

minimal. The decomposition model presented here for *Spartina* detritus indicates, however, that relatively large (4%) isotope changes can occur during the early diagenesis of lignified plant tissues and that shifts in $\delta^{13}\text{C}$ should be considered in source identification of organic matter. Indeed, recent analyses of the carbon isotope and chemical composition of ancient buried woods have shown that the remaining tissues are relatively depleted in ^{13}C and enriched in lignin relative to modern counterparts¹³.

The relative contributions of *Spartina alterniflora* grass (whole-tissue $\delta^{13}\text{C} = -12$ to -13%) and phytoplankton ($\delta^{13}\text{C} = -19$ to -23%) to estuarine organic matter have been debated for many years¹⁴⁻¹⁶. Early studies of fluxes of organic matter in salt-marsh estuaries indicated that a large portion of the detritus derived from *Spartina alterniflora* was transported to adjacent waters and sediments^{14,15}. Data from more recent studies based on the carbon isotope compositions of estuarine detritus were interpreted to indicate that *Spartina* detritus was relatively unimportant to carbon flow beyond marsh sediments¹⁷⁻²⁰. The simple mixing models typically used to distinguish different carbon sources on the basis of $\delta^{13}\text{C}$ values do not take into account shifts in isotope composition during decomposition and assimilation and, in the case of *Spartina*, may have significantly underestimated the contribution of salt-marsh vegetation to estuarine and coastal waters.

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Was the Archaean biosphere upside down?

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Photosynthesis produces reduced organic carbon and an oxidized partner in equivalent molar amounts. These compounds can react with one another, again in equivalent molar amounts, so that no net change occurs in the overall level of oxidation of the biosphere (here taken to mean the biota together with the part of the Earth with which living things interact¹). But, the reduced and oxidized partners have different susceptibilities to transport by environmental processes and so, typically, they become separated. Conservation of matter implies that for every mole of excess oxidant in an oxidizing region of the biosphere there must be a mole of excess reductant in a reducing region. Today, the oxidized partner in photosynthesis is usually free oxygen, which floats upward to accumulate in excess in the atmosphere, whereas organic matter settles downward to collect in sediments and stagnant pools. On the anoxic Archaean Earth, the oxidized partner was probably iron. As oxidized iron is markedly less soluble and mobile than organic carbon, differential transport in the Archaean biosphere would have had an effect just the opposite of that in the modern biosphere. The oxidized partner would have settled downward more rapidly than the reduced partner, resulting in the accumulation of excess oxidant in sediments and stagnant pools. An equivalent excess of the more volatile reduced compounds would have been left behind in ocean and atmosphere in the form of dissolved organic carbon and gaseous hydrocarbons. On average, therefore, the Archaean biosphere may have been oxidizing at the bottom and reducing on top.

For about the first 2,000 Myr of Earth history the world was anaerobic and inhabited only by prokaryotes². Biogeochemical cycles at this time may have differed markedly from those of the present, and an understanding of these cycles can influence ideas about the evolution of early life and the environmental interpretation of the sedimentary rock record. Our ideas about

biogeochemical cycles, however, are prejudiced by our familiarity with the abundantly oxidizing modern environment with its productive eukaryotic biota. By far the dominant form of autotrophy today is oxygenic photosynthesis, in which green plants or cyanobacteria reduce carbon dioxide to cell material and maintain oxidation balance by releasing free oxygen to the environment. This process is largely balanced on the modern Earth by aerobic respiration, in which heterotrophic organisms oxidize organic compounds using free oxygen as electron acceptor. On the Archaean Earth, the major biogeochemical cycles of production and consumption of organic matter must also have involved reduction and oxidation of carbon, but the environmentally abundant oxidation partner of this carbon cannot have been free oxygen when the world was anaerobic. Even if Archaean autotrophs released free oxygen to the environment, this oxygen must have reacted rapidly with reduced inorganic constituents of ocean and atmosphere to maintain an anaerobic environment. The oxidized products of photosynthesis or of this ambient reaction would have been used by anaerobic heterotrophs as electron acceptors.

