Methane, oxygen, photosynthesis, rubisco and the regulation of the air through time

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Rubisco I’s specificity, which today may be almost perfectly tuned to the task of cultivating the global garden, controlled the balance of carbon gases and O2 in the Precambrian ocean and hence, by equilibration, in the air. Control of CO2 and O2 by rubisco I, coupled with CH4 from methanogens, has for the past 2.9 Ga directed the global greenhouse warming, which maintains liquid oceans and sustains microbial ecology.

Both rubisco compensation controls and the danger of greenhouse runaway (e.g. glaciation) put limits on biological productivity. Rubisco may sustain the air in either of two permissible stable states: either an anoxic system with greenhouse warming supported by both high methane mixing ratios as well as carbon dioxide, or an oxygen-rich system in which CO2 largely fulfils the role of managing greenhouse gas, and in which methane is necessarily only a trace greenhouse gas, as is N2O. Transition from the anoxic to the oxic state risks glaciation. CO2 build-up during a global snowball may be an essential precursor to a CO2-dominated greenhouse with high levels of atmospheric O2.

Photosynthetic and greenhouse-controlling competitions between marine algae, cyanobacteria, and terrestrial C3 and C4 plants may collectively set the CO2 : O2 ratio of the modern atmosphere (last few million years ago in a mainly glacial epoch), maximizing the productivity close to rubisco compensation and glacial limits.

Keywords: rubisco evolution; oxygenic photosynthesis; Archaean; atmospheric composition

1. INTRODUCTION: PHYLOGENY AND EVOLUTION OF RUBISCO

Rubisco (ribulose 1,5-bisphosphate carboxylase/oxygenase) form I is today arguably the planet’s most common protein, central to the biosphere as the chief link between atmospheric and organic carbon, and essential in managing the creation of atmospheric oxygen. Throughout the life’s history, the several forms of rubisco, by facilitating gas uptake and emission into water and air, must have played a central role in directing the atmosphere. Owing to the importance of this role, and the depth of the consequent sequestration of carbon, the carbon isotopic impact of the various rubisco forms must have left an indelible geological record.

Rubisco is very ancient (Hanson & Tabita 2001; Ashida et al. 2005; Tabita et al. 2008). Form III of rubisco, comprising large subunits only, occurs in anoxic archaea, notably methanogens. Note that it is still too early to say whether all, or most, methanogens have rubisco III, though this is probable. Rubisco-like proteins (RLP or form IV), similar to the large subunit, which appear to participate in a metabolic pathway that is not the Calvin cycle, occur in some non-photosynthetic eubacteria, photosynthetic bacteria and archaea. By contrast, rubisco form I occurs in oxic organisms. With eight large (50–55 kDa) and eight small (12–18 kDa) subunits, this is the form of the enzyme that is found in plants and cyanobacteria. Form II, found in some photosynthetic proteobacteria, chemoautotrophs and dinoflagellates, has only large subunits.

Figure 1 summarizes the possible evolution of the rubisco forms. An ancestral last common ancestor may have possessed a precursor to the rubisco family. Early on, the rubiscos diverged to an archaeal lineage that led to form III, and an anoxic bacterial lineage. All this was in anoxic conditions. At some stage, the eubacterial lineage then further diversified into form IV in strictly anoxic bacteria, and more oxygen-tolerant forms II and I in photosynthetic eubacteria. Note that in figure 1, a triple divergence is assumed, but without strong evidence.

Rubisco III in methanogens may be very old. Grassineau et al. (2006) found possible (though not conclusive) C isotope evidence for methanogenesis in 3.8 Ga Isua rocks. This suggests very early branching between rubisco III and eubacterial rubiscos. If so, greenhouse warming by biogenic methane may explain the puzzle of the antiquity of water-borne sediments. Methane emission is the most likely candidate for the responsibility of keeping the planetary climate warm in the earliest Archaea, despite the faintness of the young Sun. Rubisco IV (RLP) occurs in strictly anaerobic bacteria and may have evolved in archaea (see Ashida et al. 2005; Tabita et al. 2008) in the Early or Mid-Archean, perhaps also the time of the original divergence between archaeal and eubacterial rubiscos.

