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Extrapolating feedback processes from the present to the past

J. A. Raven

Department of Biological Sciences, University of Dundee, Dundee DD1 4HN, UK

Extant terrestrial vegetation alters its physical environment via its albedo, and its influence on immediate temperature via stomatal and boundary-layer influences of energy dissipation as sensible and latent heat; aquatic vegetation also controls albedo (e.g. coccolithophorids) and, by competing with water for electromagnetic energy absorption, the depth of the mixed layer and hence the quantity of nutrients trapped for the spring bloom. Both aquatic and terrestrial vegetation have had, together with microbial and geological processes, an influence on O_2 and CO_2 levels, and hence on the availability and biological functioning of Fe, Mn, Cu, Zn, Se and P, and the relative competitive advantage of C_3 versus C_4, crassulacean acid metabolism (CAM) and carbon concentration mechanism (CCM) organisms. Less directly, changes in primary productivity impact on the production of CH_4 and N_2O which, like CO_2, are greenhouse gases, while some (marine) primary producers yield dimethyl sulphide (and hence cloud condensation nuclei, with effects on cloudiness) and halocarbons (via, in part, O_2-dependent processes), partly negating the O_3 attenuation of UV-B radiation. These effects can be related to the terrestrial embryophytic vegetation back to *ca.* 450 Ma, and to eukaryotic marine vegetation back to at least 1.7, and probably 2.1 Ga, with implications for *inter alia* C_3 versus C_4, CAM and CCM photosynthesis, and Fe acquisition mechanisms. Even earlier (3.8 Ga onwards), prokaryotes may have influenced CO_2 levels and hence controlled (as they did later) surface temperature. By producing O_2, they may have led to decreasing availability of Fe, Mn and P (and utility of Se?), and increasing availability of Cu (and Zn?) that shaped the biochemistry on which later biogeochemistry was based.

Keywords: greenhouse gases, palaeobiota, elemental availability, palaeoatmospheres, photosynthetic pathways

1. INTRODUCTION

This paper addresses the extrapolation of feedback processes among vegetation, climate, and the atmosphere from the present to the past without encroaching unduly on the areas covered by other contributors to this proceedings. I begin with a brief discussion of the sorts of feedback that are important at the present. In doing this, vegetation is considered in the broad sense as the sum of those organisms which contribute primary productivity by 'plant-type' photosynthetic processes that involve O_2 evolution in parallel with CO_2 fixation, i.e. including aquatic as well as terrestrial biota.

Considering how the feedbacks found today could have applied in the past will initially involve discussion of the last 450 Ma or so, when embryophytic vegetation on Earth greatly increased the potential for interactions between terrestrial vegetation, climate, and the atmosphere, as well as having implications for aquatic photosynthesis. Not only was this the time of the origin and evolution of terrestrial embryophytes, but also a time of very considerable change of aquatic primary producers.

The period from at least 1.7 (probably 2.1) Ga to 0.45 Ga represents the time when eukaryotes existed before the origin of embryophytes, with evidence for some terrestrial biota for at least the last half of this time (1 Ga onwards). This time, from the origin of eukaryotes onwards, marks oxygenation of the atmosphere (and oceans).

The third period considered is the time from the origin of photosynthetic O_2 evolution (3.5 billion years ago?) where extrapolation of present-day feedback processes may seem a very dubious proposition, but extant feedbacks set the scene even for very early changes in biota and in the atmosphere and climate (Raven 1997*a*,*b*).

2. PRESENT-DAY FEEDBACK PROCESSES

Extant terrestrial, predominantly embryophytic, vegetation has important implications for the physical environment. Terrestrial vegetation canopies modify albedo relative to the underlying rooting medium, and thus have an impact on the Earth's radiation balance. Another impact on vascular plant vegetation concerns the fate of the absorbed radiation (as opposed to reflected, albedo-related radiation) which is not used in photosynthesis, i.e. at least 70% of 400–700 nm radiation. The vascular plant canopy can influence the dissipation of absorbed energy as latent heat (transpiration) or sensible heat (convective radiation). This occurs by determining (i) the surface roughness of the absorptive surface, (and thus, with wind speed, the possibility of heat and water vapour exchange between the atmosphere and the canopy), and (ii) stomatal activity: closed stomata cause more sensible heat dissipation, wide open stomata bring about more dissipation as latent heat and lower canopy surface temperature. These effects of vascular plants on tmospheric environment, and hence the climate, are ed to the modulating effects of vegetation on run-off water-table levels, and the depth of rooting making water available for evaporation. All of these processes alter the temporal relation between rainfall and oration.

quatic vegetation also has influence on the physical onment in aquatic systems. The $CaCO_3$ liths of cocco- phoids increase the local albedo of the ocean (Green & lbeater 1994). Aquatic vegetation adds to radiation rption by water and dissolved substances near the ce of water bodies. A high enough density of pigment the surface can lead to a thinning of the upper mixed , thus reducing the quantity of nutrients trapped for the ng bloom' in temperate and polar water bodies (Evans sham 1993).

