GSA Data Repository 2016343

A modeling case for high atmospheric oxygen concentrations during the Mesozoic and Cenozoic

Mills et al.

APPENDIX

APPENDIX 1: ALTERATIONS TO PREVIOUSLY PUBLISHED MODEL

The COPSE and GEOCARB models

The original COPSE model (Bergman et al., 2004) is a long term biogeochemical box model, based on the GEOCARB models (Berner 1991, 1994, Berner and Kothavala, 2001). It calculates fluxes between the atmosphere/ocean and sedimentary reservoirs of oxidised and reduced carbon and sulphur to estimate changes in CO_2, O_2 and ocean sulphate over the Phanerozoic. Since publication of COPSE, GEOCARB has been extended to include calculations for the sulphur cycle and oxygen (GEOCARBSULF). In Mills et al. (2014), COPSE was updated to consider the weatherable area of different rock types, and to investigate alternative reconstructions for volcanic degassing rates (Van Der Meer et al., 2014). The model predictions were compared to variation in seawater $^{87}Sr/^{86}Sr$.

The critical difference between COPSE and GEOCARBSULF is the method used to estimate the burial rates of organic carbon and pyrite sulphur, which are the long term sources of oxygen. COPSE uses integrated cycles of limiting nutrients P and N (following Lenton and Watson 2000) to estimate these fluxes based on other model parameters, such as nutrient delivery via weathering. GEOCARBSULF uses an isotope mass balance technique (IMB: Berner 1987, 2001) which infers the burial rates from known changes in isotope ratios $\delta^{13}C$ and $\delta^{34}S$, and does not require the calculation of nutrient fluxes. Whist model predictions for CO_2 over the Phanerozoic are broadly similar, predictions for variation in O_2 are substantially different.

Model used in this work

This paper uses the latest version of the COPSE biogeochemical model (Mills et al., 2014), and adds to this a routine for calculating the burial rates of organic carbon and pyrite sulphur via isotope mass balance, mirroring the functionality of the GEOCARBSULF model (Berner, 2006; 2009). The resulting model is very similar to GEOCARBSULF, but differences remain in the assumed rate of volcanic degassing, and the weatherable area of volcanic rocks, as well as more minor quantitative differences in the calculations for weathering fluxes.

In this paper we wish to test the oxygen predictions from the isotope mass balance system, particularly with regard to the input of $\delta^{13}C$ data, which shows large uncertainty. In theory, this test can be carried out using the GEOCARBSULF model, however recent work has shown that the computational algorithm used to solve the model fails when $\delta^{13}C$ inputs are varied only slightly from the model baseline (Royer et al., 2014). The COPSE algorithm uses a variable time-step method and is therefore suited to testing wide differences in input parameters. Thus we adapt the COPSE model to test the isotope mass balance method by removing the nutrient system and replacing with the IMB equations. This has the additional benefit of testing whether the differences in the COPSE formulations for degassing and weathering have much impact on the model outputs under isotope mass balance.

To summarize the results of this exercise:

- Replacing the nutrient system in COPSE with the exact isotope mass balance system from GEOCARBSULF (including standard inputs for $\delta^{13}C$ and $\delta^{34}S$) results in oxygen predictions very similar to GEOCARBSULF. Showing that O_2 predictions are much more dependent on the assumed isotope record than other model processes.

- Replacing the standard $\delta^{13}C$ input compilation with a more recent record (Saltzman and Thomas, 2012) results in major revision of the O_2 predictions, with $pO_2 > 0.2$atm for the whole model timeframe (200-0Ma).

Rapid recycling

In order to add the isotope mass balance system to COPSE, the model must be modified to include 'rapid recycling' of sedimentary carbon and sulphur. Under this method, it is assumed that geologically young sedimentary rocks constitute the majority of interaction with the surface system, allowing the isotopic signature of buried material to be more quickly recycled to the atmosphere and oceans. This technique has been included in all isotope mass balance approaches (Berner 1987; 2006; 2009; Royer et al., 2014).

The method involves splitting the sedimentary reservoirs for organic carbon, carbonates, pyrite and gypsum sulphur into 'young' and 'ancient' boxes. The young boxes are smaller and have higher weathering rates, the ancient boxes are much larger and have lower weathering rates (see ms figure 2). The relative size of the young and ancient reservoirs, as well as the relative weathering contributions are taken directly from GEOCARBSULF, and are listed below with the other model parameters. The carbon and sulphur cycle schematic from the attached manuscript, which details the flux names, is reproduced here (A1) for convenience.

