PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY B BIOLOGICAL SCIENCES

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Phil. Trans. R. Soc. Lond. B 1994 **346**, 421-432
doi: 10.1098/rstb.1994.0159

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SUMMARY

This paper presents an attempt to reconstruct potential changes in the photosynthetic rates of terrestrial C3 leaves over the past 120 Ma. The approach has been to couple palaeoatmospheric reconstructions of O_2, CO_2 and temperature from geochemical modelling, and an independent estimate of ancient CO_2 changes from fossil porphyrins, with a mechanistic biochemical model of C3 photosynthesis. The model accounts for the effect of each of these palaeoenvironmental changes, at the biochemical level, to predict leaf photosynthesis and has been parametrized for a typical gymnosperm and angiosperm. The results indicate clear potential for increased photosynthetic C3 fixation in the warm Cretaceous for both angiosperms and gymnosperms, despite the increased O_2 content of the atmosphere prevailing at the time. Photosynthetic rates are then predicted to progressively decline into the Tertiary, as a result of global cooling. The model simulations also point towards some leaf-level ecophysiological explanations for the rise in angiosperm dominance and the concomitant decline in gymnosperms from the late Cretaceous onwards, at mid-latitudes, which have not been considered previously. This work provides a basis for scaling up to the canopy level to predict the primary productivity of ancient ecosystems and their possible feedback on atmospheric composition and climate.

1. INTRODUCTION

Over a decade ago Moore (1983) first considered the evolution of angiosperms in relation to palaeoatmospheres; since then considerable advancement has been made both in palaeoatmospheric reconstructions and in the biochemical modelling of the C3 photosynthetic C fixation pathway. Modelling and reconstruction of changes in palaeoatmospheric O_2 and CO_2 has advanced largely as a consequence of improved coupling of the N and S cycles and inclusion of the effects of vegetation and solar radiation on rock weathering rates (Lasaga *et al.* 1985; Berner & Canfield 1989; Robinson 1989; Berner 1990, 1992, 1993). Additionally, a new technique has been developed for estimating ancient CO_2 levels from the relationship between the stable carbon isotope composition of fossil chlorophyll derivatives (porphyrins) from deep sea cores, temperature and atmospheric CO_2 partial pressure (Freeman & Hayes 1992). In C3 photosynthesis the mechanistic biochemical model of Farquhar *et al.* (1980) has now been extensively validated against results from plants grown under different atmospheric CO_2 and O_2 concentrations and different regimes of irradiance and water availability (Farquhar *et al.* 1980; Sharkey 1985; Harley & Sharkey 1991; Harley *et al.* 1992). The general applicability of the Farquhar *et al.* model has seen its use in models simulating the carbon balance of leaves, canopies and ecosystems (see, for example, Kim & Verma 1991; McMurtrie *et al.* 1992), and so provides a sound basis for scaling up leaf-level observations to accurately predict whole canopy CO_2 fluxes (Hollinger *et al.* 1994). Current interest in forecasting the effects of future global change has seen its incorporation into models predicting changes in photosynthetic C fixation on a global scale (Long & Hutchin 1991; Woodward *et al.* 1995).

Modelling approaches to changes in ancient atmospheric composition and C3 photosynthesis have arisen largely in isolation from each other, possibly as a consequence of the different disciplines into which the problems have become segregated. Yet the coupling of the two now appears to hold real promise for attempting reconstructions on a geological timescale of plant physiological functions under different atmospheric and environmental conditions. In this paper an attempt is made to couple the output from geochemical models predicting temperature, O_2 and CO_2 change, and the CO_2 estimates of Freeman & Hayes (1992), to a recently published version of the Farquhar *et al.* mechanistic model of photosynthesis (Harley *et al.* 1992). The approach represents a first attempt at constructing long-term changes in *potential* photosynthetic rates of leaves of terrestrial vegetation. These predictions may be tested at a later date as more information of a quantitative nature becomes available from analysis of fossil leaf cuticles (such as stomatal dimensions and frequencies) (see Raven & Sprent 1989). These quantitative fossil characteristics

Phil. Trans. R. Soc. Lond. B (1994) **346**, 421–432
Printed in Great Britain

may be coupled with equations of diffusion theory to calculate rates of photosynthesis (Raven 1993) and stomatal conductance (Beerling & Woodward 1993). Reconstructed photosynthetic rates from this independent line of evidence will enable refinements of the first-order predictions made here. The final resolution to the problem will only be realized by a combination of the two approaches.

This paper briefly outlines (i) model results for CO_2, O_2 and temperature for the interval late Cretaceous – Present (the past 120 Ma) and (ii) the photosynthesis model employed in calculating photosynthetic rates. The photosynthesis model is then used to consider the effects of Cretaceous and Tertiary changes in atmospheric O_2, CO_2 and temperature, leading to the prediction of potential photosynthetic rates through the past 120 Ma for typical gymnosperm and woody angiosperm species under light-saturating and light-limiting conditions, assuming non-limiting water availability. The sequence of model is as follows.

1. Investigation of the separate effects of atmospheric O_2, CO_2 and temperature prevailing in the late Cretaceous and the Tertiary on the relation between photosynthetic rate (A) and intercellular leaf CO_2 concentration (c_i), (A/c_i response).
2. Investigation of the combined effects of Cretaceous and Tertiary atmospheric O_2, CO_2 content and temperatures on the A/c_i response under light-saturating and light-limiting conditions for a hypothetical species and for three species representative of taxa that evolved in either the late-Cretaceous or the Tertiary under different CO_2 concentrations.
3. Finally, the model is applied to reconstruct changes in photosynthetic rates of leaves of a typical gymnosperm and woody angiosperm in response to the continuously changing palaeoenvironments and palaeoatmospheres of the past 120 Ma.

2. PALAEOENVIRONMENTAL RECONSTRUCTIONS OF THE PAST 120 Ma

This section briefly considers the rationale for the choice of palaeodata sources and the overall trends revealed by these data.