hemical effects of terrestrial and aquatic vegetation on tmosphere include CO_2 uptake and O_2 evolution. The spheric contents of O_2 and CO_2 are, respectively, in atio 210 : 0.36 or 583 : 1, with correspondingly greater -term effects of vegetation on atmospheric CO_2 than O_2, granted a photosynthetic quotient of about 1.0. e notions of how vegetation modulates the atmo- ric CO_2 and O_2 contents are subject to revision over ds longer than a few months as a result of chemoor- trophic activity and, in the longer term, geological esses (Beran 1995; Broecker 1995; Evans & Fasham ; Walker 1994). CO_2, with CH_4, N_2O, and CFCs, are nhouse gases', and their current anthropogenic ases are apparently increasing the Earth's surface erature. The present CO_2 level, and its increase, are ably reversing the competitive advantage of C_4 (and, aps, crassulacean acid metabolism (CAM) terrestrial ts over C_3 terrestrial plants, which occurred during generally downward trend of atmospheric CO_2 over past few tens of millions of years, at least in some onments. It may also have effects on stomata, which increase the dissipation of absorbed energy as sensible r than latent heat, with consequent effects on canopy erature; however, the conclusions of Sellers *et al.* 6) may be based on some over-simplifications in their el.

the aquatic environment, the effect of altered atmo- ric CO_2 is modulated by the occurrence of carbonate linity at some 2 mol OH^- equivalent per cubic metre e ocean, and varying concentrations in inland waters. y aquatic plants can use exogenous bicarbonate, se concentration changes much less than does that of lved CO_2 when atmospheric CO_2 changes. Therefore, show less response to changed atmospheric CO_2, even the present dissolved inorganic C concentration is aturating for photosynthesis or *in situ* growth (Raven *c*). However, larger changes in dissolved inorganic C very large changes in atmospheric CO_2 can have effects on the performance of aquatic phototrophs as ole, and on the relative success of different genotypes en 1997*c*). In the aquatic, as in the terrestrial environ- , the expression of increased light-saturated osynthesis by C_3 plants with higher inorganic C s in terms of increased *in situ* growth requires that shall be little sink limitation for such growth by ed nutrient supply, or by decreased inorganic C fixa- due to limited light supply. It must be remembered that there are theoretical, and sometimes observational, reasons for believing that fewer photons are needed per inorganic C fixed, and that less N, Fe and Mn are needed per unit biomass to achieve a given biomass-specific rate of inorganic C assimilation when a plant with C_3 metabolism is growing at higher (approaching, or above, saturation) CO_2 levels, than when it is growing at lower (limiting or co-limiting with some other resource) levels. These changes in 'resource use efficiency' (*sensu lato*) may go some way to permitting the potential for increased rates of photosynthesis and growth by C_3 plants at high CO_2 levels to be realized, and thus increase their potential for outcompeting organisms with obligate C_4, CAM, and CCM (carbon concentrating mechanisms based on active H^+, CO_2 or $HCO_3{}^-$ transport across membranes; Raven 1997*c*) mechanisms of inorganic C acquisition.

These effects of changed atmospheric composition on the potential primary productivity of vegetation, and the contribution of biota with different inorganic C acquisition mechanisms, constitutes a negative feedback in that a higher CO_2 level may increase C sequestration, at least in the short-term, and vice versa. That such feedbacks are not completely effective over the time scale of decades to centuries is attested to by the current anthropogenic increase in atmospheric CO_2 (and earlier CO_2 variations: see §3). However, without vegetation the fluctuations could have been larger. Furthermore, there is little evidence of feedback of changed atmospheric CO_2 via changed plant C to other element ratios, on the availability of the 'other elements' (N, Fe, Mn), for example, by a changed C : N ratio in terrestrial plant litter altering the chemo-organotrophic N_2 fixation in soil.

Present-day plants do not significantly alter the atmospheric O_2 level over centuries to millennia, and do not directly alter the global availability of nutrient elements whose availability is altered by effects of O_2 on their redox state (Fe, Mn, Cu) or via changes in the redox state of other elements (reduced availability of P as a result of oxidation of Fe). Extant plants can make 'local arrangements' which increase the availability of these elements, e.g. terrestrial vascular plants (except grasses) create a local reducing environment (with lower pH and secretion of chelaters) in their rhizosphere when Fe-deficient in aerated soil (Raven 1997*a*–*c*). Alterations of total transpiratory water use as a function of atmospheric CO_2 levels can alter soil water content and thus have an (small) impact on the availability of redox-influenced elements *via* alterations to the likelihood of waterlogging.

The existence of O_2 in the atmosphere, and dissolved in natural waters, resulting from the activity of O_2-evolving photolithotrophs plus other biogeochemical processes (see §3), is related to the occurrence of biogenic atmospheric trace gases with profound environmental implications. Thus, a minor component of the greenhouse gas N_2O in the atmosphere results from the O_2-dependent microbial process of nitrification, while most of it results from microbial denitrification whose occurrence depends on the O_2-dependent occurrence of nitrate, albeit with denitrification occurring in localized hypoxic or anoxic environments generated by faster organic sedimentation and microbial metabolism than O_2 diffusion in aquatic (including water-logged soil) habitats. Such habitats can also yield CH_4 when electron acceptors for anoxic metabolism other than CO_2 have been exhausted. Essentially all of these electron acceptors other than CO_2 have been generated courtesy of the presence of O_2; a very striking example is the abundant sulphate in seawater. O_2 also catalyses the (non-bacterial) breakdown of atmospheric methane via photochemically produced hydroxyl radicals. Other biogenic gases which are indirectly or directly dependent on O_2 for their production and/or consumption include the halocarbons and dimethyl sulphide (DMS), as well as ozone (O_3).

