Quantitative estimates of changes in marine and terrestrial primary productivity over the past 300 million years

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Changes in marine primary production over geological time have influenced a network of global biogeochemical cycles with corresponding feedbacks on climate. However, these changes continue to remain largely unquantified because of uncertainties in calculating global estimates from sedimentary palaeoproductivity indicators. I therefore describe a new approach to the problem using a mass balance analysis of the stable isotopes ($^{18}\text{O}/^{16}\text{O}$) of oxygen with modelled O_2 fluxes and isotopic exchanges by terrestrial vegetation for 300, 150, 100 and 50 million years before present, and the treatment of the Earth as a closed system, with respect to the cycling of O_2 . Calculated in this way, oceanic net primary productivity was low in the Carboniferous but high (up to four times that of modern oceans) during the Late Jurassic, mid-Cretaceous and early Eocene greenhouse eras with a greater requirement for key nutrients. Such a requirement would be compatible with accelerated rates of continental weathering under the greenhouse conditions of the Mesozoic and early Tertiary. These results indicate possible changes in the strength of a key component of the oceanic carbon (organic and carbonate) pump in the geological past, with a corresponding feedback on atmospheric CO_2 and climate, and provide an improved framework for understanding the role of ocean biota in the evolution of the global biogeochemical cycles of C, N and P.

Keywords: palaeoclimates; palaeoproductivity; oceans; atmospheric composition

1. INTRODUCTION

Marine primary production has varied over geological time with changes in phytoplankton diversity (Knoll 1989), the fertility of the oceans, oceanic circulation patterns and sea level (Berger & Herger 1992). Photosynthetic carbon fixation by marine organisms plays a key role in determining the rate of carbon export from shallow ocean water to deep ocean sediments. It is a primary component of the biological pump for organic and carbonate carbon, influencing atmospheric CO_2 and climate (Mix 1989; Volk 1989), as well as the global biogeochemical cycles of other elements (e.g. O_2 , Fe, S, N and P) through redox reactions (Van Cappellen & Ingall 1996; Falkowski 1997). Establishing the linkage between ocean biotic processes, global biogeochemistry and climate through the Phanerozoic therefore requires quantitative estimates of the primary productivity of ancient oceans. However, uncertainties in the interpretation of sedimentary-based palaeoproductivity indicators (Pedersen & Calvert 1990; Berger & Herger 1992), and their application to specific ocean basins, preclude the derivation of global estimates (Veto *et al.* 1997). Moreover, many groups of algae contributing substantially to marine productivity and biomass are not represented in the geological record as recognizable fossils, further confounding predictive estimates of marine primary production from the sedimentary record (Knoll 1989).

To address this issue I describe a new approach quantifying gross biospheric production and its partitioning between the terrestrial and marine realms, applied to specific intervals of the past 300 million years (Myr). The approach uses a mass balance analysis of the stable isotopes ($^{18}\text{O}/^{16}\text{O}$) of oxygen (Bender *et al.* 1985, 1994; Keeling 1995; Beerling 1999) and assumes that the difference between the oxygen isotope composition of seawater in the oceans (δ_{O}) and the oxygen isotope composition of atmospheric O_2 (δ_{ATM})—the ‘Dole effect’ (Dole *et al.* 1954), presently +23.5‰ (Kroopnick & Craig 1972)—has remained constant through geological time. Temporal (seasonal) and spatial (Arctic Islands, Australia and inland cities) surveys (Dole *et al.* 1954; Kroopnick & Craig 1972) have revealed the Dole effect to be constant to at least 0.25‰; tropospheric measurements (Keeling 1995) indicate a constancy to 0.03‰. Moreover, palaeoreconstructions of the Dole effect, extending back over the last two glacial cycles (140 kyr), further indicate its remarkable stability (Bender *et al.* 1994) ($\pm 0.5\%$) despite variations in sea level and atmospheric CO_2 markedly altering the surface area of the oceans and photosynthetic carbon fixation. Its stability arises because the Earth as a whole behaves essentially as a closed system with respect to O_2 over tens of thousands of years, so that a change in one component of the system will be matched by a new steady-state isotopic value of atmospheric O_2 , at a rate depending on the O_2 content of the atmosphere and biospheric O_2 production (Berry 1992).