(*a*) *Palaeo-CO_2 reconstructions*

Cretaceous reconstructions based on atmospheric modelling (Barron & Washington 1985), geochemical modelling (Berner 1990, 1992, 1993; Lasaga *et al.* 1985), stable carbon isotopes (Freeman & Hayes 1992) and an evaluation of volcanic emissions (Caldeira & Rampino 1991) all conclude that atmospheric CO_2 concentrations during the late Cretaceous were probably four to ten times present concentrations (figure 1*a*). The results presented here are based upon an improved carbonate–silicate geochemical model of Lasaga *et al.* (1985) which predicts CO_2 values towards the higher end of the range of current models, but has the advantage of providing a high temporal resolution for the time interval concerned in the present study. This model provides an upper bound to Cretaceous – Tertiary CO_2 concentrations. Estimates of ancient CO_2 concentrations based on fossil porphyrins indicate much lower values (figure 1*a*) and these have been used to set the lower bound on the CO_2 trends. Both reconstructions show a similar overall trend with higher CO_2 concentrations in the Cretaceous, which decline moving into the Tertiary.

(*b*) *Palaeo-O_2 reconstructions*

Trends in atmospheric O_2 concentration are presented in figure 1*b*, based on the result of the model of Berner & Canfield (1989). This reconstruction is based on a variable land mass scenario, rather than the 'most likely' scenario of Berner & Canfield (1989) because of its greater realism to biological palaeodata (see Robinson 1989 for discussion). O_2 concentration in this model is calculated from rates of burial and weathering of organic carbon and pyritic sulphur. Negative feedbacks are included by assigning higher weathering rates to younger rocks.

(*c*) *Palaeotemperature reconstructions*

There are several proxy indicators of palaeotemperatures for the past 120 Ma (Frakes 1979; Tallis 1991). For modelling photosynthetic rates the present study has used the estimates of Lasaga *et al.* (1985) (figure 1*c*). This temperature curve is derived from the CO_2 model and provides a continuous temperature record in line with palaeobotanical evidence (Savin 1977). Furthermore, this record shows an Eocene temperature maximum (figure 1*c*) (*ca.* 45 Ma) that is now well recognized in palaeobotanical studies (Wolfe 1980).

3. DESCRIPTION OF PHOTOSYNTHESIS MODEL

(*a*) *Model structure*

In this paper a simplified version of the Farquhar *et al.* (1980) model of photosynthesis is used in which the limiting effect of triose phosphate utilization (TPU) has been omitted (Harley *et al.* 1992). TPU limitation is a fine-scale effect which was observed in only 14% of 109 species examined by Wullschleger (1993) and is therefore unlikely to influence the overall pattern of results described here.

Net leaf photosynthetic rate may be expressed as:

$$A = \left(1 - \frac{0.5O}{\tau c_i}\right) \min\{W_c, W_j\} - Rd, \qquad (1)$$

where A is the net leaf photosynthetic rate (μmol $CO_2\,m^{-2}\,s^{-1}$), c_i and O are the partial pressures of CO_2 and O_2 in the intercellular leaf space, W_c and W_j are the rates of carboxylation-limited Rubisco (ribulose 1,5-bisphosphate (RuBP) carboxylase–oxygenase) activity and RuBP regeneration by electron transport, respectively, Rd is the rate of CO_2 release in the light resulting from processes

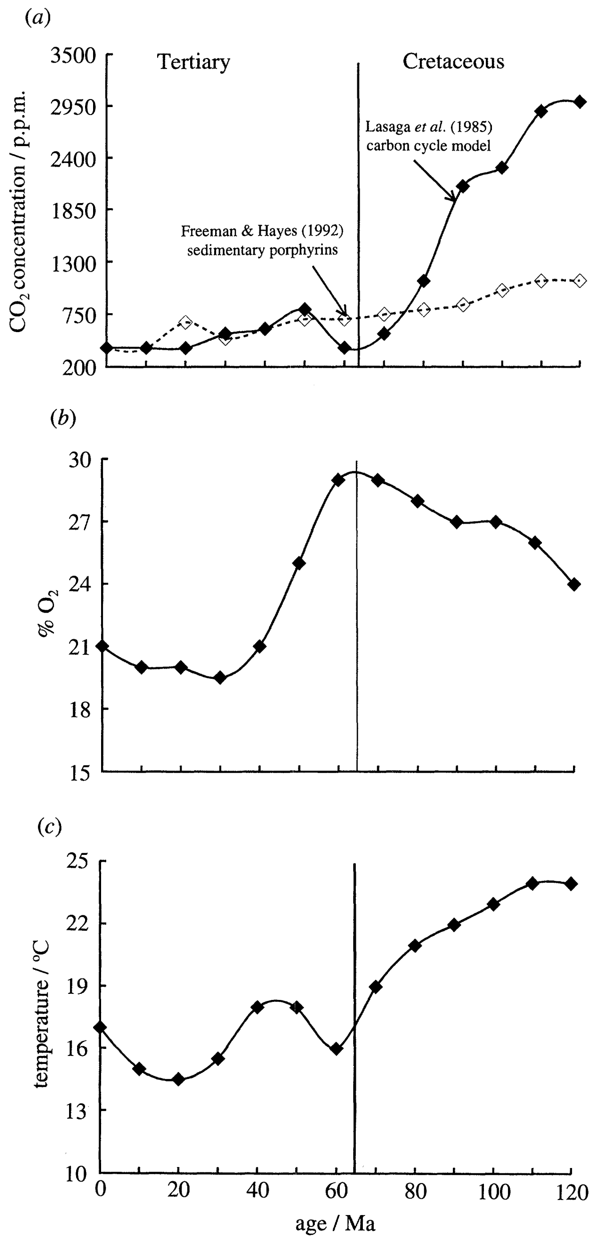

Figure 1. Palaeo-reconstructions for the past 120 Ma of (*a*) CO_2 concentrations from the results of the long-term carbon cycle model of Lasaga *et al.* (1985) (filled diamonds) and reconstructed from the isotopic composition of fossil porphyrins (open diamonds) (Freeman & Hayes 1992), (*b*) O_2 from the Berner & Canfield (1989) model and (*c*) temperature estimates from the carbon cycle model of Lasaga *et al.* (1985).

other than photorespiration, τ is the specificity of Rubisco and { } denotes the returning the 'minimum of'. No attempt has been made to model changes in *Rd*, which is difficult to measure experimentally and to predict under changing environmental conditions (Harley *et al.* 1992; Lawlor 1993).

Rubisco activity limits the carboxylation rate according to:

$$W_c = \frac{V_{\max} c_i}{c_i + K_c\left(1 + \dfrac{O}{K_o}\right)}, \tag{2}$$

where $V_{\max}$ is the maximum rate of carboxylation and K_c and K_o are the Michaelis–Menten constants for carboxylation and oxygenation, respectively.