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Anoxygenic photosynthesis and rubisco II may date from the Mid-Archaean. Nisbet et al. (2007) studied the C and S isotopic evidence for the evolution of rubisco I and concluded that oxygenesis first had planetary impact ca. 2.9 Ga ago. This is also the age of the oldest extant large-scale stromatolitic carbonate reefs (e.g. Wilks & Nisbet 1988). If so, this was when oxygenic photosynthesis began on a large scale and when oxic waters first occurred (though not necessarily free oxygen in the air). Though the 2.9 Ga date may fix the appearance of rubisco I, in aerobic settings, it does not necessarily date the divergence between rubisco I and II, which must predate the oxygenesis that rubisco I made possible. Perhaps this took place in sulphate-rich waters,

Figure 1. Outline of rubisco phylogeny (time scale adapted from Nisbet & Sleep (2001). LCA, last common ancestor.

Figure 2. Outline geological record of the atmosphere (modified from Nisbet et al. 2007), showing timings of some key parts of the rock record.
2. OXIDATION STATE AND TEMPERATURE OF THE AIR AND OCEAN IN THE ARCHAEOAN

Prior to 2.9 Ga ago, most evidence (see discussion in Nisbet et al. 2007) suggests that the air was anoxic (Hessler et al. 2004; Canfield 2005; Kasting 2006), though this consensus view has been challenged (Rosing & Frei 2004). Especially strong evidence for pre-2.9 Ga anoxia comes from non-mass-dependent fractionation of S isotopes (Farquhar & Wing 2003), which is significant, implying anoxic conditions. The S isotopic record between 2.65 and 2.9 Ga ago is more ambiguous (Farquhar et al. 2007). One explanation of the strongly fluctuating signal is that the air was indeed anoxic in most of the 2.65–2.9 Ga interval, but that local fluctuations in trace gas mixing ratios in photic zone waters may have occurred (Nisbet et al. 2007). Between 2.6 and 2.45 Ga ago, non-mass-dependent fractionation is again significant, implying anoxic conditions. Post 2.45 Ga ago, non-mass-dependent fractionation of S is absent, implying that the air has been oxidizing since the Early Proterozoic (figure 2).

The temperature of the Archaean ocean is hotly disputed. Robert & Chaussidon (2006) argued for high temperatures, while Sleep & Hessler (2006) suggested cooler conditions. Whatever the range, abundant sedimentological evidence implies that the oceans were in liquid state. Most preserved surface sediments are not obviously glacial. Maintenance of clement conditions under the faint Mid-Archaean Sun would have demanded stronger greenhouse warming than today. The geological record suggests that the air had much more CO$_2$ ca 3.2 Ga ago than today (Hessler et al. 2004). However, CO$_2$ alone might not have been capable of sustaining warm oceans, unless air pressure was markedly different. Methane is a potent greenhouse gas and Lovelock (1988), as part of a deep insight into the Archaean puzzle that raised many hypotheses still being debated today, suggested that it may have been the chief sustainer of greenhouse warming in the time from 3.5 to 2.3 Ga ago. Under the faint young Sun, only an atmosphere with high levels of CO$_2$ and CH$_4$ would be capable of sustaining a clement, or even warm, surface. Early evolution of methanogens may have kept the planet from freezing under the faint young Sun. Figure 3 shows a possible updated version of Lovelock’s (1988) hypothesis. Kharecha et al. (2005) suggested that methane mixing ratios were very much higher than today (between 100 and 35 000 ppm, or 3.5%). N$_2$O is another possible contributor to the Archaean greenhouse, though rarely discussed.

