Acta Palaeobot. Suppl. 2: 623–628, 1999 — Proceedings 5th EPPC

THE EVOLUTION OF THE CARBON CYCLE

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ABSTRACT. The manner in which carbon is circulated between the atmosphere, biosphere and geosphere is widely referred to as the carbon cycle. Its major features have changed drastically through the course of Earth history. Closely linked to this evolution of the carbon cycle have been other changes in the composition of the atmosphere, the extent to which carbon is stored in sedimentary rocks, the global climate and the nature of plant and animal life. The fossil plant record documents some of the land-marks in these processes: the appearance of photosynthetic prokaryotes, the resulting oxygenation of the atmosphere, and the occurrence of wildfire which then became possible. The palaeobotanical record also tracks the invasion of the land by plant life, and the way in which this accelerated the ensuing fall in atmospheric carbon dioxide. Plants had a dual role in this process, both in their photosynthesis and by their roots enhancing the rate of silicate weathering. Finally, the stomatal density on fossil leaves records their response to the fluctuations in global carbon-dioxide level, and the climate changes associated with them. The evolution of laminate, megaphyll leaves may also have been directly driven by the falling carbon-dioxide through the Devonian.

KEY WORDS: Carbon dioxide, photosynthesis, stomatal density, carbon burial, oxygen, wildfire, silicate weathering, laminate leaf

INTRODUCTION

In my lifetime I have seen palaeobotany and palynology change from what was the systematic study of fossil plants and spores – their structure, stratigraphic and spatial distribution – to one involving all aspects of past plant life, and above all, their interactions with the environment. The taxonomic and stratigraphic sides of the subject have not become less important, but the stimulus generated by looking at other aspects of plant life has added a new dimension to earlier approaches.

The purpose of this brief review is to consider how the study of fossil plants has contributed to our understanding of the way in which carbon moves between the atmosphere, biosphere and geosphere. More particularly, I want to consider how that movement has changed through the course of geological time.

I start not just with the story of the carbon cycle through Earth history, but by looking at the early days of palaeobotany to ask: who first began to raise such questions? Many palaeobotanists who have worked on Mesozoic or Palaeozoic plants will be familiar with the Fossil Flora of Great Britain, written by John Lindley and William Hutton (1831 et seq.). Rather fewer may have read the introduction to the first volume, where John Lindley wrote: – "the probable condition of the atmosphere at the most remote periods – what gradual changes that climate may have undergone since living things first began to exist – whether there has been from the commencement a progressive development of their organisation – all these are questions which it is either the peculiar province of the botanist to determine, or which his enquiries must at least tend very much to elucidate." He was saying in effect that botanists and palaeobotanists can tell us something not just about (evolutionary) changes in plant life through time, but changes in the climate and more remarkably, changes in the composition of the air, through time past. He was not alone in thinking along these lines; indeed Brongniart and others raised similar questions. But it is appropriate to acknowledge that these very "topical" issues were actually being considered by palaeobotanists over a hundred and fifty years ago!

THE ORIGIN OF THE CARBON CYCLE

The core of the involvement of living organisms in the present carbon cycle hinges on the photosynthetic fixation of carbon dioxide, by both terrestrial plants and marine (and freshwater) phytoplankton, to produce carbohydrate. The carbon is subsequently incorporated into a vast range of other organic compounds in living systems. This is eventually followed by respiratory breakdown of the organic matter by animals, plants fungi and bacteria, returning the carbon dioxide to the atmosphere:

$$CO_2 + H_2O = CH_2O + O_2$$

(Carbon dioxide plus water yields carbohydrate plus oxygen)

This simplistic formula for photosynthetic carbon fixation of course runs in the reverse direction for eventual release of carbon dioxide by respiration. The respiration may involve oxidation of a wide range of organic substances, including lipids, protein and their derivatives, but the eventual product is normally CO_2 in all these pathways. If breakdown of the fixed carbon does not occur, but the organic material is incorporated in sedimentary rock (as for example in a peat bog, or coal-forming swamp) then the cycle is not completed and the carbon may remain in that sense "buried" for millions of years. The oxygen generated by the photosynthesis then remains in the atmosphere. This process of oxygenation of the atmosphere by carbon burial is generally accepted as the means by which an initially high carbon-dioxide, low-oxygen atmosphere of Earth came to reach its present oxygen level of some 21%.