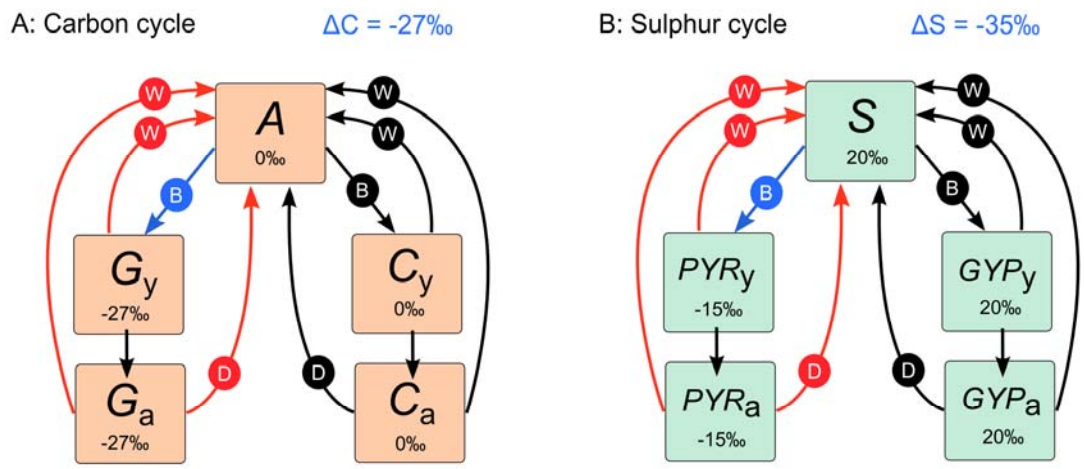

Figure DR1. Long term carbon and sulphur cycles. The carbon cycle consists of fluxes between atmosphere and ocean carbon (A), organic carbon (G) and carbonate (C). The sulphur cycle represents ocean sulphate (S), buried reduced pyrite (PYR) and oxidised gypsum (GYP). Burial (B) moves carbon and sulphur from the atmosphere and ocean to the crustal reservoirs, and it is returned by weathering (W) and degassing/metamorphism (D). Subscript (y) denotes young crustal reservoirs, (a) denotes ancient crustal reservoirs. Oxygen sources are shown in blue, sinks are shown in red. Present day isotope ratios $\delta^{13}C$ and $\delta^{34}S$ are shown for carbon and sulphur reservoirs respectively in per mil (‰), ΔC *and* ΔS *show the burial fractionation effects for carbon and sulphur respectively.*

Isotope mass balance equations for burial fluxes

With rapid recycling added to the COPSE model, and the nutrient system removed completely, the equations representing organic carbon burial and pyrite sulphur burial are copied exactly from GEOCARBSULF, the code for which was kindly sent by R. A. Berner. The mathematical derivation is published in Berner (1987) and begins with the assumption of input-output parity for ^{12}C and ^{13}C atoms (and ^{34}S and ^{32}S for sulphur). For Carbon:

$$Input \times \delta(Input) = Output \times \delta(Output) \quad (1)$$

$$W(G_y)\delta(G_y) + W(G_a)\delta(G_a) + D(G_a)\delta(G_a) + W(C_y)\delta(C_y) + W(C_a)\delta(C_a) +$$
$$D(C_a)\delta(C_a) = B(G)(\delta(A) - \Delta C) + B(C)\delta(A) \quad (2)$$

Rearranging gives:

$$\Delta C \times B(G) = \left(\delta(A) - \delta(G_y)\right) W(G_y) + \left(\delta(A) - \delta(G_a)\right)\left(W(G_a) + D(G_a)\right) +$$
$$\left(\delta(A) - \delta(C_y)\right)W(C_y) + (\delta(A) - \delta(C_a))\left(W(C_a) + D(C_a)\right) \quad (3)$$

Where δ(X) is the isotopic composition of reservoir X, W denotes weathering, D denotes degassing and B denotes burial. ΔB and ΔS are the fractionation effects for burial of carbon and sulphur respectively. This equation is mirrored for the sulphur cycle.

APPENDIX 2: FULL MODEL DESCRIPTION

The full model equations are detailed below. Aside from the addition of rapid recycling and isotope mass balance, and the removal of the nutrient system, they follow exactly the model from Mills et al., (2014). The flux names from the manuscript are simplified here for convenience:

$$W(C_y) = carbw_y, W(C_a) = carbw_a, W(G_y) = oxidw_y, W(G_a) = oxidw_a,$$
$$D(C) = ccdeg, D(G) = ocdeg, B(G) = ocb, B(C) = mccb$$

$$W(GYP_y) = gypw_y, W(GYP_a) = gypw_a, W(PYR_y) = pyrw_y, W(PYR_a) = pyrw_a,$$
$$D(GYP) = gypdeg, D(PYR) = pyrdeg, B(GYP) = mgsb, B(PYR) = mpsb$$

Reservoir calculations:

Atmosphere/ocean carbon:

$$\frac{dA}{dt} = ccdeg + carbw_y + carbw_a + oxidw_y + oxidw_a + ocdeg$$
$$-mccb - ocb - sfw \quad (4)$$

Ocean sulphate:

$$\frac{dS}{dt} = pyrw_y + pyrw_a + pyrdeg + gypw_y + gypw_y + gypdeg$$

$$-mpsb - mgsb \quad (5)$$

Buried organic C (young): $\frac{dG_y}{dt} = ocb - oxidw_y - F_{Gya}$ (6)

Buried organic C (ancient): $\frac{dG_a}{dt} = F_{Gya} - oxidw_a - ocdeg$ (7)

Buried carbonate C (young): $\frac{dC_y}{dt} = mccb - carbw_y - F_{Cya}$ (8)

Buried carbonate C (ancient): $\frac{dC_a}{dt} = F_{Cya} - carbw_a - ccdeg$ (9)

