

**Evolution of a habitable planet: A biogeochemical
modelling study of the rise of oxygen to modern levels**

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Abstract

The question of whether rising oxygen levels through Earth history have driven the evolution of life, is a subject of considerable interest. A key investigative tool in this topic has been the geochemical analyses of sedimentary rocks, from which we have gained valuable insights into Earth's changing redox landscape. Many of these geochemical proxies are marine in nature, thus only broad inferences about atmospheric oxygen levels can be made. However, some of this data can be utilised in Earth system models to generate quantitative predictions. While many such models exist for the Phanerozoic, none continuously chart atmospheric oxygen over billions of years, making it difficult to understand any link between oxygen and life.

This research aims to redress that issue by estimating atmospheric oxygen levels for the last 3.4 Gyrs. This has required the redevelopment of a well-established Phanerozoic model: GEOCARBSULF, in three distinct phases. Phase one was to understand why GEOCARBSULF predicts high oxygen levels in the early Paleozoic, contrary to geochemical evidence. It was found that GEOCARBSULF's simplified treatment of $\delta^{34}\text{S}$ fractionation leads to oxygen being tightly regulated to near modern-day levels. Using an alternative approach to the sulfur cycle generates low oxygen in the early Paleozoic with a step change to modern levels starting in the Ordovician. Phase two extended this model back to investigate the Neoproterozoic Oxygenation Event, resulting in the suggestion that the first animals evolved against a backdrop of extreme variability in oxygen levels. Phase three encompasses the last 3.4 Gyrs, including quantitative estimates for the Great Oxidation Event and subsequent 'oxygen overshoot', finding that they were near equal in magnitude but only approximately one tenth of present-day levels, converse to other predictions.

Overall, this work identifies that the Earth experienced three periods of atmospheric oxygen upheaval, with times of relative quiescence in between.

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List of abbreviations and elements

Al	Aluminium
atm	Of the atmosphere by volume
B	Boron
C	Carbon
Ca	Calcium
CAS	Carbonate associated sulfate(s)
Ce	Cerium
Ce _{anom}	Cerium anomaly
CH ₄	Methane
C _{org}	Organic carbon
CO ₂	Carbon dioxide
Cr	Chromium
DIC	Dissolved inorganic carbon
DOC	Dissolved organic carbon
f_{org}	Fraction of carbon leaving the ocean as organic carbon
f_{pyr}	Fraction of sulfur leaving the ocean as pyrite
Fe	Iron
FeO	Iron (II) oxide
Fe ₂ O ₃	Iron (III) oxide
Ga	Billion years ago (Giga annum)
GOE	Great Oxidation Event
Gyrs	Billions of years
H ₂	Hydrogen
H ₂ S	Hydrogen sulfide
Hf	Hafnium
I	Iodine
IMB	Isotope mass balance

LA-ICP-MS	Laser ablation-inductively coupled plasma-mass spectrometry
LECA	Last eukaryote common ancestor
LUCA	Last universal common ancestor
Ma	Million years ago (Mega annum)
Mg	Magnesium
MIF-O	Mass-independent fractionation of oxygen
MIF-S	Mass-independent fractionation of sulfur
Mn	Manganese
Mo	Molybdenum
MSR	Microbial sulfate reduction
Myrs	Millions of years
Nd	Neodymium
NOE	Neoproterozoic Oxygenation Event
O ₂	Oxygen
O ₃	Ozone
ODE	Ordinary differential equation
P	Phosphorus
PAL	Present atmospheric level
Pb	Lead
POE	Paleozoic Oxygenation Event
ppm	Parts per million
REEs	Rare earth elements
RSE	Redox sensitive trace element
S	Sulfur
Se	Selenium
Sm	Samarium
SO ₂	Sulfur dioxide
sd	Standard deviation
U	Uranium
UV	Ultraviolet

V

Vanadium

1. Introduction

Are there other hospitable worlds for life in our Universe? How, why and when did life evolve on our own planet? These are some of the key research questions in NASA's astrobiology roadmap (Achenbach *et al.*, 2015). It is thought that the answers to the second set of these questions may lead to an answer for the first question, by narrowing the search field to those exoplanets most suitable for hosting life, instead of general exoplanet hunting. The first order approach in the search for other habitable worlds has been to look for those planets lying within the circumstellar habitable zone – also known as the Goldilocks zone – that is, the distance from the host star where planetary surface temperatures are in the range for liquid water to be present (Kasting, Whitmire and Reynolds, 1993; Selsis *et al.*, 2007). The reasoning behind looking for liquid water first is due to its biological importance as a polar solvent, allowing other carbon-containing polar compounds to dissolve in it, and although certain hardy organisms can survive without liquid water, they become effectively dormant and are unable to reproduce or perform metabolic functions until reintroduced to water (Kasting, 2010).

Water is thought to be ubiquitous in the Universe, albeit mostly in the form of ice (Mottl *et al.*, 2007), thus in order to refine our search for habitable planets further, we can look to another essential chemical component – in terms of either production or consumption – for *almost* all life, and certainly for all animal life, on Earth: oxygen. An understanding of the evolutionary history of atmospheric oxygen (O₂) on Earth may then provide some clues as to the how's and why's behind life's emergence and diversification, which can be used in our search for habitable planets. As there are no

direct records of atmospheric oxygen composition, except for possibly (and perhaps controversially) gas inclusions in halite (Blamey *et al.*, 2016; Yeung, 2017; Blamey and Brand, 2019; Steadman *et al.*, 2020), beyond the Quaternary period, geochemical proxies are used to infer past O₂ levels (Sessions *et al.*, 2009). Unfortunately, these proxies can often only provide threshold values of O₂, rather than definitive levels. However, a wide array of biogeochemical data can be utilised by numerical models of the Earth system to provide quantitative reconstructions of the paleo atmosphere (e.g. Arvidson, Mackenzie and Guidry, 2006; Berner, 2006a; Lenton, Daines and Mills, 2018).

The aim of this thesis is to provide, for the first time, a quantitative history of the evolution of atmospheric oxygen on Earth, with the hope that the results will lead to significant advances in our thinking about the coupled evolution of Earth and life. This requires a total Earth-system and multidisciplinary approach, combining diverse fields such as: physics; chemistry; biology; geology; mathematics; and computing.

1.1. The early Earth: from Hadean to Archean

1.1.1. Earth formation and the beginning of continents

The Earth formed around 4.54 billion years ago (Ga) out of the solar nebula – the circumstellar disc of gas and dust left over after the formation of the Sun. The dust grains accreted over time, leading to clumps of rock which collided to form planetesimals, and further collisions eventually led to the formation of the terrestrial planets (Goldreich and Ward, 1973). It is difficult to definitively ascertain what conditions on the Earth during its infancy might have been like, due to the scarcity of rocks from the Hadean Eon (4.54 – 4 Ga) that have been preserved through time

(Garrels and Mackenzie, 1969; Reimink *et al.*, 2016). Although there is presently only one rock unit with a precise Hadean age – the Idiwhaa tonalitic gneiss in the Acasta Gneiss Complex, Canada ($4,019.6 \pm 1.8$ Myr) – Hadean zircons found in Archean sediments from the Mt. Narryer and Jack Hills formations in Western Australia have helped to illuminate some early earth processes (Harrison *et al.*, 2005; Watson and Harrison, 2005; Harrison, 2009; Reimink *et al.*, 2016). Zircon thermometry and oxygen isotopes have, for example, suggested that: crust formation; erosion, whether by chemical weathering from an active hydrosphere or physical processes; and sediment recycling had evolved as early as 4.35 Ga (Mojzsis, Harrison and Pidgeon, 2001; Wilde *et al.*, 2001; Watson and Harrison, 2005). Large swings in hafnium (Hf) isotope values extracted from zircons seem to imply that continental crust, felsic in nature, existed by 4.4 Ga and even as early as 4.5 Ga, but was rapidly recycled into the mantle (Harrison *et al.*, 2005), although boron (B) isotopes suggest that this recycling did not follow modern subduction-style processes until very late in the Archean (Smit *et al.*, 2019). However, U-Pb and other Hf isotope data from ~ 4.02 Ga suggest that the crust was ultramafic or mafic instead of continental (Reimink *et al.*, 2016).

1.1.2. *The Hadean atmosphere*

It is likely that the impact of Theia, a small planetary body, on the Earth (forming the Moon in the process) at $\sim 4.45 - 4.5$ Ga caused a vaporisation of a significant quantity of rock material, which upon condensation and coagulation left behind an atmosphere of water vapour, carbon dioxide (CO₂) and hydrogen (H₂), among other volatiles (Sleep, Zahnle and Neuhoff, 2001). This atmosphere would have enabled global average surface temperatures to lie within the range required (0 - 100°C) for surficial

liquid waters to exist by at least 4.2 Ga (Mojzsis, Harrison and Pidgeon, 2001) and possibly earlier (Wilde *et al.*, 2001).

1.1.3. *The Archean atmosphere and oceans*

Iron speciation analyses of marine shales point towards Archean oceans dominated by anoxic ferruginous conditions (i.e. low sulfate but with an abundance of iron; see Fig. 1.1) (Poulton and Canfield, 2011). Iron formations, which are iron and silicon dioxide rich marine sedimentary rocks, are prevalent throughout the Archean through to the Paleoproterozoic (Konhauser *et al.*, 2017). Under anoxic conditions, dissolved iron (in Fe^{2+} form) sourced at least partially via hydrothermal vents, may have precipitated close to the vents and are consequently associated with intermittent periods of enhanced volcanism (Isley and Abbott, 1999; Konhauser *et al.*, 2017). Alternatively, the iron-rich waters may have upwelled on to continental margins where the iron precipitated out due to a possible interaction with oxygenated shallow waters, which are inferred from high rhenium (Re) but low molybdenum (Mo) enrichments (Kendall *et al.*, 2010; Poulton and Canfield, 2011; Konhauser *et al.*, 2017). Re and Mo are both released from continental crust via oxidative weathering, as is sulfur (Kendall *et al.*, 2010; Catling and Zahnle, 2020). This indicates the presence of some O_2 in the atmosphere, possibly as ‘whiffs’, because although the Archean oceans were generally low in sulfate – suggesting that there was not enough O_2 to oxidise large quantities of sulfide to sulfate – there are instances of both authigenic Mo enrichments (which can occur under euxinic, i.e. anoxic and hydrogen sulfide-rich, conditions) and significant mass-dependent sulfur isotope fractionations, indicating times of elevated sulfate levels (Anbar *et al.*, 2007; Kaufman *et al.*, 2007; Reinhard *et al.*, 2009; Crowe *et al.*, 2014; Havig *et al.*, 2017).

Although geochemical data suggests transient and perhaps localised rises in O₂ in the Archean, the ubiquitous presence of the mass-independent fractionation of sulfur (MIF-S) isotopes in sediments prior to 2.45 Ga provides a general upper limit on O₂ levels (Farquhar, Bao and Thiemens, 2000; Pavlov and Kasting, 2002; Zahnle, Claire and Catling, 2006). Briefly, various mechanisms such as biological, kinetic or thermodynamic processes, can fractionate isotopes dependent on the relative mass difference between the isotopes, leading to observable and quantifiable relationships (Farquhar, Bao and Thiemens, 2000). This is mass-dependent fractionation, and using sulfur as an example, the isotopic variations can be defined (Farquhar, Bao and Thiemens, 2000; Pavlov and Kasting, 2002) as:

$$\delta^{33}\text{S} \cong 0.515 \cdot \delta^{34}\text{S} \quad (1.1)$$

$$\delta^{36}\text{S} \cong 1.91 \cdot \delta^{34}\text{S} \quad (1.2)$$

Mass-independent fractionations on the other hand, do not obey this relationship.

Under an anoxic atmosphere, volcanic sulfur dioxide (SO₂) emissions can be transformed by a series of photochemical reactions with short wave ultraviolet (UV) light to insoluble elemental sulfur (S₈) which generates a MIF-S signal (Farquhar *et al.*, 2001; Pavlov and Kasting, 2002; Zahnle, Claire and Catling, 2006). Sulfur would have likely exited the Archean atmosphere both as insoluble S₈ but also in water soluble sulfuric acid and SO₂ forms, whereas in the modern day all sulfur is oxidised to sulfate (Zahnle, Claire and Catling, 2006). The mixture of insoluble and soluble sulfur may have prevented total mixing of the various sulfur species in a low oxygen ocean, as a good proportion of the S₈ likely settled to the sediments fairly rapidly (Halevy, 2013). While some of the S₈ would have reacted with H₂S (depending on the

dissolution kinetic rate) resulting in isotopic mixing of these species, some would have formed pyrite (Halevy, 2013). If the pyrite was formed rapidly after the microbial reduction of sulfur (whether that be derived from an initial reservoir of S₈ or from oxidation of SO₂ etc.) this may have preserved the MIF-S signals of the different sulfur species (Farquhar *et al.*, 2013; Halevy, 2013).

Shortwave UV light in the modern troposphere is blocked by the presence of stratospheric ozone (Catling and Zahnle, 2020), which is formed when UV-C photolyses O₂ to produce oxygen radicals that can combine with O₂ to produce O₃. Thus, the formation of O₃ in the stratosphere would have significantly reduced, if not prevented, the photochemical creation of S₈ (Farquhar, Bao and Thiemens, 2000; Pavlov and Kasting, 2002). With the aid of photochemical modelling, an upper limit for O₂ of 10⁻⁵ PAL has been suggested, in order for the photochemical production of S₈ to take place on the scale required for MIF-S preservation (Pavlov and Kasting, 2002). However, later photochemical modelling, which includes sufficient quantities of reduced gases (e.g. CH₄) in the atmosphere, suggests that O₂ levels prior to the Great Oxidation Event (GOE) were instead <10⁻⁶ PAL (Zahnle, Claire and Catling, 2006).

There is the possibility that across the Hadean and Archean, the Earth was transiently enveloped in an organic haze, as a result of methane (CH₄) production via biological processes such as methanogenesis, and the polymerisation of CH₄ into organic particles during photolysis, when ratios of CH₄/CO₂ > ~0.1 in the atmosphere (Trainer *et al.*, 2006; Zerkle *et al.*, 2012; Izon *et al.*, 2015, 2017; Arney, Domagal-Goldman and Meadows, 2018). The haze may have blocked UV radiation, which would have affected sulfur gases in the troposphere and thus the MIF-S signal, and the correlation

of pulses of MIF-S in the sedimentary record with incidences of light organic carbon isotopes ($\delta^{13}\text{C}_{\text{org}}$) suggest variances in the CH_4/CO_2 ratio, driven by fluctuations in biogenic CH_4 production (Domagal-Goldman *et al.*, 2008; Zerkle *et al.*, 2012; Izon *et al.*, 2015, 2017).

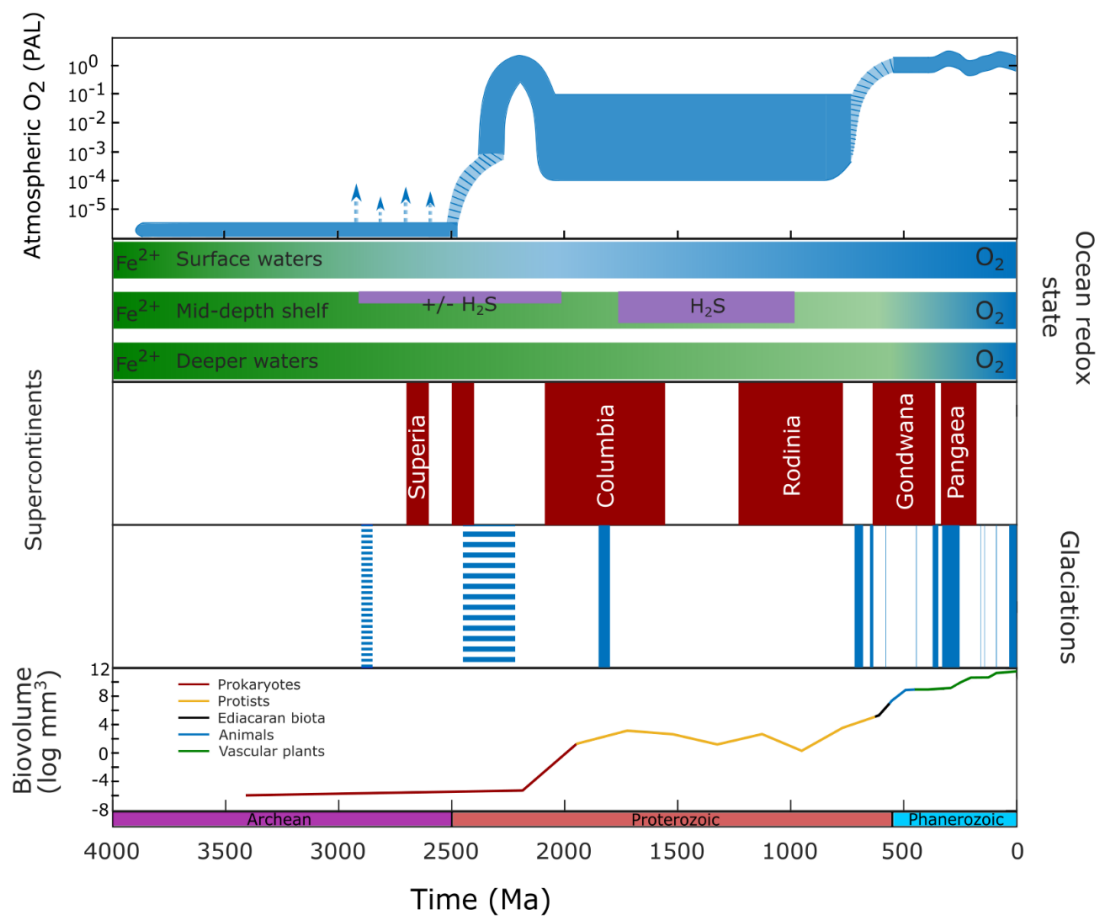


Figure 1.1 | The evolution of the Earth.

The top panel shows the currently proposed history of atmospheric O₂. The panel below shows the changing redox state of the oceans, separated into surface, mid-depth, and deep ocean layers, where Fe²⁺ represents anoxic ferruginous, H₂S is euxinic, and O₂ are oxygenated waters. The middle panel shows periods of supposed supercontinent existence. Below that: the dashed line in the Archean represents a possible localised glaciation; the dashed line at the start of the Proterozoic represents multiple glaciations; thick blue lines are periods of either extensive or long-lasting glaciations, thin blue lines are more localised or shorter glaciations. The final panel shows changes in maximum body sizes of organisms: red line-prokaryotes; yellow-protists; black-Ediacaran biota; blue-animals; green-vascular plants. The schematic is adapted from a number of sources (Och and Shields-Zhou, 2012; Lyons, Reinhard and Planavsky, 2014; Poulton, 2017; Mills et al., 2019).

1.1.4. Early life

The earliest putative evidence for life probably occurs in the Eoarchean Era (3.6 – 4 Ga), but possibly in the Hadean, in the form of fossilised microorganisms from the ferruginous (iron-containing) sediments of the Nuvvuagittuq belt in Quebec, Canada (Dodd *et al.*, 2017). These rocks have been interpreted as precipitates of seafloor hydrothermal vents, with an age between ~3.75 – 4.28 Ga depending on the aging systematics (U-Pb versus ¹⁴⁶Sm-¹⁴²Nd), and contain fossilised tubes and filaments that have similar morphologies and assemblages to those found in modern hydrothermal vent precipitates (Dodd *et al.*, 2017). This rough age for the emergence of life on Earth seems to correspond with recent work which reconsiders fossil material by employing new molecular clock analyses, and finds that the last common universal ancestor (LUCA) for cellular life is older than 3.9 Ga (Betts *et al.*, 2018). In addition,

geochemical evidence in the form of isotopically light carbon (implying biological activity) in carbonaceous inclusions extracted from apatite grains, suggest life's existence at $\sim 3.8 - 3.85$ Ga (Mojzsis *et al.*, 1996).

However, the oldest conclusive evidence for life is between $\sim 3.465 - 3.481$ Ga (in the Paleoarchean), with carbon isotopes from both microbial fossils and stromatolites, and petrographic microscopy on microfossils indicating biogenicity, possibly that of a phototrophic nature, though not necessarily that of the oxygenic kind (Sugitani *et al.*, 2015; Schopf *et al.*, 2018; Baumgartner *et al.*, 2019).

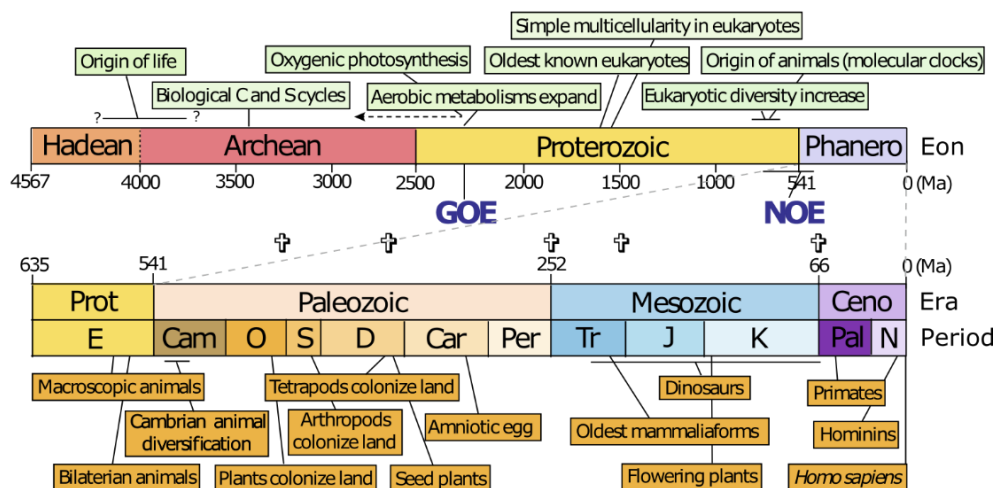


Figure 1.2 | The timetable of evolution.

Based on various data, such as fossils, environmental and geochemical proxies, and geochronology, this charts the evolution of life on Earth. The GOE is the Great Oxidation Event and NOE is the Neoproterozoic Oxygenation Event, with crosses indicating periods of major mass extinctions. Taken from Knoll and Nowak (2017).

There is substantial debate regarding the timing of the evolution of oxygenic photosynthesis, with estimates ranging from >3.7 Ga to 2.35 Ga (Rosing and Frei, 2004; Kirschvink and Kopp, 2008), but as it remains the only major source of free O₂ on Earth, its evolution must have predated or at least coincided with the GOE (see Fig. 1.2) at ~2.3 to ~2.4 Ga (Lyons, Reinhard and Planavsky, 2014). Genomic work on organisms related to photosynthetic cyanobacteria suggest that the advent of oxygenic photosynthesis occurred later, rather than earlier, in bacterial evolution, meaning that the maximum age of this process can be estimated to be ~2.5 to 2.6 Ga based on molecular clock analyses of the deviation of *Oxyphotobacteria* from *Melainabacteria* (Soo *et al.*, 2017).

1.2. The Great Oxidation Event

The GOE marked a pivotal point in Earth history: a switch from an atmosphere essentially free of O₂, to one with levels high enough to generate permanent state changes in various geological and geochemical proxies, and is the first of the two broad stepwise changes in atmospheric O₂ (see Fig. 1.1) that are thought to have occurred (Lyons, Reinhard and Planavsky, 2014). The GOE likely occurred in association with major changes to the Earth system (see Fig. 1.1), including the break-up of a possible supercontinent from the Neoproterozoic, and a number of glaciations (Kirschvink *et al.*, 2000; Reddy and Evans, 2009; Gumsley *et al.*, 2017). The MIF-S, a prominent feature of the Archean sedimentary record, essentially disappears after ~2.32 Ga (Lyons, Reinhard and Planavsky, 2014; Havig *et al.*, 2017), providing a lower limit to subsequent O₂ levels of >10⁻⁶ PAL (Zahnle, Claire and Catling, 2006), although the limit is often suggested to be >10⁻⁵ PAL (Pavlov and Kasting, 2002).

Other proxies, such as significant deposits of redox-sensitive detrital pyrite, uraninite and siderite become less ubiquitous and essentially disappear after the mid-Proterozoic, suggesting that O_2 after the GOE may have been higher than 0.01 PAL (Walker *et al.*, 1983; Rasmussen and Buick, 1999; Buick, 2008). Conversely, the GOE marks the appearance of terrestrial red beds: sedimentary rocks containing ferric oxides (Holland, 2006; Kump, 2008). Prior to the GOE, paleosols would have lost soluble Fe^{2+} during weathering processes, but the increased abundance of Fe_2O_3 compared to FeO after the GOE suggests enough O_2 in the atmosphere to oxidise Fe^{2+} to insoluble Fe^{3+} (Holland, 2006; Buick, 2008; Kump, 2008).

1.3. Earth's middle age

1.3.1. Introduction

Termed, ‘the boring billion’, Earth’s middle age from ~1.8 Ga to ~0.8 Ga has long been thought to be a period of geological, biological, and environmental stasis, with low atmospheric O_2 levels (see Fig. 1.1) and no major tectonic or climatic changes (Brasier and Lindsay, 1998; Och and Shields-Zhou, 2012; Lyons, Reinhard and Planavsky, 2014; Mukherjee *et al.*, 2018). Some of the early geochemical evidence that pointed to this stagnation in the Earth system lay with the relatively stable and flat $\delta^{13}C$ record extracted from carbonates found in Australian successions (Buick, Des Marais and Knoll, 1995; Brasier and Lindsay, 1998), with subsequent data only serving to confirm this trend (Shields and Veizer, 2002; Prokoph, Shields and Veizer, 2008). Work involving redox sensitive trace elements (RSE) and phosphorus (P) concentrations in black shales also point to a prolonged period of stability (e.g. Scott *et al.*, 2008; Robbins *et al.*, 2016; Reinhard *et al.*, 2017), however, recent studies have

suggested a more complex picture of ocean redox during this time (Doyle *et al.*, 2018; K. Zhang *et al.*, 2018).

1.3.2. Ocean chemistry

The onset of the boring billion coincides with the disappearance of banded iron formations, which was originally thought to be due to widespread ocean oxygenation (Holland, 1984), but later was considered to be the result of the formation of anoxic sulfidic (euxinic) waters (Canfield, 1998). More recently, a more complex view of ocean chemistry during the boring billion has emerged (see Fig. 1.1): that deeper waters were probably ferruginous (Poulton, Fralick and Canfield, 2010; Planavsky *et al.*, 2011; Poulton and Canfield, 2011; Guilbaud *et al.*, 2015) with possible transient episodes of oxygenation (Zhang *et al.*, 2016; Zhang *et al.*, 2018) and shallow water anoxia (Doyle *et al.*, 2018); and that euxinia was spatially limited to the more productive continental margins (Poulton, Fralick and Canfield, 2004; Scott *et al.*, 2008), with no more than ~7% of the global seafloor being euxinic (Gilleaudeau *et al.*, 2019).

1.3.3. Atmospheric oxygen predictions

Chromium (Cr) isotope data from a variety of locations suggest that Cr oxidation at the Earth's surface during much of the boring billion was inhibited, thus placing a constraint on atmospheric O₂ levels to be 0.1% PAL (alternatively written as 10⁻³ PAL) at most (Planavsky *et al.*, 2014; Cole *et al.*, 2016), though there are concerns that the samples do not contain authigenic Cr, which is of paramount importance for reconstructing past O₂ (Zhang *et al.*, 2016) and that the initial modelling to obtain this

threshold value overestimated the O₂ exposure time for Cr-bearing soils (Daines, Mills and Lenton, 2017), thus the constraint should be ~1% PAL.

An O₂ level of 0.1% PAL or lower would be inimical to animal respiration, however, enhanced Cr isotope ($\delta^{53}\text{Cr}$) fractionation and work looking at trace metals and biomarkers, alongside a carbon-oxygen model, suggest atmospheric O₂ levels above 0.1% PAL (depending on the model used) and possibly >4% PAL – above the threshold required by animals, at ~1.4 Ga (Zhang *et al.*, 2016; Canfield *et al.*, 2018). The ~4% PAL threshold has been obtained from the carbon-oxygen model by assessing the likely minimum atmospheric O₂ level required for the presence of oxygenated bottom waters for the Xiamaling Formation, considering that C_{org} reactivity (and thus oxidative respiration rate), ocean temperature and water age (i.e. the water volume in adjacent ocean layers with a constant density ratioed by the amount of water entering this volume), each impact upon ocean O₂ concentrations (Zhang *et al.*, 2016). With an estimated water age of 10 years, atmospheric O₂ estimates may vary between 1.3% PAL (low C_{org} reactivity, colder waters) and 6.2% PAL (high C_{org} reactivity, warmer waters), however, the water age is based on modern data and may not be true for 1.4 Ga (Zhang *et al.*, 2016). Nevertheless, even the lower O₂ estimate is an order of magnitude larger than previously predicted (Planavsky *et al.*, 2014).

Again, there are fears that there might be contamination of the biomarkers, and that the low V/Al ratios obtained – indicative of V removal from the sediment by oxygenated bottom waters – are just a relic of the variability in V/Al ratios that can often be seen in the present day continental crust (Planavsky *et al.*, 2016). Re-analysis of the biomarkers and comparison of the trace metals to other rock units (Zhang *et al.*, 2016) assuages these fears somewhat, and is backed by Cr isotope data from this group

suggesting O₂ levels >1% PAL (Canfield *et al.*, 2018). The debate over atmospheric O₂ levels between these research groups remains, but it may be resolved in the future, as more information about the operation of $\delta^{53}\text{Cr}$ fractionation and RSE variability under a wide range of redox settings is generated.

Other work, looking at a dataset of over 3000 LA-ICP-MS trace-element analyses on sedimentary pyrite, implies that O₂ levels were ~18% (of the atmosphere by volume, atm – roughly equivalent to 86% PAL) at 1.8 Ga, with subsequent fluctuations between 5% and 11% atm until O₂ declines to <2% atm by 1 Ga (Large *et al.*, 2019). However, in order to achieve these modelled O₂ results, the dataset is standardised either: against the outputs from the biogeochemical model, GEOCARBSULF (Berner, 2009), which has some significant issues (see Chapter 3) that introduces doubts to the veracity of these results; or against measurements of ancient O₂ trapped in fluid inclusions within halite crystals (Blamey *et al.*, 2016), which may have experienced contamination (Yeung, 2017).

1.3.4. Possible reasons for oxygen regulation

A number of drivers have been put forward to explain the low O₂ levels seen through much of the Proterozoic. A couple of studies propose that low O₂ conditions can be maintained if, for example, phosphorus (P) – the ultimate limiting nutrient over geologic timescales (Tyrrell, 1999) – is scavenged by an iron trap, which would reduce the amount available for primary productivity (Laakso and Schrag, 2014; Reinhard *et al.*, 2017). Alternatively, P may have been limited earlier in the Proterozoic due to a predominance of seafloor weathering over continental weathering, thereby reducing

the P input into the oceans (Mills, Lenton and Watson, 2014). A gradual shift to higher terrestrial weathering throughout the Proterozoic would likewise slowly increase P levels in the oceans, and although not all P is bioavailable and dissolved P concentrations are controlled by redox conditions, it is likely that primary productivity, and therefore O₂ levels, increased towards the end of the Boring Billion (Mills, Lenton and Watson, 2014; Poulton, 2017; Reinhard *et al.*, 2017).

Other possibilities for low O₂ drawn from numerical modelling are: that incomplete oxidative weathering, and tectonic recycling of organic carbon (C_{org}) could have regulated O₂ at low levels (Daines, Mills and Lenton, 2017); or that the O₂ sink via the input of reduced gases such as CH₄ was still considerable (Pavlov *et al.*, 2003).

Another hypothesis put forward is that of nitrogenase – the sole enzyme cyanobacteria utilise to fix nitrogen – inhibition when O₂ levels reach 10% PAL (Allen, Thake and Martin, 2019). In this case, the nitrogenase inhibition would have suppressed global primary productivity rates, which is corroborated by triple oxygen isotopes from 1.4 Ga sulfate minerals (Crockford *et al.*, 2018). However, the authors (Allen, Thake and Martin, 2019) argue that this would be the case until the evolution of land plants, and yet, they also acknowledge that different cyanobacterial lineages have different degrees of protection against nitrogenase, thus primary productivity and O₂ production may be dependent on the cyanobacterial ecology at that time. Alternatively, under sulfidic conditions, Fe and Mo, which are cofactors in different forms of nitrogenase, can be removed from solution to the sediments (Anbar and Knoll, 2002; Allen, Thake and Martin, 2019), thus inhibiting primary productivity in the oceans, particularly along continental margins. But, lacustrine settings may have also been an important

environment for eukaryotic life, and there is some evidence that Mo may not have been a limiting element in Mesoproterozoic lakes (Parnell *et al.*, 2015).

1.3.5. *Evolutionary advances*

Despite the general view of fairly static atmospheric O₂ levels through this period of time, from a biological standpoint, recent work points to the ‘Boring Billion’ being anything but so. There is emerging evidence that crown group eukaryotes (the last eukaryotic common ancestor: LECA) had evolved by the late Paleoproterozoic (see Fig. 1.2), with fossils preserved in ~1.6 billion-year-old sedimentary rocks interpreted to be red algae (Butterfield, 2015; Bengtson *et al.*, 2017). Micropaleontological analysis of the Mesoproterozoic aged siliciclastic rocks of the Roper group in Australia find abundant, well-preserved taxa, of which five are unambiguously eukaryotes (Javaux and Knoll, 2017). Additionally, the fossils provide evidence for certain eukaryotic features such as: a cytoskeleton; cysts with a decay-resistant coating; reproductive capabilities; and importantly, simple multicellularity (Javaux and Knoll, 2017). The end of the boring billion in the Tonian period was heralded by: an increase in the number of species of complex, organic-walled microfossils; vase-shaped tests similar to extant testate amoebae; and simple foraminifera (e.g. Porter, Meisterfeld and Knoll, 2003; Knoll, 2015), with molecular clocks (see Fig. 1.2) hinting that the last common ancestor for all animals evolved at ~800 Ma (Erwin *et al.*, 2011).

1.4. The Neoproterozoic Oxygenation Event

The second stepwise oxygenation of Earth’s atmosphere is proposed to have occurred at some point during the Neoproterozoic, with O₂ rising to roughly modern-day levels

(Och and Shields-Zhou, 2012; Lyons, Reinhard and Planavsky, 2014). The Neoproterozoic Era witnessed a number of large-scale changes to the Earth system (see Fig. 1.1). The supercontinent, Rodinia, formed in the late Mesoproterozoic to early Neoproterozoic, and following major rifting episodes at approximately 825 Ma, 780 Ma and 720 Ma, subsequently broke up into a number of low-latitude continents, before the assembly of the Gondwana supercontinent at ~540 Ma (Li *et al.*, 2008; Li, Evans and Halverson, 2013). The Era was also punctuated by three glaciations: the Sturtian (~717–659 Ma); the Marinoan (~649–635 Ma); and the Gaskiers (~580 Ma), of which the Sturtian and Marinoan are considered to be ‘Snowball Earth’ glaciations (Hoffman *et al.*, 1998; Condon *et al.*, 2005; Fairchild and Kennedy, 2007; Calver *et al.*, 2013; Pu *et al.*, 2016; Macdonald *et al.*, 2017; Cox *et al.*, 2018; Wang *et al.*, 2019).

These events have posed a challenge in terms of understanding the possible drivers of the Neoproterozoic Oxygenation Event (NOE) as, for example, volcanic degassing associated with Rodinia rifting episodes will have acted as a sink for O₂ but may have also provided ample quantities of oxidised carbon and sulfur to the ocean-atmosphere, if, for example, sufficient amounts of carbonate were subducted and decomposed to CO₂ (Sleep and Zahnle, 2001). Emissions of reduced forms of carbon and sulfur (alongside other gases, such as H₂) would have readily reacted with O₂ (sink) but the amount of reduced gases released can be dependent on the magmatic source, with some work pointing towards the eruption of oxidised magmas at ~780 Ma, thus decreasing the size of the sink (Catling and Claire, 2005; Macouin *et al.*, 2015). But ultimately bursts of volcanic activity will increase the carbon and sulfur in the ocean-atmosphere system available for reduction (and therefore O₂ production), subject to other photosynthetic or microbial sulfate reducing limitations (e.g. nutrients, light etc.)

(Berner, 1991; Rothman *et al.*, 2003; Catling and Claire, 2005; Lee *et al.*, 2016). Thus, the ratio of oxidised carbon and sulfur to reduced carbon and sulfur emitted during volcanic activity may be an important constraint on atmospheric O₂ levels through time (Macouin *et al.*, 2015).

The timing and extent of the NOE is also contentious. The onset of oxygenation is generally inferred from geochemical proxies, most of which are from the marine realm, but there is no clear consensus from these proxies about when the NOE starts. A body of research on uranium isotopes ($\delta^{238}\text{U}$), utilising geological observations, and theoretical and experimental results, points towards considerable isotopic fractionation during the reduction of U(VI) to U(IV) under anoxic (including euxinic) settings (Tissot and Dauphas, 2015; Lau, Romaniello and Zhang, 2019). Authigenic U(IV) precipitates form which are preferentially enriched in ^{238}U , leaving seawater isotopically light (e.g. Tostevin *et al.*, 2019). As there appears to be no significant isotopic fractionation between the seawater soluble U (in the form of a uranyl-tricarbonate ion) and its uptake into calcium carbonates, $\delta^{238}\text{U}$ extracted from calcium carbonates should reflect the $\delta^{238}\text{U}$ of seawater ($\delta^{238}\text{U}_{\text{sw}}$) through time (Tissot and Dauphas, 2015; G.-Y. Wei *et al.*, 2018; Lau, Romaniello and Zhang, 2019; Tostevin *et al.*, 2019). The input fluxes of $\delta^{238}\text{U}$ to the ocean seem to track bulk crustal values, thus it can be inferred that more negative $\delta^{238}\text{U}_{\text{sw}}$ values represent more reducing conditions (a larger anoxic or euxinic sink) and transitions to modern seawater values ($\sim -0.39\text{‰}$) or higher are representative of more oxidising conditions (Tissot and Dauphas, 2015; G.-Y. Wei *et al.*, 2018; Lau, Romaniello and Zhang, 2019; Tostevin *et al.*, 2019). As such, $\delta^{238}\text{U}_{\text{sw}}$ data suggests short-lived periods of ocean oxygenation during the Cryogenian and Ediacaran (Lau, Romaniello and Zhang, 2019; Tostevin *et*

al., 2019). Enrichments of RSEs, such as Cr, U, V etc. also imply multiple transitions between an anoxic and oxic ocean from the Cryogenian through to the early Cambrian (Sahoo *et al.*, 2016).

Cerium (Ce) is somewhat of an oddity compared to most of the other rare earth elements (REEs), as it can exist in both +3 and +4 valence states, rather than just the +3 state (German and Elderfield, 1990; Tostevin *et al.*, 2016; Wallace *et al.*, 2017). In anoxic settings Ce is soluble in the oceans and is found in the +3 valence state, but in the presence of O₂, Ce is scavenged by manganese (Mn) and Fe (oxyhydr)oxides, whereby the Ce is partially oxidised to the +4 state and the residual seawater is Ce-depleted compared to the other (REEs), and thus a Ce anomaly (Ce_{anom}) can be determined by normalising Ce concentrations in sediments to neighbouring REEs (German and Elderfield, 1990; Tostevin *et al.*, 2016; Wallace *et al.*, 2017). Negative Ce_{anom} values (i.e. Ce is depleted with respect to other REEs, and thus Ce_{anom} < 1) indicate oxygenation of the oceans, but Ce_{anom} data for much of the Neoproterozoic suggest the oceans were predominantly anoxic, with a brief oxygenation event at the Ediacaran-Cambrian boundary (Wallace *et al.*, 2017).

Iodine/calcium plus magnesium (I / Ca + Mg) ratios in shallow marine carbonates can be used as an oxygenation proxy, as iodate (IO₃⁻) is the dominant dissolved iodine species in oxygenated waters and co-precipitates with carbonates, whereas dissolved iodide (I⁻) is dominant in anoxic conditions and is not incorporated into carbonate minerals (Hardisty *et al.*, 2014). As with the Ce_{anom}, I / Ca + Mg ratios also hint at widespread ocean anoxia, but with an oxygenation event at ~800 Ma (Lu *et al.*, 2018;

Wörndle *et al.*, 2019). A statistical analysis of $\delta^{53}\text{Cr}$ data shows a substantial fractionation from the bulk silicate Earth value from 850 Ma onwards, hinting that the NOE may have started then (Cole *et al.*, 2016). While the $\delta^{53}\text{Cr}$ provides a lower bound for O_2 of 0.1 – 1% PAL (Planavsky *et al.*, 2014; Daines, Mills and Lenton, 2017), it is difficult to define even qualitative bounds from the other geochemical proxies, although gas inclusions in halite tentatively imply O_2 levels of ~48% PAL at 850 Ma and an average of ~40 – 46% PAL at 815 Ma (Blamey *et al.*, 2016; Blamey and Brand, 2019).

The Neoproterozoic world then, seemed to be a time of both geological and geochemical complexity, and it is likely that the biosphere was no different. Research involving hydrocarbon biomarkers extracted from shales indicates a shift from cyanobacterial domination of total primary production to an increasing abundance of algae during the Sturtian-Marinoan interglacial period (Brocks *et al.*, 2017). Biomarkers also indicate the advent of predatory protists at the same time as this increase in algae (Brocks *et al.*, 2017) and the possibility of the evolution of demosponges prior to the Sturtian glaciation (Brocks *et al.*, 2016). Later in the Neoproterozoic, the first fossils of the enigmatic Ediacaran biota are found (Knoll and Nowak, 2017). Interpretations of the biota remain complex, but palaeontological and again, biomarker evidence, have led to the identification of *Kimberella* and *Dickinsonia*, at least, as some of the first macroscopic animals on Earth (Ivantsov, 2009; Bobrovskiy *et al.*, 2018).

1.5. The Phanerozoic

The start of the Phanerozoic is marked by the Cambrian explosion: the abrupt increase of bilaterian animals in the rock record (Erwin *et al.*, 2011). As O₂ is a requirement for animal metabolism (Nursall, 1959; Erwin *et al.*, 2011) it is thought that rising O₂ levels may have fuelled the Cambrian explosion, with later rises leading to the evolution of large marine predators and an increase in size of terrestrial arthropods, for example (Berner *et al.*, 2003; Dahl *et al.*, 2010). An atmospheric O₂ minimum of ~10% PAL in the early Paleozoic has been postulated, based on possible O₂ requirements by Cambrian biota (Levin, 2003), although less complex animals, such as sponges, may have had lower requirements (Mills *et al.*, 2014).

As with the Precambrian, the broad oxygenation history of the Phanerozoic has been ascertained from the interpretation of various geochemical proxies. Iron speciation and Ce_{anom} point to the deep oceans remaining predominantly anoxic during the early Paleozoic (Sperling *et al.*, 2015; Wallace *et al.*, 2017), while $\delta^{238}\text{U}_{\text{sw}}$ and RSE data suggest fluctuating redox conditions in the Cambrian (Dahl *et al.*, 2014; Sahoo *et al.*, 2016; G.-Y. Wei *et al.*, 2018). The Devonian marked a shift to widespread ocean oxygenation, with I / Ca + Mg ratios, Mo isotopes and the Ce_{anom} all expressing values indicative of oxic conditions (Dahl *et al.*, 2010; Wallace *et al.*, 2017; Lu *et al.*, 2018). This transition in the oceans at ~400 Ma likely coincided with the evolution of vascular plants on land, with their higher C:P ratios (compared to marine photosynthesisers) leading to enhanced C_{org} burial, and thus oxygen production (Dahl *et al.*, 2010). This may have then contributed to the appearance of marine biota with high oxygen requirements, such as predatory fish, at this time (Dahl *et al.*, 2010).

In the terrestrial realm, the record of fossilised charcoal in sediments (inertinite) has been used as a proxy for atmospheric O₂ levels for the past 400 Myrs (Glasspool and Scott, 2010). Wildfires are initiated by the combustion of some form of fuel (e.g. wood, mosses) in the presence of O₂, forming charcoal as a by-product (Belcher and McElwain, 2008; Glasspool and Scott, 2010). Experimental work on combustion limits has shown that fuel, even with a low moisture content, will not combust when O₂ is <15% atm (Belcher and McElwain, 2008), and that burn probability is low until O₂ exceeds 19% atm (Belcher, Collinson and Scott, 2013; Watson and Lovelock, 2013). Armed with the knowledge of: present day O₂ levels; average inertinite percentage by volume in coals ($4.27 \pm 0.64\%$); and the assumption that at O₂ levels of 15% atm, the inertinite percentage abundance in a coal sample would equal 0.2%, inertinite data can be transformed into O₂ estimates (Glasspool and Scott, 2010; Glasspool *et al.*, 2015). The inertinite data suggests that for much of the last 400 Myrs, atmospheric O₂ remained above PAL but below 30% atm, which is not unexpected, as there is an assumption that O₂ must have remained below 30% atm that is factored into the inertinite to O₂ translations (Glasspool and Scott, 2010; Glasspool *et al.*, 2015).

Due to the limitations of other methods, much of our insight into atmospheric O₂ levels throughout the Phanerozoic is due to biogeochemical modelling (e.g. Bergman, Lenton and Watson, 2004; Falkowski *et al.*, 2005; Arvidson, Mackenzie and Guidry, 2006; Berner, 2006a). Biogeochemical models often take a surficial Earth system approach, looking at the atmosphere and ocean reservoirs, and various crustal reservoirs, estimating how they may have changed in size throughout the Phanerozoic. An understanding of these reservoirs, and how and why they have changed in size through time is the cornerstone of this thesis, and thus this is explored in Chapter 2.

1.6. This work

In Chapter 2 a comprehensive history of the evolution of the GEOCARBSULF model, including its results, flaws and limitations, is presented, and sets the scene for the rest of the work.

Chapter 3 focuses on the reconstruction of the GEOCARBSULF model, the identification of some of these shortcomings, and the effort to address these for Phanerozoic oxygen estimates. Results from the modified GEOCARBSULF model are showcased and compared to geochemical proxies and various geological and biological events. This work has been published (Krause *et al.*, 2018) and includes the further results and discussion from the supplementary information.

In Chapter 4 the modified GEOCARBSULF model is extended back through time, to investigate the existence of a possible oxygenation event in the Neoproterozoic Era, and to provide a quantitative approximation of O₂ levels during this highly dynamic period of time. Results are discussed with regards to geochemical proxies and geological events, and what this means for the Neoproterozoic Oxygenation Event.

Finally, Chapter 5 sees the extension of the model back through to the Archean and provides one way to estimate the history of the evolution of atmospheric oxygen on Earth. Notable discussions are centred on the quantification of levels during the Great Oxidation Event and the oxygen overshoot during the Lomagundi isotope excursion.

Chapter 6 discusses the main findings of this body of work, and finally, offers some suggestions for future research.

2. The evolution of the GEOCARBSULF model

2.1. Introduction

In this chapter I review the literature with regards to biogeochemical box modelling of the long-term carbon and sulfur cycles over the Phanerozoic Eon ($\sim 541 - 0$ Ma). While there are a number of box models which, for example, investigate only the carbon cycle (e.g. Sleep and Zahnle, 2001; Hayes and Waldbauer, 2006), or oceanic processes (e.g. Sarmiento and Toggweiler, 1984; Slomp and Van Cappellen, 2007), there exists three main Phanerozoic box models which attempt to reconstruct the flow of carbon and sulfur through the surficial Earth system – atmosphere, oceans, crust – and in doing so, compute changes to temperature, atmospheric O_2 and CO_2 levels, through time. These models are: GEOCARBSULF (Berner, 2006a, 2006b, 2008, 2009), COPSE (Bergman, Lenton and Watson, 2004; Lenton, Daines and Mills, 2018) and MAGic (Arvidson, Mackenzie and Guidry, 2006, 2013). All three models share commonality in their roots, but provide distinctly different results, particularly with regard to O_2 during the Phanerozoic.

An understanding of why model results diverge requires a knowledge of the origin of those roots and their subsequent evolutionary paths. Here, I focus principally on GEOCARBSULF, with the aim of developing not only a deep understanding of the underlying processes which govern its results, but also the incremental changes made to the suite of models over time and the rationale behind these updates. The reasoning behind investigating atmospheric O_2 levels through time with the GEOCARBSULF model, rather than COPSE or MAGic is due to the fact that the GEOCARBSULF model is the only ‘inverse’ model – i.e. one which starts with a set of observations, in

this case the $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ records, applies a set of laws or constraints, and from this calculates desired parameters (in this case primarily O_2 , but CO_2 predictions are also valuable) – that covers the entire Phanerozoic.

The key benefit to using GEOCARBSULF is the use of geological data for calculating organic carbon (C_{org}) and pyrite burial, rather than determining these fluxes from estimates of the input to the oceans of sedimentary material and nutrients via weathering, as is the case with COPSE and MAGic. There are of course limitations to the GEOCARBSULF model, and these are explored throughout the thesis. For completion, towards the end of this chapter there is a further, brief discussion about the differences between GEOCARBSULF and the COPSE and MAGic models in terms of both operation and O_2 results.

For each iteration of the GEOCARB and isotope mass balance (IMB) models, and eventually GEOCARBSULF itself, all of which are described below, I reconstructed the models in the MATLAB[®] programming language, based on a knowledge of the literature, rather than obtaining model code from elsewhere.

2.2. The early models

The 1970s marked the start of efforts by the scientific community to build mathematical models of various global elemental cycles to understand their individual behaviour, their influence on other cycles as a ‘coupled’ system (e.g. carbon and sulfur), and the effect that perturbations through time might have on the oxygen cycle (e.g. Holland, 1973; Garrels and Perry, 1974; Walker, 1974). However, it was the 1980s that saw the true advent of ‘box models’, which represented elemental cycles as a system of reservoirs (e.g. their various sedimentary, oceanic and atmospheric forms),

with matter transferred between them as ‘fluxes’ (Garrels and Lerman, 1981). These models considered biogeochemical processes over long timescales, and their consequent long-term feedbacks on the sediments and climate.

2.2.1. *The WHAK model*

The first model to propose long-term regulation of the climate by weathering processes was the ‘WHAK’ model, named after its authors (Walker, Hays and Kasting, 1981). Knowledge of stellar evolution decrees that the Sun’s luminosity has increased from ~70% of its present day value at 4.7 Ga (Gough, 1981). This much reduced solar luminosity would have resulted in a frozen early Earth, and yet, as far back as 3.8 Ga there is evidence for water-borne sedimentary processes having taken place (Lowe, 1980), thus necessitating the presence of greenhouse gases in the Archean atmosphere to counteract this Faint Young Sun (Sagan and Mullen, 1972; Owen, Cess and Ramanathan, 1979). While Sagan and Mullen (1972) suggested that ammonia, as well as water vapour, were the key constituents for Earth’s early greenhouse effect, Owen *et al.* (1979) proposed that CO₂ was the gas responsible for clement temperatures. However, in order to reconcile the lower solar luminosity, partial pressures of CO₂ would need to be 1000x greater than present-day levels (Walker, Hays and Kasting, 1981) and the absence of siderite (an iron carbonate mineral) in paleosols dated between 2.2 – 2.75 Ga (Rye, Kuo and Holland, 1995) imposes an upper limit of 100x present (pre-industrial: ~280 parts per million) atmospheric level (PAL): an order of magnitude in difference.

One suggestion to overcome this issue has been to invoke a lower albedo on Earth during this time (Rosing *et al.*, 2010), yet, the methodology used requires

unfeasibly large rain droplet sizes in order to create thin clouds, and nearly equal mixing ratios of CO₂ and CH₄, which would enable the formation of a stratospheric hydrocarbon haze (Goldblatt and Zahnle, 2011). The size and shape of the haze particles appear to be likely controls on whether the haze formation resulted in cooling or warming of the early Earth, as fractal (rather than spherical) shapes generate a warming, but particles >0.2 µm in diameter would lead to a cooling, thus there is some uncertainty regarding the overall effect of hydrocarbon hazes on the early Earth (Pavlov, Brown and Kasting, 2001; Arney, Domagal-Goldman and Meadows, 2018).

Nevertheless, much of this information postdates the inception of the WHAK model, which was designed to test whether it was purely coincidence that atmospheric CO₂ levels decreased through time as the solar luminosity increased. Using the Urey cycle (Urey, 1952), where CO₂ is removed from the atmosphere via the reaction of carbonic acid with silicate minerals and subsequent burial of carbonate minerals in the oceans, the WHAK model postulated that silicate weathering is a temperature dependent process, in line with riverine data from Meybeck (1979), which shows that silicate weathering is a function of either temperature or runoff (which itself is partially dependent on temperature). As such, elevated CO₂ levels and thus higher temperatures would enhance silicate weathering rates, drawing down in the process more CO₂ and leading to a decrease in temperature (Walker, Hays and Kasting, 1981). Over time then, an inverse relationship between solar luminosity and CO₂ levels is expected, and changes to this relationship are likely as a result of biological and geological perturbations – such as changes to primary productivity and/or volcanic activity, leading to a descent into, or escape from a Snowball state (e.g. Hoffman *et al.*, 2017) – or solar perturbations (e.g. Milankovitch cycles, Spiegel *et al.*, 2010).

