

A BIFURCATION MODEL FOR ATMOSPHERIC O₂ GROWTH

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Evolution of atmospheric oxygen

Isotopic evidence of perturbations in the carbon and sulfur cycles, along with the fossil record of primitive animals, suggest that significant changes in atmospheric oxygen took place during the late Neoproterozoic (Derry et al., 1992; Canfield and Teske, 1996; Runnegar, 1982). Here I explore a mass balance model for the carbon - oxygen system that includes oxygen-dependent feedback functions for organic carbon burial and weathering. One consequence of this non-linear model is the existence of multiple steady states for atmospheric oxygen. The Neoproterozoic carbon and strontium isotope records can be combined to demonstrate a perturbation to the carbon - oxygen system that was capable of moving the system from a low oxygen state to a high oxygen state characteristic of the Phanerozoic.

Oxygen mass balance terms

Free oxygen is produced by the burial of reduced carbon, and to a lesser extent, reduced sulfur. Oxygen is consumed by the oxidation of reduced mantle volatiles, and the oxidative weathering of reduced carbon and sulfur. Organic carbon burial (prior to the advent of significant terrestrial life) is a function of both net primary production and the oxygenation of the oceanic water column. Phosphorous availability in the marine environment is sensitive to the oceanic O₂ (van Cappellen and Ingall, 1996). At low pO₂, P is efficiently recycled during diagenesis, and P burial effectively decoupled from OC burial. At high pO₂ ferric iron compounds effectively sequester P in sediments, limiting the oceanic P availability. Nitrogen fixation and denitrification also depend on oceanic oxygen. At low pO₂, denitrification rates may exceed the ability of nitrogen fixing bacteria to supply fixed nitrogen. Furthermore, low bottom water oxygen levels enhance the burial of organic carbon because anoxic rates of decomposition are slower than oxic rates, although this relationship is not as simple as once assumed. Thus any function for marine organic carbon burial rate (i.e. oxygen production rate) should have a maximum at some intermediate pO₂. For the present purposes of an analytical solution we take the form of a logistic equation to represent O₂ production; however numerical solutions showing similar features result from the incorporation of

the constraints listed above without the need to adopt an arbitrary function.

For simplicity we will not consider the terms arising from the sedimentary cycle of sulfur. The sulfur cycle has a significantly smaller influence on the oxygen mass balance than carbon. We take the rate of oxygen consumption from the oxidation of mantle volatiles to be a linear function of the degassing flux. However, the oxidation rate of sedimentary organic matter is more complex. At very low pO₂, the oxidative weathering rate of kerogens must be low. At pO₂ near modern values, oxidative weathering of sedimentary organic carbon is nearly complete, except in quite limited regions of very rapid transport and reburial of recycled sediments. Thus, further increases in pO₂ cannot significantly increase the weathering rate of sedimentary carbon. Oxidative weathering of kerogen is a surface controlled reaction, and we propose the rate has the form of a surface saturation mechanism such as the Langmuir isotherm. Adsorption of O₂ on graphite follows this relationship (Brunauer et al., 1938), and recent experimental evidence suggests that oxidation of natural coal can be modeled with a Langmuir isotherm, at least over the relevant range of pO₂ (Chang and Berner, 1998).

Formally the oxygen mass balance can be stated:

$$1. \quad \frac{dO}{dt} = [\kappa O(1 - \alpha O) + \beta] - \frac{\gamma O}{(1 - \gamma O)}$$

where the first term represents oxygen production modulated by kappa, which is inversely proportional to the magnitude of the reduced volatile sink. If the volatile flux is large, kappa will be small, preventing any large accumulation of oxygen (O). Alpha controls the position of the maximum in the O₂ production curve, and is estimated by comparison with modern data. The second term has the form of the Langmuir isotherm (also of Michaelis-Menten or Monod kinetics), and gamma is the saturation constant. The value of gamma is determined empirically from data on the oxidation of coal, and is near 50 (Chang and Berner, 1998).