The rate of carboxylation, when limited solely by the rate of RuBP regeneration in the Calvin cycle, W_j, is mediated through the rate of electron transport (J):

$$W_j = \frac{J c_i}{4\left(c_i + \dfrac{O}{\tau}\right)}. \tag{3}$$

Light dependency of the model is achieved through its effects on electron transport according to:

$$J = \frac{\alpha I}{\left(1 + \dfrac{\alpha^2 I^2}{J^2_{\max}}\right)^{0.5}}, \tag{4}$$

where $J_{\max}$ is the maximum rate of electron transport, α is the efficiency of light conversion on an incident light basis (mol electrons/mol photons) (0.24) and I is photosynthetically active radiation (PAR) (μmol photons $m^{-2}\,s^{-1}$).

Temperature dependence of $V_{\max}$ and $J_{\max}$ is modelled by using fitted polynomials (McMurtrie & Wang 1993):

$$\begin{aligned} J_{\max} = J_m[1 &+ 0.0409(T-25) \\ &- 1.54 \times 10^{-3}(T-25)^2 \\ &- 9.4 \times 10^{-5}(T-25)^3]; \end{aligned} \tag{5}$$

$$\begin{aligned} V_{\max} = V_m[1 &+ 0.0505(T-25) \\ &- 0.248 \times 10^{-3}(T-25)^2 \\ &- 8.09 \times 10^{-5}(T-25)^3], \end{aligned} \tag{6}$$

where T is the temperature of the leaf (°C) and V_m and J_m are species-specific values of $V_{\max}$ and $J_{\max}$ at 25°C (μmol CO_2 $m^{-2}\,s^{-1}$ and μmol electrons $m^{-2}\,s^{-1}$, respectively). The temperature dependence of K_c, K_o and τ is each described by the exponential function

$$\text{Parameter}(K_c, K_o, \tau) = \exp\left(c - \frac{\Delta H_a}{R T_k}\right), \tag{7}$$

where c is a scaling constant, ΔH_a is an activation energy (kJ mol^{-1}), R is the gas constant (0.00831 kJ $K^{-1}\,mol^{-1}$), and T_k is the leaf temperature in kelvin. Here the value of c, and ΔH_a for K_c, K_o and τ, are those given by Harley *et al.* (1992) of 35.79, 9.59 and −3.949; ΔH_a values were 80.47, 14.51, −28.99, respectively. Note that the activation energy of τ is negative because it declines with increasing temperature. All of the above equations were encoded for computer simulations by using MATHCAD (1993).

The above model has been extensively validated against experimental observations obtained from plants growing in ambient and elevated CO_2 concentrations and under different partial pressures of oxygen (Harley *et al.* 1985, 1992). No attempt has been made to predict stomatal conductance by using the empirical relation described by Ball *et al.* (1987) which links stomatal conductance and assimilation rates. Stomatal responses to CO_2 over the past 120 Ma are unknown, although there is some evidence that the sensitivity of more recently evolved angiosperm taxa may be greater than those of gymnosperms (Robinson 1994). There is also the possibility that stomatal responses to CO_2 have changed over the course of evolutionary time since stomata must have opened under high CO_2 concentrations of the Silurian–Devonian (Ziegler 1987), implying an increased sensitivity to CO_2 in today's plants relative to those of the Siluro-Devonian. Therefore this paper focuses on the effects of palaeoatmospheres and temperatures on photosynthetic rates; stomatal conductance may be incorporated at a later date based on quantitative measurements of the fossil cuticles themselves (Beerling & Woodward 1993; Raven 1993).

(*b*) *Assumptions and limitations of the model applied to the geological past*

The above model of leaf photosynthesis has been used to investigate the effects of the increased O_2 and CO_2 content of the atmosphere, predicted from geochemical studies, by reconstructing A/c_i responses. Estimating leaf photosynthesis from these responses requires an estimate of the concentration of CO_2 inside the leaf (c_i). Recent measurements have shown that this value is typically 0.7 of the atmospheric CO_2 concentration (von Caemmerer & Evans 1991), resulting in a gradient of 30% between the inside and outside of the leaf in many C3 plants. In dealing with large historical changes in atmospheric CO_2 concentration (figure 1*a*) photosynthesis has been modelled by assuming that a 30% gradient is maintained between the leaf and the atmosphere. This assumption is in keeping with a recent theoretical analysis of plants growing under high Cretaceous CO_2 concentrations where the 'cost' of maintaining a 30% gradient is a percentage reduction in gross assimilation rate (Robinson 1994). Robinson's analysis showed that for plants growing in the Cretaceous the reduction was *ca.* 10% compared with 40% for plants growing in the present atmosphere. The modelling exercise presented in this paper assumes no major changes in the kinetic properties of Rubisco over the past 120 Ma with respect to (i) the requirement for high substrate availability, (ii) the degree of inhibition of the carboxylation function in the presence of O_2 and (iii) its ability to act as a mono-oxygenase to initiate the photorespiratory carbon cycle (Keys 1986). Sequence homologies, which test for these possible differences, indicate that no drastic changes of this nature have occurred (Troughton 1971; Badger & Andrews 1987); recent biochemical studies summarized by Raven (1993) further support this assumption.

4. EFFECTS OF CRETACEOUS AND TERTIARY PALAEOENVIRONMENTS ON LEAF PHOTOSYNTHESIS

(*a*) *O_2 effects*

From the palaeoatmospheric reconstructions it is apparent that plants growing in the Cretaceous environment would have experienced both CO_2 concentrations and temperatures higher than present (figure 1*a,c*). Together these two conditions would have dictated a capacity for high photosynthetic rates in the Cretaceous, an effect previously reported from modelling (Long 1991; Beerling & Woodward 1994) and experimental (Ryle *et al.* 1992; Mitchell *et al.* 1993) studies investigating the combined effects of elevated CO_2 and temperature on plant gas exchange. However, an important additional consideration is the O_2 content of the atmosphere, which greatly exceeded current values (figure 1*b*) at this time, and has important biological consequences for plants (Raven 1991; Raven *et al.* 1994).

In C3 plants the initial fixation of CO_2 is catalysed by the enzyme Rubisco. However, both O_2 and CO_2 compete for the Rubisco binding site, and if O_2 fixation occurs CO_2 is related by photorespiration (Brooks & Farquhar 1985; Lawlor 1993). Photorespiration is strongly dependent upon the ratio of atmospheric O_2:CO_2 and temperature. In general, an increased O_2 concentration (Harley *et al.* 1985) results in an increase in photorespiratory CO_2 losses, and an increase in temperature reduces the specificity of Rubisco for CO_2 in favour of O_2, further increasing photorespiration (Brooks & Farquhar 1985). Together both features result in a decline in photosynthetic efficiency. However, at high CO_2 concentrations photorespiration becomes suppressed (Ehleringer *et al.* 1991) by the competitive inhibition of oxygenation (Long 1991). Therefore in the Cretaceous period the question arises as to whether the high CO_2 concentration was sufficient to suppress increased photorespiration of the plants in the warmer temperatures and high O_2 content of the atmosphere.

