

Modelling major transitions in the earth system

Benjamin Mills

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Abstract

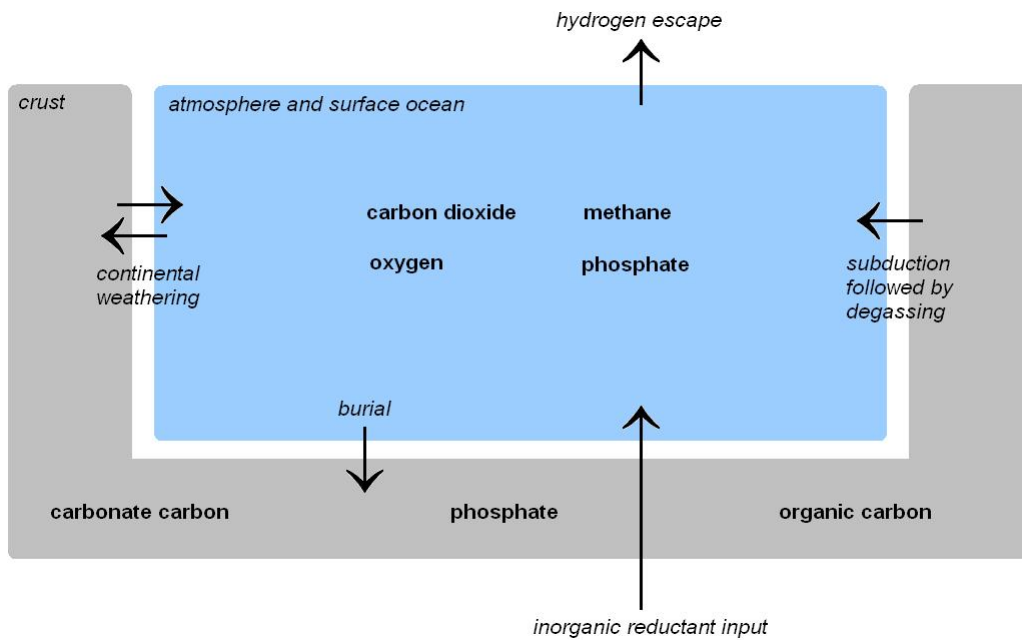
Something along the lines of :

Around 2.4 Ga oxygen went from being a trace gas to an important atmospheric constituent. Named the 'Great oxidation event', this transition caused major changes in climate. The 'boring' billion years that followed seem to show a stable atmosphere with $O_2 > 0.01$ PAL (present atmospheric level). A secondary oxidation is thought to have occurred in the neoproterozoic (1000Ma–542Ma) in which oxygen concentration approached present day level. Here we use a simple earth system model to analyse these transitions and look at possible causes and effects.

1 Model schemataic

This model links the simple ocean biology model of Goldblatt et al. [2006] to a stripped down climate, weathering and nutrient system which is based on the 'Redfield revisited' [Lenton and Watson, 2000] and 'COPSE' [Bergman et al. 2004] models.

The model consists of two boxes. One representing the atmosphere and ocean, and one representing the crust. Species are moved from the atmosphere/ocean to the crust via burial, and are returned by subduction and degassing. Continental weathering allows transfer in both directions. The system is supplied with an assumed quantity of inorganic reductant, represented chemically by ferrous iron. Hydrogen escapes to space as a result of methane reaching the upper atmosphere.



The system consists of four atmosphere and ocean reservoirs, and three crustal reservoirs.

Name	Meaning	Present day size (mol)
P	Phosphate	3.1×10^{15}
O	Oxygen	3.7×10^{19}
A	Carbon dioxide	3.193×10^{18}
M	Methane	1×10^{14}
G	Buried organic carbon	1.25×10^{21}
C	Buried carbonate carbon	5×10^{21}
Q	Buried phosphate	1.3×10^{20}

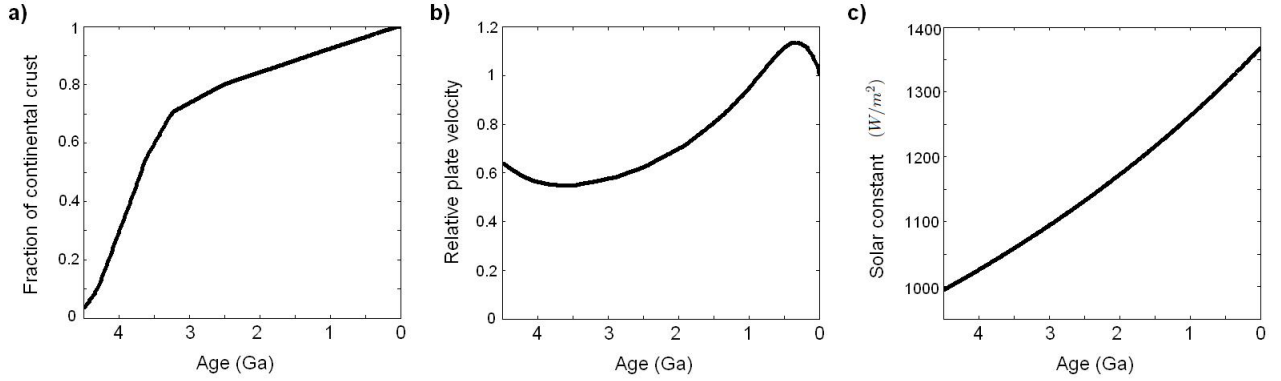
Table 1: Model reservoirs

2 Model Forcings

The model is forced with changing continental area, tectonic plate velocity and solar constant. We use the parameters ϵ and $vasc$ (both with present day value of 1) to represent biological enhancement of weathering. Following Geocarb [Berner, 1991], we assume $vasc = \frac{1}{7}$ before the evolution of vascular plants (at around 400Ma), rising to 1 thereafter. We will explore the effect of altering this value. We add ϵ to represent increased weathering for nutrients in the neoproterozoic. It is thought that rapid expansion of land-based organisms at this time may have driven a transition due to increased weathering rates [Heckman et al., 2001. Lenton and Watson, 2004] and we hope to observe the effects such an increase might have. Finally we use r to represent the amount of inorganic reductant entering the system.

Name	Meaning	Present day size	Source
U	Fraction of continental crust	1	Campbell, 2003.
V	Relative tectonic plate velocity	1	Korenaga, 2008.
S	Solar constant	$1368 W/m^2$	Bergman et al, 2003.
ϵ	Biotic weathering enhancement	1	Lenton and Watson, 2004.
$vasc$	Vascular plant weathering enhancement	1	Bergman et al, 2003.
r	Inorganic reductant input	7.5×10^{10} mol O ₂ equiv yr ⁻¹	Goldblatt et al, 2006.