Buried pyrite S (young): $\frac{dPYR_y}{dt} = mpsb - pyrw_y - F_{PYRya}$ (10)

Buried pyrite S (ancient): $\frac{dPYR_a}{dt} = F_{PYRya} - pyrw_a - pyrdeg$ (11)

Buried gypsum S (young): $\frac{dGYP_y}{dt} = mgsb - gypw_y - F_{GYPya}$ (12)

Buried gypsum S (ancient): $\frac{dGYP_a}{dt} = F_{GYPya} - gypw_a - gypdeg$ (13)

Isotope reservoir calculations:

Atmosphere/ocean carbon:

$$\frac{d(A \times \delta(A))}{dt} = ccdeg \times \delta(C_a) + carbw_y \times \delta(C_y) + carbw_a \times \delta(C_a) + oxidw_y \times \delta(G_y) +$$

$$oxidw_a \times \delta(G_a) + ocdeg \times \delta(G_a) - ocb \times (\delta(A) - \Delta C) - mccb \times \delta(A) - sfw \times \delta(A)$$

(14)

Ocean sulphate:

$$\frac{d(S\times\delta(S))}{dt} = gypdeg \times \delta(GYP_a) + gypw_y \times \delta(GYP_y) + gypw_a \times \delta(GYP_a) + pyrw_y \times \delta(PYR_y) + pyrw_a \times \delta(PYR_a) + pyrdeg \times \delta(PYR_a) - mpsb \times (\delta(S) - \Delta S) - mgsb \times \delta(S) \quad (15)$$

Buried organic C (young):

$$\frac{d(G_y\times\delta(G_y))}{dt} = ocb \times (\delta(A) - \Delta C) - oxidw_y \times \delta(G_y) - F_{Gya} \times \delta(G_y) \quad (16)$$

Buried organic C (ancient):

$$\frac{d(G_a\times\delta(G_a))}{dt} = F_{Gya} \times \delta(G_y) - oxidw_a \times \delta(G_a) - ocdeg \times \delta(G_a) \quad (17)$$

Buried carbonate C (young):

$$\frac{d(C_y\times\delta(C_y))}{dt} = mccb \times \delta(A) - carbw_y \times \delta(C_y) - F_{Cya} \times \delta(C_y) \quad (18)$$

Buried carbonate C (ancient):

$$\frac{d(C_a\times\delta(C_a))}{dt} = F_{Cya} \times \delta(C_y) - carbw_a \times \delta(C_a) - ccdeg \times \delta(C_a) \quad (19)$$

Buried pyrite S (young):

$$\frac{d(PYR_y\times\delta(PYR_y))}{dt} = mpsb \times (\delta(S) - \Delta S) - pyrw_y \times \delta(PYR_y) - F_{PYRya} \times \delta(PYR_y) \quad (20)$$

Buried pyrite S (ancient):

$$\frac{d(PYR_a\times\delta(PYR_a))}{dt} = F_{PYRya} \times \delta(PYR_y) - pyrw_a \times \delta(PYR_a) - pyrdeg \times \delta(PYR_a) \quad (21)$$

Buried gypsum S (young):

$$\frac{d(GYP_y\times\delta(GYP_y))}{dt} = mgsb \times \delta(S) - gypw_y \times \delta(GYP_y) - F_{GYPya} \times \delta(GYP_y) \quad (22)$$

Buried gypsum S (ancient):

$$\frac{d(GYP_a\times\delta(GYP_a))}{dt} = F_{GYPya} \times \delta(GYP_y) - gypw_a \times \delta(GYP_a) - gypdeg \times \delta(GYP_a) \quad (23)$$

List of fluxes

Temperature dependence of basalt weathering:

$$f_{Tbas} = e^{0.061(T-T_0)}\{1 + 0.038(T - T_0)\}^{0.65} \quad (24)$$

Temperature dependence of granite weathering:

$$f_{Tgran} = e^{0.072(T-T_0)}\{1 + 0.038(T - T_0)\}^{0.65} \quad (25)$$

Temperature dependence of carbonate weathering:

$$g_T = 1 + 0.087(T - T_0) \quad (26)$$

Pre-plant silicate weathering: $f_{preplant} = f_T \cdot \sqrt{RCO_2}$ (27)

Plant-assisted silicate weathering: $f_{plant} = f_T \cdot \left(\frac{2RCO_2}{1+RCO_2}\right)^{0.4}$ (28)

Pre-plant carbonate weathering: $g_{preplant} = g_T \cdot \sqrt{RCO_2}$ (29)

Plant-assisted carbonate weathering: $g_{plant} = g_T \cdot \left(\frac{2RCO_2}{1+RCO_2}\right)^{0.4}$ (30)

Climate forcing for silicates:

$$f_{CO2} = f_{preplant}(1 - \min(VEG \cdot W)) + f_{plant} \cdot \min(VEG \cdot W) \quad (31)$$

$f_{CO2gran}$ and f_{CO2bas} result from the f_{CO2} function with plant-weathering feedbacks using f_{Tgran} and f_{Tbas} respectively.