This question was addressed by using the model to construct hypothetical A/c_i responses with an increased atmospheric O_2 content from 15 to 35%, representative of lower Triassic to upper Cretaceous O_2 limits, respectively (Berner & Canfield 1989). At a present-day c_i of 24.5 Pa this rise in O_2 content would have reduced photosynthetic rates by *ca.* 30% (figure 2) as a result of increased photorespiration. This reduction in photosynthetic rate becomes minimized at values of c_i likely to have been experienced by plants if atmospheric CO_2 concentrations rose to towards the upper Cretaceous estimates predicted by the Lasaga *et al.* (1985) carbon cycle model (figure 2). It seems therefore from this simple modelling exercise that some photorespiratory-related reductions in photosynthetic rate would have occurred, but that these were more than compensated for by the high atmospheric CO_2 concentrations of the Cretaceous and Tertiary, with plants having photosynthetic rates greater than present for a given temperature.

(*b*) *Combined CO_2, O_2, temperature and irradiance effects*

The rate of photosynthesis of leaves is, however, dependent on the interactive effects of CO_2, O_2, temperature and irradiance. Given that all three

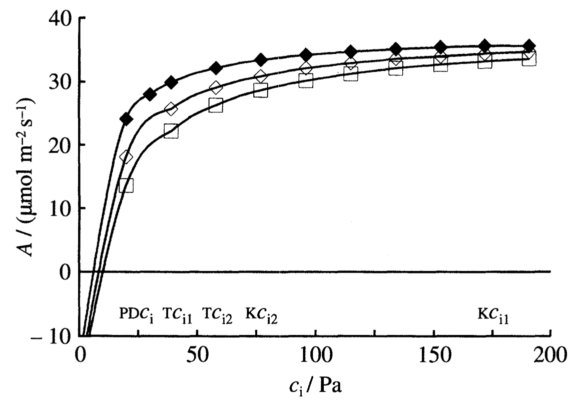

Figure 2. The effects of atmospheric O_2 concentration at 15% (filled diamonds), 25% (open diamonds) and 35% (squares) on photosynthetic rates as a function of the intercellular CO_2 concentration (c_i) in pascals. Also shown on the abscissa are average c_i values for the present day (PDc_i), the Tertiary based on the Lasaga *et al.* result (Tc_{i1}) and the Freeman & Hayes results (Tc_{i2}) and the Cretaceous based on the same two sets of results (Kc_{i1}, Kc_{i2}, respectively).

variables have been modelled or estimated for Tertiary and Cretaceous times, it becomes possible to investigate their combined effects on the theoretical A/c_i response of plants growing in these conditions. The results show that despite increased photorespiration rates, as a result of higher O_2 levels and temperatures, photosynthetic rates were probably greatest in the Cretaceous, and slightly lower in the Tertiary, relative to the present day, assuming that the c_i is approximately 70% of atmospheric concentrations (figure 3*a*).

Exposure of leaves to saturating irradiance for plants growing under field conditions in competition with other individuals is not guaranteed. Obviously, light is of crucial importance in regulating photosynthetic rates (Lawlor 1993) and in this model it determines the linear rate of electron transport from water to $NADP^+$, required in the reduced form, for the production of the acceptor molecule RuBP. At an irradiance of 300 $\mu mol\,m^{-2}\,s^{-1}$, light-limiting conditions for the leaves of many C3 species, photosynthetic rates are marginally lower in the Cretaceous than those of the present-day at c_i values of less than 100 Pa (figure 3*b*). Even above this c_i value, the photosynthetic benefit of high CO_2 concentrations is greatly diminished to the point where all the curves converge to give similar photosynthetic rates.

The modification of photosynthetic responses to increased O_2 and temperature by high and low irradiances suggests clear differences in the ability of plants to fix C by photosynthesis which are dependent upon their position and stature within the ecosystem. For example, tall conifers, with needle-like leaves and a high leaf-area index, would have been able to exploit these potentially photosynthetically productive conditions subject to modification by low water vapour pressure deficits and increased windspeeds, and the constraints of nutrient (see Lawlor *et al.* 1988) and water availability. Similarly, plants exploiting canopy gaps created by disturbance would, assuming the photosynthetic capability, also have benefited. In contrast, low-growing understorey plants receiving lower irradiance would have been unlikely to benefit to the same extent from the high atmospheric CO_2 concentration (which they experience under present conditions due to soil and (in the dark) plant respiration), in terms of photosynthetic C fixation, although a decreased vapour pressure deficit of the air and wind speed in these situations may partly offset the expected decline.

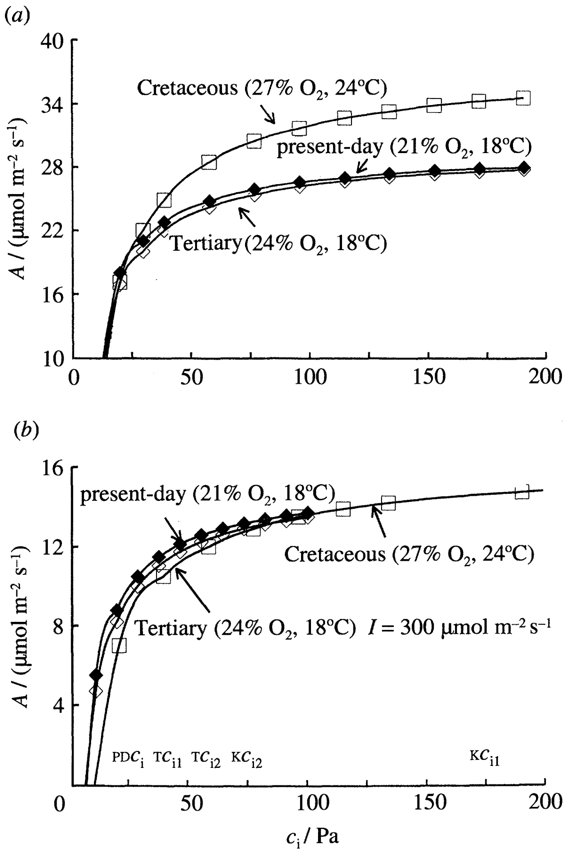

Figure 3. The combined effects of palaeo-O_2 and temperatures on the A/c_i response (*a*) at saturating irradiance (1000 $\mu mol\,m^{-2}\,s^{-1}$) and (*b*) under light-limiting conditions (300 $\mu mol\,m^{-2}\,s^{-1}$). Symbols on the abscissa as for figure 2.

