Biogeochemistry **39:** 139–164, 1997.

The role of marine biota in the evolution of terrestrial biota: Gases and genes

Atmospheric composition and evolution of terrestrial biota

JOHN A. RAVEN
Department of Biological Sciences, University of Dundee, Dundee DD1 4HN, UK

Key words: atmospheric composition, elemental composition, evolution, marine biota, soils, terrestrial biota

Abstract. There is greater biodiversity (in the sense of genetic distance among higher taxa) of extant marine than of terrestrial O_2-evolvers. In addition to contributing the genes from one group of algae (Class Charophyceae, Division Chlorophyta) to produce by evolution the dominant terrestrial plants (Embryophyta), the early marine O_2-evolvers greatly modified the atmosphere and hence the land surface when the early terrestrial O_2-evolvers grew. The earliest terrestrial phototrophs (from geochemical evidence) occurred 1.2 Ga ago, over 0.7 Ga before the Embryophyta evolved, but well after the earliest marine (cyanobacterial) O_2 evolvers (3.45 Ga) and marine eukaryotic O_2 evolvers (2.1 Ga). Even by the time of evolution of the earliest terrestrial O_2-evolvers the marine O_2-evolvers had modified the atmosphere and land environment in at least the following five ways. Once photosynthetic O_2 paralleling organic C burial had satisfied marine (Fe^{2+}, S^{2-}) reductants, atmospheric O_2 built (1) up to a considerable fraction of the extant value (although some was consumed in oxidising terrestrial exposed Fe^{2+}) and (2) provided stratospheric O_3 and thus a UV-screen. (3) CO_2 drawdown to $\sim$20–30 times the extant level is attributable to net production, and burial, of organic C in the oceans (plus other geological processes). Furthermore, (4) their production of volatile organic S compounds could have helped to supply S to inland sites but also (5) delivered Cl and Br to the stratosphere thus lowering the O_3 level and the extent of UV screening.

Introduction

Terrestrial plants today predominate over marine O_2-evolvers (photosynthetic organisms which reduce CO_2 using H_2O as the reductant) in terms of both biodiversity (about 300,000 out of 350,000 described species of O_2-evolving organisms) and contribution to global net primary productivity (60 out of 95 Pg C per year) (Raven 1995a; Norton, Melkonian & Anderson 1996; Womersley 1996). The extant marine organisms, do, however, have a much greater biodiversity at higher taxonomic levels (i.e. taxa with greater genetic distance among themselves) (Raven 1995a). Thus, all of the predominant terrestrial plants (Embryophyta, i.e. bryophytes plus tracheophytes, the latter including the flowering plants) are derivatives of one class (the Charophyceae) of one division (the Chlorophyta) of the Viridiplantae (see Graham 1993; Raven 1995a). However, marine O_2-evolvers include several taxa at or above the level of the Chlorophyta which are only distantly related to them, e.g. the divisions Rhodophyta, Dinophyta, Haptophyta, Cryptophyta and Heterokontophyta, as well as cyanobacteria and a few flowering plants (seagrasses) (Ragan & Gutell 1995; Raven 1995a; van den Hoek, Mann & Jahn 1995). While we should not ignore the role of phototrophs other than the embryophytes in terrestrial habitats (e.g. the cyanobacteria and the Chlorophyta, both of which occur free-living and in lichens on land), it is clear that marine (and freshwater) habitats have major fractions of net primary productivity shared among more higher taxa than is the case for terrestrial habitats (Raven 1995a).

One purpose of this paper is to consider the availability of marine (and, perhaps, freshwater) photosynthetic organisms as potential, and realised, ancestors for terrestrial O_2-evolvers. Specifically, we address the availability of organisms other than the immediate ancestors of the Embryophyta which might have been among the earliest terrestrial colonizers.

A second point which the paper addresses is the evidence as to the timing, and biogeochemical impact, of various episodes in the invasion of land by O_2-evolvers.

The third point, which interacts strongly with the other two, concerns the extent to which the early marine biota, and particularly O_2-evolvers, have influenced the terrestrial habitat available to the earliest terrestrial O_2-evolvers.

Time-scales of major events in the evolution of O_2-evolving organisms

(i) Aquatic organisms

Figure 1 shows that the earliest fossils closely resembling extant cyanobacteria occur in marine strata some 3.45 Ga ago in the Archaean (Schopf 1993). This considerably predates the occurrence of O_2 in the ocean or atmosphere at more than the $\leq 10^{-8}$ of the present atmospheric level which could be produced abiologically by photodissociation of H_2O (Figure 2; Holland 1984; Schidlowski 1988). The absence of free O_2 before $\sim$2.5 Ga can be accounted for by the consumption of photosynthetically produced O_2 by the oxidation of reductants in the ocean (Fe^{2+}, S^{2-}) and, after oxidation of marine reductants, subsequently, on the land surface exposed to the atmosphere which had existed since about 3.5 Ga (Buick et al. 1995; Hoffman 1995). Thus, the cyanobacteria from 3.45 Ga could have been O_2-evolving,

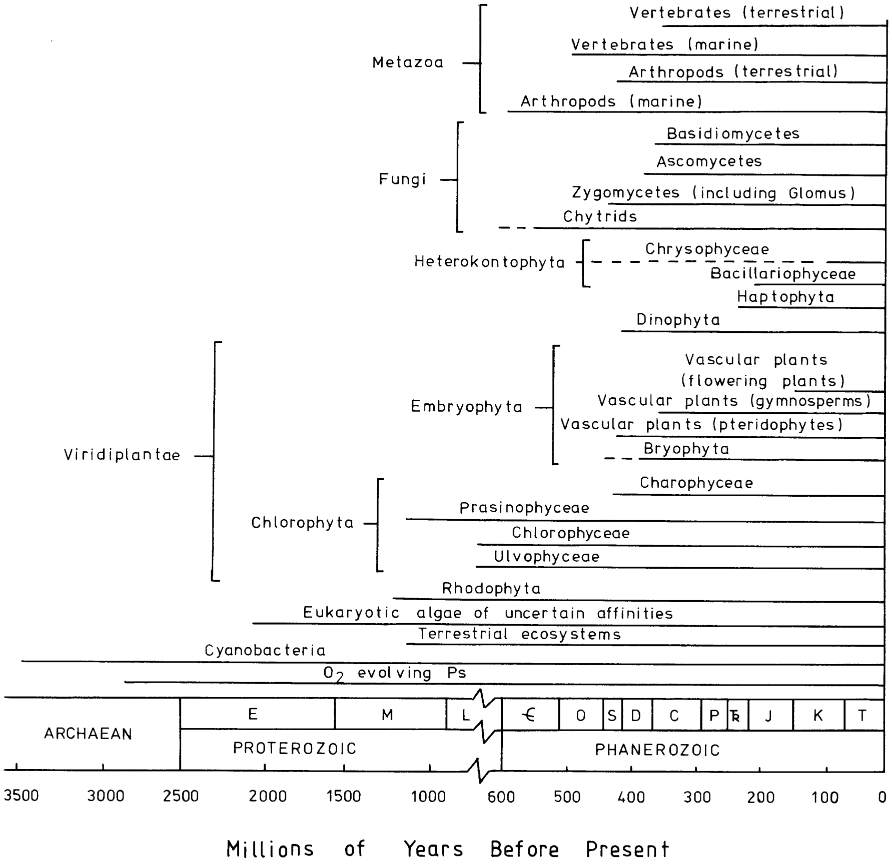

Figure 1. Major events in the evolution of aquatic and terrestrial O_2-evolvers, and of certain chemoorganotrophs. Note the change of scale between Proterozoic and Cambrian. E = Early Proterozoic, M = Middle Proterozoic, L = Late Proterozoic, ϵ = Cambrian, O = ordovician, S = Silurian, D = Devonian, P = Permian, = Triassic, J = Jurassic, K = Cretaceous, T = Tertiary. The Tertiary is divided into the Palaeogene (Palaeocene, Eocene, Oligocene) and the Neogene (Miocene, Pliocene, Pleistocene). The Pleistocene is generally accorded the status of belonging to the Quarternary. Modified from Raven (1995a), Kooistra & Medlin (1995a, b) and Berbee & Taylor (1993).

possibly (at these low external O_2 concentrations) without the aid of photosystem one (Greenbaum et al. 1995; Barber 1995; Prince 1996).

Eukaryotic O_2 evolvers are derived from phagotrophic eukaryotic ancestors which have ingested cyanobacteria as food items, but have retained them as genetically integrated photosynthetic organelles or chloroplasts (Bhattacharya & Medlin 1995; Allen & Raven 1996; Palmer & Delwiche 1996).