In addition to the photosynthetic/respiratory drive of the carbon cycle, there is an entirely different route by which carbon may be "taken out of circulation" by non-biotic processes. This involves the weathering of silicate minerals (especially calcic feldspars) contained in igneous rocks such as basalt. Carbon dioxide in the atmosphere (or more particularly in the soil atmosphere) reacts with such minerals to displace the silicate component and go into solution as bicarbonate ions balanced in solution by the calcium ions (or other cations). The net product is slow erosion of the igneous rock, coupled with movement of carbon from the atmosphere as (soluble) bicarbonate ions, eventually to be precipitated in large part as calcium carbonate in the oceans. The silica residue, less soluble than the bicarbonate, will tend to remain on the terrestrial surface. This sequence may be abbreviated from its initial components to the end product as:

$$CaSiO_3 + CO_2 = CaCO_3 + SiO_2$$

(Calcium silicate plus carbon dioxide yields calcium carbonate plus silica)

This silicate weathering pathway is not strictly an entirely "abiotic process" since the proximity of plant roots and associated microorganisms to the mineral components of the bedrock greatly facilitate accessibility of carbon dioxide to the silicate. However, silicate weathering by CO_2 undoubtedly occurred, at a much slower rate, before the evolution of plants adapted to terrestrial life. This route of movement of atmospheric carbon into carbonate on the ocean floor will also normally involve the action of phytoplankton, such as coccolithophores, or zooplankton such as foraminifera. All such organisms extract calcium and bicarbonate ions from water and precipitate calcium carbonate as part of their cell-armouring defence. A very readable and up-to-date account of these and other aspects of the carbon cycle is given in Francis and Dise (1997).

It is important to note that this silicate weathering pathway, unlike the carbon fixation effected by photosynthesis, does not involve the release of oxygen. Consequently, when it first came into action in the early history of Earth, it would not have contributed to atmospheric oxygenation.

AN EARLY ABIOTIC CARBON CYCLE

From what has been outlined above, the activity of living organisms, and most particularly the primary producers using photosynthesis – land plants and phytoplankton – drives the present-day carbon cycle. As a result, our record of fossil plants links closely with the changes that have taken place over the latter part of Earth history in the circulation of carbon. But it is appropriate to note that before the appearance of life, carbon must have been cycled between the atmosphere and the geosphere (in the form of the Earth's crust) by purely physical and chemical processes. Of course these still continue at the present day, although now playing a less important role against the background of biotic carbon cycling. Kasting (1987) has argued that in the early phase of Earth history (until say 4000 million years ago) atmospheric carbon dioxide was at 10^4 times its present level, and certainly there is a very general acceptance of the concept of a high CO_2 level in the early atmosphere (and hence of course in the oceans with which it was in equilibrium). The ensuing high rate of silicate weathering on land would have resulted in significant movement of bicarbonate, with accompanying cations, into the oceans, where at least in local restricted environments purely chemical precipitation of carbonate could occur. Further, where hot quenched lava met carbon-dioxide-rich ocean water (as in mid-oceanic ridges) the magma would have become altered and carbonated, so that the ocean floor basalt would incorporate carbon derived directly from the atmosphere. As with modern ocean floor sediments containing carbonate, the eventual fate of the carbonated basalt on the scale of geological time, would be subduction from the movement of tectonic plates. This would be followed by its subsequent re-emergence as gaseous carbon dioxide from volcanic vents returning the carbon to the atmosphere. Kasting's model is well explained in terms relevant to palaeobiologists in Francis and Dise (1997).

