÁPHIC EVIDENCE**

Water in the vicinity of modern deep-sea vents contains as much as 0.4% dissolved oxygen derived from surface exchange with the 20% oxygen atmosphere. Such saturation values indicate that for far lower oxygen values in the atmosphere, assuming Henry's Law, the oxidation states in the deep ocean would be low, probably anoxic. Clemmey and Badham (1982, p. 145) have suggested that there was some free oxygen in the atmosphere in Isua time. The near-surface ocean may be oxygenated (see Drevet, 1974) by exchange with the atmosphere. However, it is unlikely that the Archean deep ocean was ventilated prior to the development of significant oxygen in the atmosphere and concomitant glaciation to produce dense oxygen-rich water to ventilate deep water (Berry and Wilde, 1978).

**MODEL**

The following discussion hypothesizes the conditions and evolutionary pathways in pre-Iusa time leading to the initiation of the base of food webs analogous to those in the modern aerobic surface ocean. It provides an explanation for the early carbon reservoir and suggests how photosynthetic conditions could develop. Unfortunately, there is no geologic evidence for pre-Iusa conditions to guide or to test the hypothesis. However, this is a failing of all primitive earth models. Thus, each model should be evaluated on how logically it leads to an explanation of geologic conditions beginning in Isua time.

The coincidence of nonphotosynthetic bacterial activity around modern deep ocean vents and the geologic record of similar conditions in the Archean suggests that early carbon-fixing life forms could be chemosynthetic bacteria that used geothermally produced hydrogen sulfide as their primary energy source. Use of geothermal energy as the energy source for initial carbon fixers overcomes the problem of limited light transmission through a cloudy, high-CO$_2$ early atmosphere such as that seen in the modern Cytherean system (Hoffman et al., 1980; Tomasko et al., 1981).

Chemical conditions are based on the Garrels and Perry (1974) elaboration of the Sillen (1961) model in which coupling of the carbon and sulfur systems has been reaffirmed in the discussions of Veizer et al. (1980) and Schidlowski and Junge (1981).

Early biotic (pre-Iusa) conditions included an anoxic ocean (Berry and Wilde, 1978; Garrels and Perry, 1974) and an atmosphere with a high carbon dioxide content similar to the present abiotic Venus. Hydrogen sulfide or reduced sulfur from volcanic vent outgassing would persist in an anoxic ocean because of relatively high solubility of H$_2$S (Doubl and Riley, 1979). Volcanic activity and erosion of crustal rocks could result in dissolved nitrogen compounds and phosphates in the ocean (Garrels and MacKenzie, 1971, p. 281-292). Environmental conditions would be similar to those in the hydrogen sulfide zone in the Black Sea (Kriss, 1959).

Hydrogen and methane probably were present; Welham and Craig (1979) noted that ridge-rise thermal vents appear to be a major source for hydrogen and methane in the oceans. The presence of methane would insulate that nitrogen would occur as ammonia. Atmospheric and ocean temperatures would be warm to hot, primarily as a consequence of the greenhouse effect. Insolation at the sea surface would be extremely low because cloudiness would have been persistent.

The designation “Anoxium” is used here for a complex of chemosynthetic, poten-

\[ 106CO_2 + 106H_2S + 16NH_3 + H_2PO_4^- + \]
\[ 106H_2O - [Fe(H_2O)]_{10}(NH_3)_{15}(H_2PO_4)] + 106SO_4^{2-} + 106H_2O. \]

The presence of NH$_3$ is an atavistic reminder of the past. Garrels and Perry (1974) suggested that NH$_3$ was chemically dominant prior to development of significant banded iron formations. Anoxium is considered, therefore, to have evolved before Isua time. Prior to the deposition of the banded iron formations, sufficient Fe$^{2+}$ was present to inorganically produce pyrite (FeS$_2$) (Drewer, 1974) and diminish the potential for primitive sulfur heterotrophic activity or the reverse of equation 1. True sulfur heterotrophy probably did not develop until about 3.2 b.y. ago, as noted above, after most of the ferrous iron was oxidized and oxygen pressures were high enough to produce sulfite and eventually sulfate. Late development of sulfur heterotrophy would allow for increase of the C and S in organic sinks.

Organic matter formed through the reaction of equation 1 went into a “sink” in the sedimentary sequence, as the rock record of Archean graphic and carbonaceous layers indicates (Cameron and Garrels, 1980; Annahauze et al., 1968). The net result would be a decline in the amount of reactive carbon dioxide and sulfur in the oceans and atmosphere. Carbon in organic matter that went into sinks would be unavailable for reactions until released through erosion. At the same time, the amount of S$^{2-}$ would decrease, assuming autotrophic organisms utilized S$^{2-}$ more quickly than outgassing could replenish it, and inorganic processes would gradually oxidize or deplete reduced sulfur.

