

Carbon dioxide and climate over the past 300 Myr

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The link between atmospheric CO₂ levels and global warming is an axiom of current public policy, and is well supported by physicochemical experiments, by comparative planetary climatology and by geochemical modelling. Geological tests of this idea seek to compare proxies of past atmospheric CO₂ with other proxies of palaeotemperature. For at least the past 300 Myr, there is a remarkably high temporal correlation between peaks of atmospheric CO₂, revealed by study of stomatal indices of fossil leaves of *Ginkgo*, *Lepidopteris*, *Tatarina* and *Rhachiphyllum*, and palaeotemperature maxima, revealed by oxygen isotopic ($\delta^{18}\text{O}$) composition of marine biogenic carbonate. Large and growing databases on these proxy indicators support the idea that atmospheric CO₂ and temperature are coupled. In contrast, CO₂–temperature uncoupling has been proposed from geological time-series of carbon isotopic composition of palaeosols and of marine phytoplankton compared with foraminifera, which fail to indicate high CO₂ at known times of high palaeotemperature. Failure of carbon isotopic palaeobarometers may be due to episodic release of CH₄, which has an unusually light isotopic value (down to -110% , and typically -60% $\delta^{13}\text{C}$) and which oxidizes rapidly (within 7–24 yr) to isotopically light CO₂. Past CO₂ highs (above 2000 ppmv) were not only times of catastrophic release of CH₄ from clathrates, but of asteroid and comet impacts, flood basalt eruptions and mass extinctions. The primary reason for iterative return to low CO₂ was carbon consumption by hydrolytic weathering and photosynthesis, perhaps stimulated by mountain uplift and changing patterns of oceanic thermohaline circulation. Sequestration of carbon was promoted in the long term by such evolutionary innovations as the lignin of forests and the sod of grasslands, which accelerated physicochemical weathering and delivery of nutrients to fuel oceanic productivity and carbon burial.

Keywords: carbon dioxide; temperature; oxygen isotopes;
stomatal index; *Ginkgo*; *Lepidopteris*

1. Introduction

The idea that rising atmospheric CO₂ causes global warming is now much in the news, and guides international industrial and conservation policies (Houghton *et al.* 2001). The idea was first established experimentally by Tyndall (1861), then applied to calculate global warming by Arrhenius (1896). Further support came from planetary exploration, particularly as an explanation for the temperatures of Venus, Mars and the early and current Earth (Sagan & Mullen 1972). Mass-balance geochemical models of carbon sequestration and oxidation demonstrate how temporal changes

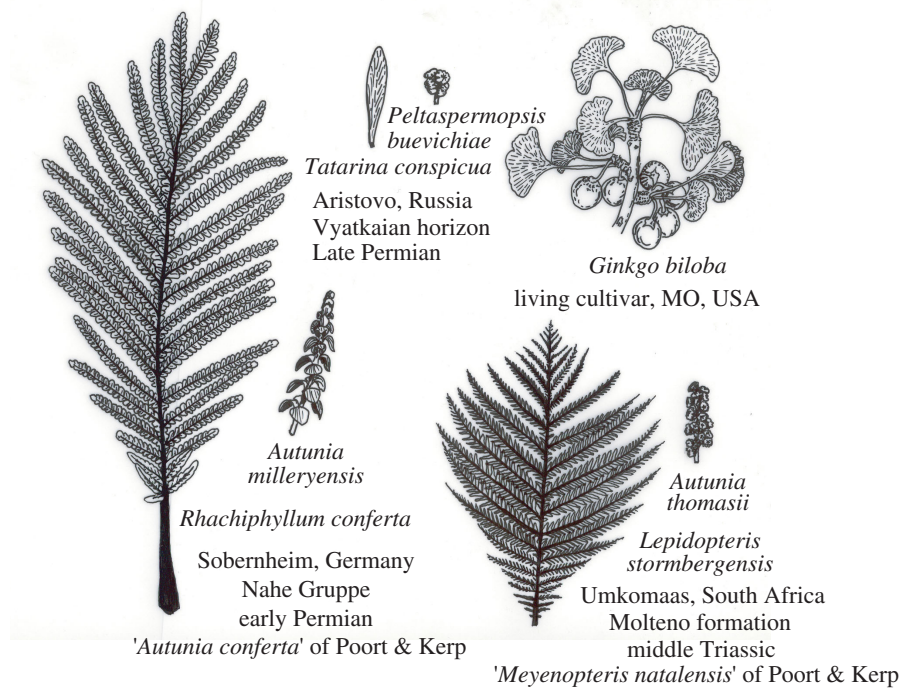


Figure 1. Leaves and ovulate structures of *Ginkgo*, *Lepidopteris*, *Tatarina* and *Rhachiphyllum*. Stomatal indices from cuticles of these taxa were used to construct palaeoatmospheric CO₂. Illustrations are adapted from Gomankov & Meyen (1986), Kerp (1988), Anderson & Anderson (1989) and Poort & Kerp (1990). Plant names follow traditional form genera, but '*Autunia conferta*' and '*Meyenopteris natalensis*' are taxa of Kerp (1988) and Poort & Kerp (1990) with unconventional typification and definition.

