

## ***Interactive comment on “The regulation of the air: a hypothesis” by E. G. Nisbet et al.***

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Reply to Review by Lee Kump (Referee RC C581)

We thank Lee Kump for a very thoughtful review, that is critically very helpful. We accept his general comment that the paper should be improved by 'being a bit more cautious in its wording'. As he says, the hypothesis is only permissive, but that it is indeed permissive is important. Given the significance of its implications we hope that it will be allowed formal publication, and that it deserves the debate that will follow.

As to the specific comments:

1. The N<sub>2</sub> budget of the air. Our nitrogen discussion is peripheral to the focus of the hypothesis of the paper, which is the O<sub>2</sub>:CO<sub>2</sub> ratio. We accept that our remarks on N<sub>2</sub> are speculative, as the thermodynamics and kinetics of nitrogenase are not as well

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investigated as rubisco I: there is as yet no equivalent for nitrogenase of the Tcherkez et al (2006) 'fine-tuning' analysis of rubisco I. However, as the nitrogen cycle is so clearly connected biologically to the carbon cycle, we introduced the speculation.

That said, we do not accept the referee's comment that atmospheric regulation of N<sub>2</sub> has 'failed' because the N<sub>2</sub> is in the atmosphere. This would imply that evolution by natural selection does not apply to nitrogenase. Indeed, this is perhaps the crux of the debate. Are nitrogenase (and rubisco) exempt from natural selection because they are monopolies? If so, then they are indeed 'inefficient' and biological control has indeed 'failed': thus inorganic controls rule. Or are the specificities of nitrogenase and rubisco indeed subject to darwinian tuning, and thus the air is under darwinian kinetic control, not control by chemical equilibria?

Thus, we would argue the size of the atmospheric N<sub>2</sub> burden may indeed be a sign of the success of natural selection. Were all life to disappear tomorrow, it is possible (though admittedly Kasting and Whitmire, Icarus 101:108-28, 1993, argued to the contrary) that inorganic fixation by lightning would create soluble N species and the atmospheric nitrogen would slowly vanish into the water and hence into hydrothermal systems that formed ammonium zeolites in oceanic crust. From there, subduction would return the N to the mantle.

But this is not so: the nitrogen is kept out of the mantle and is available for the biosphere. The combined impact of anammox planctomycete bacteria and denitrifying bacteria have created a global reservoir of N<sub>2</sub> that gives bulk to the air and the weather, helps sustain the greenhouse by pressure broadening, and provides a globally accessible N<sub>2</sub> supply for nitrogen fixation.

2. Timescales. The past is the sum of the presents. We fully agree that numerical modelling is indeed important. For example, in the glacial/interglacial changes in the past 15 ka, very rapid changes took place that seem to have driven the atmosphere/ocean system suddenly from one quasi-stable state to another (Nisbet, E.G. and Chappel-

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laz, J., (2009) Shifting gear, quickly. *Science* 324, 477-8). But within a quasi-stable episode, feedbacks do seem to be capable of maintaining long periods of stability.

3. Control on CO<sub>2</sub>. There is a misunderstanding here: we will rewrite. a) We see the atmosphere/ocean equilibration as part of the biological system. Controls on ocean/air gas exchange are not fully understood yet. Methane concentrations in seawater, for example, may be markedly out of equilibrium with air. Conversely, CO<sub>2</sub> exchange across the ocean/atmosphere interface may be greatly speeded by carbonic anhydrase emitted by plankton into the uppermost water surface. b) Modern CO<sub>2</sub> emission shows how quickly biology responds to CO<sub>2</sub> emission. The power of biological processes in the short term is shown by the 'Keeling curve'. Presently, although very roughly half the emission of CO<sub>2</sub> by humanity remains in the air, the rest is already very rapidly taken up by the biosphere (le Quere et al, 2009). Moreover, Keeling (1960) showed the close annual linkage between terrestrial biological uptake and atmospheric CO<sub>2</sub>. c) As for the C<sub>4</sub> plants, we meant to comment that these are the plants adapted to glacial conditions. In the C<sub>3</sub>/C<sub>4</sub> competition, areas under C<sub>4</sub> plants expand in glacial, while C<sub>3</sub> plants prosper in interglacial episodes. The text will be revised.

4. Feedbacks. The geochemical argument is for the independence of O<sub>2</sub> and CO<sub>2</sub> controls. Should a large CO<sub>2</sub>-influencing geological event occur (such as a massive plume eruption over a few hundred thousand to a few million years), natural selection will certainly induce an evolutionary response in rubisco specificity. But it is our argument that this in the broadest terms is an evolutionarily stable system, with rubisco fitness evolving to maximise biological survival: in other words, to sustain the equable climate. In our interpretation the CO<sub>2</sub>, O<sub>2</sub> and indeed N<sub>2</sub> burdens of the atmosphere are not independent of each other, but, to the contrary, all three co-evolve together, as managed by the biosphere.