2.2.2. *The BLAG model*

The ‘BLAG’ model (Berner, Lasaga and Garrels, 1983) was constructed to look at both CO₂ sources and sinks, and ended up making a similar conclusion with regards to a negative feedback loop affecting climate, temperature and weathering over long timescales. This model consists of five reservoirs, with separate boxes for the ocean, atmosphere, dolomitic carbonates (MgCO₃), calcium carbonates (CaCO₃), and a final box representing Ca and Mg silicate minerals. Using continental land area, and seafloor spreading rates as geological forcings, and a relationship describing the conversion of MgCO₃ to CaCO₃ and Mg-silicates, the model computes changes to atmospheric CO₂ for the last 100 Myrs. From model sensitivity analyses, it was determined that plate tectonics have held a dominant control over CO₂ levels during this time; affecting both seafloor spreading rates, which return CO₂ to the atmosphere from the subduction of carbonates, and continental land area, which determines the total rock mass available for chemical weathering.

2.2.3. *The Garrels and Lerman models*

Another model to note is one produced by Garrels and Lerman (1981) and improved upon by the same authors a few years later (1984). Although it was not the first IMB model (see for example, Holland, 1973), it was a pioneer in its use of the $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ isotope records of ancient marine carbonates and sulfates, respectively, to compute burial rates of both reduced and oxidised forms of carbon and sulfur through Phanerozoic time. As knowledge of the isotopic records of carbon and sulfur, how these isotopes fractionate (dependent on mass, see Chapter 1 for a small discussion on

the mass-independent fractionation of sulfur), and what we can infer from these records and processes are important for understanding the operation of IMB models, here follows a brief overview of these isotopes.

Carbon isotopes

Carbon has 15 known isotopes, of which three are naturally occurring, and two: ^{12}C and ^{13}C , are stable, with ^{12}C being the more abundant isotope (approximately 98.9% of all carbon isotopes), due to its formation in stars from stellar nucleosynthesis: the triple-alpha process (Burbidge *et al.*, 1957). Because of its lower mass (relative to ^{13}C) ^{12}C is preferentially taken up by biological processes due to kinetic fractionation, and the associated lower energy costs of using the lighter isotope. For example, plants and trees use ^{12}C from atmospheric CO_2 during photosynthesis, leaving the atmosphere enriched in $^{13}\text{CO}_2$. Variations in the ratio of $^{13}\text{C}:^{12}\text{C}$ can be measured by mass spectrometry and are reported as deviations in parts per mille (‰) from the ratios in a standard, as determined by equation (2.1).

$$\delta^{13}\text{C} = \left[\frac{\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{sample}}}{\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{standard}}} - 1 \right] \cdot 1000 \quad (2.1)$$

Where the standard is a reference material (usually Vienna-Pee Dee Belemnite).

Carbon exists in different forms (e.g. organic or inorganic) depending on its redox state, and these forms often exhibit differing isotopic compositions due to kinetic

fractionation. For example, the inorganic carbon in carbonate minerals exhibits little isotopic fractionation from the seawater the carbonates form from, thus in the pre-industrial cycle their isotopic value is on average $\sim 0\text{‰}$ (see Fig. 2.1, Newton and Bottrell, 2007). Meanwhile, the isotope values for plants can range from -10‰ to -33‰ depending on the photosynthetic pathway used (O’Leary, 1988).

In addition, some inferences about primary productivity, particularly during the geologic past, can be made. For example, a positive $\delta^{13}\text{C}$ value in marine carbonate rocks is often interpreted as representing a period of enhanced primary productivity, while a more negative value represents an ecosystem crash in photosynthesising organisms. As enhanced primary productivity can be extrapolated to also represent periods of enhanced C_{org} burial and thus O_2 production (Schidlowski, 1988; Karhu and Holland, 1996; Lyons, Reinhard and Planavsky, 2014), the $\delta^{13}\text{C}$ record of marine carbonates ($\delta^{13}\text{C}_{\text{carb}}$) may be used as a proxy for atmospheric O_2 production through time (e.g. Berner, 2006a; Royer *et al.*, 2014; Krause *et al.*, 2018).

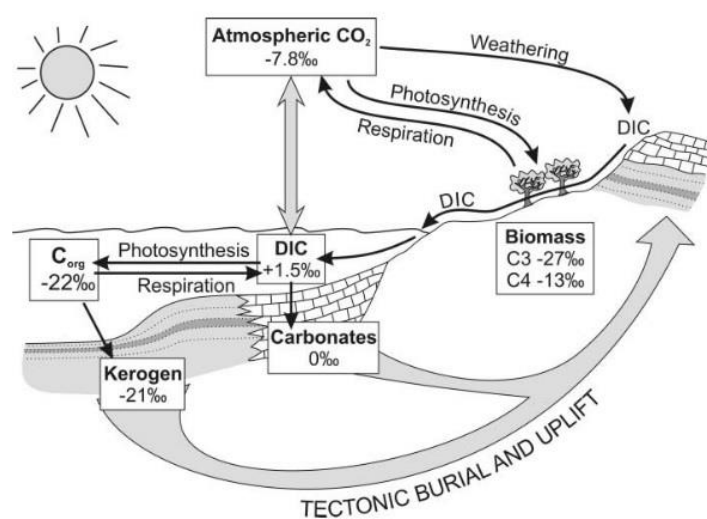


Figure 2.1 | The pre-industrial carbon cycle.

Taken from Newton and Bottrell (2007).

It has been difficult to reconcile large variations in the $\delta^{13}\text{C}_{\text{carb}}$ record – for example during the Lomagundi excursion (up to 10‰), and during the Shuram-Wonoka anomaly (as low as -12‰) – and what they mean in terms of atmospheric O_2 levels, with the information about ocean redox obtained by other geochemical proxies (Lyons, Reinhard and Planavsky, 2014). A lot of work has been conducted, in an attempt to explain the existence of these $\delta^{13}\text{C}$ variations (e.g. Rothman *et al.*, 2003; Derry, 2010; Williams and Schmidt, 2018; Shields *et al.*, 2019), and it is part of this work to investigate the links between $\delta^{13}\text{C}_{\text{carb}}$ values and atmospheric O_2 levels through time.

The $\delta^{13}\text{C}$ values of organic matter ($\delta^{13}\text{C}_{\text{org}}$) can also be obtained and used to help identify the evolutionary timescales of, for example, the different photosynthetic pathways: C3, C4 and CAM, and to distinguish the dominant photosynthetic communities across temporal or spatial scales. This is useful for trying to understand any link between the coupled evolution of the Earth and life. The paired records of $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ can also be used to try and gain an understanding of changes to the Earth system through time; please see Chapter 6 for further discussion on this. However, this thesis focuses primarily on $\delta^{13}\text{C}_{\text{carb}}$, as such, any mention of $\delta^{13}\text{C}$ refers to the $\delta^{13}\text{C}_{\text{carb}}$ record, rather than $\delta^{13}\text{C}_{\text{org}}$, unless otherwise stated.

Sulfur isotopes

Sulfur has 23 known isotopes, four of which are stable: ^{32}S ; ^{33}S ; ^{34}S ^{36}S , with ^{32}S being the most abundant (~95% of the total sulfur isotopes). Like carbon, sulfur isotopes can undergo fractionation dependent on mass. For example, some microbes in marine sediments, where oxygen has become depleted in the pore waters, preferentially utilise

isotopically light sulfate ($^{32}\text{SO}_4$) as the electron acceptor for respiration, in the process converting the sulfate to sulfide, and leaving the remaining sulfate pool enriched in ^{34}S (Thode, Wanless and Wallouch, 1954; Kaplan and Rittenberg, 1964; Bottrell and Newton, 2006).

Variations in the ratio of ^{34}S : ^{32}S can be obtained from equation (2.2):

$$\delta^{34}\text{S} = \left[\frac{\left(\frac{^{34}\text{S}}{^{32}\text{S}}\right)_{\text{sample}}}{\left(\frac{^{34}\text{S}}{^{32}\text{S}}\right)_{\text{standard}}} - 1 \right] \cdot 1000 \quad (2.2)$$

Where the standard is a reference material (usually Vienna-Canyon Diablo Troilite).

$\delta^{34}\text{S}$ values can be obtained from carbonate associated sulfates (CAS), evaporites (such as gypsum), sulfides (such as pyrite), or marine barite (Fike *et al.*, 2015). $\delta^{34}\text{S}_{\text{CAS}}$ values are often used as a geochemical proxy for past seawater sulfate isotopic composition due to the relatively minor fractionation (see Fig. 2.2) when the sulfur is incorporated into carbonate mineral lattices, the ease of extraction (compared to barite), and because the precipitation and preservation of evaporite deposits is sporadic through time (Takano, 1985; Burdett, Arthur and Richardson, 1989; Wortmann and Paytan, 2012; Fike *et al.*, 2015). There are, as with most geochemical proxies, some concerns about possible contamination of samples (Peng *et al.*, 2014), nevertheless the $\delta^{34}\text{S}$ record can provide valuable insights into the chemical evolution of the Earth. For this work, the focus is on $\delta^{34}\text{S}_{\text{sulf}}$ values (i.e. making no distinction between sulfate sources) rather than $\delta^{34}\text{S}_{\text{pyr}}$, although as with the carbon cycle, examining both the $\delta^{34}\text{S}_{\text{sulf}}$ and $\delta^{34}\text{S}_{\text{pyr}}$ records is certainly useful – see Chapter 6. As such, any reference to $\delta^{34}\text{S}$ is shorthand for $\delta^{34}\text{S}_{\text{sulf}}$, unless otherwise stated.

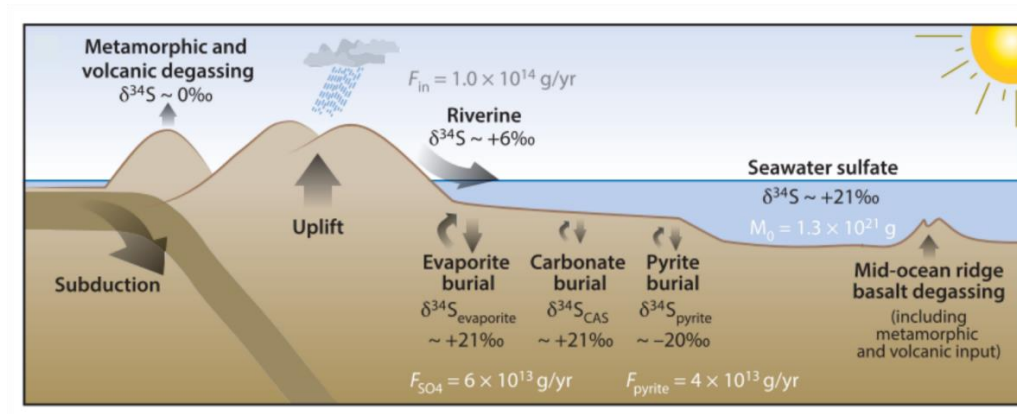


Figure 2.2 | The pre-industrial sulfur cycle.

Taken from Fike et al. (2015).

The process of microbial sulfate reduction (MSR) leads to a significant enrichment of ^{32}S in the sulfide (and thus a negative value of $\delta^{34}\text{S}$), but the exact amount of isotopic enrichment seems to vary dependent on a number of factors – notably phylogenetics – with both small isotopic fraction (2‰) and very large fractionations (up to 66‰ in some cases) being recorded in environmental settings and laboratory experiments (Detmers *et al.*, 2001; Johnston, 2011; Sim, Bosak and Ono, 2011).

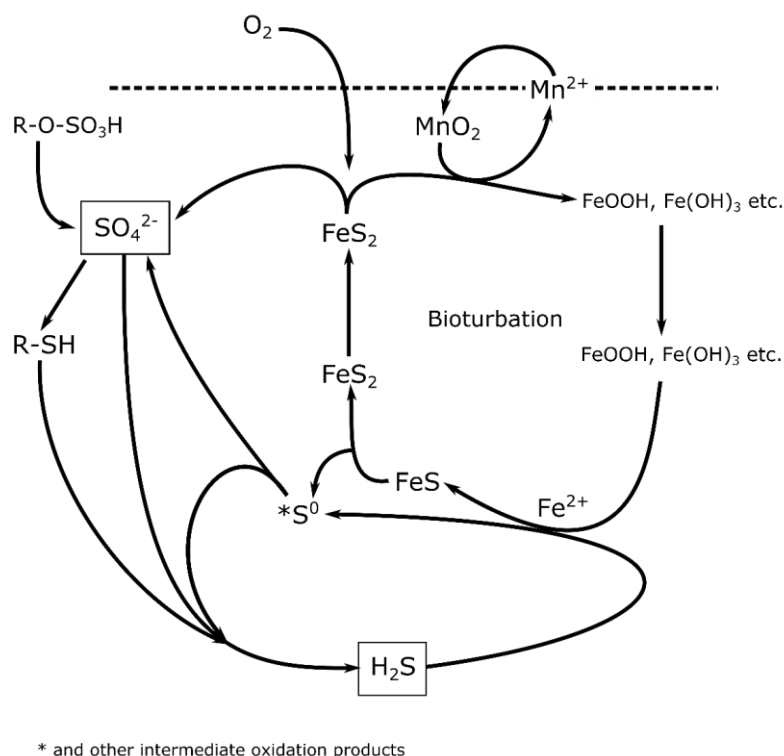


Figure 2.3 | The marine sulfur cycle.

This simplified schematic shows the pathways for inorganic and organic (R-bonded sulfur) sulfate reduction, and subsequent re-oxidisation or disproportionation, plus the influence of iron on the cycle. Adapted from: (Jørgensen and Nelson, 2004; Fakhraee, Li and Katsev, 2017).

Use of the geological record of $\delta^{34}\text{S}$ in marine sulfates to infer anything about past atmospheric O_2 levels is complicated by the nature of the marine sulfur cycle (see Fig. 2.3). Sulfates are reduced to sulfides by MSR, but only some of the sulfide, mostly in the form of pyrite, is permanently buried, with estimates ranging between 5-20% (Jørgensen and Nelson, 2004), 10-20% (Zopfi, Ferdelman and Fossing, 2004), or 10-25% (Bottrell and Newton, 2006). The rest of the sulfide is either disproportionated or re-oxidised, both of which can impact upon the isotope values recorded, in some cases

creating a fractionation of 12.5‰ or more (Pellerin *et al.*, 2019). Chapter 3 looks at this issue in the context of atmospheric O₂ predictions, in more detail.

The Garrels and Lerman model setup

A schematic of the Garrels and Lerman (1984) model (henceforth referred to as, ‘GAL’) can be seen in figure 2.4. The model consists of a combined ocean and atmosphere reservoir, and four sedimentary (or ‘crustal’) reservoirs to cover both oxidised and reduced forms of carbon and sulfur. The model is constrained in three ways: 1) the masses of sulfur and carbon in the ocean-atmosphere reservoir remain constant throughout time, thus for example, the total burial flux of carbon must equal the total weathering flux of carbon; 2) that the weathering fluxes are first order fluxes, and as such they are dependent on the reservoir size at time (t) and a rate constant; and 3) that the model is a closed system, so the total mass of sulfur and/or carbon (i.e. the summation of ocean-atmosphere and crustal reservoir masses) does not change through time (Garrels and Lerman, 1984).

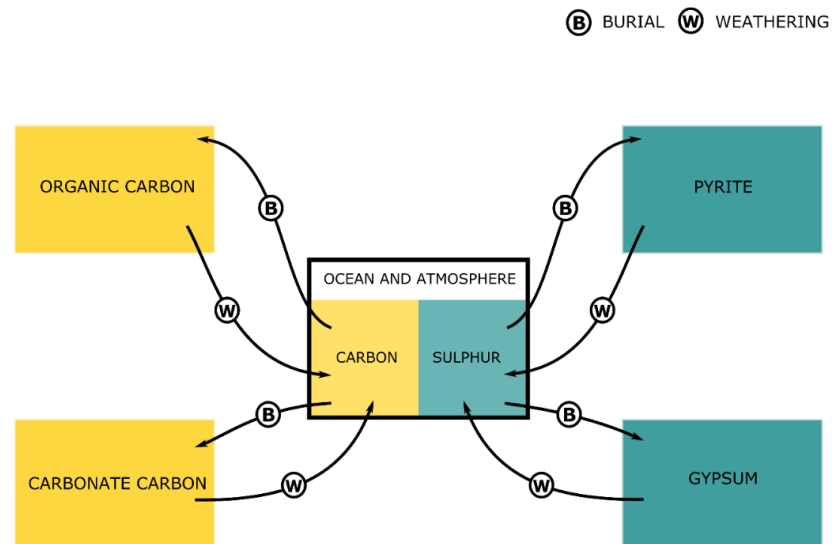
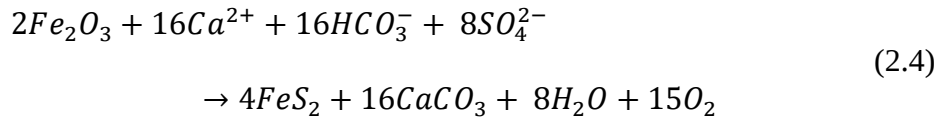
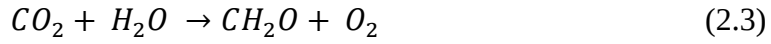


Figure 2.4 | The coupled sulfur and carbon model.

Adapted from Garrels and Lerman (1984), there are four sedimentary reservoirs, representing oxidised (carbonate and gypsum) and reduced (organic carbon and pyrite) forms of carbon and sulfur, and a combined ocean-atmosphere reservoir. The numbered fluxes from the original schematic have been replaced with letters to simplify what each flux represents – B: burial, W: weathering.

As the ocean-atmosphere remains constant, the changes to the crustal reservoir sizes through time will be of equal magnitude, but opposite sign. For example, if the oxidised crustal sulfur, represented by gypsum, were to increase by 2×10^{18} moles in 1 Myrs, then the reduced sulfur (pyrite) would decrease by 2×10^{18} moles in 1 Myrs (Garrels and Lerman, 1984). The fluxes involving C_{org} and pyrite alter the surface system redox, as burial of carbon and sulfur to the crustal reservoirs is in these reduced forms, but weathering returns carbon and sulfur to the ocean-atmosphere in their oxidised forms. Burial of C_{org} and pyrite release O_2 to the atmosphere and are

considered a ‘source’ (equations 2.3 and 2.4), whilst the weathering of these same species consumes O_2 – a ‘sink’ (reversal of equations 2.3 and 2.4).



Thus, the changing sizes of the crustal reservoirs through time can give a first order insight into the redox landscape of the Earth (Garrels and Lerman, 1984; Berner, 1987). Estimating the size and isotopic compositions of the sedimentary reservoirs, and investigating any coupling between the carbon and sulfur cycles, are the main objectives of the GAL model, rather than the explicit calculation of atmospheric O_2 (Garrels and Lerman, 1984).

Operation of the model

The GAL model is run in what Garrels and Lerman name, a “movie model” fashion, i.e. that given the estimated present-day reservoir sizes of all the reservoirs, and the seawater carbon and isotope records through the Phanerozoic and late Proterozoic, GAL can be run backwards solving a set of isotope mass balance differential equations, to obtain the sizes and isotopic compositions of the crustal reservoirs in the past (Garrels and Lerman, 1984). With this method there are two approaches:

- 1) The $\delta^{34}S$ record is used to calculate isotope and mass changes to the sulfur reservoirs, and the carbon cycle is linked to the sulfur cycle by assuming that changes

to the C_{org} reservoir are proportional to the changing size of the gypsum reservoir by 15/8. The 15/8 stoichiometry is derived from equation (2.4), where 8 moles of sulfate are required to produce 15 moles of O_2 .

2) The opposite takes place, and the $\delta^{13}C$ record is used to calculate isotope and mass changes to the carbon reservoirs, and the same relationship between changes to the sizes of the C_{org} and gypsum reservoirs holds.

Results

The estimated size of the gypsum reservoir for the last 700 Myrs, using both approaches, was plotted by Garrels and Lerman (1984) and the similarity is striking, with a maximum difference between the two curves being $\sim 25 \times 10^{18}$ moles. Thus the model suggests a strong coupling between the carbon and sulfur cycles through time, such that the oxidation of pyrite to sulfate is roughly matched by the reduction of carbonate to C_{org} over geologic timescales (Garrels and Lerman, 1984).

2.3. Bob Berner's isotope mass balance models

2.3.1. *The first iteration*

Berner's first IMB model (1987), which I have shortened to 'IMB1', built upon the foundations of the Garrels and Lerman model (1984), by taking a similar approach with regards to 'inverting' the $\delta^{13}C$ and $\delta^{34}S$ isotope records of ancient marine carbonates and sulfates to derive burial fluxes of C_{org} and pyrite. However, Berner found that using new $\delta^{13}C$ data in GAL resulted in high C_{org} burial rates during the Permo-Carboniferous and consequently O_2 levels higher than today (Berner, 1987).

The crux of the problem Berner faced is due to the reservoir setup of GAL (Fig. 2.4), where single boxes for each of the sedimentary reservoirs strongly buffer against isotopic changes of weathering inputs into the ocean-atmosphere, thus rendering the mean isotopic composition of total carbon (carbonate and C_{org}) constant over time. This leads to C_{org} burial essentially tracking the $\delta^{13}C$ marine carbonate data input into the model, and hence, although there is some mediation from the sulfur cycle, O_2 levels also track the $\delta^{13}C$ record (Berner, 1987).

To test whether a large increase in O_2 in the Permo-Carboniferous was a valid possibility, and not just an artefact of the GAL setup, Berner modified the model by splitting the sedimentary reservoirs into two: ‘young’ and ‘ancient’ sub-reservoirs (see Fig. 2.5). Splitting of the sedimentary boxes into two allows for rapid recycling of some of the freshly deposited (young) sediments back to the ocean-atmosphere via weathering, thus allowing a rapid tracing of the isotopic value of weathering inputs to the ocean-atmosphere, with the isotopic value of burial outputs.

Splitting the reservoirs also allows a transfer of mass from young to ancient reservoirs, imitating deeper sediment burial over time. The ancient reservoirs are assumed to experience a reduction in weathering rates compared to their young counterparts due to the use of different rate constants for ancient weathering, and each ancient reservoir is constant in size through time, i.e. the weathering flux for each sediment type (e.g. pyrite) equals the flux of sediment moving from the young to ancient reservoirs. The ocean-atmosphere is also in mass balance through time thus, it is only the young reservoirs which are allowed to shrink or expand in size.

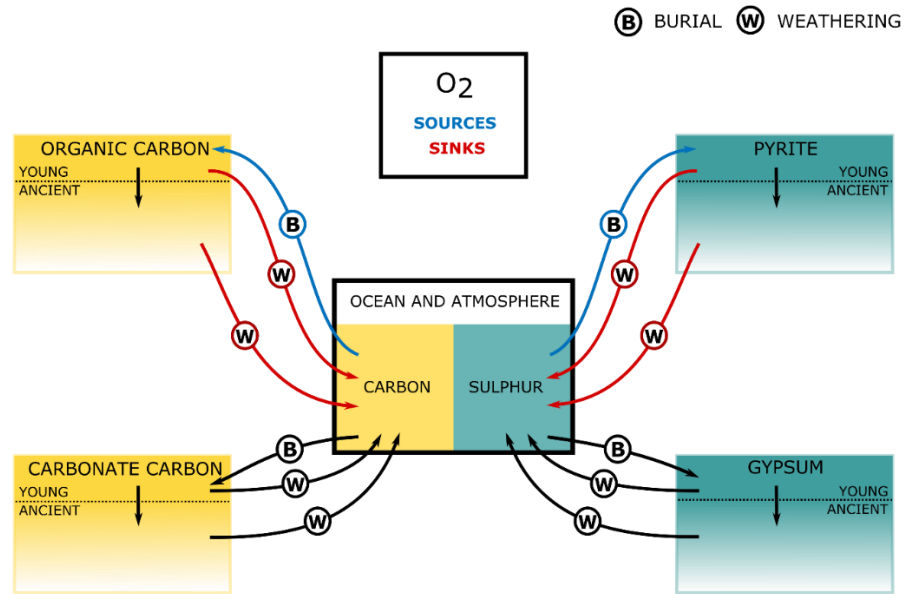


Figure 2.5 | The rapid recycling sulfur and carbon model.

Adapted from Berner (1987), the four sedimentary reservoirs of GAL are split into young and ancient sub-reservoirs, the ocean-atmosphere reservoir remains the same as GAL. The numbered fluxes from the original schematic have been replaced with letters to simplify what each flux represents – B: burial, W: weathering. The black fluxes have no effect on atmospheric oxygen calculations, whereas the blue fluxes are sources of oxygen, and the red are sinks.

The model uses a series of expressions representing the burial and weathering fluxes, to solve several differential equations for the mass and isotopic mass balance of the rock reservoirs, as well as O_2 levels through the Phanerozoic. At each 1 Myr point during the model run, it is assumed that the ocean-atmosphere reaches a new steady state position, thus the isotopic data (see figures 2.6 and 2.7) can be used to calculate the next steady state values for the various fluxes, reservoirs and isotopic reservoirs for the following 1 Myr time point. Present day conditions were assumed at model

initiation (at $t = 570$ Ma) and the model ran forward through time to the present ($t = 0$ Ma).

This approach was taken because use of the so-called, ‘Movie’ style of GAL, where present day values for the fluxes and reservoirs were used at $t = 0$ Ma and the model then run backwards to 570 Ma, resulted in numerical instability. Initial values were chosen to represent an extreme setup (e.g. young reservoir weathering fluxes were 4x as large as those for ancient reservoirs), in an attempt to reduce the Permo-Carboniferous high O_2 , whilst finishing with fluxes, reservoirs and O_2 levels reasonably close to those at the present day. As this approach was numerically stable, it led Berner to consider the possibility that the Cambrian world was perhaps not so different to the present day, albeit this is somewhat of a circular argument.

Despite this methodology working, the rapid recycling model could not entirely justify its existence by eradicating the Permo-Carboniferous high O_2 , although it could diminish it somewhat (see Fig. 2.8). As Berner (1987) notes, the problem lies in the isotope systematics of the carbon cycle in the model. The $\delta^{13}C$ values for the ocean-atmosphere (Fig. 2.6), and young carbon (both organic and inorganic) reservoirs are the only time-dependent variables when it comes to calculating C_{org} burial from equation (2.5).

$$F_{bg} = \left(\frac{1}{\alpha_c} \right) \cdot \{ [kwy \cdot C_{Ty} \cdot (\delta_{OA} - m\delta_y)] + [kwa \cdot C_{Ta} \cdot (\delta_{OA} - m\delta_a)] \} \quad (2.5)$$

Where: α_c is the isotopic fractionation factor for C_{org} and is set as a constant with value of 25‰; k_{wy} and k_{wa} are rate constants for the weathering of young carbon and ancient carbon, respectively; C_{Ty} and C_{Ta} are the sum of young carbon reservoirs, and ancient carbon reservoirs, respectively; δ_{OA} is the isotopic composition of the ocean-atmosphere; and $m\delta_y$ and $m\delta_a$ are the mean isotopic composition of the young carbon and ancient carbon reservoirs, respectively.

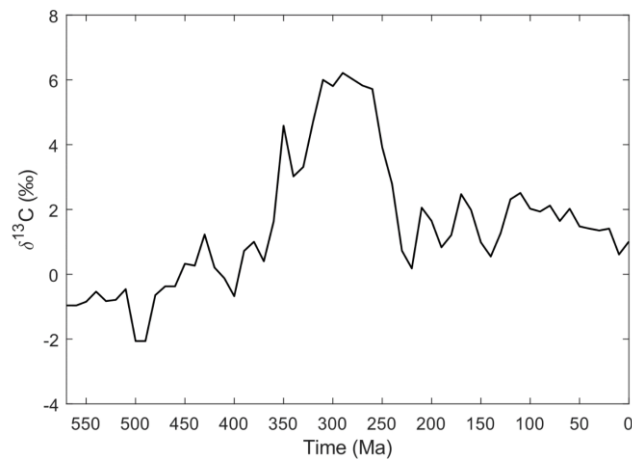


Figure 2.6 | The $\delta^{13}C$ record used in the IMB model.

The data is from Lindh (1983) and Popp et al. (1986).

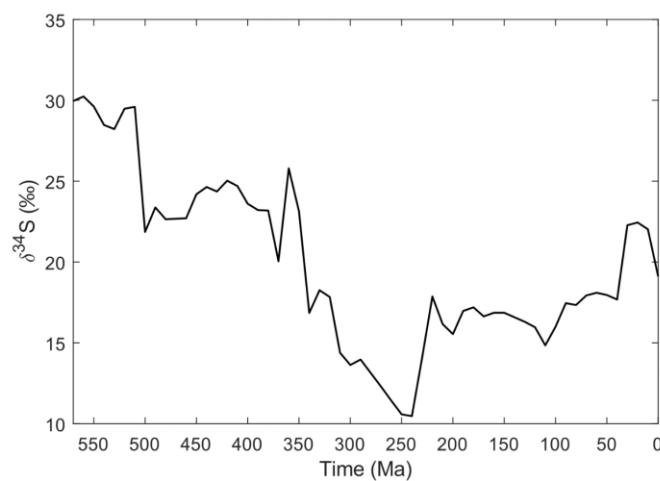


Figure 2.7 | The $\delta^{34}S$ record used by the IMB model.

The data is from Lindh (1983).

Theoretically, with the rapid recycling scheme, any significant changes to δ_{OA} should be mirrored by changes to $m\delta_y$ thus large variations in C_{org} burial would not be permitted. However, as C_{org} burial increases, as it does during the Permo-Carboniferous due to the increasing $\delta^{13}C$ values, the young C_{org} reservoir becomes larger, fed by the young carbonate reservoir due to the mass balance of the ocean-atmosphere. This causes $m\delta_y$ to decrease instead of increase as was supposed, as the isotopic composition of the young C_{org} reservoir is lighter than either the young carbonate reservoir, or the ocean-atmosphere. Thus, C_{org} burial rates increase when $\delta^{13}C$ values do.

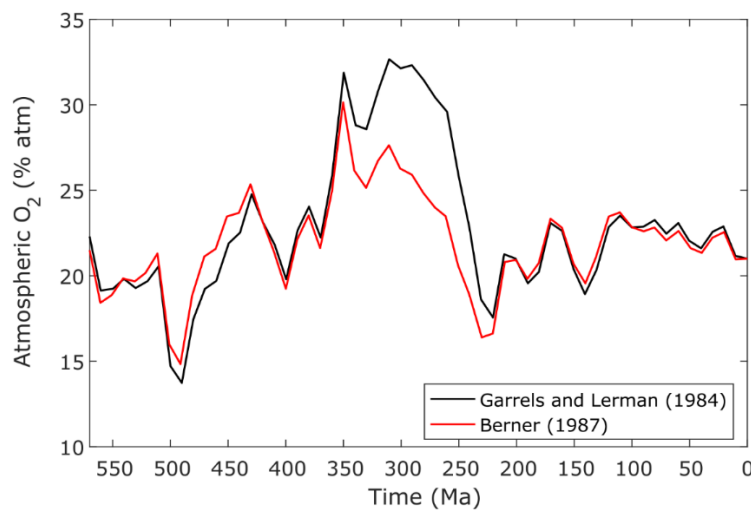


Figure 2.8 | Atmospheric O₂ results generated by the GAL model and by the rapid recycling model.

While some of these issues can be traced to comparatively smaller young reservoirs, increasing the size of the young reservoirs to match ancient reservoir sizes results in much slower isotope recycling, effectively reducing the model back to the GAL

version. So, the model could not accomplish what it set out to achieve, but it was an important advance in modelling and the use of isotopes as model drivers.

2.3.2. Improvements to the rapid recycling model (IMB2)

The updates to the rapid recycling model (Berner, 2001) are few, but complex in their nature, and are centred on a better representation of negative feedback mechanisms on O_2 levels. In the previous version of the model (Berner, 1987) an O_2 -dependent feedback was included in the weathering equations of pyrite and C_{org} , by multiplying the first order rate constant and reservoir size by normalised O_2 (i.e. $O_2(t) / O_2(0)$). This results in enhanced oxidation of pyrite and C_{org} when O_2 levels are high, thus limiting to an extent, large variations in atmospheric O_2 . This can introduce a positive feedback, as the isotopically light carbon and sulfur are returned to the ocean-atmosphere, necessitating an increase in burial of C_{org} and pyrite to maintain mass balance, and therefore a further increase in O_2 levels. Rapid recycling can, by-and-large, mitigate against this positive feedback, but not completely and thus geologically unreasonable levels of O_2 can be produced by the model.

To provide an O_2 -dependent negative feedback without the issue with IMB, an O_2 dependency on the fractionation of carbon and sulfur isotopes is introduced, and the O_2 -dependency included in the weathering equations is removed. For the carbon cycle, it is known from both theory and laboratory experiments that plants and plankton significantly fractionate carbon isotopes during photosynthesis, leaving them enriched in isotopically light ^{12}C and that increased O_2 levels can drive greater fractionation than is often seen at ambient levels (e.g. Berner, 2000). Similarly, for the sulfur cycle,

MSR can induce a fractionation of sulfur isotopes, and it is assumed, based on observations in natural settings, that higher isotopic fractionation occurs at higher O₂ levels due to a cyclicity of sulfate reduction and sulfide oxidation at the sediment-seawater interface (Canfield and Teske, 1996; Berner *et al.*, 2000). From this, equations (2.6 and 2.7) were derived.

$$\Delta c_{phot} = \Delta c_{phot}(0) + \left[J \cdot \left(\frac{O_2(t)}{O_2(0)} - 1 \right) \right] \quad (2.6)$$

$$\Delta s = \Delta s(0) \cdot \left(\frac{O_2(t)}{O_2(0)} \right)^n \quad (2.7)$$

Where: Δc_{phot} is the isotopic fractionation of carbon due to photosynthesis at time (t) – sometimes represented by α_c – and $\Delta c_{phot}(0)$ is the present-day value; J is a curve-fitting parameter, O₂(t) is atmospheric oxygen calculated at time (t) and O₂(0) is the present-day value; Δs is the isotopic fractionation of sulfur due to MSR at time (t) – sometimes represented by α_s – and $\Delta s(0)$ is the present-day value; and n is another fitting parameter.

The $\delta^{13}C$ record was also updated for the Ordovician – Cretaceous with the use of a simple order fit to the data of Veizer *et al.* (1999), while the data of Lindh (1983) was retained for the rest of the Phanerozoic (see Fig. 2.9).

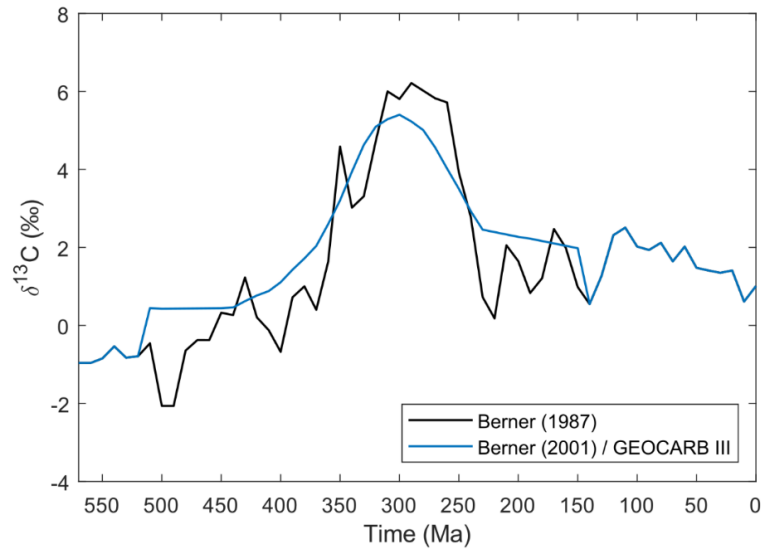


Figure 2.9 | The updated $\delta^{13}\text{C}$ record.

The data is from Veizer *et al.* (1999) and Lindh (1983).

Results

Berner (2001) conducted a number of sensitivity analyses by varying some of the equation parameters, and also compared the fractionation values derived from the new equations to geological data. It was found that the assumed present-day value for photosynthetic-based fractionation, $\Delta c_{\text{phot}}(0)$ (either 25‰ or 30‰) did not result in significant changes to calculated O_2 levels over the Phanerozoic. However, varying the fitting parameters J and n does make a considerable difference to Phanerozoic O_2 as higher values for J and n result in lower O_2 during the Permo-Carboniferous but higher O_2 during the Mesozoic and Cenozoic, compared to setting either J or n to zero.

For this reason, and also because the carbon isotope fractionation values obtained from equation (2.6) compared well with the geological data of Hayes *et al.* (1999), the preferred values of J , n and $\Delta c_{\text{phot}}(0)$ are 3, 1, and 30‰ respectively (see Fig. 2.10 for a comparison of the O_2 outputs). This results in O_2 levels of ~15% of the

atmosphere by volume (atm) for much of the Paleozoic, then a rise to somewhere between 30 – 35% atm during the Permo-Carboniferous, with a decline to ~15% atm by the end of the Triassic before a slow and steady rise to the present-day.

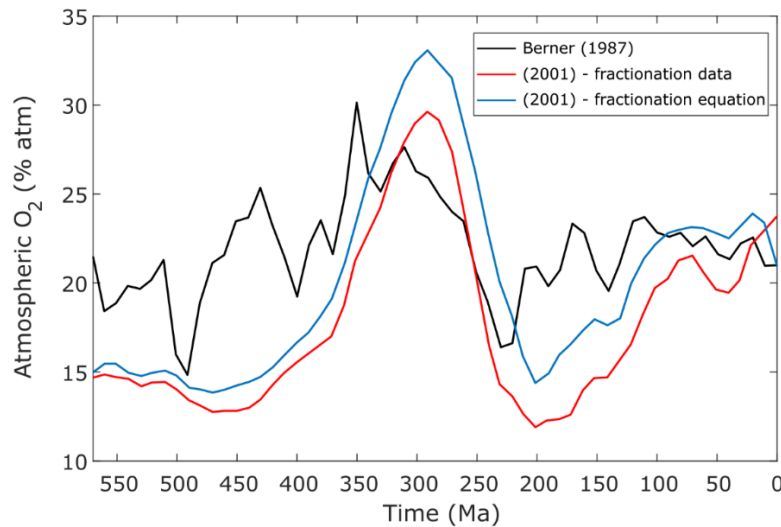


Figure 2.1 | A comparison of the O₂ outputs from IMB modelling.

This compares the first rapid recycling model (black line, Berner, 1987), with those from the second iteration (Berner, 2001) using either the fractionation equation (blue line), or fractionation data (red line, Hayes, Strauss and Kaufman, 1999) for $\delta^{13}\text{C}$.

2.4. GEOCARB

2.4.1. GEOCARB I

GEOCARB was created in an attempt to reconstruct the history of atmospheric CO₂ concentrations over the entire Phanerozoic (Berner, 1991). Building from the base of the BLAG model, what GEOCARB lost in terms of mathematical complexity – by combining all carbonate minerals into a single reservoir – it gained, with regards to

both biological and geological intricacy, and the computational efficiency to model over much longer timescales (instead of just the last 100 Myrs). Following only the carbon cycle, GEOCARB has three boxes: the ocean-atmosphere reservoir, where all of the carbon is assumed, for simplicity, to be in the form of CO_2 and marine dissolved inorganic carbon (DIC); a C_{org} crustal reservoir; and a carbonate crustal reservoir (see Fig. 2.11).

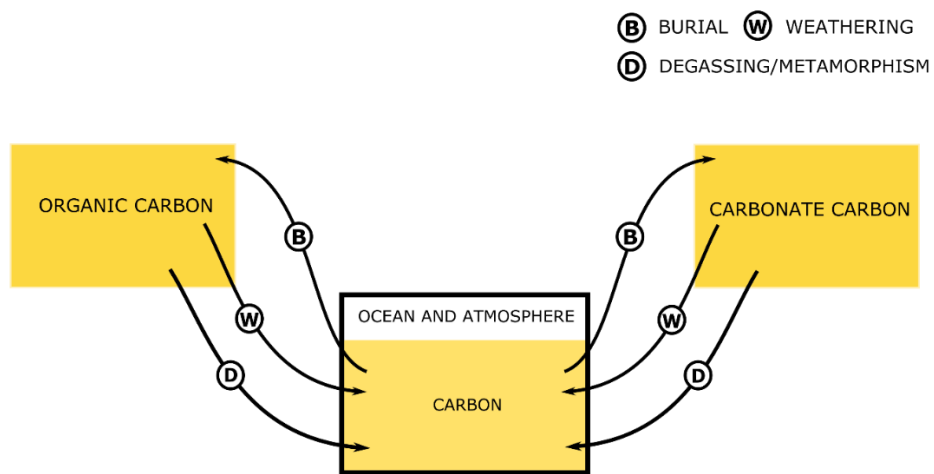


Figure 2.2 | The GEOCARB model.

Adapted from Berner (1991), there are three reservoirs: the ocean-atmosphere reservoir; and the two crustal reservoirs of organic carbon and carbonate carbon. Carbon flows through the reservoirs as a series of fluxes. The fluxes are B: burial, W: weathering, D: degassing/metamorphism.

The model uses the IMB approach of GAL (and not the rapid recycling method) but also incorporates several dimensionless parameters to represent key geological and biological factors that are used as forcings in the various fluxes. The dimensionless parameters are taken from actual data, for example the amount of continental land area at any point in time during the Phanerozoic, but the data is normalised to present-day

values. This is done to avoid the burdensome task of trying to convert the units of most of the parameters into one standard unit: moles, but also, some of the biological forcings are dimensionless to begin with.

Carbon is transferred between the boxes by burial, weathering, and degassing/metamorphism fluxes. As the ocean-atmosphere reservoir is small and responds much more rapidly than either of the crustal boxes, and the model timestep is every 1 Myrs, the equations for calculating the $\delta^{13}\text{C}$ and CO_2 values of the ocean-atmosphere can be solved as a series of steady states, following Kump and Garrels (1986). As per the rapid recycling method, the model is run from 570 Ma to 0 Ma, and starting values were adjusted so that present day values of fluxes and reservoirs were obtained at the end of the run. Data is input into the model at 10 Myr timepoints, with linear interpolation between them. The full set of dimensionless parameters are described as thus:

f_A: Total land area

This parameter (see Fig. 2.12) affects all weathering fluxes by changing the amount of continental area available for weathering (seafloor weathering was considered in GEOCARB but was found to have essentially no net effect on CO_2 levels) through time.

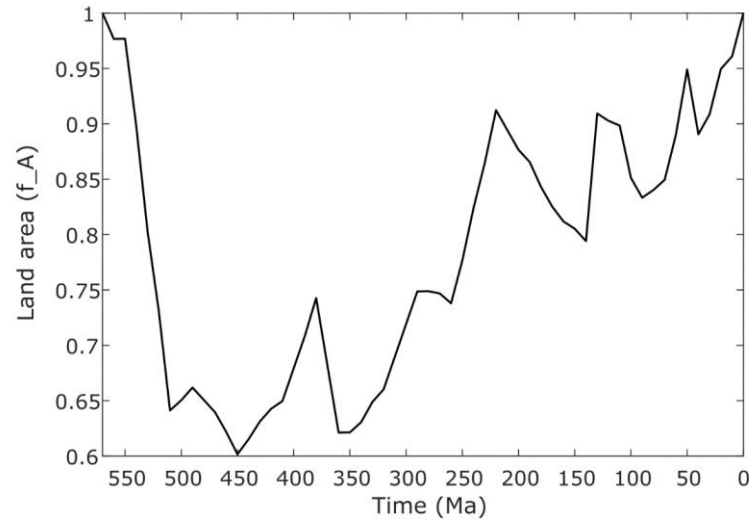


Figure 2.3 | Total land area.

For the timeframe of 570 Ma to 140 Ma the data is based on paleogeographic reconstructions by Ronov (1976), and for the rest of time is based on work by Barron et al. (1980).

f_D: Runoff

Another parameter affecting the weathering fluxes (see Fig. 2.13), this forcing reflects changing continental runoff rates due to paleogeography, and the data comes from general circulation modelling (GCM) by Tardy et al. (1989).

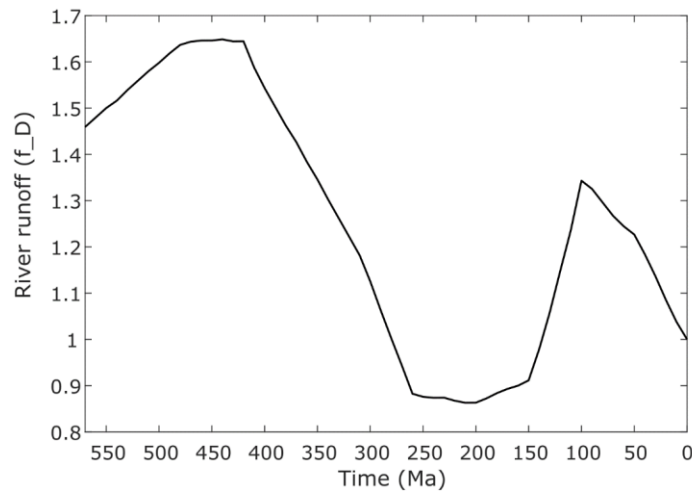


Figure 2.4 | Global river runoff.

In their work they split the Earth into 10° latitudinal slices and calculate the average runoff for each slice at the present day. Assuming these values hold true for any type of land within these slices, the continents are moved according to paleogeographic reconstructions, to ascertain how the total land area under each slice changes over time. To obtain a global average runoff at any point in time, the total runoff is calculated for each slice, the slices are summed up and the runoff value is divided by the total land area. As Berner (1991) notes, this works well as a first order approach, but does neglect the effect orogenies will have on precipitation and thus runoff rates.

f_R: Mountain uplift

This forcing (see Fig. 2.14) describes the effect of global mean land elevation on weathering rates, where it is assumed that physical erosion will expose fresh bedrock for chemical weathering but only for C_{org} and silicate weathering, as it had been previously shown that elevation has little effect on carbonate weathering (e.g. Holland,

1978). Subsequent work has shown that elevation does have some effect on carbonate weathering (Li and Elderfield, 2013).

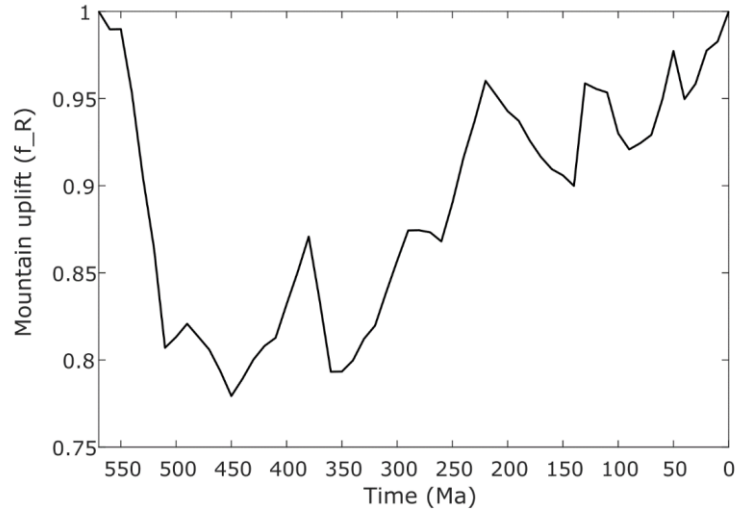


Figure 2.5 | Mountain uplift.

In GEOCARB, f_R is calculated using equation (2.8) which is based on the work by Hay *et al.* (1981).

$$f_R = 1 + \log_{10} f_A(t) \quad (2.8)$$

f_E: Biological weathering factor

This forcing (see Fig 2.15) considers the evolution of plants on land, and their contribution towards weathering enhancement through: physical destruction; and chemical degradation via biological organic acid and CO₂ production. This term is not included in C_{org} weathering, as it is thought that organic acids have negligible effect on C_{org} oxidation, and subsequently has little effect on atmospheric CO₂ levels.

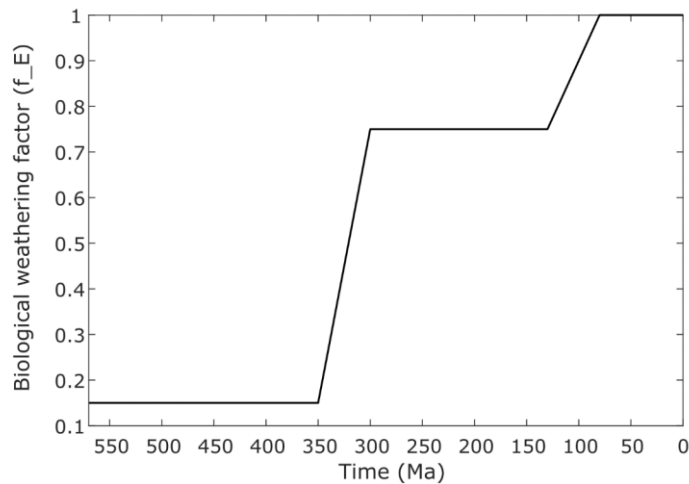


Figure 2.6 | The effect of plants on weathering.

The global effect of plants on weathering rates is somewhat uncertain at present day, and is almost entirely unknown for pre-vascular plants, with field studies suggesting that the direct effect of plants on silicate weathering is probably less than an order of magnitude, and that the presence of plants may simply shift a regime from being weathering-limited to transport-limited, which will still affect the supply of ions to the oceans (Cawley, Burruss and Holland, 1969; Schwartzman and Volk, 1989; Drever, 1994). However, rough estimates can be made, thus, from 570 Ma to 350 Ma (pre-vascular plants), Berner settled, after sensitivity testing, on using a value of 0.15. From 300 Ma to 130 Ma (pre angiosperms) f_E is set to 0.75. From 350 Ma to 300 Ma a linear mixing of pre- and post-vascular plants is used. At 130 Ma angiosperms likely evolved, bringing about more rapid weathering and less efficient nutrient recycling (Knoll and James, 1987), and attained dominance at ~80 Ma. Thus f_E rises in a linear fashion from the value at 130 Ma until it reaches 1 (the present-day value) at 80 Ma, remaining at that value for the rest of time.

f_G (also known as f_{SR}): Degassing rates

This is the change in degassing rates based on seafloor spreading (see Fig. 2.16). In theory, greater spreading rates means enhanced volcanism and metamorphic processes, and thus increased degassing, returning both C_{org} and carbonate carbon back to the ocean-atmosphere as CO₂.

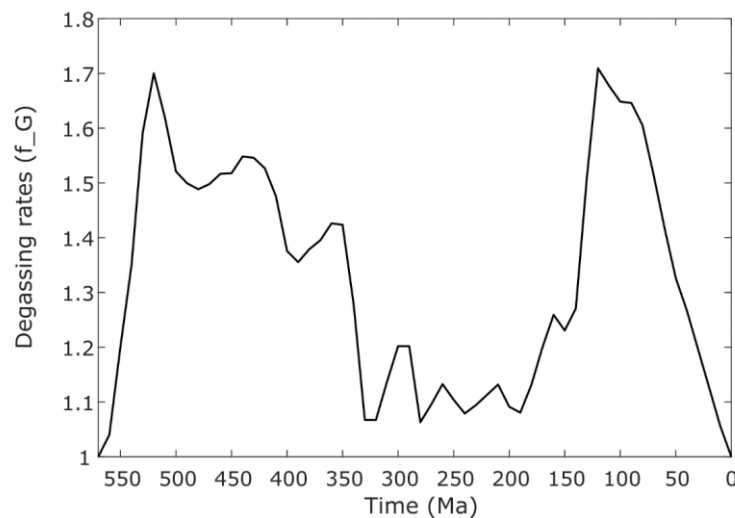


Figure 2.7 | Changing degassing rates.

As there is very little seafloor older than 150 Myrs remaining due to subduction, it is difficult to estimate seafloor generation rates using an area/age relationship (Berner, Lasaga and Garrels, 1983). Instead, Berner (1991) uses the sea-level inversion approach of Gaffin (1987), where it is assumed that changes to sea-level through time are solely due to tectonic processes, thereby neglecting the effect of glacial eustasy.

f_C: Dependence of degassing rates on burial location of marine carbonates

At ~150 Ma there is evidence for the evolution of calcareous plankton. As their remains are largely deposited in deep waters, their evolution marked a shift in the rates

of carbonate degassing (Volk, 1989). Deep water sediments are more likely to undergo subduction and thermal decomposition than those in shallow waters, where thermogenesis is only likely if sediments are deeply buried (Volk, 1989; Berner, 1991). This is especially the case for those shallow water sediments resting on stable cratons. Therefore, the last 150 Myrs should have seen a rise in the recycling of carbonates via degassing back to CO₂ (see Fig. 2.17).