Climate forcing for carbonates:

$$g_{CO2} = g_{preplant}(1 - \min(VEG \cdot W)) + g_{plant} \cdot \min(VEG \cdot W) \quad (32)$$

Vegetation feedback: $VEG = 2 \cdot E \cdot \frac{(CO_2ppm-10)}{(183.6+CO_2ppm-10)} \cdot \left(1 - \left(\frac{(T-T_0)}{T}\right)^2\right) \cdot \left(1.5 - 0.5(RO_2)\right) \cdot \frac{k_{fire}}{(k_{fire}-1+\max(586.2O_2(atm)-122.102\,,0))}$ (33)

Evolution of plants: $pevol = \left(k_{preplant} + \left(1 - k_{preplant}\right) \cdot W \cdot VEG\right)$ (34)

Basalt weathering: $basw = \%bas_0 \cdot k_{silw} \cdot f_{CO2bas} \cdot PG \cdot pevol \cdot BA$ (35)

Granite weathering:

$$granw = (1 - \%bas_0) \cdot k_{silw} \cdot f_{CO2gran} \cdot PG \cdot U \cdot pevol \cdot GA \quad (36)$$

Silicate weathering: $$silw = basw + granw \quad (37)$$

Carbonate weathering (young): $$carbw_y = k_{carbwy} \cdot g_{CO2} \cdot PG \cdot U \cdot pevol \cdot LAC_{rel} \quad (38)$$

Carbonate weathering (ancient): $$carbw_a = k_{carbwa} \cdot g_{CO2} \cdot PG \cdot U \cdot pevol \cdot LAC_{rel} \quad (39)$$

Oxidative weathering (young): $$oxidw_y = k_{oxidwy} \cdot U \cdot \sqrt{RO_2} \quad (40)$$

Oxidative weathering (ancient): $$oxidw_y = k_{oxidwa} \cdot U \cdot \sqrt{RO_2} \quad (41)$$

Transfer from C_y to C_a: $$F_{Gya} = carbw_a + ccdeg \quad (42)$$

Transfer from G_y to G_a: $$F_{Gya} = oxidw_a + ocdeg \quad (43)$$

Marine carbonate carbon burial: $$mccb = silw + carbw \quad (44)$$

Seafloor weathering is revised to include direct temperature dependence as with terrestrial basalt weathering. This assumes a direct relationship between surface temperature change and seafloor temperatures.

Seafloor weathering: $$sfw = k_{sfw} \cdot D \cdot e^{0.061(T-T_0)} \quad (45)$$

In COPSE, sulphur degassing is assumed to have the same controls as sulphur weathering, therefore the degassing terms are accounted for by larger weathering terms:

Pyrite sulphur weathering (young): $$pyrw_y = k_{pyrwy} \cdot U \cdot \frac{PYR_y}{PYR_{y0}} \sqrt{RO_2} \quad (46)$$

Pyrite sulphur weathering (ancient): $$pyrw_a = k_{pyrwa} \cdot U \cdot \frac{PYR_a}{PYR_{a0}} \sqrt{RO_2} \quad (47)$$

Gypsum sulphur weathering (young): $$gypw = k_{gypw} \cdot U \cdot \frac{GYP_y}{GYP_{y0}} \cdot \frac{carbw}{carbw_0} \quad (48)$$

Gypsum sulphur weathering (ancient): $$gypw = k_{gypw} \cdot U \cdot \frac{GYP_a}{GYP_{a0}} \cdot \frac{carbw}{carbw_0} \quad (49)$$

Transfer from GYP_y to GYP_a: $$F_{GYPya} = gypw_a + gypdeg \quad (50)$$

Transfer from PYR_y to PYR_a: $$F_{PYRya} = pyrw_a + pyrdeg \quad (51)$$

Gypsum sulphur burial: $$mgsb = k_{mgsb} \cdot \frac{S}{S_0} \cdot \frac{CAL}{CAL_0} \quad (52)$$

Organic carbon degassing: $$ocdeg = k_{ocdeg} \left(\frac{G}{G_0}\right) \cdot D \quad (53)$$

Carbonate carbon degassing: $$ccdeg = k_{ccdeg} \left(\frac{C}{C_0}\right) \cdot D \cdot B \quad (54)$$

Marine carbonate carbon burial: $$mccb = silw + carbw \quad (55)$$

Total organic carbon burial:

$$ocb = \frac{1}{\Delta C}\Big(carbw_y\left(\delta(A) - \delta(C_y)\right) + carbw_a\left(\delta(A) - \delta(C_a)\right) + oxidw_y\left(\delta(A) - \delta(G_y)\right) + oxidw_a\left(\delta(A) - \delta(G_a)\right) + ccdeg\left(\delta(A) - \delta(C_a)\right) + ocdeg\left(\delta(A) - \delta(G_a)\right)\Big) \quad (56)$$

Total pyrite sulphur burial:

$$pyrb = \frac{1}{\Delta S}\Big(gypw_y\left(\delta(S) - \delta(GYP_y)\right) + gypw_a\left(\delta(S) - \delta(GYP_a)\right) + pyrw_y\left(\delta(S) - \delta(PYR_y)\right) + pyrw_a\left(\delta(S) - \delta(PYR_a)\right) + gypdeg\left(\delta(S) - \delta(GYP_a)\right) + pyrdeg\left(\delta(S) - \delta(PYR_a)\right)\Big) \quad (57)$$

Other calculations:

Relative atmospheric O_2: $$RO_2 = \frac{\frac{O}{O_0}}{\frac{O}{O_0} + k_{O2}} \quad (58)$$

where $k_{O2} = 3.762$

Solar forcing: $$S = \frac{S_0}{1+0.38\left(\frac{t}{\tau}\right)} \quad (59)$$

where S_0 = 1368Wm^{-2}, τ=4.55x10^9 years.