The halocarbons are partly produced by immediately O_2-dependent haloperoxidase enzymes, although the specificity of the haloperoxidases means that many, largely non-volatile, halocarbons must be produced by other means (van Pée 1996). One such means is the 'carbocation' route which, while not obviously O_2-dependent, has so far only been found in aerobes (O_2-evolving photolithotrophs) (van Pée 1996). The halocarbons can produce chlorine (Cl) and bromine (Br) atoms, and ClO and BrO radicals, in the stratosphere, and thus catalyse O_3 breakdown and increase the solar UV-B flux reaching the surface of land and sea, although today their impact on stratospheric O_3 is minor relative to that of anthropogenic CFCs and the like (Lovelock 1975; Palenik *et al.* 1991; Raven 1997*b*; Rozema *et al.* 1997). In the stratosphere, O_3 is itself the product of photochemical modification of O_2; it should be noted that attenuation of UV-B by natural waters is very largely dependent on dissolved O_2 (*not* dissolved O_3!) (Kirk 1994).

Although it is a completely reduced S compound, DMS is apparently always a product of aerobes, this time as an enzymic (or otherwise) breakdown product of the compatible solute and cryoprotectant dimethyl sulphoniopropionate (DMSP) which they produce (Kiene *et al.* 1996). In the atmosphere, DMS is oxidized (again using OH radicals derived photochemically from O_2) to methane sulphonic acid and to sulphur dioxide (SO_2), and hence SO_3 which hydrates to sulphuric acid (H_2SO_4). Atmospheric H_2SO_4 can form cloud condensation nuclei which alter albedo and hence the radiation balance of affected areas. Atmospheric S derived from ocean processes (as essentially all non-volcanic S was prior to anthropogenic effects) can alleviate S-deficiency in soils.

Finally, immediate terrestrial plant products (volatile hydrocarbons) react photochemically with NO_x to produce tropospheric O_3 (Pienaar & Helas 1996), with greenhouse and UV-B screening effects, but with a predominantly damaging influence on biota. Other damaging O-containing gases, e.g. the free radicals NO and NO_2, are naturally generated by O_2-dependent reactions (a combination of N_2 and O_2 in bolide impacts, thunderstorms and forest fires and, biologically, in nitrification and denitrification (dissimilatory nitrate reduction), as well as assimilatory nitrate reduction and nitric oxide synthase which occurs in higher plants as well as metazoa: Cueto *et al.* 1996). As with SO_2 and tropospheric O_3, biologically damaging levels of NO and NO_2 are anthropogenic (bolides excepted).

Biogenic S and halide gases act *inter alia* to transfer S and halides from the sea to land. DMS production in the sea may have important implications for S supply to S-deprived land areas, although the transfer is not global (cf. the relatively localized impact of 'point' anthropogenic sources of SO_2). The production of iodocarbons from the ocean could help supply I-deficient land areas, with implications for I-requiring organisms (i.e. vertebrates).

The atmosphere also serves to carry nutrient elements from land to the sea. An example is combined N as ammonia (NH_3). Raven *et al.* (1992) point out that shoots of terrestrial plants have a higher NH_3 compensation concentration, i.e. the constant steady-state NH_3 concentration in an enclosed gas phase containing the plant shoot exceeds the NH_3 concentration in an enclosed gas phase over seawater containing phytoplankton and grazers. This means that NH_3 will be transferred from the land to the oceans in the gas phase, paralleling the combined N flux in solution and as particles down rivers. The small fraction of N assimilated from the soil which is emitted as gaseous NH_3, and the relatively short half-life of atmospheric NH_3 due to oxidation by OH radicals and rain-out, restrict the flux of NH_3 from land to the sea via the atmosphere to a *maximum* of *ca.* 2% of the total nitrogen used in primary production in the oceans, or about 8 out of *ca.* 400 Tmol N yr^{-1} (Raven *et al.* 1992).

3. EXTRAPOLATION OF FEEDBACK PROCESSES TO THE PAST

(a) *The 450 Ma or so since the origin of an embryophytic land vegetation*

The evolution of embryophytes around 450 Ma (table 1) permitted much higher primary production rates than did the pre-existing terrestrial algal flora, with a correspondingly greater weathering of soil (Yapp & Poths 1994). Both of these processes remove CO_2 from the atmosphere, with weathering of Ca and Mg aluminosilicates causing (Ca, Mg) CO_3 precipitation, removing CO_2 as sedimented carbonates in oceans. The more rapid weathering on land attendant on the evolution of herbaceous embryophyte vegetation was accentuated by deeper rooting by woody plants from the Middle Devonian onwards, which injected CO_2 (and organic acids) deeper into the soil and underlying rocks: see Berner (1997); Retallack (1997). It is important to remember that litter breakdown in soil can also increase the rate of weathering by providing more CO_2, so organic C breakdown does not necessarily return all of the resulting CO_2 directly to the atmosphere (Berner 1997). The possibility of long-term sequestration of C as organic C was increased by the evolution of less readily biodegraded polymers related to the water relations and mechanical challenges of life on land, e.g. lignin, cutin, and sporopollenin; the content of lignin as a fraction of biomass increased with the evolution of woody plants in the Upper Devonian. In addition to the short-term (geologically speaking) effect of terrestrial plant organic C sequestration with reconversion to CO_2 of most of the organic C over days to decades, there is the longer-term organic C cycle involving very little of the total net primary productivity being sedimented, with reconversion to CO_2 by weathering upon return to the Earth's surface or by events deeper in the Earth's crust. The inorganic C cycle involves the marine sedimentation of carbonate derived from terrestrial weathering of aluminosilicates, followed much later by conversion of the $CaCO_3$ (and SiO_2) to CO_2 and aluminosilicates, le 1. *Atmospheric CO_2 and O_2, surface short-wave radiation, and diversity of terrestrial and marine O_2-evolvers, today and over evolutionarily defined intervals since 3.85 Ga ago (from data cited in the text)*