Table 2: Model forcings



Name	Meaning	Size	Source
β	Burial fraction	2×10^{-3}	Goldblatt et al, 2006
k_1	Net primary production	$3.75 \times 10^{15} \text{ mol C yr}^{-1}$	Goldblatt et al, 2006
k_2	Ca associated phosphorus burial	$1.5 \times 10^{10} \text{ mol P yr}^{-1}$	Redfield revisited
k_3	Fe associated phosphorus burial	$6 \times 10^9 \text{ mol P yr}^{-1}$	Redfield revisited
k_4	Present day oxic fraction	0.86	Redfield revisited
k_5	Silicate weathering	$6.578 \times 10^{12} \text{ mol C yr}^{-1}$	For steady state at present day
k_6	Carbonate weathering	$1.335 \times 10^{13} \text{ mol C yr}^{-1}$	GEOCARB
k_7	Oxidative weathering	$6.177 \times 10^{12} \text{ mol C yr}^{-1}$	For steady state at present day
k_8	Reactive phosphorus weathering	$5.1 \times 10^{10} \text{ mol P yr}^{-1}$	For steady state at present day
k_9	Organic carbon degassing	$1.25 \times 10^{12} \text{ mol C yr}^{-1}$	GEOCARB
k_{10}	Carbonate carbon degassing	$6.65 \times 10^{12} \text{ mol C yr}^{-1}$	GEOCARB
d_γ	Respiration limitation constant	6.33×10^{18}	For steady state at present day
d_δ	Methanotrophy constant	2.73×10^{17}	Goldblatt et al, 2006
k_{oxic}	C:P burial ratio, oxic ocean	217 mol:mol	COPSE
k_{anoxic}	C:P burial ratio, anoxic ocean	4340 mol:mol	COPSE
k_{carb}	CO ₂ greenhouse approx	8°C	Haqq misra et al, 2008.
k_{meth}	CH ₄ greenhouse approx	2°C	Haqq misra et al, 2008.

Table 3: Table of constants

3 Ocean biology model

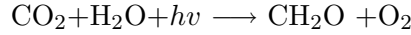
Following Goldblatt et al. (2006) the marine biosphere resolves fluxes of anoxygenic and oxygenic photosynthesis, aerobic respiration, methanogenesis and methanotrophy. To this we add a simple nutrient and anoxia system, based on the 'Redfield revisited' model [Lenton and Watson, 2000]. Throughout this derivation we track available organic carbon, \mathbf{B} , to ensure that this is conserved.

3.1 Nutrient limitation

We assume the biosphere is limited by a single nutrient, which we model as phosphate. Net primary production via oxygenic photosynthesis is assumed to be proportional to the size of the phosphate reservoir \mathbf{P} .

$$N = k_1 \left(\frac{\mathbf{P}}{\mathbf{P}_0} \right) \quad (3.1.1)$$

3.2 Oxygenic photosynthesis



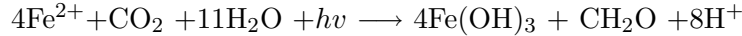
This process removes carbon dioxide and increases oxygen and available organic carbon in the atmosphere/ocean box.

$$\mathbf{A}'_{oxphoto} = -N \quad (3.2.1)$$

$$\mathbf{B}'_{oxphoto} = N \quad (3.2.2)$$

$$\mathbf{O}'_{oxphoto} = N \quad (3.2.3)$$

3.3 Anoxygenic photosynthesis



The assumed input of ferrous iron, r , is used to increase available organic carbon in the atmosphere/ocean via anoxygenic photosynthesis.

$$\mathbf{A}'_{anoxphoto} = -r \quad (3.3.1)$$

$$\mathbf{B}'_{anoxphoto} = r \quad (3.3.2)$$

3.4 Organic carbon burial

We assume a fraction, β , of the available organic carbon is buried in sediments. This decreases the organic carbon in the atmosphere/ocean box and increases organic carbon in the crust.

$$\mathbf{B}'_{orgCburial} = -\beta(N + r) \quad (3.4.1)$$

$$\mathbf{G}'_{orgCburial} = \beta(N + r) \quad (3.4.2)$$

3.5 Aerobic respiration



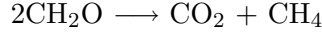
A fraction, γ , of the remaining organic carbon is decomposed by hetrotrophic aerobic respiration. This is a sink of organic carbon and oxygen, and a source of carbon dioxide. $\gamma = \frac{\mathbf{O}}{\mathbf{O}+d_\gamma}$ is a function of oxygen, and corresponds to the inhibition of aerobic respiration below the pasteur point (≈ 0.01 *PAL*). We determine the value of d_γ by assuming steady state at present day oxygen concentrations.

$$\mathbf{B}'_{resp} = -\gamma(1 - \beta)(N + r) \quad (3.5.1)$$

$$\mathbf{O}'_{resp} = -\gamma(1 - \beta)(N + r) \quad (3.5.2)$$

$$\mathbf{A}'_{resp} = \gamma(1 - \beta)(N + r) \quad (3.5.3)$$

3.6 Decomposition and methanogenesis



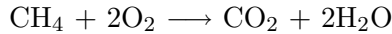
All the remaining organic carbon is assumed to be decomposed by fermentors and methanogens. This is a sink of organic carbon and a source of carbon dioxide and methane.

$$\mathbf{B}'_{methgen} = -(1 - \gamma)(1 - \beta)(N + r) \quad (3.6.1)$$

$$\mathbf{A}'_{methgen} = \frac{1}{2}(1 - \gamma)(1 - \beta)(N + r) \quad (3.6.2)$$

$$\mathbf{M}'_{methgen} = \frac{1}{2}(1 - \gamma)(1 - \beta)(N + r) \quad (3.6.3)$$

3.7 Methanotrophy



A fraction, δ , of the methane produced is used by methanotrophs. This is a sink of oxygen and methane, and a source of carbon dioxide. $\delta = \frac{\mathbf{O}}{\mathbf{O}+d_\delta}$ is a function of oxygen, following the analysis of Goldblatt et al. [2006] and Ren et al. [1997].

$$\mathbf{O}'_{methtroph} = -\delta(1 - \gamma)(1 - \beta)(N + r) \quad (3.7.1)$$

$$\mathbf{M}'_{methtroph} = -\frac{1}{2}\delta(1 - \gamma)(1 - \beta)(N + r) \quad (3.7.2)$$

$$\mathbf{A}'_{methtroph} = \frac{1}{2}\delta(1 - \gamma)(1 - \beta)(N + r) \quad (3.7.3)$$

3.8 Total effect of the biosphere

Summing the fluxes for each species we calculate the effect of the biosphere on the model reservoirs. Here we substitute $\Omega_{(\mathbf{O})} = (1 - \gamma)(1 - \delta)$ to simplify.

$$\begin{aligned}
\mathbf{O}'_{bio} &= \mathbf{O}'_{oxphoto} + \mathbf{O}'_{resp} + \mathbf{O}'_{methtroph} \\
&= N - \gamma(1 - \beta)(N + r) - \delta(1 - \gamma)(1 - \beta)(N + r) \\
&= N - (1 - (1 - \gamma)(1 - \delta))(1 - \beta)(N + r) \\
&= N - (1 - \Omega_{(\mathbf{O})})(1 - \beta)(N + r)
\end{aligned} \tag{3.8.1}$$

$$\begin{aligned}
\mathbf{M}'_{bio} &= \mathbf{M}'_{methgen} + \mathbf{M}'_{methtroph} \\
&= \frac{1}{2}(1 - \gamma)(1 - \beta)(N + r) - \frac{1}{2}\delta(1 - \gamma)(1 - \beta)(N + r) \\
&= \frac{1}{2}(1 - \gamma)(1 - \delta)(1 - \beta)(N + r) \\
&= \frac{1}{2}\Omega_{(\mathbf{O})}(1 - \beta)(N + r)
\end{aligned} \tag{3.8.2}$$