Present day values:		**Source:**
Marine organic carbon burial:	k_{mocb}=4.5x10^{12} mol C yr^{-1}	COPSE
Pyrite sulphur burial:	k_{mpsb}=5.3x10^{11} mol S yr^{-1}	COPSE
Gypsum sulphur burial:	k_{mgsb}=1x10^{12} mol S yr^{-1}	COPSE
Silicate weathering:	k_{silw} = 4.9x10^{12} mol C yr^{-1}	for steady state
Seafloor weathering:	k_{sfw} = 1.75x10^{12} mol C yr^{-1}	Mills et al. (2014)
Oxidative weathering (young):	k_{oxidwy}=7x10^{12} mol C yr^{-1}	COPSE
Oxidative weathering (ancient):	k_{oxidwa}=7.75x10^{11} mol C yr^{-1}	COPSE
Carbonate weathering (young):	k_{carbwy}=1.8x10^{13} mol C yr^{-1}	COPSE
Carbonate weathering (ancient):	k_{carbwy}=2x10^{12} mol C yr^{-1}	COPSE
Pyrite sulphur weathering (young):	k_{pyrw}=2.36x10^{11} mol S yr^{-1}	COPSE
Pyrite sulphur weathering (ancient):	k_{pyrw}=2.9x10^{11} mol S yr^{-1}	COPSE
Gypsum sulphur weathering (young)	k_{gypwy}=7.5x10^{11} mol S yr^{-1}	COPSE
Gypsum sulphur weathering (ancient)	k_{gypwy}=2.5x10^{11} mol S yr^{-1}	COPSE
Organic carbon degassing:	k_{ocdeg}=1.25x10^{12} mol C yr^{-1}	COPSE
Carbonate carbon degassing:	k_{ccdeg}=6.65x10^{12} mol C yr^{-1}	COPSE
Atmosphere and ocean CO_2:	A_0=3.193x10^{18} mol	COPSE
Ocean sulphate:	P_0=4x10^{19} mol	COPSE

Atmosphere and ocean oxygen:	O_0=3.7x10^{19} mol	COPSE
Buried organic carbon:	G_0=1.25x10^{21} mol	COPSE
Buried carbonate carbon:	C_0=6.6x10^{21} mol	COPSE
Buried pyrite sulphur:	PYR_0=1.8x10^{20}mol	COPSE
Buried gypsum sulphur:	GYP_0=2x10^{20} mol	COPSE

Forcings:	**Attributes:**
Solar forcing:	$S = \frac{S_0}{1+0.38\left(\frac{t}{\tau}\right)}$
	where S_0 = 1368Wm^{-2}, τ=4.55x10^9 years.
Relative global CO_2 degassing:	$D = 1$ for present day
Relative uplift rate:	$U = 1$ for present day
Evolution of land plants:	$E = 1$ for present day
Weathering effect of plant evolution:	$W = 1$ for present day
Carbonate burial depth:	$B = 1$ for present day
Relative basaltic area:	$BA = 1$ for present day
Relative total land area:	LA_{rel} = 1 for present day
Relative carbonate land area:	LAC_{rel} = 1 for present day
Relative granite area:	GA = LA – LAC – BA_{cont}

where BA_{cont} is the total basaltic area on continents (i.e. total basaltic area minus island arc and ocean island contributions) and LA and LAC are the total land area and carbonate land area respectively, calculated by scaling the relative areas to the present day areas.

Paleogeographical runoff effect:	$PG = 1$ for present day

Starting conditions

The model reservoir of ancient carbonates, C_a, is by far the largest store of carbon, therefore its assumed isotopic composition at the start of the model run will influence the relative carbon burial rates for this time. This parameter is set so that organic C burial rates and oxygen concentration return to present day values at the end of the run (0Ma). This requires $\delta(C_{astart}) = 1.16$ for the GEOCARB δ^{13}Cinput, and $\delta(C_{astart}) = -0.56$ for the GTS2012 input.

Model output

Figure DR2 shows IMB-COPSE model output for 3 combinations of input parameters:

1) δ^{13}C and δ^{34}S inputs follow GEOCARBSULF. Shown in green.
2) δ^{13}C input follows GEOCARBSULF, δ^{34}S inputs follow Algeo et al., (2015). Shown in orange.
3) δ^{13}C input follows GTS2012 (Saltzman and Thomas, 2012), δ^{34}S inputs follow Algeo et al., (2015). Shown in red.