in different parts of the carbon cycle regulate the CO₂ content of the atmosphere (Bernier & Kothavala 2001). Such models are judged a success by the degree to which their predicted times of high CO₂ match times of high temperature indicated by other palaeoclimatic proxies, for example the distribution of thermophilic ecosystems (fossil reefs and bauxites) and of organisms (large foraminifera and entire-margined leaves (Parrish 1998)). In this account I use as a proxy for global palaeotemperature the inverse relationship between temperature and oxygen isotopic value ($\delta^{18}\text{O}$) of marine foraminifera, molluscs and brachiopods (Veizer *et al.* 2000; Zachos *et al.* 2001). As a proxy palaeobarometer of CO₂, I extend and emend my database (Retallack 2001) on the stomatal index of fossil leaves of four closely related gymnosperms: *Ginkgo*, *Lepidopteris*, *Tatarina* and *Rhachiphyllum* (figure 1). This palaeobotanical palaeobarometer is based on the observation that plant leaves have fewer stomates when atmospheric CO₂ is high than when atmospheric CO₂ is low (Beerling *et al.* 1998). Taken together, these two proxies show strong support for CO₂–temperature coupling over the past 300 Myr. Other proxy palaeobarometers—such as the carbon isotopic composition of palaeosols (Ekart *et al.* 1999; Tanner *et al.* 2001) and of marine phytoplankton compared with foraminifera (Pagani *et al.* 1999, 2000), which appear to indicate CO₂–temperature uncoupling (Cowling 1999; Veizer *et al.* 2000)—may be compromised by isotopically unusual methane–clathrate dissociation

events (Retallack 2001). This issue of coupling–uncoupling is addressed here, as well as possible reasons for the striking fluctuation in atmospheric CO₂ and temperature over geological time-scales.

2. New and enlarged data on stomatal index of fossil leaves

The black carbonaceous film adhering to some fossil leaves has long been prized by palaeobotanists because it includes remains of external cuticle with outlines of epidermal cells, stomatal cells and other epidermal features (figure 2). Such cellular details offer insights into both botanical relationships and palaeoenvironments of fossil plants (Dilcher 1974; McElwain & Chaloner 1996; Kerp & Krings 1999). Study of cuticles from living plants has shown that stomatal density is changed by different partial pressures of atmospheric CO₂, as well as by insolation, water stress, in sun leaves rather than shade leaves, and in some taxa compared with other taxa (Kürschner *et al.* 1996; Kürschner 1997). The differing sensitivity of different taxa to CO₂ can be mitigated by confining analysis to phylogenetically related taxa, such as *Ginkgo*, *Lepidopteris*, *Tatarina* and *Rhachiphyllum* (figure 1), which include living representatives whose response to CO₂ can be studied in the greenhouse and from herbarium specimens (Beerling *et al.* 1998; Retallack 2001; Royer *et al.* 2001a). The problem of finding functionally comparable plants prevents ready extension of this stomatal record back further than the Permian (Edwards 1998; Cleal *et al.* 1999). Stomatal subsidiary cells of *Ginkgo*, *Lepidopteris*, *Tatarina* and *Rhachiphyllum* commonly have a darker (because they are thicker) cuticle than do epidermal cells of the cuticle, and hollow papillae around the stomatal pit (figure 2a), which Kräusel (1923) concluded were primitive seed plant characters, as well as functionally comparable. A mix of sun and shade leaves is suspected if there is high variance in stomatal index or hydathode-like trichomes, as is the case for some fossil species of *Lepidopteris* (Townrow 1960) and *Ginkgo* (figure 2). High water stress that might compromise cuticles as a record of past CO₂ is partly filtered out of the fossil record by the humid, lowland, preservational environments required for cuticular preservation of fossil leaves (Retallack 1998). Nevertheless, high salinity, low pH, lack of water and high insolation all have effects on epidermal cell size, and some plants have epidermal cells of different size on either side of the leaf. These compromising variables can be factored out by calculating the stomatal index (SI) in per cent (Salisbury 1927), using the formula:

$$\text{SI} = 100 \frac{N_s}{N_s + N_e},$$

where N_s is the number of stomates and N_e is the number of epidermal cells in the same area of cuticle. Because stomatal index, unlike stomatal density, is independent of cell size, it is widely used as a palaeobarometer of atmospheric CO₂ concentrations (Beerling *et al.* 1998; McElwain *et al.* 1999; Retallack 2001; Royer *et al.* 2001a).