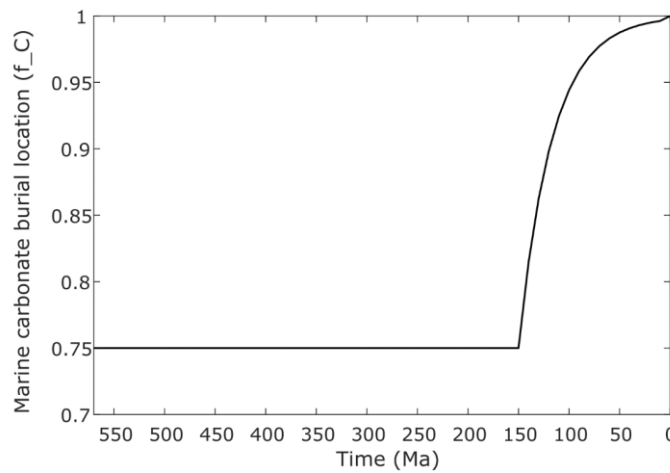


Figure 2.8 | The burial location of marine carbonates and the effect on carbonate degassing.

Before 150 Ma, f_C is set to 0.75, and thereafter values are obtained using equation (2.9), which results in a rapid increase in f_C in an exponential fashion, such that $f_C = \sim 0.9$ by 120 Ma, and is based on data from Hay *et al.* (1988).

$$f_C = 0.75 + (0.75 \cdot [1 - \exp^{-0.03 \cdot (150-t)}]) \quad (2.9)$$

f_B: Dependence of weathering on CO₂ levels

The f_B parameter relates the dependence of weathering rates to normalised CO₂ levels (RCO₂) and global average surface temperature. Higher CO₂ levels should

increase global average temperatures and plant productivity, thereby increasing both runoff and biologically assisted weathering. As plant productivity values will change depending on the evolutionary timescale of plants, f_B changes were set as:

$$(a) \ 570 - 350 \text{ Ma}, f_B = RCO_2$$

$$(b) \ 350 - 300 \text{ Ma}, f_B = \text{linear interpolation between (a) and (c)}$$

$$(c) \ 300 - 130 \text{ Ma}, f_B = (RCO_2)^{0.5}$$

$$(d) \ 130 - 80 \text{ Ma}, f_B = \text{linear interpolation between (c) and (e)}$$

$$(e) \ 80 - 0 \text{ Ma}, f_B = \left[\frac{2 \cdot RCO_2}{1 + RCO_2} \right]^{0.4} \cdot RCO_2^{0.22}$$

The exponent, 0.4, in (e) is a fertilisation factor, and signifies that only 35% of plants globally respond to changes in CO_2 levels, and that the rest are limited either by nutrient-poor soils, lack of water, or of sunlight.

Rate constants

In addition to these dimensionless parameters, GEOCARB also uses rate constants from the rapid recycling model (Berner, 1987). As degassing fluxes were not part of that model, the rate constants for carbonate weathering from the rapid recycling model were added together and that value split into three, with 2/3 apportioned to weathering, and 1/3 metamorphism/degassing, following the BLAG model (Berner, Lasaga and Garrels, 1983). The same is done for the C_{org} weathering rate constants, but the total is split into four, with 3/4 of the value corresponding to weathering and 1/4 metamorphism/degassing.

$\delta^{13}\text{C}$ input

Finally, the $\delta^{13}\text{C}$ record for the ocean-atmosphere, which is used to calculate C_{org} burial rates (see Fig. 2.18), is based on a smoothing of data from Berner (1987, 1989).

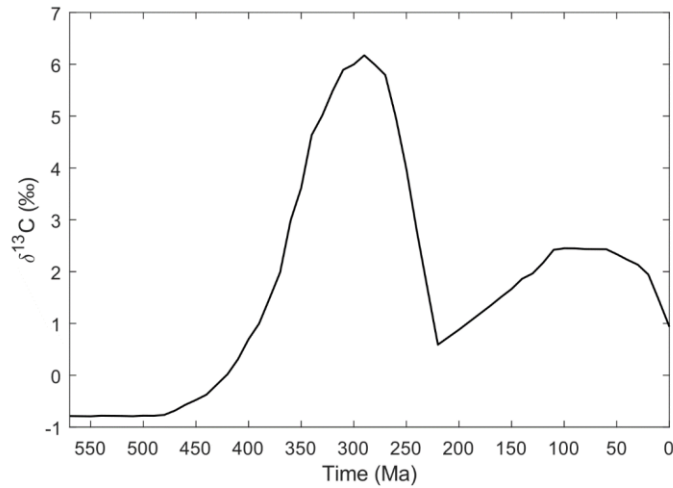


Figure 2.9 | The $\delta^{13}\text{C}$ record used in GEOCARB.

Results

The baseline run for the GEOCARB model, using the values defined in this section, results in atmospheric CO_2 levels for the Phanerozoic as seen in figure 2.19.

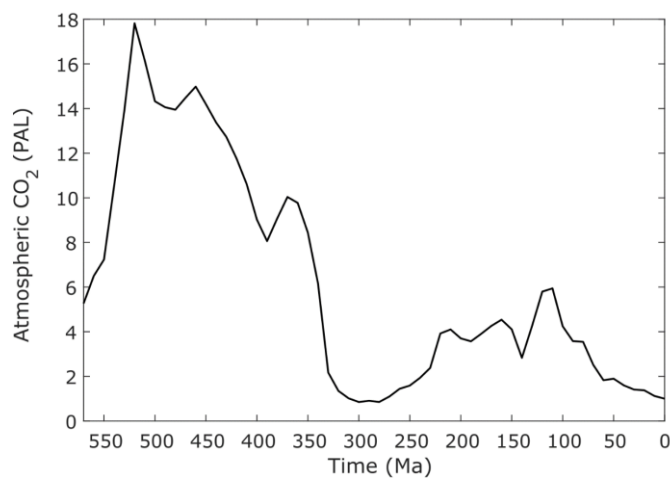


Figure 2.19 | Atmospheric CO_2 results from GEOCARB.

Here, CO₂ values are >6x PAL for much of the Paleozoic, until the Carboniferous, when levels drop to around those at present day, until towards the end of the Permian. Thereafter CO₂ increases, whilst remaining <6x PAL, until the end of the Cretaceous, where levels decline towards the present day. From analyses of model sensitivity to the various dimensionless parameters, Berner (1991) showed that while all the forcings have an effect on CO₂, some have a greater influence than others. Principally, f_G (degassing) holds a great control over atmospheric CO₂ through time, especially during the Cretaceous when f_G values are high, but f_B (dependence of weathering on CO₂ levels) and f_E (plant evolution) are also important, particularly in the Paleozoic before the evolution of vascular plants on land.

2.4.2. *GEOCARB II*

The revision of the first GEOCARB model (henceforth referred to as GEOCARB I) to become GEOCARB II saw the introduction of some new parameters, as well as a revision of data for others.

f_{LA}: Total area underlain by carbonates

In GEOCARB II, f_A: the parameter for total land area, was dropped from the equations for silicate weathering and C_{org} weathering. The reasoning behind this being: because the variations in sea-level over the Phanerozoic would have uncovered areas underlain by relatively chemically stable sediments, such as clays, changes to f_A should not appreciably effect either of these weathering fluxes, instead, physical

erosion revealing fresh rock for chemical weathering should be of greater importance (Berner, 1994). However, the uncovered areas would be underlain by carbonate minerals in some areas, therefore f_A needs to be included in the equation for carbonate weathering. Using the paleogeographic data of Bluth and Kump (1991) to obtain values for f_L : the amount of carbonate land area, the proportion of the total land area which is underlain by carbonates is calculated as $f_L \times f_A$, using the values of f_A from GEOCARB I (see Fig. 2.20 for a comparison between f_A and f_{LA}).

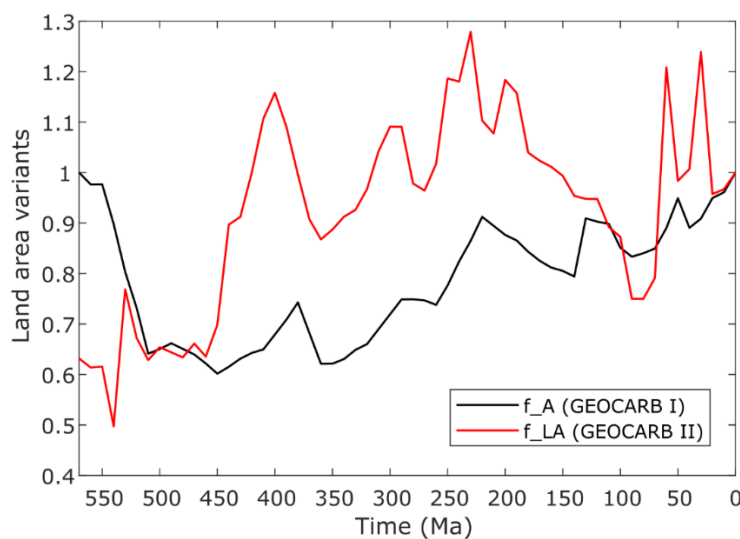


Figure 2.10 | A comparison between total land area variants.

The total land area parameter from GEOCARB I is the black line, and the total land area underlain by carbonates from GEOCARB II is the red line.

f_R : Mountain uplift

Instead of a logarithmic relationship to f_A (total land area), the values for f_R are now derived from the seawater strontium isotope record (Burke *et al.*, 1982). Sediments are uplifted and subsequently exposed to erosion and chemical weathering, but silicates and carbonates on average have different $^{87}\text{Sr}/^{86}\text{Sr}$ signatures, where

silicates exhibit high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, and carbonates have medium ratios, akin to that of seawater (Berner, 1994).

Using an isotope mass balance approach to the strontium cycle, with no fractionation when Sr is incorporated into marine carbonates, and assuming that the low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from basalt-seawater interactions are outweighed by the continental weathering fluxes, it can be inferred that higher silicate weathering rates would increase the $^{87}\text{Sr}/^{86}\text{Sr}$ composition of seawater, thus the Sr isotopic composition through time could be used as a proxy for uplift (Raymo, 1991; Francois and Walker, 1992; Richter, Rowley and DePaolo, 1992). However, there is the possibility that the Sr isotope record could result in silicate weathering rates that greatly exceed the amount of degassing due to the exposure of significantly enriched ^{87}Sr silicates (Berner, 1994). Thus, over >1 Myr timescales, the atmosphere could become completely depleted of CO_2 , and therefore, f_R requires a link between $^{87}\text{Sr}/^{86}\text{Sr}$ and the carbon cycle to constrain its influence on weathering rates.

Using equation (2.10), a curve can be calculated for the $^{87}\text{Sr}/^{86}\text{Sr}$ composition of the oceans, because of basalt-seawater interactions alone. This curve can then be compared to measured $^{87}\text{Sr}/^{86}\text{Sr}$ data from over the Phanerozoic (Burke *et al.*, 1982) to derive equation (2.11) which can be used to calculate f_R .

$$\begin{aligned} & \frac{dRoc}{dt} \\ &= \frac{[(f_G(t) \cdot F_{bas}(0)) \cdot (R_{bas} - Roc(t))] + [F_{riv} \cdot (R_{riv} - Roc(t))]}{M_{Sr}} \end{aligned} \quad (2.10)$$

$$f_R(t) = 1 - \left\{ L \cdot \left(\frac{Rocb(t) - Rocm(t)}{Rocb(t) - 0.7000} \right) \right\} \quad (2.11)$$

Where: $dRoc$ is the calculated changes to $^{87}\text{Sr}/^{86}\text{Sr}$ of the ocean over time and $Roc(t)$ is the value at a specific time point; $Fbas(0)$ is the flux of total Sr between basalt and seawater at present; $Rbas$ is the average $^{87}\text{Sr}/^{86}\text{Sr}$ of basalts; $Friv$ is the flux of Sr to oceans from rivers; $Rriv$ is the average $^{87}\text{Sr}/^{86}\text{Sr}$ of rivers; L is an uplift proportionality factor; $Rocb(t)$ are the values of $^{87}\text{Sr}/^{86}\text{Sr}$ at time (t) as calculated using equation (2.10); and $Rocm$ are the measured values of $^{87}\text{Sr}/^{86}\text{Sr}$ at time (t).

A comparison of f_R calculated using this approach, to that using the GEOCARB I formula can be seen in figure 2.21.

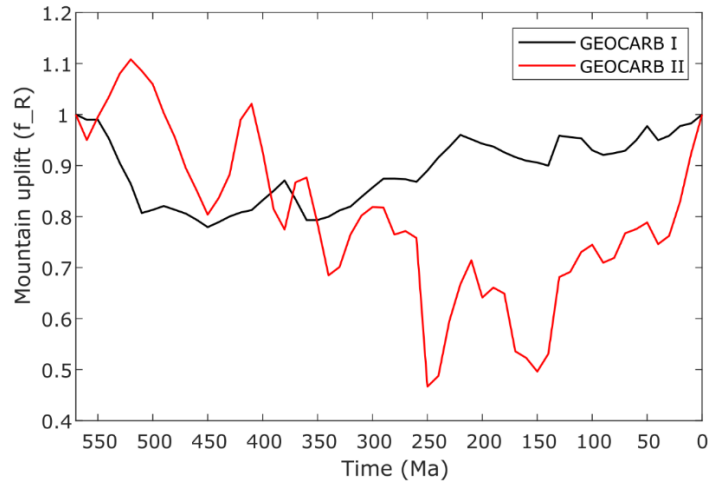


Figure 2.11 | A comparison of mountain uplift values.

The black line represents GEOCARB I's approach, using a logarithmic relationship to total land area, and the red line shows GEOCARB II's method of using Sr isotopes.

f_B: Dependence of weathering on CO₂ levels

This parameter was substantially revised in GEOCARB II to separate the effect of temperature on weathering rates from the effect of CO₂ levels, and to also include changes in solar luminosity in calculating temperature following Caldeira and Kasting (1992). The derivation for the effect of temperature on weathering is an involved process, including many factors such as regolith thickness and porosity for runoff calculations, GCM modelling for temperature response to CO₂ levels and the calculation of a solar luminosity factor etc. As such, the reader is directed to the original article (Berner, 1994) for the full details.

However, it is suffice to say that for the combined effect of CO₂ and temperature on weathering rates, there are four equations instead of one: the effect on silicate weathering before the evolution of vascular plants; and after vascular plants; the effect on carbonate weathering before vascular plants; and after vascular plant evolution. Four equations are necessary as the temperature dependency is different for silicate weathering, compared to carbonate weathering due to the different activation energies for the dissolution of these minerals. However, this means that the calculation of temperature through time has been substituted into the four equations, and thus is not calculated and preserved as a model output directly. Therefore, I do not complete this substitution, and have separate forcings as follows:

- temp: Temperature through time
- f_CO₂: Effect of changes to CO₂ on carbonate and silicate weathering
- f_Tsi: Effect of changes in temperature on silicate weathering
- f_Tcarb: Effect of changes in temperature on carbonate weathering

With the following equations:

$$temp = \{gamma \cdot \ln(RCO_2)\} - \left(W_s \cdot \frac{t}{-570} \right) + temp\_0 \quad (2.12)$$

$$f\_CO_2 = interpolation(0 - 350 - 380 - 570), (VAS \ VAS \ NOVAS \ NOVAS) \quad (2.13)$$

$$\text{Where: } VAS = \left(\frac{2 \cdot RCO_2}{1 + RCO_2} \right)^{FERT}$$

$$NOVAS = RCO_2^{0.5}$$

$$f\_Tsi = e^{ACT\_si \cdot (temp - temp\_0)} \cdot \{1 + [RUN \cdot (temp - temp\_0)]\}^{0.65} \quad (2.14)$$

$$f\_Tcarb = 1 + [ACT\_carb \cdot (temp - temp\_0)] \quad (2.15)$$

Where: gamma is the response of global average temperature to the atmospheric CO₂ greenhouse effect; W_s is the effect of solar insolation on global average temperature; temp_0 is the present day temperature (288°K); FERT is the land plant fertilisation factor from GEOCARB I; ACT_si is the activation energy for silicate minerals; ACT_carb is the activation energy for carbonate minerals; and RUN is the effect of temperature on global river runoff (other influences on river runoff, such as changing paleogeography remain represented by f_D).

These forcings can then be treated to produce an overall combined effect on silicate and carbonate weathering due to CO₂ and temperature:

$$f_{Bsi} = f_{Tsi} \cdot f_{CO2} \quad (2.16)$$

$$f_{BBcarb} = f_{Tcarb} \cdot f_{CO2} \quad (2.17)$$

f_D: Runoff

The data for this parameter were updated to use the results of Otto-Bliesner (1995) who employed GCM modelling under changes to paleogeography, with no topographic relief but changing continental size as well as latitudinal location, for 12 time slices during the Phanerozoic. The parameter has a linear scaling for carbonate weathering, as per GEOCARB I, due to the assumption that runoff in areas underlain by carbonates become saturated with those minerals. For silicate weathering, f_D is raised to the power of 0.65 to account for dilution of groundwater with other minerals. A comparison between the values used in GEOCARB I versus those in GEOCARB II can be seen in figure 2.22.

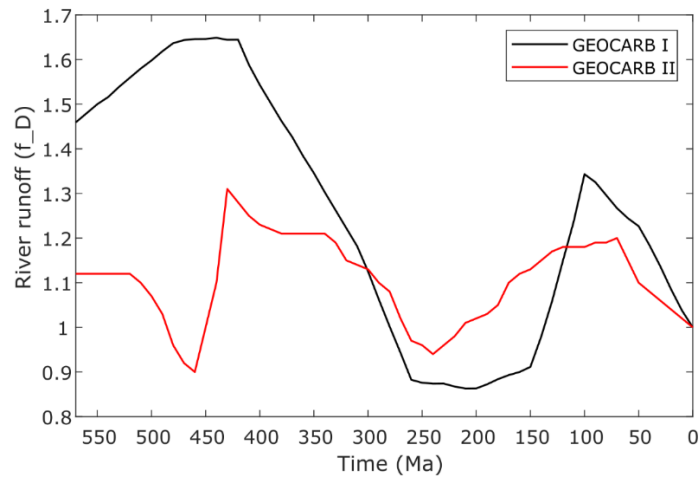


Figure 2.12 | A comparison of river runoff values.

The black line shows the values used in GEOCARB I, the red line shows the values used in GEOCARB II.

f_G: Degassing rates

For the majority of Phanerozoic time, results from the sea-level inversion approach of Gaffin (1987) are roughly maintained. However, for the last 150 Myrs, data from Engebretson *et al.* (1992), who use a fixed hotspot reference frame to calculate subduction rates over time, are used, this can be seen in figure 2.23.

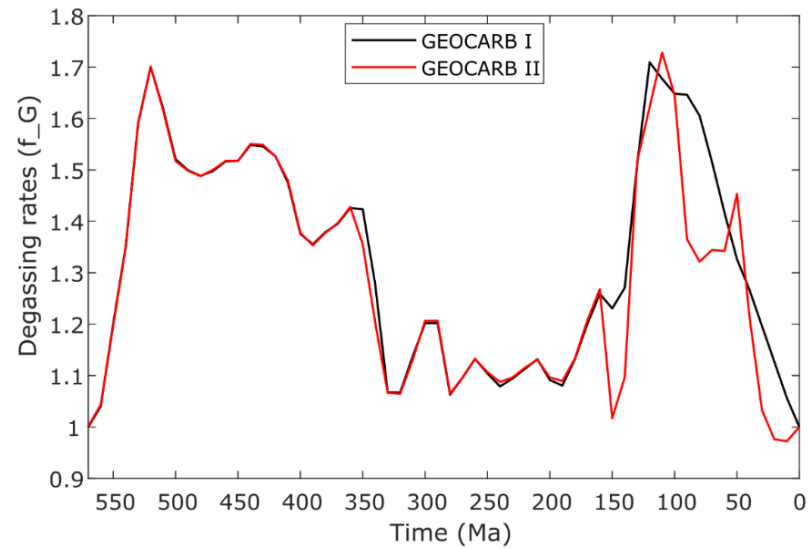


Figure 2.13 | A comparison of degassing rates.

The black line represents the values used in GEOCARB I and the red line shows the difference in degassing rates for the last 150 Myrs, as used in GEOCARB II.

f_C: Dependence of degassing rates on burial location of marine carbonates

The general approach for this forcing remains the same, however, instead of f_C reaching the present day value of 1 asymptotically, f_C rises in a linear fashion from 0.75 at 150 Ma to 1 at 0 Ma to represent a more steady transfer of carbonates to the deep ocean and into subduction zones, as can be seen in figure 2.24.

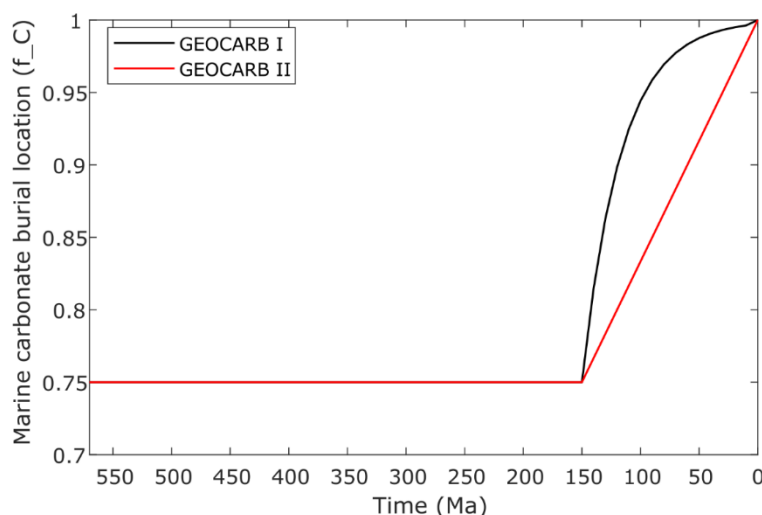


Figure 2.14 | A comparison of carbonate burial location values.

The black line shows the parameter rising in an exponential fashion (GEOCARB I) and the red line in a linear fashion (GEOCARB II) from 150 Ma to Present.

Rate constants and reservoirs

One final change for the GEOCARB II model was to remove the use of first order rate constants and reservoir size for calculating the degassing fluxes for C_{org} and carbonate. Instead, for C_{org} degassing: F_{mg} , the parameter f_G is multiplied by the degassing flux at present: F_{mg_0} , and for carbonate degassing: F_{mc} , f_G is multiplied by f_C and F_{mc_0} . The reasoning behind this change is that the shift in marine carbonate burial from shallow to deep seas would have decreased the carbonate available for weathering but should have had no bearing on the amount available for degassing, therefore this change, although has little overall effect on CO_2 predictions, is more geologically correct.

Results

There is not a major difference in CO₂ predictions between the standard runs of GEOCARB I and GEOCARB II (see Fig. 2.25). Generally, values are slightly higher for GEOCARB II during much of the Paleozoic, but it misses the Cretaceous CO₂ hump present in GEOCARB I, although sensitivity analyses of the various updated parameters produce an uncertainty window showing that Mesozoic CO₂ values can be very high indeed. Nevertheless, the general trend of CO₂ over the Phanerozoic remains the same. The results show that the first GEOCARB was a good approximation, and that updates in GEOCARB II add sophistication, with geologically more sound principles, which can act as a base for further refinement.

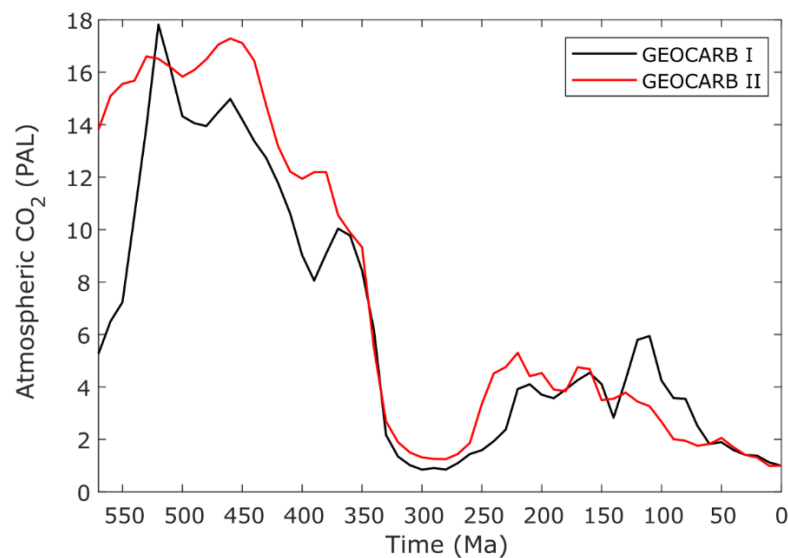


Figure 2.15 | Comparison of CO₂ outputs from GEOCARB I with GEOCARB II.

The black line shows the results from GEOCARB I and the red line shows the results from GEOCARB II.

2.4.3. GEOCARB III

The final iteration of the GEOCARB models (Berner and Kothavala, 2001) saw some revisions to various parameters due to, for example, improved GCM efforts, but there were no major changes to the general operation of the model.

f_B: Dependence of weathering on CO₂ levels

As described in section 2.4.2., this parameter is now four separate forcings: temp; f_CO2; f_Tsi; and f_Tcarb. In GEOCARB III a new parameter is added to equation (2.12) for calculating temperature: GEOG (see Fig. 2.26), which is the effect of changing paleogeography on continental surface temperature and is based on the GCM modelling by Otto-Bliesner (1995), where present-day CO₂ levels and solar luminosity are assumed.

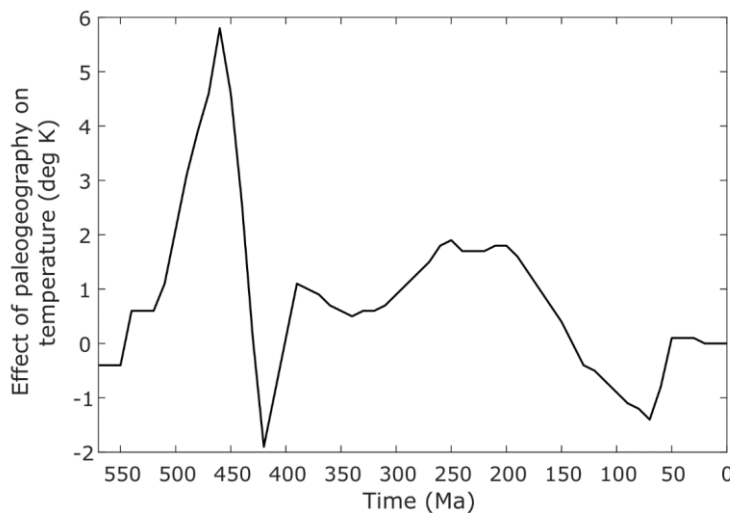


Figure 2.16 | The effect of changing paleogeography on continental surface temperature (GEOG) in °K.

Additionally, gamma (climate sensitivity to CO₂), Ws (solar luminosity), and RUN (temperature-controlled runoff) are all updated to use data from GCM modelling. In GEOCARB II the values for gamma and RUN were fixed for the entire model run time, however, work by Kothavala *et al.* (1999, 2000) showed that temperature and runoff have a lower sensitivity to CO₂ and solar forcing than previously thought. Consequently, data from their GCM modelling is used to obtain values for gamma and RUN for conditions similar to the ‘icehouse’ of the present day (340-260 Ma and 40-0 Ma), while for warmer, ‘greenhouse’ conditions, the work of Hay *et al.* (1999) is used. The Ws parameter is fixed for the entire model run and is based on Kothavala *et al.* (1999, 2000).

f_R: Mountain uplift

In GEOCARB II strontium isotopes were used as a proxy for uplift, however, as the strontium isotope composition of seawater can be affected by granites and limestones, as well as basaltic rocks, a more independent method of calculating the effect of uplift and erosion on weathering was developed, using the sediment data (sandstone and shale abundance) from Ronov (1993). Terrigenous rocks (e.g. non-carbonate, non-evaporite) form because of physical erosion, hence their abundance over time can be used as a proxy for erosion in the past.

Using the deposition-erosion modelling approach of Wold and Hay (1990), a simple relationship between f_R and erosion can be derived (equation 2.18). The Ronov data (1993) is first normalised to Miocene values, in order to exclude the excessive erosion and deposition values for the Pliocene and Quaternary, and is then input into equation (2.18).

$$f_R(t) = \text{erosion}(t)^{\frac{2}{3}} \quad (2.18)$$

The data from this approach was fit to a cubic polynomial (see equation 2.21) and compared to f_R data from the $^{87}\text{Sr}/^{86}\text{Sr}$ approach and found to be in good agreement (see Fig. 2.27). Hence, for GEOCARB III the $^{87}\text{Sr}/^{86}\text{Sr}$ data remained in use.

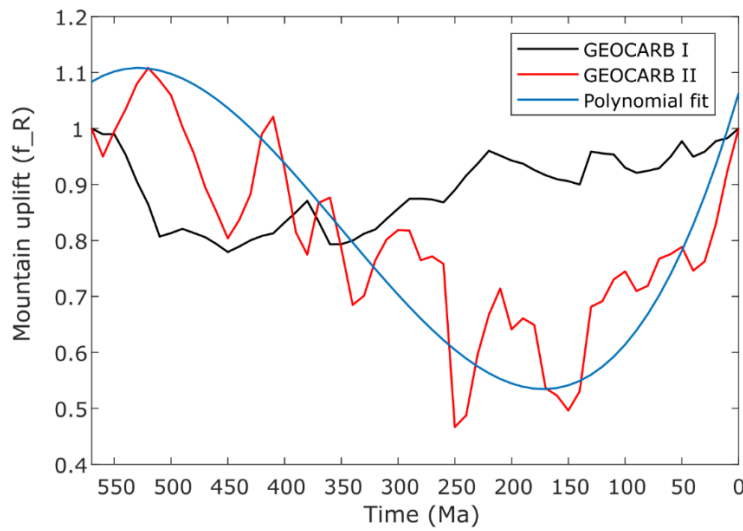


Figure 2.17 | Variations on mountain uplift values.

The black line is the logarithmic relationship to land area from GEOCARB I, the red line is the relationship to Sr isotopes from GEOCARB II, and the blue line is the polynomial fit to terrigenous sediments that is explored (but not implemented) in GEOCARB III.

f_E: Biological weathering factor

In GEOCARB I the pre-vascular plant value for f_E was set to be 15% of the present-day level. However, work by Moulton *et al.* (2000) on both tree-covered and ‘bare’ Icelandic basalts, had shown that trees provide a four-fold increase in chemical

weathering rates, thus f_E is set to be 0.25 (25% of the present-day) in GEOCARB III for the period 570 Ma to 380 Ma. Note that the evolutionary timing for trees was updated, based on work by Algeo *et al.* (1995) so that the model considers them to be evolving (linear mixing of pre and post-vascular plants) in the period 380 Ma to 350 Ma (see Fig. 2.28). From 350 Ma to 0 Ma the values of f_E remain as per GEOCARB I, although a value of $f_E = 0.875$ for gymnosperms is tested during the sensitivity analyses and is used in later modelling (Royer *et al.*, 2014).

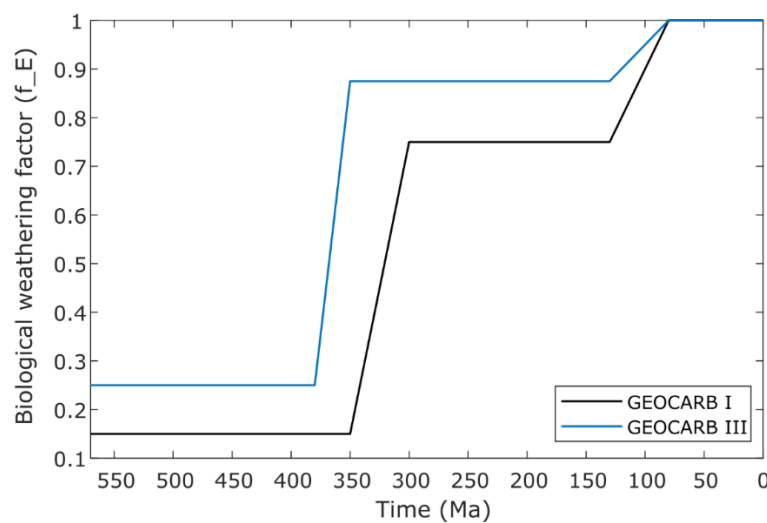


Figure 2.18 | A comparison of the biological weathering factor used in GEOCARBs I and III.

The black line represents the weathering factor used in GEOCARB I and the blue line is the factor used in GEOCARB III.

f_A : Total land area

The values used for f_A were updated based on recent data from Ronov (1994). The f_A parameter was then multiplied by f_D (global river runoff) to produce f_{AD} (global discharge from global runoff, see Fig. 2.29), and this was included in the equations for carbonate (alongside the parameter, f_{LA} : the total area underlain by

carbonates) and silicate weathering. The reasoning for this change is that values for f_D represent values for the whole of the continents, whereas Berner (1994) felt that runoff should only apply to such areas, namely mountainous areas, where most of the weathering is focused.

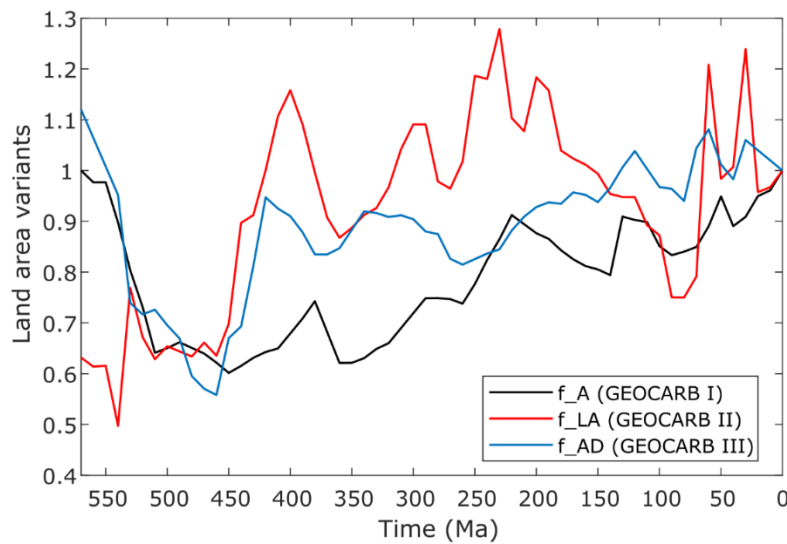


Figure 2.29 | The different variations of land area used in the GEOCARB models.

The black and red lines are from GEOCARB I and II respectively, the blue line is the new variant: global discharge from rivers.

Results

The effect of these changes on the baseline results for atmospheric CO_2 can be seen in figure 2.30. Similarly, to the comparison made between GEOCARB I and GEOCARB II, the differences between GEOCARB II and GEOCARB III are focused on the Paleozoic (particularly the Cambrian) and the Cretaceous. For both periods of time GEOCARB III predicts higher CO_2 , than GEOCARB II, and for the Cretaceous in particular, sensitivity analyses show that varying f_R or the biological factors, f_E and FERT can make a significant difference to CO_2 levels.

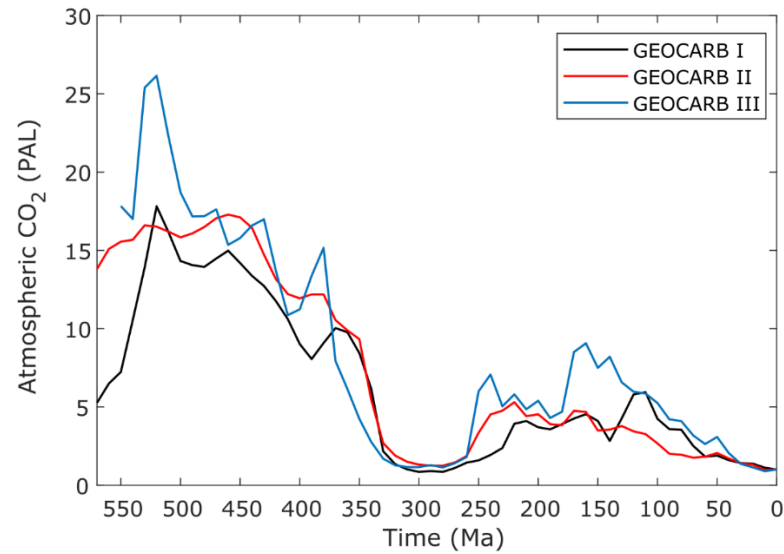


Figure 2.19 | CO_2 results from all versions of the GEOCARB model.

The black and red lines are the results from GEOCARB I and II respectively, and the blue line is from GEOCARB III.

2.5. Bringing it all together: GEOCARBSULF

2.5.1. GEOCARBSULF (2006)

In 2006, Berner combined the IMB approach of his 1987 and 2001 models to the GEOCARB models, creating the GEOCARBSULF model (see Fig. 2.31 for a schematic of the model set-up), with the express purpose of calculating, simultaneously, atmospheric O_2 and CO_2 variations over the Phanerozoic (Berner, 2006a). For the first time, dimensionless parameters were introduced to the sulfur cycle, and both rapid recycling and O_2 -dependent isotope fractionation were introduced to the GEOCARB suite.

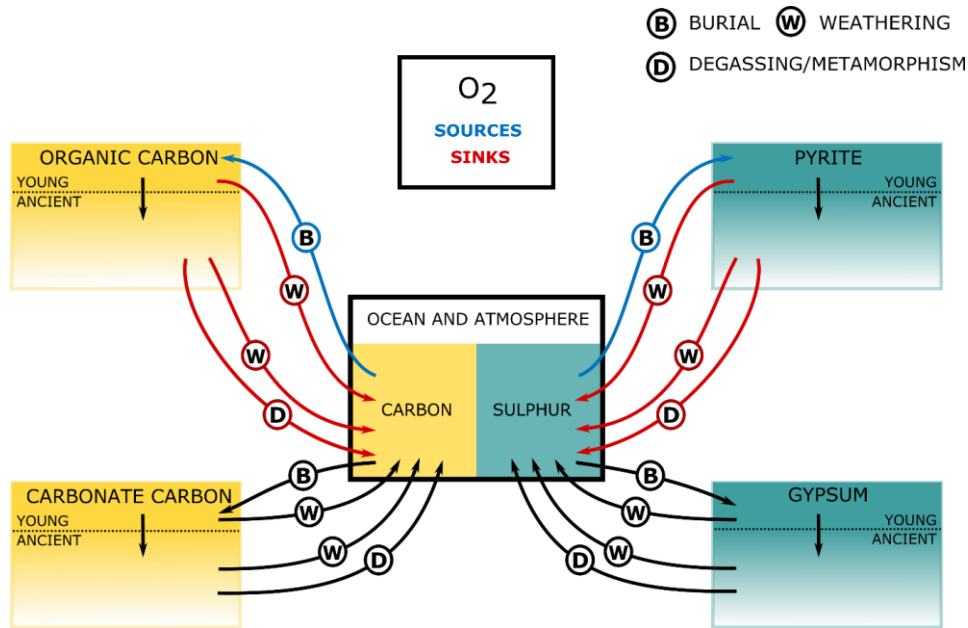


Figure 2.20 | The GEOCARBSULF model.

Adapted from Berner (2006a), the reservoirs are identical to earlier IMB models (Berner, 1987, 2001), as are the fluxes, but with the addition of degassing fluxes which recycle carbon and sulfur from the ancient reservoirs back to the ocean-atmosphere. Fluxes are: B: burial, W: weathering, D: degassing. The black fluxes have no effect on atmospheric O₂ calculations, whereas the blue fluxes are sources of O₂, and the red are sinks. Atmospheric CO₂ is calculated as the sum of all carbon weathering and degassing fluxes, minus the sum of the burial fluxes of carbon.

The various model parameters have been discussed in detail in previous sections, as such, the data used to run GEOCARBSULF is obtained from whichever model where that parameter was last updated (e.g. global river runoff values (f_D) from GEOCARB II are used, whereas the biological enhancement of weathering (f_E) is from GEOCARB III).

There are some exceptions, where the parameters are either updated or restructured.

These are:

The total land area underlain by carbonates (f_{LA}) and the total global discharge (f_{AD}) parameters are split into total land area (f_A , see Fig. 2.32), total carbonate land area (f_L , see Fig. 2.33) and global river runoff (f_D , see Fig. 2.22 in the GEOCARB II section). In GEOCARB III, the equation for C_{org} weathering contains f_{AD} , but in GEOCARBSULF river runoff (f_D) is not included. Thus, the equations for carbonate and C_{org} weathering are returned to their GEOCARB II forms.

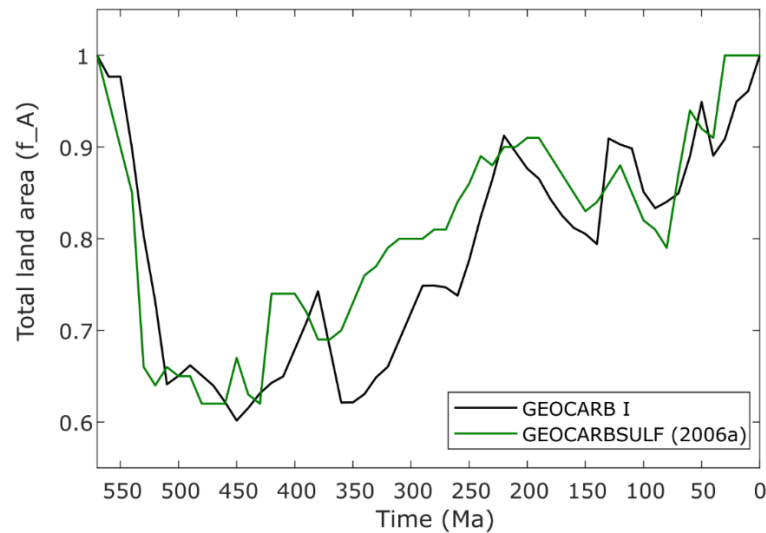


Figure 2.21 | Total land area used in GEOCARBSULF.

The black line represents the data used in GEOCARB I (and II) based on work by Ronov (1976) and Barron et al. (1980), while the green line is data from Ronov (1994) used in GEOCARB III and GEOCARBSULF.

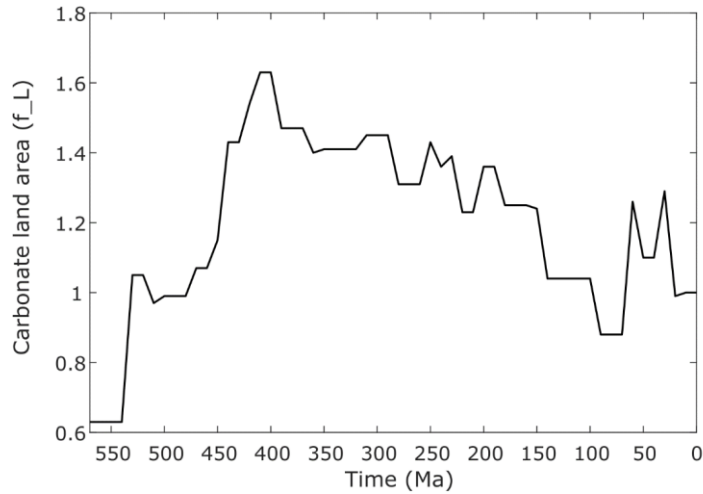


Figure 2.22 | Total carbonate land area.

The data for this parameter is obtained from Bluth and Kump (1991).

Finally, the $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ records are updated (see Figs. 2.34 and 2.35), with the $\delta^{13}\text{C}$ data compiled by Berner (2006a) from numerous sources (see reference for further details) and the $\delta^{34}\text{S}$ coming from Kampschulte and Strauss (2004).

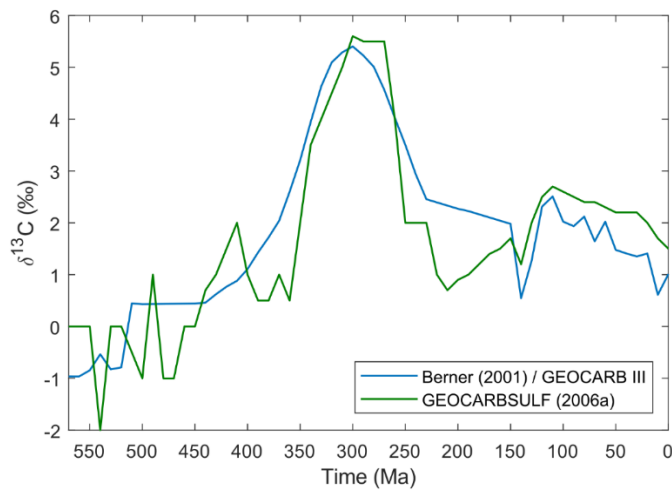


Figure 2.23 | The latest $\delta^{13}\text{C}$ compilation.

The blue line is the compilation used in GEOCARB III and IMB2, and the green line is the data used for GEOCARBSULF.

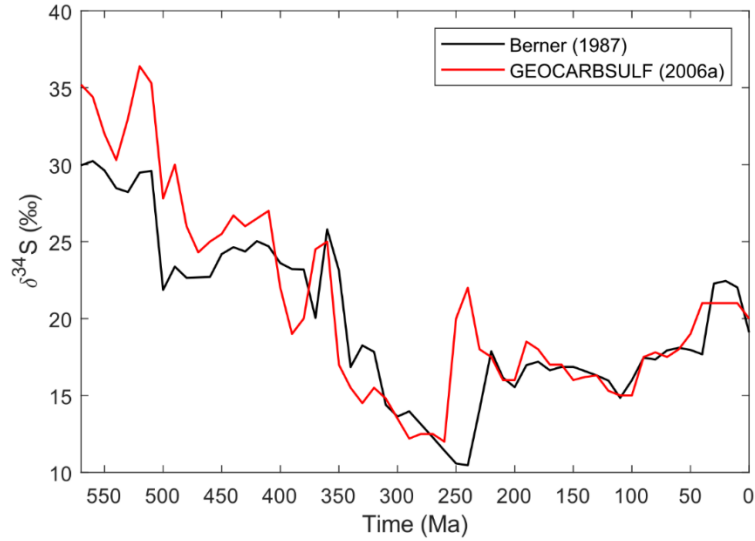


Figure 2.24 | The latest $\delta^{34}\text{S}$ compilation.

The black line is the compilation used in IMB1 and the red line is the compilation used in GEOCARBSULF.

The full list of parameters and their values, as well as model equations for GEOCARBSULF can be found in tables (2.1 – 2.6). One thing to note is that, although it is included in the sensitivity analyses for model O_2 output, the standard run for GEOCARBSULF (Berner, 2006a) uses the carbon isotope fraction (α_c) values from Hayes *et al.* (1999) rather than using the O_2 -dependent equation introduced in the earlier IMB2 modelling (Berner, 2001). The sulfur isotope fractionation in the standard run however, uses the O_2 -dependent equation (2.7) from IMB2.

As with the GEOCARB and IMB models, the timestep for GEOCARBSULF is one Myr, with data input at 10 Myr points and interpolation between. The model is initiated at 570 Ma, with the parameters having the same values at 570 and 560 Ma as they do at 550 Ma, to allow for model spin-up.

Results

In figure 2.36 the O₂ output from GEOCARBSULF can be seen and is compared to the predictions made by IMB2. Atmospheric O₂ is predicted by GEOCARBSULF to be: higher than 15% atm for most of the Paleozoic; and above present-day levels for the late Silurian to early Devonian, and for most of the Carboniferous and Permian periods. O₂ is very low (almost 10% atm) at the end of the Triassic, and then rises slowly thereafter to ~21% at the present-day – contrary to IMB2, which predicted O₂ that was a bit too high at present-day.

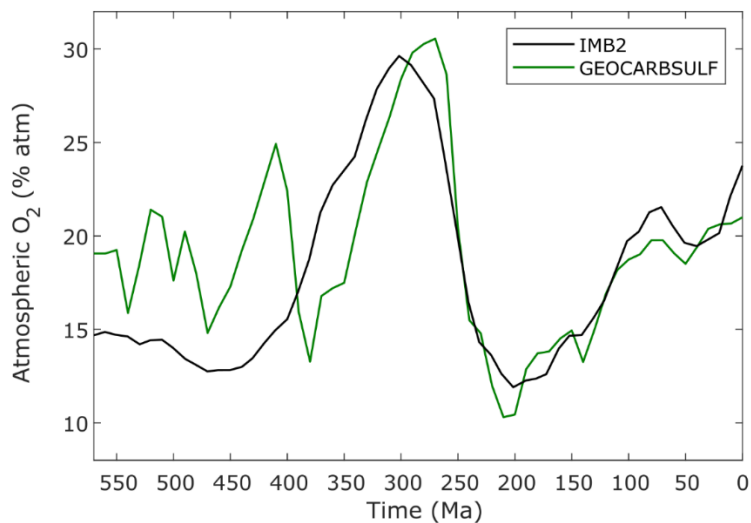


Figure 2.25 | Atmospheric O₂ predictions from IMB2 and GEOCARBSULF.

The black line is the standard run from IMB2, and the green line is the standard run from GEOCARBSULF, both of which use fractionation data from Hayes et al. (1999) to help calculate C_{org} burial rates.

Comparing figure 2.34 (the $\delta^{13}\text{C}$ record) to figure 2.36 highlights that much of the variability in O₂, particularly in the early Paleozoic and also the timing of the mid-

Carboniferous-Permian hump, can be attributed to the carbon isotopes in use, rather than the introduction of dimensionless parameters. As Berner showed, with sensitivity analyses of his GEOCARB models (Berner, 1991, 1994; Berner and Kothavala, 2001), the dimensionless parameters can exert a significant influence on atmospheric CO₂ levels. But, the results from figure 2.36 suggest that this is not the case for O₂, thus perhaps it is the oxygen sources, rather than the sinks, that hold a dominant control over atmospheric O₂ levels, during the Phanerozoic at least.

A sensitivity analysis, whereby uplift (f_R), land area (f_A) and river runoff (f_D) were set to equal 1 (i.e. present-day) for the entire model run, resulted in O₂ that is near identical to the standard run, except for a much reduced peak across the Permo-Carboniferous (Berner, 2006a). Recent research (S. Zhang *et al.*, 2018) testing the sensitivity of O₂ to weathering and degassing fluxes that have been artificially scaled (to be either lower or higher than the GEOCARBSULF standard run) back up this assertion that changes to O₂ sources, in the Phanerozoic at least, are more important than changes to the sinks.

There is little difference between GEOCARB III and GEOCARBSULF atmospheric CO₂ predictions (see Fig. 2.37). The key forcings that affect CO₂ in this type of box modelling are f_G and f_R (Mills *et al.*, 2019), however, as the degassing values are the same for both GEOCARB III and GEOCARBSULF, and the Sr isotope approach for f_R is retained, it is possibly the splitting of the land area variants back into their constituent parameters which is generating the differences in CO₂ predictions. The

effect of chemical weathering on CO₂ levels is explored further in the next couple of sections.

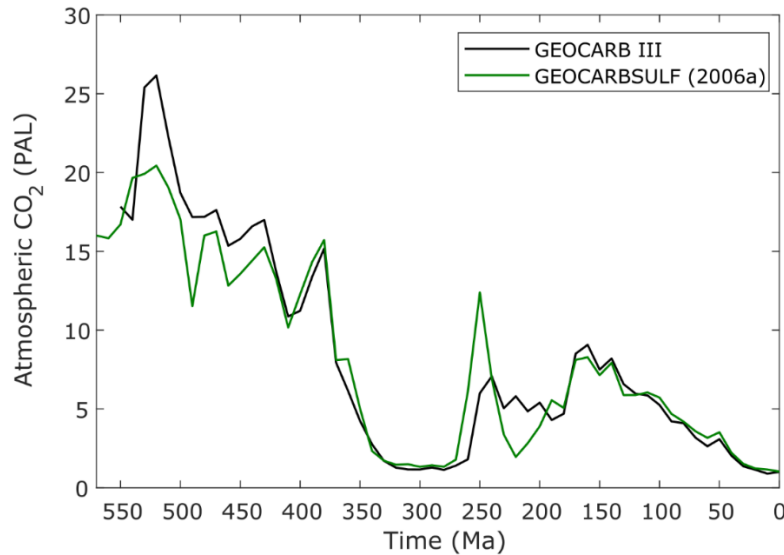


Figure 2.26 | CO₂ predictions from GEOCARB III and GEOCARBSULF.

The black line is CO₂ output from GEOCARB III, and the green line is from GEOCARBSULF (Berner, 2006a), which does not include additional equations and parameters to distinguish between the weathering of volcanic and non-volcanic rocks (Berner, 2006b).