The object in exploring this early phase of Earth history is simply to make the point that the carbon cycle did not begin with photosynthesis; indeed, the carbon cycle was not "invented" by living organisms, but rather their activities simply accelerated and added new dimensions to an existing system.

PHOTOSYNTHESIS AND OXYGENATION OF THE ATMOSPHERE

The fossil record of photosynthetic organisms really begins with our recognition of fossil cyanobacteria. The appearance of chains of cells which closely resemble those of living cyanobacteria from about 3500Ma

(Schopf 1992), is generally taken as our earliest structural evidence for autotrophic organisms. By analogy with their living counterparts these fossil prokaryotes must have been photosynthesising using chlorophyll a, and releasing oxygen into their environment. Most students of Earth history would see photosynthesis – initially by photosynthetic prokaryotes, and later by eukaryotes (algae, higher plants) as having brought about the oxygenation of our atmosphere, largely accomplished by the end of the Precambrian. As mentioned earlier, this resulted in conversion of a more or less non-oxygenic atmosphere rich in carbon dioxide to one in which the oxygen far outweighs the carbon dioxide. Details of actual oxygen levels at different time intervals remain unclear, but there is a wealth of detail from physical evidence of progressive, but perhaps erratic, rising atmospheric oxygen through the Precambrian.

The oxygenation of Earth's atmosphere is probably the most far-reaching and significant change in the environment brought about by living organisms. Microorganisms which had a metabolism based on an oxygen-free environment (especially a number of bacterial anaerobes) were driven into very restricted habitats where a low oxygen concentration was locally sustained. The effect on other forms of life was of course immense. The metabolic pathway of enzymic breakdown of organic matter in an anoxygenic atmosphere must originally have been limited to "fermentation", the breakdown of carbohydrates to CO_2, alcohols or acids. With abundant oxygen, respiration could effect total oxidation of the carbon to CO_2 with a far higher energy yield. Once the atmosphere had attained a high level of free oxygen, higher organisms could recover the full energy value of the biomass that they had consumed or accumulated by their photosynthesis.

A further effect of progressive oxygenation was that plant biomass accumulated by photosynthesis could now burn in the air; wildfire (and eventually, as large trees evolved, forest fire) became possible. This is considered further below.

A NON-PHOTOSYNTHETIC BIOTA

Most biologists instinctively see photosynthesis based on solar radiation as the ultimate energy source for all primary production in any ecosystem. It is only some twenty years ago that biologists first became aware of the extraordinary metabolism of the submarine communities which have colonised hydrothermal vents along mid-oceanic ridges. We now have a picture of this remarkable ecosystem which is based on geochemical energy rather than solar radiation (see Fowler & Tunnicliffe 1997). The marine invertebrates which dominate the ecosystem are using the bacteria called archaea as their source of organic matter. These prokaryotes use hydrogen sulphide in the hot, hydrothermal fluids as an energy source, and employ the chemical energy to fix carbon dioxide, just as plants use light energy. The whole ecosystem operates in the total darkness of the deep ocean so that photosynthesis plays no part in the energy flow of the food web. Some of the animals graze the free-living archaea, while others such as the giant tube-worms have a symbiotic relationship with the sulphide archaea and bacteria. Since such hydrothermal vents are known to have existed well back into the Archaean (at least prior to 2500 Ma) these communities with their non-photosynthetic energy source could clearly have had a very ancient origin. Indeed, they raise significant questions concerning the nature of pre-photosynthetic life, and indeed the origin of photosynthesis itself.

THE "GREENING OF THE LAND"

When green plants colonised the land, they were to make what was perhaps the second most significant impact of life on the global environment. For as long as there have been cyanobacteria (and, later, algae) able to fix carbon, there must have been green life in a range of terrestrial habitats. It is reasonable to suppose that they colonised land surfaces wherever there was enough moisture (perhaps only seasonally) to sustain them. Many such habitats are occupied by a range of algae and bacteria today, from intertidal muds and river banks to "bare" rock surfaces, where a film of flowing water keeps them moist. There is no reason to doubt that this must equally have been the case from at least 2000 Ma, and probably earlier.