Rarefaction analysis showed that at least 500 epidermal cells should be counted in order to be within the standard deviation of a count of 6000 cells (Retallack 2001). Eighty-seven fossil leaf records passed this minimal standard and allowed construction of a preliminary curve for stomatal index variations over the past 300 Myr. This curve was converted to estimates of CO₂ concentration in ppmv using a transfer function derived from the stomatal index of greenhouse *Ginkgo* leaves grown under known CO₂ and of herbarium specimens of *Ginkgo* that span the known post-industrial rise

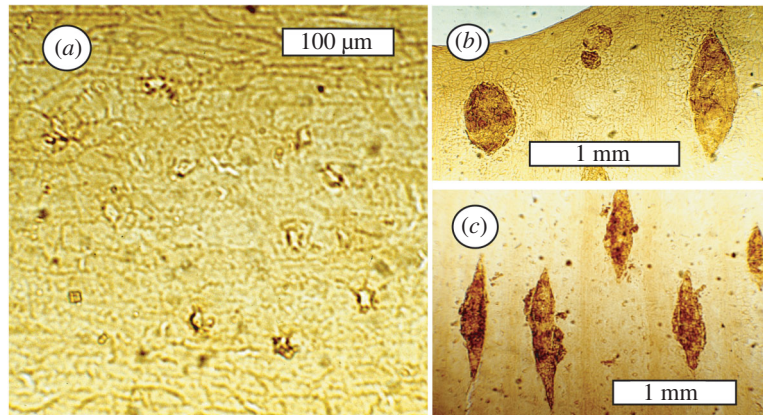


Figure 2. Cuticles of *Ginkgo adiantoides* from the Middle Miocene (16 Ma), Upper Cedarville Formation at 49 Camp, Washoe County, NV (Lamotte 1936), showing papillate subsidiary cells to stomates (a), and large multicellular trichomes, here interpreted as hyathodes ((b), (c)). This is University of California, Berkeley, Museum of Paleontology, cuticle preparation 849.

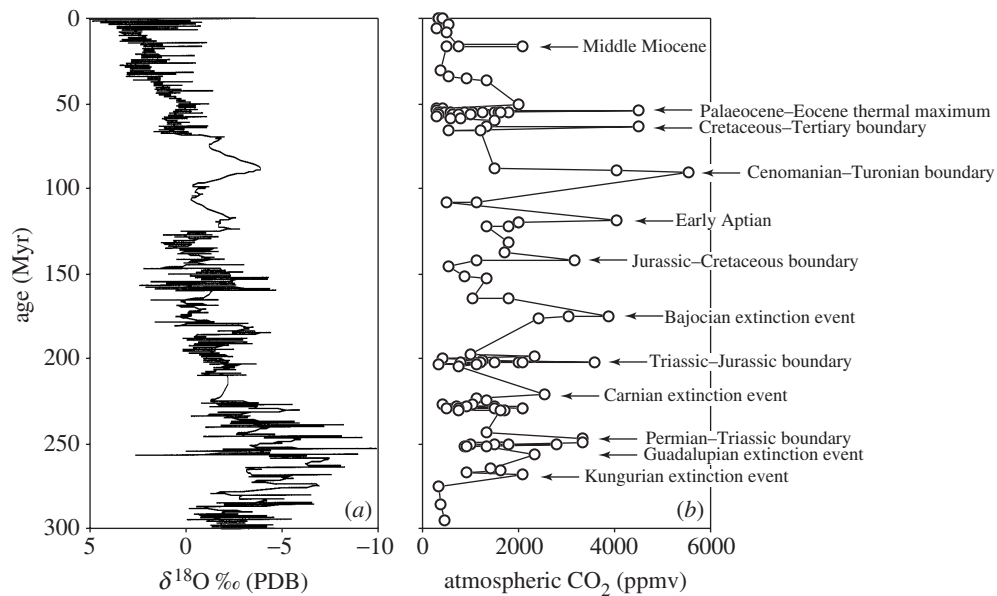


Figure 3. Over the past 300 Myr, maxima in palaeotemperature estimated from oxygen isotopic values ($\delta^{18}\text{O}$) of marine biogenic carbonate (part (a) data from Veizer *et al.* (2000), Zachos *et al.* (2001)) align with maxima in the CO_2 concentration of the atmosphere estimated from the stomatal index of fossil leaves (part (b) data from Retallack (2001), Royer *et al.* (2001a), supplemented here). The oxygen isotopic data have been corrected for the terminal Permian at 250 Ma and terminal Triassic at 200 Ma (following Retallack 2001), and smoothed by a five-point moving average, but not detrended.

of CO_2 (Retallack 2001). Subsequently, new determinations of stomatal index and an alternative transfer function have been published (Royer *et al.* 2001a), which, along with a new record reported here (figure 2), bring the total number of records to 115