(*c*) *Species-specific examples*

Standard values have been assigned to the maximum rates of carboxylation by Rubisco *in vivo* (V_{max}) and to the maximum rate of electron transport (J_{max}) to run the model for environments representing different geological periods. In reality the values of these two key regulatory parameters of leaf photosynthesis are species-specific and have been found to vary greatly across a wide range of C3 species with different ecological traits (Wullschleger 1993). Realistic modelling must take this variation into account.

The approach taken has been to investigate the different effects of palaeoenvironmental conditions of the past on taxa with different evolutionary histories. Selection of species from particular families follows the rationale of Robinson (1994) who has suggested that fast-evolving taxa are most likely to manifest stomatal optimization behaviour (see Cowan (1977) and Cowan & Farquhar (1977)). It is reasoned that where plants evolved in a low-CO_2 atmosphere, selection would have favoured the ability to optimize stomatal regulation of water loss, particularly in environments where light and water availability were variable. Consequently, Robinson (1994) suggests that CO_2 starvation favoured recently evolved grasses and discriminated against hard, needle-like leaf forms. Her literature review supported this interpretation, with stomatal sensitivity to environmental variables including light, humidity, leaf water potential and temperature increasing in the order herbs > woody angiosperms > gymnosperms. Therefore, assuming that the atmospheric history of the different groups has also influenced their photosynthetic capacity, as well as stomatal sensitivity (since both are linked to improved plant 'fitness'), three species were selected: one each to represent a gymnosperm, a woody angiosperm and a grass. The photosynthesis model has been parametrized for values of $V_{\max}$ (maximum rate of carboxylation) and $J_{\max}$ (maximum rate of electron transport) for *Pinus taeda* (gymnosperm), *Quercus rubra* (woody angiosperm) and *Festuca arundinacea* (grass) using the values reported by Wullschleger (1993). These species belong to the families Pinaceae, Fagaceae and Gramineae, the first two thought to have evolved in the early and late Cretaceous, respectively, and the latter in the early Tertiary (Thomas & Spicer 1987). Consequently, these species represent families with evolutionary origins at times of a progressively declining atmospheric CO_2 concentration. Selection of these contrasting evolutionary histories has been made on the assumption that these characteristics are retained in the present-day plants from these families.

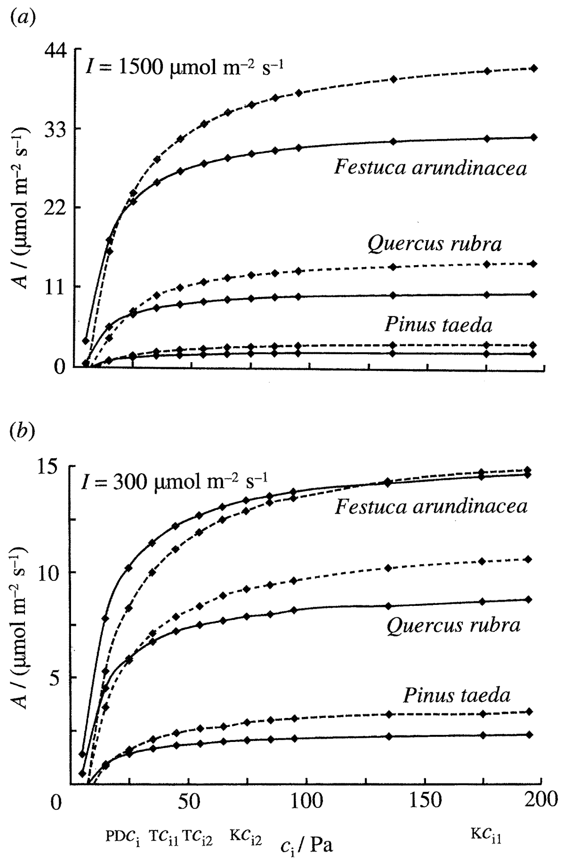

Figure 4. Species-specific examples of A/c_i responses in present atmospheric composition and temperature (continuous lines) and in Cretaceous atmospheres and temperatures (broken lines) under (*a*) saturating light conditions (1000 μmol m^{-2} s^{-1}) and (*b*) light-limiting (300 μmol m^{-2} s^{-1}) conditions. Values of $V_{\max}$ for *P. taeda*, *Q. rubra* and *F. arundinacea* were 18, 30 and 118 and of $J_{\max}$ were 20, 72 and 226 μmol m^{-2} s^{-1}, respectively (taken from Wullschleger 1993). Symbols on the abscissa as for figure 2.

Under saturating irradiance the grass *F. arundinacea* shows the greatest increase in photosynthetic rates of the three species as c_i increases towards Cretaceous levels, with a progressive decline in proportional benefit through *Q. rubra* and *P. taeda* (figure 4*a*). Under light-limiting conditions both *Q. rubra* and *P. taeda* still benefit, although to a lesser extent (figure 4*b*). The grass *F. arundinacea*, however, shows a decrease in photosynthetic rates at c_i values typical of the Tertiary and the Cretaceous (based on the Freeman & Hayes (1992) estimates of CO_2) not evident in the other two species. It is not until c_i reaches a value expected under the high CO_2 concentrations of the Lasaga *et al.* (1985) model, i.e. over 125 Pa, that some marginal benefit to photosynthesis accrues. These results emphasize the need for further palaeo-CO_2 estimates under these conditions to predict the gas exchange of plants growing in the geological past (figure 4*b*), especially in light-limiting conditions. Contrasting taxa serve to illustrate A/c_i responses for plants with different photosynthetic properties. The approach may be limited in its predictive capacity because possible adaptations, e.g. altered efficiency of light conversion (α in equation 7) in shade leaves relative to sun leaves (Givnish 1988), can be expected to play modifying roles not currently addressed by the model.