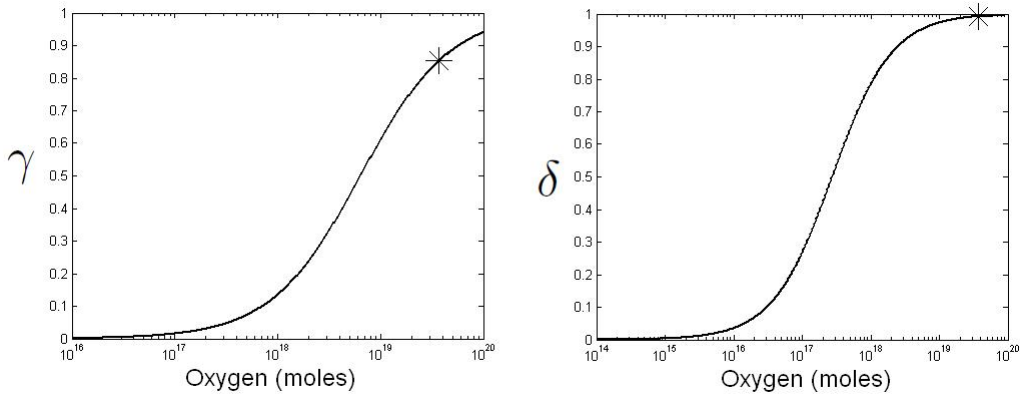
$$\begin{aligned}
\mathbf{A}'_{bio} &= \mathbf{A}'_{oxphoto} + \mathbf{A}'_{anoxphoto} + \mathbf{A}'_{resp} + \mathbf{A}'_{methgen} + \mathbf{A}'_{methtroph} \\
&= -N - r + \gamma(1 - \beta)(N + r) + \frac{1}{2}(1 - \gamma)(1 - \beta)(N + r) + \frac{1}{2}\delta(1 - \gamma)(1 - \beta)(N + r) \\
&= -N - r + (1 - \frac{1}{2}(1 - \gamma)(1 - \delta))(1 - \beta)(N + r) \\
&= -N - r + (1 - \frac{1}{2}\Omega_{(\mathbf{O})})(1 - \beta)(N + r)
\end{aligned} \tag{3.8.3}$$

$$\begin{aligned}
\mathbf{G}'_{bio} &= \mathbf{G}'_{orgCburial} \\
&= \beta(N + r)
\end{aligned} \tag{3.8.4}$$

$$\begin{aligned}
\mathbf{B}'_{bio} &= \mathbf{B}'_{oxphoto} + \mathbf{B}'_{anoxphoto} + \mathbf{B}'_{orgCburial} + \mathbf{B}'_{resp} + \mathbf{B}'_{methgen} \\
&= N + r - \beta(N + r) - \gamma(1 - \beta)(N + r) - (1 - \gamma)(1 - \beta)(N + r) \\
&= 0
\end{aligned} \tag{3.8.5}$$

Substituting $N = k_1 \left(\frac{\mathbf{P}}{\mathbf{P}_0} \right)$ we have:

$$\begin{aligned}
\mathbf{O}'_{bio} &= k_1 \left(\frac{\mathbf{P}}{\mathbf{P}_0} \right) - (1 - \Omega_{(\mathbf{O})})(1 - \beta) \left(k_1 \left(\frac{\mathbf{P}}{\mathbf{P}_0} \right) + r \right) \\
\mathbf{M}'_{bio} &= \frac{1}{2} \Omega_{(\mathbf{O})} (1 - \beta) \left(k_1 \left(\frac{\mathbf{P}}{\mathbf{P}_0} \right) + r \right) \\
\mathbf{A}'_{bio} &= -k_1 \left(\frac{\mathbf{P}}{\mathbf{P}_0} \right) - r + \left(1 - \frac{1}{2} \Omega_{(\mathbf{O})} \right) (1 - \beta) \left(k_1 \left(\frac{\mathbf{P}}{\mathbf{P}_0} \right) + r \right) \\
\mathbf{G}'_{bio} &= \beta \left(k_1 \left(\frac{\mathbf{P}}{\mathbf{P}_0} \right) + r \right)
\end{aligned} \tag{3.8.6}$$



4 Nutrient burial

The nutrient, assumed to be phosphate, can exist either in the atmosphere/ocean or the crust. Burial fluxes for phosphate are adapted from Redfield revisited. All of these reduce the amount of phosphate in the atmosphere/ocean, \mathbf{P} , and increase the crustal reservoir of phosphate, \mathbf{Q} .

Rates of nutrient burial are believed to be dependent on the degree of ocean anoxia, we calculate this using the balance between free oxygen and new production.

$$anox = 1 - k_4 \left(\frac{\mathbf{O}/\mathbf{O}_0}{\mathbf{P}/\mathbf{P}_0} \right) \tag{4.0.7}$$

Organic phosphate burial is calculated using the organic carbon burial flux and the carbon

to phosphorus burial ratio, which we call CP_{sea} .

$$\mathbf{Q}'_{orgP_{burial}} = \frac{G'_{orgP_{burial}}}{CP_{sea}} = \frac{\beta(k_1\left(\frac{\mathbf{P}}{\mathbf{P}_0}\right) + r)}{Cp_{sea}}$$

$$\mathbf{P}'_{orgP_{burial}} = -\frac{\beta(k_1\left(\frac{\mathbf{P}}{\mathbf{P}_0}\right) + r)}{Cp_{sea}} \quad (4.0.8)$$

Van Capellan and Ingall (1994, 1996) suggest that this burial ratio is heavily dependant on anoxia and calculate

$$CP_{sea} = \frac{k_{oxic} \cdot k_{anoxic}}{(1 - anox(\mathbf{O}, \mathbf{P})) \cdot k_{anoxic} + anox(\mathbf{O}, \mathbf{P}) \cdot k_{oxic}} \quad (4.0.9)$$

Following COPSE, we take the constants k_{oxic} and k_{anoxic} to be 217 and 4340 respectively. This is so that $CP_{sea} = 250$ for present day anoxia. This process will give a strong negative feedback on oxygen levels, so we will also test the model with CP_{sea} held constant.