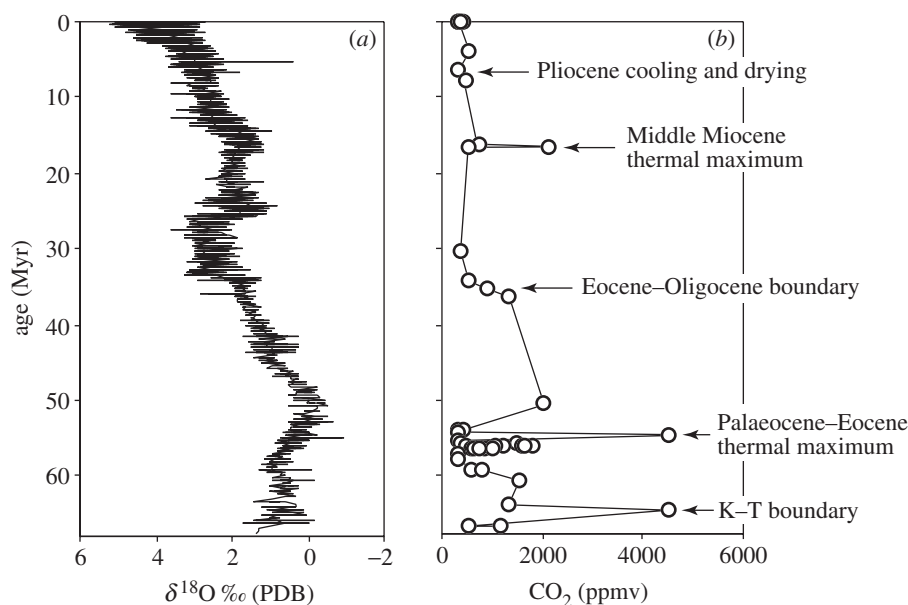


Figure 4. Variation over the past 67 Myr of oxygen isotopic composition ($\delta^{18}\text{O}$) of marine biogenic carbonate (part (a), from Zachos *et al.* (2001)), and of the CO_2 concentration of the atmosphere estimated from the stomatal index of selected fossil leaves (part (b), from Retallack (2001), Royer *et al.* (2001a), with additional data explained in the text).

for the past 300 Myr. These new stomatal indices are incorporated into the compilations presented here (figures 3 and 4). However, the transfer function of Royer *et al.* (2001a) is an inverse that declines to an asymptote at stomatal index 6, and so cannot be used for the stomatal indices of less than 6 in my compilation (Retallack 2001). My quadratic transfer function (Retallack 2001) is also preferred for the time being, because preliminary modelling using Fickian diffusion (by my colleague Jonathan Wynn) suggests that it is a theoretically better fit.

There is much room for improvement on these data, and on theoretical and empirical transfer functions for atmospheric CO_2 . Kerp (2002) has indicated mistaken labelling of plant cuticles in his publications (Kerp 1988, 1990) that affect one of my data points (see the supplementary information in Retallack (2001)). ‘*Autunia conferta*’ (he uses that name to include both *Autunia milleryensis* and *Rhachiphyllum conferta* from conventional-form generic nomenclature) said to be from ‘Sobernheim’ and ‘Lebach’ is really from Langenthal, for which the emended stomatal index should be 8.6 ± 1.1 (standard deviation of three fragments including 797 epidermal cells and 80 stomates), with a geological age better given as 285 ± 3 Ma (following Lippolt & Hess 1989).

I have also recently been able to study the cuticle of *Ginkgo adiantoides* (figure 2) from the Middle Miocene, Upper Cedarville Formation at 49 Camp, Washoe County, NV (Lamotte 1936). The 49 Camp flora is sandwiched by volcanic ashes dated at 16.28 ± 0.02 and 15.84 ± 0.05 Ma (Bonham 1969; Perkins *et al.* 1998), and much more accurately dated than the Middle Miocene leaves from Zakarnatskie, Russia, in my original compilation (Retallack 2001). I counted 34 separate fields of view at magnifications of 160 for a total of 11 623 epidermal cells and 945 stomates

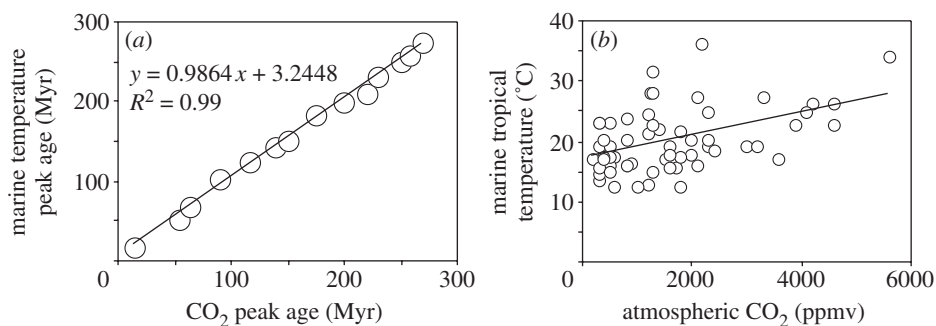


Figure 5. Correlations between (a) times of palaeotemperature maxima estimated from marine biogenic oxygen isotopic minima versus atmospheric CO₂ maxima estimated from stomatal index minima, and (b) marine palaeotemperature estimated from the detrended oxygen isotopic composition ($\delta^{18}\text{O}$) of marine biogenic carbonate and the CO₂ concentration of the atmosphere estimated from the stomatal index of selected fossil leaves interpolated at 5 Myr increments over the past 300 Myr. The timing of peaks in temperature and CO₂ is highly correlated (a), but their relative magnitude is not (b).