Multiple steady states

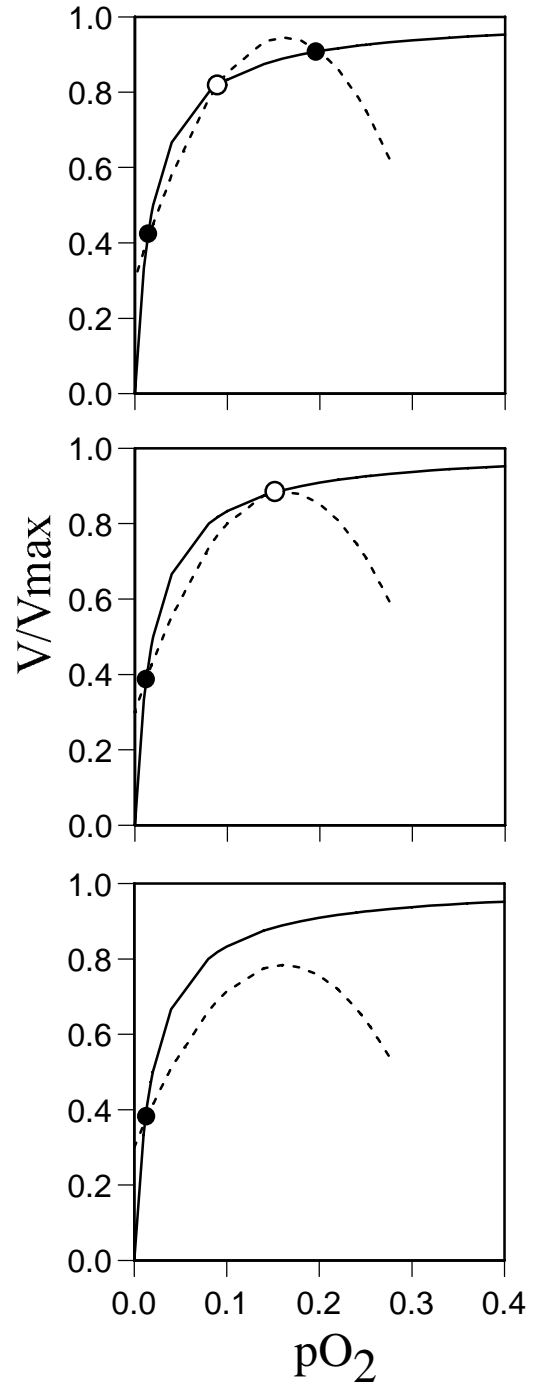
Equation 1 may be rewritten in steady state form as:

$$2. \quad [\kappa O(1 - \alpha O) + \beta] = \frac{\gamma O}{(1 - \gamma O)}$$

This equation has one, two, or three solutions depending on the value of kappa. If kappa is small, only one steady state solution exists at low pO_2 (the exact value is determined by beta), but as kappa increase, the system undergoes a transcritical bifurcation at a critical point and a second steady state solution appears (Figure 1). This second solution is transient and unstable, however further increase in kappa results in the establishment of three nodes, two of which are stable steady state solutions. In physical terms the decrease in the reduced volatile flux allows the creation of a second steady state at high pO_2 once a threshold value of the reduced volatile flux has been passed.

The possibility of multiple steady states in the atmospheric oxygen balance was explored briefly by Lasaga (1981), who noted that “autocatalytic” or non-linear feedback behavior was a prerequisite for their existence. Equations 1 and 2 describe a system in which the reduced volatile flux acts as a “master variable”, controlling the shape of solution space and the number of possible solutions. Regardless of the production of oxygen, if the volatile flux is sufficiently high only one stable state can exist, that of low pO_2 . If the volatile flux drops below the critical threshold, a second stable steady state can exist, but this state will not be “occupied” unless a sufficiently large perturbation increases pO_2 enough to allow the system to settle into the new, higher steady state. Both the low and high nodes are locally stable, and any small perturbations will result in a return to the initial state. In order to change occupancy of the stable nodes, the perturbation must increase pO_2 past the unstable node, conceptually equivalent to an “activation energy barrier.” Once the system occupies this high O_2 steady state, a large perturbation to low values is necessary to return to the low O_2 steady state. Alternatively, an increase in the reduced volatile flux could simply eliminate the high steady state, and then the system would necessarily return to the low O_2 steady state.