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Continued expansion of Anoxium would reduce the amount of $S^2$ to such an extent that the environmental optimum conditions for Anoxium would be restricted to the vicinity of those vents outgassing H$_2$S. An environmental gradient of available hydrogen sulfide away from the vents would have developed. The development of such a gradient about Canadian Archean vents has been indicated by Cameron and Garrels (1980). They noted that "moderate to large amounts" of carbon and sulfur are present in shales deposited near Archean thermal vents on the Canadian Shield, but that shales distant from thermal vents are "generally low in these elements."

Peripheral isolates in Anoxium populations on the outer reaches of the gradients would be at a disadvantage in competition for $S^2$ as an electron source. Any organisms among the peripheral isolates able to exploit other electron sources would have an advantage in competition for needed electron resources. As the vents became inactive, or the quantity of outgassed H$_2$S diminished, competition for survival would increase. Photic energy from sunlight would be a potential energy source only for those Anoxium population isolates on gradients that came near the sea surface. Assuming the ancient vents were on ridge rise systems in the deep ocean, isolates at the sea surface would be remote from their energy source, which would place them under pressure to use a nonsulfur energy source.

Continued fixation of carbon dioxide by Anoxium and loss of organic matter to sedimentary sinks gradually would diminish the greenhouse effect. As the ambient temperature dropped, cloudiness would be reduced, thus increasing light quality. The exact qualitative effects on solar radiation due to changes in CO$_2$ and water-vapor content are still topics of controversy (see Broecker et al., 1971, p. 312–317). However, there is agreement that decreased CO$_2$ will reduce temperatures, which in turn will reduce water vapor and cloudiness in the atmosphere, improving the amount of light received at the surface. On the basis of a cloud cover of 50% (Møller, 1963) a 1% reduction in cloudiness would produce a net loss of 0.8 mcal/cm$^2$-min. As the decline in transmission coefficient is smooth toward lower wavelengths (Williams, 1970, p. 18), reduction in CO$_2$ and cloudiness would permit more transmission of lower wavelengths with time.

On Venus, at the surface, solar radiation shining through the 96% CO$_2$ and perpetually cloudy lower atmosphere is concentrated at the red end (600 to 900 mM) and is essentially devoid of lower wavelengths (Tomasko et al., 1981, p. 8179–8180). Blue and shorter wavelengths penetrate only to an altitude of about 30 km, to the top of the lower Hadley convection cell. The absorption appears to be due to sulfur compounds, primarily SO$_2$, in the Cytherean clouds (Pollack et al., 1979, p. 79). By analogy (Fig. 1), purple and green photobacteria would be favored in such an early high-CO$_2$ cloudy atmosphere. Accordingly, photo-organisms using shorter wavelengths could not develop until that niche appeared with the combination of oxidation of SO$_2$ absorbers and decrease in CO$_2$-derived cloudiness.

With increased quality and quantity of light, selection would favor those peripheral isolates among Anoxium populations that had or incorporated organelles that used light as an alternative energy source. Such organelles could include the photomitochondria of Woese (1977). Olson (1978, p. 1) postulated a common ancestor that "existed approximately 3.5 billion years ago" for purple and green bacteria and blue-green algae because they all have similar chlorophylls, cytochromes, ferredoxins, and quinones. Different evolutionary pathways could develop under those circumstances. In one, organisms similar to modern purple and green sulfur bacteria could arise (see Fig. 2). They would oxidize hydrogen sulfide in the presence of light and fixed carbon dioxide. Miller (1963, p. 861) noted "it is easier to split H$_2$S than to split H$_2$O, and so it seems likely that organisms would develop photo-

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**Figure 1.** Comparison of light characteristics of Cytherean atmosphere as analog of primitive terrestrial atmosphere with absorption by terrestrial photic organisms. Cytherean data after Tomasko et al. (1981, p. 8179). Spectra for altitudes above Cytherean surface in kilometres: a = 0.1; b = 5; c = 16.2; d = 31.4; e = 47.9; f = 49.7; g = 57.5; h = 61.3; i = 64.3. Terrestrial organisms: 1, diatom = Navicula minima after Tanada (1951); 2, blue-green alga = Anacystis; 3, green bacterium = Chlorobium; 4, purple bacterium = Rhodopseudomonas; after Stanier et al. (1970, p. 220).
synthesis with sulfur first." The first step would be oxidizing $S^2_-$ to elemental sulfur or photosystem I (Towe, 1978):

$$\text{CO}_2 + 2\text{H}_2\text{S} \rightarrow \text{CH}_3\text{O} + \text{H}_2\text{O} + 2\text{S}^0. \quad (2)$$