An evolutionary interpretation of figure 4(*a*,*b*) suggests that the grass *F. arundinacea*, representative of a taxon evolving under low CO_2 concentrations, has developed an innate capacity to increase CO_2 fixation rapidly should CO_2 become available, by virtue of its $V_{\max}$ and $J_{\max}$ characteristics. For the two taxa that have evolved under high CO_2 concentrations this capacity is much less. It appears, therefore, that species have evolved inherited differences in photosynthetic capacity at the biochemical level, possibly related to the CO_2 concentration under which the taxa first evolved. High innate photosynthetic capacity is apparently coupled with high stomatal sensitivity, ensuring that these species are able to maximize photosynthetic C fixation when conditions are suitable. Some evidence supporting the assumption that traits arising from plants with different evolutionary histories are retained through time comes from an analysis of A/c_i responses by Wullschleger (1993). This analysis of the $V_{\max}$ and $J_{\max}$ values for the 109 species reported indicates a significant difference for both $V_{\max}$ and $J_{\max}$ between conifers and woody angiosperms, but similar values for herbs and agricultural monocotyledons (figure 5).

It is interesting to note that concomitant with the rise of the angiosperms in the late Cretaceous there was a gradual decline in gymnosperms (Knoll 1986; Crane 1987; Spicer 1989*a*). The photosynthetic modelling studies (figures 2–4) and surveys of V_{max} and J_{max} for the two groups (figure 5) provide a mechanism at the scale of the individual leaf by which the angiosperms may have been able to express this effect in a competitive context, with the angiosperms becoming more efficient at photosynthetic C fixation at mid-latitudes. A further ecophysiological impact during the rise of the angiosperms, which could have been at the expense of the gymnosperms, may be related to the water-use efficiency (WUE) (units of C fixed per unit of water lost) of the two groups. Available climate data, summarized by Hendry (1993), indicate that over the past 65 Ma the climate of mid-latitudes became progressively drier and cooler. Therefore in mid-latitudes more efficient water use may have been a competitive advantage. On a global scale, present-day measurements indicate that gymnosperms in general have a lower WUE than angiosperms, as inferred from discrimination against ^{13}C (D. J. Beerling & F. I. Woodward, in preparation) and instantaneous transpiration rates (Woodward & Smith 1994*a*). This appears to arise in part through lower stomatal sensitivities of the gymnosperms (Robinson 1994; Körner 1994). Therefore the angiosperms, from an ecophysiological point of view, may have functioned in the late Cretaceous at mid-latitudes with a higher water-use efficiency and higher C fixation rate, both of which are features that would be predicted to contribute to their successful domination of the gymnosperms. At higher latitudes the advantages of angiosperm C gain may have been offset by the evergreen habit of conifers, allowing C fixation to continue throughout the year and reducing the large energy expenditure required to re-establish a deciduous canopy at the beginning of the growing season. At these higher latitudes the apparently xerophytic morphology of gymnosperm needles, including sunken stomata, thick cuticles and epicuticular waxes (Larcher 1973), and other ecophysiological traits (Woodward 1987) significantly reduce transpirational water losses relative to angiosperms.

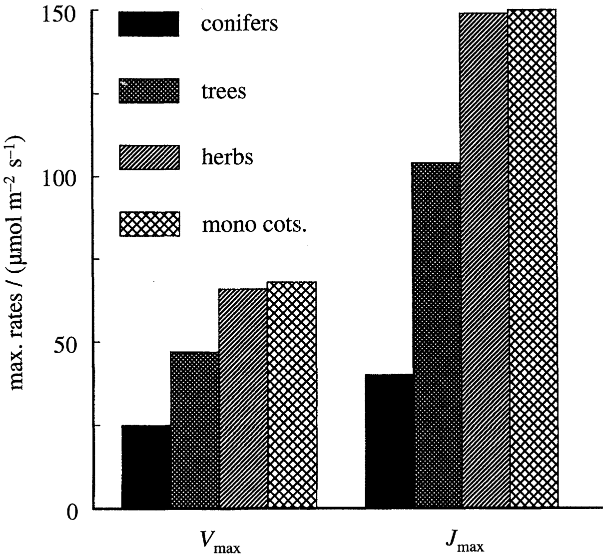

Figure 5. Mean values of V_{max} and J_{max} for conifers, angiosperm trees, herbs and agricultural monocotyledons, as reported by Wullschleger (1993); $n = 10$, 19, 10 and 12, respectively. Significant differences ($p < 0.001$) were detected between V_{max} and J_{max} values of conifers and angiosperm trees (orthogonal contrasts).

It is not being suggested that the differences in photosynthetic C fixation and WUE between angiosperms and gymnosperms in response to palaeoatmospheric and environmental change over the past 120 Ma are solely responsible for the changes in the dominance of these two groups. Possible explanations for this phenomenon have recently been reviewed in relation to this topic (Friis *et al.* 1987; Crane 1987); rather, the model results indicate that these ecophysiological differences may also have contributed to the switch in dominance of the two groups and that this has not previously been highlighted by use of a mechanistic model of photosynthesis.

5. PHOTOSYNTHETIC RATES RECONSTRUCTED THROUGH GEOLOGICAL TIME

So far this paper has considered the effects of Cretaceous–Tertiary environments on the potential photosynthetic rates of leaves by means of a mechanistic biochemical model capable of including the effects of light, CO_2, O_2 concentrations and temperature for taxa that evolved under different CO_2 concentrations. The continuously changing palaeoenvironmental conditions of the past 120 Ma, however, require a continuous modelling approach to view an overall pattern of changing photosynthetic rates. This is particularly apparent given the contrasting changes in atmospheric O_2 and CO_2 content over this time (figure 1*a*,*b*).

This approach has been adopted in the following section for representatives of the gymnosperm and angiosperm groups, based on the palaeo-CO_2 estimates of Lasaga *et al.* (1985) and Freeman & Hayes (1992). Continuous photosynthetic rates have been modelled at saturating (1000 µmol m^{-2} s^{-1}) and light-limiting conditions (300 µmol m^{-2} s^{-1}) using values of V_{max} and J_{max} for the gymnosperm *P. taeda* reported by Wullschleger (1993) (figure 6*a*). The overall trend shows one of decreasing photosynthetic rates over the past 120 Ma. Despite high Cretaceous O_2 levels prevailing until the K–T boundary (65 Ma BP), photosynthetic rates were still above those expected in the Tertiary because of the warmer temperatures. The high CO_2 concentrations of the Cretaceous and Tertiary largely saturate Rubisco and substantially reduce the oxygenation reaction, so that photosynthetic rates seem to be controlled by temperature. This overall pattern of responses does