Figure 1: Phase plane plot of oxygen model. Rates of oxygen consumption (solid curve) and production (dashed curve) from Equation 2 as a function of pO_2 . V/V_{max} is the rate of O_2 consumption as a fraction of the maximum theoretical rate. Solid circles indicate stable nodes, open circles indicate unstable nodes. The constant κ increases from the lower panel to the upper, all other parameters remain fixed. The lower panel shows a system with only one steady state, all perturbations away from this value must eventually return to the stable node. The middle panel shows the onset of the transcritical bifurcation at the threshold value of κ . The upper panel shows two stable steady states, separated by an unstable node (“repelling point”). It is necessary to perturb the system and cross the unstable node to move between the two stable steady state solutions. All local perturbations will return to the stable node they began from, unless they are sufficiently large to cross into the attracting region of the other stable node.



The above analysis suggests that, rather than a continuous or gradual increase in pO_2 through the Precambrian, there was at least one rapid, locally irreversible, change in the size of the O_2 reservoir. This increase is in part a function of the thermal evolution of the Earth. Gradually decreasing heat flow should imply decreasing reduced volatile fluxes from the deep interior and would permit the establishment of a potential high O_2 reservoir. The establishment of such a state would be relatively sudden, as would its subsequent occupancy following a perturbation in the carbon cycle.

Neoproterozoic C, S and Sr data

Carbon isotope data from the Neoproterozoic show a prolonged period of very high values punctuated by brief excursions to strongly negative values associated with major glaciations (Knoll et al., 1986). Following the last of these glaciations (the Varanger, ca. 590 Ma) $\delta^{13}\text{C}$ in carbonates returns to high values ($\approx +5$ to $+8$ ‰) in the lower Vendian (Kaufman et al., 1991, Narbonne et al., 1994). $\delta^{13}\text{C}$ values afterwards decline and again show a pronounced negative excursion at the Precambrian-Cambrian boundary (Saylor et al., 1998). The prolonged periods of high $\delta^{13}\text{C}$ indicate burial of a large mass fraction of organic carbon in global sediments during the post-Varanger interval. The same Vendian interval is characterized by a dramatic increase in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seawater (Derry et al., 1989; Kaufman et al., 1993). The increase in the strontium isotopic ratio of seawater appears to reflect collisional tectonics in the Pan-African orogeny. The rate of increase exceeds that known for the Cenozoic, associated with the India-Asia collision. The India-Asia collision resulted in a reorganization of plate motions and possible decrease in overall spreading rates in the Pacific during the late Eocene – early Oligocene. Beginning in the Oligocene, clastic fluxes to the oceans began to increase, with dramatic increases in the Neogene. This increased particle flux is associated with increased burial of organic matter (France-Lanord and Derry, 1997). By analogy, the Vendian – Cambrian increase in marine $^{87}\text{Sr}/^{86}\text{Sr}$ also likely began with plate motion reorganization and a decrease in hydrothermal fluxes from the oceanic crust (Derry et al., 1989). The rapid rise probably also reflects significantly increased erosion and sedimentation rates, although not necessarily large changes in chemical weathering rates. The combination of high fractional burial of organic carbon indicated by the $\delta^{13}\text{C}$ mass balance, and high cycling rates of sedimentary carbon indicated by the increasing $^{87}\text{Sr}/^{86}\text{Sr}$ values implies a period of significant growth of the sedimentary organic carbon reservoir (Derry et al., 1992). These authors showed that there was potential for substantial perturbation of the oxygen reservoir within a fairly short (ca. 10 Ma) window of time during the Vendian, using a mass balance model for the organic carbon reservoir that incorporates both the $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ information.