The combined activity of the photosynthesisers as well as the chemosynthesisers would reduce $S^2_-$ significantly as an available electron source, except at outgassing vents. Pure sulfur chemosynthesisers would be restricted and the opportunities for organisms similar to certain modern purple and green sulfur bacteria would be enhanced at the sea surface, particularly in tidal areas. A second line would be from peripheral isolates in the Anoxium complex to organisms similar to modern cyanobacteria, such as *Oscillatoria limnatica* (Cohen et al., 1975). Such cyanobacteria exist in anoxic and aerobic environments, and they appear to be able to alternate between chemotaurophic growth using hydrogen sulfide and photosynthetic growth (Cohen et al., 1975; Garlick et al., 1977; Oren and Padan, 1978; Oren et al., 1979). Photosystem II (Towe, 1978) would develop in the photosynthetic phase, producing free oxygen:

$$\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{O} + \text{H}_2\text{O} + \text{O}_2. \quad (3)$$

Reduced sulfur ($S^-, S^-$) concentrations would decrease by inorganic oxidation of sulfur compounds to sulfate in the presence of free O$_2$. Eventually, with free O$_2$ available locally in the absence of reduced sulfur, the second step in sulfur oxidation from elemental sulfur to sulfate would be possible:

$$3\text{CO}_2 + 2\text{S}^- + 5\text{H}_2\text{O} \rightarrow \text{CH}_3\text{O} + 4\text{H}^+ + 2\text{SO}_4^{2-}. \quad (4)$$

Monster et al. (1979, p. 412) proposed photo-tobiogenic sulfate formation in the absence of free oxygen:

$$0.5\text{H}_2\text{S} + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{CH}_3\text{O} + \text{H}^+ + 0.5\text{SO}_4^{2-}. \quad (5)$$

Such a direct photo-oxidative transfer of 8 electrons implies an ample light source. Such a development would be evolutionarily later than or contemporaneous with the development of the sulfur cyanobacteria. Direct sulfate formation as in equation 5 has been reported by Parkin and Brock (1981) for green sulfur bacteria in a Michigan lake (under present atmospheric conditions, of course).

In the ocean, as PO$_2$ increased, geo-thermal $S^-$ oxidized to SO$_3^{2-}$ and SO$_4^{2-}$, and NH$_3$ oxidized to NO$_2^-$ and NO$_3^-$. Subsequently, organisms similar to *Desulfovibrio* evolved to use organic matter and SO$_3^{2-}$ and eventually SO$_4^{2-}$. This would have re-established anoxic environments locally and regenerated H$_2$S. Photosynthetic organisms would be producing the major part of the organic matter in the oceans by this step.

With loss of $S^-$ by oxidation, non-sulfur photosynthesizing organisms would be favored. Particularly with increased light availability as these organisms expanded, increasing quantities of free oxygen escaped to the atmosphere. As atmospheric oxygen increased, surface waters of the oceans were ventilated more fully through wind mixing, and an opportunity opened for development of prototye thiobacilli at the boundary between oxygenated and anoxic waters now seen in the Black Sea (Sorokin, 1964).

**SUMMARY**

The postulated progressive development from certain possible preprokaryotic to prokaryotic organisms is summarized in Figure 2. It should be emphasized that, as a consequence of numerous examples of convergent evolution among bacteria (Swartz and Dayhoff, 1978; Fox et al., 1980), organisms occupying certain niches today may not be related phylogenetically to organisms that occupied similar niches in the Archean.

The principal organic carbon-fixing activity thus shifted from anoxic chemotaurophic to aerobic photosynthesisers operative in the oxygenated surface mixed layer of the ocean. This accelerated the production of oxygen and organic matter, beginning the modern food web in the oceans as illustrated by the Richards (1965) plankton equation:

$$106\text{CO}_2 + 122\text{H}_2\text{O} + 16\text{HNO}_3 \rightarrow \text{H}_3\text{PO}_4 + ([\text{CH}_2\text{O}]_{106}(\text{NH}_3)_{14}[\text{H}_3\text{PO}_4]) + 138\text{O}_2. \quad (6)$$
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