The obvious oxidation partners for photosynthetic carbon on the early Earth are sulphur or iron. Iron is, of course, geochemically much more abundant than sulphur. Nearly all sulphur in igneous rocks is in the form of the iron sulphide, pyrite. When pyrite weathers under aerobic conditions today, sulphur enters solution in the oxidized form as sulphate; insoluble iron oxide remains behind as a solid. Sulphur is therefore more abundant in ocean and atmosphere today than iron, but it would not have been more abundant on the anaerobic Earth³. Weathering under anaerobic conditions would not mobilize highly insoluble pyrite, but would allow the iron in abundant iron silicate minerals to enter solution in the soluble ferrous oxidation state. It is therefore likely that dissolved iron was considerably more abundant than dissolved sulphur in the Archaean hydrosphere. Iron could have been the oxidation partner of carbon that permitted productive biogeochemical cycles without free oxygen. For the purposes of my argument it does not matter whether the iron was oxidized directly in the metabolic apparatus of the photosynthetic organisms or indirectly as a result of reactions in the ambient medium between dissolved reduced iron and the oxidized direct product of photosynthesis. What matters is that the

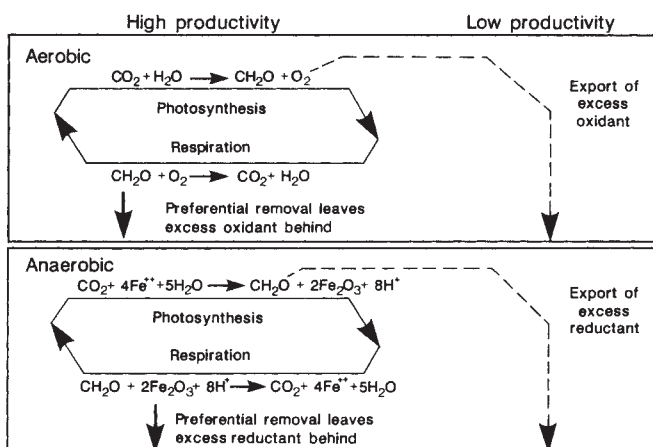


Fig. 1 Schematic view of the biogeochemical cycles of photosynthesis and respiration, contrasting an aerobic biosphere (top) with an anaerobic biosphere (bottom). The chemical reactions indicate the geochemical consequences of these metabolic processes, not necessarily the specific metabolic reactions involved. The symbol CH_2O represents organic matter. Reduction of carbon in the aerobic biosphere is coupled to the release of free oxygen; in the anaerobic biosphere it is coupled to oxidation of iron. Photosynthesis and respiration produce and consume oxidized and reduced compounds in equivalent amounts, so the biogeochemical cycle is nearly closed.

oxidizing partners of the reduced organic compounds produced by photosynthesis appeared, in the environment, largely as oxidized iron.

On thermodynamic grounds the reaction of organic matter with ferric iron is expected to release more energy than reaction with sulphate. Measurement of pore-water composition in anoxic sediments shows that iron is mobilized in diagenesis before sulphate is reduced⁴. In short, there is no reason to suppose that heterotrophs on the early Earth did not breathe iron in preference to sulphate. This suggestion is novel. Although Cloud⁵ suggested that iron might have consumed the oxidizing products of photosynthesis on the anaerobic Earth, he did not point out that oxidized iron could have served as the oxidized partner in a closed biogeochemical cycle by supporting heterotrophic respiration.

Oxygen is more volatile than cell material. On the aerobic Earth there is a tendency for oxygen to rise into the atmosphere while organic matter remains at the ground or in particulate or dissolved form in the hydrosphere. Dissolved organic carbon or reduced biogenic gases are consumed in reactions with the excess oxygen in ocean and atmosphere. Particulate organic carbon tends to be denser than water and therefore to settle more rapidly than oxygen to the bottom of oceans or lakes. There, excess organic matter accumulates in soils or lake or ocean sediments to produce locally anaerobic environments. Because oxidized and reduced compounds are produced and consumed in stoichiometrically equivalent amounts, the key to the development of oxidizing or reducing local environments is differential transport of oxidized and reduced compounds. The modern biosphere is oxidizing on the top and reducing on the bottom.

This partitioning of the biosphere, illustrated schematically in Fig. 1, is a consequence of the physical properties of oxygen and organic matter and is not a consequence of any general property of oxidized and reduced chemical compounds. In particular, oxidized iron is less volatile, less soluble, less mobile and more dense than cell material and organic compounds. It is for these reasons that almost all iron on the modern Earth is in solid or particulate form. The partitioning of the Archaean biosphere should therefore have been just the opposite of that of today, with oxidized iron settling more rapidly than reduced compounds to the bottom of water bodies to produce local

concentrations of oxidized sediments in a generally anaerobic world. The more volatile organic compounds, such as methane, would have diffused upwards into the atmosphere more rapidly than oxidized iron to yield a generally reducing atmosphere. It is in this sense that the Archaean biosphere may have been upside down, oxidizing on the bottom and reducing on the top (see Fig. 1).