Table 1. Mean annual land surface climates, globally averaged oxygen isotope composition of precipitation (δ_p) and atmospheric gas composition of each geological era

era	mean annual temperature (°C)	mean annual precipitation (mm d ⁻¹)	mean annual relative humidity (%)	δ_p (‰)	atmospheric composition ^a	
					CO ₂ (%)	O ₂ (%)
Carboniferous (300 Myr BP)	7.0	1.1	74.9	−9.2	0.03	35
Late Jurassic (150 Myr BP)	18.5	2.6	68.2	−6.1	0.120	21
mid-Cretaceous (100 Myr BP)	19.7	2.6	70.5	−5.1	0.090	22
early Eocene (50 Myr BP)	16.6	3.1	70.9	−6.2	0.060	24
present day (1990s)	11.3	1.9	63.7	−9.3	0.035	21

^aAtmospheric CO₂ and O₂ content from Berner (1994) and Berner & Canfield (1989), respectively.

2. MATERIAL AND METHODS

The Dole effect can be quantitatively described by (Bender *et al.* 1994):

$$\text{Dole effect} = \left[\left(\frac{F_{\text{TGPP}}}{F_{\text{TGPP}} + F_{\text{MGPP}}} \right) \times T + \left(\frac{F_{\text{MGPP}}}{F_{\text{TGPP}} + F_{\text{MGPP}}} \right) \times O \right] - \delta_{\text{SD}}, \quad (1)$$

where F_{TGPP} and F_{MGPP} are the annual one-way total O₂ fluxes (Pmol yr⁻¹) produced by terrestrial vegetation and the oceans respectively, T and O are the terrestrial and oceanic Dole effects (i.e. net isotopic fractionations associated with F_{TGPP} and F_{MGPP}) and δ_{SD} accounts for stratospheric diminution resulting from the O isotopic exchange between the O₂ and CO₂ (0.4‰).

Under steady-state conditions, i.e. with gross O₂ production by terrestrial photosynthesis and photorespiration equal to gross O₂ consumption by respiration, T is defined by

$$T = \delta_E + \delta_R, \quad (2)$$

where δ_E is the globally averaged oxygen isotopic composition of chloroplast water, weighted by gross O₂ production, and δ_R is the net isotopic fractionation by respiration and varies depending on the CO₂:O₂ ratio of the atmosphere (table 1). Similarly, under steady-state conditions, O is given by

$$O = \delta_{\text{ME}} + 18.9, \quad (3)$$

where δ_{ME} is the isotopic composition of seawater, derived for specific intervals of the Phanerozoic from measurements on low-Mg calcite shells of marine organisms (Veizer *et al.* 1997), and the composite value 18.9‰ represents discrimination against ¹⁸O during deep- and surface-water marine respiration (Bender *et al.* 1994). Substituting equation (2) and equation (3) into equation (1) and solving for F_{MGPP} gives

$$F_{\text{MGPP}} = -F_{\text{TGPP}} \times \frac{(\text{Dole effect} - \delta_E - \delta_R + \delta_{\text{SD}})}{(\text{Dole effect} - \delta_{\text{ME}} - 18.9 + \delta_{\text{SD}})}. \quad (4)$$

To estimate F_{MGPP} from equation (4), δ_E and F_{TGPP} were calculated here with off-line couplings between a process-based terrestrial vegetation–biogeochemistry model (VBM) (Woodward *et al.* 1995; Beerling 1999) and four global palaeoclimate simulations by the UK Universities Global Atmospheric Model-

ling Programme (UGAMP) general circulation model (GCM). The VBM models, under steady-state conditions, the physiological processes of nutrient uptake, photosynthesis, respiration and stomatal limitation of transpiration, and uses these to determine the net (and gross) primary production of vegetation, its structure in terms of leaf-area index, and litter formation (Woodward *et al.* 1995). The productivity model is dynamically coupled to the Century biochemistry model (Parton *et al.* 1993) simulating the cycling of C and N in soils, thereby completing the terrestrial carbon cycle. At equilibrium, the extent of ¹⁸O enrichment of leaf water (due to the slower transpiration of H₂¹⁸O compared to H₂¹⁶O) was determined on a monthly basis using the Craig–Gordon evaporative enrichment model (CGM), with all parameterizations as described previously (Farquhar *et al.* 1993; Beerling 1999), and weighted by gross O₂ production (photosynthetic and photorespiratory O₂ production). The CGM requires the isotopic composition of precipitation (δ_p) and atmospheric water vapour (δ_v). Here δ_p was calculated from its relationship between annual mean temperature, elevation and precipitation (Farquhar *et al.* 1993), and δ_v was taken as a constant 10‰ depletion everywhere with respect to precipitation, but weighted by monthly plant-canopy transpiration, since δ_v reflects a mixture of water vapour from plant canopies and air entrained from above the canopy (Beerling 1999).