to determine a mean stomatal index of 7.6 ± 1.3 . The four cuticle fragments from 49 Camp are covered in abundant, dark, lenticular-ellipsoidal features (figure 2b, c), averaging $615 \pm 296 \mu\text{m}$ long by $210 \pm 52 \mu\text{m}$ wide. These were originally interpreted by Lamotte (1936) as infestations, but none shows necrotic reaction rims, giant cells, or cellular deformation expected from fungal decay, nematode or insect galls (Meyer & Maresquelle 1983; Waggoner 1999). Furthermore, such lenticular features have been found on ginkgo-like leaves of Rhaetian (200 Ma (Kirchner 1992, plate 1, fig. 5)), Callovian (160 Ma (Krassilov 1972, plate X, fig. 6)) and Aptian age (117 Ma (Krassilov 1972, plate VII, fig. 5)). I interpret them as hydathodes (water-regulatory trichomes (Uphof 1962)), comparable with the blisters of fossil *Lepidopteris* (Townrow 1960), pearl glands of living *Leea* (Ampelidaceae), and peltate trichomes of living *Clerodendron* (Verbenaceae (Metcalf & Chalk 1950)). This interpretation is especially indicated by the tubular aperture visible at either end (figure 2c), and is compatible with water stress to be expected at high temperatures, indicated by the associated flora (Graham 1999) and its lake margin habitat (Lamotte 1936).

In addition to stomatal index, plant-cuticle thickness and stomatal size also appear to be sensitive to atmospheric CO₂. The cuticles of earliest Triassic '*Dicroidium*' *callipteroides* (better assigned to *Lepidopteris* (Retallack 2000a)) have an unusually low stomatal index, indicating CO₂ levels of $3314 \pm 1097 \text{ ppmv}$ (12 ± 4 times the present atmospheric level (PAL) (Retallack 2001)). Maceration in Schultz's solution (Kerp & Krings 1999), which takes minutes or hours for most fossil plants, takes days or weeks for '*D.*' *callipteroides*. The cuticles are unusually thick (5–10 μm), with internal flanges that reach down as much as 10 μm between the periclinal walls of the stomatal and epidermal cells. Stomatal guard cells of '*D.*' *callipteroides* are also small ($24 \pm 4 \mu\text{m}$ long): about a third of the length of guard cells in Permian *Rhachiphyllum* from Crock, Germany ($62 \pm 11 \mu\text{m}$) and about half the length of guard cells in Middle Miocene *Ginkgo* from 49 Camp ($41.4 \pm 5 \mu\text{m}$) and in living *Ginkgo* ($42 \pm 5 \mu\text{m}$ on leaves picked in Eugene in 2000 and $45 \pm 5 \mu\text{m}$ on leaves picked in East Lansing in 1888 (Retallack 2001)). This size difference is not obvious from illustrations of

cuticle, because the epidermal and subsidiary cells of ‘*D.*’ *callipteroides* cuticles are all proportionally small.

3. CO₂–temperature coupling

Temperature–CO₂ coupling is demonstrated well by 300 Myr time-series for oxygen isotopic composition of marine biogenic carbonate and for CO₂ concentrations derived from plant stomatal index, which show striking coincidences in peaks and valleys (figures 3 and 4; see also Kürschner (2001)). The degree of correspondence is shown well by the cross-correlation of ages of palaeotemperature peaks inferred from oxygen isotopic values for marine biogenic carbonate (Veizer *et al.* 2000) and of CO₂ peaks inferred from stomatal index (Retallack 2001). Thus times of warm palaeotemperature in the ocean from oxygen isotopic values correspond with times of high atmospheric CO₂ from stomatal index (figure 5*a*). The magnitudes of the temperature and CO₂ excursions also correlate positively, but not significantly (figure 5*b*). For this comparison, data were resampled at 5 Myr intervals, CO₂ partial pressure was calculated from the stomatal index using the transfer function of Retallack (2001), and (using detrending and the 3/6 smoothing of Veizer *et al.* (2000)) oxygen isotopic values were converted to temperatures using the transfer function of Arthur *et al.* (1983). The lack of strong correlation between the magnitudes of the excursions may be because of inadequate sampling or differing sensitivity of either proxy. Even with 12 709 oxygen isotope values compiled from Veizer *et al.* (2000) and Zachos *et al.* (2001), data remain sparse for the mid-Cretaceous and Late Triassic. Foraminiferal oxygen isotope composition can be compromised by early diagenetic recrystallization (Pearson *et al.* 2001). It is likely that other greenhouse gases such as CH₄ and water vapour play a role in temperature as well as CO₂. Nevertheless, the correlation of oxygen isotopic and stomatal index data support CO₂–temperature coupling over the past 300 Myr. A case can also be made for CO₂–temperature coupling before that time as well (Retallack 1997, 2000*b*), but significant uncertainties remain for Early Palaeozoic palaeoclimatic proxies (Veizer *et al.* 2000).