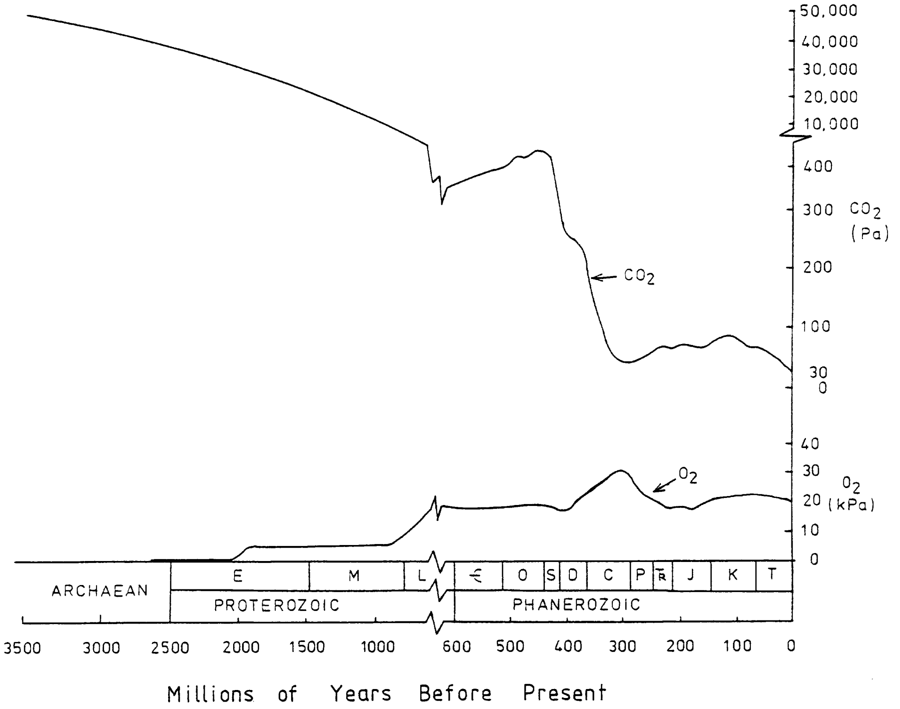

Figure 2. Atmospheric O_2 and CO_2 over the last 3.5 billion years. Note the change of scale between Proterozoic and Cambrian. Abbreviations for Geological Periods as for Figure 1. From Raven (1995a) and Mora, Driese & Colarusso (1996) using data in Appenzeller (1993), Anning & Canfield (1992), Berner (1990, 1993), Berner & Canfield (1989), Holland (1984, 1994), Kasting (1993) and Rye et al. (1995).

The earliest fossil evidence for eukaryotes is from 2.1 Ga (Palaeoproterozoic) strata in the form of the marine *Grypanea spiralis* (Han & Runnegar 1992; see also Hackstein & Mackenstedt 1995). This fossil seems to represent a (eukaryotic) alga of unknown affinities, as do the excellently preserved (including cell organisation in the thallus) specimens up to 34 mm long from 1.6 Ga (Shixing & Huineng 1995). The first eukaryotic O_2-evolvers possibly referable to extant higher taxa occur from about 1.9 Ga onwards as acritarchs, generally thought to be the cyst (phycoma) stage of the class Prasinophyceae (Chlorophyta). The assignment of acritarchs to the class Prasinophyceae is much less certain than for later, Neoproterozoic and Phanerozoic acritarchs (1.0 Ga onwards) and the pre-Neoproterozoic acritarchs are not so assigned in Figure 1 (Knoll 1994). Possible examples of algae in the Heterokontophyta (e.g. possible Chrysophyceae, Tribophyceae (= Xanthophyceae), Fucophyceae (= Phaeophyceae)) occur in strata from 1.0 Ga (earliest Proterozoic) onwards (Knoll 1994; cf. Kooistra & Medlin 1996a,b). The final 'non-green' algal taxon known from Proterozoic is the Rhodophyta, for which excellently preserved fossils referable to the extant family Bangiaceae are known from Neoproterozoic, probably nearly 1.4 Ga, strata (Knoll 1994; Butterfield, Knoll & Swett 1990).

The Charophyceae (Chlorophyta) gave rise to the embryophytes (higher land plants) around 450 Ga, at least 1 Ga after the class Prasinophyceae (the 'basal' Chlorophyta). The (mainly marine) Ulvophyceae *sensu lato* and, less certainly, the (mainly freshwater) Chlorophyceae *sensu lato,* are known from the latest Neoproterozoic (0.6 Ga); Raven (1995a). The fourth major class of the Chlorophyta, the Charophyceae *sensu lato*, are not known as fossils before $\sim$428 Ma, i.e. rather later than fossil (spore) evidence for the earliest embryophytes (Raven 1995a; Edwards, Abbott & Raven 1996). The evidence suggesting that the Charophyceae are the green algal class which is closest to the embryophytes has come, sequentially, since the time of recognition of the class Charophyceae, from (1) 'classical' phylogenetic analysis using ultrastructural, enzymic and chemical criteria, then (2) the use of cladistic analyses of the data used in (1) and finally (3) application of molecular phylogenetic analyses (see discussion in Graham 1993; Raven 1987, 1995a; McCourt 1995; van den Hoek et al. 1995). Such analyses suggests that, within the Charophyceae *sensu lato*, it may well not have been the Charophyceae *sensu* van den Hoek et al. (1995), i.e. the order Charales known from $\sim$428 Ma which are the closest relatives of the ancestors of the embryophytes which originated $\sim$450 Ma. The closest relatives may have belonged to the *Klebsormidium* and *Coleochaete* (both in the Klebsormidiophyceae *sensu* van den Hoek et al. 1995), the latter resembling the Devonian *Parka* (see later).

These data show (Figure 1) that, in addition to the cyanobacteria, at least 4 classes of (eukaryotic) algae occurred in the Precambrian, i.e. Prasinophyceae, Chlorophyceae, Ulvophyceae and Rhodophyceae (subsuming Bangiophyceae and Florideophyceae), and, much less certainly, three classes of the Heterokontophyta.

(ii) Non-embryophytic O_2-evolvers on land

Turning to the evidence for photosynthetic life on land, continental crust exposed to the atmosphere has existed for 3.5 Ga (Buick et al. 1995; Hoffman 1995), and the work of Horodyski & Knauth (1994) suggests that photosynthetically supported terrestrial communities have existed for 1.2 Ga (late Mesoproterozoic). The evidence involves weathering rates which can best be explained by CO_2 concentrations in the material weathering to produce the palaeosal which exceeds that likely to have occurred in the atmosphere 1.2 Ga ago. The most likely source of this CO_2 is the activities of chemoorganotrophic organisms on organic C percolating downward from photolithotrophs which had fixed atmospheric CO_2. The nature of the photolithotrophic components of such communities is not indicated by fossils. Cyanobacteria, present at that time in the sea, are obvious candidates, since they are significant components of extant terrestrial communities, and especially those inimical to the growth of embryophytes (Bell 1993). Chlorophycean green algae, and diatoms, are also significant non-embryophyte terrestrial photolithotrophs today, but were not known to be present 1.2 Ga ago (see above, and Figure 1). Chlorophyte algae living in/on soil today include the Chroolepidaceae and the pleurastrophytes which are not readily assigned to any members of the four green algal classes (Prasinophyceae, Charophyceae, Chlorophyceae, Ulvophyceae, all *sensu lato*) already mentioned, and which have no known pre-Phanerozoic fossil record (Friedl 1995; Raven 1995a; van den Hoek et al. 1995). None of these organisms (cyanobacteria, diatoms and green algae) today form structures reaching more than a millimetre or two above the (mineral) soil surface. This microbial mat structure means that the area for CO_2 uptake from the atmosphere, and from which diffusion of inorganic C to photosynthetic cells, is approximately equal to the projected ground area. The need for aqueous-phase diffusion of CO_2 from the atmosphere-mat interface to individual photosynthetic cells limits productivity by these terrestrial microbial mats in today's atmosphere, but higher productivities could have occurred in the past with higher atmospheric CO_2 levels. Thus, microbial mats on land which today achieve productivities of some 2 μmol (m^2 ground area)$^{-1}$ s^{-1} at optimal hydration could have achieved values of 6 μmol (m^2 ground area)$^{-1}$ s^{-1} in the higher CO_2 partial pressures of the Proterozoic (Raven 1995a; Figure 2). These poikilohydric primary producers are generally desiccation-tolerant (Potts 1996; Raven 1995a).

The only non-embryophytic primary producers reaching heights of centimetres or more on land today are lichens, whose fungal components (ascomycetes and, to a lesser extent, basidiomycetes) apparently did not evolve till the Silurian and later; the earliest fossil lichen having recently been reported from the Lower Devonian (see Raven 1995a).

While the photobionts in some extant lichens are cyanobacteria which were present 1.2 billion years ago, most of them are green algae of the Chroolepidaceae or pleurastrophytes which, as we have just seen, have no relevant fossil record. Another extant cyanobacterium-fungus symbioses, but involving *endo*symbiosis of the cyanobacterium, is *Geosiphon*. Here the fungal partner is a zygomycete from the Glomales, i.e. closely related to the fungal component of (vesicular-) arbuscular mycorrhizas of embryophytes (Gehrig, Schüssler & Kluge 1995; Schüssler et al. 1995). While the zygomycetes evolved before the ascomycetes and basidiomycetes they were probably not present before the Silurian (see Figure 1 and Raven 1995a), thus rendering

Geosiphon-like symbioses unlikely as components of the earliest terrestrial communities.

(iii) Non-photosynthetic terrestrial life

The emphasis thus far has been on the photolithotrophic components of early terrestrial communities, with a brief mention of (vesicular) arbuscular mycorrhizas which were very important in uptake of nutrients of the soil by early embryophytes (Nicolson 1975; Newsham, Fitter & Watkinson 1995; Raven 1995a; Edwards, Abbott & Raven 1996). As for pathogens, grazers and decomposers which are today involved in recycling organic matter generated by photolithotrophs, bacteria and viruses would have been available to the earliest terrestrial ecosystems. Eukaryotic decomposers and pathogens could have included heterokontophytan ‘pseudofungi’ (oomycetes) and, from the early Palaeozoic onwards, ‘true’ fungi starting with chytrids (Cambrian: ∼500 Ma) and followed by zygomycetes (Ordovician: ∼450 Ma) and asco- and basidiomycetes by the late Devonian (∼380 Ma (see Figure 1, and Berbee & Taylor 1993). The true fungi seem to have evolved on land.

The role of metazoa in the Lower Palaeozoic terrestrial communities at the time of diversification of embryophytes seems to have initially been as detritus-feeding and carnivores, with grazing of living plants being less well-developed early in the terrestrial existence of both arthropods (on land from the Silurian onwards) and vertebrates (on land from the Upper Devonian onwards): Edwards et al. (1995b); Raven (1995a). By contrast with the green algae-embryophyte line, the arthropods and vertebrates came onto land as organisms of similar size and level of complexity to their truly terrestrial descendants; only a few terrestrial metazoans of arthropod affinities are desiccation-tolerant (Kinchin 1994).