This statement should have been true in an average sense, applying to the overall properties of the biosphere without regard for local heterogeneity. Consideration of the consequences of heterogeneity in biological productivity reveals that the Archaean biosphere was probably back to front as well as upside down. Regions of high biological productivity today tend to be underlain by sediments rich in organic carbon. The oxygen released when this organic matter was synthesized has been left behind in ocean and atmosphere, where it has been redistributed around the globe. In biologically unproductive regions of the Earth this extra oxygen, stoichiometrically equivalent to the extra organic matter preserved in the sediments below productive regions, consumes what organic matter there is so that the deserts of the world, both on land and at sea, are underlain by oxidized sediments containing little or no organic matter.

Because of the immobility of oxidized iron, the situation would have been quite the opposite on the anaerobic Earth. There, regions of high biological productivity would have been underlain by sediments rich in more rapidly deposited oxidized iron and deficient in organic matter, whereas the more mobile organic matter would have been left in excess in ocean and atmosphere and redistributed around the globe. In unproductive regions of the globe this excess of reduced organic compounds would have made possible the complete consumption of any oxidized iron produced locally. In due course the excess organic matter would have been incorporated into sediments deficient in oxidized iron that accumulated beneath biologically unproductive regions. Because oxidized and reduced compounds are produced and destroyed in stoichiometrically equivalent amounts, the preservation of oxidant in the sediments of one region must have been balanced by the preservation of an equivalent amount of reductant in the sediments of another region. In short, on an anaerobic world, regions of high biological productivity would have deposited oxidized sediments deficient in organic carbon, and the world's deserts would have deposited reduced sediments containing more organic matter than oxidized iron.

Both types of sedimentary rock are known for the Archaean and early Proterozoic Earth. Clastic deposits containing low concentrations of organic matter and essentially no oxidized iron are common⁶. In my interpretation they would have marked the unproductive regions of the globe. The sedimentary rocks rich in oxidized iron and deficient in organic carbon are the banded iron formations that formed in abundance only on the anaerobic Earth^{7,8}. I follow Cloud⁵ in attributing these deposits to the more productive regions of the Archaean biosphere.

There is no contradiction in the suggestion that banded iron formations, which now contain very little organic matter, were deposited under regions of unusually high biological productivity. High biological productivity yielded abundant insoluble oxidized iron, which settled relatively rapidly into sediments to attack and destroy any organic matter incorporated in those sediments. The product of the oxidation of organic matter in banded iron formations can be detected by isotopic analysis of the carbon incorporated in the carbonate minerals they contain^{9,10}. This carbonate exhibits lower relative amounts of the heavy isotope of carbon than does the oxidized carbon in sea water. Isotopically light carbon is characteristic of the organic matter produced by autotrophic organisms, including photosynthetic organisms. The isotopically light carbonate in banded iron formations is evidence that a significant fraction of this carbonate was produced by diagenetic oxidation of isotopically light organic matter incorporated into the sediments when they

were deposited. Diagenesis has consumed organic carbon and ferric iron, leaving a record in the form of isotopically light carbonate minerals.

I suggest, therefore, that biogeochemical cycles on the anaerobic Earth would have yielded relative vertical and horizontal distributions of reduced and oxidized compounds that are just the opposite of those of the aerobic Earth. These ideas offer an explanation of why banded iron formations are deficient in organic matter; they also suggest that Archaean sediments rich in organic carbon are not indicative of high biological productivity in the overlying water column—quite the reverse. This analysis also carries the surprising implication that photosynthesis on the anaerobic Earth, even oxygenic photosynthesis, could have increased the concentrations of reduced gases in the atmosphere¹¹. The peculiar aspects of an anaerobic biosphere should be considered when the environments of early life are being deduced from the sedimentary rock record.

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Nuclear β -decay and the origin of biomolecular chirality

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The origin of homochirality in terrestrial life has long been debated¹. Asymmetric decomposition of racemic mixtures of biomolecules by longitudinally polarized β -rays has been described as a possible mechanism for inducing optical activity². Here I present an extension of former estimates given by Hegstrom³ with respect to this process. I derive the energy dependence and sign of the relative asymmetries in radiolysis cross-sections for both β^+ - and β^- -radiation, and the connection of these cross-sections with the decomposition rate constants. In the light of the amplification model devised by Kondepudi and Nelson^{4–7}, I compare the chiral selectivity of β -rays with that of weak neutral current effects in handed molecules^{8,9}. I argue that the exceptional prebiotic conditions required do not favour asymmetric β -radiolysis as the selector of the exclusive signature of optical activity in living nature.