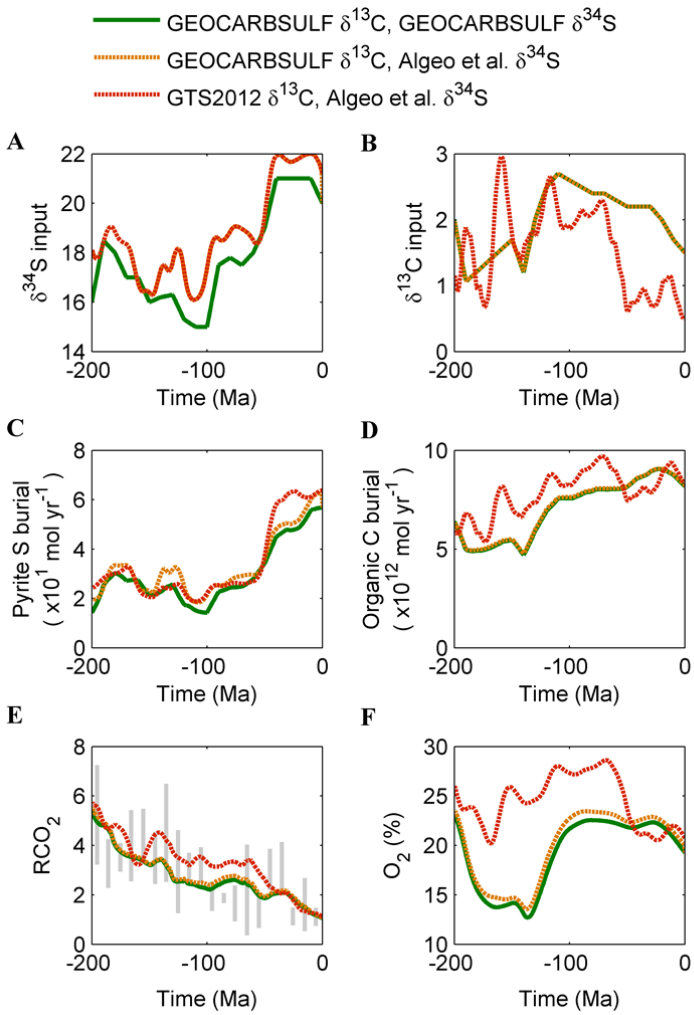

Figure DR2. IMB-COPSE model output for different isotope input scenarios. Relative atmospheric CO_2 concentration plotted against compilation of Park and Royer (2011).

Under the GEOCARBSULF inputs, the IMB-COPSE model predicts very similar variations in atmospheric oxygen to the original GEOCARBSULF model (Berner, 2009; see manuscript). When $\delta^{34}S$ input is altered to follow Algeo et al., (2015), oxygen variation is only slightly affected, owing to the minor alteration to the input (around one 5th of the range), and to the significantly smaller fluxes of oxygen associated with the sulphur system when

compared to carbon. When the $\delta^{13}C$ input parameter is also altered, predicted oxygen concentration is significantly changed, and is higher over the model timeframe. This stems from the assumption that Mesozoic $\delta^{13}C$ was higher than present, equating to greater organic carbon burial in this model variant.

APPENDIX 3: ADDITIONAL MODEL EXPERIMENTS

Sensitivity of O_2 predictions to input parameters other than carbonate $\delta^{13}C$

In the manuscript we show extreme sensitivity of modelled oxygen predictions to carbonate $\delta^{13}C$ inputs. In figure DR3 we test additional uncertainty by including error estimates for other model processes. The grey area shows the extent of the range of model predictions when run with $\pm 1\sigma$ variation in carbonate $\delta^{13}C$, but also with variation between the minimum and maximum estimates for the rate of volcanic CO_2 degassing and the global area of weatherable volcanic rocks. This mirrors the sensitivity window shown in Mills et al., (2014). The effects on atmospheric oxygen predictions are small when compared to the results under variation in carbonate $\delta^{13}C$ alone (blue dotted lines). It has been shown (Royer et al., 2014) that multi-parameter error analysis on all GEOCARBSULF input parameters, despite minimal variation in the $\delta^{13}C$ input, can give similar uncertainty ranges for model O_2 predictions as are calculated here by varying only the $\delta^{13}C$ input. The grey error window we show could therefore be extended using this method, but the best-guess predictions, which are the subject of this paper, would not be altered. Nevertheless it should be noted that it is possible for this model to predict a period of low O_2 (<15%) during the Jurassic, but such prediction would rely on a fortuitous combination of parameter variations.

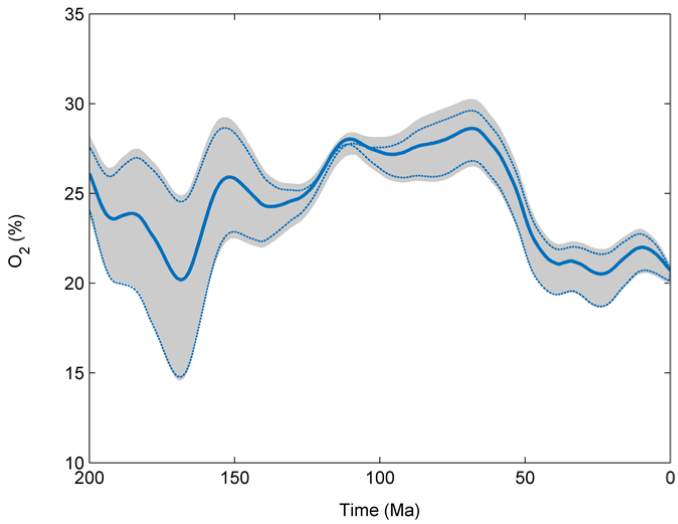

Figure DR3. Model error window (grey) when subject to max/min variation in inputs for carbonate $\delta^{13}C$, volcanic CO_2 degassing rate and weatherable area of volcanic rocks. See Mills et al., (2014) for details of these processes. Compared to model error window under $\pm 1\sigma$ in carbonate $\delta^{13}C$ input (blue dashed lines).