(iv) Embryophytic plants on land

Regardless of whether terrestrial photolithotrophs occurred as early as 1.2 Ga, there is no evidence of embryophytic vegetation on land before the mid-Ordovician (∼450 Ma). The earliest evidence of embryophytes comes from permanent tetrads and dyads of trilete spores from the Mid-Ordovician to at least the latest Lower Silurian (Gray 1993; see Raven 1995a). These were most likely to have been produced by the sporophyte (diploid) phase of embryophytes, and would have germinated to produce the gametophyte (haploid) phase which, after gametogenesis and syngamy, regenerates the sporophyte (Kenrick 1994). They were certainly aerially dispersed and produced by meiosis. There are no vegetative remains confidently assignable to the sporophyte phase of embryophytes before the Upper Silurian, and of the gametophyte phase before the Lower Devonian (Kenrick 1994; Edwards, Duckett & Richardson 1995a). The work of Edwards et al. (1995a) is of especial interest; the Lower Devonian material they analysed has clear affinities with extant liverworts (bryophyta). The fossils they examined was of gametophyte and sporophyte material containing spores in permanent tetrads, as in the Mid-Ordovician to Lower Silurian dispersed spore material. This work of Edwards et al. (1995) is consistent with the Mid-Ordovician spores having been produced by liverwort-like plants. Taylor (1995a,b) has also pointed out the resemblance of Lower Silurian dyad spores to those of extant bryophytes in the Sphaerocarpales and to the bipartite exospores of the Devonian non-vascular plants *Parka* and *Protosalvinia*. Graham (1993) points out the similarity of the vegetative structure of *Parka* to that of early developmental stages of the gametophyte of the extant moss *Sphagnum* and to the (haploid) vegetative thallus of the extant green alga *Coleochaete* (Charophyceae *sensu lato*; Klebsormidiophyceae *sensu* van der Hoek et al. 1995). It is thus tempting to think of *Parka* as a derivative of the organisms which gave rise to the embryophytes in the Ordovician and that it is closely related to the Klebsormidiophyceae.

These data are consistent with the earliest embryophytes being relatively low-growing, poikilohydric plants, i.e. unable to maintain their water content away from thermodynamic equilibrium with the environment for long (>hours) periods by the deployment of the stomata/xylem/intercellular space/cuticle system (Raven 1995a). These homoiohydric attributes were present in sporophytes of at least some embryophytes in the Upper Silurian and later strata, albeit not always with true xylem in the Upper Silurian and Lower Devonian (Raven 1995a). Cladistic analyses suggest that the order of evolution of these attributes was cuticle, then stomata (plus intercellular gas spaces), and finally (polyphyletically) xylem and xylem-like tissue, i.e. the hydrome of bryophytes and the water-conducting tissues of *Aglaophyton* (Raven 1995a).

The evolution of embryophyte attributes should be considered in the context of biogeochemical data on Ordovician palaeosols (Yapp & Poths 1994). Yapp & Poths measured the content of $Fe(CO_3)OH$ in goethite in Ordovician palaeosols as a proxy for soil CO_2 partial pressure, which could be related to the organic C input from primary productivity. The conclusion was that terrestrial primary productivity was similar to extant values. Given the range of extant values this suggestion only gives us a broad band of organic C production rates. Raven (1993, 1995a) points out that, even with the high CO_2 partial pressures in the Upper Ordovician (16–17 times extant values; Figure 2), primary productivities at the upper end of the present-day range (tens of μmol CO_2 (m^2 ground area)$^{-1}$ s^{-1} would require more than a simple microbial mat. As explained above, this relates to problems with inorganic C diffusion through the mat in the aqueous phase. Structural complexity which amplifies the surface area available for CO_2 exchange to values of several times the ground area could be achieved by organisms at the liverwort level of organisation by either the presence of several layers of unistratose leaves or by the presence of intercellular gas spaces in a ventilated thallus (i.e. with intracellular gas spaces) with a surface area equal to the ground area.

Returning to the homoiohydric sporophytes (and perhaps certain gametophytes; see Kenrick 1994) of vascular plants (and their close relatives, e.g. *Aglaophyton*, with xylem-like tissues rather than true xylem) from the Upper Silurian onwards, these organisms can carry out photosynthesis in the absence of continual water input to a greater extent than poikilohydric plants. This would especially have been the case after development of root systems (Rayner 1984) which allow the exploitation of water deeper in the soil. Furthermore, it is an empirical observation that only homoiohydric plants can grow to heights in excess of 1–2 m, so that the shrub- and tree-dominated communities found from the Upper Devonian onwards could only have been possible with homoiohydric plants. Furthermore, as the CO_2 level decreased (on average) over the last 400 million years, the need for amplification of the surface area for CO_2 absorption over the ground area becomes even more crucial in bringing the achieved CO_2 fixation rate per unit ground area closer to the theoretical maximum permitted by light intercepted under otherwise optimal conditions (Raven 1995a).

This restriction in height also appears to apply to vegetative desiccation tolerance (see Oliver 1996; Raven 1995a), although some desiccation-tolerant members of the Veloziaceae may be rather taller. Furthermore, the (later) development of N_2-fixing symbioses with homoiohydric plants permitted symbiotic diazotrophy and photolithotrophy by the host to show essentially identical responses to water availability (Raven & Sprent 1989; Sprent & Raven 1986, 1992). The fixation of N_2 by poikilohydric free-living (cyanobacteria) and symbiotic (some lichens, and bryophytes) photolithotrophs again shows a parallelism between N_2 fixation and CO_2 fixation, but here the occurrence of both processes is much more dependent on wetting events (Raven 1995a).

The emphasis here has been on embryophytes and organisms resembling their likely ancestors (e.g. *Parka*; *Protosalvinia*; see above) as macroscopic primary producers in the Ordovician-Lower Devonian. While this emphasis is perhaps acceptable in the context of the evolution of the components of the land flora which have dominated terrestrial ecosystems from at least the Lower Devonian onwards, other macroscopic primary producers were, or could have been, present. Among the organisms which were present were the enigmatic *Nematothallus* (latest Ordovician – Lower Devonian: Edwards et al. 1996) and *Prototaxites* (which are not referable to any extant taxa) as well as lichens (Early Devonian ($\sim$400 Ma): Taylor et al. 1995). Raven (1986) discusses possible reasons why lichens have never evolved into homoiohydric photolithotrophs. It might also be worth considering why another cyanobacterium-fungus association, in this case the *Geosiphon* endosymbiosis, has not given rise to larger, and possibly homoiohydric, organisms (Gehrig et al. 1995; Schüssler et al. 1995, 1996). However, the ascomycetes and basidiomycetes which give the macroscopic structure to lichens also produce morphologically complex subaerial structures when not lichenised, while the Glomales (to which *Geosiphon*) belongs do not produce any such structures when non-symbiotic. Furthermore, while there is no fossil evidence of *Geosiphon*, the Glomales can be traced at least as far back as the Silurian on both fossil and molecular clock evidence (see Berbee & Taylor 1993; Raven 1995).

The role of marine biota in modifying atmospheric composition and its impact on the evolution of terrestrial organisms

(i) What we know about past atmospheres

Figure 2 shows the changes in the major atmospheric gases O_2 and CO_2 over the last 3.5 Ga. The time scale in this Figure is such that the detailed CO_2 measurements from ice cores in Greenland and Antarctica representing the last 150,000 years are not represented. The Phanerozoic (550 Ma onwards) data on O_2 come from chemical mass balances of oxidised and reduced C, Fe and S, and for CO_2 from mass balances of inorganic and organic C. Proterozoic and Archaean values come from more disputable data.

Examples of data from which atmospheric O_2 concentrations in the Proterozoic have been estimated include the oxidation state of palaeosols, the nature of uranium ones, the history of red beds, the trace element content of black shales, the age distribution of banded iron formations, the evolution of eukaryotes, and $^{34}S/^{32}S$ and $^{13}C/^{12}C$ ratios in sulfides and of organic and inorganic carbon (Anbar & Holland 1992; Canfield & Teske 1996; Habicht & Canfield 1996; Holland 1984, 1994; Knoll 1996). The sum of evidence from these data is that there was in increase in atmospheric O_2 partial pressure between $\sim$2.2 and $\sim$2.0 Ma from little more than 10 Pa to perhaps 4 kPa, with a rise to values closer to the present 21 kPa between 0.64 and 1.05 Ma (Figure 2). The mechanisms which regulate atmospheric O_2 levels today are still incompletely understood (Kump & MacKenzie 1996; Van Cappeller & Ingall 1996). For CO_2 we rely on arguments from the greenhouse effect, i.e.

the need for a larger greenhouse effect earlier in the earth's history to explain the continuous occurrence of unfrozen oceans despite the lower total radiant output of the 'weak young sun' (Newman 1979), and the occurrence and nature of silicate and carbonate minerals in palaeosols and the weathering rates of terrestrial rocks (cf. Horodyski & Knauth 1994; Yapp & Poths 1994; Rye, Kuo & Holland 1995). The palaeosol data of Holland (1994) and Rye et al. (1995) suggest lower atmospheric CO_2 values 2.2–2.75 Ga than are needed by present models of the greenhouse effect to account for surface temperatures at those times.