The evidence of larger plants, with vascular structure for water conduction, a cuticle, stomata for gas exchange and spores structured for wind dispersal, dates from approximately 400 Ma. (Kenrick & Crane 1997). With their appearance and rapid rise to global dominance in the terrestrial realm, the land surface (in suitable habitats) became covered with vegetation with an "in depth" capacity for carbon fixation. Dispersed spores and cuticle fragments somewhat predate these earliest vascular plants, and offer incomplete evidence of their possible antecedents. From the early Devonian onwards, upright vascular plants must have produced a sward of green vegetation in many habitats globally; through the course of the Devonian this vegetation was to evolve into forest trees, at least in some favourable habitats. By the end of the Devonian, vertebrates were able to follow the arthropods which had moved onto the plant-covered land surface from the earliest Devonian times. Plant life with its offer of shade, a moist sheltered habitat and primary production of foodstuffs had made possible the colonization of the land by animals. Whereas plant life accomplished this only in a single evolutionary clade (Kenrick & Crane 1997), the animal kingdom seems to have made the air-breathing adaptation to terrestrial life independently in at least five separate clades, in several different phyla (arthropods, molluscs and vertebrates).

PHOTOSYNTHESIS, CARBON DIOXIDE AND CLIMATE

The impact of land-adapted higher plants on the fixation of carbon seems to have had a very powerful effect on the global atmospheric carbon dioxide level. The rapid diffusion of both oxygen and carbon dioxide through the atmosphere contrasts with its slow movement by diffusion through water. Even so, the carbon fixation by oceanic phytoplankton is probably limited far more by nutrient availability than by carbon-dioxide availability. The limitations on the bioproductivity of land vegetation is more complex, and is limited by an interaction of temperature, light intensity, moisture and nutrients. But the simple comparison of the part played by oceanic versus terrestrial carbon fixation today is illustrated by their roles in primary production. The net primary production of the Earth's terrestrial plant communities (ca. 110×10^9 dry tons/yr; Chapman & Reiss 1992) is estimated to be about double that of the global oceanic biomass production (60×10^9 dry tons/yr) despite the fact that the area of the oceans is more than double that of the vegetated land area. Berner (1997) has suggested that the impact of land vegetation drew down the atmospheric carbon dioxide from around 20 times its present level prior to the Devonian, to approximately the present level by the end of the Carboniferous. Much of this carbon was buried in the form of extensive coal deposits of Mississippian and principally Pennsylvanian age.

While photosynthesis by land plants was driving the fall in atmospheric carbon dioxide, another carbon-burial process was being influenced by the action of plant life. Silicate weathering must have been enormously accelerated as plants evolved more structurally complex and deep-penetrating roots through the course of the Devonian (Algeo & Scheckler 1998). The deeper, humus-rich soils generated by root penetration beneath the expanding forests of the late Devonian and Carboniferous must have had a major effect on the access of carbon dioxide to silicate minerals derived from the bedrock (Berner 1998). The ensuing transport of bicarbonate ions (accompanied by calcium and magnesium ions) into the oceans was of course the route by which the massive limestones and dolostones of the Upper Palaeozoic came to store the carbon previously held in the atmosphere. This pathway of carbon burial, like that produced by the coal swamps, was accelerated by the nature of the rapidly diversifying land flora. The effect of the falling carbon dioxide level through Upper Palaeozoic time was not merely as a diminished source of carbon for the photosynthetic plant life. The reduced green-house effect of the lowered carbon dioxide may have played a central role in the onset of the great Carbo-Permian southern-hemisphere glaciation, as Berner (1997) has suggested. It is a most suggestive coincidence that the carbon dioxide level is so relatively low at the time of the two major global Phanerozoic ice ages, of the Carbo-Permian and Pleistocene. Each of these was associated with a low carbon dioxide "ice-house" climatic pattern, in the language of palaeoclimatologists. At least this gives support to the proposition that the plant-mediated atmospheric carbon dioxide level was a major factor influencing global climate.