The VBM was forced with global climate simulations by the UGAMP GCM (3.75° latitude × 3.75° longitude) performed at the University of Reading for specific intervals of geological time representing the late Carboniferous (300 Myr before present (BP)), the Late Jurassic (150 Myr BP), the mid-Cretaceous (100 Myr BP) and the early–middle Eocene (50 Myr BP). Detailed descriptions of the boundary conditions of each simulation (solar inputs, orbital parameters, landmass configurations, sea surface temperatures, etc.), and extensive validation of the resulting climates against the worldwide distribution of climate proxies (coals, evaporites and bauxites) are given elsewhere (Price *et al.* 1995, 1997; Valdes *et al.* 1995; Valdes & Crowley 1998). For comparison, a further simulation was performed using GCM global climates averaged for the 1990s (Mitchell *et al.* 1995), representative of a modern climate. Mean land surface characteristics of each climate and the atmospheric composition used for each simulation are given in table 1. Calculated in this way, the productivity of the terrestrial biosphere

Table 2. Globally averaged values for the oxygen isotope composition of leaf water enrichment (δ_E), respiration (δ_R), seawater (δ_O) and gross primary productivity of the terrestrial (F_{TGPP}) and marine (F_{MGPP}) biospheres, response time of the Dole effect and oceanic nutrient requirements through geological time ($1 \text{ Pmol} = 1 \times 10^{15} \text{ mol}$)

era	δ_E (‰)	δ_R^a (‰)	δ_O^b (‰)	F_{TGPP}^c (Pmol O ₂ yr ⁻¹)	F_{MGPP}^d (Pmol O ₂ yr ⁻¹)	sensitivity of F_{MGPP}^e (Pmol O ₂ yr ⁻¹)		marine net primary production ^f (Pmol C yr ⁻¹)	nutrient supply ^g (10 ¹² mol yr ⁻¹)	
						+	-		nitrogen	phosphorus
Carboniferous (300 Myr BP)	11.8	18.5	-2.0	12.2 (45)	11.0 (1.0)	1.6	1.8	3.2	483.0	30.2
Late Jurassic (150 Myr BP)	11.6	17.2	0.0	33.2 (6)	33.2 (1.0)	6.0	7.3	12.7	1917.0	120.0
mid-Cretaceous (100 Myr BP)	10.9	17.3	-1.0	32.6 (10)	23.5 (1.4)	5.1	4.3	8.4	1267.2	79.2
early Eocene (50 Myr BP)	11.3	17.6	-2.0	41.4 (19)	29.7 (1.4)	4.8	4.6	11.1	1675.5	104.7
present day (1990s)	9.6	17.9	0.0	19.6 (31)	11.0 (1.7)	n/a		3.8	573.6	35.8

^a Flux-weighted average for the discrimination against ¹⁸O associated with the three main respiration pathways in plants (dark respiration, Mehler reaction and photorespiration), based on values summarized by Bender *et al.* (1994).

^b Data from Veizer *et al.* (1997).

^c Values in brackets indicate the proportion of GPP derived from photorespiration (Bender *et al.* 1994). The net primary productivity of the terrestrial biosphere was estimated by the VBM for the 1990s (F_{TNPP}) to be 4.3 Pmol C yr⁻¹, a value closely compatible with a recent published estimate based on remote sensing information (4.9 Pmol C yr⁻¹) (Field *et al.* 1998).

^d Values in brackets indicate the terrestrial to marine GPP ratio.

^e Error estimates determined from the mass balance analysis by varying the Dole effect by $\pm 0.5\%$. It is recognized that the mass balance analyses rest on the assumption of relatively minor shifts in the Dole effect over geological time. Such stability has only been demonstrated for the last 0.14 Myr and, ultimately, the best test of this assumption requires global isotopic tracer simulations with coupled vegetation-atmosphere-ocean climate models for each era.

^f Calculated by removing respiratory O₂ consumption according to its scaled relationship with F_{MGPP} (Duarte & Agusti 1998) for marine planktonic and benthic communities and an O₂:C ratio for new marine organic matter (Laws 1991) of 1.4:1. Estimated in this way, global NPP of the contemporary ocean equals 3.8 Pmol C yr⁻¹ identical to that calculated independently from coastal zone colour scanner data for the world's oceans (Falkowski *et al.* 1998) (3.8 Pmol O₂ yr⁻¹). The scaling relationship between F_{MGPP} and respiratory O₂ consumption was assumed constant for all eras since changes in the atmospheric CO₂ content have less of an impact on aquatic plant productivity due to buffering by carbonate alkalinity in the oceans (Falkowski & Raven 1997).