Calcium-bound phosphorus burial is assumed to be proportional to organic carbon burial:

$$\mathbf{Q}'_{Ca-P_{burial}} = k_2 \left(\frac{k_1\left(\frac{\mathbf{P}}{\mathbf{P}_0}\right) + r}{k_1 + r_0} \right) \quad (4.0.10)$$

$$\mathbf{P}'_{Ca-P_{burial}} = -k_2 \left(\frac{k_1\left(\frac{\mathbf{P}}{\mathbf{P}_0}\right) + r}{k_1 + r_0} \right) \quad (4.0.11)$$

Iron-sorbed phosphorous burial is taken to be a function of anoxia:

$$\mathbf{Q}'_{Fe-P_{burial}} = \frac{k_3}{k_4} (1 - anox(\mathbf{O}, \mathbf{P})) \quad (4.0.12)$$

$$\mathbf{P}'_{Fe-P_{burial}} = -\frac{k_3}{k_4} (1 - anox(\mathbf{O}, \mathbf{P})) \quad (4.0.13)$$

Combining these equations we have our phosphate burial flux:

$$\begin{aligned} \mathbf{Q}'_{nutrientburial} &= \mathbf{Q}'_{orgP_{burial}} + \mathbf{Q}'_{Ca-P_{burial}} + \mathbf{Q}'_{Fe-P_{burial}} \\ &= \frac{\beta(k_1\left(\frac{\mathbf{P}}{\mathbf{P}_0}\right) + r)}{Cp_{sea}} + k_2 \left(\frac{k_1\left(\frac{\mathbf{P}}{\mathbf{P}_0}\right) + r}{k_1 + r_0} \right) + \frac{k_3}{k_4} (1 - anox(\mathbf{O}, \mathbf{P})) \end{aligned} \quad (4.0.14)$$

$$\begin{aligned}
\mathbf{P}'_{nutrientburial} &= \mathbf{P}'_{orgPburial} + \mathbf{P}'_{Ca-Pburial} + \mathbf{P}'_{Fe-Pburial} \\
&= -\frac{\beta(k_1\left(\frac{\mathbf{P}}{\mathbf{P}_0}\right) + r)}{Cpsea} - k_2\left(\frac{k_1\left(\frac{\mathbf{P}}{\mathbf{P}_0}\right) + r}{k_1 + r_0}\right) - \frac{k_3}{k_4}(1 - anox(\mathbf{O},\mathbf{P}))
\end{aligned} \tag{4.0.15}$$

5 Climate

The system is subject to a solar forcing, S . We calculate average surface temperature using an energy balance model, adding terms for greenhouse warming by carbon dioxide and methane.

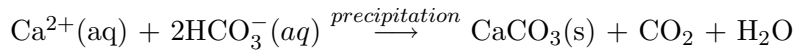
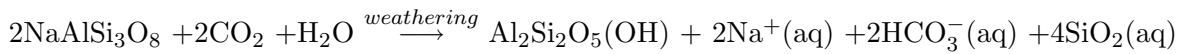
$$T = \sqrt[4]{\frac{(1 - \alpha)S}{4\sigma}} + k_{carb} \log\left(\frac{\mathbf{A}}{\mathbf{A}_0}\right) + k_{meth} \log\left(\frac{\mathbf{M}}{\mathbf{M}_0}\right) + k_{norm} \tag{5.0.16}$$

Here $\alpha = 0.3$ is planetary albedo which we assume is constant. $k_{norm} = -239.9$ is a normalisation constant so that under present day conditions we have $T = 15^\circ C$. For simplicity, we assume a constant temperature rise for every order of magnitude increase in greenhouse gasses. From a rough approximation of the results of Haqq Misra et al. (2008) we obtain $k_{carb} = 8^\circ C$ and $k_{meth} = 2^\circ C$. This approximation is only valid for $\frac{\mathbf{A}}{\mathbf{A}_0}, \frac{\mathbf{M}}{\mathbf{M}_0} \geq 1$.

6 Continental weathering

Following COPSE, we resolve fluxes of silicate, carbonate, oxidative and nutrient weathering. All weathering is assumed to happen on the land, so fluxes are proportional to the relative continental area, U .

6.1 Silicate weathering



Weathering removes 2C from the atmosphere, precipitation returns 1C. So overall, this process removes carbon dioxide from the atmosphere and increases carbonate carbon in the crust.

$$\mathbf{A}'_{silw} = -k_5 \cdot fCO_2 \cdot U \cdot vasc \tag{6.1.1}$$

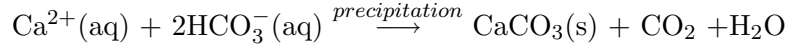
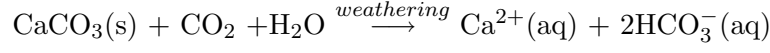
$$\mathbf{C}'_{silw} = k_5 \cdot fCO_2 \cdot U \cdot vasc \tag{6.1.2}$$

Normalised continental area, U , and the weathering enhancement of vascular plants, $vasc$,

affect this flux. COPSE uses the function fCO_2 to describe the dependence of silicate weathering on surface temperature and pCO_2 and we use the same.

$$fCO_2(T, \mathbf{A}) = e^{0.09(T-T_0)}(1 + 0.038(T - T_0))^{0.65} \sqrt{\frac{\mathbf{A}}{\mathbf{A}_0}} \quad (6.1.3)$$

6.2 Carbonate weathering



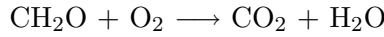
The precipitation reaction is the reverse of the weathering reaction so there is no net effect on the system. However we will require this flux to approximate the weathering of nutrients. Normalised continental area, U , and the weathering enhancement of vascular plants, $vasc$, also affect carbonate weathering.

$$\mathbf{F}_{carbw} = k_6 \cdot gCO_2 \cdot U \cdot vasc \quad (6.2.1)$$

Where gCO_2 (again from COPSE) describes temperature and pCO_2 dependence:

$$gCO_2(T, \mathbf{A}) = (1 + 0.087(T - T_0)) \sqrt{\frac{\mathbf{A}}{\mathbf{A}_0}} \quad (6.2.2)$$

6.3 Oxidative weathering



We assume the rate of oxidative weathering is proportional to the continental area, U , and to the amount of buried organic carbon in the crust, \mathbf{G} . Following Lasaga and Ohmoto (2002) we also assume a square root dependence on pO_2 .

$$\mathbf{G}'_{oxidw} = -k_7 \cdot U \cdot \frac{\mathbf{G}}{\mathbf{G}_0} \sqrt{\frac{\mathbf{O}}{\mathbf{O}_0}} \quad (6.3.1)$$

$$\mathbf{O}'_{oxidw} = -k_7 \cdot U \cdot \frac{\mathbf{G}}{\mathbf{G}_0} \sqrt{\frac{\mathbf{O}}{\mathbf{O}_0}} \quad (6.3.2)$$

$$\mathbf{A}'_{oxidw} = k_7 \cdot U \cdot \frac{\mathbf{G}}{\mathbf{G}_0} \sqrt{\frac{\mathbf{O}}{\mathbf{O}_0}} \quad (6.3.3)$$

6.4 Weathering of nutrients

Following COPSE, we calculate the weathering flux of phosphate by scaling to the other weathering fluxes. This follows the assumption [Van Capellan and Ingall, 1994, 1996.] that organically buried phosphorus is weathered with organic matter, calcium associated phosphorus is weathered with carbonates and iron-sorbed phosphorus is weathered with silicates.

$$\mathbf{P}'_{phosw} = \epsilon \cdot k_8 \left(\frac{2}{12} \frac{silw}{silw_0} + \frac{5}{12} \frac{carbw}{carbw_0} + \frac{5}{12} \frac{oxidw}{oxidw_0} \right) \quad (6.4.1)$$

$$\mathbf{P}'_{phosw} = \epsilon \cdot k_8 \cdot U \left(\frac{2}{12} fCO_2 \cdot vasc + \frac{5}{12} gCO_2 \cdot vasc + \frac{5}{12} \frac{\mathbf{G}}{\mathbf{G}_0} \sqrt{\frac{\mathbf{O}}{\mathbf{O}_0}} \right) \quad (6.4.2)$$

7 Subduction and degassing

Crustal deposits of organic and carbonate carbon are assumed to undergo subduction at a rate proportional to the tectonic plate velocity, V . We assume all products are degassed.