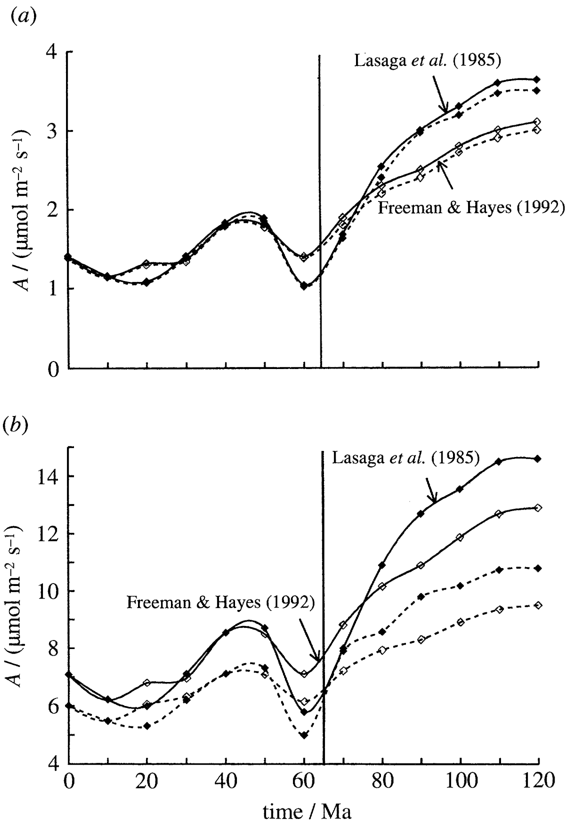

Figure 6. Reconstructed photosynthetic rates for the past 120 Ma for (*a*) the gymnosperm *P. taeda* and (*b*) the angiosperm tree *Q. rubra* at saturating (continuous lines) ($1000\,\mu mol\,m^{-2}\,s^{-1}$) and light-limiting (broken lines) ($300\,\mu mol\,m^{-2}\,s^{-1}$) conditions, based on the CO_2 estimates of Lasaga *et al.* (1985) and Freeman & Hayes (1992). V_{max} and J_{max} values as for figure 4.

not appear to differ under light-limiting conditions (figure 6*a*); because Rubisco is largely saturated even at the atmospheric CO_2 concentrations estimated by Freeman & Hayes (1992), both curves show photosynthetic rates of a similar magnitude and a similar pattern of change.

A second set of predictions have been made for the woody angiosperm *Q. rubra* as a representative of the Fagaceae, which evolved in the late Cretaceous. Despite the late appearance of the family in the fossil record it is instructive to model changes in the photosynthetic rate of this species over the past 120 Ma for comparison with the gymnosperm response. The curve shows the same general decline in photosynthetic rates as for the gymnosperm (figure 6*b*). Although the absolute rates of leaf photosynthesis are about three times greater than for *P. taeda*, this time the rate of decline from the late Cretaceous to the Tertiary is steeper and there is much more pronounced effect of reduced irradiance on the photosynthetic rates of *Q. rubra*. Nevertheless, this effect does not change the overall pattern through time, indicating the dominance of temperature in controlling photosynthesis. Interestingly, the curves of both species (figure 6*a*,*b*) show a pronounced increase in photosynthetic rates during the Eocene temperature maximum which occur largely in response to the warm temperatures and to the decline in O_2 content reducing photorespiratory CO_2 losses.

The saturation of Rubisco at the CO_2 concentrations prevailing in the Cretaceous and Tertiary, by either estimate of CO_2 (figure 1), largely reconciles the paradox of the productivity of C3 plants at high latitudes (Spicer 1989*b*). Spicer (1989*b*) argued that at high latitudes the high atmospheric O_2 content and temperatures of the Cretaceous ought to have been detrimental to C3 systems, because of enhanced photorespiration, yet the palaeobotanical evidence indicates that high-latitude vegetation was extremely productive during this time. The present modelling studies show that in fact the high atmospheric O_2 content and temperatures of the Cretaceous were not sufficient to depress photosynthetic rates because of the overriding effect of increased atmospheric CO_2 concentration, which allowed vegetation to realize a high productivity. This is an effect that has recently been demonstrated by observations of field-grown plants exposed to increased O_2 and temperature while growing under CO_2 enrichment (Sage & Sharkey 1987).

An important feature not included on the photosynthesis curves (figure 6*a*,*b*) is the effect of a Cretaceous–Tertiary boundary impact event characterized by an initial decline in global temperatures and light intensities (Wolf & Upchurch 1986; Wolfe 1991). Recent calculations suggest that the impact of a bolide *ca.* 5 km in radius onto carbonate-rich terrain would have elevated atmospheric CO_2 levels by two to ten times globally for several million years, and probably longer if CO_2 degassing from the photic zone of the ocean was accounted for (O'Keefe & Ahrens 1989). Consequently, plants establishing after this event would have experienced a globally warmed atmosphere with a high concentration of atmospheric CO_2, and increased precipitation, at least in mid-latitudes (Spicer 1989*a*): conditions ideal for maximizing photosynthetic C fixation. We might expect therefore, at some point after 65 Ma before present (BP), a short-lived increase in leaf photosynthesis, which has not been accounted for in the present study.

6. DISCUSSION

From long-term Phanerozoic models of CO_2 change (Berner 1990, 1992, 1993) it is clear that plants evolved in an atmospheric CO_2 concentration well above that of the present-day. In Silurian atmospheres the Rubisco of extant C3 terrestrial plants would have been CO_2-saturated (Raven 1993) and in Cretaceous and Tertiary atmospheres leaf photosynthesis would have been similarly CO_2-saturated, with the rate controlled by electron transport (J_{max}) and temperature. The former effect is shown in figure 3(*a*,*b*) where typical Cretaceous and Tertiary c_i values correspond to the asymptotic portion of the curves. In contrast, terrestrial vegetation growing in the present concentrations of atmospheric CO_2 and O_2 realizes only 60–70% of its photosynthetic potential (Bowes 1993), because of the kinetic constraints imposed by Rubisco.