THE ROLE OF WILDFIRE

The relationship between carbon burial and oxygen level in the atmosphere has already been touched on. Berner and Canfield (1989) offer a model of oxygen levels in the Phanerozoic atmosphere based on estimates of the rates of carbon (and sulphide) burial and of their subsequent weathering. On the basis of this modelling, those authors suggest that there have been significant excursions of oxygen, following to some extent the reverse form of the CO_2 curve (Berner & Canfield 1989). From the work of Watson *et al*. (1978), we know that there are both upper and lower limits to the level of atmospheric oxygen within which wildfire ("forest fire", where woodland burning is involved) would have been a natural and regular occurrence in the terrestrial ecosystem. The tangible evidence of the pyrolysis of plant material by wildfire is the occurrence of fossil charcoal (fusinite) in the fossil record (Jones & Chaloner 1991). From this fossil record, which extends from the Devonian to the Recent, it appears that the level of oxygen has lain within the "fire window" of 13% to 35% throughout the Phanerozoic (Robinson, Chaloner & Jones 1997). Although this constraint lies within the range suggested by Berner and Canfield the difference is slight, and it appears that the feed-back on oxygen level represented by the frequency of wildfire may have served to stabilise the oxygen level in the atmosphere, as was envisaged by Watson *et al*. (1978).

Our fossil record of wildfire carries with it the concept that there must have been a point in Earth history when the rising oxygen level made the ignition of natural (plant) biomass possible for the first time. The igniting agency would presumably have been lightning. Just when this might have occurred remains, of course, pure speculation. The event could well have pre-dated by many millions of years the accumulation of ignitable biomass from land-adapted vascular plants. Indeed, it might have consisted of the burning of algal biomass (marine or freshwater) accumulated and dried out on some lee shore of ocean or lake. Although a purely hypothetical "first event", it would have represented a landmark in the history of both the carbon cycle and of the global oxygen level.

STOMATAL RESPONSE TO CHANGING CO_2

Two observations that have made their mark in the last twenty years relate to the significance of the rising atmospheric CO_2 level. The first is the record from Mauna Loa that the ambient CO_2 level in the global atmosphere has been rising steadily since year-by-year measurements have been made. The other is the evidence from the Russian Vostok Antarctic ice cores that show the close correlation between CO_2 level and global temperature over the last 200 thousand years (Jouzel *et al*. 1993). These two records of changing atmospheric CO_2, more than any other evidence, appears to have generally persuaded the public – and more important, policy makers – of the importance of changes in atmospheric CO_2 (Chaloner 1989). It is now widely believed that the production of CO_2 from fossil fuel burning is driving the increase in that green house gas which could result in a dangerous degree of global warming. This demonstrable link between global temperature and CO_2 has had an enormous impact on the politics of fossil fuel burning on a world-wide scale.

During this period of rising interest in the human influence on CO_2 levels, Woodward (1987) published the striking evidence that modern tree leaves show a fall in the density of stomata as the atmospheric CO_2 has risen. This inevitably raised the question of what might be learnt from the stomatal density of fossil leaves. Woodward demonstrated that over the past century and more, the leaves of a number of native British forest trees showed a reduction in the density of stomata (and specifically, the stomatal index, the ratio of stomata to epidermal cells) as the carbon dioxide has risen. More important, he showed that experimental observation on tree seedlings exposed to controlled CO_2 levels demonstrated the same response. Using the ice-core data on past CO_2 levels, Beerling *et al*. (1993) demonstrated that Pleistocene fossil *Salix herbacea* leaves showed changes in stomatal index which corresponded with the ice-core record. Similarly, Van der Burgh *et al*. (1993) demonstrated that fossil *Quercus* leaves showed changing stomatal index values which matched the CO_2-greenhouse-driven climate of the Pliocene recorded in fossil pollen spectra. Chaloner and McElwain (1997) extended the same methodology to stomatal density from the earliest land plants, and showed that the falling CO_2 from the Devonian to the Carbo-Permian, modelled by Berner, is reflected in rising stomatal density in plants ranging from the early Devonian to early Permian in Europe. It appears that the density of stomata on fossil leaves is in effect recording changes in the global CO_2 level, as plants responded by maximizing their "water use efficiency" (the number of molecules of carbon dioxide that they fix divided by the number of molecules of water lost by transpiration).