7.1 Organic carbon degassing



We assume all of the degassed organic carbon reacts with oxygen in the atmosphere. This is a sink of oxygen and organic carbon, and a source of carbon dioxide. The rate of degassing is proportional to plate velocity, V , and the relative amount of organic carbon, \mathbf{G} , in the crust.

$$\mathbf{G}'_{orgCdegass} = -k_9 \cdot V \cdot \frac{\mathbf{G}}{\mathbf{G}_0} \quad (7.1.1)$$

$$\mathbf{O}'_{orgCdegass} = -k_9 \cdot V \cdot \frac{\mathbf{G}}{\mathbf{G}_0} \quad (7.1.2)$$

$$\mathbf{A}'_{orgCdegass} = k_9 \cdot V \cdot \frac{\mathbf{G}}{\mathbf{G}_0} \quad (7.1.3)$$

7.2 Carbonate carbon degassing

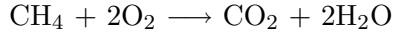
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This reduces the amount of carbonate in the crust and increases carbon dioxide in the atmosphere/ocean box. The rate of degassing is proportional to plate velocity, V , and the relative amount of carbonate carbon, \mathbf{C} , in the crust.

$$\mathbf{C}'_{carbCdegass} = -k_{10} \cdot V \cdot \frac{\mathbf{C}}{\mathbf{C}_0} \quad (7.2.1)$$

$$\mathbf{A}'_{carbCdegass} = +k_{10} \cdot V \cdot \frac{\mathbf{C}}{\mathbf{C}_0} \quad (7.2.2)$$

8 Methane oxidation



Methane and oxygen react together in the atmosphere. The effect of oxygen concentration on rate of oxidation is complex (due to the formation of an ozone layer with sufficient oxygen) and can be approximated from photochemical models, we follow Goldblatt et al (2006) and use their approximation:

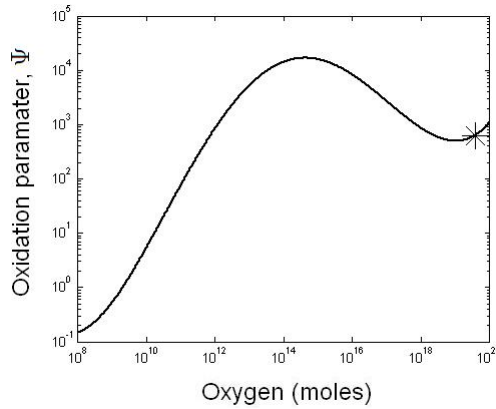
$$\mathbf{M}'_{methox} = -\frac{1}{2}\Psi(\mathbf{O}) \cdot \mathbf{M}^{0.7} \quad (8.0.3)$$

$$\mathbf{O}'_{methox} = -\Psi(\mathbf{O}) \cdot \mathbf{M}^{0.7} \quad (8.0.4)$$

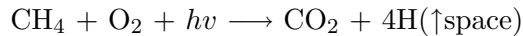
$$\mathbf{A}'_{methox} = \frac{1}{2}\Psi(\mathbf{O}) \cdot \mathbf{M}^{0.7} \quad (8.0.5)$$

where $\Psi(\mathbf{O}) = 10^{a_1(\log \mathbf{O})^4 + a_2(\log \mathbf{O})^3 + a_3(\log \mathbf{O})^2 + a_4(\log \mathbf{O}) + a_5}$

$a_1 = 0.003$, $a_2 = -0.1655$, $a_3 = 3.2305$, $a_4 = -25.8343$ and $a_5 = 71.5398$



9 Hydrogen escape



This process is a sink of oxygen and methane, and a source of carbon dioxide. We assume hydrogen escape is diffusion limited, so can set a constant $s = 3.7 \times 10^{-5}$ [Claire et al. 2006] such that:

$$\mathbf{M}'_{H-escape} = -s\mathbf{M} \quad (9.0.6)$$

$$\mathbf{O}'_{H-escape} = -s\mathbf{M} \quad (9.0.7)$$

$$\mathbf{A}'_{H-escape} = s\mathbf{M} \quad (9.0.8)$$

10 Full model equations

Summing sources and sinks for each reservoir we arrive at the equations representing the whole system.

$$\begin{aligned}
\mathbf{P}' &= \mathbf{P}'_{phosw} + \mathbf{P}'_{nutrientburial} \\
&= \epsilon \cdot k_8 \cdot U \left(\frac{2}{12} fCO_2 \cdot vasc + \frac{5}{12} gCO_2 \cdot vasc + \frac{5}{12} \frac{\mathbf{G}}{\mathbf{G}_0} \sqrt{\frac{\mathbf{O}}{\mathbf{O}_0}} \right) \\
&\quad - \frac{\beta(k_1 \left(\frac{\mathbf{P}}{\mathbf{P}_0} \right) + r)}{Cpsea} - k_2 \left(\frac{k_1 \left(\frac{\mathbf{P}}{\mathbf{P}_0} \right) + r}{k_1 + r_0} \right) - \frac{k_3}{k_4} (1 - anox(\mathbf{O}, \mathbf{P}))
\end{aligned}$$

$$\begin{aligned}
\mathbf{O}' &= \mathbf{O}'_{bio} + \mathbf{O}'_{oxidw} + \mathbf{O}'_{orgCdegass} + \mathbf{O}'_{methox} + \mathbf{O}'_{H-escape} \\
&= k_1 \left(\frac{\mathbf{P}}{\mathbf{P}_0} \right) - (1 - \Omega_{(\mathbf{O})})(1 - \beta)(k_1 \left(\frac{\mathbf{P}}{\mathbf{P}_0} \right) + r) - k_7 \cdot U \cdot \frac{\mathbf{G}}{\mathbf{G}_0} \sqrt{\frac{\mathbf{O}}{\mathbf{O}_0}} \\
&\quad - k_9 \cdot V \cdot \frac{\mathbf{G}}{\mathbf{G}_0} - \Psi(\mathbf{O}) \cdot \mathbf{M}^{0.7} - s\mathbf{M}
\end{aligned}$$

$$\begin{aligned}
\mathbf{A}' &= \mathbf{A}'_{bio} + \mathbf{A}'_{silw} + \mathbf{A}'_{oxidw} + \mathbf{A}'_{orcCdegass} + \mathbf{A}'_{carbCdegass} + \mathbf{A}'_{methox} + \mathbf{A}'_{H-escape} \\
&= -k_1 \left(\frac{\mathbf{P}}{\mathbf{P}_0} \right) - r + (1 - \frac{1}{2}\Omega_{(\mathbf{O})})(1 - \beta)(k_1 \left(\frac{\mathbf{P}}{\mathbf{P}_0} \right) + r) - k_5 \cdot fCO_2 \cdot U \cdot vasc \\
&\quad + k_7 \cdot U \cdot \frac{\mathbf{G}}{\mathbf{G}_0} \sqrt{\frac{\mathbf{O}}{\mathbf{O}_0}} + k_9 \cdot V \cdot \frac{\mathbf{G}}{\mathbf{G}_0} + k_{10} \cdot V \cdot \frac{\mathbf{C}}{\mathbf{C}_0} + \frac{1}{2}\Psi(\mathbf{O}) \cdot \mathbf{M}^{0.7} + s\mathbf{M}
\end{aligned}$$