istry, physics, y	today	0.45–0.0 Ga	2.1–0.45 Ga	3.85–2.1 Ga
at sea level	36.5 Pa	less than present in the Pleistocene, especially in glaciations, otherwise similar (Upper Carboniferous) or higher ($\leqslant$600 Pa)	higher than present ($\leqslant$3 kPa?)	higher than present ($\leqslant$3 kPa?)
sea level	20.8 kPa	similar to present day, but higher in Upper Carboniferous	initially low ($\leqslant$1 kPa); from 0.55 Ga similar to present	<200 µPa; localized O_2 around O_2-evolving photolithotrophs in ocean?
tratospheric, tor)		about the same as today	$\leqslant$ today	0
ce photosyntheti- active radiation, 700 µm	$\leqslant$2 mmol photon m^{-2} s^{-1}	$\leqslant$2 mmol photon m^{-2} s^{-1}	initially $\leqslant$1.9 mmol photon m^{-2} s^{-1}	initially $\leqslant$1.6 mmol photon m^{-2} s^{-1}
ce UV-B radiation, 320 nm	$\leqslant$5 µmol photon m^{-2} s^{-1}	$\leqslant$5 µmol photon m^{-2} s^{-1}	initially higher than today	much higher than today (10×?)
ce temperature ve to today	—	generally warmer but with glacial episodes	generally warmer (?) but with glacial episodes	generally warmer (?) but with glacial episodes
ne volvers	cyanobacteria Chlorophyta Rhodophyta Heterokontophyta Dinophyta Haptophyta	cyanobacteria Chlorophyta Rhodophyta Heterokontophyta (from 0.28 Ga?) Dinophyta (from 0.35 Ga?) Haptophyta (from 0.16 Ga?)	cyanobacteria Chlorophyta (from 1.7 Ga?) Rhodophyta (from 1.7 Ga?)	cyanobacteria (from 3.45 Ga?)
strial volvers	cyanobacteria (free living and in lichens) Chlorophyta (free living and in lichens) Embryophyta (bryophytes; pteridophytes; gymnosperms; angiosperms)	cyanobacteria (in lichens from 0.40 Ga?) Chlorophyta (in lichens from 0.40 Ga?) Embryophyta (bryophytes; pteridiophytes from *ca.* 0.42 Ga, gymnosperms from *ca.* 0.35 Ga; angiosperms from *ca.* 0.12 Ga)	cyanobacteria (from 1.2 Ga) Chlorophyta (from 1.2 Ga)	none

deep in the Earth's crust (Broecker 1995; Walker). Berner (1997) also points out that stands of vegeta- can increase weathering by recycling water in spiration and rainfall, thus providing temporal conti- of wet, weatherable sediment, and by anchoring minerals rather than letting them erode.

ne *general* downward trend in atmospheric CO_2 over last 450 Ma may be related in part (quantified by er (1997), and references therein) to the activity of strial plants in increasing weathering and hence sedi- tation of inorganic C, and also sedimentation of nic C, against a background of variable resupply of from long-term sedimented inorganic and organic C ner 1997; Retallack 1997), and with a contribution to nic and inorganic C sequestration from marine photo- trophs (see below).

Over most of the last 450 Ma, and certainly over the last 380 Ma, the predominant terrestrial photolithotrophs have been the sporophytes of vascular plants (Raven 1993*b*; table 1). The predominance of stomata as the means of gas exchange between plants and the atmosphere has implications for the water cost of plant growth, but may also alter the near-canopy temperature as a result of the variable, stomatally controlled allocation of absorbed radiant energy, which is not converted to chemical energy in photosynthesis, between latent heat of evaporation of water in transpiration and mainly convective loss as sensible heat. Models of this energy partitioning in relation to increased CO_2 from the present concentration of *ca.* 360 µmol mol^{-1} to *ca.* 720 µmol mol^{-1} suggest an increase in air temperature just above the canopy of a degree or more (Sellers *et al.* 1996) although with some imperfect inputs. Such models, when refined, will clearly have relevance to the previous 420 Ma of terrestrial vegetation with stomata, since the atmospheric CO_2 level during this time has been higher than the present value except for the last few million years and (probably) during the Upper Carboniferous.

Stomatal responses to CO_2 take place at the development level (acclimatory changes in stomatal index and density: Woodward 1987), and the functional level (changes in aperture) as well, probably, at the evolutionary level (genotypically determined changes in stomatal index, density, and possibly of function: McElwain & Chaloner 1996). The genotypic and/or phenotypic changes in stomatal index/density with time since the Lower Devonian show an inverse relationship with the atmospheric CO_2 deduced from soil carbonate $\delta^{13}C$ values and biogeochemical models (McElwain & Chaloner 1996; Berner 1997; cf. Poole *et al.* 1996). How these stomata responded to the CO_2 levels in which they functioned is not completely clear. The relatively constant $\delta^{13}C$ value of terrestrial organic C over the last 400 Ma or so (see Raven & Spicer 1996) suggests that the organisms were functioning at a similar ratio of intracellular to atmospheric CO_2 concentration, as do extant terrestrial C_3 plants. This interpretation is based on the model of Farquhar *et al.* (1982), assuming constancy over the last 400 Ma of (i) the $\delta^{13}C$ of atmospheric CO_2, (ii) the discrimination between $^{13}CO_2$ and $^{12}CO_2$ by ribulose bisphosphate carboxylase (RUBISCO), and (iii) the kinetics of RUBISCO of terrestrial C_3 plants, and also that there have been no diagenetic changes in $\delta^{13}C$, and that the preserved material reflects the mean $\delta^{13}C$ of the live plant (see Raven 1997*a*). Such interpretations, if taken at face value, suggest a relative constancy of *mean* stomatal functioning, in relation to the optimization strategies defined by Cowan & Farquhar (1977), since stomata evolved, with implications for water costs of growth and of canopy temperature as a function of CO_2 level (Beerling 1997; Sellers *et al.* 1996). A constant ratio of intracellular to atmospheric CO_2 would yield decreased water costs of photosynthesis, and higher rates of CO_2 fixation in C_3 plants at high atmospheric CO_2 levels, although the large changes in stomatal density with varying atmospheric CO_2 through time (McElwain & Chaloner 1996) combined with the $\delta^{13}C$ data suggest an inverse relation of photosynthetic capacity and atmospheric CO_2 level. An increased canopy temperature with the high bulk tropospheric temperatures common in a high-CO_2 world is less of a problem for C_3 plants if their RUBISCO is CO_2-saturated, in agreement with the interpretation of the $\delta^{13}C$ data in terms of a relatively constant ratio of intracellular to atmospheric CO_2 concentration (see Long 1991; Raven & Spicer 1996). However, Robinson (1994*a*) shows that Late Tertiary and Quarternary decreases in atmospheric CO_2 levels (from 500 to 200 μmol mol^{-1}) are correlated with a higher (less negative) $\delta^{13}C$ of Indian peat deposits from C_3 plants, suggesting an emphasis on minimizing the water cost of growth at the expense of growth rate under low CO_2 conditions.