The role of marine biota in bringing about the Archaean and Proterozoic changes in O_2 and CO_2 is known in at least semi-quantitative terms. Clearly the production of O_2 above 10^{-8} of the present level is *absolutely* dependent on photolithotrophic O_2 production; photodissociation of H_2O could only account for $10^{-14} - 10^{-8}$ of the present level (Holland 1984; Schidlowski 1988). The *quantity* of O_2 left as a fossil of previous photosystems depends on the amount which is not removed in oxidising Fe(II) and S(II) and the quantity of organic C which has been sedimented and not subsequently oxidised. Accordingly, the early occurrence of more than 10^{-8} of the present atmospheric level of O_2 is absolutely dependent on photosynthesis as the source of O_2 and on an excess of net burial of organic cover net O_2 consumption by reduced S and Fe species. As for CO_2, the net conversion of CO_2 to organic C (sedimented) in photosynthesis causes a drawdown of CO_2, but the situation is complicated by other reactions, e.g. the precipitation of $CaCO_3$ in the ocean from the (presently) supersaturated solution, and which is (presently) largely under biological control. It is important to note that the precipitation of $CaCO_3$ *per se* is a CO_2-*producing* reaction (Frankignoulle, Canon & Gattuso 1994). Weathering of silicates on land can, however, remove CO_2 from the atmosphere:

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2$$

Marine photolithotrophs have thus a significant impact on atmospheric composition before, and during the early evolution of, terrestrial ecosystems, as far as the major components O_2 and CO_2 are concerned. Their influence on N_2 partial pressures were much smaller (Raven & Sprent 1989).

The presence of an oxidising O_2-containing atmosphere at the time of origin of the first terrestrial communities had implications for the supply of a number of essential resources for the growth of photolithotrophs. Among these we consider C, N, Fe, P, Zn, Cu and S, and influences on UV-B damage and on damage by toxic O radicals.

(ii) Carbon availability

During the Proterozoic the trend was for atmospheric O_2 to increase and for CO_2 to decrease (Figure 2). This has important implications for photosynthetic O_2-evolving organisms since at least 95% of the C they contain has been fixed by the enzyme RUBISCO (ribulose bisphosphate carboxylase-oxygenase) (Raven 1991a; Raven et al. 1994; Graham et al. 1995). As its name suggests this enzyme catalyses not only a carboxylase activity (CO_2 assimilation, forming a C-C bond) but also an oxygenase activity (O_2 assimilation, forming a C-O bond). The oxygenase activity is competitive with the carboxylase activity, and once the CO_2 concentration had fallen to a value at which RUBISCO was CO_2-limited the extent of oxygenase relative to carboxylase activity could be deduced from the CO_2 and O_2 concentrations and the selectivity factor τ (high τ mean high selectivity for CO_2 relative to O_2). The decreasing CO_2 and increasing O_2 concentrations in the later Precambrian, and even those suggested for the latest Proterozoic (Figure 1) would in the simplest case only have had a minor impact on RUBISCO carboxylase activity. The case considered is diffusive entry of CO_2 and efflux of O_2 in a small organism (e.g. a phytoplankton cell) which gives a lower CO_2 concentration and higher O_2 concentration at the site of RUBISCO than in the bulk aqueous medium. Even with the relatively low τ RUBISCOs of extant cyanobacteria and many extant green algae the late Proterozoic and early Phanerozoic (Cambrian – Lower-Devonian) CO_2 and O_2 levels would not cause significant CO_2 limitation of RUBISCO activity, or expression of oxygenase activity. However, RUBISCO-containing organisms in microbial mats under water or on land and stromatolites under water could be CO_2-limited and subject to O_2 inhibition of RUBISCO carboxylase activity and the corresponding occurrence of RUBISCO oxygenase activity, at least for the photosynthetic cells far from the bulk CO_2 supply yet still not deeply shaded by other cells so that they can still absorb enough photons to photosynthesize. $^{13}C/^{12}C$ data for organic and inorganic C are consistent with the occurrence of diffusive CO_2 entry to RUBISCO in phototrophs in the Precambrian ocean, and with CO_2 diffusion not being the major determinant of the rate of photosynthesis (Schidlowski 1988; Raven 1991a, 1996, 1997).

However, all extant cyanobacteria and most extant green (and other) algae have a CO_2 concentrating mechanism based on energized transport of inorganic C across a membrane(s). Such mechanisms increase the CO_2 concentration, and the CO_2/O_2 ratio, around RUBISCO and thus favour the carboxylase activity and suppress the oxygenase activity of that enzyme (Raven 1991a, 1996, 1997). CO_2 concentrating mechanisms are correlated with relatively low τ values for RUBISCO at least in cyanobacteria and green algae. CO_2 concentrating mechanisms based on a carboxylation/decarboxylation cycle preceding the action of RUBISCO occur in C_4 and CAM (Crassulacean Acid Metabolism) tracheophytes, once more with a tendency to lower τ values for RUBISCO. The higher τ values for RUBISCO in the green algae and their descendants the embryophytes are in organisms which depend on diffusive entry of CO_2 to RUBISCO, e.g. the terrestrial green alga *Coccomyxa* (Palmqvist et al. 1995) and the C_3 embryophytes. The high τ values of these C_3 terrestrial plants presumably relates to natural selection as CO_2 levels, and CO_2/O_2 ratios, declined. Even higher τ values are found for RUBISCO from aquatic algae of the Rhodophyta and Heterokontophyta. These high τ values may result from the non-cyanobacterial prokaryotes from which these algae derived their RUBISCO, with the possibility of a higher mechanistically determined upper limit on τ available to natural selection as a result of the different antecedence of RUBISCO.

The evolutionary increase in the τ value of RUBISCO as the CO_2 level, and CO_2/O_2 ratio, in the atmosphere declined has probably occurred in parallel in RUBISCOs in different phyletic lines which originated in a high CO_2, high CO_2/O_2 ratio environment. This is also the case for the C_4 and CAM versions of CO_2 concentrating mechanisms in the embryophytes. Despite the low CO_2 and low CO_2/O_2 in the late Carboniferous atmosphere (Figure 2) C_4 metabolism does not seem to have arisen then. Strong evidence of C_4 photosynthesis occurs not earlier than $\sim$12.8 million years ago in the mid-Miocene. C_4 metabolism has arisen at least 20 times independently from C_3 ancestors, presumably in response to the Micocene to recent trend of a decline in CO_2 and CO_2/O_2 ratio in the atmosphere (Cerling, Wang & Quade 1993; McFadden & Cerling 1994). CAM is also polyphyletic although its time(s) of origin are very poorly known (Raven & Spicer 1996).

Low CO_2, and CO_2/O_2 ratios, at the site of action of RUBISCO would have occurred earlier in aquatic organisms. As indicated earlier, this results from the low diffusion coefficients of CO_2 and O_2 in water relative to those in air, combined with the long diffusion path for these gases in microbial mats, stromatolites and bulky organisms. Accordingly, there would have been selective advantage for organisms with CO_2 concentrating mechanisms considerably earlier (late Proterozoic/early Phanerozoic) in aquatic than in terrestrial habitats (taking terrestrial microbial mats which only function at high water contents as honorarily aquatic). Nevertheless, the conditions in which CO_2 concentrating mechanisms would have been advantageous considerably post-dated the origin of cyanobacteria (Archaean) and of diverse taxa of eukaryotic algae (Palaeo- and Meso-proterozoic), suggesting a polyphyletic origin of membrane-associated CO_2 concentrating mechanisms. This accords, at least for eukaryotes, with the diversity of membrane-based mechanisms of inorganic C acquisition (Raven 1997). It is of interest that some extant terrestrial O_2-evolvers use such membrane-associated CO_2 concentrating mechanisms, e.g. free-living and lichenised cyanobacteria, some free-living and lichenised green algae, and even the hornworts *Anthoceros* and *Phaeoceros* (Embryophyta): Smith & Griffiths (1996a,b). Presumably these CO_2 concentrating mechanisms were inherited from the aquatic ancestors of these terrestrial organisms, and retained through the varying atmospheric conditions (Figure 2) over at least the last 400 Ma (a late estimate of the first occurrence of hornworts). A specifically terrestrial aspect of C limitation is that net CO_2 acquisition from the atmosphere has a H_2O cost in terms of the H_2O lost in evaporation as CO_2 is taken up. The C_4 and, especially, CAM modes of photosynthesis are widely acknowledged as having reduced H_2O cost of C gain relative to organisms carrying out C_3 photosynthesis in a similar environment. It is less widely acknowledged that reductions in the H_2O cost of C gain can also occur in poikilohydric plants exposed to air when a CO_2 concentrating mechanism is operating (Raven 1994). This applies to terrestrial cyanobacteria and (many) terrestrial green algae, and to *Anthoceros* and *Phaeoceros*, as well as to intertidal marine algae.

(iii) Nitrogen supply

Turning to N, the occurrence of (biogenic) O_2 poses problems for any terrestrial diazotrophs as well as for their marine ancestors. Essentially similar solutions (e.g. heterocysts) are employed in extant terrestrial as in extant aquatic cyanobacterial diazotrophs. Inputs of combined N to terrestrial as well as aquatic habitats occur today in the form of $NO/NO_2/HNO_3$ from electrical storm activity. Evidence of past electrical storms comes from ‘fossilized lightning strikes’ (fused silica) in sandstones. Even before the presence of significant O_2 in the atmosphere electrical storms could have generated NO, HNO_2 and HNO_3 which, after reaching the ocean as ‘acid rain’, be reduced to NH_3 by the abundant Fe(II) (Summers & Chang 1993). The present-day mechanism ($N_2 + O_2 \rightarrow 2\ NO$) could have occurred at the O_2 partial pressure in the Mesoproterozoic ($\sim$2 Ga) to have given significant combined N inputs (0.2 nmol N $m^{-2}\ s^{-1}$, averaged worldwide). Lest it be thought that this is not significant in the context of a potential photosynthetic rate of 6 μmol C $m^{-2}\ s^{-1}$, it must be remembered that 0.2 nmol $m^{-2}\ s^{-1}$ is an *average* N input while the C fixation rate is the *peak* rate found at optimal hydration, and that the C:N atomic ratio of terrestrial microalgae with a mucilage sheath may be 10:1 or more. Lovelock (1975, 1978) emphasizes that the extinction of all life on earth would mean that $N_2 + O_2 \rightarrow 2NO$ in thunderstorms would be a major inorganic sink for O_2 previously produced in photosynthesis, yielding (ultimately) nitric acid, and O_2-free atmosphere with an N partial pressure at sea level of $(78 - (21/3))$ or 71 kPa.