Another proxy of past atmospheric CO₂ is the boron isotopic composition of marine foraminifera, insofar as it tracks oceanic pH. Published data for the Cenozoic (Pearson & Palmer 2000) are not at variance with the stomatal index record presented here (figure 4), including a significant, though small, Middle Miocene CO₂ spike. This record is compromised by covariance of boron isotopic values with changes in river-water input into the ocean (Lemarchand *et al.* 2000). Model estimates of past atmospheric CO₂ are also in agreement with the stomatal index record (Retallack 2001) if allowance is made for the coarse temporal resolution of the mass-balance models. A 10-point running average applied to my stomatal index data (figure 3) gives a curve similar to that of Berner & Kothavala (2001).

Other proxies of atmospheric CO₂ show no correlation with proxies of temperature and have led to the concept of CO₂–climate uncoupling (Cowling 1999). For example, Royer *et al.* (2001*a*) failed to find a significant decrease in the stomatal index of *Ginkgo* and *Metasequoia* leaves at the Middle Miocene thermal optimum, well known as a time of unusual global warmth from the high-latitude spread of laterites and bauxites (Schwarz 1997), of *Liquidambar* and other thermophilic plants (Graham 1999), and of large foraminifera (Itoigawa & Yamanoi 1990; McGowran & Li 1997). The fossil leaves studied by Royer *et al.* (2001*a*) temporally straddle the thermal

optimum, which is now captured by the cuticles reported here from 49 Camp, NV (figures 2 and 4). Other fossil plants at 49 Camp, like other western US floras such as Fingerrock, Pyramid, Mascall and Latah indicate an unusually warm and wet palaeoclimate at 16 Ma, but much drier and cooler climates by 15 Ma (Graham 1999). Similarly, in Oregon marine rocks, large foraminifera and corals are found in the Astoria Formation for only a restricted interval at *ca.* 16 Ma, whereas other parts of the formation have less diverse molluscan faunas (Moore 1963), and such cool climate indicators as glendonites (ikaite pseudomorphs (Boggs 1972)). The short-lived spike of the Middle Miocene thermal optimum is also apparent from palaeosols and marine foraminifera and molluscs of Japan (Itoigawa & Yamanoi 1990) and South Australia (McGowran & Li 1997).

Another important CO₂ palaeobarometer has been derived from palaeosols, in which the carbon isotopic composition of pedogenic carbonate becomes heavier with higher partial pressure of atmospheric CO₂ diffusing further into the soil to dilute isotopically light CO₂ from respiration of plants and their debris. Unfortunately this palaeobarometer gives low CO₂ levels (and some negative concentrations!) at times of known global warmth, such as the earliest Triassic (250 Ma), Early Jurassic (200–190 Ma), Early Cretaceous (117 Ma) and Late Palaeocene (55 Ma (Ekart *et al.* 1999; Tanner *et al.* 2001)). Other isotopic studies demonstrate that each of these were times of massive dissociation of methane clathrates, flooding the atmosphere with CH₄, another greenhouse gas (Bains *et al.* 1999; Krull & Retallack 2000; Krull *et al.* 2000; Hesselbo *et al.* 2000; Jahren *et al.* 2001). Methanotrophic CH₄ is isotopically light (–110‰ and typically –60‰ δ¹³C), and this distinctive composition is an invaluable tracer of the temporal and geographic variation in abundance of CH₄ (Whiticar 2000). Methane oxidizes to isotopically light CO₂ within 7–24 yr (Khalil *et al.* 2000), but observed perturbations of organic carbon isotopic composition attributed to methane hydrate dissociation lasted for hundreds of thousands of years (Bains *et al.* 1999; Krull & Retallack 2000; Krull *et al.* 2000; Hesselbo *et al.* 2000; Jahren *et al.* 2001). Carbon isotopic palaeobarometers of CO₂ from palaeosols assume a gradient of isotopically light CO₂ from respiration of soil organic matter to isotopically heavy atmospheric CO₂. If atmospheric CO₂ is isotopically light from methanogenic CH₄ oxidation, then even with high atmospheric CO₂, the isotopic composition of soil organic and inorganic carbon will be light and give the misleading impression that soil respiration was dominant and atmospheric CO₂ low.