Although GEOCARBSULF was not quite the first model to simultaneously calculate O₂ and CO₂, as the first version of the COPSE model predates it (Bergman, Lenton and Watson, 2004), it nevertheless presented a more-detailed construction of the history of atmospheric O₂ over the Phanerozoic. It also allowed an inter-model comparison with COPSE, to look for general trends in O₂, and to examine whether there might be links between changing O₂ levels and the evolution of life.

2.5.2. *GEOCARBSULFvolc*

In this update (Berner, 2006b) to the GEOCARBSULF model, an attempt was made to quantify the weathering of volcanic rocks, and their influence on atmospheric CO₂ levels over the Phanerozoic. Berner noted that research by, for example, Gaillardet *et al.* (1999) implied that the weathering of volcanic rocks plays a significant contribution to global silicate weathering rates, due to their rich Mg- and Ca-silicate mineral composition (Berner, 2004) and faster weathering rates (e.g. Meybeck, 1987).

Following an assumption that: seawater $^{87}\text{Sr}/^{86}\text{Sr}$ values through time are faithfully recorded in carbonates and represent mixing of the various inputs; volcanic rocks record an average $^{87}\text{Sr}/^{86}\text{Sr}$ which is known (0.703 is assumed here); and that non-volcanic rocks generally have a higher $^{87}\text{Sr}/^{86}\text{Sr}$ composition, the Sr isotope record through time (see Fig. 2.38) can be used to split the contribution to total silicate weathering from volcanic and non-volcanic rocks (Kump, 1989; Berner and Rye, 1992; Francois and Walker, 1992; Taylor and Lasaga, 1999). Thus, instead of using Sr isotopes to calculate uplift (f_R) – as was the case for GEOCARBSULF and GEOCARB II and III – GEOCARBSULFvolc utilises the polynomial fit to sediment data for f_R , and the Sr isotopes are used to distinguish between volcanic and non-volcanic weathering (Berner, 2006b).

To calculate the fraction of volcanic rock weathering to the overall silicate weathering flux through time, the $^{87}\text{Sr}/^{86}\text{Sr}$ for volcanic rocks remains static throughout the entire model run, whereas the $^{87}\text{Sr}/^{86}\text{Sr}$ for non-volcanic rocks is computed as a function of an arbitrary parameter (NV) and f_R at each time step, such that the modern day

$^{87}\text{Sr}/^{86}\text{Sr}$ for non-volcanic rocks reaches 0.717, equating to a 30% contribution of volcanic rock weathering (Xvolc) to total silicate weathering (Berner, 2006b).

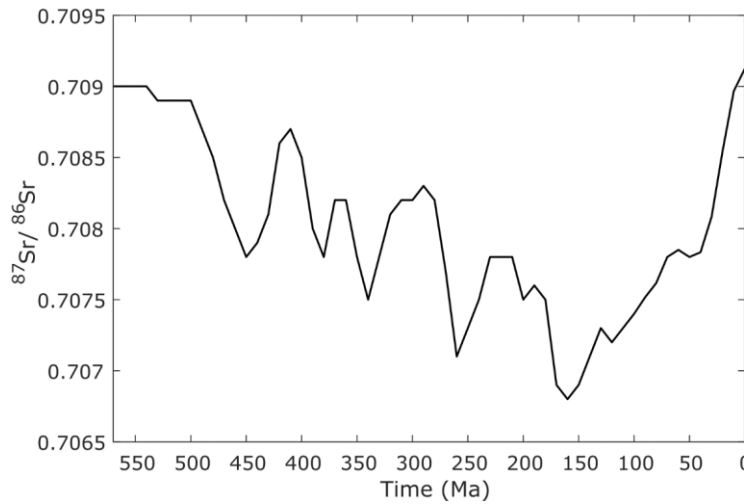


Figure 2.27 | The strontium isotope record used in GEOCARBSULFvolc.

The data is from Burke et al. (1982)

Results

In figure 2.39 the CO_2 results from GEOCARBSULF and GEOCARBSULFvolc (where NV is set to be 0.015) are compared to one another (Berner does not plot the O_2 output from this version of GEOCARBSULFvolc). Although the two versions of the model follow the same broad trends, GEOCARBSULFvolc predicts lower CO_2 in the early and mid-Paleozoic, but generally higher levels in the Mesozoic. Prior to ~320 Ma, the overall effect of including the weathering of volcanic rocks (f_{volc} – see equations 2.55-2.60) is >1 meaning that total silicate weathering is amplified and therefore more CO_2 is drawn down from the atmosphere during this time in GEOCARBSULFvolc compared to GEOCARBSULF.

For the later Paleozoic, despite $f_{\text{volc}} < 1$ and a significant difference in f_R , these changes exert little effect on CO_2 levels, presumably because the temperature dependence on silicate weathering rates holds a greater control. For the Cenozoic, f_{volc} is close to 1 and f_R is similar, thus it is unsurprising that there is little change to CO_2 levels during this time. For much of the Mesozoic, $f_{\text{volc}} > 1$ implying increased silicate weathering rates, but for the majority of this Era, CO_2 estimates are higher in GEOCARBSULFvolc. However, this is easily explained by very low f_R rates from the polynomial fit, whereas the f_R rates from Sr isotopes show a greater degree of variability.

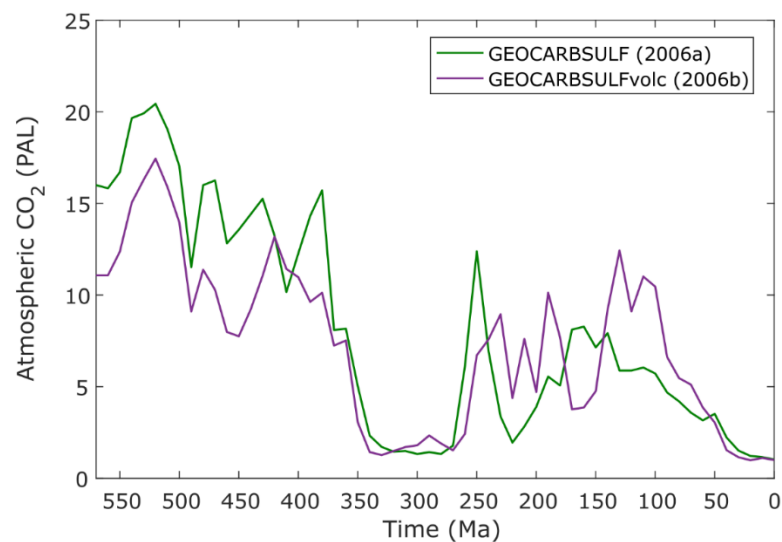


Figure 2.39 | GEOCARBSULF vs. GEOCARBSULFvolc CO_2 predictions.

The green line is from the GEOCARBSULF model (Berner, 2006a) and the purple line is the output from GEOCARBSULFvolc (where $NV = 0.015$) (Berner, 2006b).

2.5.3. Addendum to GEOCARBSULFvolc

The changes in the GEOCARBSULFvolc addendum (Berner, 2008) were fairly minimal. A new parameter was included: VNV – which represents a ratio of chemical

weathering in volcanic to non-volcanic silicate rocks. The rate of exchange of Ca and Mg between basalt and seawater at present day (F_{bo_0}) was judged to have been too low in the previous version of GEOCARBSULFvolc (0.75×10^{18} mol myr⁻¹) and was revised upwards to 5×10^{18} mol myr⁻¹. The present day $^{87}\text{Sr}/^{86}\text{Sr}$ for non-volcanic rocks was also increased, to 0.722, and finally, the uplift (f_R) was revised so that $f_R = 1$ at Present (see equations (2.20 and 2.21) and figure 2.40).

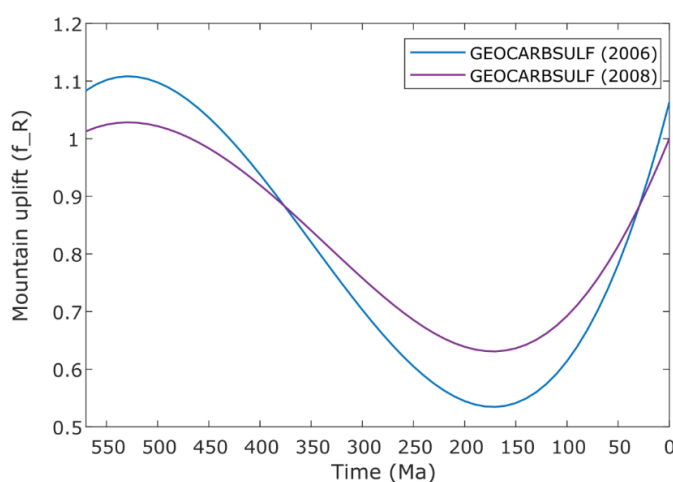


Figure 2.28 | The revised uplift rates.

Results

A range of sensitivity tests were conducted to ascertain the effect on CO_2 estimates from including VNV and revising F_{bo_0} (see Berner (2008) for further details). A value of $VNV = 2$ was settled on, and the results from this can be seen in figure 2.41. Although there is little variation between the 2006 and 2008 versions of GEOCARBSULFvolc for the Paleozoic and Cenozoic, CO_2 in the Mesozoic has been significantly dampened, which is likely due to the revision to higher values of uplift rates through this time, and therefore an increase in silicate weathering rates in the 2008 version, compared to the 2006 version.

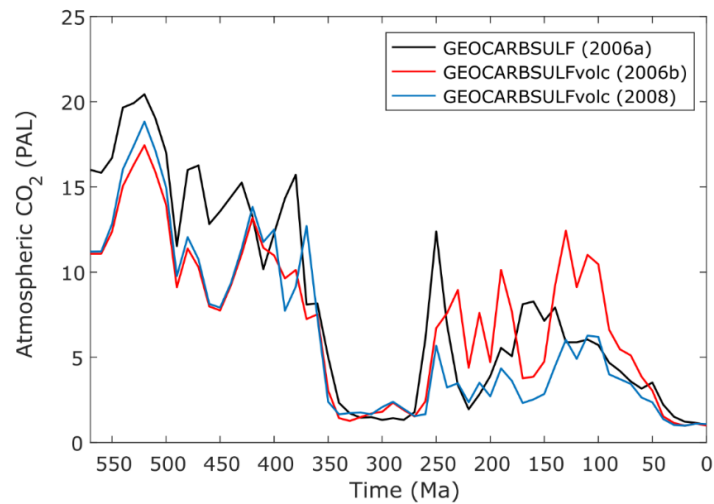


Figure 2.29 | CO_2 estimates from the different variations of GEOCARBSULF.

2.5.4. The final update by Berner

In 2009, Bob Berner made his final updates to the GEOCARBSULF model (Berner, 2009). The two updates to the model were to: revise the $\delta^{13}C$ record (see Fig. 2.42), incorporating data from Permo-Carboniferous brachiopod shells (Grossman *et al.*, 2008) with the data smoothed across a window of 12 Myrs, with an output every 10 Myrs; and to switch from using the carbon isotopic fractionation data of Hayes *et al.* (1999) to using an O_2 -dependent equation, but with different values for the present-day fractionation and J fitting parameter to those previously explored in IMB2 (Berner, 2001).

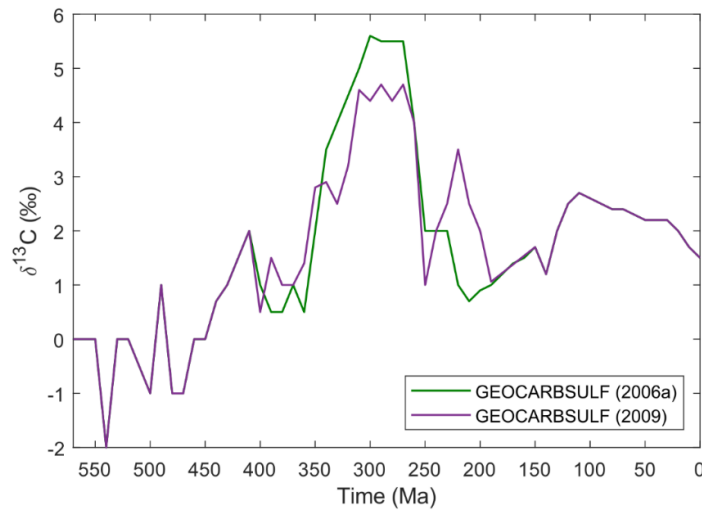


Figure 2.30 | The final update to the $\delta^{13}\text{C}$ record.

The green line is from the 2006 (GEOCARBSULF) version, and the purple line is from the 2009 (GEOCARBSULFvolc) version.

Results

The updates result in O_2 levels (see Fig. 2.43) that are not $<15\%$ atm for such a long swathe of time (just the Jurassic and very briefly in the Cretaceous, instead of continuously from the Triassic to early Cretaceous). The 2009 version also does not exhibit quite such a dramatic decrease in O_2 levels in the Devonian. A comparison of the $\delta^{13}\text{C}$ data used across the model versions (Fig. 2.42) shows no isotopic change prior to the Devonian or from the Jurassic to the Present, yet, pre-Devonian the O_2 results across both versions of the models are nearly identical, but this is not true post-Triassic. Although the weathering of volcanic rocks has been included in the 2009 version, this would have little overall effect on O_2 predictions, instead, it is the switch to an O_2 -dependent equation (equation 2.6) for calculating $\delta^{13}\text{C}$ fractionation which appears to exert a considerable influence on O_2 , particularly in the Mesozoic and Cenozoic. The results suggest that either the fractionation equation is matching the

Hayes *et al.* (1999) isotopic data pre-Devonian, or that the carbon cycle is not the dominant control on O₂ levels during this time. The answer appears to be that the O₂-dependent equation produces $\delta^{13}\text{C}$ fractionation a few per mille lower than records suggest occurred (Hayes, Strauss and Kaufman, 1999), leading to a reduction in O₂ production from the carbon cycle. However, this is counter-balanced by increased pyrite burial and O₂ production from the sulphur cycle due to the $\delta^{34}\text{S}$ fractionation equation, which is discussed further in Chapter 3.

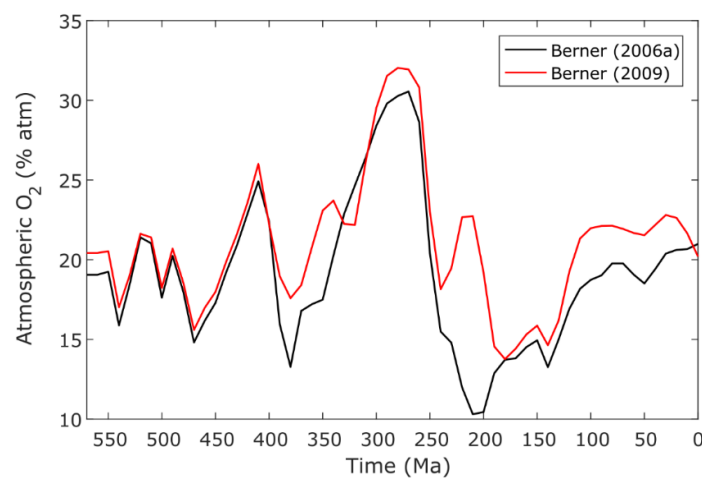


Figure 2.31 | A comparison of O₂ predictions made by the 2006 and 2009 versions of GEOCARBSULF.

The black line is from 2006a, and the red line is from the 2009 version.

For the late Paleozoic through to the Present, the isotopic fractionation generated by the equation is likely to be quite different to the Hayes *et al.* (1999) data, although the new $\delta^{13}\text{C}$ data for the Permo-Carboniferous will also have a strong influence on O₂ results, as evidenced during Triassic, where the 2009 version of GEOCARBSULF shows a rise, instead of continued decrease, in O₂. The fractionation data from Hayes *et al.* (1999) is marine in nature, and thus neglects terrestrial C_{org} burial, which likely has a different effect on fractionation and therefore exhibits a different isotopic

signature, hence the fractionation equation likely results in O_2 predictions representative of a mixing of marine and terrestrial $\delta^{13}C$ fractionation (Beerling *et al.*, 2002; Berner, 2009).

2.5.5. GEOCARBSULF, COPSE and MAGic

Now that all of Berner's updates to his GEOCARBSULF model have been documented, it is interesting to see how the O_2 predictions fare against the COPSE (Lenton, Daines and Mills, 2018) and MAGic (Arvidson, Mackenzie and Guidry, 2013) model estimates (see Fig. 2.44). For much of the last 400 Myrs, the O_2 output from all three models follows the same broad trends, with a significant rise in O_2 in the Carboniferous (although the models disagree on the magnitude) and another rise in the Cretaceous. GEOCARBSULF dips below the wildfire limit of 15% atm during the Jurassic, whereas COPSE and MAGic do not, and the reason for this addressed in section 2.5.7.

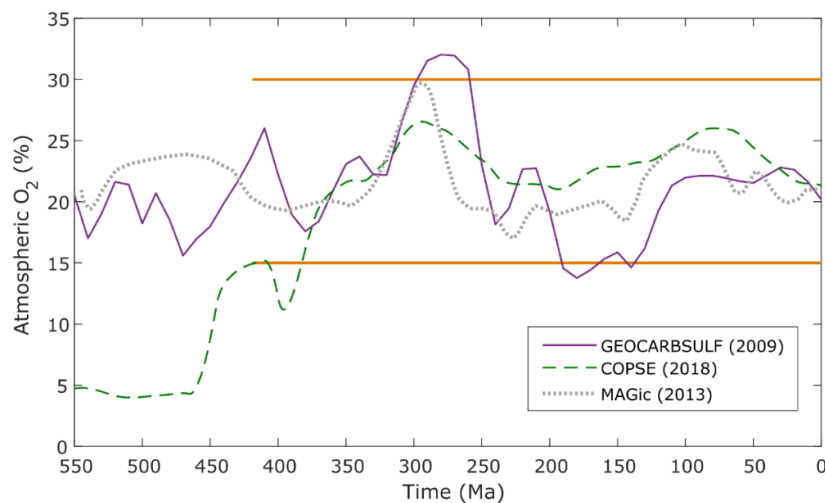


Figure 2.32 | O_2 predictions made by three Phanerozoic box models.

The purple line is the O₂ output from GEOCARBSULF (Berner, 2009), the green dashed line is from COPSE (Lenton, Daines and Mills, 2018), and the grey dotted line is from MAGic (Arvidson, Mackenzie and Guidry, 2013). The orange lines are the wildfire limits (Belcher and McElwain, 2008; Watson and Lovelock, 2013).

The main disagreement between the models lies in O₂ estimates for the early Paleozoic, where GEOCARBSULF and MAGic favour approximately present-day levels, and COPSE predicts much lower O₂ levels. GEOCARBSULF's results are tied to its isotope approach to C_{org} and pyrite burial and are explored in further detail in Chapter 3, yet COPSE and MAGic – both nutrient and therefore productivity driven models – display differing estimates for O₂ prior to ~375 Ma.

Both models utilise the dimensionless parameters from GEOCARB III to help calculate certain weathering fluxes, although MAGic also has a separate ocean reservoir, while COPSE (and GEOCARBSULF) does not. MAGic and COPSE also have an O₂-dependent (degree of anoxia) influence on: marine primary productivity, whereby more anoxic conditions results in more phosphorus recycling from the sediments back into the water column; and on pyrite burial, as more oxygenated conditions limits the preservation of pyrite in sediments (Arvidson, Mackenzie and Guidry, 2013; Lenton, Daines and Mills, 2018).

MAGic does have a greater number of reservoirs than either COPSE or GEOCARBSULF, including a pool of sedimentary clay, and like BLAG, has separate dolomite and calcite reservoirs, and it also has a more detailed approach to seawater chemistry, but these differences are more likely to affect the inorganic side of the

carbon cycle (Berner, Lasaga and Garrels, 1983; Berner, 2006a; Arvidson, Mackenzie and Guidry, 2013; Lenton, Daines and Mills, 2018).

MAGic does assume that the burial of terrestrial C_{org} is only a small fraction of the total C_{org} burial flux, which explains why there is no rise in O_2 concurrent with the evolution of land plants, but it does not explain the high O_2 levels in the early Paleozoic (Arvidson, Mackenzie and Guidry, 2006, 2013). It is possible that the model is initiated with an O_2 level that is too high and subsequently has insufficient negative feedbacks or not enough spin-up time to allow O_2 levels to drop, but this is possibly an avenue for research in the future.

2.5.6. Error analysis of GEOCARBSULF's O_2 and CO_2 predictions

GEOCARBSULF has over 60 input parameters, some of which – the $\delta^{13}C$ record, for example – have a degree of uncertainty associated with them (Royer *et al.*, 2014). Although error envelopes have been calculated for O_2 and CO_2 for previous GEOCARB(SULF) models, these were the result of varying only a couple of parameters – either singly or in tandem – and so do not produce the full range of possible model results.

The objective of the work by Royer *et al.* (2014) was to update certain parameters (listed below), and then to generate a window of uncertainty for O_2 and CO_2 predictions using a 10,000 run Monte Carlo simulation, assuming a Gaussian distribution for most variables. They found that the updated model produced high O_2 in the Permo-Carboniferous and low O_2 at the end of the Triassic, which are discussed

in more detail below and in section 2.5.7. For CO₂, they found that levels were elevated in the early Paleozoic and early Mesozoic, and that the model is particularly sensitive to the relationship between CO₂ and temperature, and plant-assisted weathering (Royer *et al.*, 2014).

f_D: Runoff

The river runoff due to paleogeography was updated to use the coupled carbon-GCM model by Godd  ris *et al.* (2012), although not the exact results from that paper, as the results include the influences of variable CO₂ and solar luminosity on river runoff, whereas GEOCARBSULF deals with these separately (Royer *et al.*, 2014). The Godd  ris *et al.* model has significant advantages over the previous model (Otto-Bliesner, 1995), as it has a higher spatial resolution, topographical features, vegetation, and allows for continental ice sheet growth during the late Paleozoic and second half of the Cenozoic. The f_D results from the model can be seen in figure 2.45.

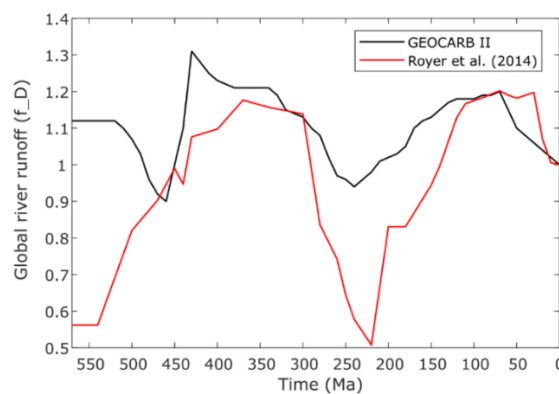


Figure 2.33 | Updated river runoff due to paleogeography rates.

The black line is the river runoff used in GEOCARB II right through to GEOCARBSULF, and the red line are the values used by Royer *et al.* (2014).

GEOG: Changing paleogeography on average continental surface temperature

As with river runoff, the *GEOG* values are taken from the Godd ris *et al.* model which has been re-run to use present day CO₂ and solar luminosity. In this model, only grid cells that exhibit chemical weathering (i.e. river runoff >0) are included for calculating *GEOG*, thus cold and dry environments – which can have an overly large influence on average continental temperatures – are excluded (Berner and Kothavala, 2001; Royer *et al.*, 2014). The new *GEOG* estimates (see Fig. 2.46) suggest that the continental configuration during the early Paleozoic would have resulted in colder temperatures on average, but the Mesozoic would have been much warmer.

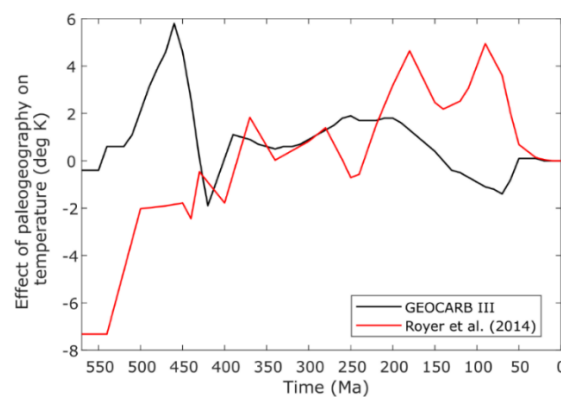


Figure 2.34 | The difference in *GEOG* values.

The black line shows the effect of paleogeography on temperature as used in *GEOCARB III* and *GEOCARBSULF*, while the red line shows the updated values used by Royer *et al.* (2014).

f_{AW}: The fraction of total land area undergoing chemical weathering

This is a new parameter introduced into the *GEOCARBSULF* model by Royer *et al.* (2014) and again, is based on the Godd ris *et al.* model. At any point in time, the total land area undergoing chemical weathering will not be 100% of the total land area

because of glacial coverage, large continental mass leading to arid interiors etc. (Berner and Kothavala, 2001; Royer *et al.*, 2014). Consequently, there is a need for this to be reflected in box modelling, as it may significantly affect weathering rates over time.

In figure 2.47, the fraction of land area that will experience chemical weathering through time is plotted and is based on non-zero runoff grid cells from the Godd ris *et al.* model. The black line represents the values as used in Royer *et al.* (2014), however, the authors have not normalised these results to the present-day fraction, as is the case with all other time-dependent variables (e.g. uplift, river runoff etc.) and thus this may unduly affect chemical weathering rates through time. The red line represents a normalisation of f_{AW} , and these values are used in later chapters.

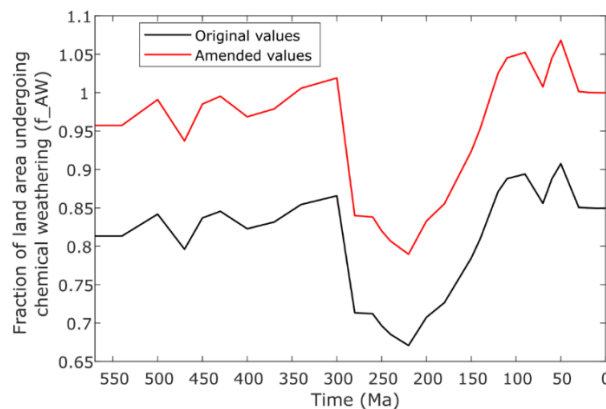


Figure 2.35 | The fraction of land that will undergo chemical weathering.

The black line shows the original values derived by Royer *et al.* (2014), while the red line shows the values amended so that they are normalised to the present-day, in line with other dimensionless parameters.

f_A: Total land area

The total land area parameter itself is updated, based on 22 time slices from the Godd  ris *et al.* model, with linear interpolation between the slices so that there is data to input every 10 Myrs, as is the standard for GEOCARBSULF. As can be seen in figure 2.48, there is little difference between this update and the previous values (differences are exacerbated by the y-axis scale), except during the early Paleozoic.

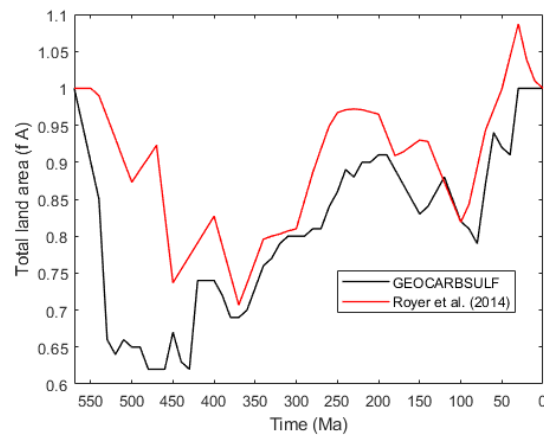


Figure 2.36 | The final update to the total land area parameter.

The black line is the land area values used in GEOCARBSULF (2006 – 2009) and the red line shows the updated data used in Royer et al. (2014).

The $\delta^{34}\text{S}$ record

Finally, the $\delta^{34}\text{S}$ values input into the model (see Fig. 2.49) are updated to a more recent compilation (Wu *et al.*, 2010). The new data are very similar to those used previously, except for the values use in the spin-up period: 550-570 Ma, which are considerably lighter.

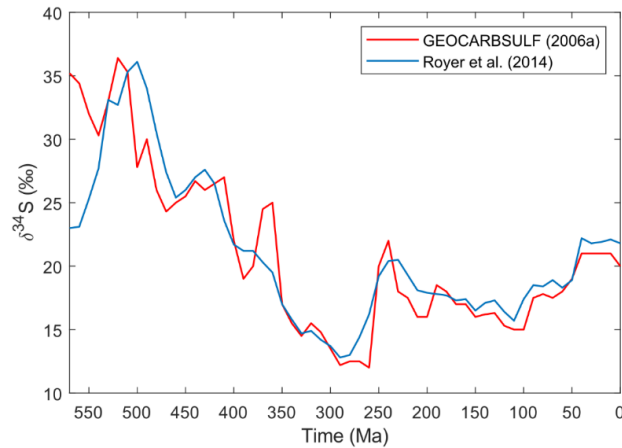


Figure 2.49 | The final update to the $\delta^{34}\text{S}$ record used in GEOCARBSULF.

The red line shows the values used in GEOCARBSULF (2006 – 2009) which are taken from Kampschulte and Strauss (2004), and the blue line shows the values used by Royer *et al.* (2014) which are taken from Wu *et al.* (2010).

Results

The mean results of the Monte Carlo simulation conducted by Royer *et al.* (2014), for both CO_2 and O_2 , are plotted in figures 2.50 and 2.51. CO_2 results are not too dissimilar to those from Berner (2008), with the notable exceptions of much higher CO_2 in the Cambrian, and lower estimates in the Jurassic and Cretaceous. The $\sim 2\times$ higher CO_2 in the Cambrian is due to a mixture of low river runoff rates, lower land area and low *GEOG*, all of which contribute to decreased silicate weathering rates. For the Jurassic and Cretaceous, *GEOG* is significantly higher and leads to increased silicate weathering rates, and thus lower CO_2 .

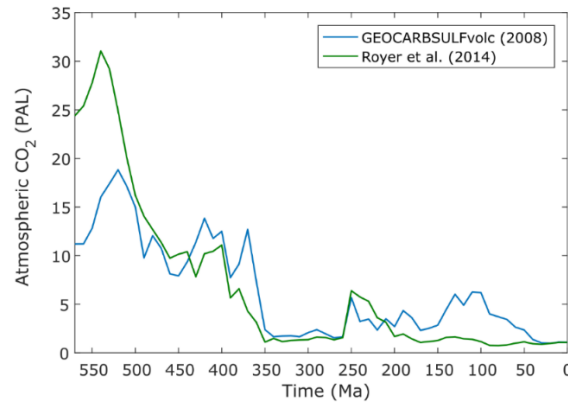


Figure 2.37 | CO₂ predictions made by different versions of GEOCARBSULF.

The blue line is GEOCARBSULFvolc (2008), the green line from Royer *et al.* (2014).

The O₂ results from Royer *et al.* (2014) are strikingly similar to Berner (2009). It is possible that the lower O₂ from 550 to 570 Ma is due to the lighter $\delta^{34}\text{S}$ record here, suggesting less pyrite burial and hence O₂ production. At the start of the Jurassic, O₂ plummets to ~10% atm, below the wildfire limit (Belcher and McElwain, 2008). It is not clear if there is a single underlying mechanism behind this drop, as there is little difference in $\delta^{34}\text{S}$ here to act as a possible explanation. Instead, it is perhaps a cumulative effect of changes to *GEOG*, *f_D*, etc. or it is a legacy of the averaging of 10,000 Monte Carlo runs, and the real result lies somewhere in the uncertainty envelope.

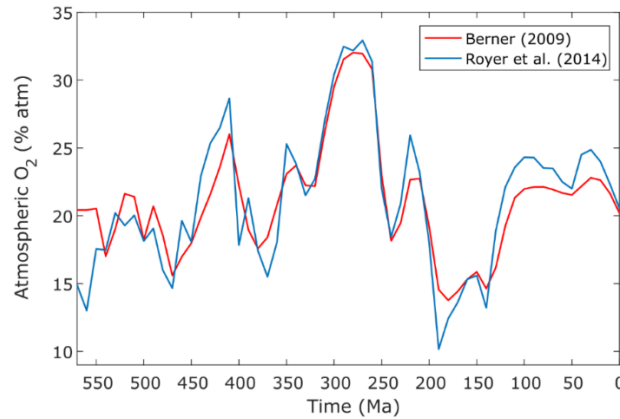


Figure 2.38 | O_2 predictions made by different versions of GEOCARBSULF.

The red line is from GEOCARBSULF (2009), the blue line from Royer *et al.* (2014).

2.5.7. Resolution of low O_2 predictions in the Mesozoic

GEOCARBSULF, both in the original papers (Berner, 2006a, 2009) and in the update by Royer *et al.* (2014) predict atmospheric O_2 to be between ~10 – 13% atm during the Jurassic. Experimental work on combustion limits, allied with evidence of inertinite in the geological record suggest that O_2 must have been above 15% atm during the Jurassic, contrary to GEOCARBSULF's predictions (Belcher and McElwain, 2008; Berner, 2009; Glasspool and Scott, 2010; Royer *et al.*, 2014). As GEOCARBSULF O_2 predictions are often considered the 'best guess', this mismatch between model outputs and experimental/geological data presents a quandary with regards to the reliability of the model. However, as can be seen in figure 2.52, this is a problem easily remedied with the use of updated $\delta^{13}C$ data (Mills *et al.*, 2016).

Implementing new $\delta^{13}C$ data into the original GEOCARBSULF model code is problematic, as even modest changes to this, or other variables can easily result in

model failure (Royer *et al.*, 2014; S. Zhang *et al.*, 2018). By incorporating an IMB approach to calculating C_{org} and pyrite burial in COPSE, instead of using the usual nutrient and productivity driven method, it has been shown that the O_2 predictions from the hybrid, IMB-COPSE model are indeed highly sensitive to the $\delta^{13}C$ data used (Mills *et al.*, 2016). This is because the present-day $\delta^{13}C$ of the oceans is very important, as the model is parameterised based on modern values (in terms of fluxes, reservoir sizes etc.) and GEOCARBSULF has a $\delta^{13}C$ of $\sim 2\%$, whereas more recent data compiled by Saltzman and Thomas (2012) shows that $\delta^{13}C$ is closer to 0% at present (Mills *et al.*, 2016).

Thus, during the Jurassic, GEOCARBSULF has a $\delta^{13}C$ input which is lower than at present, effectively meaning less C_{org} burial (which is the major source of O_2) during this time, whereas the Saltzman and Thomas (2012) data shows the opposite and hence predicts O_2 levels above the wildfire limit of 15% atm (Belcher and McElwain, 2008; Mills *et al.*, 2016).

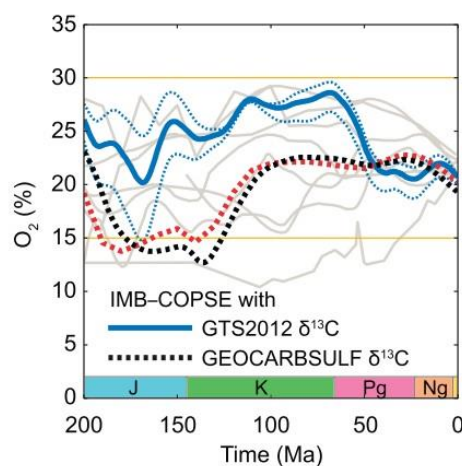


Figure 2.39 | O_2 predictions for the last 200 Myrs from the IMB-COPSE model.

The red dashed line is the output from the original GEOCARBSULF (2009), the black dashed line shows the results from the IMB-COPSE model using the GEOCARBSULF $\delta^{13}\text{C}$ data, the blue lines are the IMB-COPSE model results using updated $\delta^{13}\text{C}$ data – solid blue is the mean and the dashed lines are the $\pm 1\text{sd}$. Taken from Mills et al. (2016).

2.5.8. High O_2 predictions in the early Paleozoic

Now that a history of the GEOCARBSULF model has been charted, and one issue with its predictions has been resolved, attention can now be given to another problem with its O_2 estimates: high levels of O_2 in the early Paleozoic. One attempt was made to investigate the root cause behind GEOCARBSULF's high O_2 predictions in the early Paleozoic, contrary to geochemical proxies (Sperling *et al.*, 2015; S. Zhang *et al.*, 2018). Using the GEOCARBSULF model, reconstructed in the R programming language by Royer *et al.* (2014), different O_2 evolution scenarios for the Paleozoic were fed into the model, and optimised scaling factors were added to the weathering and degassing fluxes for all carbon and sulfur species, such that the model estimated the required flux sizes to achieve the O_2 value at each timestep (S. Zhang *et al.*, 2018).

It was found that: similar to prior efforts (Royer *et al.*, 2014), this update to GEOCARBSULF was also prone to failure; the scaling factors sometimes varied by geologically unfeasible amounts (i.e. carbonate weathering dropped from a scaled factor of 1 to 0 – no carbonate weathering at all – within only 20 Myrs); and that changes to the weathering and degassing fluxes alone could not produce stable, low O_2 in the early Paleozoic (S. Zhang *et al.*, 2018). Thus, it is likely that some other

mechanism is controlling O₂ levels in the early Paleozoic, and this is explored in detail in the next chapter.

2.6. GEOCARBSULF parameters and equations

2.6.1 Full model parameters

Table 2.1: Present day parameters used in GEOCARBSULF

Parameter	Algebraic Representation	Value
Atmosphere and ocean CO ₂	A0	3.193x10 ¹⁸ mol
Atmosphere and ocean O ₂	O0	3.8x10 ¹⁹ mol
Atmosphere and ocean sulfate	OA_S_0	3.8x10 ¹⁹ mol
Temperature	<i>temp_0</i>	288 K
Silicate weathering	<i>F_ws_0</i>	6.67x10 ¹⁸ mol myr ⁻¹
Weathering rate of ancient pyrite	<i>F_wp_a0</i>	0.25x10 ¹⁸ mol S myr ⁻¹
Weathering rate of ancient gypsum	<i>F_wgyp_a0</i>	0.5x10 ¹⁸ mol S myr ⁻¹
Weathering rate of ancient C _{org}	<i>F_wg_a0</i>	0.5x10 ¹⁸ mol C myr ⁻¹
Weathering rate of ancient carbonate	<i>F_wc_a0</i>	2x10 ¹⁸ mol C myr ⁻¹
Degassing rate of ancient pyrite	<i>F_mp_0</i>	0.25x10 ¹⁸ mol S myr ⁻¹
Degassing rate of ancient gypsum	<i>F_ms_0</i>	0.5x10 ¹⁸ mol S myr ⁻¹
Degassing rate of ancient C _{org}	<i>F_mg_0</i>	1.25x10 ¹⁸ mol C myr ⁻¹
Degassing rate of ancient carbonate	<i>F_mc_0</i>	6.67x10 ¹⁸ mol C myr ⁻¹
*Rate of exchange of Ca and Mg between basalt and seawater	<i>F_bo_0</i>	5x10 ¹⁸ mol myr ⁻¹
Fraction of total Ca and Mg silicate weathering derived from volcanic rocks	Xvolc_0	0.35

*Royer *et al.* (2014) use a value of 4x10¹⁸ mol myr⁻¹ for this parameter.

Table 2.2: Constant parameters used in GEOCARBSULF

Parameter	Algebraic Representation	Value
Normalized activation energy for silicates	ACT_{si}	0.09 K^{-1}
Normalized activation energy for carbonates	ACT_{carb}	0.087 K^{-1}
Effect of solar insolation on temperature	Ws	7.4°
Proportion of plants fertilized by increasing CO_2	$FERT$	0.4
Curve fitting parameter for effect of O_2 on $\delta^{13}\text{C}$ fractionation	J	4
Average value of $^{87}\text{Sr}/^{86}\text{Sr}$ of sub-aerial and submarine volcanic rocks	Rv	0.704
*Ratio of chemical weathering in volcanic to non-volcanic silicate rocks	VNV	2
*Parameter used to calculate the average $^{87}\text{Sr}/^{86}\text{Sr}$ of non-volcanic silicate rocks	NV	0.015
Young pyrite weathering rate constant	k_{wp}	0.01 myr^{-1}
Young gypsum weathering rate constant	k_{wgyp}	0.01 myr^{-1}
Young C_{org} weathering rate constant	k_{wg}	0.018 myr^{-1}
Young carbonate weathering rate constant	k_{wc}	0.018 myr^{-1}

*For these parameters, Royer *et al.* (2014) use $VNV = 5$ and $NV = 0.0075$

Table 2.3: Time dependent parameters used in GEOCARBSULF

Parameter	Algebraic Representation	Notes
Total land area	f_A	Time array
Fraction of land area experiencing chemical weathering	f_{AW}	Time array – introduced by Royer <i>et al.</i> (2014)
Global river runoff	f_D	Time array
Effect of change in paleogeography on temperature	$GEOG$	Time array
Proportion of land area underlain by carbonates	f_L	Time array
Δ Degassing rate due to tectonics / seafloor spreading	f_G or f_{SR}	Time array - the same values are used by Royer <i>et al.</i>
Ocean $\delta^{13}C$ carbonate record	δ_{OA_C}	Time array
Dependence of weathering rate on soil biological activity due to land plants	f_E	0-80 Ma $f_E = 1$ 130-350 Ma $f_E = 0.875$ 380-550 Ma $f_E = 0.25$ Linear interpolation between 80-130 Ma and 350-380 Ma
Mean land elevation	f_R	Cubic fit – See equations (2.20) and (2.21)

Dependence of degassing rate on relative proportions of carbonates on shallow platforms or deep ocean	f_C	150-550 Ma $f_C = 0.75$ 0-150 Ma is a time dependent equation, see equation (2.19)
Ocean ^{87}Sr record for use in calculating silicate weathering	R_{ocm}	Time array
*Response of global mean temperature to atmospheric CO_2 greenhouse effect	γ	For 0-40 Ma and 260-330 Ma: $\gamma = 4$ All other time: $\gamma = 3.3$
Temperature controlled runoff factor	RUN	0-40 Ma and 260-340 Ma: RUN $= 0.045$ All other time: $RUN = 0.025$
Effect of changes to CO_2 on carbonate and silicate weathering	f_{CO_2}	0-350 Ma: $f_{\text{CO}_2} = \text{VAS}$ 380-550 Ma: $f_{\text{CO}_2} = \text{NOVAS}$ Linear interpolation between 350-380 Ma - see equations (2.14-2.17 and 2.25-2.26)

^Both of these terms are used throughout the literature, but in GEOCARBSULF they are treated as the same thing.

*Royer et al. (2014) use $\gamma = 8.6562$ for 0-40 Ma and 260-330 Ma. For the rest of the time: $\gamma = 4.3281$

Table 2.4: Starting reservoir sizes of GEOCARBSULF

Parameter	Algebraic Representation	Value
Young pyrite	Pyr_y	20×10^{18} mol
Ancient pyrite	Pyr_a	280×10^{18} mol
Young gypsum	Gyp_y	150×10^{18} mol
Ancient gypsum	Gyp_a	150×10^{18} mol
Young C_{org}	G_y	250×10^{18} mol
Ancient C_{org}	G_a	1000×10^{18} mol
Young carbonate	C_y	1000×10^{18} mol
Ancient carbonate	C_a	4000×10^{18} mol
Young pyrite isotope mass balance (IMB)	$\delta_{p\_y} \cdot Pyr\_y$	$-10 \cdot 20 \times 10^{18}$
Ancient pyrite IMB	$\delta_{p\_a} \cdot Pyr\_a$	$-10 \cdot 280 \times 10^{18}$
Young gypsum IMB	$\delta_{gyp\_y} \cdot Gyp\_y$	$35 \cdot 150 \times 10^{18}$
Ancient gypsum IMB	$\delta_{gyp\_a} \cdot Gyp\_a$	$2.0133 \cdot 150 \times 10^{18}$
Young C_{org} IMB	$\delta_{g\_y} \cdot G\_y$	$-23.5 \cdot 250 \times 10^{18}$
Ancient C_{org} IMB	$\delta_{g\_a} \cdot G\_a$	$-23.5 \cdot 1000 \times 10^{18}$
Young carbonate IMB	$\delta_{c\_y} \cdot C\_y$	$3 \cdot 1000 \times 10^{18}$
Ancient carbonate IMB	$\delta_{c\_a} \cdot C\_a$	$-1.5774 \cdot 4000 \times 10^{18}$

2.6.2. Full model equations

The full model equations are listed below. Note, some equations are out of sequence, as they appear earlier in the chapter.

Table 2.5: Flux and parameter equations

f_{C} for $t < 150$ Ma:	$f_{\text{C}} = 0.75 + \left[\left(\frac{0.25}{150} \right) \cdot (150 + t) \right]$	[2.19]
Mean land elevation:	$f_{\text{R}} = \left(\frac{f_{\text{RT}}}{1.063} \right)^{0.67}$	[2.20]
Where:	$f_{\text{RT}} = \left(25.269 \cdot \left(\frac{t}{1000} \right)^3 \right) + \left(26.561 \cdot \left(\frac{t}{1000} \right)^2 \right) + \left(6.894 \cdot \left(\frac{t}{1000} \right) \right) + 1.063$	[2.21]
Ratio of CO ₂ relative to present day:	$\text{RCO}_2 = \frac{\text{CO}_2(t)}{A_0}$	[2.22]
Ratio of O ₂ relative to present day:	$\text{O}_{2\text{mr}} = \frac{\text{O}_2(t)}{\text{O}_0}$	[2.23]
Conversion of relative O ₂ to atmospheric %:	$\text{O}_{2\text{atm}} = \left(\frac{\text{O}_{2\text{mr}}}{\text{O}_{2\text{mr}} + 3.762} \right) \cdot 100$	[2.24]

Effect of changes in CO ₂ on carbonate and silicate weathering:	$VAS = \left(\frac{2 \cdot RCO2}{1 + RCO2} \right)^{FERT}$ $NOVAS = RCO2^{0.5}$	[2.25]
Global average temperature:	$temp = (gamma - \ln RCO2) - \left(Ws \cdot \frac{t}{-570} \right) + GEOG + temp_0$	[2.26]
Temperature effect on silicate weathering:	$f\_Tsi = e^{(ACT\_si \cdot [temp - temp_0])} \cdot \{1 + [RUN \cdot (temp - temp_0)]\}^{0.65}$	[2.14]
Temperature and CO ₂ effect on silicate weathering:	$fBsi = f\_Tsi \cdot f\_CO2$	[2.16]
Temperature effect on carbonate weathering:	$f\_Tcarb = 1 + [ACT\_carb \cdot (temp - temp_0)]$	[2.15]
Temperature and CO ₂ effect on carbonate weathering:	$f\_BBcarb = f\_Tcarb \cdot f\_CO2$	[2.17]
Weathering of young pyrite:	$F\_wp\_y = f\_R \cdot f\_A \cdot k\_wp \cdot Pyr\_y(t)$	[2.27]
Weathering of ancient pyrite:	$F\_wp\_a = f\_R \cdot F\_wp\_a0$	[2.28]
Weathering of young gypsum:	$F\_wgyp\_y = f\_D \cdot f\_A \cdot k\_wgyp \cdot Gyp\_y(t)$	[2.29]
Weathering of ancient gypsum:	$F\_wgyp\_a = f\_D \cdot f\_A \cdot F\_wgyp\_a0$	[2.30]

Weathering of young C_{org} :	$F_{wg\_y} = f_R \cdot f_A \cdot k_{wg} \cdot G_y(t)$	[2.31]
Weathering of ancient C_{org} :	$F_{wg\_a} = f_R \cdot F_{wg\_a0}$	[2.32]
Weathering of young carbonate:	$F_{wc\_y} = f_{BBcarb} \cdot f_L \cdot f_A \cdot f_D \cdot f_E \cdot k_{wc} \cdot C_y(t)$	[2.33]
Weathering of ancient carbonate:	$F_{wc\_a} = f_{BBcarb} \cdot f_L \cdot f_A \cdot f_D \cdot f_E \cdot F_{wc\_a0}$	[2.34]
Degassing of ancient pyrite:	$F_{mp} = f_{SR} \cdot F_{mp\_0}$	[2.35]
Degassing of ancient gypsum:	$F_{ms} = f_{SR} \cdot F_{ms\_0}$	[2.36]
Degassing of ancient C_{org} :	$F_{mg} = f_{SR} \cdot F_{mg\_0}$	[2.37]
Degassing of ancient carbonate:	$F_{mc} = f_{SR} \cdot f_C \cdot F_{mc\_0}$	[2.38]
Fractionation of $\delta^{13}C$:	$\alpha_C = 27 + [J \cdot (O_2mr - 1)]$	[2.6]
Fractionation of $\delta^{34}S$:	$\alpha_S = 35 \cdot (O_2mr)^{1.5}$	[2.7]
Young pyrite isotopes:	$\delta_{p\_y} = \frac{\delta_{p\_y}(t) \cdot Pyr\_y(t)}{Pyr\_y(t)}$	[2.39]
Ancient pyrite isotopes:	$\delta_{p\_a} = \frac{\delta_{p\_a}(t) \cdot Pyr\_a(t)}{Pyr\_a(t)}$	[2.40]
Young gypsum isotopes:	$\delta_{gyp\_y} = \frac{\delta_{gyp\_y}(t) \cdot Gyp\_y(t)}{Gyp\_y(t)}$	[2.41]

Ancient gypsum isotopes:	$\delta_{gyp\_a} = \frac{\delta_{gyp\_a}(t) \cdot Gyp\_a(t)}{Gyp\_a(t)}$	[2.42]
Young C _{org} isotopes:	$\delta_{g\_y} = \frac{\delta_{g\_y}(t) \cdot G\_y(t)}{G\_y(t)}$	[2.43]
Ancient C _{org} isotopes:	$\delta_{g\_a} = \frac{\delta_{g\_a}(t) \cdot G\_a(t)}{G\_a(t)}$	[2.44]
Young carbonate isotopes:	$\delta_{c\_y} = \frac{\delta_{c\_y}(t) \cdot C\_y(t)}{C\_y(t)}$	[2.45]
Ancient carbonate isotopes:	$\delta_{c\_a} = \frac{\delta_{c\_a}(t) \cdot C\_a(t)}{C\_a(t)}$	[2.46]
Burial of C _{org} :	$F_{bg} = \frac{1}{\alpha_C}$ $\cdot \{[(\delta_{OA\_C} - \delta_{c\_y}) \cdot F_{wc\_y}]$ $+ [(\delta_{OA\_C} - \delta_{c\_a}) \cdot F_{wc\_a}]$ $+ [(\delta_{OA\_C} - \delta_{g\_y}) \cdot F_{wg\_y}]$ $+ [(\delta_{OA\_C} - \delta_{g\_a}) \cdot F_{wg\_a}] + [(\delta_{OA\_C} - \delta_{c\_a}) \cdot F_{mc}]$ $+ [(\delta_{OA\_C} - \delta_{g\_a}) \cdot F_{mg}]\}$	[2.47]
Burial of carbonate:	$F_{bc} = F_{wg\_y} + F_{wc\_y} + F_{wg\_a} + F_{wc\_a} + F_{mg} + F_{mc} - F_{bg}$	[2.48]

Burial of pyrite:	$F_{bp} = \frac{1}{\alpha_S} \cdot \{[(\delta_{OA_S} - \delta_{gyp_y}) \cdot F_{wgyp_y}] + [(\delta_{OA_S} - \delta_{gyp_a}) \cdot F_{wgyp_a}] + [(\delta_{OA_S} - \delta_{p_y}) \cdot F_{wp_y}] + [(\delta_{OA_S} - \delta_{p_a}) \cdot F_{wp_a}] + [(\delta_{OA_S} - \delta_{gyp_a}) \cdot F_{ms}] + [(\delta_{OA_S} - \delta_{p_a}) \cdot F_{mp}]\}$	[2.49]
Burial of gypsum:	$F_{bgyp} = F_{wp_y} + F_{wgyp_y} + F_{wp_a} + F_{wgyp_a} + F_{mp} + F_{ms} - F_{bp}$	[2.50]
Young to ancient pyrite flux:	$F_{ya_p} = F_{wp_a} + F_{mp}$	[2.51]
Young to ancient gypsum flux:	$F_{ya_gyp} = F_{wgyp_a} + F_{ms}$	[2.52]
Young to ancient C _{org} flux:	$F_{ya_g} = F_{wg_a} + F_{mg}$	[2.53]
Young to ancient carbonate flux:	$F_{ya_c} = F_{wc_a} + F_{mc}$	[2.54]
Convert strontium isotopes to $^{87}\text{Sr}/^{86}\text{Sr}$:	$R_{oc} = \frac{R_{ocm}}{10000} + 0.7$	[2.55]
Average value of $^{87}\text{Sr}/^{86}\text{Sr}$ for young carbonates undergoing weathering:	$R_{cy} = R_{cy}(t) + \left[(R_{oc} - R_{cy}(t)) \cdot \frac{F_{bc}}{C_y(t)} \right]$	[2.56]

Average value of $^{87}\text{Sr}/^{86}\text{Sr}$ for ancient carbonates undergoing weathering:	$R_{\text{ca}} = R_{\text{ca}}(t) + \left[(R_{\text{cy}} - R_{\text{ca}}(t)) \cdot \frac{F_{\text{ya\_c}}}{C_{\text{a}}(t)} \right]$	[2.57]
$^{87}\text{Sr}/^{86}\text{Sr}$ of non-volcanic silicates:	$R_{\text{nv}} = 0.722 - \left[NV \cdot \left(\frac{1 - f_{\text{RT}}}{1.063} \right) \right]$	[2.58]
Fraction of total Ca and Mg silicate weathering derived from volcanic rocks:	$X_{\text{volc}} = \frac{\{ [f_{\text{SR}} \cdot F_{\text{bo\_0}} \cdot (R_{\text{v}} - R_{\text{oc}})] + (F_{\text{wc\_y}} \cdot R_{\text{cy}}) + (F_{\text{wc\_a}} \cdot R_{\text{ca}}) - (R_{\text{oc}} \cdot F_{\text{bc}}) + (R_{\text{nv}} \cdot F_{\text{ws}}) \}}{F_{\text{ws}} \cdot (R_{\text{nv}} - R_{\text{v}})}$	[2.59]
Volcanic weathering effect:	$f_{\text{volc}} = \frac{(VNV \cdot X_{\text{volc}}) + (1 - X_{\text{volc}})}{(VNV \cdot X_{\text{volc\_0}}) + (1 - X_{\text{volc\_0}})}$	[2.60]
*Silicate weathering:	$F_{\text{ws}} = f_{\text{volc}} \cdot f_{\text{Bsi}} \cdot (f_{\text{AW}} \cdot f_{\text{A}} \cdot f_{\text{D}})^{0.65} \cdot f_{\text{R}} \cdot f_{\text{E}} \cdot F_{\text{ws\_0}}$	[2.61]

* f_{AW} was introduced by Royer *et al.* (2014) and is not present in earlier incarnations of GEOCARBSULF.