Combined N could also have been transferred from the ocean to the land as NH_3. Combined N supplied to the ocean as NO_x from thunderstorms could be assimilated by marine algae and ultimately be released as NH_3 after (e.g.) viral lysis or herbivory. Similarly, any N_2 fixed by cyanobacteria would ultimately be released as NH_3. Much of this NH_3/NH is today reassimilated by primary producers or (if released at depth) nitrified.

Thus extant marine biota maintain NH_4^+ at low concentrations at the ocean surface ($\leq$1 mmol m^{-3}) corresponding, with the observed pK_a of NH_3/NH_4^+ and solubility of gaseous NH_3, to a lower NH_3 partial pressure in the marine atmosphere than over land. The higher partial pressure of NH_3 over land is partly of anthropogenic origin and partly results from the relative ‘leakiness’ of the shoots of terrestrial plants (Raven et al. 1993). At the time of evolution of the earliest terrestrial biota the NH_3 partial pressure over abiotic land would have been even lower than the (low) value over the sea (cf. Rye et al. 1995). Accordingly, the net flux of NH_3 vapour would have been from the sea to the land, with dry and wet deposition competing with oxidative conversion of NH_3 to NO_x (which could also serve as combined N sources for terrestrial biota) (see above). The quantitative significance of this flux would have been small relative to the other combined N inputs to early land biota (thunderstorms; N_2 fixation; direct transfer of oxidised N from marine metabolism).

Less likely to have been important in supplying N to early terrestrial biota are the gaseous combined N products (mainly N_2O; some NO) of marine nitrification/denitrification. (Codispotti 1995; Ganeshram et al. 1995) and probably (for NO) as a ‘leak’ from assimilatory NO reduction by phytoplankton (Soeder et al. 1996). The quantity of NO is very small, and N_2O is only of doubtful utility to photolithotrophs (cf. Grundmann, Lensi & Chalamet 1993).

(iv) Iron supply

Fe availability to marine biota would have been decreased as initially UV-B photochemistry, and later the accumulation of O_2 produced in photosynthesis converted Fe(II) to Fe(III) in the ocean (Anbar & Holland 1992; Holland 1994). Presumably production of siderophores (capable of chelating Fe(III)), and the Fe(III)-siderophore can then be taken up by cells) and catalysis of Fe(III) reduction to Fe(II) at the cell surface, followed by Fe(II) uptake overcame this problem for marine biota. The extent of blue radiation- and UV-powered reduction of Fe(III) to Fe(II) with organic C as reductant in seawater would have been minimal unless seawater pH was much lower than the present value (Finden et al. 1984; Waite & Morel 1984). Once O_2 reached the atmosphere it would have oxidised any Fe(II) at the earth’s surface rendering it unavailable for organisms unless they used siderophores or surface reduction by cells (Raven 1995a). The reduction of Fe(III) by solar radiation in soil with organic C would have been less important on land than in the sea: radiation does not penetrate far into soil or (most) rocks. While anoxic microenvironments produced by waterlogging of soils rich in organic C could reduce Fe(III) to Fe(II), such (dark) habitats would by definition not support the growth of small photolithotrophs (although large, vascular photolithotrophs can span an anoxic root medium and an oxic shoot medium). The earliest terrestrial photolithotrophs presumably used Fe-acquisition mechanisms (siderophores, surface reduction) which they inherited from their marine ancestors (Raven 1995).

(v) Phosphorus availability

The oxidation of Fe(II) to Fe(III) has implications for P availability. Binding of inorganic phosphate to Fe_2O_3/Fe_3O_4 is added to the (redox-independent) binding to Al_2O_3 and precipitation as Ca salts (especially at high pH) as physicochemical factors limiting P availability (Marschner 1995). Accordingly, the build-up of O_2 tends to restrict P availability in the sea and freshwater and on land, unless anoxic microenvironments (waterlogged soils for rhizophytes) are available. This lack of P availability could have been a major selective force favouring (vesicular)-arbuscular mycorrhizas in some of the earliest terrestrial rhizophytes (Nicolson 1975; Newsham, Fitter & Watkinson 1995; Raven 1995a).

(vi) Zinc availability

The free Zn concentration in the early anoxic ocean was less than 10^{-4} of that in today's oxic ocean (Table 10.4 of Williams & Frausto da Silva 1996), so that the potential for the use of Zn in biological catalysts increased as the ocean became more oxidised. Thus, the 'zinc finger' DNA transcription factors only occur in eukaryotes. Of particular relevance to the role of atmospheric changes in the availability of elements, and of how these elements interact with CO_2 and O_2, are the roles of Zn in carbonic anhydrase and in Cu-Zn superoxide dismutase (Williams & Frausto da Silva 1996). The roles of carbonic anhydrase in extant plants largely relate to the relatively low inorganic C levels in present environments (Badger & Price 1994; Raven 1995b, 1997), so the role of Zn in carbonic anhydrase may not have been as crucial before the O_2 increase $\sim$2 Ma ago than it has subsequently become. In any case, Co^{2+} can substitute for Zn^{2+} in extant carbonic anhydrase (Sunda & Huntsman 1995; Yee & Morel 1996), and Co^{2+} was more available than Zn^{2+} in the early anoxic ocean (Williams & Frausto da Silva 1994). The occurrence of Cu-Zn superoxide dismutases (an enzyme which limits the damage caused by toxic O radicals) in photolithotrophs is restricted to the Charophyceae *sensu lato* and the embryophytes, and is probably a relatively late acquisition (possibly early Phanerozoic). Whilst this enzyme first occurred in aquatic algae, most of the extant photolithotrophs containing Cu-Zn superoxide dismutase are terrestrial, despite the fact that terrestrial photolithotrophs are generally subjected to lower *intracellular* O_2 concentrations than are aquatic photolithotrophs (Raven et al. 1994). It is not clear what advantages there are in the Cu-Zn superoxide dismutase rather than the Mn form (also found in Charophyceae and embryophytes) and Fe form of the enzyme which could have occurred much earlier in the evolution of photolithotrophs.

(vii) Copper availability

Cu was essentially unavailable in the anoxic ocean, being precipitated as Cu_2S (Williams & Frausto da Silva 1996). Oxygenation of the oceans, and then the land, oxidised S^{2-} and Cu^{+} and made Cu^{2+} available. This element is used in cytochrome oxidase, but some (mainly terrestrial) photolithotrophs have an additional requirement for Cu in the photosynthetic catalyst plastocyanin (most marine O_2-evolvers use cytochrome c_6) and Cu-Zn superoxide dismutase (most marine O_2-evolvers only have Fe or Mn versions of this enzyme) (Raven 1995a). As was pointed out by Henry & Hall (1977) and Henry, Halliwell & Hall (1976) the availability of O_2 permitted the use of Cu in catalysts, one of which (Cu-Zn superoxide dismutase) has a specific role in dealing with toxic O radicals. The evolution of Cu-Zn superoxide dismutase would probably have been restricted by Cu, rather than Zn, availability in the ocean as the oxidation level increased.

(viii) Toxic oxygen radicals and increased cell damage

Another aspect of the increase in O_2 partial pressure which might impact differentially on early terrestrial photolithotrophs and their marine (or freshwater) relatives is damage to DNA and other cell components.

O_2 and radicals (especially O_2 and $^{\cdot}OH$) derived from O_2 by photochemistry or redox thermochemistry can cause damage to DNA, proteins, lipids and other cell components (Halliwell & Gutteridge 1989). These damaging effects become more pronounced with high O_2 concentrations and/or faster metabolic rates (mol O_2 (m^3 cell volume)$^{-1}$ s^{-1}) (Raven et al. 1994; Allen & Raven 1996). Terrestrial photolithotrophs will generally be subjected to a *lower* intracellular O_2 concentration than will corresponding organisms under water under photosynthetic conditions and with a similar photon flux density since *extracellular* accumulation of O_2 is more likely underwater (taking due recognition of the relevance of dissolved O_2 concentration rather than the equilibrium gas-phase O_2 concentration) (Raven et al. 1994). This applies especially to submerged microbial mats and stromatolites, and high intertidal rock pools. However, there may be a low rate of O free radical generation at a given O_2 concentration in the light in deep-growing photosynthesis organisms as a result of the lower photon flux density incident on deep-growing aquatic organisms than on surface-dwelling or terrestrial organisms under a given land or water surface irradiance regime.

It appears, then, that the earliest terrestrial photolithotrophs will have been subjected to similar rates of generation of toxic O species to those encountered by their marine ancestors. Accordingly, the selective factors determining the balance of damage avoidance (scavenging/quenching of O free radicals and the precursors), damage repair (replacement of damaged nucleotides in DNA, and of whole damaged polypeptides) and damage tolerance which the organisms encountered in their marine/freshwater habitats also apply to the terrestrial environment.