5. N:P ratio. There are essentially three states of the atmosphere/ocean system: 1) the present system with oxic air and oxygenated ocean, sustained by oxygenic (rubisco I) photosynthesis; 2) the early-mid Archaean anoxic ocean/atmosphere, prior to the

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evolution of rubisco I, but with anoxic photosynthesis (rubisco II), and also rubisco III methanogenesis; 3) in the late Archaean and earliest Proterozoic, an episode of perhaps 500 Ma after the evolution of rubisco I (Nisbet et al 2007), when the ocean and atmosphere were broadly anoxic but widespread oxygen 'oases' existed in the photic zone of the uppermost ocean and in coastal lagoons. Planctomycetes are ancient and it is likely they played an important role in such conditions, producing N<sub>2</sub> by reacting NH<sub>4</sub><sup>+</sup> from anoxia with NO<sub>3</sub><sup>-</sup> from oxic settings.

6. Carbon burial draws down CO<sub>2</sub>, and this can take place rapidly. For example the immense peat deposits of NW Siberia and the Hudson Bay lowlands have accumulated remarkably quickly, beginning less than 10 ka ago. Likewise, tropical peat formation in Amazonia and the Congo accelerated then, and the accumulation of C in the Black Sea floor. Thus the global change in primary production after Termination 1B (at the start of the Holocene) did indeed cause an immediate change in C burial rate. Sequestration is not necessarily linked to essential nutrients as elements in short supply (Fe, P etc.) are recycled: many coals are very pure C with little residual Fe; in contrast, Precambrian banded ironstones (laid down when Fe was abundant in anoxic oceans) are very poor in C.

7. Figure 3 is illustrative – our purpose in suggesting the hypothesis is indeed to trigger a full quantitative investigation. But the basic point that the greenhouse gases CO<sub>2</sub> and CH<sub>4</sub> govern surface temperature is surely strong, and thus that which sets CO<sub>2</sub> and CH<sub>4</sub> sets the environment.

8. Archaean CO<sub>2</sub>:O<sub>2</sub>.. The hypothesis is about Rubisco I specificity. We have argued that Rubisco I did not evolve until about 2.9 Ga ago (Nisbet et al., 2007). Prior to this, the controls we suggest in our hypothesis would have been absent. However, both methanogenesis and anoxygenic photosynthesis were active before 2.9 Ga, and the rubisco family may have originated as a rubisco III-like form, in a strictly anaerobic methanogen. It is not improbable that natural selection may have acted to balance the CH<sub>4</sub> greenhouse created by rubisco-III methanogens during the long period from the

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origin of methanogens to the late Archaean.

9. We do not in any way deny the validity and essential control of the inorganic equilibria – indeed, our hypothesis depends on them, but as a consequence of the control on thermodynamic state variables imposed by the greenhouse and pH, which are themselves consequences of evolutionary selection of CO<sub>2</sub> over O<sub>2</sub> controlled by the action of natural selection on rubisco specificity. Once the greenhouse forcing of the air is set, then the oceanic pH and temperature follow, and from them, the inorganic equilibria. Moreover, in an evolutionarily stable system there is no need for constant CO<sub>2</sub>:O<sub>2</sub> – indeed, the glacial/interglacial changes at the start of the Holocene shows that this ratio can change by up to 40% within a millennium. In episodes of rapid albedo or solar change, the large O<sub>2</sub> reservoir and the even larger N<sub>2</sub> burden act as 'memories', helping the global average plant specificity to maximise survival, given albedo and insolation. Again, we disagree with the referee's statement that the N<sub>2</sub> atmospheric burden is 'demonstrably' not under the control of the biological nitrogen cycle.

The referee concludes with helpful remarks about future modelling, with which we concur: there may be much to be learned by coupling geochemical modelling with the biological constraints provided by rubisco's systematics.

Minor points: thanks; will be acted on.

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Final remarks on all comments

In another Comment on this paper, Marcel Andre discusses the tail wagging the dog. To change the analogy slightly, from our experience involving occasional over-near elephants, comparison can be made with an elephant's tracks: footprints and droppings. The impressions on the solid Earth, the footprints, show both the mass of the elephant and its motion. A skilled tracker can use prints to tell how big the elephant is, and its behaviour – browsing, running, playing. The elephant droppings are equally informa-

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tive – they give the flux of food, the type of food, and indeed reflect the general state of the vegetation (rainfall, seasonal cycle, etc.). Similarly, the sedimentary record, like the elephant's prints, accurately records the mass of the biosphere, and the organic deposits reflect the metabolism. From these, the history of the atmosphere can be reconstructed. But just as the footprint and dung do not control the elephant, so we argue that the flux of inorganic carbonate and organic deposits do not control the atmosphere. The footprints and dung happen because of what the elephant does, and our elephant is the biosphere.

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Interactive comment on Solid Earth Discuss., 3, 769, 2011.

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