^g Nutrient supply required to support marine NPP assuming a conserved Redfield atomic ratio of 106:16:1 (C:N:P) for marine organic matter.

and the oceans were both strongly compatible with recent estimates based on remotely sensed information, validating the approach under a contemporary climate and atmospheric CO₂ content (table 2).

3. RESULTS AND DISCUSSION

The global simulations (figure 1) provide the first quantitative picture of changes in gross O₂ production (photosynthetic and photorespiratory) by terrestrial vegetation through geological time. For all three intervals representing the Earth in the largely ice-free greenhouse world of the Mesozoic and early Tertiary (Late Jurassic, mid-Cretaceous and early-middle Eocene), the terrestrial oxygen flux (F_{TGPP}) was nearly double that estimated for the present day (table 2), due to the high CO₂ concentration and warm climates. Substantial productivity was modelled to occur at high palaeolatitudes in all three cases (figure 1*b-d*), in line with the evidence from the fossil record demonstrating the existence of high-latitude polar forests at these times (Vakhrameev 1991). In contrast, the cool, high O₂ environment of the late Carboniferous curtailed vegetation productivity (figure 1*a*) and compressed it to within a narrow latitudinal band close to the equator. Photorespiration constituted some 45% of the global annual (one-way) O₂ flux from the terrestrial biosphere in the Carboniferous (table 2).

The average isotopic composition of leaf water in the terrestrial biosphere (δ_E) shows variations of *ca.* 2‰ over the past 300 Myr BP (table 2), which, together with the terrestrial O₂ fluxes, imply (equation (4)) large changes in the gross primary production of the oceans (F_{MGPP}) at corresponding intervals (table 2). In the Carboniferous, F_{MGPP} is slightly above that of the present-day oceans, but there is some uncertainty attached to the high O₂ content of the atmosphere at this time (table 1) with a direct influence on vegetation activity. Therefore, a further off-line simulation between the VBM and UGAMP Carboniferous climate was made but with a contemporary O₂ content (21%). This procedure yielded values for δ_E , δ_R and F_{TGPP} of 9.6‰, 18.4‰ and 16.0 Pmol O₂ yr⁻¹ respectively, and a value for F_{MGPP} of 9.3 Pmol O₂ yr⁻¹. Oceanic primary production in the Carboniferous therefore is estimated to be low and/or similar to today's oceans, a conclusion quite robust regardless of the O₂ content of the atmosphere. Ecological and geological data indicate the Carboniferous period was characterized by extremely low phytoplankton diversity (Knoll 1989) and oligotrophic marine surface waters (Martin 1995), in agreement with these results.

In contrast to the Carboniferous, F_{MGPP} in the Late Jurassic, middle Cretaceous and early-middle Eocene were substantially greater than the contemporary oceans (table 2). Late Jurassic mid-latitude ocean sediments

Figure 1. Global patterns of gross primary production in the (a) late Carboniferous (300 Myr BP), (b) Late Jurassic (150 Myr BP), (c) mid-Cretaceous (100 Myr BP), (d) early-middle Eocene (50 Myr BP) and (e) the present day. The scale bar is in units of mol O_2 produced by photosynthesis and consumed by photorespiration $\text{m}^{-2} \text{ yr}^{-1}$.

Figure 2. Global patterns of leaf-water enrichment in ^{18}O (δ_E) in the (a) late Carboniferous (300 Myr BP), (b) Late Jurassic (150 Myr BP), (c) mid-Cretaceous (100 Myr BP), (d) early-middle Eocene (50 Myr BP), and (e) the present day. The scale bar is in units of per mil (‰).

record extremely thick sequences of carbonates and organic carbon-rich shales (DeWever & Baudin 1996; Weissert & Mohr 1996), and deep-sea sediment cores of the middle Cretaceous (Aptian through Cenomanian) record fluctuating sequences of carbonates and organic-rich black shales (Weissert & Mohr 1996; Herbert 1997). During the Tertiary, the palaeoproductivity of the Indian ocean peaked in the early–middle Eocene, due to the abrupt reorganization of oceanic circulation patterns (Siesser 1995). Although the sedimentary evidence provides some qualitative support for the described theoretical approach to estimating past oceanic production, uncertainties in carbonate chemistry in seawater (Berger & Herger 1992) and the controls on organic matter preservation in ocean sediments (e.g. anoxia versus productivity) (Pedersen & Calvert 1990) necessarily limit the use of such tests.

