



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

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Our thanks to Tyler Volk for posting this helpful statement of the 'geochemistry-first' standpoint.

As a general response, we do not see the problem of inorganic precipitation versus biological controls as 'either/or' . Instead, our position is that the two are mutually interactive. The fundamental control, however, is the key link between abiotic carbon and organic carbon, and that is the specificity of rubisco. On this single point depends the vast bulk of the biosphere.

We argue that biological kinetics will always outpace abiotic equilibria, and that therefore biology leads, though its direct and rapid control of CO₂. The inorganic reactions do indeed work to attain equilibria, and we do not dispute the conclusions drawn from the models depending on long-term inorganic equilibrium.

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However, we argue that inorganic chemistry is compelled to operate in the ambient environment which is set by biology, in particular by the mechanism of rubisco's specificity. The inorganic equilibria are thus attained in an external environment set by the pH, pCO₂ and T that are controlled by the action of natural selection on rubisco. To take a historic analogy, humans eat drink and are merry in Washington today just as they did in ancient Rome and Nineveh. But the ways in which they eat, drink and are merry depend on the local tax collection and revenue spending system, and that can be very different in its impact on the broad society. Chemistry rules, whether on Mars, Venus or Earth, but biochemical kinetics can set the framework in which the system of getting and spending operates: T, pH, atmospheric pressure, phases of water.

Now to the specific questions: 1. Lower CO₂ in ice ages favours marine rubisco over terrestrial, and C₄ over C₃ plants: there will be strong selective pressures. Marcel Andre has commented on the C₃/C₄ competition. The C₄ option, which has evolved in multiple lines, approximates the pre-concentration stage in laboratory analysis of carbon, in that the carbon is pre-concentrated before presentation to the rubisco. This enables the plant to thrive in low CO₂ settings, but at an energy cost compared to C₃ plants. CAM plants (e.g. pineapple) also have a pre-collection stage. As noted in our Fig 3, the feedbacks in the system may oscillate rather like a domestic heating control. We do not argue against externally-driven change, and biology clearly must responds to Milankovitch forcings. What is a surprise is the size of the oscillations. Indeed, the land/ocean selective competition may be important here, with dominance switching between on the one hand marine cold-loving photosynthesis and C₄ land plants, and on the other hand the terrestrial C₃ biosphere. All use rubisco I, but in competing ways. To quote Tcherkez et al., 2006 "so-called higher specificity Rubiscos will have higher specificities only at low temperatures; at higher temperatures, the tables will be turned."

2. Re the question about the early history of the atmosphere, when the O₂/CO₂ ratio of the air was millions of time smaller than today. We have elsewhere argued that

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Rubisco Form 1 (oxygenesis) evolved around 2.9 Ga ago, long prior to the Great Oxidation Event, and that other forms of Rubisco are significantly older, with rubisco in anoxygenic bacteria dating from at least the mid-Archaeon, and rubisco forms in anaerobes such as methanogens perhaps being older yet (Nisbet et al., The age of Rubisco: the evolution of oxygenic photosynthesis *Geobiology*. 5, 311-335; see also Nisbet, E.G. and Fowler, C.M.R. The Evolution of the Atmosphere in the Archaean and early Proterozoic. *Chinese Science Bulletin*, 55, 1-10).

More generally, we note that CO₂ and O₂ crossing points are inverse and obverse of the same biological coin – they cannot be separately controlled. Nor, for that matter, can N₂ – the carbon/oxygen and nitrogen cycles are intricately interlinked biochemically.

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