$$\begin{aligned}
\mathbf{M}' &= \mathbf{M}'_{bio} + \mathbf{M}'_{methox} + \mathbf{M}'_{H-escape} \\
&= \frac{1}{2}(1 - \Omega_{(\mathbf{O})})(1 - \beta)(k_1 \left(\frac{\mathbf{P}}{\mathbf{P}_0} \right) + r) - \frac{1}{2}\Psi(\mathbf{O}) \cdot \mathbf{M}^{0.7} - s\mathbf{M}
\end{aligned}$$

$$\begin{aligned}
\mathbf{G}' &= \mathbf{G}'_{bio} + \mathbf{G}'_{oxidw} + \mathbf{G}'_{orgCdegass} \\
&= \beta(k_1 \left(\frac{\mathbf{P}}{\mathbf{P}_0} \right) + r) - k_7 \cdot U \cdot \frac{\mathbf{G}}{\mathbf{G}_0} \sqrt{\frac{\mathbf{O}}{\mathbf{O}_0}} - k_9 \cdot V \cdot \frac{\mathbf{G}}{\mathbf{G}_0}
\end{aligned}$$

$$\begin{aligned}
\mathbf{C}' &= \mathbf{C}'_{silw} + \mathbf{C}'_{carbCdegass} \\
&= k_5 \cdot fCO_2 \cdot U \cdot vasc - k_{10} \cdot V \cdot \frac{\mathbf{C}}{\mathbf{C}_0}
\end{aligned}$$

$$\begin{aligned}
\mathbf{Q}' &= \mathbf{Q}'_{nutrientburial} + \mathbf{Q}'_{phosw} \\
&= \frac{\beta(k_1 \left(\frac{\mathbf{P}}{\mathbf{P}_0} \right) + r)}{Cpsea} + k_2 \left(\frac{k_1 \left(\frac{\mathbf{P}}{\mathbf{P}_0} \right) + r}{k_1 + r_0} \right) + \frac{k_3}{k_4} (1 - anox(\mathbf{O}, \mathbf{P})) \\
&\quad - \epsilon \cdot k_8 \cdot U \left(\frac{2}{12} fCO_2 \cdot vasc + \frac{5}{12} gCO_2 \cdot vasc + \frac{5}{12} \frac{\mathbf{G}}{\mathbf{G}_0} \sqrt{\frac{\mathbf{O}}{\mathbf{O}_0}} \right)
\end{aligned}$$

11 Proterozoic-phanerozoic transition

11.1 Steady state solutions at 750Ma

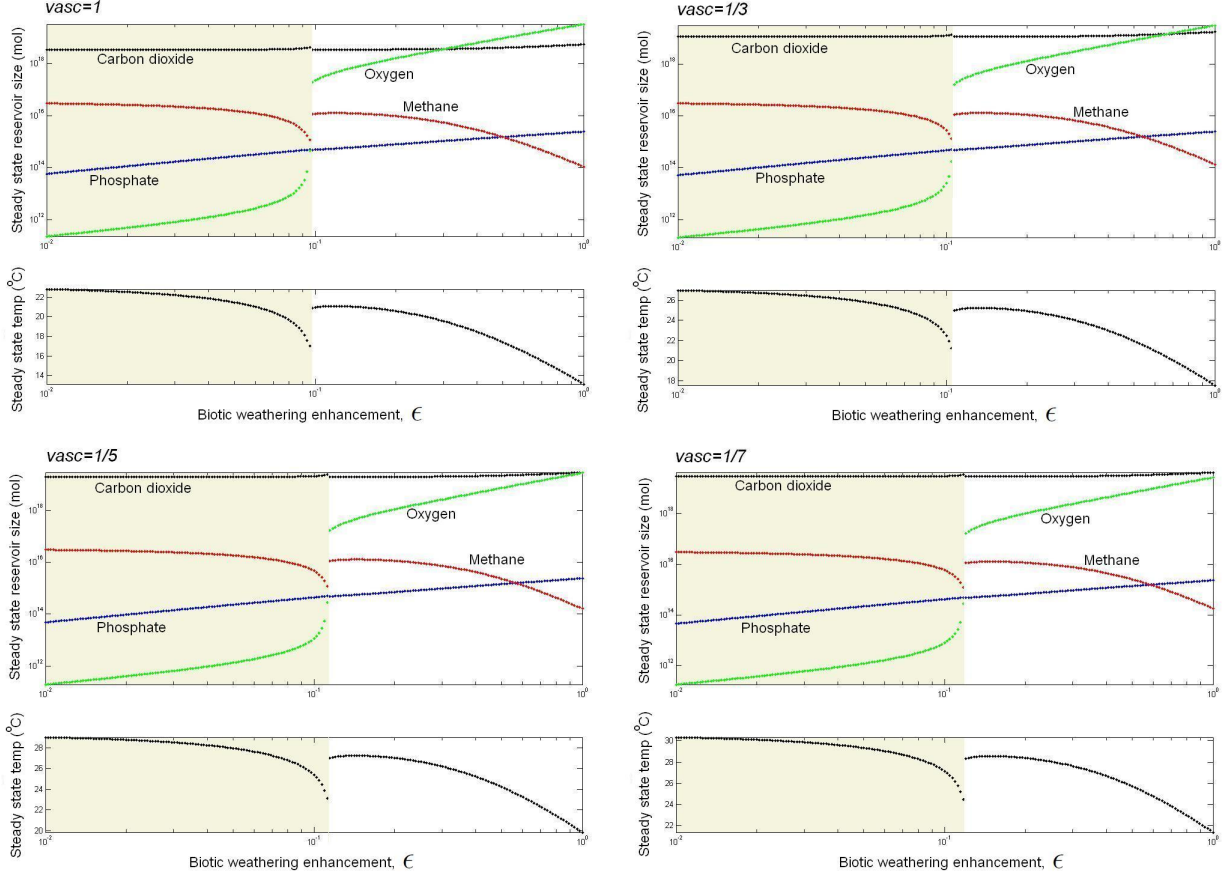


Figure 1: Steady state solutions at 750Ma for $10^{-2} \leq \epsilon \leq 1$. Pre-vascular weathering is set to 1, 1/3, 1/5 and 1/7 \times present day level respectively. The shaded areas (left on each) shows transition to a low-oxygen solution with no ozone layer. We hold \mathbf{G} and \mathbf{C} at ~ 90 percent of present day level in accordance with Hayes and Waldbauer [2006].