(ix) Ozone, UV-B screening and decreased cell damage

As the O_2 build-up involved organisms in toxic O radical avoidance, repair and tolerance, the concomitant O_3 build-up acted to screen UV-B and thus reduce its toxic effects (Kasting & Donahue 1980). UV-B (defined here as 280–320 nm) can damage DNA (Karentz, Cleaver & Mitchell 1991) as well as genetically downstream components with appropriate absorption spectra, e.g. polypeptides and quinones. UV-B is screened (absorbed) relative to photosynthetically active radiation (400–700 nm) by marine and fresh waters containing dissolved O_2, regardless of their overall attenuation of radiation by organic matter in solution or particles (alive or dead) (Kirk 1994a,b). This in turn means that growth of photolithotrophs deeper in a water body will lower the ratio of UV-B to photosynthetically active ratio incident on them, and thus permit significant avoidance of UV-B without excessive reduction of photosynthetic radiation input (Raven & Sprent 1989; Raven 1991b). Nevertheless, the marine photolithotrophs of the Mesoproterozoic ($\sim$2 Ga) would have had at least some of the screening or behavioural responses (avoidance) and damaged nucleotide replacement or whole damaged polypeptide or quinone replacement (repair) found in extant photolithotrophs, and these would have been (genetically) available to their terrestrial descendants (Raven 1991b). The need for screening of UV-B or repair of UV-B damage would have been even greater on land for the earliest terrestrial biota than for their aquatic ancestors, since there would have been no screening of UV-B relative to photosynthetically active radiation external to the organisms (including any UV-B-screening sheaths which they produce): Raven (1991b); Garcia-Pichel

Table 1. Biogenic inputs of C, sulfur and halides to the atmosphere from methane and its sulfur and halogen derivatives. For comparison terrestrial biota exchange ≥ 5 Pmol C y^{-1} as CO_2 with the atmosphere and marine biota exchange 2.9 Pmol C y^{-1} as CO_2 with the surrounding seawater (Raven et al. 1993).

Compound	Input to atmosphere (G mol)					Reference
	C	S	Cl	Br	I	
CH_4	2.3×10^4	0	0	0	0	Houghton et al. (1990)
$(CH_3)_2S$	$1.3–3.6 \times 10^3$	$0.65–1.8 \times 10^3$	0	0	0	Kelly et al. (1994)
CH_3Cl	58–158	0	58–158	0	0	Harper (1994)
$CHCl_3$	3	0	9	0	0	Khalil et al. (1983)
CH_3Br	0.11–3.2	0	0	7.8–9.3	0	Harper (1994); Lobert et al. (1994)
$CHBr_3$	2.6–3.1	0	0	7.8–9.3	0	Harper (1994)
CH_3I	2.1–9.2	0	0	0	2.1–9.2	Harper (1994)

& Castenholz (1991); Post & Larkum (1993). This contrasts with conclusions arrived at earlier about the generation of toxic O radicals (other than by UV-B) in different habitats.

Extant marine biota, and especially marine photolithotrophs, are important sources of trace atmospheric gases; some of these gases (halocarbons) can destroy stratospheric O_3. Table 1 shows some of the gases which marine biota produce today, and quantitative information on the global flux to the atmosphere each year. Methane is mainly produced today in freshwater wetlands and sediments by non-phototrophic organisms; most of the S- and halogen-containing compounds are produced by marine photolithotrophs.

Volatile halocarbons can impact on the marine biota which produced them and on terrestrial biota *via* their influence on the (mainly stratospheric) O_3 screen. The extent to which the volatile halocarbons produced by extant marine biota can reach the stratosphere is variable. Those that do reach the stratosphere are oxidised there to produce Cl, Br, ClO and BrO radicals which catalyse the breakdown of O_3 *via* chain reactions. The synthetic pathways of these compounds are incompletely understood (Collén 1994; Collén et al. 1994; Kaim & Schwederski 1994; Nightingale, Malin & Liss 1995). One pathway involves the vanadoenzyme haloperoxidase and depends on the O_2-dependent production of H_2O_2 which is consumed in the reaction:

$$H_2O_2 + XH + Ha^- \rightarrow H_2O + XHa + OH^-$$

where XH is an organic compound and Ha^- is Br^- or Cl^-. This haloperoxidase pathway could only have produced potentially O_3-destroying halocarbons *after* the free O_2 needed for O_3 production become available. A second pathway involves S-adenosylmethionine as an intermediate and is not explicitly O_2-dependent so that it might have produced atmospheric halocarbons prior to the O_2 build-up. Regardless of the timing of the biogenesis of volatile halocarbons relative to the O_2 build-up, the presence in the atmosphere of both halocarbons and O_2 permits both the photochemical production of O_3 and the oxidation of halocarbons by $\cdot$OH to Ha and HaO radicals which can destroy O_3. The extent to which any such Proterozoic halocarbons could have reduced the O_3 partial pressure, and hence its effectiveness as a UV-screen, is not clear. Higher taxa containing organisms which today produce halocarbons in the marine environment have representatives in strata up to 600 Ma old for the Ulvophyceae (Butterfield, Knoll & Swett 1988) and 1.4 Ga for the Rhodophyta (Butterfield, Knoll & Swett 1990). The role of volatile iodocarbons in providing I to I-deficient (for growth of vertebrates) terrestrial habitats (Lovelock & Margulis 1974) would not have been significant before the Upper Devonian and the first terrestrial vertebrates.

(x) Sulphur supply

Another very important gas produced by extant marine photolithotrophs is dimethylsulphide (DMS), a breakdown product of the compatible solute dimethylsulphoniopropionate (DMSP) produced by (*inter alia*) members of the Dinophyta, Haptophyta, Pelagophyceae and Ulvophyceae (Keller, Bellows & Guillard 1989; Karsten, Wiencke & Kirst 1991; Andreae & Jaeschke 1992; De Yoe, Chan & Suttle 1995). Atmospheric DMS is oxidised in part to CH_3SO_3H (methanesulphonic acid or MSA) which is not further oxidised in the atmosphere but is deposited back in the ocean or on land where it is (by poorly defined means) used as an S-source by micro-organisms (Kelly et al. 1994; cf. Vairavamurthy et al. 1994). The rest of the DMS is oxidised to SO_2 and thence SO_3 which is (slowly: Steudel 1995) hydrated to H_2SO_4. After deposition the $SO_2/SO_3/H_2SO_4$ can be used as an S source by plants and microbes in the sea and on land. The role of atmospheric H_2SO_4 in forming cloud condensation nuclei, thus altering albedo, rainfall and temperature, is still the subject of debate as regards its quantitative importance (Mitchell et al. 1995). The role of DMS and MSA in supplying S to S-deficient terrestrial habitats in undisputed. The extent to which S-deficiency is an (evolutionary) ‘expectation’ of photolithotrophs is seen in the ability of extant cyanobacteria to replace the normal apoproteins of their light-harvesting phycobilins with variants containing lower contents of their S-containing amino-acids cysteine and methionine (Mazel & Marliere 1989).

Assessment of the potential role of S transfer from the sea to land *via* DMS at the time of origin of terrestrial biota requires consideration of (1) the likely extent of S deficiency on land at that time and (2) the occurrence of DMSP, and hence DMS, in marine biota in the time of origin of terrestrial biota. With regard to the supply of S to early land biota, a demand for S in excess of that provided from *in situ* weathering of rocks is possible (Andreae & Jaeschke 1992). As to the occurrence of DMSP-producing marine biota in the Proterozoic, the Ulvophyceae, which today produce DMSP, are known from sediments from 600 Ma (Butterworth, Knoll & Swett 1988), although other present-day marine producers of DMSP are not known as fossils until the Phanerozoic (550 Ma onwards) (Dinophyta, Haptophyta), or are not known as fossils at all (Pelagophyceae). DMSP production is probably a polyphyletic trait and could have originated earlier in the Proterozoic than the earliest known Ulvophyceae.

Conclusions

(1) Extant terrestrial biota are derived from a small fraction of the marine biodiversity present at the time that terrestrial communities became established.
(2) Metabolic activities of marine biota had large influences on the terrestrial environment before, during and after the first occurrence of terrestrial biota.

Acknowledgements

Discussions with past and present colleagues in Dundee, and with Professors WG Chaloner, D Edwards, P Liss and RA Spicer, and Drs K Abrahamsson, R Bateman, M Chamberlain, J Collén and M Pedersén, have greatly helped my appreciation of palaeobiogeochemistry. Dr H D Holland and an anonymous referee have made very helpful contributions to the paper.

References

Anbar AD & Holland HD (1992) The photochemistry of manganese and the origin of banded iron formations. Geochim. Cosmochim. Acta 56: 2595–2603

Allen JF & Raven JA (1996) Free-radical induced mutation *vs* redox regulation: Costs and benefits of genes in organelles. J. Mol. Evoln. 42: 482–492

Andreae MD & Jaeschke WA (1992) Exchange of sulphur between biosphere and atmosphere over temperate and tropical regions. In: Howarth RW, Stewart JWB & Ivanov JB (Eds) Sulphur Cycling in the Continents (pp 27–61). John Wiley, Chichester

Appenzeller T (1993) Searching for clues to ancient carbon dioxide. Science 259: 908–909

Badger MR & Price GD (1994) The roles of carbonic anhydrase in photosynthesis. Ann. Rev. Plant Physiol. Plant Mol. Biol. 45: 369–392

Barber J (1995) Photosynthesis: Short-circuiting the Z-scheme. Nature 376: 388–389

Bell RA (1993) Cryptoendolithic algae of semi-arid lands and deserts. J. Phycol. 29: 123–129

Berbee ML & Taylor JW (1993) Dating the evolutionary radiations of the true fungi. Can. J. Bot. 71: 1114–1127

Berner RA (1990) Atmospheric carbon dioxide levels over Phanerozoic time. Science 249: 1382–1386

Berner RA (1993) Palaeozoic atmospheric CO_2: importance of solar radiation and plant evolution. Science 261: 68–70

Berner RA & Canfield DE (1989) A new model for atmospheric oxygen over phanerozoic time. Am. J. Sci. 289: 333–361

Bhattacharya D & Medlin L (1995) The phylogeny of plastids: a review based on comparisons of small-subunit ribosomal RNA coding regions. J. Phycol. 31: 489–498

Buick R, Thornett JR, McNaughton NJ, Smith JB, Barley ME & Savage M (1995) Record of continental crust $\sim$3.5 billion years ago in the Pilbara Craton of Australia. Nature 375: 574–577