Model sensitivity to carbonate reservoir variations.

Our model assumes an increase in the degassing rate of carbonates at ~140Ma, aiming to represent the subduction of deep ocean carbonate deposits after the evolution of calcareous plankton (burial depth forcing *B* above, following from GEOCARB modelling). However, carbonate subduction may be more dependent on longer term basin dynamics and may therefore produce a destabilizing effect on the carbon cycle (Edmond and Huh, 2003). In figure DR4 we replace the *B* forcing with a new flux from the young carbonate reservoir to the atmosphere/ocean. This represents tectonic control of carbonate subduction and follows Edmond and Huh (2003; panel A). As discussed by these authors, this flux can have a considerable impact on model CO_2 predictions. This follows from the idea that the modern day steady state does not include some significant past processes. The impact on our oxygen

predictions is however relatively small: the increase in carbon fluxes only represents around 10% of the total gross throughput, and therefore does not greatly alter the mass balance calculation for O_2 (see manuscript).

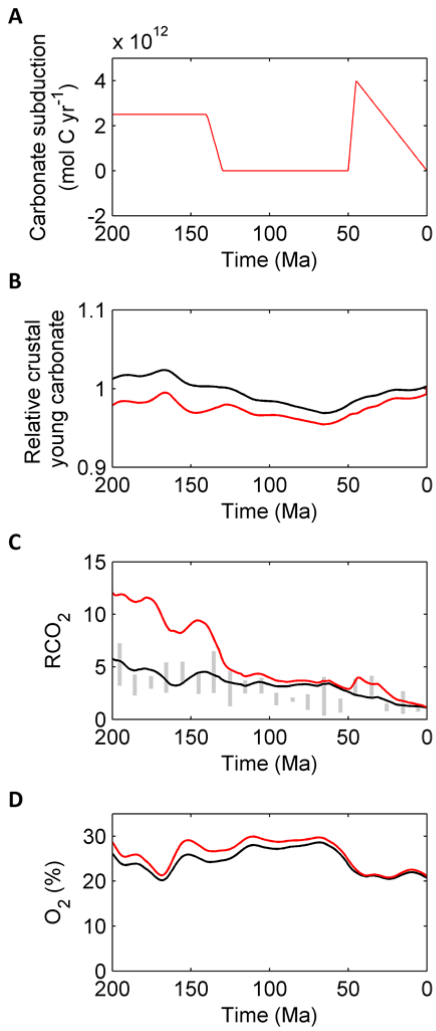

Figure DR4. Model configured with additional carbonate subduction flux from young carbonates to atmosphere/ocean (red). Compared to original model (black).

Model sensitivity to pyrite burial constraints.

The quantity f_{pyr} represents pyrite burial as a fraction of total sulphur burial. In GEOCARB and COPSE modelling f_{pyr} is around 0.3-0.4 at the present day. It has however

been suggested, based on direct estimation of the sulphate burial rate, that f_{pyr} may have been as high as 0.9 and stable at this fraction for the whole Phanerozoic (Halevy et al., 2012). To close the isotope mass balance under this constraint requires a fixed time-evolution of the isotopic composition of sulphate inputs (figure DR5, panel A), although this is not supported by available data on the composition of sulphur in coals (Canfield, 2013). In figure DR5 we run the model with an imposed $\delta^{34}S$ of sulphate inputs, and an increased rate of pyrite burial at present day (Halevy et al., 2012). Variation in oxygen predictions is again small. This is because the rate of oxygen production from pyrite burial is still much smaller than via organic carbon burial (around 20%), and also because the higher and more stable rate of pyrite burial in the altered model acts to reduce the overall variation in oxygen production rates.

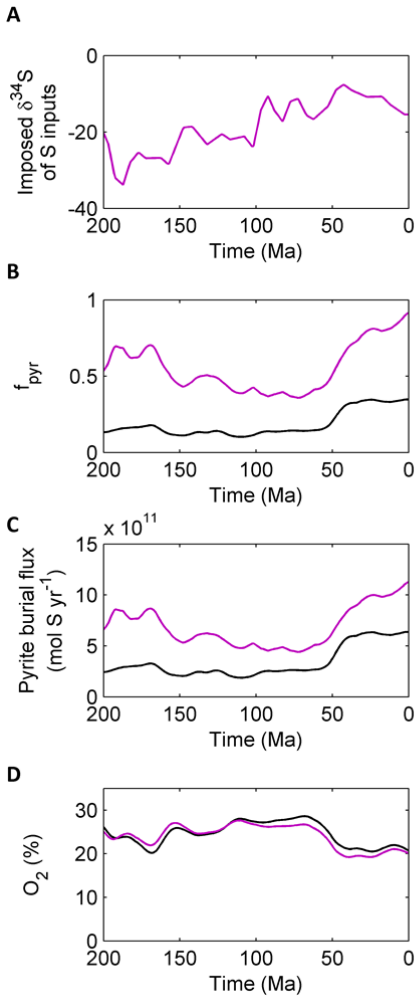

Figure DR5. Model configured with higher rate of pyrite burial and imposed $\delta^{34}S$ value for sulphate inputs (purple). Compared to original model (black).