Another aspect of stomatal functioning in the past has been raised by Robinson (1994*b*) in relation to the rate and extent of stomatal responses in different higher taxa to any environmental cue (relative humidity, light, CO_2). The scant data available suggest that 'later-evolving' taxa (angiosperms and, especially, fast-evolving flowering plants such as grasses and some forbs) have greater stomatal responsiveness (rate of response) than do gymnosperms and, particularly, pteridophytes (noting that grasses and other herbaceous angiosperms were once, evolutionarily, pteridophytes and inherited stomata from them!). If the slower responses of the stomata of 'early-evolving' taxa are confirmed by subsequent work, then the capacity for 'minute-by-minute' optimization of stomatal aperture in response to changing environmental conditions would be less in pteridophytes than in grasses. While $\delta^{13}C$ values for extant C_3 terrestrial vascular plants suggest that the *mean* intracellular CO_2 concentration maintained during photosynthesis does not vary systematically among major taxa, the variability in the data could disguise ecophysiologically significant differences (Raven 1997*a*). Cowan (1986) rightly asserts that there must be a trade-off between the benefit of optimizing water loss relative to carbon gain in a rapidly fluctuating environment by equally rapid stomatal responses and the cost of such rapid stomatal movements, but does not give a quantitative cost–benefit analysis such as Raven (1989) attempted for another nastic response, leaflet folding as a possible protection against photoinhibition from sunflecks in shade plants. Such a cost–benefit analysis for stomatal response times would be beneficial in deciding if the fastest-operating stomata are limited in their rate of response by evolutionary optimization considerations (not worth having them work faster) or mechanistic constraints (cannot make them work faster). It may be that the response rate of the biochemistry of photosynthesis to (e.g. to light changes, changes in RUBISCO activation, state transitions) may limit the extent to which more rapid stomatal changes could be capitalized on in integrated photosynthesis and transpiration in a rapidly fluctuating environment.

It is likely that any feedback mechanisms that operated between atmospheric CO_2 and vascular plant vegetation before about 15 Ma ago did so solely in the context of C_3 physiology—which does not saturate short-term photosynthesis (and, under otherwise optimal conditions, growth) until the atmospheric CO_2 level is at least 500 μmol mol^{-1}. Both C_4 and CAM have higher affinities for CO_2, but the earliest well-authenticated occurrence of C_4 photosynthesis is *ca.* 14 Ma ago, while CAM is not conclusively known from earlier than about 40 000 years ago, but is probably at least millions of years old (Raven 1997*a*,*b*; Raven & Spicer 1996). While the CO_2 level was higher than that present during most of the time between 450 and 15 Ma ago, it was probably similar to extant values in the Upper Carboniferous (Berner 1997), a time at which O_2 apparently made its sole significant excursion above present levels since 450 Ma ago (Berner & Canfield 1989; Graham *et al.* 1995; Raven *et al.* 1994). This means that the $O_2 : CO_2$ ratio in the Upper Carboniferous atmosphere was probably as high as at any time in the last 450 Ma, including the last glacial maximum. Despite this, there is little evidence for C_4 or CAM metabolism in the Carboniferous from $\delta^{13}C$, or anatomical evidence (Raven 1997*a*). The only organisms that could have fixed CO_2 on land with as high a CO_2 affinity as C_4 and CAM ts in the last 450 Ma are certain lichens and horn- s. The algal photobionts of some extant lichens have Ms, as do certain extant hornworts (Smith & Griffiths a,b). Fossil lichens appear about 395 Ma ago, while is cladistic and molecular genetic evidence for the ence of the (embryophytic) hornworts for at least Ma (Raven 1997*a*,*b*). These poikilohydric organisms d probably never have been such major contributors rrestrial productivity as C_4 (and CAM) plants are y.

oday, CO_2 pumps (including C_4, CAM and CCMs) be important for photolithotrophs exposed to air, in s of permitting lower water costs of CO_2 assimilation; is certainly the case for C_4 plants, and may also be ficant for astomatous organisms (lichens; anthocerote etophytes) to the extent that their relatively unregu- water loss after a wetting event can occur with a er CO_2 gradient between the atmosphere and the t's surface, thus permitting more C to be fixed per ing event (Surif & Raven 1990). Whether this was as ficant with the much higher bulk air CO_2 levels for of the last 450 Ma needs further analysis.