Sedimentary sulfur isotope data show an inverse correlation with $\delta^{13}\text{C}$ data during the Phanerozoic, indicating that the oxidation of organic carbon is globally coupled to the reduction of sulfate, and vice versa (Veizer et al., 1980). Prior to the mid-late Cambrian, the existence of this correlation is less clear, although there may be a general negative correlation at long time scales (Strauss, 1993). Canfield and Teske (1996) have proposed that isotopic evidence for sulfide oxidation begins in the Neoproterozoic, and use this to place a bound on atmospheric $p\text{O}_2$ prior to that time of about 10% of present atmospheric level (PAL). Careful examination of available $\delta^{34}\text{S}$ data suggest that clear evidence of sulfide oxidation is not found until the lower Vendian. Thus we take 10% PAL as an approximate boundary condition for atmospheric O_2 until the base of the Vendian. The model calculations of O_2 evolution are not highly sensitive to this boundary condition.

Numerical simulations using the above relationships and boundary conditions demonstrate that it is possible to increase $p\text{O}_2$ from 10% PAL to $>50\%$ PAL within the time frame of the post-Varanger positive $\delta^{13}\text{C}$ excursion. The new, higher value of $p\text{O}_2$ appears as a stable solution, in the manner of the analytical model developed above. The change represents an increase in the atmospheric O_2 mass of ca. $20 - 30 \times 10^{18}$ moles of O_2 . In fact,

models run without a stabilizing negative feedback such as the oxidative weathering model proposed above give rise to very large changes in $p\text{O}_2$ and do not stabilize.

Thus I propose a model for the evolution of atmospheric oxygen during the Neoproterozoic as a transition between two steady states of a non-linear system. The creation of multiple steady states is itself coupled to the long term thermal evolution of the Earth. It is possible that plate reorganizations associated with Pan-African collisional events resulted in a reduction of the submarine hydrothermal flux, a major carrier of reduced mantle volatiles to the atmosphere. This change could have dropped the volatile flux below the level necessary for the type of transcritical bifurcation shown in Figure 1. Such a scenario is consistent with the record of $^{87}\text{Sr}/^{86}\text{Sr}$ in marine carbonates, but the exact timing of the change is not critical to the model. Once this second, higher steady state became potentially available, the strong perturbation of the carbon - oxygen system that took place in the lower Vendian allowed the system to move into the stability well around the high O_2 solution. The atmospheric oxygen budget since that time has apparently been stable near 100 % PAL, with the possible exception of very high values in the Carboniferous and Permian associated with the radiation of vascular plants and the burial of extensive coals (Berner, 1999). This stability argues for the existence of a locally stable steady state at $p\text{O}_2 \approx 0.2$ atmospheres. Such a state is buffered by the coupling between the sedimentary carbon and sulfur redox cycles, and the efficient oxidative weathering of reduced carbon. In the Phanerozoic, it is likely that oxidation of reduced volatiles has not been a major sink for O_2 . Other feedbacks, such as those involving phosphorous control proposed by Kump (1988) or Van Cappellen and Ingall (1996) may be important stabilizing mechanisms during the Phanerozoic.

Prior to the Vendian “catastrophe”, a low O_2 steady state was maintained by oxidation of mantle volatiles, and a nearly linear weathering feedback. In the region below 0.05 to 0.1 atm $p\text{O}_2$, our model suggests strong feedback between $p\text{O}_2$ and the rate of oxidative weathering. Even given the presence of a second, higher steady state, only a significant perturbation of the carbon – oxygen system can be expected to push $p\text{O}_2$ high enough to enter a new region of stability.

The well-documented rise of the early metazoa occurs during this interval of rapid and dramatic environmental change (e.g. Knoll and Walter, 1992). It is likely that the Ediacaran fauna had requirements for dissolved O_2 levels consistent with atmospheric oxygen levels of 50 – 100% PAL (Runnegar, 1982). Thus it is plausible to tie the radiation of large-bodied animals and the ensuing development of skeletonization to the Vendian “step” in atmospheric O_2 levels. The combination of the long term thermal evolution of the Earth with the particular tectonic and sedimentary events of the Neoproterozoic appears to have resulted in a major transformation in the Earth’s surface environment, one that has endured over the ensuing 550 million years.

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