Butterfield NJ, Knoll AH & Swett K (1988) Exceptional preservation of fossils in an upper Proterozoic shale. Nature 334: 424–427

Butterfield NJ, Knoll AH & Swett K (1990) A bangiophyte red alga from the Proterozoic of Arctic Canada. Science 250: 104–107

Canfield DE & Teske A (1996) Late Proterozoic rise in atmospheric oxygen concentration inferred from phylogenetic and sulphur-isotope studies. Nature 382: 127–132

Cerling TE, Wang Y & Quade J (1993) Expansion of C_4 ecosystems as an indicator of global ecological change in the late Miocene. Nature 361: 344–345

Codispotti LA (1995) Is the ocean losing nitrate? Nature 376: 724

Collén J (1994) Production of Hydrogen Peroxide and Volatile Halocarbons by Macroalgae. PhD Thesis, University of Uppsala

Collén J, Ekdahl A, Abrahamsson K & Pedersén M (1994) The involvement of hydrogen peroxide in the production of volatile halogenated compounds by *Meristella gelidium*. Phytochemistry 36: 1197–1202

De Yoe HR, Chan AM & Suttle CA (1995) Phylogeny of *Aureococcus anophagefferens* and a morphologically similar bloom-forming alga from Texas as determined by 18S ribosomal RNA sequence analysis. J. Phycol. 31: 413–418

Edwards D, Abbott GD & Raven JA (1996) Cuticles in early land plants: A palaeoecophysiological evaluation. In: Kierstens G (Ed) Plant Cuticles (pp 1–31). Bios Scientific Publishers, Oxford

Edwards D, Duckett JG & Richardson JB (1995a) Hepatic characters in the earliest land plants. Nature 374: 635–636

Edwards D, Selden PA, Richardson JB & Axe L (1995b) Coprolites as evidence for plant-animal interactions in Siluro-Devonian terrestrial systems. Nature 377: 329–331

Finden DAS, Tipping E, Jaworski GHM & Reynolds CS (1984) Light-induced reduction of natural iron (III) oxide and its relevance to phytoplankton. Nature 309: 783–784

Frankignoulle M, Canon C & Gattuso J-P (1994) Marine calcification as a source of carbon dioxide: Positive feedback of increasing atmospheric CO_2. Limnol. Oceanogr. 39: 458–462

Friedl T (1995) Inferring taxonomic positions and testing genus level assignments in coccoid green lichen algae: A phylogenetic analysis of 18S ribosomal RNA sequences from *Dictyochloropsis reticulata* and from members of the genus *Myrmecia* (Chlorophyta, Trebouxiophyceae Cl. Nov.). J. Phycol. 31: 632–639

Ganeshram RS, Pedersén TF, Calvert SE & Murray JW (1995) Large changes in oceanic nutrient inventories from glacial to interglacial periods. Nature 376: 755–757

Garcia-Pichel F & Castenholz RW (1991) Characterization and biological implications of scytonemin, a cyanobacterial sheath pigment. J Phycol. 27: 395–409

Gehrig H, Schüssler A & Kluge M (1995) Molecular characteristics of the taxonomy of *Geosiphon pyriforme*. In: Ratajczak R & Ullrich C (Eds) Abstracts of the International Symposium of SFB 199 'Ecophysiology of Plants: Molecules, Membranes and Mechanisms' (pp 26–27). Ebernburg (Nahe), March 1995

Graham LE (1993) Origin of Land Plants. Wiley, New York

Graham JB, Dudley R, Auilar NM & Gans C (1995) Implications of the late Palaeozoic oxygen pulse for physiology and evolution. Nature 375: 117–120

Gray J (1993) Major Palaeozoic land plant evolutionary bio-events. Palaeogeogr. Palaeoclimatol. Palaeoecol. 104: 153–169

Greenbaum E, Lee JW, Tevault CV, Blankenship SL & Mets LJ (1995) CO_2 fixation and photoevolution of H_2 and O_2 in a mutant of *Chlamydomonas* lacking photosystem I. Nature 376: 438–441

Grundmann GL, Lensi R & Chalamet A (1993) Delayed NH_3 and N_2O uptake by maize leaves. New Phytol. 124: 259–263

Habicht KS & Canfield DE (1996) Sulphur isotope fractionation in modern microbial mats and the evolution of the sulphur cycle. Nature 382: 342–343

Hackstein JHP & Mackenstedt U (1995) A photosynthetic ancestry of all eukaryotes? Trends Ecol. Evoln. 10: 247

Halliwell B & Gutteridge JMC (1989) Free Radicals in Biology and Medicine (Second Edition). Clarendon Press, Oxford

Han TM & Runnegar B (1992) Megascopic eukaryotic algae from the 2.1 billion-year old Negaunee Iron Formation, Michigan. Science 257: 232–235

Harper DB (1994) Biosynthesis of halogenated methanes. Bioch. Soc. Trans. 22: 1007–1011

Harrison MJ & van Buuren ML (1993) A phosphate transporter from the mycorrhizal fungus *Glomus versiforme*. Nature 328: 626–629

Henry LEA, Halliwell B & Hall DO (1976) The superoxide dismutase activity of various organisms measured by a new and rapid assay procedure. F.E.B.S. Letters 66: 303–306

Henry LEA & Hall DO (1977) Superoxide dismutase in green algae – an evolutionary survey. Special Issue of Plant and Cell Physiology: 377–382

Hiltonen T, Karlsson J, Palmqvist K, Clarke AK & Samuelsson G (1995) Purification and characterisation of the intracellular carbonic anhydrase of the green alga *Coccomyxa*. Planta 195: 345–351

Hoffman PF (1995) Oldest terrestrial landscape. Nature 375: 537–538

Holland MD (1984) The Chemical Evolution of the Atmosphere and Oceans. Princeton University Press

Holland HD (1994) Early Proterozoic atmospheric change. In: Bengtson S (Ed) Early Life on Earth. Nobel Symposium No.84 (pp 237–224). Columbia University Press, New York

Horodyski RJ & Knauth LP (1994) Life on land in the Precambrian. Science 263: 494–498

Houghton JT, Jenkins GI & Ephraums JJ (Eds) (1990) Climate Change. The IPCC Scientific Assessment. Cambridge University Press

Kaim W & Schwederski B (1994) Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life. An Introduction and Guide. Wiley, Chichester

Karentz D, Cleaver JE & Mitchell DL (1991) Cell survival characteristics and molecular responses of Antarctic phytoplankton to ultraviolet-B radiation. J Phycol. 27: 326–341

Karsten U, Wiencke C & Kirst GO (1991) The effect of salinity changes upon the physiology of eulittoral green macroalgae from Antarctica and Southern Chile. II Intracellular inorganic ions and organic compounds. J. Exp. Bot. 42: 1533–1539

Kasting JF (1993) Earth's early atmosphere. Science 259: 920–926

Kasting JF & Donahue TM (1980) The evolution of atmospheric ozone. J. Geophys. Res. 85: 3255–3263

Kelly DP, Wood AP, Jordan SL, Padden AN, Gorlenko VM & Dubinina GA (1994) Biological production and consumption of gaseous organic sulphur compounds. Biochem. Soc. Trans. 22: 2011–2015

Keller MD, Bellows WK & Guillard RPK (1989) Dimethylsulphide production and marine phytoplankton: An additional source. In: Cosper EM, Bricelj VM & Carpenter EJ (Eds) Novel Phytoplankton Blooms (pp 57–75). Springer-Verlag, Berlin

Kenrick P (1994) Alternation of generations in land plants: New phylogenetic and palaeobotanical evidence. Biol. Rev. 69: 293–330

Khalil MAK, Rasmussen RA & Hoyt SD (1983) Atmospheric chloroform ($CHCl_3$): Ocean-air exchange and global mass balance. Tellus 35B: 266–274

Kinchin IM (1994) The Biology of Tardigrades. Portland Press, London

Kirk JTO (1994a) Light and Photosynthesis in Aquatic Ecosystems. Second Edition. Cambridge University Press

Kirk JTO (1994b) Optics of UV-B in natural waters. Arch. Hydrobiol. Beich. 43: 1–16

Knoll AM (1994) Proterozoic and Early Cambrian protists: evidence for accelerating evolutionary tempo. Proc. Natnl. Acad. Sci. Wash. 91: 6743–6750

Knoll AH (1996) Breathing room for early animals. Nature 382: 111–112

Kooistra WHCF & Medlin L (1996a) The origin of the pigmented heterokonts and diatoms. J. Phycol. 32: 25s

Kooistra WHCF & Medlin L (1996b) The origin and evolution of the pigmented heterokonts. Abstracts of the First European Phycological Congress, Cologne, July 1996, p 37. Cambridge University Press

Kump LR & Mackenzie FT (1996) Regulation of atmospheric O_2: Feedback in the microbial feedbag. Science 271: 459–460

Lobert JM, Butler JH, Montzkas A, Geller LS, Myers RS & Elkins JW (1995) A net sink for atmospheric CH_3Br in the East Pacific Ocean. Science 267: 1002–1005

Lovelock JE (1975) Thermodynamics and the recognition of alien biospheres. Proc. Roy. Soc. Lond. B. 189: 167–181

Lovelock JE (1979) Gaia. A New Look at Life on Earth. Oxford University Press

Lovelock JE & Margulis L (1974) Atmospheric homoeostasis by and for the biosphere: The Gaia hypothesis. Tellus 26: 2–9

McCourt RM (1995) Green algal phylogeny. Trends Ecol. Evoln. 10: 159–163

McFadden BJ & Cerling TE (1994) Fossil horses, carbon isotopes and global change. Trends Ecol. Evoln. 9: 481–486

McElwain JC & Chaloner WG (1995) Stomatal density and index of fossil plants track atmospheric carbon dioxide in the Palaeozoic. Ann. Bot. 76: 389–395