THE ORIGIN OF THE PLANATED LEAF

There is a further effect of falling CO2 through the Devonian and early Carboniferous which has received little attention. A picture of early Devonian plants is generally one of a sward of dichotomising terete axes. Because of the presence of stomata on these axes, they must have functioned as the major photosynthetic organs of the plant. It is not until the late Devonian that any number of vascular plants begin to show flat, planated megaphyll leaves (such as those shown by *Archaeopteris*), believed to be derived from planation and webbing of a dichotomously divided axial system. This was Zimmermann's picture of the origin of the megaphyll leaf, and it has not been seriously questioned since he first advanced it in the 1930s (see e.g. Gifford & Foster 1988). Taken at face value, this means that vascular plants took about 25 million years, from the appearance of Lower Devonian vascular plants with their terete branching systems, until the majority of land plants were producing megaphyll leaves with a significant proportion of thin, laminate tissue. Did it really take so long to acquire such a productive adaptation which green algae had arrived at, (in environments where CO_2 may have been much more limiting) many millions of years earlier?

Van der Burgh (1996) has remarked on this seemingly long "delay" in the appearance of laminate leaves, and suggested that they were an adaptation to unidirectional light becoming a dominant feature of the environment only in the late Devonian. This he suggests contrasted with the cloudy, diffuse light environment of the "greenhouse world" of early Devonian time. He sees the falling CO_2 level through the Devonian, which we have already noted, as driving the global climate from one dominated by dense cloud cover to one of direct sunlight from cloud-free skies. As he writes, "when at last in the Upper Devonian the atmosphere cleared and the sun came through... plants reacted by developing flat leaves which could be directed towards these rays". He suggests that leaf evolution took this quantum leap in response to that climatic change. I like his thesis, but I think the role of falling CO_2 may have operated differently; that the evolution from photosynthetic cylinders to thin plates of tissue was a direct response to falling CO_2 and not an indirect one related to cloud cover. Rather, I suggest that when the atmospheric CO_2 was ten or more times the present level, cylindrical photosynthetic axes were an adequate basis for carbon fixation. With a high external CO_2 level the steep concentration gradient within the depths of the robust axial photosynthetic tissue maintained adequate diffusion of CO_2, despite limited stomatal access. As the CO_2 fell, it became necessary to increase the stomatal density and to limit the depth of photosynthetic tissue to maximise the diffusion from a very tenuous level of atmospheric CO_2. This is illustrated by a comparison of the photosynthetic cortical tissue in *Rhynia* compared with that of the corresponding mesophyll tissue in a typical dicot leaf, which represents only about one fifth of that thickness.

I have no basis to refute Van der Burgh's cloud cover theory – indeed I rather like it – but I suggests that the falling CO_2 itself represents an adequate environmental factor which would have driven the rise of the megaphyll leaf in the same direction.

CONCLUSIONS

In the fossil record of plant life we can see a series of steps which record some of the interlinked key processes of the global system, involving changes in the atmosphere, climate and vegetation. These include the rise of photosynthetic bacteria and algae that oxygenated the atmosphere; the appearance of plants on land, their impact in rooting on silicate weathering, and their photosynthesis on biomass production and so the increased burial of carbon; and the effect of atmospheric oxygen in making wildfire possible, and its record as fossil charcoal. Finally, the plant fossil record demonstrates the response to changing CO_2 as seen in stomatal densities, and the evolution of the planate leaf. All these interactions represent links between the processes included in "earth system science", and the record of past plant life which is the matrix of palaeobotany. Their study has brought a new dimension to the relevance of palaeobotany for earth scientists.

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