ther terrestrial vegetation–atmosphere–climate inter- ns that would have qualitatively, if not quantitatively, e past as they do now include the production of volatile ocarbons and NO, with subsequent photochemical uction of tropospheric O_3, and the evolution of NH_3. ocarbon production would probably have occurred flowering plants and conifers, although what the eozoic terrestrial vascular plants would have contrib- is not clear since few data are available for ocarbon emissions from extant pteridophytes. At all ts the low NO levels would have limited O_3 production n-toxic levels. For NH_3, any influence of N fertilizers, erbated by artificial selection of crops for the capacity apid consumption of high soil N levels, in increasing release to the atmosphere would mean a lower ous NH_3 release in the past than pertains today en *et al.* 1992).

urning to the marine environment over the last 450 Ma, hanges in primary producers in the sea have been more ound than the evolution of terrestrial embryophytes, at if change is taken as genetic distance among biota, and ossil record calibrations of the molecular clock for such er taxa as the Heterokontophyta (e.g. diatoms and n algae) are accepted as showing that photosynthesis is Division arose within the last 280 Ma (see Raven a,b; table 1). Regardless of when the heterokonts me photosynthetic, the fossil record tells us that ms have only been catalysing SiO_2 sedimentation for than 280 Ma. Furthermore, regardless of when the ophyta evolved, the $CaCO_3$-sedimenting role of cocco- phorids has only been evident for the last 160 Ma or so en & Leadbeater 1994; table 1). While SiO_2 deposition has an indirect effect on the C cycle and, especially, the sphere, the precipitation of $CaCO_3$ can reduce, or even se at a high enough ratio of particulate inorganic to nic C production, the CO_2 decrease in solution resulting net primary productivity. The influence on sea-surface can increase the atmospheric CO_2 content relative to ame amount of marine primary production by a non- fied organism, with a positive feedback effect of asing background CO_2 levels (Frankignoule *et al.* 1994). Such effects might be significant over periods of millions of years (e.g. in the Cretaceous). A further atmospherically significant property of the Haptophyta is the production of DMS (see Kiene *et al.* 1996); this occurs in non-coccolithophorids (e.g. *Phaeocystis* spp.) as well as calcifying haptophytes. Other major sources of DMS today are marine dinoflagellates (Dinophyta; from 0.35 Ga?) and pelagophytes (a class of the Heterokontophyta), with contributions from certain marine macroalgae and maritime higher plants (Kiene *et al.* 1996). It is possible that all of the phytoplanktonic algae producing DMS evolved less than 450 Ma ago (see Raven 1997*a*,*b*; table 1). However, this begs the question of whether their *non-photosynthetic* marine ancestors, prior to acquisition of plastids by secondary endosymbiosis of a pre-existing eukaryotic microalga, produced DMS, and if so, whether their abundance was such as to make them significant sources of DMS in the context of the global climate. Even if they were significant sources of DMS, these 'pre-photolithotrophic' ancestors of major DMS-producing algal taxa scarcely qualify as vegetation for present purposes. Halocarbon production (and hence O_3 destruction) by marine phototrophs using haloperoxidase could have occurred in this time interval, since a haloperoxidase gene occurs in extant cyanobacteria (Kaneko *et al.* 1996).

(b) *The period between the origin of eukaryotic photolithotrophs and the origin of embryophytic land vegetation*

Eukaryotic marine vegetation can be dated to at least 1.7 Ga ago using the well-preserved fossils of a macroalga described by Shixing & Huineng (1995), and probably to the (presumed) eukaryotic macroalga *Grypanea* at 2.1 Ga ago (Han & Runnegar 1992). Eukaryotic marine phytoplankton, in the form of acritarchs of a morphology referable to resting stages of prasinophycean green algae, can be found back to at least 1.2 Ga ago (see Raven 1997*b*). Red algae are known from at least 0.7 Ga, and very probably 1.4 Ga ago, and they and the green algae diversified from 0.65–0.55 Ga ago onwards (Raven 1997*a*,*b*; table 1). Cyanobacteria (and hence halocarbon production (Kaneko *et al.* 1996)) were, of course, present throughout.

The earliest geochemical evidence for photosynthetic life on land comes from the work of Horodyski & Knauth (1994) on weathering rates 1.2 Ga ago. The argument here is that the weathering rates exceeded those expected from the atmospheric CO_2 level, which is in turn derived from greenhouse effect considerations; the observed weathering rates are attributed to surface-dwelling photolithotrophs, products of whose photosynthesis were biologically converted to organic acids and CO_2 in the upper part of the substratum, leading to increased weathering rates. However, there is no evidence as to the nature of the organisms involved in the 'CO_2 pump' from the atmosphere to the upper substratum layers (Raven 1997*b*), although cyanobacteria and green algae (common soil algae today) could have been involved.

Atmospheric composition over the period 2.1–0.45 Ga ago is less well constrained up to the beginning of the Cambrian (0.55 Ga ago) than between 0.55 and 0.45 Ga ago. In this latter 100 Ma, the concentration of CO_2 was much higher (at least 10-fold) than that of today, while

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY B BIOLOGICAL SCIENCES

O_2 was similar to extant values (table 1). It is likely that the atmospheric O_2 level was adequate for the synthesis of specifically embryophytic components, e.g. lignin, well before the first evidence of embryophytes and of lignin (Raven 1997*a*,*b*). Before 0.55 Ga ago, the O_2 concentration was lower, with the origin of eukaryotes 2.1 Ga ago corresponding to the first major occurrence of atmospheric O_2 at levels in excess of the value (10^{-8} of the present level) attained by photolysis of water vapour (table 1). Before 0.55 Ga ago, CO_2 was probably at least up to 100 times the present level, based on greenhouse considerations (noting the occurrence of glaciations: Kaufman 1997; Evans *et al*. 1997) in relation to lower radiant energy output by the younger sun (table 1).