Support for the concept of CO₂–temperature uncoupling has also come from a carbon isotopic palaeobarometer that uses the difference in carbon isotopic composition of particular organic compounds that are biomarkers for phytoplankton compared with the carbon isotopic composition of associated foraminifera in oligotrophic, deep marine sequences. Detailed studies of deep sea cores using this technique showed near-modern CO₂ levels during the Miocene, with a slight increase rather than decrease toward the present, and they failed to detect a CO₂ rise during the Middle Miocene thermal optimum (Pagani *et al.* 1999, 2000). There are problems with palaeoproductivity, palaeotemperature, palaeosalinity, palaeoalkalinity and purity of chemical extracts that could compromise this approach, but these difficulties were all addressed by Pagani *et al.* (1999). The covariance between CO₂ and the differential isotopic composition of phytoplankton organic and foraminiferal carbonate carbon reaches a plateau at values in excess of those equivalent to 750–1250 ppmv CO₂ in the atmosphere, which is an effective upper limit of the technique's sensitivity (Royer *et*

al. 2001*b*). A more fatal flaw in this method, like that outlined above for the palaeosol CO₂ palaeobarometer, is its vulnerability to methane hydrate dissociation and oxidation events. Foraminifera calcify in direct proportion to the degree of carbonate saturation (Lea *et al.* 1995), and grow to large sizes and great abundance in sewage outlets and natural-gas seepages (Yanko *et al.* 1994). On the other hand, marine phytoplankton decrease photosynthetic carbon fixation at high CO₂ levels (Paasche 1964; Hinga *et al.* 1994). Why this happens is unclear: it may be due to limitations in diffusion of CO₂ into the cell or inactivity of the RUBISCO enzyme, or perhaps a result of the narcotizing effect of high CO₂. As mentioned above, vascular plants respond to high CO₂ by reducing the density and size of their stomates and increasing the thickness of their cuticles, but thickening of cell walls is the only option available for marine phytoplankton. The critical experiments remain to be performed: on the effects of different CO₂ levels on the wall thickness and isotopic composition of coexisting marine phytoplankton and foraminifera. Nevertheless, from the experiments noted above, massive amounts of isotopically light CO₂ from methanogenic CH₄ oxidation would lighten the isotopic composition of foraminifera in the surface ocean, bringing their isotopic composition closer to that of associated phytoplankton, which would not become comparably isotopically lighter, because of reduced photosynthetic carbon fixation as a physiological response to high CO₂. Such a reduced difference in isotopic composition of foraminifera and phytoplankton would then be misinterpreted as a result of low CO₂. Thus the phytoplankton–foraminiferal palaeobarometer could also be compromised by temporal and geographical variation in the isotopic composition of atmospheric CO₂.

4. Causes of CO₂ variation

An unexpected result of both the oxygen isotopic and stomatal index time-series (figures 3 and 4) is abrupt swings on geologically short time-scales. Even in the Early Tertiary, there were times of near-modern CO₂ levels (Royer *et al.* 2001*a*), punctuated by periods of high CO₂. It is thus a broad and unrealistic generalization to speak of an Early Tertiary greenhouse, let alone a Jurassic or Mesozoic greenhouse. Average CO₂ levels were high during these time-spans, but CO₂ maxima were sometimes very high and CO₂ minima only a little higher than present CO₂ levels. There is more variation here than would have been expected from early versions of the Gaia hypothesis (Lovelock 1979), which envisaged tight biotic control of greenhouse gases. What creates and limits these fluctuations?

(a) Atmospheric CO₂ highs

Some of the CO₂ highs revealed by stomatal index data are remarkably sharp, such as the Late Palaeocene thermal maximum (55 Ma), which is defined by a close temporal resolution of stomatal index measurements (Royer *et al.* 2001*a*). The carbon isotopic excursion during the terminal Palaeocene is so profound that it can only be explained by dissociation of isotopically light CH₄ from clathrate deposits (Dickens *et al.* 1995; Bains *et al.* 1999). Methane clathrate dissociation events are also the only feasible interpretation of large carbon isotopic excursions during the earliest Triassic (Krull & Retallack 2000), Early Jurassic (Hesselbo *et al.* 2000) and Early Cretaceous (Jahren *et al.* 2001). Some contribution of methane to the negative carbon isotopic

anomaly is also likely at the Cretaceous–Tertiary boundary (Max *et al.* 1999) and during the Middle Miocene thermal optimum (herein), but in these cases the recorded magnitude of the negative carbon isotopic excursion (Arens & Jahren 2000; Zachos *et al.* 2001) is less than at the other times listed above, and can be explained by a variety of mechanisms, such as abrupt drops in productivity, as well as by methane release.

Other CO₂ highs are less sharply focused and asymmetric in time, suggesting a short, sharp rise, followed by longer-term decay (figures 3 and 4). These peaks may represent catastrophic disruption of the carbon cycle followed by long-term repair. Many of these were times of likely asteroid or comet impact, such as the terminal Permian (Retallack *et al.* 1998; Becker *et al.* 2001), terminal Jurassic (Bice *et al.* 1996; Ward *et al.* 2001), and terminal Cretaceous (Alvarez *et al.* 1995). Many are times of flood basalt eruptions, such as the terminal Permian Siberian Traps, terminal Triassic Drakensburg Basalt, terminal Cretaceous Deccan Traps and Middle Miocene Columbia River Basalts (Wignall 2001). These dramatic forcings of the carbon cycle would be expected to leave transient residues in the atmosphere.