3. ATMOSPHERIC CONTROL: CO$_2$ : O$_2$ RATIO AND METHANE

The actions of life sustain the modern air in internal disequilibrium (O$_2$ and CH$_4$ coexisting in the same air mass) and also in disequilibrium with the geochemical setting. Dioxygen is the obverse of the carbon dioxide coin. For each O$_2$ molecule liberated, a molecule of CO$_2$ is fixed, and the reverse. At the heart of the atmospheric system are CO$_2$ and CH$_4$. These, with N$_2$O, are the ‘managing’ greenhouse gases, with water vapour being the chief responding gas. Climate (and the stability of oceans) is set by these gases.
CO₂ and water are taken up and O₂ is released by reactions linked to rubisco I. Though methane is generated by methanogens, today the atmospheric mixing ratio of CH₄ is also directly connected to oxygenesis and photosynthetic carbon fixation. Atmospheric CH₄ is destroyed by OH and methanotrophs, both supported by O₂. Any atmosphere that has significant O₂ thus can only contain trace amounts of CH₄. In water, oxygenesis increases sulphate supply. Methane in sediment and water is subject to anaerobic methane oxidation by sulphate-supported archael/bacterial consortia. Conversely, methane emission depends on photosynthetic carbon uptake, which eventually creates dead organic matter. From this, sedimentation of fixed carbon enters or creates anaerobic settings such as organic-rich sediment and eventually re-enters the ocean/atmosphere system as biologically released methane.

Several questions thus arise, given the dominance of rubisco in global biospheric carbon cycling, as follows.

(i) Does rubisco I set the O₂ : CO₂ ratio of the atmosphere, and hence indirectly control CH₄ and O₂?

(ii) Has the evolution of rubisco in all its forms been the factor that controlled the history of the atmospheric greenhouse?

If so,

(iii) Has rubisco evolution, over the aeons, by its management of the greenhouse, sustained planetary habitability under a slowly brightening Sun, by controlling the radiative impact of CO₂ and CH₄, as amplified by water feedbacks?

The centre of the atmospheric puzzle is the CO₂ : CH₄ : O₂ relationship. Rubisco I, supplemented by rubisco II, controls the CO₂ : O₂ ratio, and by its oxygen emission destroys methane in oxic air, while rubisco III facilitates the creation of methane, which provides an alternative mechanism of greenhouse feedback and fosters anoxia, in which rubisco IV cells flourish.

(a) Rubisco specificity

Both CO₂ and O₂ can act as substrates for rubisco catalysis. Rubisco I’s selection of CO₂ over O₂, or ‘specificity’ (i.e. its choice for C against O—Tolbert et al. 1995; Tcherkez et al. 2006), subjects the atmosphere to the limits in CO₂—O₂ space beyond which rubisco is incapable of capturing carbon from the air/ocean system (Hahn 1987).

The specificity of rubisco I determines the O₂ : CO₂ balance around a cell carrying out oxygenesis. This simple synopsis is complicated by carbon-concentrating mechanisms that aid transport. However, these are typically very efficient, so the control focuses on rubisco. Broadly, if O₂ and CO₂ are present in a living community that is entirely microbial (e.g. Early Precambrian), and other nutrients are available to a cyanobacterial cell in seawater, then the CO₂ : O₂ balance is attained when accessible CO₂ is in tens to hundreds of parts per million (ppm), and oxygen is in per cent.

(b) Rubisco compensation: O₂–Γ and CO₂–Γ

Rubisco molecular specificity, supported by very efficient CO₂ transport into and around the cell by carbonic anhydrase, is expressed on the macroscopic scale as ‘compensation’ controls (see discussion in Hahn 1987; Tolbert 1994; Tolbert et al. 1995). If ambient O₂ is below rubisco’s O₂ compensation (known as the O₂–Γ), then there is uptake of CO₂ from the air, with the reduction of the carbon into organic matter, and plants grow. Conversely, if ambient dioxygen in the environment is above the O₂–Γ there is net photosynthetic uptake of O₂ from the environment and reduced CO₂ fixation, and plants die. The O₂–Γ level increases linearly with the mixing ratio of ambient CO₂ in the air (Tolbert 1994; Tolbert et al. 1995). Similarly, there is a CO₂–Γ level, defining carbon dioxide compensation, when carbon fixation falls to zero. When CO₂ is below compensation, net uptake of carbon by photosynthetic cells ceases. The CO₂–Γ level similarly increases linearly with ambient O₂ mixing ratio in the air (figure 4). These compensation boundaries limit the conditions under which the oxygenic biosphere is viable, because the balance between photosynthesis and photospiration limits the removal of CO₂ by oxygenic photosynthesis from the air.