Decreasing the weathering of phosphate results in a stable state with lower oxygen concentrations and higher methane concentrations. Steady state carbon dioxide is only weakly affected and acts to counter the loss of methane. In this model, stable oxygen concentrations of around 0.01 PAL require at most a ten-fold reduction in weathering for nutrients compared to the paleozoic. An increase in weathering of this size during the neoproterozoic could explain large phosphorus deposits (ref...etc). This model suggests that a low oxygen proterozoic

(around 0.01 PAL) could face a collapse of oxygen due to a small decrease in nutrient supply. The choice of $vasc$ changes carbon dioxide concentration (and therefore surface temperature) but does very little to the other reservoirs. Steady state temperature is up to 2 degrees warmer with the allowed decrease in ϵ (i.e. not so much as to lose the ozone layer). (unfortunately it looks like 8 in the diagram due to a mistake with logs and log10s which i have just noticed! The temp was calculated after the runs from the sizes of A and M so other results are ok but that one needs redoing!).

11.2 Time dependent solutions

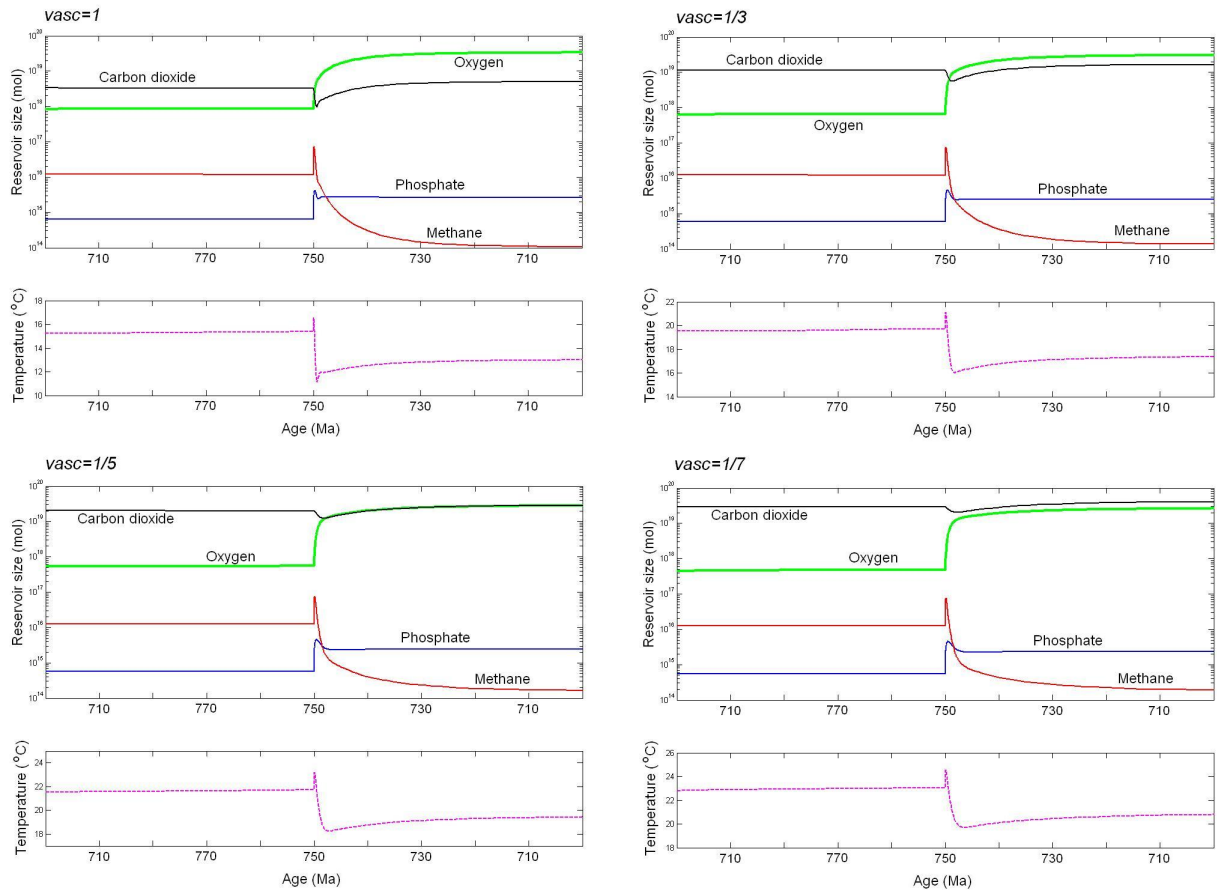


Figure 2: Time dependent solutions for a step change in ϵ at 750Ma. Pre-vascular weathering is set to 1, 1/3, 1/5 and 1/7 \times present day level respectively.

Biotic weathering enhancement, ϵ , is set to 0.15, changing to 1 at 750Ma. An increase in weathering for nutrients causes phosphate and oxygen concentrations to rise sharply, carbon

dioxide concentration falls quickly but is restored after around 10 Myr. Methane levels drop and remain low after the transition.

Simultaneous drops in Methane and Carbon dioxide concentrations cause a maximum of $\sim 4^\circ\text{C}$ cooling in each case.