The occurrence of atmosphere O_2 above the level attainable by photolysis of water is absolutely dependent on photosynthetic O_2 evolution being in excess of respiratory (and other) processes consuming O_2. The production of O_2 probably started with the evolution of cyanobacteria some 3.45 Ga ago, but it was largely consumed by inorganic oxidations (Fe^{2+} to Fe^{3+}; S^2 to SO_4^2). The occurrence of free O_2 at the time of origin of eukaryotes permitted them to perform aerobic respiration (courtesy of endosymbiotic proteobacteria termed mitochondria), and provides a UV-B screen via photochemical production of stratospheric O_3, and in natural waters by the absorption of UV-B by dissolved O_2. The stratospheric O_3 could (as indicated earlier) be partly removed by volatile halocarbons, which are produced *inter alia* by O_2-dependent processes. The presence of O_2 also permits the expression of the oxygenase activity of RUBISCO, provided the CO_2 concentration at the site of RUBISCO activity is not so high (as a result of a high external CO_2 level with diffusive CO_2 entry, or as a result of CO_2 pumps of the C_4, CAM or CCM types) as to suppress the oxygenase activity. Free O_2 also increases the availability of Cu, which is needed for ubiquitous cytochrome oxidase as well as plastocyanin and Cu, and Zn superoxide dismutase found in some eukaryotic O_2-evolvers (Charophyceae, in the Division Chlorophyta, and Embryophyta). Negative effects of O_2 on O_2-evolvers include the production of damaging O species in and around the organism (e.g. H_2O_2, O_2^-, OH radicals and $^1O_2$) and a decrease in the availability of Fe (and hence P) and Mn (Raven 1997*a*,*b*), and in the stability of -SeH (Lee & Berry 1996). The earliest-evolving enzymes that remove O_2^- (Fe, Mn superoxide dismutase) and H_2O_2 (catalase; glutathione peroxidase) have, as essential components, elements Fe, Mn, and Se, whose availability or utility is reduced by the presence of O_2, which is responsible for production of the damaging O species (see Kaneko *et al*. 1996; Raven 1997*a*,*b*; Price & Harrison 1988; Takedo *et al*. 1993).

The occurrence of O_2 in the atmosphere and dissolved in natural waters thus had a number of very important effects on the availability of resources to photosynthetic organisms (including O_2 itself as the terminal oxidant), and the extent of damage by UV-B and toxic species derived from O_2. This comprises a set of very important feedbacks of the O_2 produced in photosynthesis on the organisms that produced the O_2. The extent to which the quantity of O_2 in the atmosphere can be related to the functioning of plants in a way which can itself alter the O_2 content of the atmosphere is still a matter of controversy. It has been suggested that high O_2 levels in the atmosphere could decrease net photosynthesis by increasing photorespiratory O_2 uptake and CO_2 loss *and* decreasing gross photosynthetic CO_2 uptake and O_2 evolution, thus reducing the atmospheric O_2 levels as O_2 is consumed in other processes, and vice versa for low O_2 levels (Tolbert 1994). However, the complexities of the O_2 cycle make it difficult to defend the notion that photosynthesis controls atmospheric O_2; rather, photosynthesis acts as the O_2-generating component of a cycle involving sedimentation of organic C and reduced S and Fe, and reoxidation of this material when it is returned to the surface by tectonic activity (Broecker 1995; Walker 1994).

The CO_2 levels in the atmosphere 2.1–0.45 Ga ago were probably higher than any values found subsequently, based on greenhouse effect arguments for the time up to 0.55 Ga ago (table 1; cf. Rye *et al*. 1995). These high CO_2 levels, combined with O_2 levels no higher than the present value, and significantly lower for most of the 2.1 Ga–0.45 Ga period, meant that diffusive CO_2 would suppress the oxygenase activity of RUBISCO unless the diffusion boundary layer limitation on CO_2 diffusion was extreme (e.g. in a bulky microbialite); such circumstances would also restrict O_2 efflux, and further decrease the $CO_2 : O_2$ ratio at the site of RUBISCO activity (Raven 1997*a*,*b*,*c*). The occurrence of the oxygenase activity of RUBISCO in microbialites would help to explain the occurrence of P glycolate phosphatase (preventing P sequestration in P glycolate) as an ancient feature of photolithotrophs (Raven 1997*a*,*b*,*c*), with perhaps less ancient CCMs as a mechanism found in parallel with P glycolate phosphatase in some photolithotrophs (Raven 1997*a*,*b*,*c*).

(c) *The period between the origin of photolithotrophy and the earliest eukaryotic photolithotrophs*