Table 2.6: Reservoir equations

Young pyrite:	$\frac{d(Pyr_y)}{dt} = F_{bp} - F_{wp_y} - F_{ya_p}$	[2.62]
Ancient pyrite:	$\frac{d(Pyr_a)}{dt} = F_{ya_p} - F_{wp_a} - F_{mp}$	[2.63]
Young gypsum:	$\frac{d(Gyp_y)}{dt} = F_{bgyp} - F_{wgyp_y} - F_{ya_gyp}$	[2.64]
Ancient gypsum:	$\frac{d(Gyp_a)}{dt} = F_{ya_gyp} - F_{wgyp_a} - F_{ms}$	[2.65]
Young C_{org} :	$\frac{d(G_y)}{dt} = F_{bg} - F_{wg_y} - F_{ya_g}$	[2.66]
Ancient C_{org} :	$\frac{d(G_a)}{dt} = F_{ya_g} - F_{wg_a} - F_{mg}$	[2.67]
Young carbonate:	$\frac{d(C_y)}{dt} = F_{bc} - F_{wc_y} - F_{ya_c}$	[2.68]
Ancient carbonate:	$\frac{d(C_a)}{dt} = F_{ya_c} - F_{wc_a} - F_{mc}$	[2.69]
Young pyrite IMB:	$\frac{d(\delta_{p_y} \cdot Pyr_y)}{dt}$ $= [(\delta_{OA_S} - \alpha_S) \cdot F_{bp}]$ $- (\delta_{p_y} \cdot F_{wp_y}) - (\delta_{p_y} \cdot F_{ya_p})$	[2.70]
Ancient pyrite IMB:	$\frac{d(\delta_{p_a} \cdot Pyr_a)}{dt}$ $= (\delta_{p_y} \cdot F_{ya_p}) - (\delta_{p_a} \cdot F_{wp_a})$ $- (\delta_{p_a} \cdot F_{mp})$	[2.71]

Young gypsum IMB:	$\frac{d(\delta_{gyp\_y} \cdot G_{yp\_y})}{dt}$ $= (\delta_{OA\_S} \cdot F_{bgyp})$ $- (\delta_{gyp\_y} \cdot F_{wgyp\_y})$ $- (\delta_{gyp\_y} \cdot F_{ya\_gyp})$	[2.72]
Ancient gypsum IMB:	$\frac{d(\delta_{gyp\_a} \cdot G_{yp\_a})}{dt}$ $= (\delta_{gyp\_y} \cdot F_{ya\_gyp})$ $- (\delta_{gyp\_a} \cdot F_{wgyp\_a})$ $- (\delta_{gyp\_a} \cdot F_{ms})$	[2.73]
Young C _{org} IMB:	$\frac{d(\delta_{g\_y} \cdot G_{\_y})}{dt}$ $= [(\delta_{OA\_C} - \alpha_C) \cdot F_{bg}]$ $- (\delta_{g\_y} \cdot F_{wg\_y}) - (\delta_{g\_y} \cdot F_{ya\_g})$	[2.74]
Ancient C _{org} IMB:	$\frac{d(\delta_{g\_a} \cdot G_{\_a})}{dt}$ $= (\delta_{g\_y} \cdot F_{ya\_g}) - (\delta_{g\_a} \cdot F_{wg\_a})$ $- (\delta_{g\_a} \cdot F_{mg})$	[2.75]
Young carbonate IMB:	$\frac{d(\delta_{c\_y} \cdot C_{\_y})}{dt}$ $= (\delta_{OA\_C} \cdot F_{bc}) - (\delta_{c\_y} \cdot F_{wc\_y})$ $- (\delta_{c\_y} \cdot F_{ya\_c})$	[2.76]
Ancient carbonate IMB:	$\frac{d(\delta_{c\_a} \cdot C_{\_a})}{dt}$ $= (\delta_{c\_y} \cdot F_{ya\_c}) - (\delta_{c\_a} \cdot F_{wc\_a})$ $- (\delta_{c\_a} \cdot F_{mc})$	[2.77]
Atmospheric oxygen:	$\frac{d(O_2)}{dt} = \left[F_{bg} + \left(\frac{15}{8} \cdot F_{bp} \right) \right] - (F_{wg\_y} + F_{wg\_a} + F_{mg})$ $- \left[\frac{15}{8} \cdot (F_{wp\_y} + F_{wp\_a} + F_{mp}) \right]$	[2.78]

3. Stepwise oxygenation of the Paleozoic atmosphere

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The author contributions to this work are:

A.J.K. and B.J.W.M. designed the research. A.J.K. performed the modelling. A.J.K., B.J.W.M. and S.W.P. wrote the paper, with input from S.Z., N.J.P. and T.M.L.

The Methods section of the paper has been moved to an earlier part of the text, for better integration, but as this is a published paper, the figure numbering does not follow the normal pattern. Additionally, the relatively short-form style of *Nature Communications* necessitated much of the model validation and sensitivity analyses, as well as full model equations and parameters to be moved to the supplementary information for the paper. These are now found in this chapter, as subsections of 3.6.

3.1. Introduction

Oxygen plays a vital role in planetary habitability, but the precise history of atmospheric oxygen on Earth remains a puzzle. The first rise in atmospheric O₂ concentration to appreciable levels around 2.45-2.32 Ga, termed the Great Oxidation Event (GOE), is well-defined due to the loss of mass-independent sulfur isotope fractionation as stratospheric ozone abundance increased (Farquhar, Bao and

Thiemens, 2000). The presence of fossilized charcoal (inertinite) in sediments younger than 419 Ma defines another oxygen threshold, indicating that pO_2 exceeded the levels required for combustion during this period (Belcher and McElwain, 2008; Glasspool and Scott, 2010; Glasspool *et al.*, 2015). However, the absence of fossil charcoal before 419 Ma does not necessarily point to lower atmospheric O_2 , and may simply reflect the absence of readily-combustible fuel before the evolution of woody plants (lignophytes) (Glasspool and Scott, 2010).

A variety of geochemical methodologies have been developed and applied to constrain the redox state of the ancient oceans and atmosphere between the GOE and the Devonian period (Arnold *et al.*, 2004; Poulton, Fralick and Canfield, 2004; Brocks *et al.*, 2005; Scott *et al.*, 2008; Frei *et al.*, 2009; Dahl *et al.*, 2010; Reinhard *et al.*, 2013; Guilbaud *et al.*, 2015; Sperling *et al.*, 2015; Wallace *et al.*, 2017; Stolper and Keller, 2018). Several studies point to a Neoproterozoic Oxygenation Event (Och and Shields-Zhou, 2012), but geochemical proxies also show widespread anoxia in early Paleozoic oceans. However, while marine geochemical proxies provide insightful baseline observations, it is difficult to quantitatively infer atmospheric oxygen levels from reconstructions of ocean redox chemistry (Lenton and Daines, 2017). Nevertheless, such data may be utilized and enhanced by whole Earth system biogeochemical models.

Biogeochemical ‘box models’ calculate how atmospheric oxygen concentrations may have fluctuated over the Phanerozoic Eon (541-0 Ma), with a particular strength lying in the potential for high-resolution temporal reconstruction of variability in

atmospheric oxygen levels. These models make predictions by estimating source and sink fluxes in the geological oxygen cycle, which are the burial, weathering, and tectonic recycling of organic carbon (C_{org}) and pyrite sulfur. This is possible because the residence time of O_2 in the surface system (i.e. atmosphere and ocean) is very long (>1 Myr). Box models for Phanerozoic oxygen can be computed in a number of ways with regard to the representation of elemental cycles, and how they calculate weathering and burial fluxes that transfer mass between the crust and surface system. The most prominent of these models, GEOCARBSULFvolc (Berner, 2006a, 2006b, 2009; Royer *et al.*, 2014), hereafter referred to simply as GEOCARBSULF, provides a detailed O_2 reconstruction, as it uses the extensive carbon and sulfur isotope records from sedimentary rocks, as well as time-dependent, normalized Earth system parameters (such as river runoff) to derive changes to carbon and sulfur cycling (Berner, 2006a). Other prominent box models (e.g. COPSE (Lenton, Daines and Mills, 2018) and MAGic (Arvidson, Mackenzie and Guidry, 2013)) opt instead to calculate productivity and burial of organic C and pyrite through an internal scheme of nutrient delivery and recycling. This gives them greater power to interrogate possible drivers of Earth system change but reduces the ability to make detailed predictions directly from known geological data. For example, the COPSE model's reconstructions of O_2 levels are in large part driven by the evolution of the terrestrial biosphere, through changes to the C:P ratio of biomass and rates of primary productivity on the continents, which is imposed in the model based on paleobotanical evidence (Bergman, Lenton and Watson, 2004; Lenton *et al.*, 2016; Lenton, Daines and Mills, 2018). The MAGic model (Arvidson, Mackenzie and Guidry, 2013) is similarly biosphere-driven, utilizing a dataset of the C_{org} content of the Phanerozoic sedimentary rock record (Budyko, Ronov and Yanshin, 1987) to derive a terrestrial C_{org} burial flux, rather than

using isotopic data. Because these models are driven by broad, long-term changes, they produce O_2 curves that have less detail than GEOCARBSULF. The GEOCARBSULF reconstructions, or other isotope-derived curves, are most commonly used beyond the immediate field of O_2 modelling, for example when considering O_2 impacts on animal evolution (Falkowski *et al.*, 2005; Clapham and Karr, 2012; Lyons, Reinhard and Planavsky, 2014; Schachat *et al.*, 2018).

Despite differences in the way these models operate, GEOCARBSULF, COPSE, and MAGic generally agree on the broad changes in atmospheric O_2 over the last ~400 Myrs, whereby pO_2 rose to a peak of around 25-30% atm in the Permo-Carboniferous (~300 Ma), and remained above ~18% atm thereafter (Hansen and Wallmann, 2003; Bergman, Lenton and Watson, 2004; Berner, 2009; Arvidson, Mackenzie and Guidry, 2013; Mills *et al.*, 2016; Lenton, Daines and Mills, 2018). This broad picture is also supported by the inertinite record (Glasspool and Scott, 2010). In contrast, there is considerable uncertainty in atmospheric oxygen levels during the early Paleozoic. Here, GEOCARBSULF predicts roughly present day levels of atmospheric oxygen, which are not borne out by other models (Bergman, Lenton and Watson, 2004; Lenton, Daines and Mills, 2018). More importantly, these predictions conflict both with proxy evidence for widespread anoxia, which indicate that pO_2 was below roughly half the present level (Dahl *et al.*, 2010; Sperling *et al.*, 2015; Stolper and Keller, 2018), and with the growing body of evidence for a step-change in surface oxygen levels during the Paleozoic (Fig. 3.1). This problem is further highlighted by recent work updating carbon isotope inputs in GEOCARBSULF (Schachat *et al.*, 2018), which cause the model to predict even higher levels of oxygen in the early Paleozoic, with 37% and ~35% atm in the Cambrian and Silurian, respectively (see Fig. 3.1). These results

suggest that the original GEOCARBSULF model produces increasingly unstable oxygen predictions during the Carboniferous period, back through to the Precambrian, as the pO_2 oscillations become larger.

To summarize, GEOCARBSULF is the most widely-used resource for reconstructing Phanerozoic oxygen concentrations, but the severe conflict with proxy records for the Paleozoic highlights that there may be a major problem in the model construction. Here we revisit GEOCARBSULF and challenge some of the underlying assumptions of the model, to ultimately produce a revised model and a new high-resolution reconstruction of Phanerozoic atmospheric O_2 . Our new reconstruction differs considerably from the original and is compatible with available proxy records, supporting a step-change in O_2 during the Paleozoic.

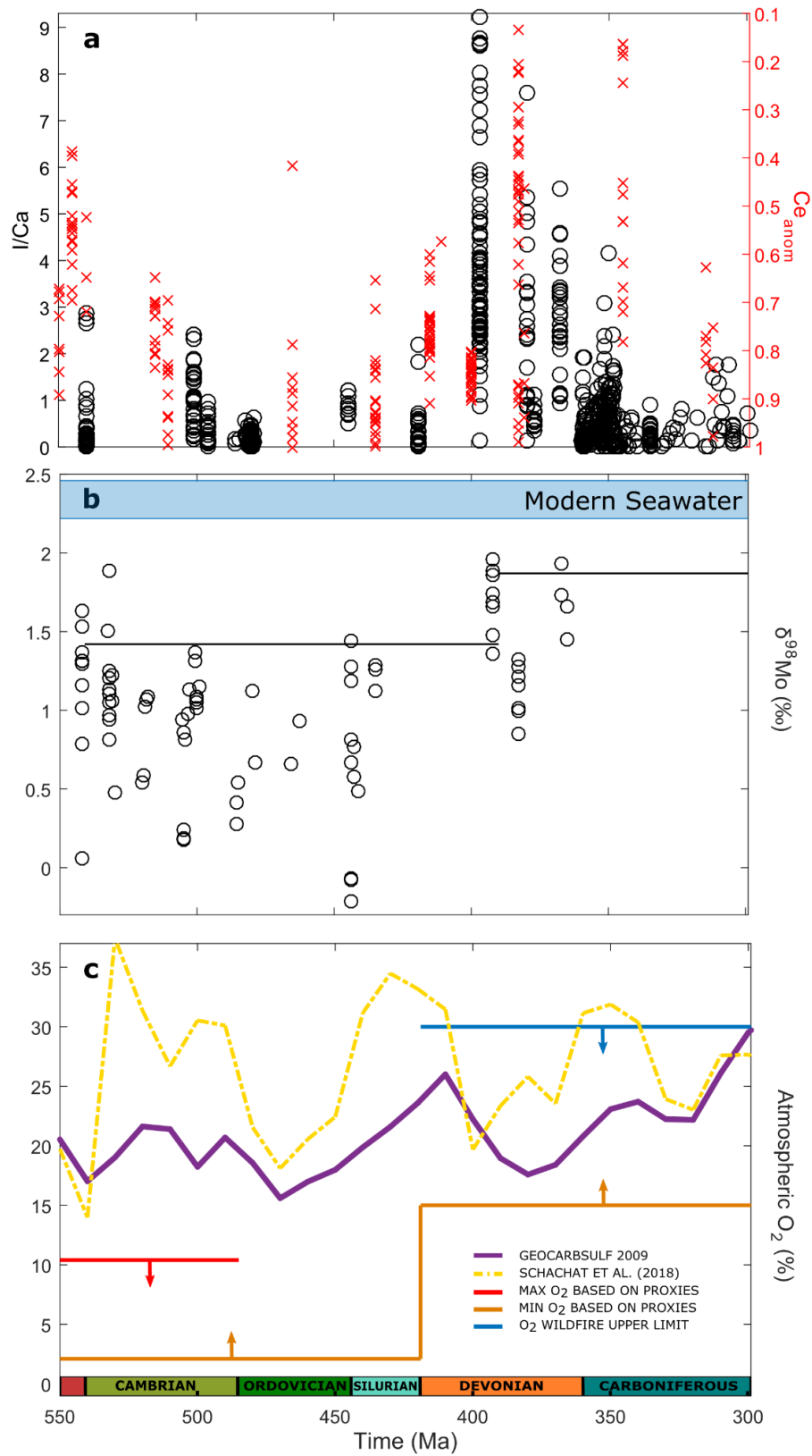
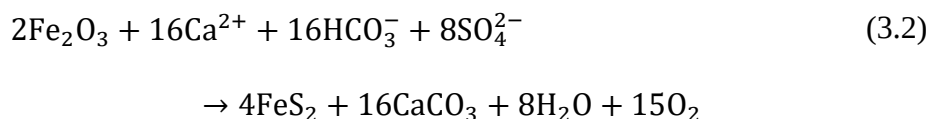
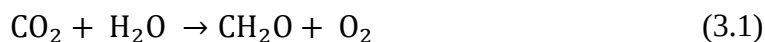


Figure 3.1 | Atmospheric O_2 levels during the early-mid Paleozoic predicted by GEOCARBSULF, compared to geochemical proxy data.

A: Iodine to calcium ratios (Lu et al., 2018), and cerium anomaly data (Wallace et al., 2017), taken from marine carbonates. Note: higher iodine to calcium ratios, and lower cerium anomaly values indicate oceanic oxygenation. B: molybdenum isotope values for the early to mid-Paleozoic, where the solid black lines represent 90% percentiles for the two time periods (Dahl et al., 2010). C: The purple line represents the atmospheric O₂ output from GEOCARBSULF (Berner, 2009), the yellow dot-dash line shows recent work to update the $\delta^{13}\text{C}$ record in GEOCARBSULF (Schachat et al., 2018), and the red line shows the approximate maximum atmospheric O₂ (10.4% atm) for the Cambrian and earlier, based on geochemical water column redox data and allowing for modelling uncertainties (Canfield, 1998, 2014; Sperling et al., 2015). The orange line is the approximate O₂ minimum, based on the same redox data, as well as Cambrian biota and wildfire oxygen requirements (Belcher and McElwain, 2008; Glasspool et al., 2015; Sperling et al., 2015). The blue line is a likely oxygen maximum, based on wildfire feedbacks, but geochemical mass balance studies suggest pO₂ levels as high as 35% atm may be permissible (Watson, 1978; Berner and Canfield, 1989; Glasspool et al., 2015).

3.2. Paleozoic oxygen controls

Box models calculate the concentration of atmospheric oxygen by estimating the geological source and sink terms. These sources and sinks are related to the cycling of carbon and sulfur: both cycles produce reduced species (photosynthetic C_{org} and pyrite sulfur derived from microbially-produced H₂S) which, when buried in sediments, leads to net oxygenation of the surface system, following equations (3.1) and (3.2) (Berner, 1987):



When these sediments are oxidatively weathered – usually following atmospheric exposure due to uplift – or are subject to metamorphism/diagenesis, the reverse of equations (3.1) and (3.2) takes place, and pyrite sulfur and C_{org} are oxidised, thus decreasing the amount of free oxygen in the system. Ultimately, the concentration of atmospheric oxygen is determined by the rates of burial of organic C and pyrite S, versus the consumption of oxygen by the weathering of these same reduced species over geologic time (Garrels and Lerman, 1984).

The GEOCARBSULF model (Bernier, 2006a; Royer *et al.*, 2014), and its predecessors (Bernier, 1987, 2001), calculate these burial rates using isotope mass balance (IMB). Both photosynthesis and microbial sulfate reduction bestow significant isotopic fractionation effects, allowing their rates to be ‘inverted’ from the known isotopic compositions of sedimentary carbonates and sulfates. However, a major uncertainty in these models is the degree to which these isotopic fractionation effects are dependent on global O_2 levels. Such a dependence of fractionation on oxygen concentration provides stabilizing negative feedback in the model, whereby higher O_2 levels imply a higher degree of carbon and sulfur isotopic fractionation, which decreases the rate of organic C and pyrite burial calculated by the inversion approach, as less organic C or pyrite needs to be buried to achieve the same change in global isotope ratios.

The fractionation between carbonates and C_{org} is reasonably well understood from plant and plankton growth experiments and theory (Berner *et al.*, 2000; Beerling, Osborne and Chaloner, 2001; Beerling *et al.*, 2002), and thus a simple equation fitted to the data is possible. By contrast, the fractionation of sulfur isotopes between sulfate and sulfide (α_s) due to bacterial sulfate reduction, is a complex process. Only ~5 – 20% of sulfide produced by sulfate reduction in shelf sediments is permanently buried as pyrite, with the remainder subject to disproportionation or reoxidation to sulfate via numerous byzantine pathways, with each step likely impacting upon the isotopic signature (Berner, 2001; Jørgensen and Nelson, 2004; Zopfi, Ferdelman and Fossing, 2004; Johnston, 2011).

For GEOCARBSULF, the sulfur isotope system was simplified and a sulfur isotope fractionation equation was derived (see equation (3.63)) based on the simple observation of larger fractionations at higher O_2 levels (Canfield and Teske, 1996), with the underlying principle being that recycling of sulfur via reoxidation and disproportionation produced the high sulfur fractionations that were not observed in existing laboratory experiments of bacterial sulfate reduction (Canfield and Thamdrup, 1994; Habicht, Canfield and Rethmeier, 1998; Sørensen and Canfield, 2004). More recent experimental studies (e.g. Sim, Bosak and Ono, 2011) have, however, shown that large sulfur isotope fractionations can be obtained from microbial sulfate reduction alone, without the need for disproportionation, although the significance of this contribution to the global sulfur isotope fractionation record over geologic time remains unclear. Furthermore, as Jørgensen and Nelson (2004) note, pyrite can be oxidized in anoxic settings through abiotic pathways (e.g. via manganese oxides), and thus the disproportionation pathway for large sulfur isotope fractionation is not

necessarily dependent on higher pO_2 levels. Additionally, the source of sulfate and its isotopic signature are important to know in order to derive fractionation values. While most sulfate in marine settings comes from bottom water sulfate, some fraction comes from the oxidation of organic sulfur compounds in particulate organic matter (Fakhraee, Li and Katsev, 2017). A lot of work has gone into elucidating the cryptic nature of the marine sulfur cycle, but it remains difficult to determine a quantitative relationship between oxygen concentration and sulfur isotope fractionation on a global scale, due to the nature of this cycling, which may have also changed over geologic time. Consequently, the equation used in GEOCARBSULF contains a considerable amount of uncertainty.

Crucially, the formulation chosen results in a very strong O_2 feedback from the sulfur cycle in GEOCARBSULF. As pO_2 levels begin to decrease, the sulfur isotope fractionation value calculated by the model also decreases. This smaller fractionation results in an increase in pyrite burial calculated from isotope mass balance, and subsequently, a rise in O_2 production (see Fig. 3.2). Atmospheric oxygen levels <10% atm therefore result in an unrealistically low sulfur isotope fractionation (less than 10‰) and generate extremely large (~1 – 2 orders of magnitude higher than present day) amounts of pyrite burial. The concentration of atmospheric oxygen is thus tightly constrained by the sulfur cycle in the model, resulting in Paleozoic pO_2 values that are close to present day (see Fig. 3.1), with low values of atmospheric oxygen being unobtainable.

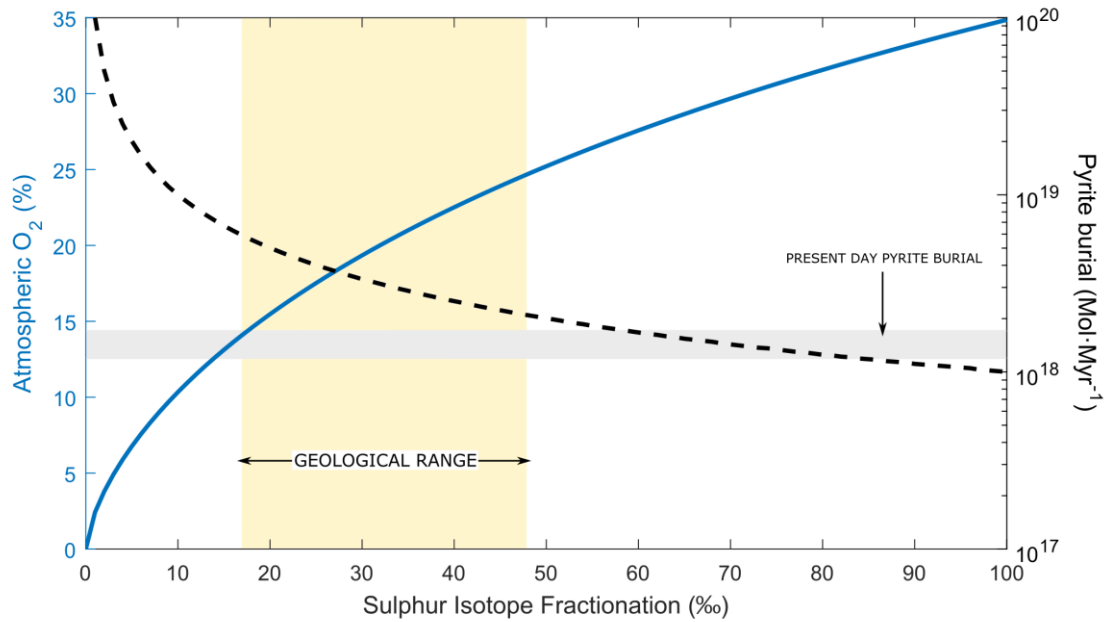


Figure 3.2 | The relationship between sulfur isotope fractionation and oxygen concentration in GEOCARBSULF.

The blue line shows the sulfur isotope fractionation (α_s) generated by the equation used in the original GEOCARBSULF model for different concentrations of atmospheric O_2 , and the dashed black line shows the resultant pyrite burial flux. The yellow box represents the bounds of the geologic record for sulfur isotope fractionation between sulfate and pyrite over the last 570 Myrs, based on datasets from Wu et al. (2010) and the grey box represents estimated modern day pyrite burial levels (Berner, 1982; Hu and Cai, 2011).

3.3. Model development

3.3.1. Introduction

We update the GEOCARBSULF model to incorporate a process-based sulfur cycle that does not depend on inverting the $\delta^{34}\text{S}$ isotope record to calculate fluxes, and therefore does not rely on estimating oxygen-related changes in the fractionation factor. To do this we replace the equations which calculate the weathering and burial rates of both reduced (i.e. pyrite) and oxidized (i.e. gypsum) sulfur species with those used in the COPSE model (Bergman, Lenton and Watson, 2004). In this modified system, the O_2 source from pyrite burial depends on the concentration of oceanic sulfate, the supply of organic matter to sediments, and the average oceanic dissolved oxygen concentration, thus retaining some level of $p\text{O}_2$ -dependent feedback (see section 3.3.4. for further details). We also make modifications to the model which follow previous work: the carbon isotope record used to drive the model is updated to the latest compilation (Saltzman and Thomas, 2012; Mills *et al.*, 2016), and oxidative weathering of fossil C_{org} is assumed to be sensitive to $p\text{O}_2$ (Daines, Mills and Lenton, 2017). Rather than alter existing code, we build the new model from scratch and name the new model GEOCARBSULFOR, indicating that it uses a ‘forwards’ sulfur system, wherein sulfur cycle dynamics are calculated from other model processes, instead of the $\delta^{34}\text{S}$ record. The isotope record is used instead for model validation.

3.3.2. Model reconstruction

The GEOCARBSULF (Berner, 2006a, 2009) model was reconstructed in MATLAB and, using a four-stage implicit Runge-Kutta method, was solved numerically

(Shampine and Reichelt, 1997; Ashino, Nagase and Vaillancourt, 2000). The Runge-Kutta method uses a variable-step, variable-order, stiff ODE solver, which allows the model to generate outcomes with a high accuracy, whilst retaining stability, thus permitting updates to several parameters, with a reduction in model failure compared to the original model code (Shampine and Reichelt, 1997; Ashino, Nagase and Vaillancourt, 2000; Royer *et al.*, 2014).

3.3.3. Data updates

The $\delta^{13}\text{C}$ record was updated to use data from Saltzman and Thomas (2012), to which we applied a 10 Myr moving average, and the data was smoothed to eliminate variations in the short term. The $\delta^{34}\text{S}$ record, which was required for testing our model, was updated to use data from Wu *et al.* (2010). The dimensionless parameters: f_{A} ; f_{D} ; f_{L} ; $GEOG$, as well as γ , all of which are defined in Chapter 2 but again in section 3.6.2. in this chapter, were revised to those employed by Royer *et al.* (2014), some of which are based on the work of Godd  ris *et al.* (2012) An additional parameter f_{AW} , used by Royer *et al.* (2014) was included, but we observe that their original data for this parameter was not normalized to the present, as all other parameters for GEOCARBSULF are, thus we have updated these values.

3.3.4. Sulfur cycle

The weathering and burial equations for young pyrite and gypsum were altered to those used in the COPSE model (Bergman, Lenton and Watson, 2004).

The weathering equations follow the reasoning that most gypsum is weathered with carbonate rocks, and most pyrite is weathered with silicate rocks, therefore they can include a dependency on the carbonate and silicate weathering functions (Berner and Canfield, 1989). As COPSE does not utilize the rapid recycling inherent in GEOCARBSULF, changes were made to the young weathering fluxes. The ancient weathering fluxes remained as per GEOCARBSULF, but with an oxidative feedback function added to the weathering of ancient pyrite.

The pyrite burial equation was altered to eliminate the reliance on the sulfur isotope fractionation present in GEOCARBSULF, whilst retaining an oxygen dependent feedback on the amount of pyrite buried at each time step. As the model remains close to steady state throughout its run, the gypsum burial equation was modified to reduce the limitation the original equation imposed on pyrite burial. The new weathering and burial equations are as follows:

$$F_{wp\_y} = \frac{F_{ws}}{F_{ws\_0}} \cdot new\_kwp \cdot \frac{Pyr\_y(t)}{Pyr\_0} \cdot O_{2mr}^{0.5} \quad (3.3)$$

$$F_{wgyp\_y} = \frac{F_{wc\_y}}{F_{wc\_y0}} \cdot new\_kwgyp \cdot \frac{Gyp\_y(t)}{Gyp\_0} \quad (3.4)$$

$$F_{bp} = k_{bp} \cdot \frac{OA\_S(t)}{OA\_S\_0} \cdot \frac{F_{bg}(t)}{F_{bg\_0}} \cdot \frac{1}{O_{2mr}} \quad (3.5)$$

$$F_{bgyp} = k_{bgyp} \cdot \frac{OA\_S(t)}{OA\_S\_0} \cdot Calc \quad (3.6)$$

Where:

F_{wp_y} is the young pyrite weathering flux; F_{wgyp_y} is the young gypsum weathering flux; F_{bp} is the pyrite burial flux; and F_{bgyp} is the gypsum burial flux.

F_{ws} is the silicate weathering flux at time (t); F_{ws_0} is the present day silicate weathering flux; new_kwp is the pyrite weathering rate constant; $Pyr\_y(t)$ is the size of the young pyrite reservoir at time (t); Pyr_0 is the size of the young pyrite reservoir at present day. F_{wc_y} is the carbonate weathering flux at time (t); F_{wc_y0} is the present day carbonate weathering; new_kwgyp is the gypsum weathering rate constant; $Gyp\_y(t)$ is the size of the young gypsum reservoir at time (t); and Gyp_0 is the size of the young gypsum reservoir at present day. $OA\_S(t)$ is the size of the ocean sulfate reservoir at time (t); OA_S_0 is the size of the ocean sulfate reservoir at present day; $F_{bg}(t)$ is the C_{org} burial flux at time (t); F_{bg_0} is the C_{org} burial flux at present day; k_{bp} is the pyrite burial rate constant; and k_{bgyp} is the gypsum burial rate constant.

$Calc$ is the normalized calcium reservoir (Horita, Zimmermann and Holland, 2002), which is dimensionless, as is O_{2mr} : the normalized amount of O_2 in the ocean-atmosphere reservoir. All other reservoir sizes are in moles, and fluxes are in moles per Myr.

Finally, we make some alterations to the total amount of sulfur, and the apportioning of this to the various reservoirs, in the model. In the original GEOCARBSULF, the total amount of sulfur in the system is 638×10^{18} moles. First, we reduce the total amount of sulfur in the system to 418×10^{18} moles; we have conservation of mass in the model, so this reduction allows the model to run with a total sulfur value roughly equivalent to that used by Kump and Garrels (1986). Next, we challenge GEOCARBSULF's assumption that the initial sizes of the pyrite and gypsum

reservoirs are equal to each other (combined young and ancient pyrite is 300×10^{18} moles, as is the combined young and ancient gypsum). Following the work of Canfield and Farquhar (2009), who provide evidence for a Proterozoic dominated by pyrite burial, with low gypsum deposition across the Ediacaran-Cambrian boundary, we adjust the balance of the sulfur distribution across the sedimentary reservoirs. We retain GEOCARBSULF's ocean-atmosphere reservoir value of 38×10^{18} moles, and then start the model run at 570 Ma, with total gypsum equal to 100×10^{18} moles, and total pyrite equal to 280×10^{18} moles (see section 3.6.1. and Fig. 3.12 for further information), thus changing the pyrite to gypsum ratio from 1:1 to 2.8:1.

3.3.5. Changes to other fluxes and reservoirs

The changes we made to the sulfur cycle resulted in the need to update other fluxes in the model. In the original GEOCARBSULF, degassing fluxes are contingent on spreading rates at time (t) multiplied by the present-day rate, while ancient reservoirs are forced to remain at steady state throughout an entire model run. These formulations introduce a rigidity to the model's operations, which can be a source of failure, as the model cannot stabilize itself quickly enough following large perturbations. The following changes make the model more dynamic, allowing it to respond faster to fluctuations in the system.

We modified the original equations for the degassing of ancient reservoirs of pyrite, gypsum, C_{org} , and carbonate, so the degassing flux calculated at each time step was dependent on the total amount of material in each reservoir, multiplied by a rate constant and the spreading rate at time (t), with an additional dependence on the

relative proportions of carbonates on shallow platforms or the deep ocean for carbonate degassing.

The weathering equations for ancient C_{org} and ancient carbonates were also updated: replacing the terms: F_{wg_a0} and F_{wc_a0} – the modern day weathering fluxes for ancient C_{org} and ancient carbonates respectively – with a rate constant multiplied by the total amount of material in each reservoir at each time step; we also include an oxidative feedback to the weathering equations for young and ancient C_{org} .

Finally, the equations governing the flux of material from young to ancient reservoirs at each iteration were altered, to allow the total amount stored in the ancient reservoirs to vary, instead of remaining constant over geologic time. This young to ancient flux is now dependent on the total amount stored in the respective young reservoir multiplied by a rate constant. The model remains in a steady state, but the total mass apportioned to each reservoir at each time step, by the model, has greater variance.

3.4. Model predictions

Our GEOCARBSULFOR model generates significantly different predictions for Phanerozoic pO_2 levels, relative to those generated by the original GEOCARBSULF model (Fig. 3.3). This is particularly evident in the early Paleozoic, where O_2 levels from GEOCARBSULFOR are much lower than the modern-day levels predicted by the original, and generally agree with geochemical redox proxies for this time period (Dahl *et al.*, 2010; Sperling *et al.*, 2015; Wallace *et al.*, 2017; Lu *et al.*, 2018). A

number of O₂ variations in the new model can be linked to geobiological events, denoted with numbers in Figure 3.3. The model calculates a transient rise in oxygen coincident with the Cambrian explosion (#1), which relaxes as bioturbation intensifies during Cambrian Stages 2 to 4 (Boyle *et al.*, 2014) (#2). Bioturbation likely resulted in the increased burial of bioavailable phosphorus in sediments, thus limiting primary productivity and oxygen production, and exposed C_{org} and pyrite buried in anoxic sediments, to the overlying oxic water column, which led to oxidation (Boyle *et al.*, 2014; van de Velde *et al.*, 2018). A second transient increase in *p*O₂ begins around 500 Ma, driven in the model by the Steptoean positive carbon isotope excursion (#3), which suggests high rates of C_{org} burial and subsequently oxygen production (Saltzman *et al.*, 2011).

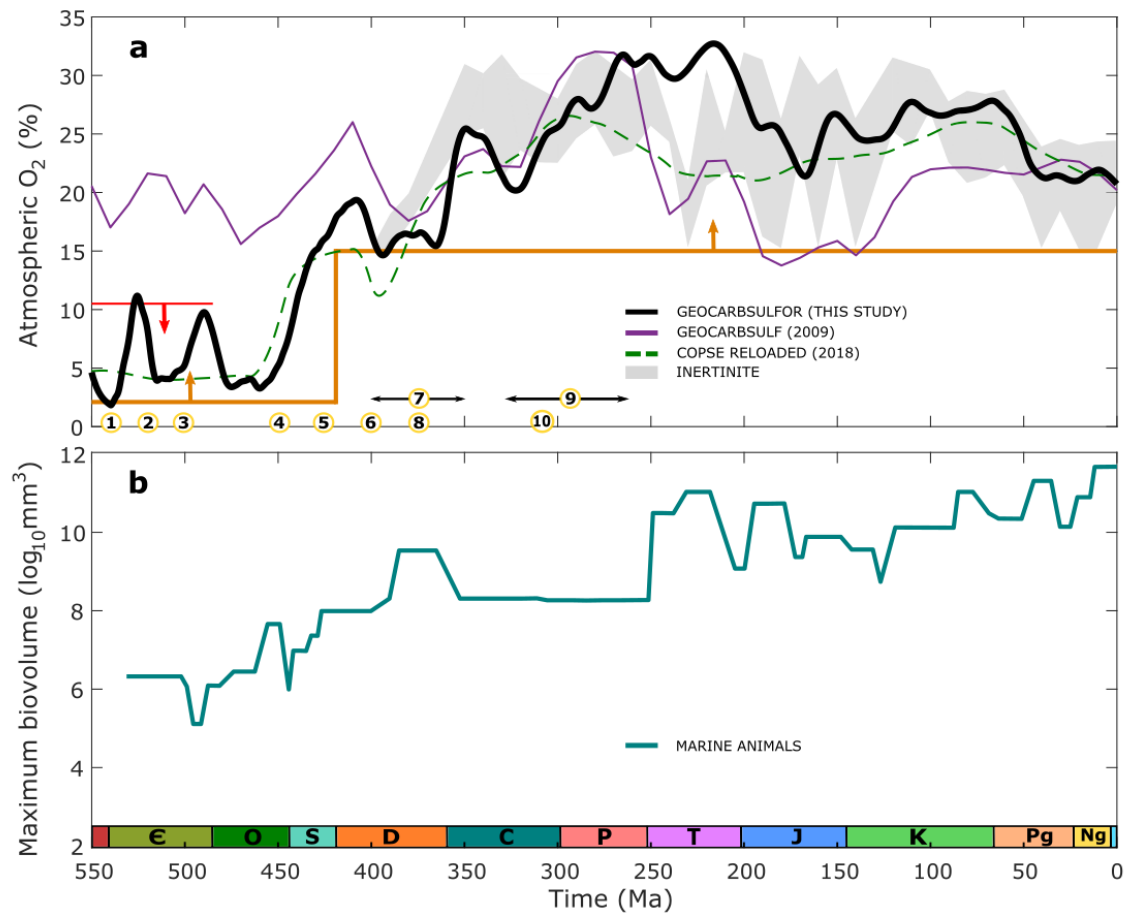


Figure 3.3 | Results of GEOCARBSULFOR compared to GEOCARBSULF (2009), the COPSE model, and to geochemical proxies.

A: The black line represents the results from GEOCARBSULFOR, the purple line is the original GEOCARBSULF (Berner, 2009) and the green line is COPSE (Lenton, Daines and Mills, 2018). The grey envelope shows pO_2 predictions from inertinite data (Glasspool and Scott, 2010), and the arrowed lines show the boundaries from Figure 3.1. The numbered circles denote: 1) the beginning of the Cambrian explosion and a decrease in cerium anomaly values 2) bioturbation intensification 3) the Steptoean positive carbon isotope excursion event 4) the Great Ordovician Biodiversity Event and evidence of the first land plant spores 5) earliest evidence for vascular land plants 6) initial evidence for a rise in $\delta^{98}Mo$ and I/Ca and a decrease in cerium anomaly values 7) a reduction in abundance of fossilized charcoal 8) the

first forests 9) widespread mires 10) a collapse in coal forests, and a rise to dominance of tree ferns (Sahney, Benton and Falcon-Lang, 2010; Saltzman et al., 2011; Belcher, Collinson and Scott, 2013; Boyle et al., 2014; Glasspool et al., 2015; Edwards et al., 2017; Wallace et al., 2017; Lu et al., 2018). B: Marine animal body size (Heim et al., 2015) evolution over the Phanerozoic. C – Cambrian, O – Ordovician, S – Silurian, D – Devonian, C – Carboniferous, P – Permian, T – Triassic, J – Jurassic, K – Cretaceous, Pg – Paleogene, Ng – Neogene.

GEOCARBSULFOR predicts a clear rise in pO_2 during the mid-Paleozoic at the time of the Great Ordovician Biodiversity Event (#4). At roughly the same time, the maximum biovolume of marine animals began to increase from 10^6 mm^3 to $>10^9 \text{ mm}^3$ in the Devonian (Fig. 3.3, panel B), which ties in with the radiation of large predatory fish that had increased oxygen demands (Dahl et al., 2010; Heim et al., 2015). While atmospheric O_2 concentration oscillated between ~2-11% atm during the Cambrian to mid-Ordovician, the mid-Paleozoic rise (the timing of which is in broad agreement with recent work, (Lenton et al., 2016; Edwards et al., 2017; Lenton, Daines and Mills, 2018; Stolper and Keller, 2018)) to near modern-day levels in the Devonian coincides with the rise of vascular plants (#5). This marked a transition to an Earth system with pO_2 levels generally above 15% – the level required to sustain smouldering fires (Belcher and McElwain, 2008) and a level complemented by the results from several novel geochemical proxies (#6) (Dahl et al., 2010; Wallace et al., 2017; Lu et al., 2018). A nadir of ~14.5% atm in the mid-Devonian (across the Emsian-Eifelian boundary at ~393 Ma) and generally lower pO_2 predictions during the mid-Emsian to end Famennian stages (~400-360 Ma) are compatible with the scarcity (but not total absence) of fossilized charcoal (#7) during this period, and with both modelling and

experimental work exhibiting the low probability of achieving combustion when $pO_2 < 19\%$ atm (Scott and Glasspool, 2006; Belcher and McElwain, 2008; Belcher, Collinson and Scott, 2013; Glasspool *et al.*, 2015).

GEOCARBSULFOR, and the original GEOCARBSULF, are driven primarily by the carbon isotope record, and as such, the model distinguishes a major change in the carbon cycle from the Ordovician to Carboniferous periods, which we attribute to the expansion of land plants and the rise of the first forests (#8), due in part, to terrestrial biomass having a much greater C:P ratio than marine organic matter (Bergman, Lenton and Watson, 2004). This is consistent with the biosphere driven method of COPSE (Lenton, Daines and Mills, 2018), which in a recent iteration of the model, assumes an increase in total C_{org} burial with the rise of land plants from ~470 Ma onwards, generating a rise in pO_2 at this time (green dashed line in Fig. 3.3). The MAGic model, on the other hand, assumes that land plant material makes a relatively small contribution to total C_{org} burial today – which contrasts with data suggesting a large contribution (Burdige, 2005, 2007). Therefore, in MAGic, land plant evolution has little effect on C_{org} burial, and thus does not replicate this oxygenation event (Arvidson, Mackenzie and Guidry, 2013).

In the mid-Carboniferous (Bashkirian, 323 Ma), the pO_2 output from GEOCARBSULFOR briefly dips to ~20%, having been >25% in the early Mississippian. This decrease generally matches a drop in sea level at the time (van der Meer *et al.*, 2017), which possibly exposed previously buried organic C to oxidative weathering. Following this, pO_2 levels rise once more to >20%, and this is concurrent

with the appearance of widespread mires (#9), firstly in Euramerica, and then in Gondwana, Cathaysia and Angara, which provided ideal conditions for enhanced preservation of buried organic C (Scott and Glasspool, 2006; Glasspool *et al.*, 2015). Towards the end of the Carboniferous there was a collapse in the coal forests (#10), and opportunistic tree ferns took over as the dominant land plant species, probably due to aridification (Sahney, Benton and Falcon-Lang, 2010). Despite this change to vegetation, pO_2 levels in our model do not drop, as swamp and mire conditions remained prevalent until near the end of the Permian, and thus organic C continued to be preserved (Glasspool *et al.*, 2015).

The model results match well those from the oxygen proxy from inertinite data (Glasspool and Scott, 2010) – which back calculates pO_2 based on charcoal abundance in mire settings – for most of the Phanerozoic, and provides a better fit to this proxy than the original GEOCARBSULF. However, there is a large discrepancy between GEOCARBSULFOR and this inertinite proxy, and between both GEOCARBSULFOR and GEOCARBSULF/COPSE, in the Triassic. The original GEOCARBSULF predicts a rapid decline in pO_2 at the Permian-Triassic boundary, and while no early Triassic coals have yet been found, the inertinite proxy suggests that pO_2 would have declined substantially (to ~18.5%) by the mid-Triassic (Glasspool and Scott, 2010). Yet, GEOCARBSULFOR suggests that atmospheric oxygen was around 30% for this entire period.

There are two reasons for this conflict; first, the isotope record used by the original GEOCARBSULF indicated a ~4‰ decrease in $\delta^{13}C$ at the end of the Permian, whereas

the more recent records used for GEOCARBSULFOR shows a decrease of only ~1.5%. As such, there is a rapid decline in the amount of C_{org} buried in GEOCARBSULF, which is not matched to the same degree in GEOCARBSULFOR. Uncertainties surrounding the carbon isotope record are discussed further below. Secondly: pyrite burial in GEOCARBSULFOR is now partially dependent on the amount of sulfate in the ocean. During the Triassic, GEOCARBSULFOR predicts – and is validated by geochemical proxies and other modelling work (see Fig. 3.10) – quite high levels of sulfate, with only a moderate decline over this period. This means pyrite burial rates for GEOCARBSULFOR do not decrease as substantially as they did in GEOCARBSULF, as sulfate levels buffer, to a degree, the changes to the C_{org} burial rates at this time. In the latest version of COPSE (Lenton, Daines and Mills, 2018), the C:P land plant stoichiometry was updated, to factor in a decrease in C:P (from 2000:1 to 1000:1) over 345 – 300 Ma, and a new forcing: coal basin depositional area, was introduced, with a high depositional area in the Carboniferous and a sharp decline at the end of the Permian. These forcings in the COPSE model serve to keep predicted pO_2 levels much lower than those by GEOCARBSULFOR, over the end of the Permian and the Triassic.

3.5. Discussion

The key differences between the Paleozoic predictions of GEOCARBSULFOR and the original GEOCARBSULF model arise from the modified sulfur cycle, rather than the new isotope data. We tested this by inputting the new $\delta^{13}C$ record, taken from Saltzman and Thomas (2012), into the original GEOCARBSULF model, and then using the $\delta^{13}C$ record from the 2009 GEOCARBSULF paper to drive

GEOCARBSULFOR (see Fig. 3.4). Using the new C isotope data in the original model results in early Paleozoic pO_2 levels which are broadly similar to those from the original model. However, using the older isotope record in our new model produces low pO_2 in the early Paleozoic, followed by near identical results from the mid-Carboniferous onwards. This leads us to conclude that atmospheric oxygen levels in the early Paleozoic are highly dependent on the sulfur cycle, although the carbon cycle helps to constrain some of the timings and magnitude of changes to pO_2 .

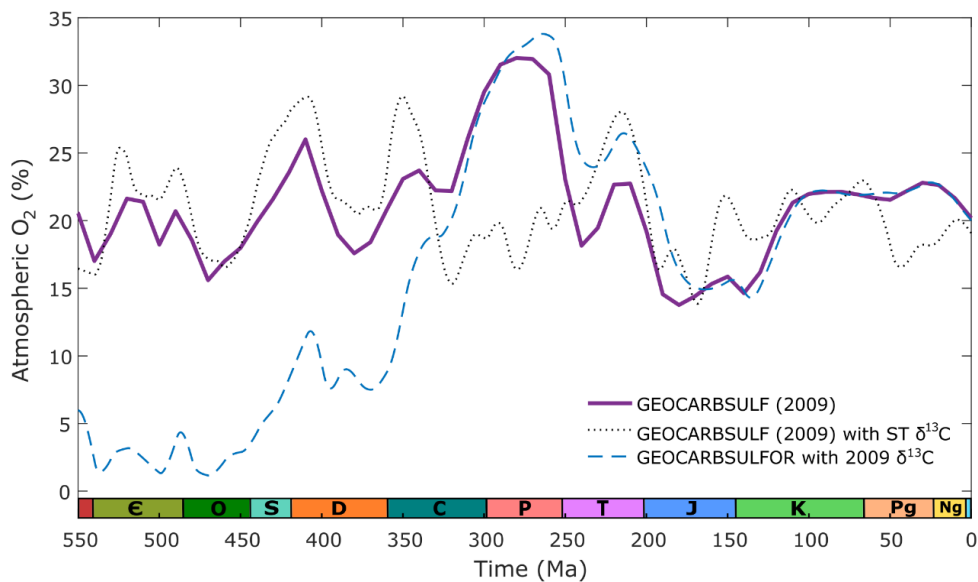


Figure 3.4 | Sulfur cycle versus carbon isotope modifications.

The purple line is the original GEOCARBSULF pO_2 prediction (Berner, 2009), the black dotted line is the original GEOCARBSULF model but with the $\delta^{13}C$ record updated to use data from Saltzman and Thomas (2012), and the blue dashed line is GEOCARBSULFOR but with the isotope data from the original GEOCARBSULF model.

As our model computes the sulfur cycle mechanistically, rather than relying on isotope inversion, it can output a synthetic $\delta^{34}\text{S}$ record, which may be compared to geological data. The model output does not reproduce the full degree of variability in measured $\delta^{34}\text{S}$, but it does remain within, or very close to, the data range defined by the record, giving confidence that the modified sulfur cycle is an accurate representation (Fig. 3.7).

Several uncertainties regarding O_2 levels are still inherent within the model; including the definitions of the mass fluxes and uncertainties in the carbon isotope record itself. The carbon cycle, primarily via C_{org} burial, in GEOCARBSULF is heavily dependent on the $\delta^{13}\text{C}$ record input into the model. The compilation by Saltzman and Thomas (2012) provides a comprehensive set of data for all geologic time, but as they acknowledge, differences in the materials analysed (calcareous organisms, bulk versus component), sediment sources (epeiric seas vs. open oceans), temperature, diagenetic alteration (in the case of high Mg calcite brachiopod shells) etc., can demonstrate variability in the isotopic signature they produce (Buggisch and Joachimski, 2006; Panchuk, Holmden and Leslie, 2006; Mills *et al.*, 2016).

We conducted a sensitivity analysis to test the effect of variations in the $\delta^{13}\text{C}$ dataset on $p\text{O}_2$ predictions for our model (see Fig. 3.5). An initial attempt was made to run the model with a $\pm$ one standard deviation to the $\delta^{13}\text{C}$ record, with all other parameters remaining as they were in our baseline run (GEOCARBSULFOR – red line in Fig. 3.5). The model deals adequately with the plus one standard deviation change, however, the minus one standard deviation results in model failure almost

immediately, as pO_2 crashes to 0%. Although our treatment of the Saltzman and Thomas (2012) data has smoothed out some of the more extreme $\delta^{13}C$ excursions, and our numerical method has made the model more resilient, the model may be missing some additional stabilising feedbacks that can counter particularly negative $\delta^{13}C$ values, especially at model initiation. The model thus remains highly sensitive to the $\delta^{13}C$ record used, but the general trend in oxygenation remains the same. Further revisions to the Saltzman and Thomas (2012) compilation or a different treatment of the data may, however, result in significant differences to the computed evolution of Phanerozoic oxygen levels.