Experiments by Tolbert et al. (1995) suggested that the minimum practical limit for CO₂, assuming ambient temperature and pressure, is a few tens of ppm CO₂. This limit rises as O₂ rises. Tolbert et al. studied chloroplasts in tobacco plants at 20°C. Their results define a linear CO₂ compensation trend with oxygen:
CO₂ (ppm) = 2.12 O₂ (%) + 3.89 ppm. The maximum O₂ limit is orders of magnitude different: per cent, not ppm. This is a steep line with O₂ (%) = 0.025 CO₂ ppm + 18%. For net growth, atmospheric CO₂ levels must be above the CO₂ line and O₂ below the O₂ line.

If tobacco plant chloroplasts exposed to abundant ambient CO₂ in the air are a representative model for the global population of oxygenic photosynthesizers, then CO₂ uptake will occur until CO₂ is drawn down to approximately 4 ppm. However, this is in optimum conditions in seedling plant cells that take CO₂ directly from the air. At sea (e.g. in the Precambrian), CO₂ is drawn from photic zone water that must access CO₂ by equilibration via carbon concentrating mechanisms with the surrounding water and thence the overlying air. In sunlight, CO₂ is rapidly depleted in local photic waters hosting a cyanobacterial bloom. For such picoplankton, the limiting local external CO₂ abundance in the air above the sea surface is therefore much higher.

Nevertheless, though seedlings have much easier access to CO₂ than microbial plankton, the Tolbert et al. (1995) model may have general applicability. Evolution has exquisitely tuned rubisco specificity (Gutteridge & Pierce 2006). Given the rapid turnover of microbial populations, this tuning is likely to be very ancient. Note, however, that this conclusion is qualitative. Hahn (1987) successfully modelled the balance between modern photosynthesis and photo-respiration: as yet this model has not been applied to Archaean conditions.

4. REGULATION OF THE AIR: THE AIR COMPOSITION/GREENHOUSE TEMPERATURE PERMUTATION

Tolbert et al. (1995) showed that the late glacial (prehuman) atmosphere of 190 ppm CO₂ and 21% O₂ was very close to the average effective compensation limits of rubisco I from plants and algae. The implication is that it is not only the atmospheric CO₂ that is near compensation but also O₂. Evolution has driven the air to both limits, presumably to maximize productivity in a warm wet world with strong chemical erosion of nutrients from rocks. If correct, this implies long-term control by rubisco I of the CO₂ : O₂ ratio of the global atmosphere. In other words, by maximizing productivity (and hence ‘fitness’) of competing biomes (e.g. C4 grasslands versus C3 forests) and ecosystems, evolution has constrained the air composition/greenhouse temperature permutation close to the rubisco compensation control. If any perturbation occurred (e.g. volcanism, or externally driven temperature change) that pushed the atmosphere off the control line, the subsequent change in productivity would drive the system back to the compensation line on a vector in O₂ : CO₂ space according to the molecular balance of the uptake of the two gases.

There is a striking disproportion between the O₂ and CO₂ levels. Compensation is attained when O₂ in air, even under Proterozoic Sun (somewhat fainter than today), was very close to the average effective compensation limits of rubisco I from plants and algae. The implication is that it is not only the atmospheric CO₂ that is near compensation but also O₂. Evolution has driven the air to both limits, presumably to maximize productivity in a warm wet world with strong chemical erosion of nutrients from rocks. If correct, this implies long-term control by rubisco I of the CO₂ : O₂ ratio of the global atmosphere. In other words, by maximizing productivity (and hence ‘fitness’) of competing biomes (e.g. C4 grasslands versus C3 forests) and ecosystems, evolution has constrained the air composition/greenhouse temperature permutation close to the rubisco compensation control. If any perturbation occurred (e.g. volcanism, or externally driven temperature change) that pushed the atmosphere off the control line, the subsequent change in productivity would drive the system back to the compensation line on a vector in O₂ : CO₂ space according to the molecular balance of the uptake of the two gases.

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past. The role in the Archaean greenhouse of N₂O has been little studied.

There is evidence for within-cell linkage between control of nitrogen fixation by nitrogenase and the rubisco-led carbon cycle (Joshi & Tabita 1996). Globally, lightning destroys N₂ if O₂ is present; note that lightning in turn depends on atmospheric water vapour (the chief greenhouse gas and albedo controller), while NH₃ is involved in photospiration.