ADDITIONAL REFERENCES

Berner, R. A., 1991, A model for atmospheric CO_2 over Phanerozoic time: American Journal of Science, v. 291, p. 339-376.

Berner, R. A., 1994, Geocarb II: A revised model of atmospheric CO_2 over Phanerozoic time: American Journal of Science, v. 294, p. 56-91.

Berner, R. A., and Kothavala, Z., 2001, Geocarb III: A revised model of atmospheric CO_2 over Phanerozoic time: American Journal of Science, v. 301, p. 182-204.

Canfield, D. E., 2013, Sulfur isotopes in coal constrain the evolution of the Phanerozoic sulfur cycle. PNAS v. 110, p. 8443-8446.

Edmond, J. M. and Huh, Y., 2003, Non-steady state carbonate recycling and implications for the evolution of atmospheric pCO_2. EPSL v. 216, p. 125-139.

Halevy I, Peters S. E. and Fischer W. W., 2012, Sulfate burial constraints on the Phanerozoic sulfur cycle. Science v. 337, p. 331–334.

Park, J., and Royer, D. L., 2011, Geologic constraints on the glacial amplification of Phanerozoic climate sensitivity: American Journal of Science, v. 311, p. 1-26.

Table DR1

Time (Ma)	O2 (%)
0	20.7203
1	20.90787
2	21.10574
3	21.29921
4	21.47945
5	21.63717
6	21.76217
7	21.86486
8	21.94267
9	21.991
10	22.00081
11	21.9663
12	21.89003
13	21.77882
14	21.64491
15	21.51127
16	21.37791
17	21.23873
18	21.08635
19	20.92225
20	20.77339
21	20.65584
22	20.57248
23	20.53019
24	20.51837
25	20.53857
26	20.5876
27	20.66192
28	20.75761
29	20.87008
30	20.97992
31	21.07253
32	21.13904
33	21.1932
34	21.24337
35	21.21574
36	21.17132
37	21.13311
38	21.07065
39	21.08161
40	21.15327
41	21.22717
42	21.34263
43	21.51468
44	21.71011
45	21.92514
46	22.17332
47	22.45822
48	22.79785
49	23.21467
50	23.69693
51	24.21096
52	24.71846
53	25.17477

54	25.57653
55	25.94122
56	26.28865
57	26.62366
58	26.93158
59	27.19963
60	27.43125
61	27.62742
62	27.81581
63	28.01337
64	28.20434
65	28.38152
66	28.5151
67	28.58899
68	28.62058
69	28.61372
70	28.57787
71	28.52064
72	28.44578
73	28.36056
74	28.27406
75	28.18909
76	28.10798
77	28.03518
78	27.97244
79	27.91927
80	27.87161
81	27.82921
82	27.79203
83	27.76068
84	27.73364
85	27.70503
86	27.67008
87	27.62493
88	27.56844
89	27.49885
90	27.41725
91	27.33634
92	27.27568
93	27.23141
94	27.19957
95	27.18076
96	27.1764
97	27.18818
98	27.21245
99	27.26183
100	27.31913
101	27.37768
102	27.43131
103	27.48736
104	27.55737
105	27.64465
106	27.74074
107	27.84057
108	27.93398

109	28.00096
110	28.03066
111	28.01916
112	27.96382
113	27.86179
114	27.7136
115	27.52366
116	27.29644
117	27.03823
118	26.75404
119	26.46771
120	26.1865
121	25.91493
122	25.65914
123	25.42765
124	25.22901
125	25.06348
126	24.91935
127	24.8013
128	24.71552
129	24.65866
130	24.6121
131	24.55371
132	24.48669
133	24.42469
134	24.36716
135	24.31882
136	24.28727
137	24.2729
138	24.27183
139	24.29023
140	24.34646
141	24.45507
142	24.60671
143	24.77658
144	24.94143
145	25.10279
146	25.26483
147	25.42797
148	25.58519
149	25.72532
150	25.83525
151	25.89968
152	25.91018
153	25.86315
154	25.75403
155	25.57453
156	25.31393
157	24.96454
158	24.53729
159	24.05196
160	23.52542
161	22.97639
162	22.41143
163	21.86963

164	21.35323
165	20.8912
166	20.53184
167	20.30169
168	20.19866
169	20.20379
170	20.31175
171	20.50601
172	20.76394
173	21.06746
174	21.40152
175	21.73367
176	22.04475
177	22.33281
178	22.58603
179	22.82386
180	23.07903
181	23.34865
182	23.58118
183	23.74602
184	23.84306
185	23.88353
186	23.8813
187	23.84355
188	23.79601
189	23.73907
190	23.66712
191	23.5984
192	23.58279
193	23.65363
194	23.81065
195	24.05719
196	24.39755
197	24.8072
198	25.25489
199	25.69296
200	26.10529