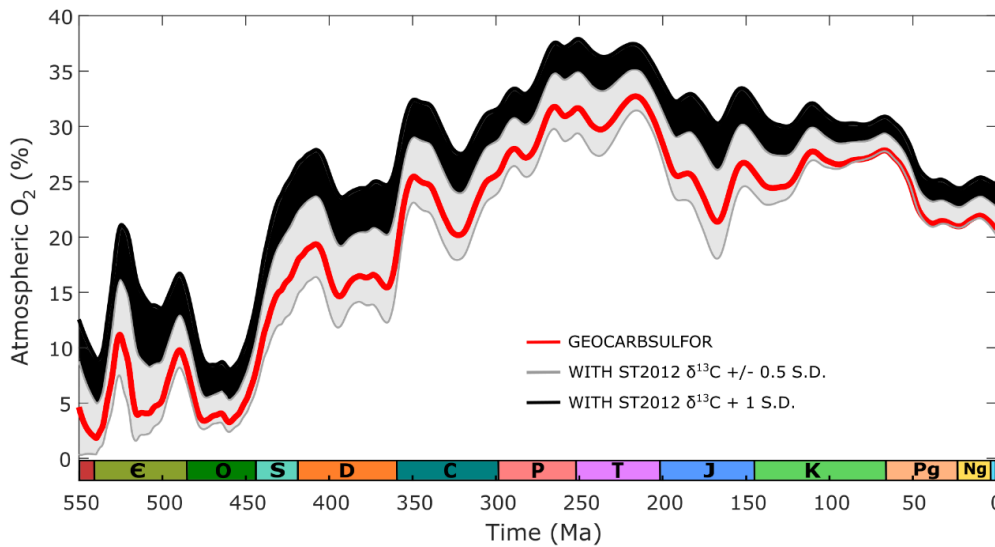


Figure 3.5 | Atmospheric O_2 sensitivity to changes in the $\delta^{13}C$ record.

The red line is our GEOCARBSULFOR model with updates as described in the main paper, the grey envelope is the atmospheric O_2 generated by $\pm$ half a standard deviation change to the ocean-atmosphere $\delta^{13}C$ record, based on the Saltzman and Thomas (2012) data, and the black envelope is the + one standard deviation.

We performed a further sensitivity analysis, by investigating the effect of changes to the parameter, J , which is used in the model to alter the effects of oxygen concentration on carbon isotope fractionation (see equation (3.29)). In our baseline run, following the original model, we use $J = 4$. A recent study by Edwards *et al.* (2017), has used this equation to estimate atmospheric oxygen concentrations from the $\delta^{13}\text{C}$ record in organic C and carbonates, using values for J of 2.5 to 7.5. We compare our results in Figure 3.6.

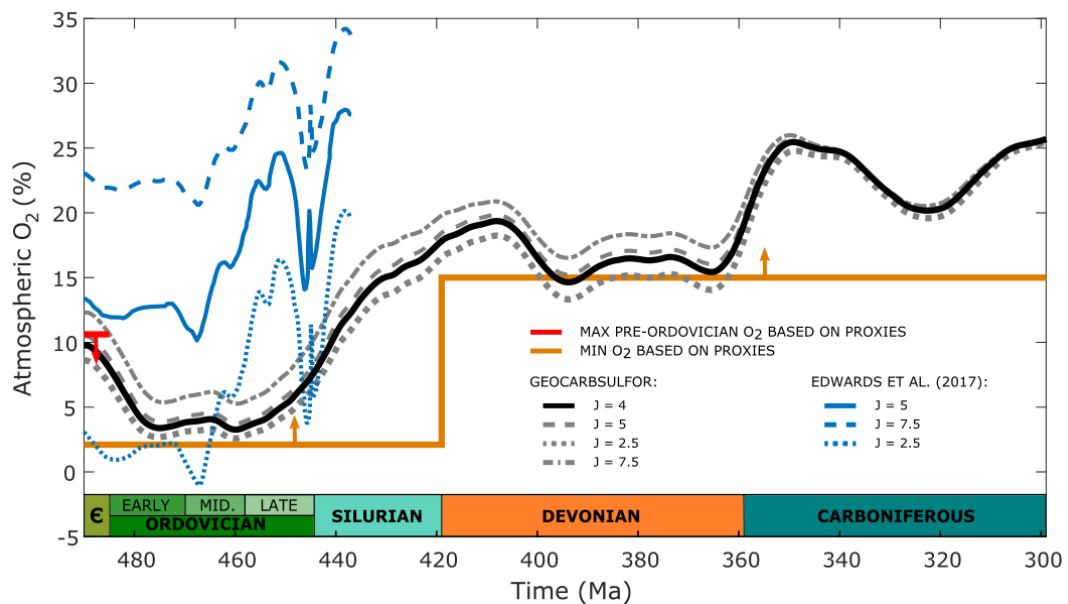


Figure 3.6 | The effect of the parameter, J , on GEOCARBSULFOR oxygen outputs, compared to another method of calculating atmospheric oxygen.

The black line is our baseline model run with $J = 4$. The grey dashed line is $J = 5$, the grey dotted line is $J = 2.5$, and the grey dot-dash line is $J = 7.5$ for our GEOCARBSULFOR model. The blue line is $J = 5$, the dashed line is $J = 7.5$ and the dotted line is $J = 2.5$ from Edwards *et al.* (2017) The red line shows the approximate maximum atmospheric O_2 (10.4% atm) for the Cambrian and earlier, based on

geochemical water column redox data and allowing for modelling uncertainties (Canfield, 1998, 2014; Sperling et al., 2015). The orange line is the approximate O_2 minimum, based on the same redox data, as well as Cambrian biota and wildfire oxygen requirements (Belcher and McElwain, 2008; Glasspool et al., 2015; Sperling et al., 2015).

GEOCARBSULFOR does not show as great a temporal variability in pO_2 levels during this period and shows considerably less sensitivity to changes in the J parameter due to the much greater complexity of the model adding negative feedbacks that buffer against change. Nevertheless, both methods show an increase in atmospheric O_2 between the mid Ordovician and early Silurian. Additional sensitivity analyses and comparisons to other work were performed to confirm the robustness of low early Paleozoic O_2 and provide further validation of our model. These can be found in section 3.6.1.

Overall, GEOCARBSULFOR shows a clear transition from an Earth with relatively low pO_2 (in terms of % atm), to a planet with an abundance of free atmospheric oxygen, in the process paving the way for the evolution of large terrestrial fauna. This well-defined, stepwise oxygenation – a Paleozoic Oxygenation Event (POE) – was coincident with the advent of terrestrial vascular plants, which fundamentally changed the geologic oxygen cycle. Our prediction of low pO_2 in the early Paleozoic removes a central disagreement between the results of GEOCARBSULF with those of other models, and between the model and geochemical proxies. More importantly, we develop here a robust, detailed model for Phanerozoic O_2 evolution that shows a number of potential links between atmospheric composition and biosphere evolution.

This model provides a baseline against which to further investigate these ideas, and the opportunity to extend these approaches to investigate the Precambrian and the Neoproterozoic Oxygenation Event (Och and Shields-Zhou, 2012).

3.6. Supplementary information

3.6.1. Model validation and further sensitivity analyses

In order to check the robustness of our new model, GEOCARBSULFOR, we conducted a number of tests, to compare various model outputs to available geologic data. We also completed a further sensitivity analysis, to measure the effect different formulations of pyrite weathering have on atmospheric oxygen levels.

We generated a synthetic ocean $\delta^{34}\text{S}$ sulfate record from the model, for comparison against the geological record (Fig. 3.7). Using a static sulfur isotope fractionation factor (α_s) for the entire time period, we conducted three model runs, with: $\alpha_s = 16.7\text{‰}$ – the lowest value recorded by Wu *et al.* (2010); $\alpha_s = 48.1\text{‰}$ – the highest value recorded by Wu *et al.* (2010); and $\alpha_s = 35.95\text{‰}$ – the average for the period 570 Ma to Present, calculated using the Wu *et al.* (2010) dataset.

Our GEOCARBSULFOR model is sensitive to the fractionation factor used, but the average value generates an ocean $\delta^{34}\text{S}$ sulfate record which is in good agreement with the geologic record for almost the entire run. The highest fractionation factor provides

a $\delta^{34}\text{S}$ sulfate record that closely matches the geologic record from the end-Permian onwards, and this is coincident with an actual rise to higher fractionation values (Wu *et al.*, 2010) during this time period. Although the $\delta^{34}\text{S}$ output using the lowest fractionation value is very low for the entire run, the actual sulfur isotope fractionation is only very low ($\leq 22.1\text{‰}$) for the period 570 – 540 Ma, with higher values ($\geq 27.5\text{‰}$) for the Phanerozoic itself (Wu *et al.*, 2010). Model runs with separate fractionation values for the periods 570 – 540 Ma, and 530 Ma – Present, give $\delta^{34}\text{S}$ records which are closer to the geological one. Additionally, the $\delta^{34}\text{S}$ output is sensitive to the starting $\delta^{34}\text{S}$ value of the sulfur reservoir. We use a value of 23‰ for 570 Ma, following Wu *et al.* (2010) for consistency, however, using the original GEOCARBSULF value of 35.2‰ and the highest fractionation (48.1‰) produces a $\delta^{34}\text{S}$ record which for the last 250 Ma is near identical to the geologic record.

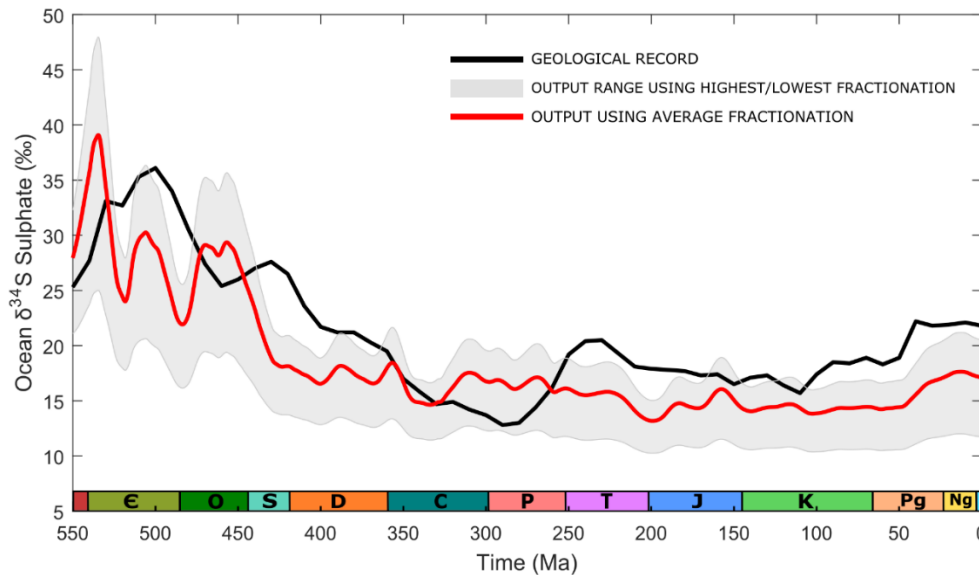


Figure 3.7 | Ocean sulfate isotope predictions for the Phanerozoic from our GEOCARBSULFOR model.

The red line is the ocean $\delta^{34}\text{S}$ output using a static average isotopic fractionation from 570 Ma to Present (35.95‰), calculated from the Wu *et al.* (2010) dataset. The

grey envelope is the ocean $\delta^{34}\text{S}$ output using the lowest (16.7‰) and highest (48.1‰) fractionation values from Wu et al. (2010) The black line is the geologic $\delta^{34}\text{S}$ data from Wu et al. (2010).

We conducted a test to ascertain whether simply substituting the sulfur isotope fractionation equation in the original GEOCARBSULF with the Wu et al. (2010) fractionation data, would produce low $p\text{O}_2$ in the early Paleozoic, as Wu et al. (2010) take into account the effects of reoxidation and disproportionation on sulfide (though not the possibility of other sinks, such as organic sulfur) changing the isotopic signature of sedimentary pyrite. This change leads to unfeasibly high (considering geochemical redox data, e.g. Sperling et al., 2015; Wallace et al., 2017) oxygen concentrations of >35% atm in the early Paleozoic, and negative O_2 during the late-Mesozoic to Cenozoic. Therefore, a $p\text{O}_2$ dependent feedback embedded somewhere in the sulfur cycle is a requirement for the model to produce reasonable levels of atmospheric O_2 .

As GEOCARBSULFOR can calculate the amount of pyrite and sulfate being buried at each time-step, we examined whether the model was generating reasonable values for the fraction of total sulfur leaving the ocean as pyrite (f_{pyr}), by comparing the model outputs to other modelling approaches (Canfield and Farquhar, 2009; Halevy, Peters and Fischer, 2012). We tried two different methods to compute f_{pyr} : one was a direct method, using the burial fluxes, following equation (3.64). The second method uses our synthetic ocean $\delta^{34}\text{S}$ sulfate record and static α_s values from Figure 3.7 to calculate records for the $\delta^{34}\text{S}$ sedimentary pyrite and sulfate, which, combined with a constant

$\delta^{34}\text{S}_{\text{in}}$ value of 5‰ (Canfield and Farquhar, 2009), can be used to calculate f_{pyr} using equation (3.65).

The direct method generates f_{pyr} values (Fig. 3.8 [A]) which are similar to the various parameterized models by Halevy *et al.* (2012), but are not as high as those predicted by Canfield and Farquhar (2009) in the early Paleozoic. However, GEOCARBSULFOR does end with an f_{pyr} value for the present day which is in line with all the different models, and there is a noticeable transition from higher f_{pyr} values in the early Paleozoic, to lower values for the rest of the Phanerozoic. Our isotope method (Fig. 3.8 [B]) generates f_{pyr} values which also decrease over the course of the Phanerozoic. Using a static α_s value of 16.7‰ delivers f_{pyr} values that are equal or close to those predicted by Canfield and Farquhar (2009) for the early Paleozoic and for much of the Mesozoic and Cenozoic, but are too high for the Permian and Triassic. The static α_s value of 48.1‰ predicts comparable results to Canfield and Farquhar (2009) for the Permian, Triassic and modern-day, but are otherwise too low. Both static values result in f_{pyr} values which compare favourably with Halevy *et al.* (2012). As with our synthetic ocean $\delta^{34}\text{S}$ sulfate record in Figure 3.7, these f_{pyr} results suggest a transition from lower to higher (persistently >35.9‰ – the average value over the last 570 Ma) sulfur isotope fractionation values in the Permian, and this can be seen in the geologic record.

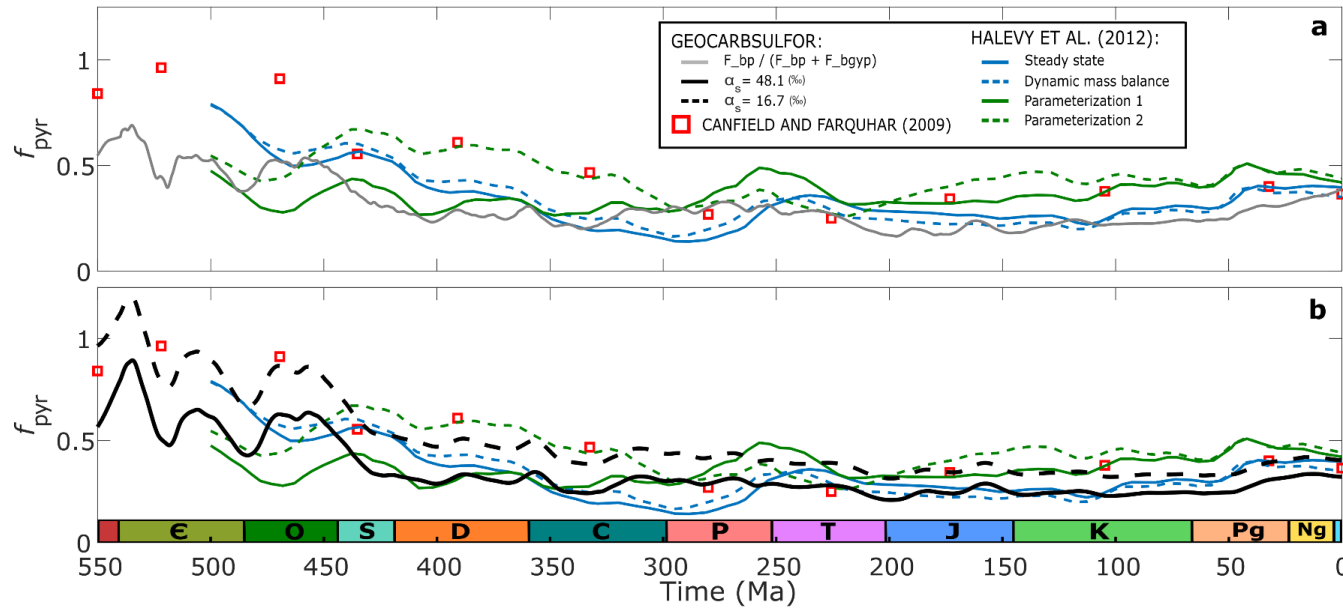


Figure 3.8 | The fraction of total sulfur leaving the ocean as pyrite in GEOCARBSULFOR.

[A] The grey line is the fraction of total sulfur leaving the ocean as pyrite, calculated by GEOCARBSULFOR's burial fluxes over time. [B] The black lines are the fraction of total sulfur leaving the ocean as pyrite, calculated by GEOCARBSULFOR using the synthetic ocean $\delta^{34}\text{S}$ sulfate record and equation (3.65); the solid black line uses a static α_s of 48.1‰ and the dashed black line uses a static α_s of 16.7‰. The red squares in [A] and [B] are f_{pyr} values taken from Canfield and Farquhar (2009), the blue and green lines are taken from different input model runs in Halevy et al. (2012).

In GEOCARBSULF, Berner (2006a) contends that erosive stripping is a more important process in the weathering of pyrite (and organic matter) than oxygen levels, and although the recent iteration of COPSE (Lenton, Daines and Mills, 2018) concurs, the original COPSE (Bergman, Lenton and Watson, 2004) model and others (Lasaga and Ohmoto, 2002; Kanzaki and Kump, 2017), include a dependency on atmospheric oxygen levels when considering the weathering of reductants (e.g. pyrite). In Figure 3.9 we conduct a sensitivity analysis of the model to an oxidative feedback term in the equations for young and ancient pyrite weathering, as well as an analysis of the importance of linking young pyrite weathering to the weathering of silicates.

In Figure 3.9, the black line is our GEOCARBSULFOR baseline, while the grey line is almost the same, but with the oxidative feedback ($O_2mr^{0.5}$) removed from the pyrite weathering equations (equations (3.3) and (3.23)). The magenta line is a model identical to GEOCARBSULFOR but the pyrite weathering equations are those used in the original GEOCARBSULF (Berner, 2006a), while the green line is the same as the magenta line, but with oxidative feedback included into Berner's equations. Finally, the yellow line is as the magenta line, but with a fixed uplift rate (f_R) of 1, for the entire run.

Our results show that although there is some sensitivity to the inclusion of an oxidative feedback term in pyrite weathering, it does not alter the general trend of the evolution of pO_2 as predicted by GEOCARBSULFOR. Comparison of our baseline GEOCARBSULFOR (black line) to no oxidative feedback (grey line) reveals a

difference of $\sim 1 - 2\%$ atm in predicted oxygen levels for most of the model run, apart from the Devonian which has a difference of $\sim 2 - 3\%$ atm, both of which would likely lie within an error analysis of the model. Similarly, tying the weathering of pyrite to the weathering of silicates makes little difference to oxygen predictions for much of the Phanerozoic, with the only real difference in predictions (green line compared to black) coming in the Cretaceous, where the effect of uplift (which is included in the silicate weathering equation (3.46)) is dampened in GEOCARBSULFOR.

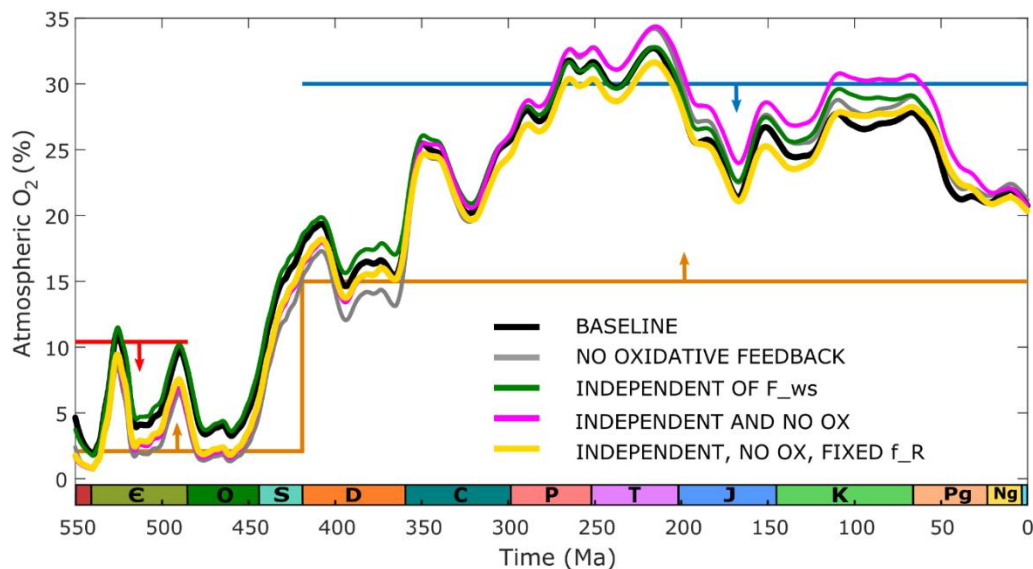


Figure 3.9 | Pyrite weathering sensitivity tests.

The black line is the baseline GEOCARBSULFOR oxygen (as seen in Fig. 3.3). The grey line includes no oxidative feedback in the pyrite weathering equations, while the green line decouples pyrite weathering from silicate weathering. The magenta line has no oxidative feedback and is not linked to silicate weathering. The yellow line is the same as the magenta line, but uplift is fixed (to the modern-day value of 1) for the entire Phanerozoic.

Two final tests were conducted, to assess the robustness of our model outputs. These tests were to evaluate both the amount of sulfate assigned to the ocean-atmosphere reservoir by the model (Fig. 3.10), and the CO₂ levels generated (Fig. 3.11), against other models and geochemical proxies. In both tests, GEOCARBSULFOR outputs compare favourably with both the proxy data and other modelling efforts. CO₂ levels predicted by GEOCARBSULFOR are on the low side of the proxy bands, particularly during the Cretaceous and Paleogene. The Paleogene low is a common issue with previous work involving GEOCARBSULF (Bernier, 2008; Royer *et al.*, 2014; Van Der Meer *et al.*, 2014), and requires the seafloor spreading rate to be ~3x the present day value in order to reconcile the model predictions with the proxy record. The discrepancy between model predictions and proxy estimates is possibly due to underrepresentation, or absence, of all plate boundary types and their contribution to CO₂ degassing (Brune, Williams and Müller, 2017). However, recent work on this issue has resulted in GEOCARBSULF predictions that better match the Paleogene record, but are subsequently too high for the Neogene (Brune, Williams and Müller, 2017). Nevertheless, we believe that our model has been comprehensively checked against the available geologic data and provides a good fit to our understanding of various geochemical indices, and thus GEOCARBSULFOR gives a compelling indication of low pO_2 in the early Paleozoic.

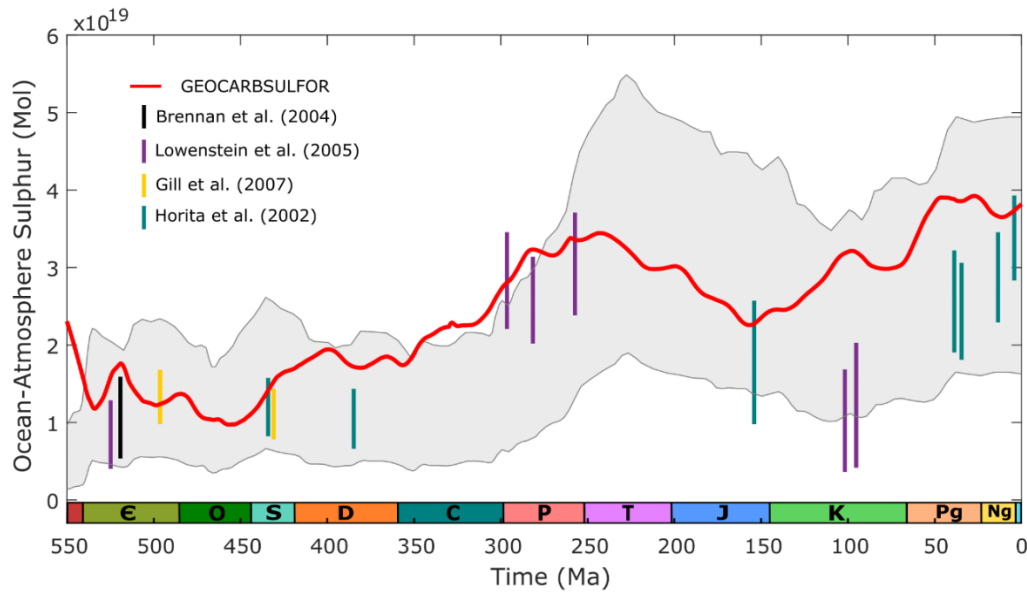


Figure 3.10 | The ocean-atmosphere sulfur reservoir generated by our GEOCARBSULFOR model, compared with proxies and other model outputs.

The red line is the amount of sulfate in the ocean-atmosphere reservoir throughout the Phanerozoic as generated by our GEOCARBSULFOR model. The vertical lines are estimates based on fluid-inclusion data (Horita, Zimmermann and Holland, 2002; Brennan, Lowenstein and Horita, 2004; Lowenstein et al., 2005) and modelling studies (Gill et al. 2007). The grey envelope is the $\pm 1\sigma$ uncertainty range from Algeo et al. (2015).

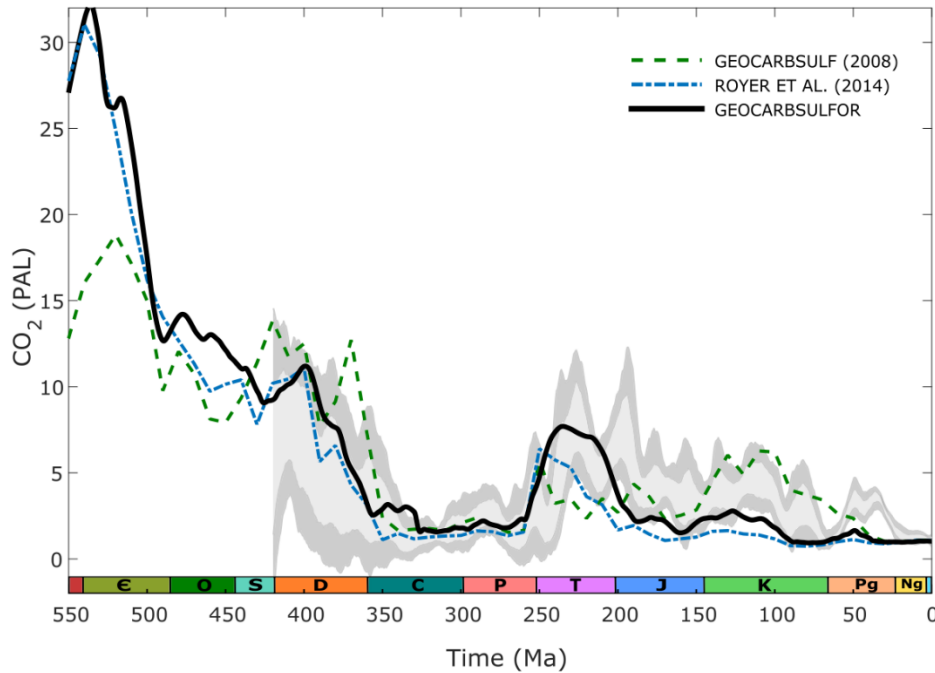


Figure 3.11 | Atmospheric CO₂ levels generated by our GEOCARBSULFOR model, compared with other model outputs and CO₂ proxies.

The black line is our GEOCARBSULFOR model output, the green dashed line is taken from Berner (2008) where basalt/granite weatherability = 2, $NV = 0.015$, $fB(0) = 5$, the blue dot-dash line is the median output from Royer et al. (2014) and the light and dark grey bands are 68% and 95% confidence intervals, respectively, of CO₂ proxy data (Foster, Royer and Lunt, 2017). Outputs are measured as multiplications of the present atmospheric level (PAL), which in GEOCARBSULF is taken as the mean Quaternary value of 250ppm.

Finally, to ensure completeness, we checked that the model adequately apportions the total mass of sedimentary sulfur between the gypsum and pyrite reservoirs, over time, starting with a pyrite-dominated Paleozoic (Canfield and Farquhar, 2009), and finishing with near equal reservoir values (total pyrite of 180×10^{18} moles and total

gypsum of 200×10^{18} moles) in the Present (Kump and Garrels, 1986); GEOCARBSULFOR achieves this (Fig. 3.12), with values at the end of its run that are very close to those at Present, indicating that our model is robust.

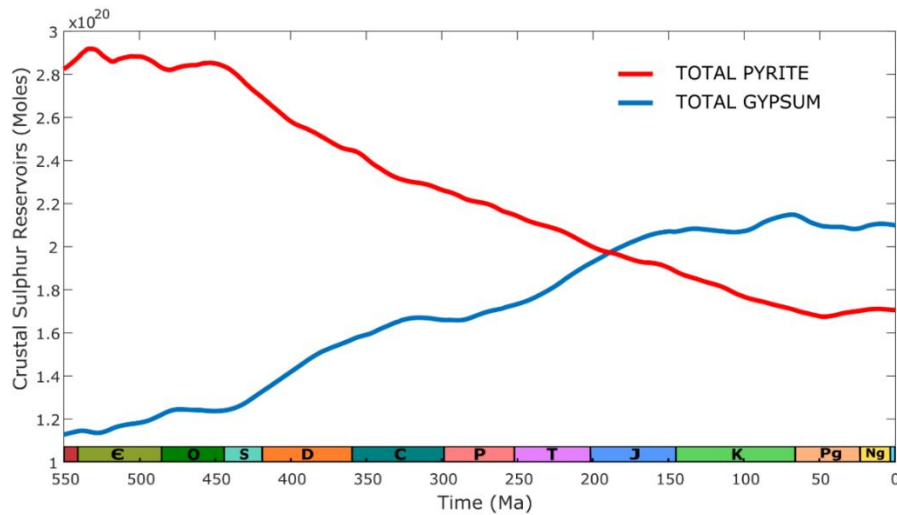


Figure 3.12 | GEOCARBSULFOR predictions of total sedimentary sulfide (pyrite) and total sedimentary sulfate (gypsum) over the Phanerozoic.

The red line is total pyrite (young plus ancient reservoirs), and the blue line is total gypsum (young plus ancient reservoirs).

3.6.2. Full model parameters

For the following tables, where we mention GEOCARBSULF as a source, we mean the final values as used in Berner (2009), some of which are unchanged from, for example, GEOCARB II (Berner, 1994).

Table 3.1: Present day parameters used in GEOCARBSULFOR

Parameter	Algebraic Representatio n	Value	Source
Atmosphere and ocean CO ₂	A0	3.193x10 ¹⁸ mol	COPSE (Bergman <i>et al.</i> , 2004)
Atmosphere and ocean O ₂	O0	3.8x10 ¹⁹ mol	GEOCARBSULF (Berner, 2009)
Atmosphere and ocean sulfate	OA_S_0	3.8x10 ¹⁹ mol	GEOCARBSULF
Young buried pyrite sulfur*	<i>Pyr_0</i>	12.8571x10 ¹⁸ mol	COPSE / GEOCARBSULF
Young buried gypsum sulfur*	<i>Gyp_0</i>	100x10 ¹⁸ mol	COPSE / GEOCARBSULF
Temperature	<i>temp_0</i>	288 °K	
Silicate weathering	<i>F_ws_0</i>	6.67x10 ¹⁸ mol myr ⁻¹	GEOCARBSULF
Young carbonate weathering*	<i>F_wc_y0</i>	11.35x10 ¹⁸ mol C myr ⁻¹	COPSE / GEOCARBSULF
Burial rate of C _{org}	<i>F_bg_0</i>	5x10 ¹⁸ mol C myr ⁻¹	(Berner and Canfield, 1989)
Rate of exchange of Ca and Mg between basalt and seawater	<i>F_bo_0</i>	5x10 ¹⁸ mol myr ⁻¹	GEOCARBSULF
Fraction of total Ca and Mg silicate weathering derived from volcanic rocks	<i>Xvolc_0</i>	0.35	GEOCARBSULF

* Values are taken from COPSE but then split into young and ancient values following the proportions set out in GEOCARBSULF. Only present young values are required for the model.

Table 3.2: Constant parameters used in GEOCARBSULFOR

Parameter	Algebraic Representation	Value	Source
Normalized activation energy for silicates	ACT_{si}	0.09 K^{-1}	GEOCARBSULF
Normalized activation energy for carbonates	ACT_{carb}	0.087 K^{-1}	GEOCARBSULF
Effect of solar insolation on temperature	Ws	7.4°	GEOCARBSULF
Proportion of plants fertilized by increasing CO_2	$FERT$	0.4	GEOCARBSULF
Curve fitting parameter for effect of O_2 on $\delta^{13}\text{C}$ fractionation	J	4	GEOCARBSULF
Average value of $^{87}\text{Sr}/^{86}\text{Sr}$ of sub-aerial and submarine volcanic rocks	Rv	0.704	GEOCARBSULF
Ratio of chemical weathering in volcanic to non-volcanic silicate rocks	VNV	2	GEOCARBSULF
Parameter used to calculate the average $^{87}\text{Sr}/^{86}\text{Sr}$ of non-volcanic silicate rocks	NV	0.015	GEOCARBSULF
Young pyrite weathering rate constant*	new_kwp	$4.6 \times 10^{17} \text{ myr}^{-1}$	This study
Young gypsum weathering rate constant*	new_kwgyp	$1.2 \times 10^{18} \text{ myr}^{-1}$	This study
Young C_{org} weathering rate constant	k_{wg}	0.018 myr^{-1}	GEOCARBSULF
Young carbonate weathering rate constant	k_{wc}	0.018 myr^{-1}	GEOCARBSULF

Ancient pyrite weathering rate constant	$kwpa$	$0.000893 \text{ myr}^{-1}$	This study
Ancient gypsum weathering rate constant	$kwgypa$	0.0033 myr^{-1}	This study
Ancient C_{org} weathering rate constant	$kwga$	0.0005 myr^{-1}	This study
Ancient carbonate weathering rate constant	$kwca$	0.00125 myr^{-1}	This study
Ancient pyrite degassing rate constant	$kmpa$	$0.000893 \text{ myr}^{-1}$	This study
Ancient gypsum degassing rate constant	$kmgypa$	0.0033 myr^{-1}	This study
Ancient C_{org} degassing rate constant	$kmga$	0.0005 myr^{-1}	This study
Ancient carbonate degassing rate constant	$kmca$	$0.001668 \text{ myr}^{-1}$	This study
Pyrite burial rate constant*	k_{bp}	$1.15 \times 10^{18} \text{ myr}^{-1}$	This study
Gypsum burial rate constant*	k_{bgyp}	$1.6 \times 10^{18} \text{ myr}^{-1}$	This study
Pyrite young to ancient flux rate constant	k_{p_ya}	0.01 myr^{-1}	This study
Gypsum young to ancient flux rate constant	k_{gyp_ya}	0.01 myr^{-1}	This study
C_{org} young to ancient flux rate constant	k_{g_ya}	0.018 myr^{-1}	This study
Carbonate young to ancient flux rate constant	k_{c_ya}	0.018 myr^{-1}	This study

* The values for these parameters are so much larger as they are multiplied by normalized reservoirs, instead of a reservoir at time (t).

Table 3.3: Time dependent parameters used in GEOCARBSULFOR

Parameter	Algebraic Representation	Source	Notes
Total land area	f_A	(Royer <i>et al.</i> , 2014)	Time array
Fraction of land area experiencing chemical weathering	f_{AW}	Royer <i>et al.</i>	Time array
Global river runoff	f_D	Royer <i>et al.</i>	Time array
Effect of change in paleogeography on temperature	$GEOG$	Royer <i>et al.</i>	Time array
Proportion of land area underlain by carbonates	f_L	Royer <i>et al.</i>	Time array
Degassing rate due to tectonics / seafloor spreading*	f_G or f_{SR}	GEOCARBSULF	Time array - the same values are used by Royer <i>et al.</i>

Ocean $\delta^{13}\text{C}$ carbonate record	delta_OA_C	(Saltzman and Thomas, 2012)	Time array
Normalized calcium reservoir	Calc	(Horita, Zimmermann and Holland, 2002)	Time array – generated from Ca fluid inclusion data
Dependence of weathering rate on soil biological activity due to land plants	f_E	GEOCARBSULF	0-80 Ma $f_E = 1$ 130-350 Ma $f_E = 0.875$ 380-550 Ma $f_E = 0.25$ Linear interpolation between 80-130 Ma and 350-380 Ma
Mean land elevation	f_R	GEOCARBSULF	Cubic fit – See equations (3.8) and (3.9)
Dependence of degassing rate on relative proportions of carbonates on shallow platforms or deep ocean	f_C	GEOCARBSULF	150-550 Ma $f_C = 0.75$ 0-150 Ma is a time dependent equation, see equation (3.7)

Ocean ^{87}Sr record for use in calculating silicate weathering	R_{ocm}	Royer <i>et al.</i>	Time array
Response of global mean temperature to atmospheric CO_2 greenhouse effect	γ	Royer <i>et al.</i>	For 0-40 Ma and 260-330 Ma: $\gamma = 8.6562$ All other time: $\gamma = 4.3281$
Temperature controlled runoff factor	RUN	GEOCARBSULF	0-40 Ma and 260-340 Ma: $RUN = 0.045$ All other time: $RUN = 0.025$
Effect of changes to CO_2 on carbonate and silicate weathering	f_{CO_2}	GEOCARBSULF	0-350 Ma: $f_{\text{CO}_2} = \text{VAS}$ 380-550 Ma: $f_{\text{CO}_2} = \text{NOVAS}$ Linear interpolation between 350-380 Ma - see equations (3.13 – 3.18)

* Both of these terms are used throughout the literature, but in GEOCARBSULF they are treated as the same thing.

For all time arrays we apply interpolation between data points.

Table 3.4: Starting reservoir sizes of GEOCARBSULFOR

Parameter	Algebraic Representation	Value	Source
Ocean and atmosphere sulfur	OA_S	38×10^{18} mol	GEOCARBSULF
Ocean and atmosphere carbon	OA_C	35.5×10^{18} mol	For attaining PAL
Young pyrite	<i>Pyr_y</i>	20×10^{18} mol	This study
Ancient pyrite	<i>Pyr_a</i>	260×10^{18} mol	This study
Young gypsum	<i>Gyp_y</i>	50×10^{18} mol	This study
Ancient gypsum	<i>Gyp_a</i>	50×10^{18} mol	This study
Young C _{org}	<i>G_y</i>	250×10^{18} mol	GEOCARBSULF
Ancient C _{org}	<i>G_a</i>	1000×10^{18} mol	GEOCARBSULF
Young carbonate	<i>C_y</i>	1000×10^{18} mol	GEOCARBSULF
Ancient carbonate	<i>C_a</i>	4000×10^{18} mol	GEOCARBSULF
Young C _{org} isotope mass balance (IMB)	$\delta_{g\_y} \cdot G_y$	$-23.5 \cdot 250 \times 10^{18}$	GEOCARBSULF
Ancient C _{org} IMB	$\delta_{g\_a} \cdot G_a$	$-23.5 \cdot 1000 \times 10^{18}$	GEOCARBSULF
Young carbonate IMB	$\delta_{c\_y} \cdot C_y$	$3 \cdot 1000 \times 10^{18}$	GEOCARBSULF
Ancient carbonate IMB	$\delta_{c\_a} \cdot C_a$	$-1.5774 \cdot 4000 \times 10^{18}$	GEOCARBSULF

3.6.3. Full model equations

The full set of equations for the model are documented below, except the new burial equations for pyrite and gypsum, and weathering equations for young pyrite and young gypsum (equations 3.3 – 3.6), which can be found in section 3.3.4. These are taken from the COPSE (Bergman, Lenton and Watson, 2004) model. All other equations have been taken from GEOCARBSULF, but we note where alterations to the original equations have been made.

Table 3.5: Flux and parameter equations

f_{C} for $t < 150$ Ma:	$f_{\text{C}} = 0.75 + \left[\left(\frac{0.25}{150} \right) \cdot (150 + t) \right]$	[3.7]
Mean land elevation:	$f_{\text{R}} = \left(\frac{f_{\text{RT}}}{1.063} \right)^{0.67}$	[3.8]
Where:	$f_{\text{RT}} = \left(25.269 \cdot \left(\frac{t}{1000} \right)^3 \right) + \left(26.561 \cdot \left(\frac{t}{1000} \right)^2 \right) + \left(6.894 \cdot \left(\frac{t}{1000} \right) \right) + 1.063$	[3.9]
Ratio of CO ₂ relative to present day:	$\text{RCO}_2 = \frac{\text{CO}_2(t)}{\text{A0}}$	[3.10]

Ratio of O ₂ relative to present day:	$O_{2mr} = \frac{O_2(t)}{O_0}$	[3.11]
Conversion of relative O ₂ to atmospheric %:	$O_{2atm} = \left(\frac{O_{2mr}}{O_{2mr} + 3.762} \right) \cdot 100$	[3.12]
Effect of changes in CO ₂ on carbonate and silicate weathering:	$VAS = \left(\frac{2 \cdot RCO_2}{1 + RCO_2} \right)^{FERT}$ $NOVAS = RCO_2^{0.5}$	[3.13]
Global average temperature:	$temp = (gamma - \ln RCO_2) - \left(Ws \cdot \frac{t}{-570} \right) + GEOG + temp_0$	[3.14]
Temperature effect on silicate weathering:	$f_{Tsi} = e^{(ACT_{si} \cdot [temp - temp_0])} \cdot \{1 + [RUN \cdot (temp - temp_0)]\}^{0.65}$	[3.15]
Temperature and CO ₂ effect on silicate weathering:	$f_{Bsi} = f_{Tsi} \cdot f_{CO_2}$	[3.16]
Temperature effect on carbonate weathering:	$f_{Tcarb} = 1 + [ACT_{carb} \cdot (temp - temp_0)]$	[3.17]
Temperature and CO ₂ effect on carbonate weathering:	$f_{BBcarb} = f_{Tcarb} \cdot f_{CO_2}$	[3.18]
*Weathering of young C _{org} :	$F_{wg\_y} = f_R \cdot f_A \cdot k_{wg} \cdot G_y(t) \cdot O_{2mr}^{0.5}$	[3.19]
*Weathering of ancient C _{org} :	$F_{wg\_a} = f_R \cdot kwga \cdot G_a(t) \cdot O_{2mr}^{0.5}$	[3.20]
Weathering of young carbonate:	$F_{wc\_y} = f_{BBcarb} \cdot f_L \cdot f_A \cdot f_D \cdot f_E \cdot k_{wc} \cdot C_y(t)$	[3.21]

Weathering of ancient carbonate:	$F_{wc\_a} = f_{BBcarb} \cdot f_L \cdot f_A \cdot f_D \cdot f_E \cdot kwca \cdot C_a(t)$	[3.22]
*Weathering of ancient pyrite:	$F_{wp\_a} = f_R \cdot kwpa \cdot Pyr\_a(t) \cdot O_2mr^{0.5}$	[3.23]
*Weathering of ancient gypsum:	$F_{wgyp\_a} = f_A \cdot f_D \cdot kwgypa \cdot Gyp\_a(t)$	[3.24]
*Degassing of ancient pyrite:	$F_{mp} = f_{SR} \cdot kmpa \cdot Pyr\_a(t)$	[3.25]
*Degassing of ancient gypsum:	$F_{ms} = f_{SR} \cdot kmgypa \cdot Gyp\_a(t)$	[3.26]
*Degassing of ancient C _{org} :	$F_{mg} = f_{SR} \cdot kmga \cdot G\_a(t)$	[3.27]
*Degassing of ancient carbonate:	$F_{mc} = f_{SR} \cdot f_C \cdot kmca \cdot C\_a(t)$	[3.28]
Fractionation of $\delta^{13}C$:	$\alpha_C = 27 + [J \cdot (O_2mr - 1)]$	[3.29]
Young C _{org} isotopes:	$\delta_{g\_y} = \frac{\delta_{g\_y}(t) \cdot G\_y(t)}{G\_y(t)}$	[3.30]
Ancient C _{org} isotopes:	$\delta_{g\_a} = \frac{\delta_{g\_a}(t) \cdot G\_a(t)}{G\_a(t)}$	[3.31]
Young carbonate isotopes:	$\delta_{c\_y} = \frac{\delta_{c\_y}(t) \cdot C\_y(t)}{C\_y(t)}$	[3.32]
Ancient carbonate isotopes:	$\delta_{c\_a} = \frac{\delta_{c\_a}(t) \cdot C\_a(t)}{C\_a(t)}$	[3.34]

Burial of C_{org} :	$F_{bg} = \frac{1}{\alpha_C}$ $\cdot \{[(\delta_{OA_C} - \delta_{C_y}) \cdot F_{wc_y}]$ $+ [(\delta_{OA_C} - \delta_{C_a}) \cdot F_{wc_a}]$ $+ [(\delta_{OA_C} - \delta_{G_y}) \cdot F_{wg_y}]$ $+ [(\delta_{OA_C} - \delta_{G_a}) \cdot F_{wg_a}]$ $+ [(\delta_{OA_C} - \delta_{C_a}) \cdot F_{mc}]$ $+ [(\delta_{OA_C} - \delta_{G_a}) \cdot F_{mg}]\}$	[3.35]
*Burial of carbonate:	$F_{bc} = F_{ws} + F_{wc_y} + F_{wc_a}$	[3.36]
*Young to ancient pyrite flux:	$F_{ya_p} = k_{p_ya} \cdot Pyr_y(t)$	[3.37]
*Young to ancient gypsum flux:	$F_{ya_gyp} = k_{gyp_ya} \cdot Gyp_y(t)$	[3.38]
*Young to ancient C_{org} flux:	$F_{ya_g} = k_{g_ya} \cdot G_y(t)$	[3.39]
*Young to ancient carbonate flux:	$F_{ya_c} = k_{c_ya} \cdot C_y(t)$	[3.40]
Convert strontium isotopes to $^{87}Sr/^{86}Sr$:	$Roc = \frac{R_{ocm}}{10000} + 0.7$	[3.41]

Average value of $^{87}\text{Sr}/^{86}\text{Sr}$ for young carbonates undergoing weathering:	$R_{\text{cy}} = R_{\text{cy}}(t) + \left[(R_{\text{oc}} - R_{\text{cy}}(t)) \cdot \frac{F_{\text{bc}}}{C_{\text{y}}(t)} \right]$	[3.42]
Average value of $^{87}\text{Sr}/^{86}\text{Sr}$ for ancient carbonates undergoing weathering:	$R_{\text{ca}} = R_{\text{ca}}(t) + \left[(R_{\text{cy}} - R_{\text{ca}}(t)) \cdot \frac{F_{\text{ya_c}}}{C_{\text{a}}(t)} \right]$	[3.43]
$^{87}\text{Sr}/^{86}\text{Sr}$ of non-volcanic silicates:	$R_{\text{nv}} = 0.722 - \left[NV \cdot \left(\frac{1 - f_{\text{RT}}}{1.063} \right) \right]$	[3.44]
Fraction of total Ca and Mg silicate weathering derived from volcanic rocks:	$X_{\text{volc}} = \frac{\{[f_{\text{SR}} \cdot F_{\text{bo}_0} \cdot (R_{\text{v}} - R_{\text{oc}})] + (F_{\text{wc}_y} \cdot R_{\text{cy}}) + (F_{\text{wc}_a} \cdot R_{\text{ca}}) - (R_{\text{oc}} \cdot F_{\text{bc}}) + (R_{\text{nv}} \cdot F_{\text{ws}})\}}{F_{\text{ws}} \cdot (R_{\text{nv}} - R_{\text{v}})}$	[3.45]
Volcanic weathering effect:	$f_{\text{volc}} = \frac{(VNV \cdot X_{\text{volc}}) + (1 - X_{\text{volc}})}{(VNV \cdot X_{\text{volc}_0}) + (1 - X_{\text{volc}_0})}$	[3.46]
*Silicate weathering:	$F_{\text{ws}} = f_{\text{volc}} \cdot f_{\text{Bsi}} \cdot (f_{\text{AW}} \cdot f_{\text{A}} \cdot f_{\text{D}})^{0.65} \cdot f_{\text{R}} \cdot f_{\text{E}} \cdot F_{\text{ws}_0}$	[3.47]

N.B. In our model code we run from -570 to 0 Ma at 10 Myr time-steps instead of +570 to 0 Ma, so some of the equations have a slightly different formulation with regard to the positive or negative sign of t or '570', compared to the original versions in GEOCARBSULF. The period -570 to -550 Ma uses the same values and formulations at -560 Ma and -570 Ma, as those used for -550 Ma, and allows for model spin-up.

* These equations have been altered from those in the original GEOCARBSULF model.

Table 3.6: Reservoir equations

Ocean and atmosphere sulfur:	$\frac{d(OA_S)}{dt} = F_{wp\_y} + F_{wgyp\_y} + F_{wp\_a} + F_{wgyp\_a} + F_{mp} + F_{ms} - F_{bp} - F_{bgyp}$	[3.48]
Ocean and atmosphere carbon (CO ₂):	$\frac{d(CO_2)}{dt} = F_{wg\_y} + F_{wc\_y} + F_{wg\_a} + F_{wc\_a} + F_{mg} + F_{mc} - F_{bg} - F_{bc}$	[3.49]
Young pyrite:	$\frac{d(Pyr\_y)}{dt} = F_{bp} - F_{wp\_y} - F_{ya\_p}$	[3.50]
Ancient pyrite:	$\frac{d(Pyr\_a)}{dt} = F_{ya\_p} - F_{wp\_a} - F_{mp}$	[3.51]
Young gypsum:	$\frac{d(Gyp\_y)}{dt} = F_{bgyp} - F_{wgyp\_y} - F_{ya\_gyp}$	[3.52]
Ancient gypsum:	$\frac{d(Gyp\_a)}{dt} = F_{ya\_gyp} - F_{wgyp\_a} - F_{ms}$	[3.53]
Young C _{org} :	$\frac{d(G\_y)}{dt} = F_{bg} - F_{wg\_y} - F_{ya\_g}$	[3.54]
Ancient C _{org} :	$\frac{d(G\_a)}{dt} = F_{ya\_g} - F_{wg\_a} - F_{mg}$	[3.55]
Young carbonate:	$\frac{d(C\_y)}{dt} = F_{bc} - F_{wc\_y} - F_{ya\_c}$	[3.56]
Ancient carbonate:	$\frac{d(C\_a)}{dt} = F_{ya\_c} - F_{wc\_a} - F_{mc}$	[3.57]
Young C _{org} IMB:	$\begin{aligned} \frac{d(\delta_{g\_y} \cdot G\_y)}{dt} &= [(\delta_{OA\_C} - \alpha_C) \cdot F_{bg}] \\ &\quad - (\delta_{g\_y} \cdot F_{wg\_y}) - (\delta_{g\_y} \cdot F_{ya\_g}) \end{aligned}$	[3.58]

Ancient C _{org} IMB:	$\frac{d(\delta_{g\_a} \cdot G\_a)}{dt}$ $= (\delta_{g\_y} \cdot F_{ya\_g}) - (\delta_{g\_a} \cdot F_{wg\_a})$ $- (\delta_{g\_a} \cdot F_{mg})$	[3.59]
Young carbonate IMB:	$\frac{d(\delta_{c\_y} \cdot C\_y)}{dt}$ $= (\delta_{OA\_C} \cdot F_{bc}) - (\delta_{c\_y} \cdot F_{wc\_y})$ $- (\delta_{c\_y} \cdot F_{ya\_c})$	[3.60]
Ancient carbonate IMB:	$\frac{d(\delta_{c\_a} \cdot C\_a)}{dt}$ $= (\delta_{c\_y} \cdot F_{ya\_c}) - (\delta_{c\_a} \cdot F_{wc\_a})$ $- (\delta_{c\_a} \cdot F_{mc})$	[3.61]
Atmospheric oxygen:	$\frac{d(O_2)}{dt} = \left[F_{bg} + \left(\frac{15}{8} \cdot F_{bp} \right) \right] - (F_{wg\_y} + F_{wg\_a} + F_{mg})$ $- \left[\frac{15}{8} \cdot (F_{wp\_y} + F_{wp\_a} + F_{mp}) \right]$	[3.62]

Table 3.7: Equation for GEOCARBSULF sulfur isotope fractionation

Formulation used for $\delta^{34}\text{S}$ fractionation in the original GEOCARBSULF	$\alpha_{S} = 35 \cdot (O_2\text{mr})^{1.5}$	[3.63]

Table 3.8: Equations for model tests

Fraction of the total sulfur leaving the ocean as pyrite (burial flux approach):	$f_{\text{pyr}} = \frac{F_{bp}}{F_{bp} + F_{bgyp}}$	[3.64]
Fraction of the total sulfur leaving the ocean as pyrite (isotope approach) (Canfield and Farquhar, 2009):	$f_{\text{pyr}} = \frac{\delta^{34}\text{S}_{\text{in}} - \delta^{34}\text{S}_{\text{sulfate}}}{\delta^{34}\text{S}_{\text{sulfide}} - \delta^{34}\text{S}_{\text{sulfate}}}$	[3.65]

4. Extreme instability in atmospheric oxygen levels in the late Precambrian

This chapter has been written in the style of a *Nature* article, and is out for review with that journal, although the Methods section of the intended article has been moved to an earlier part of the text, for better integration. Additionally, the relatively short-form style of *Nature* means that much of the model validation and sensitivity analyses, as well as full model equations and parameters will be included in the supplementary information for the paper, thus these are found in this chapter as subsections of 4.5.