Some CO₂ highs were times of geographical spread and adaptive radiation of tropical taxa to high latitudes, such as the Early Cretaceous adaptive radiation (Jahren *et al.* 2001), and the rise to dominance of flowering plants (Retallack & Dilcher 1986) and ornithischian dinosaurs (Bakker 1986; Benton 1987). Middle Miocene (16 Ma) fossil floras of North America had unusually high percentages of exotic plants whose modern relatives live in Southeast Asia (Graham 1999), which is the likely source of elephants, gelocid deer and other mammals immigrant to North America at the same time (Janis *et al.* 1998). Times of markedly elevated CO₂ were also times of warm tropical marine palaeotemperature, as indicated by the oxygen isotopic composition of shellfish and foraminifera (Veizer *et al.* 2000; Kürschner 2001). Many CO₂ highs follow times of elevated extinctions both on land and in the sea, such as the earliest Kazanian (mid-Permian), earliest Tatarian (Late Permian), earliest Griesbachian (earliest Triassic), Anisian (Middle Triassic), Carnian (Late Triassic), Hettangian (earliest Jurassic), Toarcian (Early Jurassic), Bathonian (Middle Jurassic), Berriasian (earliest Cretaceous), Aptian (Early Cretaceous), Cenomanian (mid-Cretaceous), Danian (earliest Palaeocene) and Ypresian (earliest Eocene (Benton 1987; Stanley & Yang 1994; Sepkoski 1996; Hallam & Wignall 1997)). It thus appears that CO₂ levels above 2000 ppmv and tropical marine palaeotemperatures above 25 °C are not compatible with high biological diversity. Or, as put more colourfully by Lovelock (2000), Earth's biota is sick when it runs a high temperature.

Also apparent from the data on stomatal index (figure 3) are extended periods during the Early Tertiary, mid-Cretaceous, Middle Jurassic and Early Triassic, when CO₂ levels were moderately high (500–1000 ppmv). It is only in the Early Permian that values as low as modern are found. Perhaps some of these episodes can be explained by metamorphic or volcanic CO₂ degassing rates higher than at present (Beck *et al.* 1995), but an alternative view is that they come from ecosystems with a consumer–producer ratio higher than at present (Olsen 1993). The carbon-oxidizing effects of termites and dinosaurs may explain generally higher levels of CO₂ minima during the Mesozoic. This broader pattern is overridden by numerous catastrophic carbon-oxidizing events.

(b) Atmospheric CO₂ lows

The numerous CO₂ lows seen in stomatal index records (figures 3 and 4) reflect processes of carbon sequestration within biomass and by burial in carbonate and carbonaceous rocks. Two abiotic mechanisms proposed for carbon sequestration are mountain uplift and ocean-current upwelling. Uplift of the Himalaya beginning some 45 Ma has been argued to stimulate erosion and weathering in grasslands of the Tibetan plateau, which latter consumes CO₂ by hydrolysis of newly exposed mineral grains and delivers more organic sediment and nutrients to the ocean (Raymo & Ruddiman 1992). Thermal isolation of Antarctica by completion of the Circum-Antarctic current with opening of the Drake Passage at some 30 Ma increased upwelling of dissolved nutrients and phytoplankton productivity in the southwest Pacific Ocean, thus increasing carbon burial there (Kennett 1982). Neither of these events has quite the right timing to explain the principal CO₂ drawdowns seen in the Tertiary stomatal index record (figure 4) during the Palaeocene (60 Ma), Late Eocene (34 Ma) and mid-late Miocene (15 Ma). Both mechanisms depend on biological amplification of soil carbon fixation and of oceanic carbon burial, which could have occurred for purely evolutionary reasons, for example by the evolution of lignin and thick peat in forests (Retallack 1997; Berner 1997), and of sod and organic crumb peds in grassland soils (Retallack 2001). In Olsen's (1993) view, times of low CO₂ were times when plants and plant-like microbes were thriving, reducing and fixing carbon by photosynthesis, at rates that exceeded carbon oxidation by actinobacteria, fungi or animals. The overall effect of life has been to cool our planet from long-term increase in solar radiation (Schwartzmann 1999).

5. Conclusions

The link between atmospheric CO₂ and temperature is now well accepted and widely assumed by political and industrial accords. It is thus important that the theory is based on sound science. Beyond its confirmation in physical chemistry, planetary geology and current global monitoring, the link between CO₂ and planetary temperature can also be tested from time-series of geological data. Some time-series from carbon isotopic studies (Pagani *et al.* 1999; Ekart *et al.* 1999; Tanner *et al.* 2001) have failed to show the link between CO₂ and temperature, but these isotopic records are compromised by large variations in atmospheric isotopic composition from episodic dissociation of methane clathrates. The most comprehensive time-series for CO₂ from the stomatal index of fossil leaves (Retallack 2001; Royer *et al.* 2001a) compared with copious oxygen isotopic data as a proxy for palaeotemperatures (Veizer *et al.* 2000; Zachos *et al.* 2001), support a link between atmospheric CO₂ and planetary temperature for at least the past 300 Myr. Each proxy record could be greatly improved, and should be, given the importance of the CO₂ greenhouse to life on this planet.

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