Marschner H (1995) Mineral Nutrition of Higher Plants (Second Edition). Academic Press, London

Mazel D & Marliere P (1989) Adaptive eradication of methionine and cysteine from cyanobacterial light-harvesting proteins. Nature 341: 245–248

Mitchell JBF, Johns TC, Gregory JM & Tett SFB (1995) Climate response to increasing levels of greenhouse gases and sulphate aerosols. Nature 376: 501–504

Mora CI, Dries SG, Colarusso LA (1996) Middle to late Palaeozoic atmospheric CO_2 levels from soil carbonate and organic matter. Science 271: 1105–1107

Newman MJ (1979) The evolution of the solar constant. Origins of Life 10: 105–110

Newsham KK, Fitter AH & Watkinson AR (1995) Multi-functionality and biodiversity in arbuscular mycorrhizas. Trends Ecol. Evoln. 10: 407–411

Nicolson TH (1975) Evolution of vesicular-arbuscular mycorrhizas. In: Saunders FE, Mosse B & Tinker PB (Eds) Endomycorrhizas (pp 25–34). Academic Press, New York

Nightingale PD, Malin G & Liss PR (1995) Production of chloroform and other low-molecular-weight halocarbons by some species of macroalgae. Limnol. Oceanogr. 40: 680–689

Norton TA, Melkonian M & Anderson RA (1996) Algal Biodiversity. Phycologia 35: 308–326

Oliver MJ (1996) Desiccation tolerance in vegetative plant cells. Physiologia Plantarum 97: 779–787

Palmer JD & Delwiche CF (1996) Second-hand chloroplasts and the case of the disappearing nucleus. Proc. Natnl. Acad. Sci. Wash. 93: 7432–7435

Palmqvist K, Sültemeyer D, Baldet P, Andrews TJ & Badger MR (1995) Characterization of inorganic carbon fluxes, carbonic anhydrase(s) and Rubisco in the green unicellular alga *Coccomyxa*. Comparisons with low-CO_2 cells of *Chlamydomonas reinhardtii*. Planta 197: 352–361

Poole T, Weyers JDB, Lawson T & Raven JA (1996) Variations in stomatal density and index: Implications for palaeo-climatic reconstructions. Plant Cell Environm. 19: 705–712

Post A & Larkum AWD (1993) UV-absorbing pigments, photosynthesis and UV exposure in Antarctica: Comparison of terrestrial and marine algae. Aq. Bot. 45: 231–243

Potts M (1996) The anhydrobiotic cyanobacterial cell. Physiologia Plantarum 97: 788–794

Prince RC (1996) Photosynthesis: The Z-scheme revisited. Trends Biochem. Sci. 21: 121–122

Ragan, MA & Gutell RR (1995) Are red algae plants? Bot. J. Linn. Soc. 118: 81–105

Raven JA (1986) The evolution of plant life forms. In: Givnish TJ (Ed) On the Economy of Plant Form and Function (pp 421–492). Cambridge University Press, Cambridge

Raven JA (1987) Biochemistry, biophysics and physiology of chlorophyll *b*-containing algae: Implications for taxonomy and phylogeny. Progr. Phycol. Res. 5: 1–122

Raven JA (1991a) Implications of inorganic C utilization: Ecology, evolution and geochemistry. Can. J. Bot. 69: 908–924

Raven JA (1991b) Responses of aquatic photosynthetic organisms to increased solar UV-B. J. Photochem. Photobiol. B: Biol. 9: 239–244

Raven JA (1993) The evolution of vascular land plants in relation to quantitative function of dead water-conducting cells and of stomata. Biol. Revs. 68: 49–64

Raven JA (1994) Photosynthesis in aquatic plants. In: Schulze ED & Caldwell MH (Eds) Ecophysiology of Photosynthesis (Studies in Ecology Volume 100) (pp 299–318). Springer Verlag, Berlin

Raven JA (1995a) The early evolution of land plants: aquatic ancestors and atmospheric interactions. Bot. J. Scotland 47: 151–175

Raven JA (1995b) Photosynthetic and non-photosynthetic roles of carbonic anhydrase in algal and cyanobacteria. Phycologia 34: 93–101

Raven JA (1996) Inorganic carbon assimilation by marine biota. J. Exp. Mar. Biol. Ecol. 203: 39–47

Raven JA (1997) Inorganic carbon acquisition by marine autotrophs. Adv. Bot. Res. 27: 85–209

Raven JA & Spicer RA (1996) The evolution of crassulacean acid metabolism. In: Winter K & Smith JAC (Eds) Crassulacean (Ecological Studies Volume 114) (pp 360–385). Springer Verlag

Raven JA & Sprent JI (1989) Phototrophy, diazotrophy and palaeoatmospheres, biological catalysts and the H, C, O and N cycles. J. Geol. Soc. Lond. 146: 512–518

Raven JA, Wollenweber B & Handley LL (1993) The quantitative role of ammonia/ammonium metabolism and transport in the global nitrogen cycle. Physiol. Plant 89: 512–518

Raven JA, Johnston AM, Parsons R & Kübler (1994) The influence of natural and experimental high CO_2 concentrations on O_2-evolving phototrophs. Biol. Revs. 69: 61–94

Rayner RJ (1984) New finds of *Drepanophycus spinaeformis* Göppert from the Lower Devonian of Scotland. Trans. Roy. Soc. Edinb., Earth Sci. 75: 353–363

Robinson JM (1994) Speculations on carbon dioxide starvation. Late Tertiary evolution of stomatal regulation and floristic modernisation. Plant Cell Environm. 17: 345–354

Rye R, Kuo PH & Holland HD (1995) Atmospheric carbon dioxide concentrations before 2.2 billion years ago. Nature 378: 603–605

Schidlowski M (1988) A 3,800 million-year-old isotopic record of life from carbon in sedimentary rocks. Nature 333: 313–318

Schopf JW (1993) Microfossils of the early Archaen Apex Chert: New evidence for the antiquity of life. Science 260: 95–111

Schüssler A, Schepf E, Mollenhauer D & Kluge M (1995) Structural and functional characteristics of the endosymbiosis *Geosiphon pyriforme*. In: Ratajczak R & Ullrich C (Eds) Abstracts of the International Symposium of SFB 199 ‘Ecophysiology of Plants: Molecules, Membranes and Mechanisms’, pp 24–25. Ebernburg (Nahe), March 1995

Schüssler A, Gehrig H, Bonfante P, Schnepf E, Mollenhauer D & Kluge M (1996) *Geosiphon pyriforme*: Lectin binding sites on the symbiosome and SSU rRNA sequence analysis. Abstracts of the First European Phycological Congress, Cologne, July 1996, p 7. Cambridge University

Shixing Z & Huinerg C (1995) Megascopic multicellular organisms from the 1700 – 1 million-year-old Tuanchazi Formation in the Jixian Area, North China. Science 270: 620–622

Simon L (1996) Phylogeny of the Glomales: Deciphering the past to understand the present. New Phytol. 135: 95–101

Smith EC & Griffiths H (1996a) The occurrence of the chloroplast pyrenoid is correlated with the activity of a CO_2-concentrating mechanism and carbon isotope discrimination in lichens and bryophytes. Planta 198: 6–16

Smith EC & Griffiths H (1996b) A pyrenoid-based carbon-concentrating mechanism is present in terrestrial bryophytes of the class Anthcerotae. Planta 200: 203–212

Soeder CJ, Mohn FH, Pappke H & Rockel P (1996) *Scenedesmus* can produce nitric oxide (NO). Abstracts of the First European Phycological Congress, Cologne, July 1996, p 52. Cambridge University Press

Sprent JI & Raven JA (1986) Evolution of nitrogen fixing symbioses. Proc. Roy. Soc. Edinb. B 85: 215–237

Sprent JI & Raven JA (1992) Evolution of nitrogen-fixing symbioses. In: Stacey G, Burris RH & Evans HJ (Eds) Biological Nitrogen Fixation (pp 491–496). Chapman and Hall, New York

Steudel R (1995) Sulfuric acid from sulfur trioxide and water – a surprisingly complex reaction. Angew. Chem. Int. Ed. Eng. 34: 1313–1315

Summers DP & Chang S (1993) Prebiotic ammonia from reduction of nitrite by iron (II) on the early earth. Nature 365: 630–633

Sunda WG & Huntsman SA (1995) Cobalt and zinc interreplacement in marine phytoplankton: Biological and geochemical implications. Limnol. Oceanogr. 40: 1404–1417

Taylor TN, Hass H, Remy W & Kerp H (1995) The oldest fossil lichen. Nature 378: 244

Taylor WA (1995a) Spores in earliest land plants. Nature 373: 391–392

Taylor WA (1995b) The case for hepatics on land in the Ordovician. Am. J. Bot. 82(supp 1): 92

Vairavamurthy A, Zhou W, Eglinton T & Marowitz B (1994) Sulfonates: A novel class of organic sulfur compounds in marine sediments. Geochim. Cosmochim. Acta 58: 4681–4687

van Cappellen P & Ingall ED (1996) Redox stabilization of the atmosphere and oceans by phosphorus-limited marine productivity. Science 271: 493–496

van den Hoek C, Mann DG & Jahns HM (1995) Algae. An Introduction to Phycology. Cambridge University Press

Waite DT & Morel FMM (1984) Photoreductive dissolution of colloidal iron oxides in natural waters. Environ. Sci. Technol. 18: 860–868

Williams RJP & Frausto da Silva JJR (1996) The Natural Selection of the Chemical Elements. The Environment and Life's Chemistry. Clarendon Press, Oxford

Womersley HBS (1996) The Marine Benthic Flora of Southern Australia, Part IIIB. Australian Biological Resources Study, Canberra

Yapp CJ & Poths H (1994) Productivity of pre-vascular continental biota inferred from the $Fe(CO_3)OH$ contents of goethite. Nature 368: 49–51