12 Archean-proterozoic transition

12.1 Steady state solutions at 2400Ma

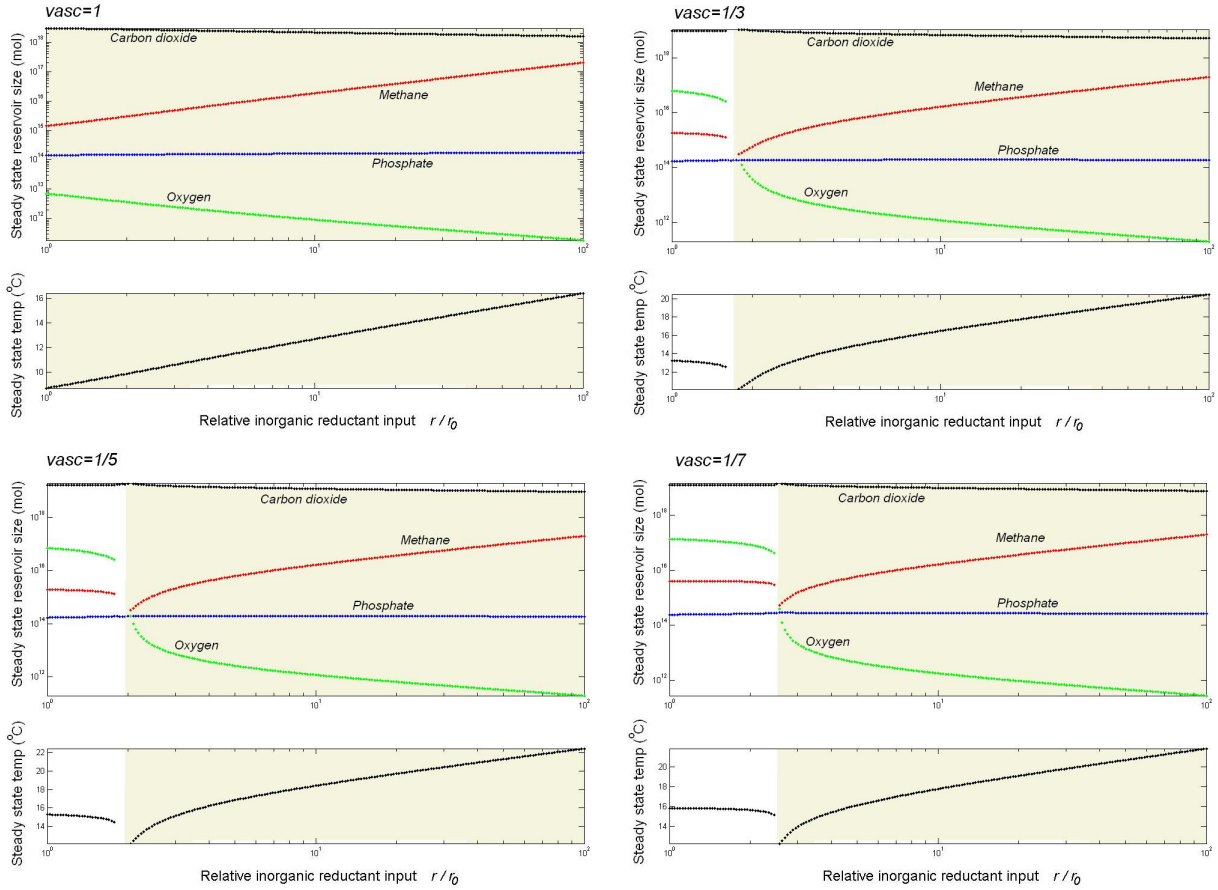


Figure 3: Steady state solutions at 2400Ma for $1 \leq \frac{r}{r_0} \leq 100$. Pre-vascular weathering is set to 1, $1/3$, $1/5$ and $1/7 \times$ present day level respectively and ϵ is set to 0.15. The shaded area (right) shows transition to a low-oxygen solution with no ozone layer. We hold \mathbf{G} and \mathbf{C} at ~ 40 percent of present day level [Hayes and Waldbauer, 2006].

(In the case of $vasc = 1$ the high oxygen state cannot exist for our choices of r . Setting $vasc = 1$ implies that vascular plants gave no enhancement to weathering so i'll probably do $vasc = 2$ instead or just leave it out.)

Higher inorganic reductant input causes lower steady state oxygen concentration, sufficient input causes the switch to the low oxygen solution. Input of reductants in the archaean is likely to have been higher than present day [refs... crust oxidation, serpentinization etc.]. Higher reductant input gives higher methane concentrations and higher temperatures, although carbon dioxide is reduced due to higher rates of anoxygenic photosynthesis.

(again the temperature is incorrect here - i'm doing more diagrams now with higher resolution so i'll fix it in those).

12.2 Time dependent solutions

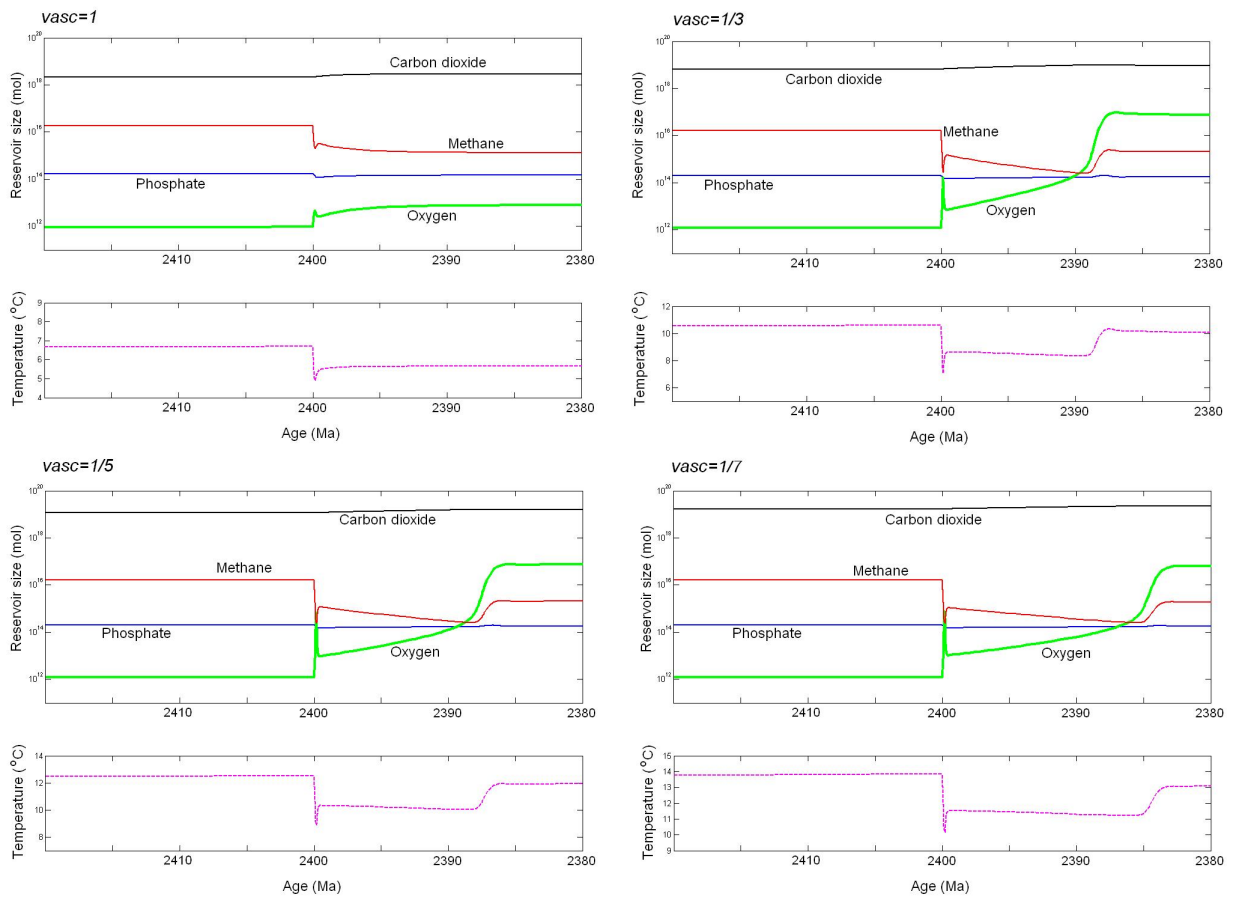


Figure 4: Time dependent solutions for a step change in r at 2400Ma. Pre-vascular weathering is set to $1, 1/3, 1/5$ and $1/7 \times$ present day level respectively.

Inorganic reductant input, r , is set to 7.5×10^{11} , changing to 7.5×10^{10} at 2400Ma. The step decrease in reductant causes oxygen concentration to increase steadily until it reaches the ozone layer threshold ($\sim 10^{-5}$ PAL). Positive feedback between ozone shielding and hydrogen escape then rapidly increase oxygen until the system stabilizes at the high oxygen state (with ozone layer). Both methane concentration and temperature decrease as oxygen increases up to the ozone formation threshold, they then increase during the positive feedback process.

A drop in methane due to rising oxygen levels prior to the oxygenation event causes $\sim 2^\circ\text{C}$ cooling in each case.

I'm going to ditch the step increase/decrease during the next runs as they give stupid spikes on the graphs. Some smoothish step thing will be better.