The atmospheric pressure feeds back into greenhouse management by pressure broadening of the spectral absorption by greenhouse gases (C. Goldblatt 2008, unpublished data, http://www.researchpages.net/people/colin-goldblatt). This feedback on radiative forcing may have been a significant control. Pressure is mainly set by nitrogen. Most atmospheric modelling assumes one bar atmospheric pressure, but this assumes a partitioning of the N reservoir between air, ocean (e.g. nitrate), crust (e.g. ammonium zeolite) and mantle that may not have been valid on the Archaean planet under sustained anoxic conditions.

(a) Management of the atmospheric greenhouse
Greenhouse management by rubisco is, in control engineering parlance, a ‘ramp’ type of control system. In the atmospheric system, the small CO₂ signal controls the water greenhouse and albedo feedbacks, but the CO₂ is itself stabilized by the large O₂ reservoir. Short-term fluctuation does not easily shift this huge O₂ reservoir. Blips in CO₂ uptake or emission have little impact on O₂. Oxygen has a lifetime of tens of millions of years in the air compared to annual production. The sharp disproportion between per cent oxygen and ppm carbon dioxide may thus sustain rubisco’s long-term control on global carbon management and on the greenhouse.

Perturbations to the system are thus damped by the size of the O₂ reservoir in comparison with any probable additions or removals. Geological injections of carbon dioxide make very little impact on oxygen (see figure 6). Even doubling the CO₂ burden of the atmosphere by a volcanic emission, and increased subsequent photosynthetic release of a balancing number of moles of oxygen, will barely shift the oxygen reservoir. The system will regress to the compensation line within a few hundred thousand years, returning to the control line only very slightly upwards in O₂ space, unless it is already at the O₂ ½ limit. This inertia implies that the global atmosphere will absorb millions of years of progressive natural increment or excrement of CO₂ before oxygen changes significantly, especially as there are other factors at work that store reduced carbon in near-perfect laboratory conditions, not C3 and C4 plants and algal, bacterial and archaeal planktons competing for local resources, the comparison may be close. The mixing ratio of CO₂ in the air is certainly not in the per cent range.

The disproportion between CO₂ and O₂ when rubisco is close to compensation suggests two stable states of the greenhouse in which life can flourish. One state is anoxic and has greenhouse warming by a mixture of long-lived CO₂ and methane, in which trace oxygen has a short lifetime. The other state has higher CO₂, but as a result free oxygen is permitted, and in its presence only short-lived trace methane can occur. Note that N₂O can be a significant ‘warming assistant’. Rubisco biochemistry permits these two general options. Within these biologically set bounds on CO₂ : O₂ ratio, the norms of inorganic geochemistry then operate, for example, setting pH of the oceans and, more widely, responding to tectonic controls to drive the fluctuation of climate (Lowe & Tice 2007). But the biology sets the rules within which the chemistry operates, not the reverse. Goldblatt et al. (2006) considered the same problem of bistability. They pointed out that when O₂ mixing ratios exceed 10⁻³ of present atmospheric level, the troposphere is shielded from ultraviolet by ozone. This shielding then causes non-linear increase in O₂. There is here a mechanism for a catastrophic switch to anoxic stable state, in which CO₂ levels would then be governed by the compensation controls.

5. PAST RECORDS OF CO₂, CH₄ AND O₂
Consider now the impact on the planet of the first evolution of oxygenic photosynthesis, say 2.9 Ga ago (Nisbet et al. 2007). Prior to this, the anoxic ocean/atmosphere system was probably kept warm by the combined greenhouse impact of both CO₂ and CH₄, say at 1000 ppm each (Kasting 2006; Kasting & Ono 2006), possibly also with trace N₂O or NH₃ or both, from the nitrogen cycle. These gases and N₂ would have been managed collectively by a biospheric consortium of methanogenic archaea, anammox planctomycetes and anoxicogenic photosynthizers.