Estimates of the palaeophotosynthetic rates of terrestrial C3 plants over geological timescales provide an indication of possible rates of drawdown of CO_2 by individual leaves exposed to potentially non-limiting and limiting irradiance without water limitation. At this point the model represents only the initial enzymic fixation of CO_2 in the chloroplast by Rubisco for leaves in the upper and lower layers in the canopy. Note that the model makes no predictions for changes in the *amount* of Rubisco under the different atmospheres of the Cretaceous and Tertiary. Evaluating the possible impact of Cretaceous and Tertiary atmospheres and temperatures on gross photosynthetic CO_2 drawdown requires scaling the model to estimate canopy photosynthesis, using estimates of palaeo-leaf area index from the fossil record and a consideration of N supply from the soils (Woodward & Smith 1994*a*,*b*). N-uptake rates may be estimated by use of Cretaceous and Tertiary palaeosol C values (Cerling 1984, 1991) and applying them to the relation established experimentally, and in the field, between N-uptake rate by plants and soil C (Woodward & Smith 1994*a*,*b*). This canopy model would then require application in a global context by using globally reconstructed patterns of vegetation types (Barron & Washington 1985; Wolfe 1985; Tallis 1991) and climate (Barron & Washington 1982; Barron *et al.* 1993) for distinct intervals in the Cretaceous and Tertiary periods. Estimates of gross photosynthetic CO_2 drawdown made in this way may then provide fine-scale modification of the long-term CO_2 dynamics (Olson *et al.* 1985) controlled by carbonate weathering (Berner 1993) on timescales of millions of years. Scaling to the canopy and application of the canopy model globally may also be used to estimate the primary productivity of fossil forests, which can then be compared with those obtained from measuring the diameters of fossilized tree trunks and sequences of ring-widths (Creber & Francis 1987; Chaloner & Creber 1989). These will be future model developments.

Validation or testing of the predictions of ancient photosynthetic rates presented here may be achieved by (i) studies on the carbon isotope composition ($\delta^{13}C$) of organic material and (ii) reconstructed gas-exchange processes from quantitative calculations based on analysis of fossilized leaf cuticles. Isotopic studies hold real promise for testing these results in a semi-quantitative manner (Farquhar *et al.* 1982). At present there have been no continuous estimates of changes in $\delta^{13}C$ from analyses of leaf material spanning the Cretaceous and Tertiary from which it may be possible to estimate limitations of photosynthesis by the biochemical and diffusional components of leaves. So far, $\delta^{13}C$ analyses of the C content of marine sediments have only been able to confirm that phototrophic organisms were operating at higher CO_2 concentrations in the Cretaceous ($\geqslant 4$ times) and that this situation changed in the Tertiary (Schidlowski 1987; Raven & Sprent 1989). Further $\delta^{13}C$ measurements on C3 leaf material are clearly required, to improve our understanding of the physiological functioning of plants in the Cretaceous and Tertiary.

Reconstructions of the gas exchange rates of plants (Raven 1993; Beerling & Woodward 1993; Beerling 1994) based on quantitative measurements of fossil cuticles may be used to make comparisons with the predictions made here. A test of the present model has been devised by using the quantitative reconstructions reported by Raven (1993) for a land plant axis (1 mm in diameter, 100 mm tall) photosynthesizing in the Silurian – early Devonian atmosphere. Raven (1993) estimated that a stoma-bearing embryophyte growing in the prevailing concentrations of CO_2 and O_2 had a potential photosynthetic rate of *ca.* $20\,\mu mol\,m^{-2}\,s^{-1}$. By comparison the biochemical model of C3 photosynthesis used here, given the same values of CO_2, O_2, temperature and irradiance and parametrized for a *Lobelia* spp.-type axis, predicts a photosynthetic rate of $16\,\mu mol\,m^{-2}\,s^{-1}$. The similarity of these two estimates provides evidence for the ability of both approaches to arrive at comparable rates of photosynthesis for plants growing in the geological past, although the best test of the modelling approach will ultimately come from quantitative reconstructions based on measurements of stomatal dimensions of Cretaceous and Tertiary cuticles.

Water availability is a key consideration likely to modify the photosynthetic rates of plants locally and globally. Water availability impacts indirectly on photosynthesis by affecting stomatal conductance, and hence the intercellular CO_2 concentration (c_i). Stomatal conductance is also influenced by additional factors including wind speed and vapour pressure deficit through changes in the leaf and canopy boundary layer conductance (Grace 1977; Friend & Woodward 1990; Kim & Verma 1991). Therefore we may expect that the c_i values given in figures 2–4 would have been altered in a manner consistent with palaeo-changes in these variables. At present the sensitivity of leaf photosynthesis to these changes has not been included in the model because of the requirement for an estimate of stomatal conductance (Ball *et al.* 1987; Aphalo & Jarvis 1993). Estimates of stomatal conductance, either from modelling or measurements made on fossil cuticles, could then be used to incorporate these effects, based on reconstructions of humidity and water availability from dust profiles (Rea *et al.* 1985), leaf physiognomy (Spicer & Parrish 1990) and general circulation models (Barron *et al.* 1993). However, these fine-scale refinements of the model would have to result in a CO_2 gradient between the leaf and the atmosphere of over 70%, twice the present-day situation, to affect leaf photosynthetic rates. Besides water availability, the ability of a plant to develop its root system adequately, because of soil restrictions, may also prove important in regulating photosynthesis. Experiments on plants grown in elevated CO_2 concentrations have shown that when root growth is restricted the activity of Rubisco decreases (Thomas & Strain 1991); this decrease indicates the possible existence of a feedback mechanism whereby source–sink balance, rather than atmospheric CO_2 alone, may regulate photosynthesis. Consideration of this aspect of plant responses to CO_2 in the Cretaceous and Tertiary is difficult to envisage;

nevertheless, it remains an important conceptual issue.

7. CONCLUSION

The approach of coupling geochemical model outputs of CO_2, O_2 and temperature, and estimates of CO_2 by isotopic fractionation represented in fossil porphyrins, with mechanistic models of leaf biochemistry, provides a method of reconstructing past rates of C3 photosynthesis of terrestrial vegetation. The philosophy behind this paper has been to explore the effects of changing palaeoatmospheres on leaf photosynthesis, and although Moore (1989) rightly states 'the responses of plants now extinct to atmosphere variations [of the type considered here] can never be fully known' the approach adopted here provides some insights with which to reconcile the palaeobotanical evidence with mechanistic ecophysiological explanations. Testing and validation of the results is required based upon quantitative reconstructions from fossil cuticles and stable carbon isotope analyses and these will be the subject of future study in Sheffield.

I thank Professor W. G. Chaloner, Professor D. J. Read, Professor F. I. Woodward, Dr G. A. F. Hendry, Dr P. L. Mitchell, Dr W. P. Quick and Miss S. Diamond for helpful discussions during the preparation of this manuscript.

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Received 29 March 1994; accepted 6 May 1994