Radiolysis can be regarded as the knocking-out of a bonding electron in a molecule with a typical bonding energy of a few eV. It has been shown³ that the asymmetry in this process of ionization can be described by means of a bound-helical-electron model, in which the asymmetry is a result of the helicity, h , of the electrons moving in molecular orbits. This helicity is predicted to exist in optically active molecules owing to the perturbation of the electron bound state by the spin-orbit interaction. It is of the order $h \sim \eta(\alpha Z)^2$, where Z is the atomic number of the chiral centre and η is a molecular asymmetry factor ($\sim 10^{-3}$ to 10^{-4} (ref. 10)), which takes into account the degree of asymmetry in the molecular structure.

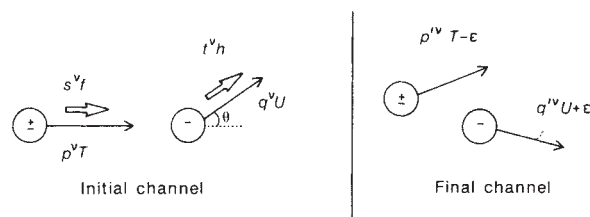


Fig. 1 Helicity-dependent free-lepton-electron scattering. The initial and final momentum four-vectors of the incoming particle (β^+ or β^-) are p^ν and p'^ν . Its spin four-vector is s^ν . The corresponding quantities of the molecular electron are q^ν , q'^ν and t^ν . The angle between \bar{p} and \bar{q} is θ . The particles have helicities f and h , and kinetic energies T and U . The energy ϵ , which will be transferred from the incoming to the molecular particle, can have the values $-U < \epsilon < T$. The angle ϕ (not shown) is the azimuth of $(\bar{p}' - \bar{q}')$ relative to $(\bar{p} + \bar{q})$.

For β^- -radiation, where the leptons are identical, it is the interference between the direct and exchange term that leads to a non-zero asymmetry³. The indistinguishability of the two electrons, causing the exchange effect, will be most important in collisions with large energy transfer. In this case the binding energy of the molecular electrons plays a secondary role and we can consider the electrons as free. This reduces the problem to the calculation of free-electron-electron (Møller) scattering. Kim and Inokuti¹¹ applied this free-electron approximation successfully to calculate corrections of ionization cross-sections for the exchange effect; here it will be used to obtain a helicity-dependent correction.

Figure 1 shows the scattering process. As the particles are longitudinally polarized, their spin four-vectors can be written as

$$s^\nu = \frac{f}{m} (p, (T+m)\hat{p}) \quad (1)$$

and similarly for t^ν . Here m is the electron rest mass, and for convenience I take $c = 1$. The total ionization cross-section is

$$\sigma^- = \int_I^{\frac{1}{2}(T-U)} d\epsilon \frac{d\sigma^-}{d\epsilon} \quad (2)$$

where I is the ionization energy of the molecular electron. The differential cross-section $d\sigma^-/d\epsilon$ can be written as the sum of a spin-independent and a spin-dependent term¹²:

$$\frac{d\sigma^-}{d\epsilon} = \frac{d\sigma_1^-}{d\epsilon} + fh \frac{d\sigma_2^-}{d\epsilon} \quad (3)$$

From (2) and (3) the helicity-dependent correction $\Delta\sigma^-$ in the ionization cross-section, averaged over all the directions of \bar{q} , is

$$\Delta\sigma^- = \frac{1}{2} \int_{-1}^1 d \cos \theta \int_I^{\frac{1}{2}(T-U)} d\epsilon \frac{d\sigma_2^-}{d\epsilon} \quad (4)$$

for the incident and molecular electrons having the same helicity ($fh = +1$), and $-\Delta\sigma^-$ for particles with opposite helicity ($fh = -1$).

For electrons the spin-dependent part of equation (3) is the sum of a direct term, an exchange term and an interference term^{13,14}:

$$fh \frac{d\sigma_2^-}{d\epsilon} = \frac{4m^2 r_0^2}{\sqrt{u(u-4m^2)}|\bar{p} + \bar{q}|} \int d\phi \left[\frac{A^-}{v^2} + \frac{B^-}{w^2} - \frac{C^-}{vw} \right] \quad (5)$$

with

$$A^- = -m^2 p' \cdot s q' \cdot t - m^2 v s \cdot t, \quad (6a)$$

$$B^- = -m^2 q' \cdot s p' \cdot t - m^2 w s \cdot t \quad (6b)$$

$$C^- = (w - m^2) p' \cdot s q' \cdot t + (v - m^2) q' \cdot s p' \cdot t + m^2 q \cdot s p \cdot t + \frac{1}{2}(vw - 2m^2(u - 2m^2))s \cdot t \quad (6c)$$

where $u = (p + q)^2$, $v = (p - p')^2$ and $w = (p - q')^2$ are the Man-