Global marine net primary production over the past 300 Myr (table 2), a key component of the oceanic carbon (organic and carbonate) pump, was two to four times stronger than present during the three ancient greenhouse eras represented in this study (Late Jurassic, middle Cretaceous and early–middle Eocene). Export of organic carbon from surface waters to the ocean interior preferentially removes ^{12}C , so that the $^{13}\text{C}:^{12}\text{C}$ ratio is several per mil more positive than deep-water carbon (Broecker & Peng 1982). Therefore, assuming appropriate controls for diagenesis, a positive $\delta^{13}\text{C}$ excursion in deep-water organic and/or carbonate carbon broadly mirrors the response of the marine organic and inorganic carbon pump, and significant C-isotope excursions have been recorded in marine sedimentary records of the Late Jurassic (Weissert & Mohr 1996), middle Cretaceous (Weissert & Mohr 1996; Herbert 1997) and early Eocene (Siesser 1995), independently corroborating the predictions for these times (table 2). The new approach described here attaches quantitative estimates of oceanic primary production to sedimentary carbon isotope excursions. Changes in the magnitude of total and export production of organic carbon to oceanic interiors strongly influence atmospheric CO_2 concentration and climate on geological time-scales (Mix 1989; Volk 1989; Falkowski *et al.* 1998), with the clear potential for ocean biota to have exerted an important feedback on both in the Mesozoic and early Tertiary, but to a lesser extent in the Carboniferous.

Changes in oceanic net primary production through geological time would also be expected to affect the evolution of the biogeochemical cycles of other elements (Van Cappellen & Ingall 1996; Falkowski 1997). To sustain the high productivity of the world's oceans in the Mesozoic and early Tertiary, marine phytoplankton required a greater-than-present supply of nitrogen (N) and phosphorus (P), assuming a conserved Redfield ratio of N and P for marine organic matter (table 2). Given that iron may limit N_2 fixation in the oceans on geological time-scales (Falkowski 1997; Falkowski *et al.* 1998) some increased transport of this, and possibly other trace elements, would be required. Increased fluxes of continentally derived minerals would be compatible with observations from modelling studies of Mesozoic and early Tertiary climates that mid-latitude depressions, important for generating storms, were both intense and frequent (Price *et al.* 1995, 1997; Valdes *et al.* 1995) and

continental arid regions extensive (cf. figure 1a,b). In addition, increased rates of continental weathering under the ancient 'greenhouse' conditions, is also thought to have accelerated the fluvial transfer of nutrients from the continents to the major oceanic basins (Worsley *et al.* 1986; Follimi 1996; Weissert & Mohr 1996).

The use of an O_2 isotopic mass balance to calculate oceanic productivity leads to uncertainties in the estimates due mainly to evolutionary changes in discrimination against ^{18}O by marine and terrestrial respiration, shifts in surface water and deep ocean respiratory fractionations, global sea-level variations and oceanic conditions, estimates of the oxygen isotope composition of seawater and the accuracy of the global palaeoclimate simulations. Nevertheless, the global maps of terrestrial vegetation O_2 fractionation should be testable by measurement of the oxygen isotope ratio of fossilized cellulose ($\delta^{18}\text{O}_{\text{cel}}$) isolated from terrestrial plant materials (assuming no major diagenetic effects) because the ^{18}O enrichment of leaf water (δ_{E}) is passed, via the action of carbonic anhydrase, to CO_2 molecules that diffuse into and out of the leaves (Farquhar *et al.* 1993), some of which become fixed by photosynthesis and converted to leaf cellulose. Consequently, $\delta^{18}\text{O}_{\text{cel}}$ is influenced by δ_{E} and has the potential to be used to record it (DeNiro & Epstein 1979). At the global scale, the simulations for each geological era show distinct asymmetries between hemispheres in the geographical patterns of modelled δ_{E} values arising because of the influence of the different climatic regimes, especially relative humidity, on the evaporative enrichment model and vegetation activity (figure 2). These inter-hemispheric differences are quite large (up to 10‰, figure 2) and well within the detection limits of mass spectrometers. Within any one individual era, there is also marked geographical variation in δ_{E} (figure 2) providing a basis for testing the broad-scale GCM palaeoclimate simulations for a particular interval.

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