The earliest evidence for RUBISCO-based inorganic C assimilation comes from $^{13}C/^{12}C$ evidence some 3.85 Ga ago (Eiler *et al*. 1997, and references therein), with evidence for cyanobacteria 3.45 Ga ago. The only photolithotrophs that could evolve O_2 until 2.1 Ga ago were the cyanobacteria, when they were supplemented by eukaryotes with chloroplasts derived from cyanobacteria. The geochemical record suggests that free O_2 was very low until about 2.1 Ga ago, with all O_2 produced being consumed in oxidizing inorganic reductants. Such an almost complete absence of free O_2 before 2.1 Ga conflicts with molecular genetic evidence for the occurrence of cytochrome oxidase in a range of prokaryotes prior to the evolution of eukaryotes *ca*. 2.1 Ga ago (Schäfer *et al*. 1996). There are two problems here: one is that cytochrome oxidase has O_2 as its normal oxidant, and so presumably evolved in relation to the presence of that oxidant; the other is that cytochrome oxidase requires Cu, which would have been essentially unavailable in the absence of O_2. It also appears that the Cu-containing plastocyanin, complementing the Fe-containing cytochrome-c_6 in cyanobacteria, has a very ancient origin (Clarke & Campbell 1996; Kaneko *et al*. 1996), posing further problems in terms of Cu availability before O_2 built up. Localized availability of free O_2 in the oceans, but not necessarily in the atmosphere, could have permitted this evolutionary feedback of photosynthetically produced O_2 on the occurrence of Cu-requiring osynthesis, and Cu-requiring respiration with O_2 as lectron acceptor.

he CO_2 level before 2.1 Ga ago was probably not more 100 times the present value (Rye *et al.* 1995); this hemical (weathering rate)-based value leaves a short- in the extent of greenhouse warming needed to unt for the observed surface temperature in the ext of the 'weak young sun'. At all events the CO_2 was high enough to saturate extant cyanobacterial ISCOs with diffusive CO_2 entry, unless they were in y microbialites where diffusive CO_2 influx and O_2 x could possibly give a lower CO_2 concentration, and ite $O_2 : CO_2$ ratio despite the absence of all but loca- external O_2 (Raven 1997*a*,*b*,*c*; Watson & Tabita 1997).

he extent to which facilitation of intracellular inor- C diffusion, and intracellular CO_2 to HCO_3^- conversion by carbonic anhydrase, would be needed 2.1 Ga ago in the high-CO_2 environment is not clear en 1997*c*). All extant carbonic anhydrases seem to use s their optimal catalytic metal, and Zn was less avail- in the early anoxic world (Raven 1997*c*). However, Co alternate catalytic metal) was probably at least as able before 2.1 Ga as it is today (Raven 1997*c*).

here is evidence for emergent (exposed to the atmo- re) continental crust about 3.56 Ga ago (Buick *et al.*). However, there is no evidence for life in terrestrial ats before 1.2 Ga ago (see above), so that the supply mospheric CO_2 to terrestrial photolithotrophs was problem 3.45–2.1 Ga ago. Any intertidal stromato- might have been limited by atmospheric CO_2 supply w tide at the CO_2 levels suggested by Rye *et al.* (1995). O_2 levels were *much* higher than those suggested by *t al.* (1995), then this limitation by CO_2 would not be ved; at very high CO_2 levels (sufficient to significantly ase atmospheric pressure), the diffusion coefficients of are lower than at the present atmospheric pressure 3 kPa), so that increasing CO_2 partial pressures in the sphere do not lead to linearly increasing CO_2 avail- ty by diffusion.

ONCLUSIONS

edbacks between vegetation, the atmosphere, and the ronment in the past as extrapolations of what occurs e moment clearly become less likely as we go further the past.

ver the last 0.45 Ga, both atmospheric composition, the photosynthetic biota involved, were generally ar (but with higher CO_2 levels) to those found today, significant terrestrial primary productivity impacting duced C storage and the rate of chemical weathering. ine primary productivity over the last 0.45 Ga cata- $CaCO_3$ and SiO_2 deposition, as well as organic C sition, and generated volatile organic sulphur and le compounds which had impacts on cloudiness and spheric O_3 (and hence the Earth's surface UV-B .

etween 2.1 Ga and 0.45 Ga, CO_2 was substantially er, and O_2 and O_3 were lower (at least before Ga) than today, with no embryophytic land vegeta- although algae could have occurred on land from a, effecting an influence on terrestrial weathering. In eas the main primary producers were green and red algae, and cyanobacteria, with (probably) less production of volatile halocarbons and DMS than occurred later.

Before 2.1 Ga there was negligible free O_2 (and O_3) in the atmosphere, but perhaps localized O_2 in oceans around sites of high primary productivity, brought about solely (among O_2-evolvers) by cyanobacteria. The consumption of photosynthetic O_2 by inorganic oxidants meant that trace element availability was very different from conditions after 2.1 Ga, and especially after 0.55 Ga; this early anoxic phase of evolution permitted large metabolic roles for elements (e.g. Fe, Mn) which, subsequent to the accumulation of O_2, became much less available.

Past and present colleagues have stimulated my thinking and curbed some of my wilder excesses.

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Discussion

M. A. Mercy (*Department of Geology and Geophysics, Yale University, New Haven, CT, USA*). Has other evidence been found to suggest the existence of land plants as early as 1.2 Ga besides increased weathering rates relative to those expected from the atmospheric CO_2 levels at that time? Have the kinetics of weathering reactions under different atmospheric conditions (especially those of earlier Earth history) been constrained sufficiently to rule out abiotic weathering rate enhancement?

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY B BIOLOGICAL SCIENCES

RAVEN. I know of no fossil evidence for terrestrial 12 billion years ago, and would not completely rule abiotic weathering as the cause of the 'increased' hering rates.

ENTON (*School of Environmental Sciences, University of East 'a, Norwich, UK*). The evolution of difficult-to-biode- e land plant structural materials such as lignin esented a novel form of organic carbon, more likely to be buried than its predecessors. Wouldn't this have tended to force up atmospheric oxygen, especially considering the delay before fungi evolved the ability to biodegrade lignin?

J. A. RAVEN. Yes. See, for example, Robinson, J. M. 1989 The burial of organic carbon as affected by the evolution of land plants. *Historical Biol.* **3**, 189–201.

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY B BIOLOGICAL SCIENCES