The chapter is in review as the following:

Krause, A.J., Mills, B.J.W., Merdith, A.S., Lenton, T.M. and Poulton, S.W. (in review)
Extreme instability in atmospheric oxygen levels in the late Precambrian.

The author contributions to this work are:

A.J.K. and B.J.W.M. designed the research. A.J.K. performed the NEOCARBSULF modelling. A.S.M. performed the tectonic plate modelling. A.J.K., B.J.W.M. and S.W.P. wrote the paper, with input from A.S.M. and T.M.L.

4.1. Introduction

It is widely believed that atmospheric oxygen rose in three broad steps during the course of Earth's 4.5-billion-year history (Lyons, Reinhard and Planavsky, 2014; Lenton *et al.*, 2016; Krause *et al.*, 2018; Alcott, Mills and Poulton, 2019). The first and

third of these steps: The Great Oxidation Event (GOE) and the Paleozoic Oxygenation Event (POE), are reasonably well understood in terms of their timings and general dynamics. For the GOE at ~2.4 Ga, key pieces of geological and geochemical evidence undergo permanent state changes across the event, some of which can provide broad constraints on atmospheric O₂ concentrations. The loss of mass-independent sulfur isotope fractionation (Farquhar, Bao and Thiemens, 2000) suggests O₂ levels since the GOE have remained above 0.001% PAL (Pavlov and Kasting, 2002) (Fig. 4.1, #1), while the rise of terrestrial red beds and the loss of detrital pyrite and uraninite in fluvial sediments, point to O₂ > 1% PAL (Rye and Holland, 1998; Holland, 2006; Buick, 2008) (Fig. 4.1 #3). Similarly for the ~400 Ma POE, a substantial increase in the abundance of sedimentary charcoal (Glasspool and Scott, 2010) (Fig. 4.1, #8), as well as accompanying step-changes in cerium anomalies (Azmy *et al.*, 2011; Wallace *et al.*, 2017) and the oxidation state of marine basalts (Stolper and Keller, 2018), all point to a stepwise increase in oxygen levels.

However, there is substantial debate over the timing and tempo of the second O₂ step – the Neoproterozoic Oxygenation Event (NOE) (Och and Shields-Zhou, 2012) – and it is not clear whether the current view (Lyons, Reinhard and Planavsky, 2014) (Fig. 4.1, blue lines - #1, 2, 7 and 8) of a stepwise change to near-modern O₂ levels, is correct. A stepwise shift towards a new stable O₂ level is somewhat difficult to reconcile with the dynamic nature of the Earth system during this time period, as the supercontinent Rodinia fractured into a multitude of low-latitude microcontinents (Li *et al.*, 2008), and the Earth experienced two ‘Snowball Earth’ glaciations (the Sturtian at ~717 – 659 Ma, and the Marinoan at ~649 – 635 Ma) and their ‘super-greenhouse’

aftermaths (Hoffman *et al.*, 1998; Condon *et al.*, 2005; Fairchild and Kennedy, 2007; Calver *et al.*, 2013; Macdonald *et al.*, 2017; Cox *et al.*, 2018; Wang *et al.*, 2019).

More directly, terrestrial proxies provide conflicting lines of evidence as to atmospheric O₂ levels during the Mesoproterozoic and early Neoproterozoic. Chromium isotopes ($\delta^{53}\text{Cr}$), where a greater fractionation from the bulk silicate Earth (BSE) pool is indicative of oxidative weathering of Cr (Frei *et al.*, 2009; Planavsky *et al.*, 2014; Cole *et al.*, 2016), have historically been interpreted to imply O₂ levels <0.1% PAL (Fig. 4.1, #4) before 800 – 750 Ma (Planavsky *et al.*, 2014; Cole *et al.*, 2016). This level is based on the assumption that Cr oxidation is dependent on the amount of time spent in a weathering environment in close contact with O₂ (Planavsky *et al.*, 2014). Other work (Daines, Mills and Lenton, 2017) has shown that soils beyond the upper layers would have been anoxic, therefore O₂ exposure during fluvial transport to the oceans is more important, suggesting an O₂ level of ~1% PAL. Furthermore, additional analyses utilising $\delta^{53}\text{Cr}$ have indicated extensive isotopic fractionation, and therefore O₂ concentrations of >0.1% PAL throughout the Mesoproterozoic (Fig. 4.1, #6) (Gilleaudeau *et al.*, 2016; Canfield *et al.*, 2018). In addition, the appearance of terrestrial red beds suggests O₂ concentrations >1% PAL since the GOE (Fig. 4.1, #3) (Holland, 2006), and in the marine realm, redox sensitive trace elements (RSE) suggest the possibility of O₂ concentrations above 4% PAL as early as 1400 Ma (Fig. 4.1, #5) (Shuichang Zhang *et al.*, 2016).

Marine geochemical proxies do not appear to agree on resilient oceanic oxygenation during the Neoproterozoic either. The I / (Ca + Mg) proxy, which is used to track

shallow ocean oxygenation, suggests low O₂ levels throughout, until a temporary rise at ~800 Ma (Lu *et al.*, 2017, 2018; Wörndle *et al.*, 2019). In turn, cerium anomalies infer generally progressive ocean oxygenation in the aftermath of the Marinoan through to the Devonian (Azmy *et al.*, 2011; Huang *et al.*, 2011; Ling *et al.*, 2013; Wallace *et al.*, 2017; W. Wei *et al.*, 2018; Wu *et al.*, 2019), while uranium isotopes ($\delta^{238}\text{U}_{\text{SW}}$) – which are considered to reflect global trends in ocean redox – tend to suggest the ocean experienced multiple oxygenation events across the Cryogenian, Ediacaran and Cambrian (Dahl *et al.*, 2014; Kendall *et al.*, 2015; Lau *et al.*, 2017; G. Wei *et al.*, 2018; Zhang *et al.*, 2018; Tostevin *et al.*, 2019). Such fluctuations are in general agreement with RSE in black shales (Sahoo *et al.*, 2016), as well as iron speciation analyses that point to spatially and temporally restricted episodes of deep ocean oxygenation (Canfield, Poulton and Narbonne, 2007; Canfield *et al.*, 2008) (see Fig. 4.1, bottom panel). Thus, a complex picture exists of intervals of ocean oxygenation during the Neoproterozoic, with no clear grasp on O₂ levels in the atmosphere and surface ocean, leading to major uncertainty in terms of oxygen controls on metazoan evolution.

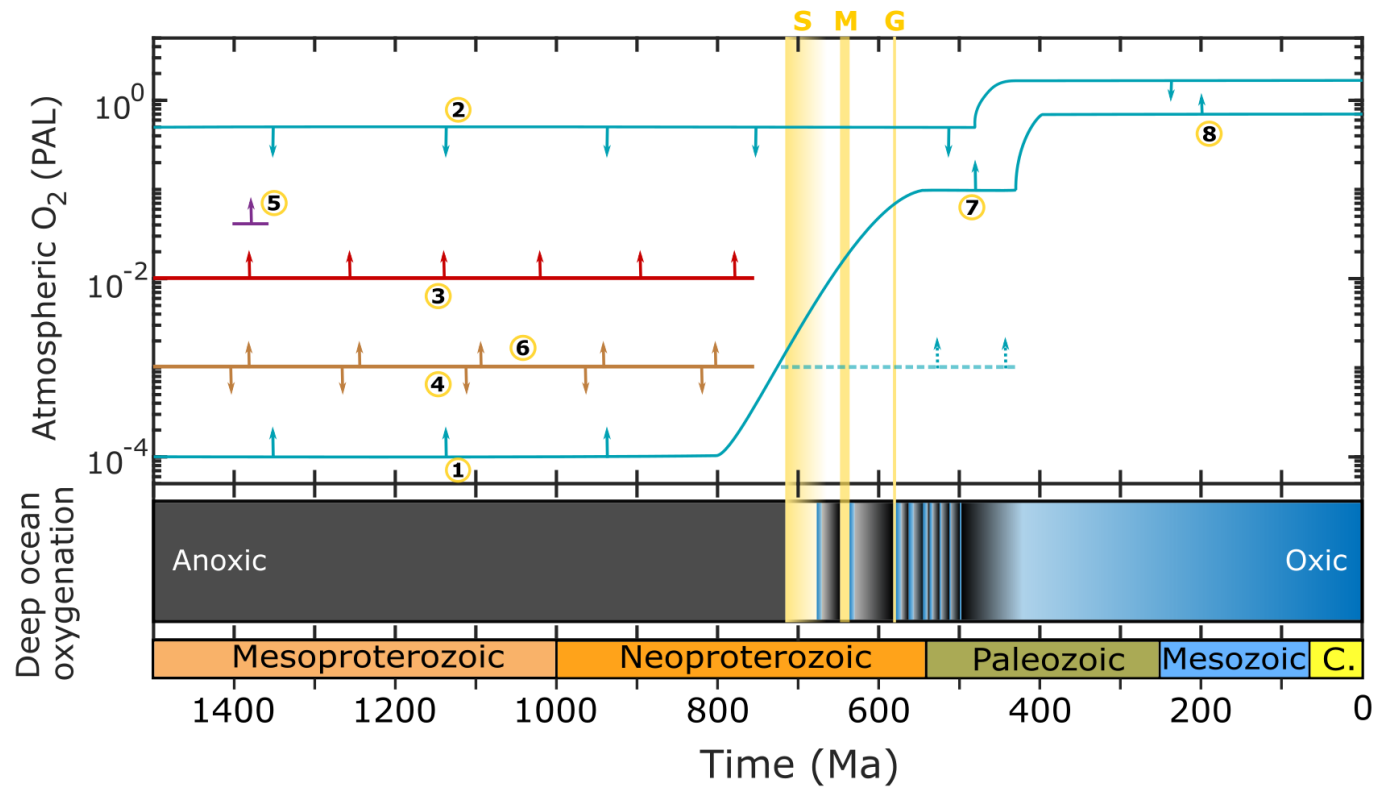


Figure 4.1 | Current ‘best guess’ estimates for atmospheric O₂ evolution over the last 1500 Myrs, and deep ocean oxygenation based on multiple geochemical proxy records.

The current view of atmospheric oxygen levels since 1500 Ma (Lyons, Reinhard and Planavsky, 2014) (top panel) and deep ocean oxygenation (bottom panel, where the black represents anoxia in the deep ocean, and the blue lines are oceanic oxygenation events as inferred from global marine proxies such as $\delta^{238}\text{U}$ and RSE (Sahoo et al., 2016; Tostevin et al., 2019), grading to a fully oxic ocean at present day). The numbered circles denote: (1) A lower boundary for O_2 based on the loss of the MIF-S ($\text{O}_2 > 0.001\%$ PAL)(Farquhar, Bao and Thiemens, 2000; Pavlov and Kasting, 2002) but minimal $\delta^{53}\text{Cr}$ fractionation ($\text{O}_2 < 0.1\%$ PAL, see also (4)) (Planavsky et al., 2014), (2) an upper limit of $<50\%$ PAL until ~ 420 Ma, based on geochemical water column redox data and allowing for modelling uncertainties (Canfield, 1998, 2014; Sperling et al., 2015), (3) the appearance of terrestrial red beds and loss of detrital pyrite and uraninite (Holland, 2006), (4) minimal $\delta^{53}\text{Cr}$ fractionation, (5) RSE data indicating $\text{O}_2 > \sim 4\%$ PAL at 1400 Ma (Shuichang Zhang et al., 2016), (6) instances of significant $\delta^{53}\text{Cr}$ fractionation during the Mesoproterozoic ($\text{O}_2 > 0.1\%$ PAL) (Gilleaudeau et al., 2016; Canfield et al., 2018), (7) likely minimum $\text{O}_2 (>10\%$ PAL) required by late Ediacaran and Cambrian biota (Levin, 2003), (8) both upper and lower O_2 limits for the last 420 Myrs are based on the wildfire record from sedimentary charcoal abundance and modelling studies (Belcher and McElwain, 2008; Glasspool and Scott, 2010). Yellow bands represent the two potential ‘snowball’ Earth glaciations (Sturtian and Marinoan) and the later Gaskiers glaciation of the Neoproterozoic.

Here, we employ a biogeochemical technique called isotope mass balance to directly infer atmospheric oxygen concentrations from 1500 Ma to the present day. This approach was first developed by Garrels and Lerman (1984) and Berner (1987), and

was subsequently used to build the GEOCARBSULF model for estimating Phanerozoic O₂ concentrations (Berner, 2006a). Isotope mass balance uses the isotopic composition of sedimentary material, alongside major tectonic material fluxes, to estimate the source and sink fluxes in the geological oxygen cycle, which are the burial of organic carbon (C_{org}) and pyrite sulfur, and the weathering and tectonic recycling of these same species, respectively. The approach still remains at the heart of Phanerozoic O₂ estimation (Krause *et al.*, 2018), and is here applied to earlier Earth history, in a framework we call NEOCARBSULF.

4.2. Methods

4.2.1. Model overview

The NEOCARBSULF model is an extension of GEOCARBSULFOR and is solved numerically in MATLAB, using an implicit variable-order ODE method (Shampine and Reichelt, 1997). The original GEOCARBSULF model (Berner, 2006a) was solved using a Euler approach, but the differential equations employed by the model are ‘stiff’, therefore previous attempts at updating the model (Royer *et al.*, 2014; S. Zhang *et al.*, 2018) often resulted in model failure due to numerical instability. Using the ODE15s solver in MATLAB permits a dynamic step size, easily adapting to areas of stiffness.

4.2.2. Data updates

The $\delta^{13}\text{C}$ record is updated to use data from Krissansen-Totton *et al.* (2015) for the Mesoproterozoic and early Tonian, and Saltzman and Thomas (2012) for the rest of

the Neoproterozoic and Phanerozoic. To this data we applied a 10 Myr moving average with smoothing to eliminate variations over very short timescales and obtained a $\pm 1\text{sd}$ for our Monte-Carlo analysis. The values for mountain uplift and erosion rates (f_R) used in NEOCARBSULF are based on the reconstruction of original masses of sediment deposited during geologic intervals (Hay *et al.* 2006). The values for tectonic degassing (f_G) are based on subduction zone and rift lengths (Merdith *et al.* 2019). The data for the land area (f_A) is the same as is used in previous modelling (Krause *et al.*, 2018) for the Phanerozoic. For the Mesoproterozoic and Neoproterozoic we derive land area values using the crustal volume and thickness data (Hawkesworth *et al.*, 2016) and the present-day crustal volume value (Schubert and Sandwell, 1989).

4.2.3. Rift and plate boundary modelling

Plate boundary lengths from 1000 Ma to the Present were analysed using a full-plate model that combines existing models that discretely cover the last 1000 Myrs (Merdith *et al.*, 2019). Rift events over the last 1000 Myrs were taken from the compilation by Merdith *et al.* (2019) for the Neoproterozoic, as well as compilations of Şengör and Natal'in (2001) as digitised in Brune *et al.* (2017) for the Phanerozoic. These rifting events, which include failed rifts, are incorporated into the tectonic models as digitised polylines in *GPlates* (www.gplates.org). Subduction zone length was calculated using the *pyGPlates* python library (www.gplates.org/pygplates) after Merdith *et al.* (2019).

4.2.4. Carbon cycle changes

To employ isotope mass balance for long periods of Earth history (i.e. beyond the timeframes in which the large crustal reservoirs could be considered close to steady state) we make a number of changes to the calculation of the carbon cycle fluxes.

We modify the carbon cycle such that, instead of using the model-derived crustal carbon reservoir sizes in the weathering and degassing equations for young and ancient organic and carbonate carbon, as is the case with previous iterations of the model (Berner, 2006a; Royer *et al.*, 2014; Krause *et al.*, 2018) we use the results generated by Hayes and Waldbauer (2006), where they demonstrate that the crustal carbon inventory has increased steadily over time (Fig. 4.2D). We normalised their results to their present day value of 8500×10^{18} moles and then multiplied this normalised value by the starting reservoir sizes of the different forms of carbon (see table 4.4), using the total crustal carbon value of 6250×10^{18} moles from the original GEOCARBSULF (Berner, 2006a).

We have, however, changed the split of crustal carbon between inorganic and organic forms to be in the ratio of 0.23, instead of the prior 0.2, as this allows for various model processes, including atmospheric O_2 to finish the model run with present-day values, but remains within the range permitted by a statistical analysis of the $\delta^{13}C$ record (Krissansen-Totton, Buick and Catling, 2015). The total amount of carbon in the model (i.e. the summation of all crustal reservoirs plus the ocean-atmosphere reservoir) is in mass balance through the entire model run time, but our changes to the carbon cycle alter the throughput of crustal carbon to the ocean-atmosphere reservoir by way of steadily increasing weathering and degassing fluxes through time. This allows the model to buffer against geologically large, positive (and negative to an extent – see the sulfur cycle changes section) swings in the $\delta^{13}C$ record

in the Precambrian, but also to mitigate against times when the record is relatively static.

We also simplified the equation to calculate C_{org} burial (equation 4.29), using the approach of Rothman *et al.* (2003), where: the total amount of carbon entering the ocean-atmosphere reservoir ($F_{\text{total\_c}}$) is multiplied by the fraction of the atmosphere-ocean carbon pool that will leave as organic carbon (f_{org}). This change was utilised as the previous approach, using the carbon isotope values generated by the model for each carbon rock reservoir (e.g. Berner, 2006a; Krause *et al.*, 2018), are very uncertain and can introduce unintended feedbacks into the model, generating unrealistic values of C_{org} burial over longer timescales.

4.2.5. Sulfur cycle changes

We introduce scaling factors (see Fig. 4.2E and 4.2F, and sections 4.5.2 and 4.5.3) to: the equation for gypsum burial (equation 4.34), to simulate basin-scale evaporite deposition during the Tonian; the equations for young and ancient gypsum weathering (equations 4.19 and 4.20 respectively), to represent dissolution of the evaporite deposits during 560 – 580 Ma, roughly coincident with the Shuram-Wonoka anomaly; and to the equation for pyrite burial (equation 4.33) during the Shuram-Wonoka anomaly, effectively turning a majority of the extra sulfate in the ocean, as a result of evaporite dissolution, into pyrite. This follows previous work (Shields *et al.*, 2019) and prevents the ocean-atmosphere becoming depleted in O_2 during the Shuram-Wonoka when the $\delta^{13}\text{C}$ record is extremely negative (see Fig. 4.2A).

4.2.6. Monte-Carlo setup

In order to capture some of the uncertainty in the model parameterisation we run a Monte-Carlo analysis of the NEOCARBSULF model, where a number of parameters are sampled from within defined limits, following a flat (instead of normal) distribution, at each timestep (see table 4.5). Although we vary 10 parameters in our analysis, the three key parameters involved are: the $\delta^{13}\text{C}$ record (see Fig. 4.2A) which will greatly influence the amount of O_2 produced by way of C_{org} burial; the tectonic degassing (f_{G}) values used (Fig. 4.2B), which can change the amount of O_2 consumption from both pyrite and C_{org} oxidation as well as the total carbon throughput; and mountain uplift (f_{R} , Fig. 4.2C) which, like tectonic degassing, will affect O_2 consumption and total carbon throughput.

The NEOCARBSULF model is run 5,000 times, instead of 10,000 times as used in previous modelling (Royer *et al.*, 2014), as this was considered adequate for the number of parameters involved in this Monte-Carlo simulation (see figure 4.5 and associated text in section 4.5.1. for further details).

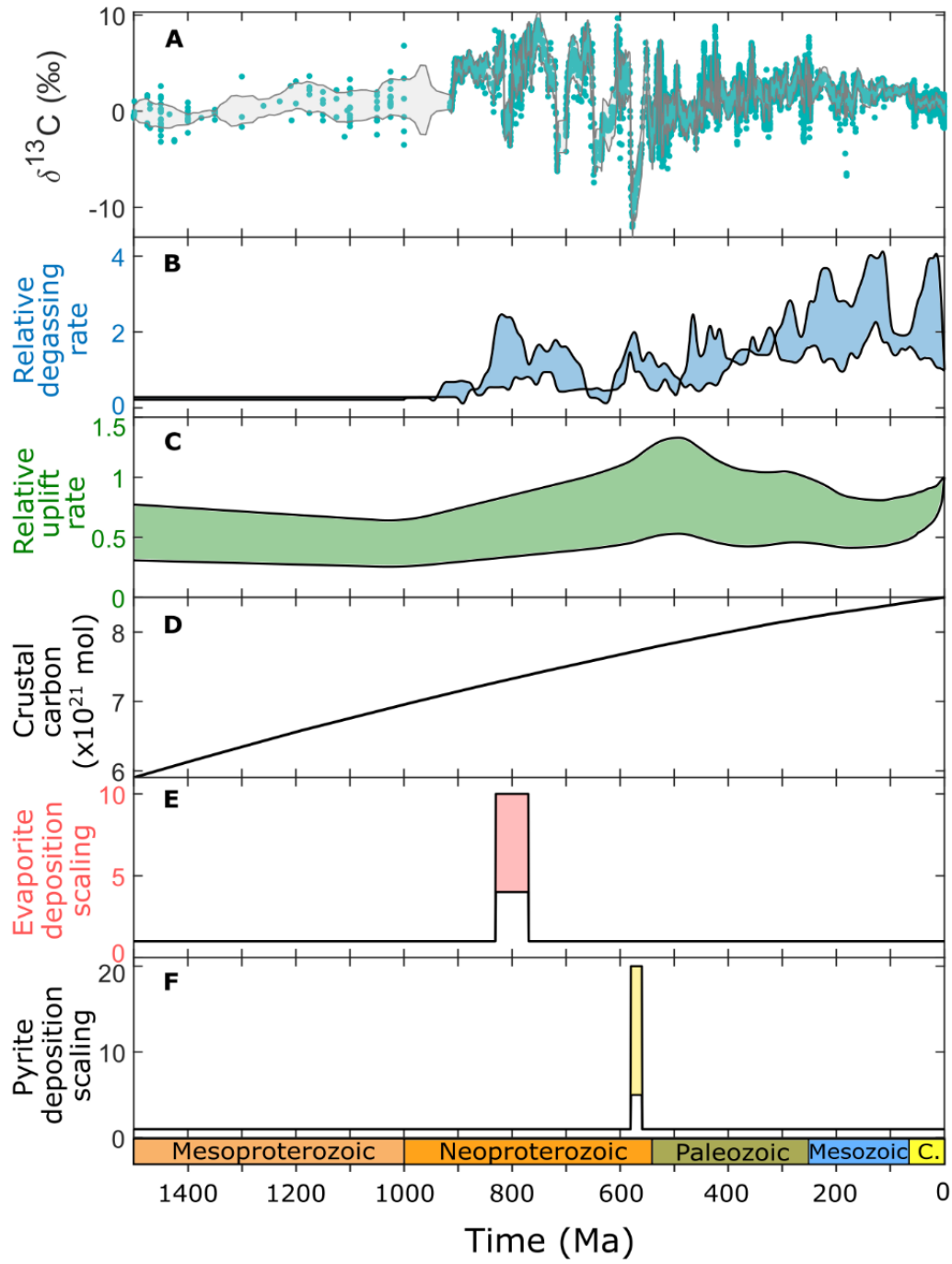


Figure 4.2 | Key parameters in the NEOCARBSULF model.

A) A compilation of $\delta^{13}\text{C}$ through time (teal dots), with the grey band representing $\pm 1\text{sd}$ of a moving average. The data are taken from the compilations of Krissansen-Totton et al. (2015) and Saltzman and Thomas (2012) and references therein. B) Tectonic degassing, normalised to the present day, where the black boundaries represent the Monte Carlo sampling limits. C) Mountain uplift normalised to the present day, where the black boundaries represent the Monte Carlo sampling limits. D) An increase in the crustal carbon reservoir since 1500 Ma (Hayes and Waldbauer, 2006). E) A scaling factor introduced into the model to simulate large-scale evaporite deposition in the Tonian. F) A scaling factor introduced to replicate a proposed increase in pyrite burial coincident with the Shuram-Wonoka anomaly.

See Methods for further details.

4.3. Results

The O_2 results from NEOCARBSULF (Fig. 4.3) show a first significant rise in oxygen at ~ 900 Ma, when O_2 rises from $\sim 1\%$ PAL to $>5\%$ PAL, although an earlier rise could be masked by the transition from relatively sparse to dense $\delta^{13}\text{C}$ data. Generally, O_2 continues to rise steadily (except for a brief reversal which begins at 816 Ma just prior to, and is probably driven by, the Bitter Springs negative $\delta^{13}\text{C}$ excursion) until a peak of $\sim 50\%$ PAL at ~ 750 Ma. Predicted O_2 levels then begin to decline and eventually return to the low levels of the Mesoproterozoic, as the Earth entered the Sturtian glaciation. During the interglacial, O_2 rises to $\sim 20\%$ PAL before dropping again as the Earth entered the Marinoan glaciation.

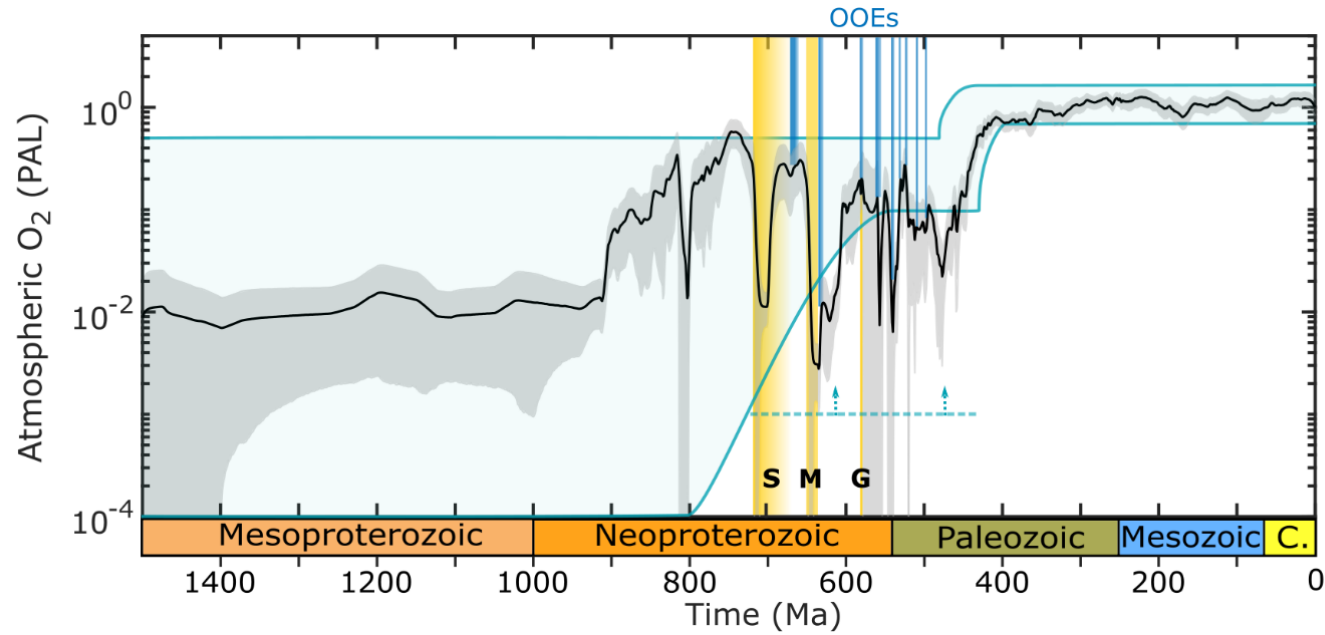


Figure 4.3 | Reconstructed O_2 evolution from 1500 Ma to present.

Atmospheric oxygen results estimated from the NEOCARBSULF model, where the black line is the mean result of 5,000 model runs. The grey shaded band represents $\pm 1sd$, which may include very low values on occasion. The blue shaded band is the O_2 'best guess' estimate from Fig. 4.1 (top panel), and the blue lines are the oceanic oxygenation events as seen in Fig. 4.1 (bottom panel). The blue dashed line with arrows is the minimum O_2 level previously defined by substantial $\delta^{53}Cr$ fractionation (Planavsky et al., 2014; Cole et al., 2016). The yellow lines are the glaciations, S: Sturtian, M: Marinoan, G: Gaskiers.

Post-Marinoan, O₂ enters a period of more rapid variability across most of the Ediacaran and Cambrian periods. Another low is recorded during the early Ordovician (485.4 – 470 Ma), before O₂ begins its inexorable rise to modern-day levels at the end of the Ordovician, in agreement with earlier work using isotope mass balance calculations (Krause *et al.*, 2018).

4.4. Discussion

Arguably these highly dynamic results for atmospheric O₂ are a better match to geochemical proxy data than the generally assumed stepwise increase in atmospheric O₂. Firstly, our model predicts a rise in O₂ at ~850 Ma from ~8%, reaching ~34% PAL by 815 Ma, which corresponds to a statistically significant difference in $\delta^{53}\text{Cr}$ fractionation in post 850 Ma shales (Cole *et al.*, 2016). Furthermore, $\delta^{238}\text{U}_{\text{sw}}$ values at the onset of the Bitter Springs C isotope excursion (810 Ma, Halverson *et al.*, 2005) are below that of modern seawater, indicating widespread anoxia at a time when our results suggest that O₂ was in temporary decline (Gilleaudeau *et al.*, 2019), but O₂ rapidly recovers at 803 Ma, before the end of the isotope excursion (at ~800 Ma), which is consistent with increased I / (Ca + Mg) ratios signifying shallow ocean oxygenation at this time (Lu *et al.*, 2017; Wörndle *et al.*, 2019). Meanwhile, $\delta^{53}\text{Cr}$ data suggest a rise in O₂ at ~750 Ma (giving a sizeable fractionation from the BSE), consistent with our results indicating O₂ levels of ~30% PAL.

NEOCARBSULF predicts that O₂ decreases at the onset of the Sturtian glaciation, and this is clearly reasonable, considering that glacial advance would have started to restrict the flux of nutrients and sunlight to the ocean, leading to a collapse in primary productivity (Hoffman *et al.*, 1998). Our results suggest that O₂ recovers after the Sturtian, in good agreement with $\delta^{238}\text{U}_{\text{sw}}$ data from limestones deposited at the termination of the glaciation, recording an average value (-0.47‰) which is not dissimilar to that of modern seawater ($-0.39 \pm 0.01\text{‰}$) (Lau *et al.*, 2017). When coupled with box modelling, this suggests extensive, albeit temporary, seafloor oxygenation before the Earth began its descent into the Marinoan glaciation, whereupon NEOCARBSULF O₂ levels begin to decline and the $\delta^{238}\text{U}_{\text{sw}}$ average drops (to -0.70‰) (Lau *et al.*, 2017).

Atmospheric O₂ does recover after the Marinoan, which can be tracked by the enrichment of RSEs in shales at this time (Sahoo *et al.*, 2016), but the slow speed of its recovery correlates with minimal $\delta^{53}\text{Cr}$ variation from the BSE value that is observed until 570 Ma (Frei *et al.*, 2013; Cole *et al.*, 2016; W. Wei *et al.*, 2018).

We predict that O₂ steadily rose in the early Ediacaran, but that levels in the Ediacaran and Cambrian were variable and still below 20% PAL. Generally, NEOCARBSULF predictions of rises (or high levels, compared to the rest of this timeframe) in O₂ in the Ediacaran and Cambrian are in agreement with RSE enrichments (Sahoo *et al.*, 2016) at ~580, ~560, ~535 and ~525 Ma. The only exception is where the RSE data predicts an oceanic oxygenation event at ~540 Ma, when NEOCARBSULF indicates temporarily low O₂ (~0.64% PAL). However, this may be due to low $\delta^{13}\text{C}$ values at this time (-5‰) from which NEOCARBSULF will infer deoxygenation, but rapid

inputs of other oxidants like sulfate can maintain or even expand the O₂ reservoir (Shields *et al.*, 2019). We follow Shields *et al.* (2019) in inputting a large pulse of sulfate coincident with the >10 Myr Shuram negative carbon isotope excursion (see Methods), which prevents deoxygenation during that time, but it is possible that we have missed other, smaller sulfate-induced O₂ peaks, given that evaporite dissolution leaves no clear signal in the rock record. Generally speaking, the predicted variability in atmospheric O₂ across the Ediacaran and Cambrian suggests that fluctuating oxygen levels, rather than progressive oxygenation of the oceans, accompanied the Cambrian explosion (G.-Y. Wei *et al.*, 2018; He *et al.*, 2019).

Our biogeochemical framework allows us to test the robustness of our oxygen results by making predictions for other Earth system metrics with known quantities. In Fig. 4.4 we compare these model outputs to various geochemical proxies and other kinds of modelling studies. Our f_{org} output – the fraction of carbon leaving the ocean as C_{org} – is compared to both the Kernel and LOWESS regression curves (Krissansen-Totton *et al.*, 2015), which are based on an independent statistical analysis of the $\delta^{13}\text{C}$ record. Generally, our results oscillate around the regression curves, indicating that if a similar smoothing was conducted on our results, our f_{org} would be similar to that of Krissansen-Totton *et al.* (2015). This is to be expected, particularly for the Mesoproterozoic and early Tonian, as we use the $\delta^{13}\text{C}$ data compiled by Krissansen-Totton *et al.* (2015) for this timeframe, and both studies invert the $\delta^{13}\text{C}$ record in some way to obtain f_{org} .

Our f_{pyr} (Fig. 4B) – the fraction of sulfur leaving the ocean as pyrite – is also a reasonable fit to the record: the model predicts fairly high pyrite burial in the

Precambrian, apart from a period of sustained gypsum deposition between 830 – 770 Ma, which has been imposed on the model in light of evidence for substantial Tonian evaporite giants, which were later weathered during the Ediacaran (Shields *et al.*, 2019). Our Phanerozoic predictions are very close to previous modelling (Canfield and Farquhar, 2009), apart from f_{pyr} values that are slightly lower in the Ordovician, and slightly higher during the Triassic.

Our model output for the ocean sulfate reservoir (Fig. 4C) captures the long-term trend of increasing sulfate concentration over the last 1500 Myrs, and correlates to several fluid-inclusion data points and prior modelling efforts. Finally, instead of inverting the $\delta^{34}\text{S}$ record in the model to help derive pyrite burial, as per the original GEOCARBSULF (Berner, 2006a), our new model can make a prediction as to what the global $\delta^{34}\text{S}$ record might be over time. Our model prediction (Fig. 4D) matches the geological record reasonably well. The clearest area of mismatch is the Cryogenian, where $\delta^{34}\text{S}$ is lower than in the geological record by around 10‰, but f_{pyr} is broadly in agreement. This may represent a period of enhanced pyrite weathering (with low $\delta^{34}\text{S}$ values) in response to the extra gypsum burial we enforce in the model. However, the long-term trend remains robust. Other model outputs are compared to geological data in the SI and are generally in agreement.

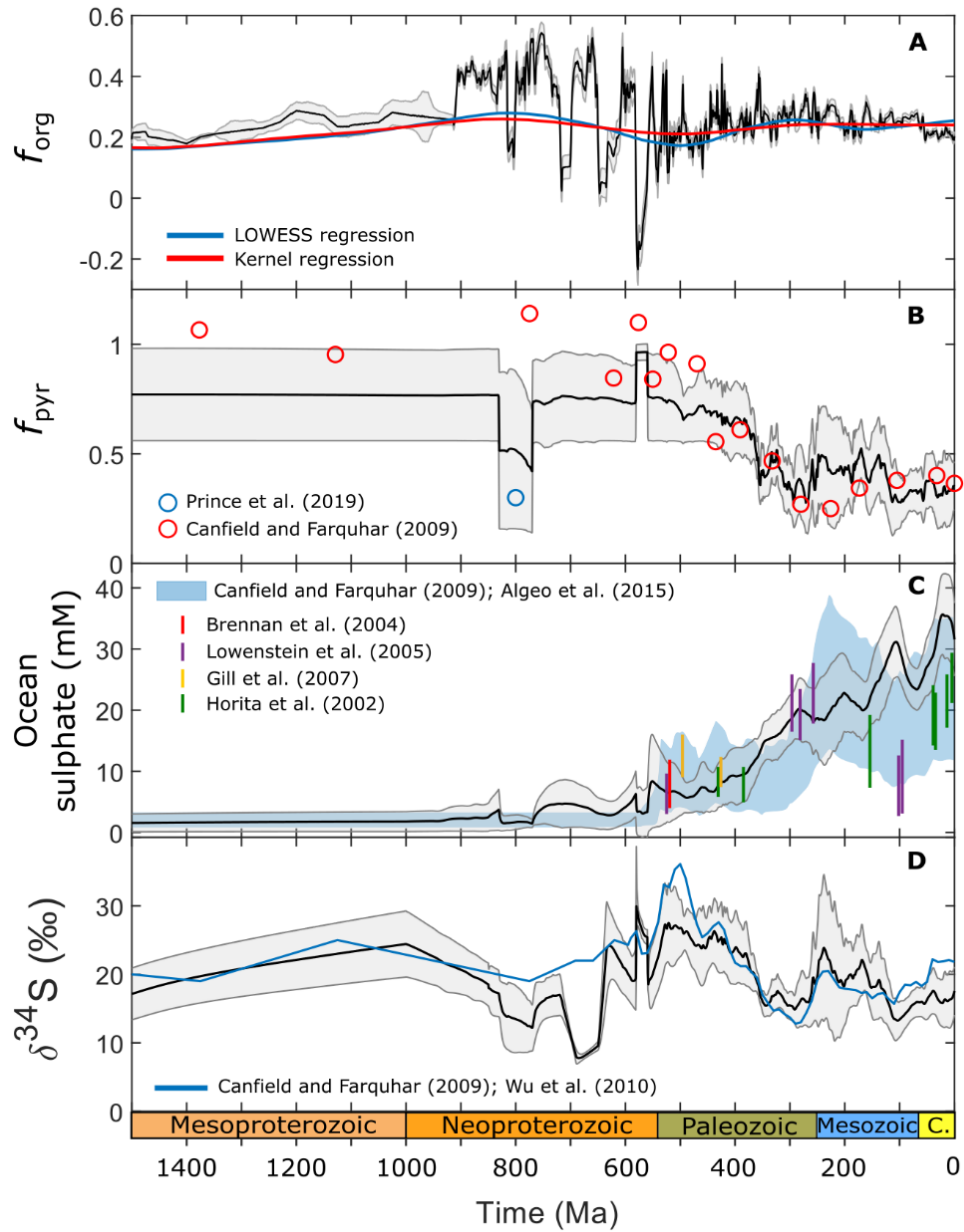


Figure 4.4 | Additional outputs from the NEOCARBSULF model compared to geochemical data and other modelling studies.

For all panels the black line is the mean result of 5,000 model runs, and the grey window represents $\pm 1\text{sd}$. A) The fraction of total carbon burial that is in the form of C_{org} . The blue and red lines are LOWESS and kernel regression smoothed curves, respectively, based on a statistical analysis of the $\delta^{13}\text{C}$ record (Krissansen-Totton, Buick and Catling, 2015). B) The fraction of total sulfur burial that is in the form of pyrite, compared to modelling of $\delta^{34}\text{S}$ data (Canfield and Farquhar, 2009; Prince, Rainbird and Wing, 2019). C) The sulfate concentration of the ocean over time. The light blue band represents the $\pm 1\text{sd}$ uncertainty range of a previous reconstruction (Algeo et al., 2015), and the vertical coloured bands are values based on fluid-inclusion studies or modelling (Horita, Zimmermann and Holland, 2002; Brennan, Lowenstein and Horita, 2004; Lowenstein et al., 2005; Gill, Lyons and Saltzman, 2007). D) The modelled prediction of the global average $\delta^{34}\text{S}$ record through time, compared to geochemical data (Canfield and Farquhar, 2009; Wu et al., 2010).

A key aspect driving our prediction is the overall increase in crustal carbon storage and tectonic recycling rate over Earth history. Traditionally, there has been something of a paradox surrounding the long-term stability of $\delta^{13}\text{C}$ around 0‰, which indicates that the fraction of carbon buried organically (and therefore the key O_2 source) did not see any long term increase or decrease (e.g. Schidlowski, 1988), and has been seen as contradictory to increasing levels of atmospheric O_2 . Our work here confirms that this long term $\delta^{13}\text{C}$ stability can be maintained in tandem with rising O_2 levels, partially because the total rate of carbon cycling is increasing, but also because the weathering rate of organic matter is oxygen-dependent (Daines, Mills and Lenton, 2017).

Our results suggest that, while there was a definite regime change for oxygen in the Neoproterozoic leading to some form of Neoproterozoic Oxygenation Event (Och and Shields-Zhou, 2012), this was not a unidirectional step change, but rather a series of oxygen oscillations. This is likely in response to the global tectonic regime during the Cryogenian-Cambrian, as the supercontinent Rodinia broke apart (ca. 800–600 Ma) and Gondwana began to coalesce (ca. 650–500 Ma), and was exacerbated by internal feedbacks within the oxygen cycle (e.g. Alcott, Mills and Poulton, 2019).

From this arises two possible explanations for equilibrium of the Earth system, and consequently atmospheric O₂ levels: (1) the evolution of land plants was the key event which precipitated this stabilisation, paving the way for the existence of marine animals with a high O₂ demand, and eventually, animal life in the terrestrial realm; (2) stabilisation occurred once the deep ocean became resiliently oxygenated, limiting the ability of changes in marine redox to cause major shifts in nutrient cycling. Testing these hypotheses will require different kinds of models with more complex ocean chemistry, which will be fruitful avenues for further research.

4.5. Supplementary information

4.5.1. Further model validation and sensitivity analyses

In addition to the model outputs discussed in the main text (Fig. 4.4), NEOCARBSULF can also predict atmospheric CO₂ and global average surface temperature changes over time. We plot these results (Fig. 4.5 and Fig. 4.6 respectively) and compare them to geochemical proxy compilations where available

(Mills *et al.*, 2019). Our model CO₂ predictions show good agreement with the proxy window for the majority of the last ~420 Myrs, with the mean of model runs lying within, or very close to, the proxy window. The notable exception is during the end of the Lower Cretaceous and much of the Upper Cretaceous (~74 – 106 Ma) where the model predicts CO₂ values significantly different to those suggested by the proxy record.

The spreading rates used in NEOCARBSULF during this time (Fig. 4.2B) are higher than those used in GEOCARBSULF(OR) (Royer *et al.*, 2014; Krause *et al.*, 2018), which experience similar discrepancies. However, for the majority of the Lower Cretaceous, spreading rates based on rift lengths alone are very high and decrease sharply towards the end of the Lower Cretaceous, while spreading rates based on subduction zone lengths experience only a minor decline. This results in a skewing of the Monte-Carlo simulation, generating a modelled Earth system with higher CO₂ and thus temperature, earlier in the Cretaceous, than would otherwise be predicted if NEOCARBSULF used the sea level inversion results from previous GEOCARB(SULF) modelling (Berner, 1991, 2006a; Royer *et al.*, 2014).

This high CO₂ and temperature would have facilitated enhanced silicate weathering and drawdown of CO₂ during the later Cretaceous right at the same time as degassing rates, both based on rift lengths and subduction lengths, decline to below 2x present day levels. This ties in with earlier work that suggests 3x the present day spreading rate is required to maintain elevated CO₂ levels during this time (Royer *et al.*, 2014).

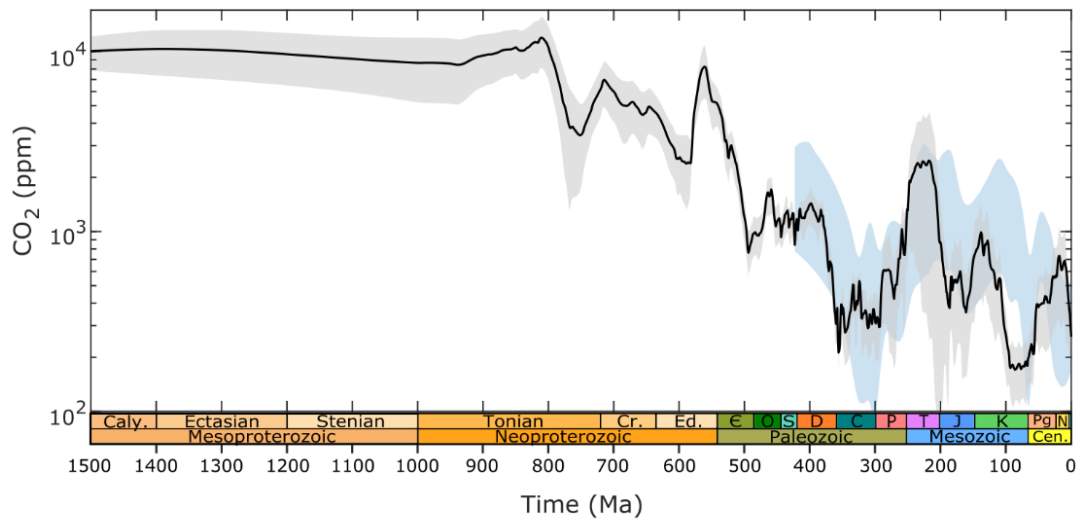


Figure 4.5 | Atmospheric CO₂ predictions compared to geochemical proxies.

The black line is the mean of 5,000 model runs and the grey window is the ± 1 sd of the runs. The blue window is a compilation of various geochemical proxies for CO₂ for the last ~420 Myrs (Mills et al., 2019).

Our temperature predictions are also in good agreement with the geochemical proxy compilation for much of the last 750 Myrs. Again, there is an issue with temperature predictions which are too low during the end of the Lower Cretaceous and much of the Upper Cretaceous, which is probably due to the low CO₂ values generated by the model here. There is also a large discrepancy between the model and proxies during the end Ediacaran through to the end Ordovician. This is partly due to a correlation with declining CO₂ values, however, it may also be due to the climate sensitivity value in use, which perhaps does not accurately capture the relationship between CO₂ and temperature during this time.

For our baseline model runs we use an Earth system sensitivity (*gamma*, which is number of °K per CO₂ doubling) fixed at 3°K for the entire 1500 Myrs. In previous

modelling (Royer *et al.*, 2014; Krause *et al.*, 2018) the value of *gamma* changes, depending on whether the Earth is in an icehouse or greenhouse state.

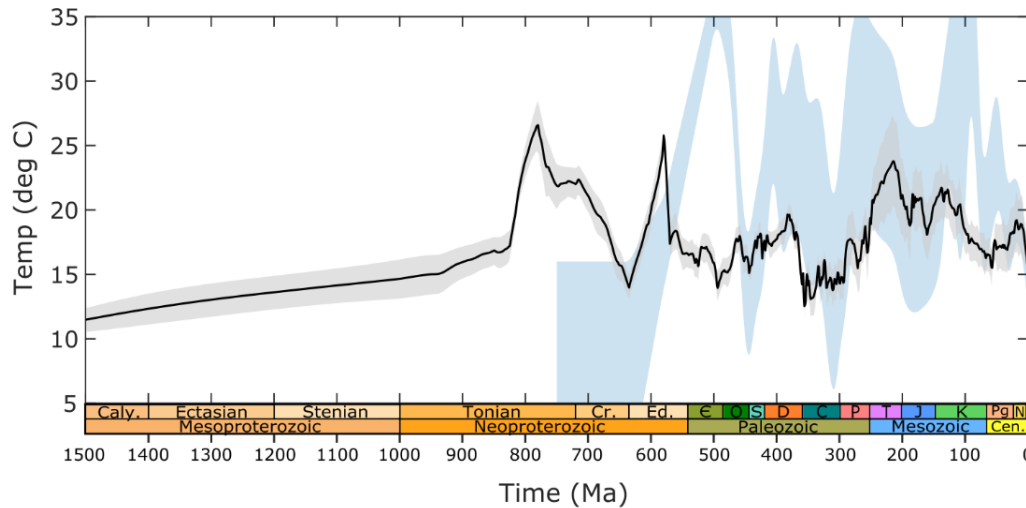


Figure 4.6 | Global average surface temperature predictions compared to geochemical proxies.

The black line is the mean of 5,000 model runs and the grey window is the ± 1 sd of the runs. The blue window is a compilation of various geochemical proxies for CO_2 for the last ~750 Myrs (Mills *et al.*, 2019).

In figure 4.7 we test the effect a changing climate sensitivity (*gamma*) has on our O_2 , CO_2 and temperature predictions. Changing *gamma* has little effect on O_2 , apart from during the Marinoan glaciation, which is a period that is particularly sensitive to variations in model parameters. Surprisingly, this is also the case for CO_2 and temperature, where there is little variation, except during the Cryogenian which displays a marked difference, due to a probable sensitivity surrounding the ice-albedo feedback (Mills *et al.*, 2019).

It is possible then, that during the Cambrian (and the Upper Cretaceous) *gamma* would need to be much lower, perhaps as little as 1°K per CO_2 doubling, in order to generate the high temperatures suggested by the proxy record, and during the Cryogenian it would need to be closer to a 10°K sensitivity (Royer, 2016; Mills *et al.*, 2019).

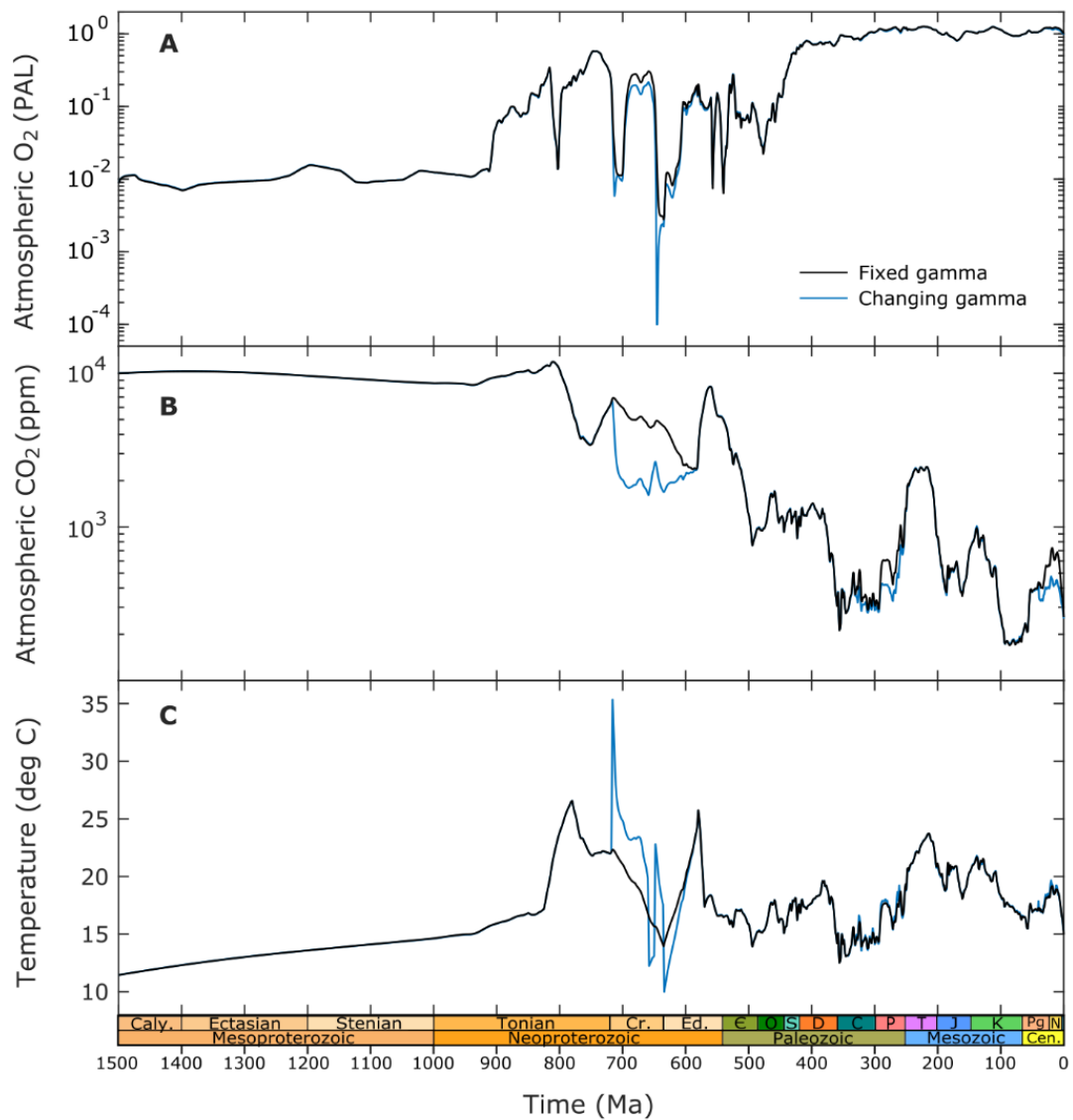


Figure 4.7 | A comparison of different values for *gamma*, the response of global mean temperature to atmospheric CO_2 greenhouse effect.