Photosynthetic emission of oxygen by cyanobacteria into the anoxic 2.9 Ga atmosphere would have introduced a new source of free O₂ emission. Initially, O₂ would only be at trace levels. With O₂ so low, rubisco I compensation would be attained by drawing down CO₂ to very low levels (figure 4), though as this took place, in photic zone water, local oxygen levels in the water would begin to rise. Even given the problems of accessing atmospheric CO₂ into seawater, and given the rising oxygen oases created by the new oxygenesis, CO₂ could be drawn down to, say, a few tens of ppm. In a methane-rich anoxic atmosphere, released O₂ would be short lived. Moreover, O₂ abundance would be limited by the prior mole-equivalent CO₂ inventory. Over time, eventual conversion of most of the prior atmospheric reservoir of CO₂ (say, 1000 ppm) would release a molecular equivalent amount of O₂ in the ppm range.

It is possible that, with a sudden bloom of newly evolved oxygenic cyanobacteria, rapid conversion of most of the CO₂ inventory of the air, down to

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compensation levels at low O₂, could trigger glaciation, especially if the methane greenhouse were reduced too. Ice cover would then limit further biological productivity. Thus, O₂ would remain in very low abundance as a minor trace gas in the air (see Farquhar et al. 2007).

Glaciation is not the only possible fate of a newly oxygenic biosphere. In parallel with oxygenesis, the increase in biological productivity would increase methane release by methanogens reprocessing newly abundant organic carbon. This methane could restore greenhouse warming. Though the new oxygen (and hence OH) would challenge atmospheric CH₄, while more abundant sulphate in water would challenge methane in the sediment as it was emitted, total methane emission would be in the long-term balance oxygen output. Thus, the newly productive methanogens would support the methane mixing ratio in the air. In an anoxic prior setting with dominant CH₄ (and hence long methane lifetime, but short O₂ life), a relatively small flux of methane could sustain a significant atmospheric burden.

A possible resultant Late Archaean scenario would be the following:

(i) a methane-rich atmosphere with abundant long-lived CH₄, low CO₂ and short-lived trace O₂,
(ii) water in which oxygenic photosynthesis was occurring, and
(iii) methane-rich sediment, emitting CH₄ that escaped to the water and thence to the air past zones of anaerobic oxidation of methane by sulphate (figure 5).

In these anoxic-air conditions, with atmospheric oxygen only as a trace component, there would be little or no atmospheric ozone. Unless a methane smog occurred, there would be high UVB flux to the surface, as shown by the 533S record (Farquhar & Wing 2003). This would suppress the productivity of the newly evolved cyanobacteria (Tolbert 1994). The atmospheric emission of dioxygen would eventually be taken up by the oxidation of the land surface and by the formation of seawater chemical species such as sulphate.

Figure 5. Synopsis of possible Late Archaean atmospheric conditions.

Figure 6. CO₂ emission spikes compared with recovery from Snowball Events. (i) CO₂ emission spike (e.g. from eruption of a large igneous province). Strong release of CO₂ (e.g. doubling atmospheric CO₂) causes short-term warming and flourishing photosynthesis. However, when the CO₂ has been taken up and mole-equivalent O₂ released, the impact on the much larger O₂ inventory is small. The system thus regresses close to the starting point on the compensation line (probably within a few hundred thousand years). Control by the large O₂ inventory gives stability to the system. The Palaeocene/Eocene thermal maximum may be an example. (ii) During a snowball, CO₂ from volcanic gases builds up until greenhouse warming is sufficient to initiate melting. This may occur only when CO₂ is approximately 12% (Caldeira & Kasting 1992). Once warming begins, photosynthesis restarts and this large CO₂ inventory allows a mole-equivalent O₂ release. The system regresses to the compensation line at very much higher O₂ and thus at higher CO₂, allowing much warmer higher O₂ conditions to be sustained, compared with the system prior to the event.

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Removal of CO₂ and methane collapse as the CH₄ lifetime shortened could occur, as oxygen emission continued until sulphate abundance overcame other reductants in the exposed sediment. The collapse of atmospheric methane would end the non-mass-dependent signal in sulphur isotopes (Zahnle et al. 2006). This would have posed a sharp challenge to the global greenhouse, possibly initiating glaciation.

The danger of runaway cooling would be constrained. Any cooling would have been to some extent self-correcting, as it would have suppressed photosynthesis. The sediment mass is a capacitor for methane and methane hydrate. Methane emissions would continue for tens of millions of years even if the productivity of the biosphere declined or nearly ceased. Thus, though glaciation may have reduced oxygen emission, methane-driven greenhouse warming would continue, perhaps until methanotrophs and anaerobic methane oxidizers imposed equilibrium.

6. SNOWBALL EVENTS

Nevertheless, major glaciations did occur. Global glaciation may have occurred on several occasions in the Proterozoic (e.g. Hoffman et al. 1998). It is possible that prolonged so-called ‘Snowball’ Events (in the widest sense of the term) took place in the Early and Late Proterozoic. Consider the way the system would respond to the major challenge of such an event, initiated by some external process or internal dynamic. In global glaciation, photosynthesis would have been virtually shut down for tens of millions of years. If so, in these abiological conditions, the atmosphere/ocean system could have departed from the compensation line as build-up of volcanic emissions raised CO₂, perhaps up to 12% CO₂ (Caldeira & Kasting 1992).

Greenhouse warming from such a huge inventory of volcanic CO₂ would eventually cause catastrophic breakdown of the snowball. Part of the CO₂ would then be taken up by acidophile cyanobacterial growth in the photic zone of the nutrient-rich anoxic sea. This would release equivalent moles of O₂. Uptake of CO₂ by both organic photosynthesis and carbonate precipitation would simultaneously drive down the atmospheric CO₂ burden until, with rising O₂ and pH, and simultaneously falling CO₂, the O₂ : CO₂ ratio reached the compensation barriers. This would be at the high end of the CO₂ G line, with significant free O₂ in the air (figure 6).

Recovery after a prolonged Late Proterozoic Snowball may have driven the system against the O₂ G barrier. The long-term result would be a stable oxygen-rich biosphere, with CO₂ high enough up the CO₂ G line to be the dominant managing greenhouse gas under the brighter older Sun. Possibly N₂O and other gases contributed, but once the atmospheric O₂ burden had increased, then CO₂ would dominate the forcing of water vapour, the main responding greenhouse gas, with methane’s role reduced to being a short-lived trace supplementary helper. In this context, it would be interesting to introduce methane and greenhouse feedbacks into the photosynthesis/photorespiration model of Hahn (1987).

7. CONCLUDING HYPOTHESES

Consideration of the interaction of the various forms of rubisco with the atmosphere/ocean system leads to the hypothesis that rubisco has guided the evolution of the global atmosphere. By setting the O₂ : CO₂ ratio, and hence also the maximum abundance of CH₄ and water vapour in the air, rubisco I specificity may have controlled the greenhouse over nearly 3 Ga. In turn,
the maintenance of advantageous greenhouse conditions would confer success on cyanobacterial picoplankton, so the evolution of specificity would, conversely, be controlled by the greenhouse. The system would co-evolve.

Several further hypotheses are plausible as follows.

(i) That rubisco compensation, the macroscopic expression of rubisco’s specificity on the molecular level, is today just as finely tuned as is specificity. Together with the carbon-concentrating mechanisms, natural selection of specificity and hence of the compensation controls may maximize productivity not only of individual cells but also of consortia and biomes. This fine tuning should apply to plants, algae and cyanobacteria, according to their different settings and biochemical skills.

(ii) That this fine tuning is very ancient, first achieved by evolutionary selection in the Archaean soon after the start of oxygenogenesis.

(iii) That under anoxic air from 3.8 until 2.9 Ga ago, the greenhouse warming from methane (from rubber-III methanogens) and CO₂ (in part controlled by anoxicogenic rubber-II photosynthesizers) sustained the liquid state of the oceans.

(iv) That between 2.9 Ga ago and the Great Oxidation Event 2.4 Ga ago, both methanogens and rubber-I oxygenic photosynthesizers operated, in oxic photic zone waters under an anoxic global atmosphere with sufficient CH₄ to maintain liquid oceans, until reservoirs of reduction power (such as the deep ocean and uppermost sediments) were overwhelmed by sulphate (figure 7).

(v) That since 2.4 Ga ago, rubber-I specificity, expressed through CO₂ and O₂ compensation, has determined the atmospheric disproportion of CO₂ (ppm) and O₂ (per cent), restricting CH₄ to trace gas status, while CO₂ alone has dominated the management of global greenhouse warming.

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REFERENCES