For all panels the black line is the mean of model runs using a gamma value of 3 for the entire model run (the baseline value for this study), and the blue line is the mean of model runs using gamma values of 6 for icehouse periods and 3 for greenhouse periods of time (these values are used by GEOCARBSULFOR (Krause et al., 2018)).

A) The effect on atmospheric O₂. B) The effect on atmospheric CO₂. C) The effect on global average surface temperature.

Another parameter of consideration is W_s , the effect of changing solar insolation on temperature. In Phanerozoic models (Berner, 2006a; Royer *et al.*, 2014; Krause *et al.*, 2018; Lenton, Daines and Mills, 2018) W_s is set to 7.4° . This is based on equation (4.51) for which Berner used values for: $temp = 288^\circ\text{K}$; $temp\_0 = 288^\circ\text{K}$; $gamma = 3.3^\circ\text{K}$; $\text{RCO}_2 = 8.7\times$ present atmospheric level (PAL); *model run time* = 570 Myrs; and $t = 550$ Myrs, as a result of global circulation modelling (Berner, 2004).

This RCO_2 value is probably fine for Phanerozoic modelling, although in retrospect, 8.7 PAL for the end of the Ediacaran appears low, based on model predictions for this time (Berner, 2008; Krause *et al.*, 2018; Lenton, Daines and Mills, 2018). However, extending the model through the Proterozoic necessitates a change to the value of W_s as the model run time is substantially different, and the solar luminosity at 1500 Ma would also be considerably lower then, compared to 550 Ma.

If we hold RCO_2 and $temp\_0$ to the same values, and use a *gamma* value of 4.3281 (*gamma* of 3 but divided by the natural log of 2, following Royer *et al.* (2014) – see also equation (4.6)), update both t and *model run time* to 1600 (as we include a 100 Myr spin-up time within the model), and factor in a moderate decrease in the average global surface temperature, $temp$, from 288°K to 284.5°K for the

Mesoproterozoic, putting these values into equation (4.51) we end up with $W_s = 12.9^\circ\text{K}$. In fact, this value for W_s is the same as is used in GEOCARBII (Berner, 1994), based on prior GCM sensitivity analyses to CO_2 and solar luminosity (Marshall *et al.*, 1994).

The effect of using 12.9°K instead of 7.4°K can be seen in figure 4.8. This update has little effect on O_2 predictions, nor does it substantially change CO_2 and temperature estimates for the Phanerozoic, but it does result in higher CO_2 and lower temperature values in the Proterozoic, particularly the Mesoproterozoic. With our new W_s value, the model predicts a temperature of 11.5°C (or 284.5°K) at 1500 Ma, which rises to 14.6°C by the start of the Neoproterozoic, both of which agree very well with other modelling results (Krissansen-Totton, Arney and Catling, 2018). This suggests that our temperature assumption for calculating W_s is reasonable. As NEOCARBSULF predicts similar CO_2 and temperature values for the Phanerozoic using our new W_s , we believe that this update captures reasonably well the changing solar luminosity and its effect on climate over the last 1500 Myrs, however, actual GCM modelling in the future may help to refine this value further.

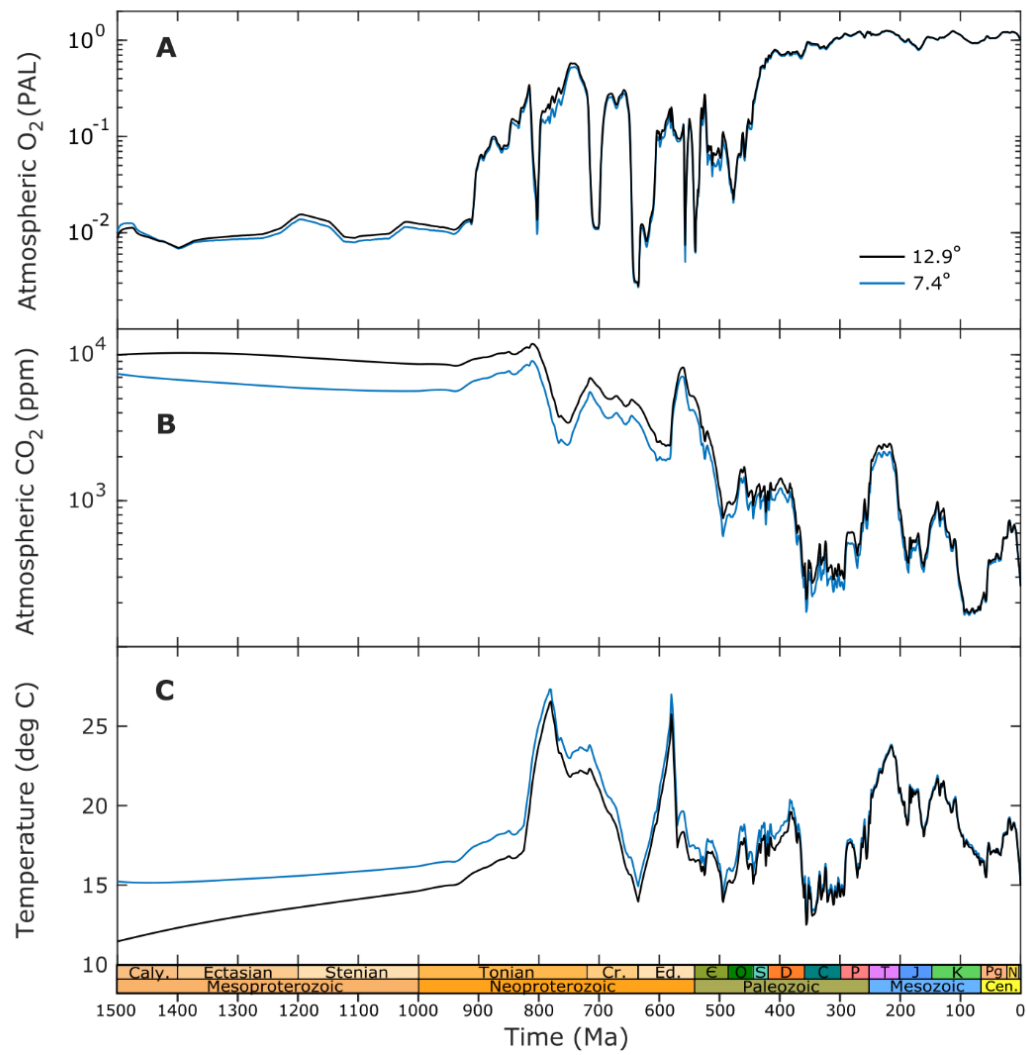


Figure 4.8 | A comparison of different values for W_s , the effect of solar insolation on temperature.

For all panels the black line is the mean of model runs using $W_s = 12.9^\circ$ (the baseline value for this study), and the blue line is the mean of model runs using $W_s = 7.4^\circ$ (the baseline value used for GEOCARBSULFOR (Krause et al., 2018)). A) The effect on atmospheric O_2 . B) The effect on atmospheric CO_2 . C) The effect on global average surface temperature.

Previous modelling work using a Monte-Carlo simulation approach (Royer *et al.*, 2014) utilised 10,000 model runs to ascertain sensitivity to various parameters in the GEOCARBSULF model. In our modelling we only use 5,000 model runs, partly due to the computational time 5,000 runs takes (approximately 60 hours using a 4-core i5 processor), but also partly due to the fact that we do not employ as many parameters in our sensitivity analysis. However, it is possible that the model has not run to completion and computed every single O₂ value possible after only 5,000 model runs. We decided to compare O₂ results from 2,000 runs to those from our 5,000 run baseline version. As can be seen in figure 4.9, there is no difference in mean O₂ between 2,000 and 5,000 model runs, and there is insignificant variation in the ± 1 sd values, thus we are certain that running NEOCARBSULF 5,000 times is sufficient and the model has run to completion.

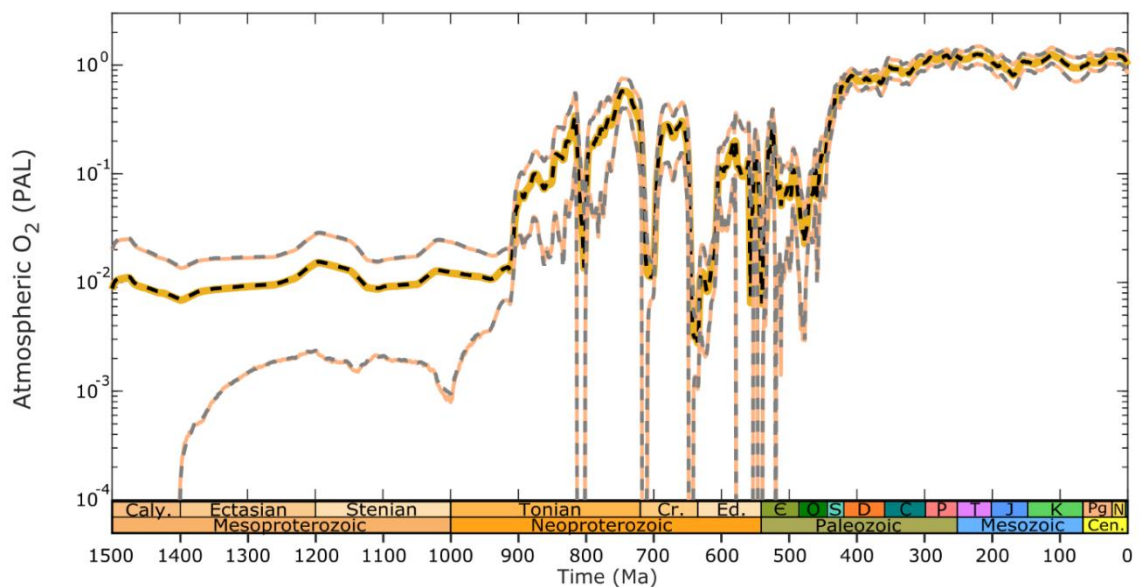


Figure 4.9 | Comparison of 5,000 vs. 2,000 model runs for Monte-Carlo analysis.

The black dashed line is the mean result of 5,000 model runs, and the yellow solid line is the mean result of 2,000 runs. The grey dashed lines are the ± 1 sd of 5,000 runs, and the peach solid lines are the ± 1 sd of 2,000 runs.

We plot a number of fluxes generated by the model, to check that NEOCARBSULF returns present day values at the end of its run (at 0 Ma). In figure 4.10 we plot the estimated C_{org} burial flux over the last 1500 Myrs, which is dependent on the $\delta^{13}\text{C}$ record and total carbon in the atmosphere-ocean reservoir through time (see equations 4.25, 4.26, 4.28, 4.29).

There is a general trend of steadily increasing C_{org} burial rates over the last 1500 Myrs, punctuated by present day levels in the Tonian, and negative values during the Shuram-Wonoka anomaly, which could be taken as the remineralisation of a large pool of C_{org} that otherwise would be buried within oceanic sediments (Rothman *et al.*, 2003; Shields *et al.*, 2019). NEOCARBSULF returns a present day burial rate of $7.06 \times 10^{18} \text{ Mol Myr}^{-1}$, which lies in the middle of other estimated present day rates of $5 \times 10^{18} \text{ Mol Myr}^{-1}$ by Berner (1987) and $9 \times 10^{18} \text{ Mol Myr}^{-1}$ in COPSE (Bergman, Lenton and Watson, 2004) giving confidence that NEOCARBSULF is returning reasonable burial rates.

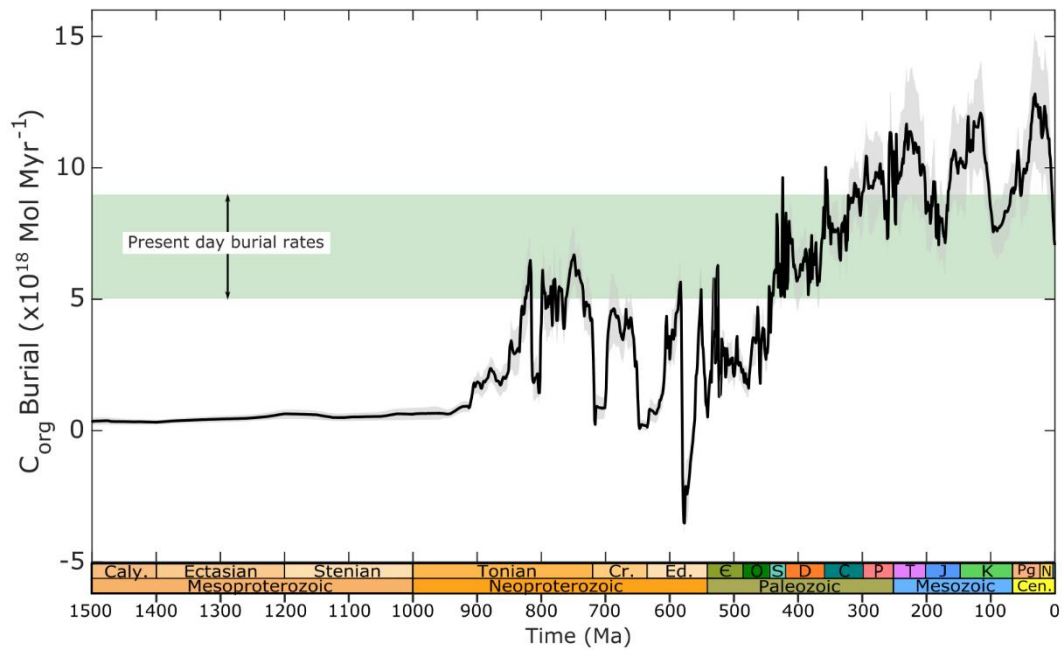


Figure 4.10 | Organic carbon burial rates for the last 1500 Myrs.

The black line is the mean of 5,000 model runs and the grey window is the ± 1 sd of the runs. The green window represents different estimates of present day burial rates (Berner, 1987; Bergman, Lenton and Watson, 2004).

In figure 4.11 we plot the pyrite burial rates from NEOCARBSULF. Unlike C_{org} burial, our results show that there has not been a significant change in pyrite burial rates over the last 1500 Myrs. Rather, the change in f_{pyr} (the fraction of sulfur leaving the ocean as pyrite; see figure 4.4B and equation (4.27)) from high values in the Precambrian to a much lower fraction in the Phanerozoic, is a result of increasing oceanic sulfate and O_2 concentrations generated by the model, which would constrain pyrite burial rates and enable more substantial gypsum deposition. In the non-model world, alongside a rise in O_2 concentrations and sulfate from the weathering of terrestrial sulfides, it is possible that the evolution of bioturbation also promoted the reoxidation of marine sulfides back to sulfate (Bottrell and Newton, 2006; Canfield and Farquhar, 2009).

The peak in pyrite burial from ~560 to 580 Ma, during the Shuram-Wonoka anomaly is the result of a scaling of gypsum weathering and subsequent pyrite burial, newly introduced into the model (see tables 4.2, 4.3 and 4.5, and equations (4.19, 4.20 and 4.33) for more details), in order to deal specifically with the negative C_{org} burial rates (Fig. 4.10) inferred by the $\delta^{13}C$ record, which would have entirely depleted the ocean-atmosphere system of O_2 .

In our Monte-Carlo simulation we use a minimum scaling value of 5, this results in a pyrite burial flux of $1.7 \times 10^{18} \text{ Mol Myr}^{-1}$, which is insufficient to counteract the large, negative C_{org} burial flux, thus suggesting that the Shuram-Wonoka anomaly was a time of substantial pyrite deposition, which is reflected in our model computation of f_{pyr} of ~1 (Fig. 4.4B) and previous work implying $f_{pyr} > 1$ (Canfield and Farquhar, 2009). NEOCARBSULF predicts pyrite burial rates of $\sim 1.3 \times 10^{18} \text{ Mol Myr}^{-1}$ at present day, which is within the bounds of previous estimates (Berner, 1982; Hu and Cai, 2011).

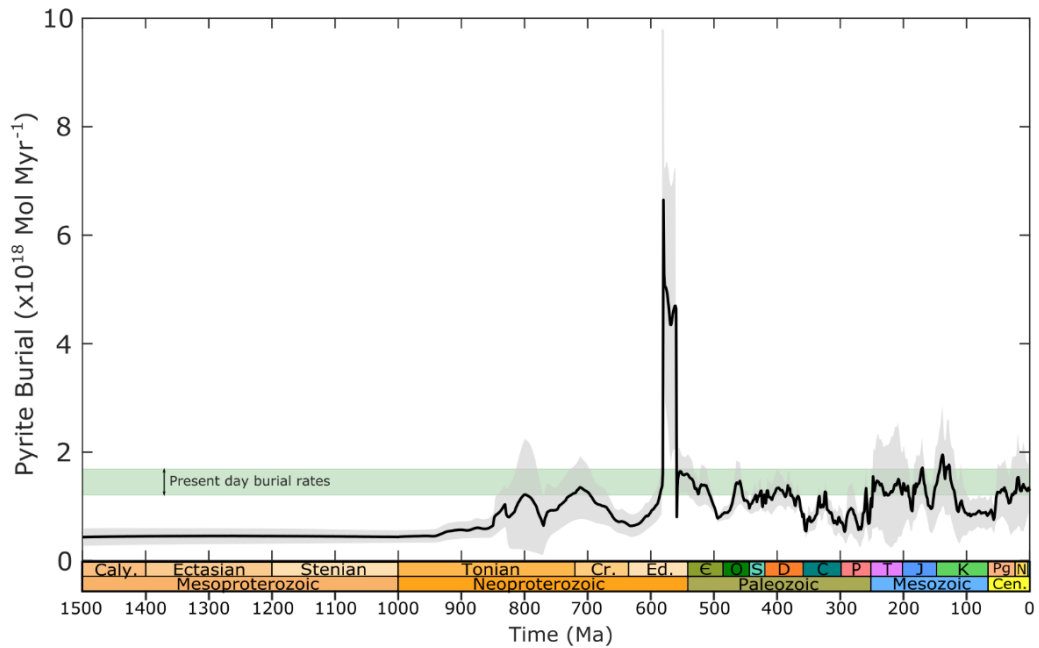


Figure 4.11 | Pyrite burial rates for the last 1500 Myrs.

The black line is the mean of 5,000 model runs and the grey window is the ± 1 sd of the runs. The green window represents different estimates of present day burial rates (Berner, 1982; Hu and Cai, 2011).

We also plot the silicate weathering flux from NEOCARBSULF (Fig. 4.12) as one more test to see if the model obtains present day rates in line with real-world estimates. Overall, there is a strong relationship between relative degassing rates through time with silicate weathering rates. Higher degassing of both forms of carbon would have increased the concentration of CO_2 , temperature and thus silicate weathering. However, higher than present day degassing rates during the Tonian (Fig. 4.2B) do not quite result in present day silicate weathering rates, and this is due to mountain uplift (f_R , see Fig. 4.2C) values of <1 which tempers the amount of material available to undergo weathering during this time. The mean silicate weathering flux at the end of the model runs is $6.1 \times 10^{18} \text{ Mol Myr}^{-1}$ which is close to the $6.7 \times 10^{18} \text{ Mol Myr}^{-1}$ value

used by Berner in the original GEOCARB model (Berner, 1991), with the + 1sd of our results giving a flux value of 7.0×10^{18} Mol Myr⁻¹.

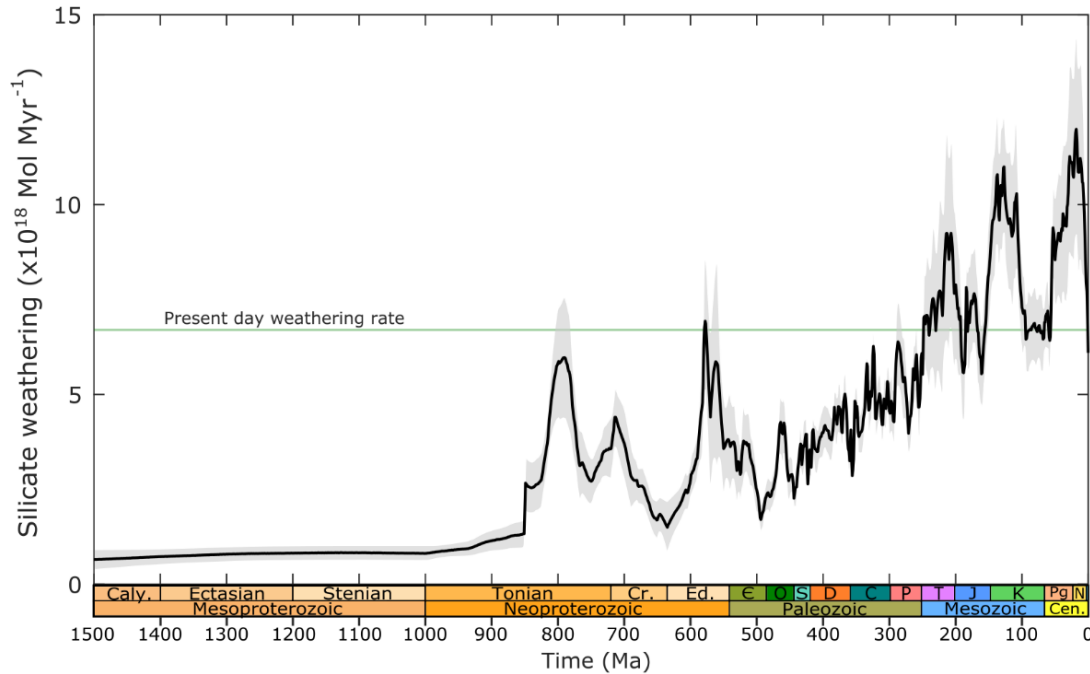


Figure 4.12 | Silicate weathering rates for the last 1500 Myrs.

The black line is the mean of 5,000 model runs and the grey window is the ± 1 sd of the runs. The green line is the weathering rate assigned as present day in the original GEOCARB model (Berner, 1991).

Finally, we checked that the model correctly portions the total mass of crustal sulfur between the gypsum and pyrite reservoirs over time, starting with a pyrite-dominated Precambrian (Canfield and Farquhar, 2009), with a steady decline in pyrite and corresponding increase in gypsum over the Phanerozoic, and finishing with near equal reservoir values (total pyrite of 180×10^{18} moles and total gypsum of 200×10^{18} moles) in the Present (Kump and Garrels, 1986); NEOCARBSULF achieves this (Fig. 4.13),

with values at the end of its run that are very close to those at present day, indicating that our model is robust.

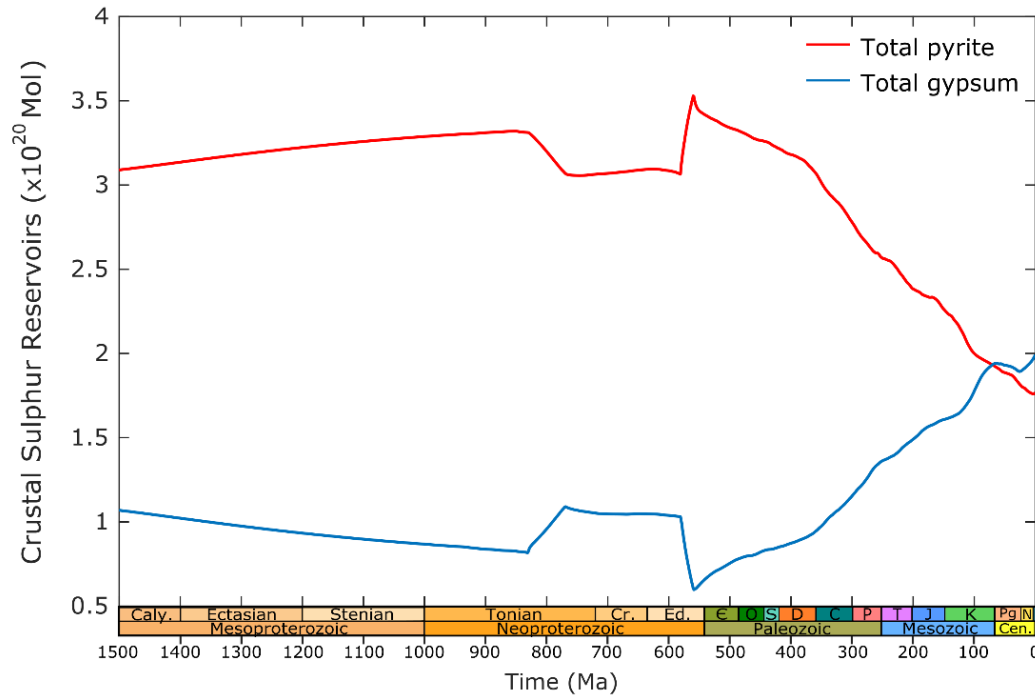


Figure 4.13 | *NEOCARBSULF* predictions of total pyrite (red) and total gypsum (blue) over the last 1500 Myrs.

4.5.2. Full model parameters

For the following tables, where we mention GEOCARBSULF as a source, we mean the final values as used in the 2009 (Berner, 2009) paper, some of which are unchanged from, for example, GEOCARB II (Berner, 1994).

Table 4.1: Present day parameters used in NEOCARBSULF

Parameter	Algebraic Representation	Value	Source
Atmosphere and ocean CO ₂	A0	3.193x10 ¹⁸ mol	COPSE (Bergman, Lenton and Watson, 2004)
Atmosphere and ocean O ₂	O0	3.8x10 ¹⁹ mol	GEOCARBSULF (Berner, 2009)
Atmosphere and ocean sulfate	OA_S_0	3.8x10 ¹⁹ mol	GEOCARBSULF
Young buried pyrite sulfur	<i>Pyr_0</i>	12.8571x10 ¹⁸ mol	GEOCARBSULFOR (Krause <i>et al.</i> , 2018)
Young buried gypsum sulfur	<i>Gyp_0</i>	100x10 ¹⁸ mol	GEOCARBSULFOR
Temperature	<i>temp_0</i>	288 °K	
Silicate weathering	<i>F_ws_0</i>	6.67x10 ¹⁸ mol myr ⁻¹	GEOCARBSULF
Young carbonate weathering	<i>F_wc_y0</i>	11.35x10 ¹⁸ mol C myr ⁻¹	GEOCARBSULFOR
Total crustal carbon	<i>crustal_carbon_0</i>	8500x10 ¹⁸ mol	(Hayes and Waldbauer, 2006)
Dissolved organic carbon pool	<i>DOC_0</i>	1.2566 x10 ¹⁷ mol	This study

Table 4.2: Constant parameters used in NEOCARBSULF

Parameter	Algebraic Representation	Value	Source
Normalised activation energy for silicates	ACT_{si}	0.09 K^{-1}	GEOCARBSULF
Normalised activation energy for carbonates	ACT_{carb}	0.087 K^{-1}	GEOCARBSULF
Effect of solar insolation on temperature	Ws	12.9°	GEOCARBII
Proportion of plants fertilised by increasing CO_2	$FERT$	0.4	GEOCARBSULF
Curve fitting parameter for effect of O_2 on $\delta^{13}\text{C}$ fractionation	J	4	GEOCARBSULF
Young pyrite weathering rate constant*	k_{wp}	$4.6 \times 10^{17} \text{ myr}^{-1}$	This study
Young gypsum weathering rate constant*	k_{wgyp}	$6 \times 10^{17} \text{ myr}^{-1}$	This study
Young C_{org} weathering rate constant	k_{wg}	0.02 myr^{-1}	This study
Young carbonate weathering rate constant	k_{wc}	0.02 myr^{-1}	This study
Ancient pyrite weathering rate constant	$kwpa$	$0.000895 \text{ myr}^{-1}$	This study

Ancient gypsum weathering rate constant	<i>kwgypa</i>	0.0026 myr ⁻¹	This study
Ancient C _{org} weathering rate constant	<i>kwga</i>	0.00055 myr ⁻¹	This study
Ancient carbonate weathering rate constant	<i>kwca</i>	0.00055 myr ⁻¹	This study
Ancient pyrite degassing rate constant	<i>kmpa</i>	0.000895 myr ⁻¹	This study
Ancient gypsum degassing rate constant	<i>kmgypa</i>	0.0026 myr ⁻¹	This study
Ancient C _{org} degassing rate constant	<i>kmga</i>	0.00129 myr ⁻¹	This study
Ancient carbonate degassing rate constant	<i>kmca</i>	0.00129 myr ⁻¹	This study
Pyrite burial rate constant*	<i>k_bp</i>	1.35x10 ¹⁸ myr ⁻¹ 1	This study
Gypsum burial rate constant*	<i>k_bgyp</i>	2.1x10 ¹⁸ myr ⁻¹	This study
Pyrite young to ancient flux rate constant	<i>k_p_ya</i>	0.01 myr ⁻¹	GEOCARBSULFOR
Gypsum young to ancient flux rate constant	<i>k_gyp_ya</i>	0.01 myr ⁻¹	GEOCARBSULFOR
C _{org} young to ancient flux rate constant	<i>k_g_ya</i>	0.018 myr ⁻¹	GEOCARBSULFOR
Carbonate young to ancient flux rate constant	<i>k_c_ya</i>	0.018 myr ⁻¹	GEOCARBSULFOR

A pulse of gypsum weathering	S_{pulse}	5 (baseline)	This study, see also table 4.5
A pulse of pyrite burial	Pyr_{pulse}	5 (baseline)	This study, see also table 4.5
A pulse of gypsum deposition	$Evap_{\text{pulse}}$	7 (baseline)	This study, see also table 4.5
Average isotopic composition of all crustal carbon	δ_{in}	-5‰	(Holser <i>et al.</i> , 1988)
Oceanic fraction of atmosphere and ocean CO ₂	$ocfrac$	0.98386	This study
Present day global average albedo	$albedo_0$	0.2992	Equation (4.5) using present day global average temperature
Response of global mean temperature to atmospheric CO ₂ greenhouse effect	γ	3	(Royer <i>et al.</i> , 2014)

* The values for these parameters are so much larger as they are multiplied by normalized reservoirs, instead of a reservoir at time (t).

Table 4.3: Time dependent parameters used in NEOCARBSULF

Parameter	Algebraic Representation	Source	Notes
Total land area	f_A	(Hawkesworth, Cawood and Dhuime, 2016); Royer <i>et al.</i>	Time array
Fraction of land area experiencing chemical weathering	f_{AW}	Royer <i>et al.</i>	Time array
Global river runoff	f_D	Royer <i>et al.</i>	Time array
Effect of change in paleogeography on temperature	$GEOG$	(Godd��ris <i>et al.</i> , 2017); Royer <i>et al.</i>	Time array
Proportion of land area underlain by carbonates	f_L	Royer <i>et al.</i>	Time array

Degassing rate due to tectonics / seafloor spreading*	f_G or f_{SR}	This study; (Merdith <i>et al.</i> , 2019)	Time array
Ocean $\delta^{13}C$ carbonate record	δ_{OA_C}	(Krissansen-Totton, Buick and Catling, 2015); (Saltzman and Thomas, 2012)	Time array
Dependence of weathering rate on soil biological activity due to land plants	f_E	GEOCARBSULF	0-80 Ma $f_E = 1$ 130-350 Ma $f_E = 0.875$ 380-470 Ma $f_E = 0.25$ 635-850 Ma $f_E = 0.1$ 850-1500 Ma $f_E = 0.05$ Linear interpolation between 80-130 Ma, 350-380 Ma and 470-635 Ma
Mean land elevation	f_R	(Hay <i>et al.</i> , 2006)	Time array

Dependence of degassing rate on relative proportions of carbonates on shallow platforms or deep ocean	f_C	GEOCARBSULF	150-1500 Ma $f_C = 0.75$ 0-150 Ma is a time dependent equation, see equation (4.1)
Temperature controlled runoff factor	RUN	GEOCARBSULF	0-40 Ma, 260-340 Ma, 635-649 Ma and 659-717 Ma: $RUN = 0.045$ All other time: $RUN = 0.025$
Effect of changes to CO ₂ on carbonate and silicate weathering	f_{CO2}	GEOCARBSULF	0-350 Ma: $f_{CO2} = VAS$ 380-1500 Ma: $f_{CO2} = NOVAS$ Linear interpolation between 350-380 Ma - see equations (4.7 – 4.12)
A scaling factor for enhanced gypsum weathering during the Shuram-Wonoka anomaly	$S_{scaling}$	This study / (Shields <i>et al.</i> , 2019)	0-559 and 581-1500 Ma: $S_{scaling} = 1$ 560-580 Ma: $S_{scaling} = S_{pulse}$ Linear interpolation between 559-560 and 580-581 Ma

A scaling factor for enhanced pyrite burial during the Shuram-Wonoka anomaly	<i>Pyr_scaling</i>	This study / Shields <i>et al.</i>	0-559 and 581-1500 Ma: <i>Pyr_scaling</i> = 1 560-580 Ma: <i>Pyr_scaling</i> = <i>Pyr_pulse</i> Linear interpolation between 559-560 and 580-581 Ma
A scaling factor for enhanced gypsum deposition in the Tonian period	<i>Evap_scaling</i>	This study / Shields <i>et al.</i>	0-769 and 831-1500 Ma: <i>Evap_scaling</i> = 1 770-830 Ma: <i>Evap_scaling</i> = <i>Evap_pulse</i> Linear interpolation between 559-560 and 580-581 Ma
Evolution of the Earth's crustal carbon content	<i>crustal_carbon</i>	Hayes and Waldbauer	Time array
Sulfur isotope fractionation	<i>alpha_S</i>	(Canfield and Farquhar, 2009); (Wu <i>et al.</i> , 2010)	Time array

* Both of these terms are used throughout the literature, but in GEOCARBSULF they are treated as the same thing.

For all time arrays we apply interpolation between data points.

Table 4.4: Starting reservoir sizes of NEOCARBSULF

Parameter	Algebraic Representation	Value	Source
Ocean and atmosphere sulfur	OA_S	38×10^{18} mol	GEOCARBSULF
Young pyrite	Pyr_y	20×10^{18} mol	GEOCARBSULFOR
Ancient pyrite	Pyr_a	260×10^{18} mol	GEOCARBSULFOR
Young gypsum	Gyp_y	50×10^{18} mol	GEOCARBSULFOR
Ancient gypsum	Gyp_a	50×10^{18} mol	GEOCARBSULFOR
Young C_{org}	G_y	330.625×10^{18} mol	This study
Ancient C_{org}	G_a	1106.875×10^{18} mol	This study
Young carbonate	C_y	1106.875×10^{18} mol	This study
Ancient carbonate	C_a	3705.625×10^{18} mol	This study

Table 4.5: Monte-Carlo simulation parameters

Parameter	Algebraic Form	Lower Limit	Upper Limit	Non Monte-Carlo Value
Ocean $\delta^{13}\text{C}$ carbonate record	$\delta_{\text{OA\_C}}$	Smoothed average – 1sd	Smoothed average + 1sd	Smoothed average
Degassing rate due to tectonics / seafloor spreading	f_{G}	Normalised degassing at subduction zones only	Normalised degassing at rift margins only	Normalised degassing at subduction zones only
Mean land elevation	f_{R}	Normalisation to Pleistocene deposition values	Normalisation to Miocene deposition values	Normalisation to Miocene deposition values
Proportion of land area underlain by carbonates	f_{L}	Time array – 0.5	Time array + 0.5	Time array
Fraction of land area experiencing chemical weathering	f_{AW}	Time array – 0.5	Time array + 0.5	Time array
Global river runoff	f_{D}	Time array – 0.5	Time array + 0.5	Time array

A scaling factor for enhanced gypsum weathering during the Shuram-Wonoka anomaly	<i>S_scaling</i>	5	20	5
A scaling factor for enhanced pyrite burial during the Shuram-Wonoka anomaly	<i>Pyr_scaling</i>	5	20	5
A scaling factor for enhanced gypsum deposition in the Tonian period	<i>Evap_scaling</i>	4	10	7
Inclusion of a normalised dissolved C _{org} pool dependency, for pyrite burial	<i>norm_DOC</i>	Yes	No	No

4.5.3. Full model equations

The full set of equations for the model are documented below. The majority of the equations are from GEOCARBSULFOR (Krause *et al.*, 2018), which themselves are mostly taken from GEOCARBSULF (Berner, 2006a) or COPSE (Lenton, Daines and Mills, 2018). Equations that are starred (*) are those which have been modified from GEOCARBSULFOR, and equations with references are newly introduced to the model. Those few equations with both a star and a reference number are fluxes that were previously in GEOCARBSULFOR but have been significantly modified for this study, in line with the referenced work. For equations that have the hash symbol (#), in the model code we add a function to the equation that effectively sets the value returned as zero if the model would otherwise calculate this flux as a negative value. The exception to this is equation (4.25), where it is specifically the ratio of O₂ relative to present day which is set to zero if there is the possibility of the model returning it as a negative value, *alpha*_C (the $\delta^{13}\text{C}$ fractionation factor) itself is allowed to be negative. The letter ‘t’ represents time and model run time is 1600 Myrs, to allow for 100 Myrs of spin-up time.

Table 4.6: Flux and parameter equations

f_C for $t < 150$ Ma:	$f_C = 0.75 + \left[\left(\frac{0.25}{150} \right) \cdot (150 + t) \right]$	[4.1]
Ratio of CO ₂ relative to present day:	$RCO_2 = \frac{CO_2(t)}{AO}$	[4.2]
Ratio of O ₂ relative to present day:	$O_{2mr} = \frac{O_2(t)}{OO}$	[4.3]
Effect of changes in CO ₂ on carbonate and silicate weathering:	$VAS = \left(\frac{2 \cdot RCO_2}{1 + RCO_2} \right)^{FERT}$ $NOVAS = RCO_2^{0.5}$	[4.4]
Global average albedo relative to present day (Caldeira and Kasting, 1992):	$\frac{1.4891 - (0.0065979 \cdot temp(t)) + (8.567 \times 10^{-6} \cdot temp(t)^2)}{albedo_0}$	[4.5]
*Global average temperature:	$temp = \left(gamma \cdot \left(\frac{\ln RCO_2}{\ln 2} \right) \right) - \left(Ws \cdot \frac{t}{-model\ run\ time} \right) + GEOG + temp_0$ $+ albedo_0$	[4.6]

Effect of changes in temperature on silicate weathering:	$f_{\text{Tsi}} = e^{(ACT_{\text{si}} \cdot [temp - temp_0])} \cdot \{1 + [RUN \cdot (temp - temp_0)]\}^{0.65}$	[4.7]
Combined effect of changes to temperature and CO ₂ on silicate weathering:	$f_{\text{Bsi}} = f_{\text{Tsi}} \cdot f_{\text{CO2}}$	[4.8]
Effect of changes in temperature on carbonate weathering:	$f_{\text{Tcarb}} = 1 + [ACT_{\text{carb}} \cdot (temp - temp_0)]$	[4.9]
Combined effect of changes to temperature and CO ₂ on carbonate weathering:	$f_{\text{BBcarb}} = f_{\text{Tcarb}} \cdot f_{\text{CO2}}$	[4.10]
#Oxygen dependency for C _{org} weathering:	$ox_{\text{weather}} = O_2 mr^{0.5}$	[4.11]
Total crustal carbon normalised to present day (Hayes and Waldbauer, 2006):	$relative\_crustal\_carbon = \frac{crustal\_carbon(t)}{crustal\_carbon_0}$	[4.12]
*#Weathering of young C _{org} :	$F_{\text{wg}_y} = f_R^{0.33} \cdot f_A \cdot k_{\text{wg}} \cdot relative\_crustal\_carbon \cdot G_y \cdot ox_{\text{weather}}$	[4.13]
*#Weathering of ancient C _{org} :	$F_{\text{wg}_a} = f_R^{0.33} \cdot k_{\text{wga}} \cdot relative\_crustal\_carbon \cdot G_a \cdot ox_{\text{weather}}$	[4.14]

*Weathering of young carbonate:	$F_{wc\_y} = f_{BBcarb} \cdot f_L \cdot f_A \cdot f_D \cdot f_E \cdot k_{wc} \cdot \text{relative\_crustal\_carbon} \cdot C_y \cdot f_R^{0.9}$	[4.15]
*Weathering of ancient carbonate:	$F_{wc\_a} = f_{BBcarb} \cdot f_L \cdot f_A \cdot f_D \cdot f_E \cdot kwca \cdot \text{relative\_crustal\_carbon} \cdot C_a \cdot f_R^{0.9}$	[4.16]
*Weathering of young pyrite:	$F_{wp\_y} = \frac{F_{ws}}{F_{ws\_0}} \cdot new\_kwp \cdot \frac{Pyr\_y(t)}{Pyr\_0}$	[4.17]
*Weathering of ancient pyrite:	$F_{wp\_a} = f_R^{0.33} \cdot kwpa \cdot Pyr\_a(t)$	[4.18]
*Weathering of young gypsum:	$F_{wgyp\_y} = \frac{F_{wc\_y}}{F_{wc\_y0}} \cdot new\_kwgyp \cdot \frac{Gyp\_y(t)}{Gyp\_0} \cdot S\_scaling$	[4.19]
*Weathering of ancient gypsum:	$F_{wgyp\_a} = f_A \cdot f_D \cdot kwgypa \cdot Gyp\_a(t) \cdot S\_scaling$	[4.20]
Metamorphism / degassing of ancient pyrite:	$F_{mp} = f_{SR} \cdot kmpa \cdot Pyr\_a(t)$	[4.21]
Metamorphism / degassing of ancient gypsum:	$F_{ms} = f_{SR} \cdot kmgypa \cdot Gyp\_a(t)$	[4.22]
*#Metamorphism / degassing of ancient C_{org} :	$F_{mg} = f_{SR} \cdot kmga \cdot \text{relative\_crustal\_carbon} \cdot G_a$	[4.23]
*Metamorphism / degassing of ancient carbonate:	$F_{mc} = f_{SR} \cdot f_C \cdot kmca \cdot \text{relative\_crustal\_carbon} \cdot C_a$	[4.24]
#Fractionation of $\delta^{13}C$:	$\alpha_C = 27 + [J \cdot (O_{2mr} - 1)]$	[4.25]

All carbon associated fluxes into the atmosphere-ocean:	$F_{total\_c} = F_{wc\_y} + F_{wc\_a} + F_{wg\_y} + F_{wg\_a} + F_{mc} + F_{mg}$	[4.26]
Fraction of the total sulfur leaving the ocean as pyrite (burial flux approach):	$f_{pyr} = \frac{F_{bp}}{F_{bp} + F_{bgyp}}$	[4.27]
Fraction of the atmosphere-ocean carbon pool that will leave as C_{org} (Rothman <i>et al.</i> , 2003):	$f_{org} = \frac{\delta_{OA\_C} - \delta_{in}}{\alpha\_C}$	[4.28]
*Burial of C_{org} (Rothman <i>et al.</i> , 2003):	$F_{bg} = f_{org} \cdot F_{total\_c}$	[4.29]
Burial of carbonate:	$F_{bc} = F_{ws} + F_{wc\_y} + F_{wc\_a}$	[4.30]
*Oxygen dependency for pyrite burial:	$fox = 2 \cdot \left(\frac{1}{1 + e^{-5(-O_2mr + 1)}} \right)$	[4.31]
Normalised dissolved C_{org} pool (Rothman <i>et al.</i> , 2003):	$norm\_DOC = \frac{\left(\frac{CO_2(t) \cdot ocfrac}{25} \right)}{DOC_0}$	[4.32]
*Burial of pyrite:	$F_{bp} = k_{bp} \cdot \frac{OA\_S(t)}{OA\_S_0} \cdot fox \cdot norm\_DOC \cdot Pyr\_scaling$	[4.33]
*Burial of gypsum:	$F_{bgyp} = k_{bgyp} \cdot \frac{OA\_S(t)}{OA\_S_0} \cdot Evap\_scaling$	[4.34]

Young to ancient pyrite flux:	$F_{ya\_p} = k_{p\_ya} \cdot Pyr\_y(t)$	[4.35]
Young to ancient gypsum flux:	$F_{ya\_gyp} = k_{gyp\_ya} \cdot Gyp\_y(t)$	[4.36]
Young to ancient C _{org} flux:	$F_{ya\_g} = k_{g\_ya} \cdot G\_y(t)$	[4.37]
Young to ancient carbonate flux:	$F_{ya\_c} = k_{c\_ya} \cdot C\_y(t)$	[4.38]
*Silicate weathering:	$F_{ws} = f_{Bsi} \cdot (f_{AW} \cdot f_A \cdot f_D)^{0.65} \cdot f_R^{0.33} \cdot f_E \cdot F_{ws\_0}$	[4.39]

Table 4.7: Reservoir equations

Ocean and atmosphere sulfur:	$\frac{d(OA\_S)}{dt} = F_{wp\_y} + F_{wgyp\_y} + F_{wp\_a} + F_{wgyp\_a} + F_{mp} + F_{ms} - F_{bp} - F_{bgyp}$	[4.40]
Ocean and atmosphere carbon:	$\frac{d(CO_2)}{dt} = F_{wg\_y} + F_{wc\_y} + F_{wg\_a} + F_{wc\_a} + F_{mg} + F_{mc} - F_{bg} - F_{bc}$	[4.41]
Young pyrite:	$\frac{d(Pyr\_y)}{dt} = F_{bp} - F_{wp\_y} - F_{ya\_p}$	[4.42]
Ancient pyrite:	$\frac{d(Pyr\_a)}{dt} = F_{ya\_p} - F_{wp\_a} - F_{mp}$	[4.43]
Young gypsum:	$\frac{d(Gyp\_y)}{dt} = F_{bgyp} - F_{wgyp\_y} - F_{ya\_gyp}$	[4.44]

Ancient gypsum:	$\frac{d(Gyp\_a)}{dt} = F\_ya\_gyp - F\_wgyp\_a - Fms$	[4.45]
Young C _{org} :	$\frac{d(G\_y)}{dt} = F\_bg - F\_wg\_y - F\_ya\_g$	[4.46]
Ancient C _{org} :	$\frac{d(G\_a)}{dt} = F\_ya\_g - F\_wg\_a - Fmg$	[4.47]
Young carbonate:	$\frac{d(C\_y)}{dt} = F\_bc - F\_wc\_y - F\_ya\_c$	[4.48]
Ancient carbonate:	$\frac{d(C\_a)}{dt} = F\_ya\_c - F\_wc\_a - Fmc$	[4.49]
Atmospheric oxygen:	$\frac{d(O_2)}{dt} = \left[F\_bg + \left(\frac{15}{8} \cdot F\_bp \right) \right] - (F\_wg\_y + F\_wg\_a + Fmg) - \left[\frac{15}{8} \cdot (F\_wp\_y + F\_wp\_a + Fmp) \right]$	[4.50]

Table 4.8: Non-model equations

Effect of solar insolation on temperature:	$W_s = \frac{temp(t) - temp\_0 - (gamma \cdot \ln(RCO_2))}{\left(\frac{t}{-model\ run\ time} \right)}$	[4.51]

5. A history of atmospheric oxygen

This chapter has been written in the style of a *Nature* article, ready for journal submission, although the Methods section of the intended article has been moved to an earlier part of the text, for better integration. Additionally, the relatively short-form style of *Nature* means that much of the model validation and sensitivity analyses, as well as full model equations and parameters will be included in the supplementary information for the paper, thus these are found in this chapter as subsections of 5.5.

5.1. Introduction

The Earth has changed dramatically across the course of its 4.54 Gyr history: shifting from greenhouse to icehouse to greenhouse climatic regimes (e.g. Hoffman *et al.*, 1998; Veizer, Godderis and François, 2000; Zachos, Dickens and Zeebe, 2008; Mills *et al.*, 2019), experiencing variations in global tectonism (e.g. Ernst *et al.*, 2013; Hawkesworth, Cawood and Dhuime, 2016; Merdith *et al.*, 2019), and changing from a reduced to oxidised surficial system (Farquhar, Bao and Thiemens, 2000; Holland, 2006; Anbar *et al.*, 2007; Buick, 2008; Zerkle *et al.*, 2012; Lyons, Reinhard and Planavsky, 2014; Yang, Gaillard and Scaillet, 2014), with life evolving amidst these, often chaotic, revolutions to the Earth (Knoll and Nowak, 2017).

The geologic cycle of oxygen may be the crucial link between all these events; either through their impact on the cycling of key elements (e.g. carbon, sulfur and phosphorus) which affect the sources and sinks of O₂, as is the case with tectonism for example, or via the postulated link between rising O₂ levels and the evolution of life

(Nursall, 1959; Catling *et al.*, 2005). As such, the questions of when and why atmospheric O₂ has changed over time, have been extensively researched and hotly debated, with the prevailing view that the Earth has experienced three oxygenation events in its history (Holland, 1994; Och and Shields-Zhou, 2012; Lyons, Reinhard and Planavsky, 2014; Krause *et al.*, 2018).

The first of these events: the Great Oxidation Event (GOE), is reasonably well understood in terms of its timing and broad dynamics, thanks to state changes in various geological and geochemical proxies (Rye and Holland, 1998; Farquhar, Bao and Thiemens, 2000; Scott *et al.*, 2008; Partin *et al.*, 2013). However, unlike the other two oxygenation events (Bergman, Lenton and Watson, 2004; Sperling *et al.*, 2013; Planavsky *et al.*, 2014; Krause *et al.*, 2018, Krause *et al.*, in review), only limited quantitative reconstructions of atmospheric O₂ levels during the GOE exists, and are based either on: simple extrapolations from the $\delta^{13}\text{C}$ record (e.g. during the Lomagundi positive isotope excursion, where $\delta^{13}\text{C}$ values reach >10‰, leading to a hypothesised O₂ overshoot, Fig. 5.1, #3) (Des Marais *et al.*, 1992; Karhu and Holland, 1996; Bekker and Holland, 2012); or on inferences from relatively simple carbon cycle models which are not constrained by geological data (Lee *et al.*, 2016; Eguchi, Seales and Dasgupta, 2020).

There exists a ‘best guess’ of O₂ levels during the Archean and Paleoproterozoic (Fig. 5.1) based on the limits inferred by geological and geochemical data. Prior to the GOE, there is evidence for the existence of mass-independent sulfur isotope fractionation (MIF-S) in the rock record, which constrains O₂ to be below 10⁻⁵ PAL (Fig. 5.1, #1)

(Farquhar, Bao and Thiemens, 2000; Pavlov and Kasting, 2002), although more recent modelling suggests O₂ would have been below 10⁻⁶ PAL (Zahnle, Claire and Catling, 2006).

After the GOE, the appearance of terrestrial red beds, and the loss of major detrital siderite, pyrite and uraninite grains in fluvial sediments imply an approximate O₂ level of >10⁻² PAL (Fig. 5.1, #4) (Rye and Holland, 1998; Holland, 2006; Buick, 2008). Minimal fractionation of Cr isotopes ($\delta^{53}\text{Cr}$) suggest that O₂ may have been <10⁻³ PAL until the Neoproterozoic (Fig. 5.1, #6) (Planavsky *et al.*, 2014; Cole *et al.*, 2016), however, this limit has been ascertained using a model which assumes a soil contact time with O₂ which is perhaps overly long (Daines, Mills and Lenton, 2017). Furthermore, significant $\delta^{53}\text{Cr}$ fractionation at ~1400 Ma (Canfield *et al.*, 2018) and ~1100 Ma (Gilleaudeau *et al.*, 2016) (Fig. 5.1, #8), alongside low V/Al ratios (Shuichang Zhang *et al.*, 2016) (Fig. 5.1, #7) indicate that Mesoproterozoic O₂ may have been greater than 10⁻³ PAL and perhaps as high as ~0.04 PAL, at least episodically.

However, while some proxies (e.g. $\delta^{238}\text{U}_{\text{sw}}$ and I / Ca + Mg)(Hardisty *et al.*, 2014; Wang *et al.*, 2018) show temporary oxygenation of the oceans during the GOE, or transient ‘whiffs’ (Fig. 5.1, #2) of O₂ prior to it (Anbar *et al.*, 2007; Scott *et al.*, 2008), a general lack of data makes it difficult to make any inference about the full extent of ocean oxygenation during this time and how this might be extrapolated to ascertain quantitative estimates of atmospheric oxygenation.

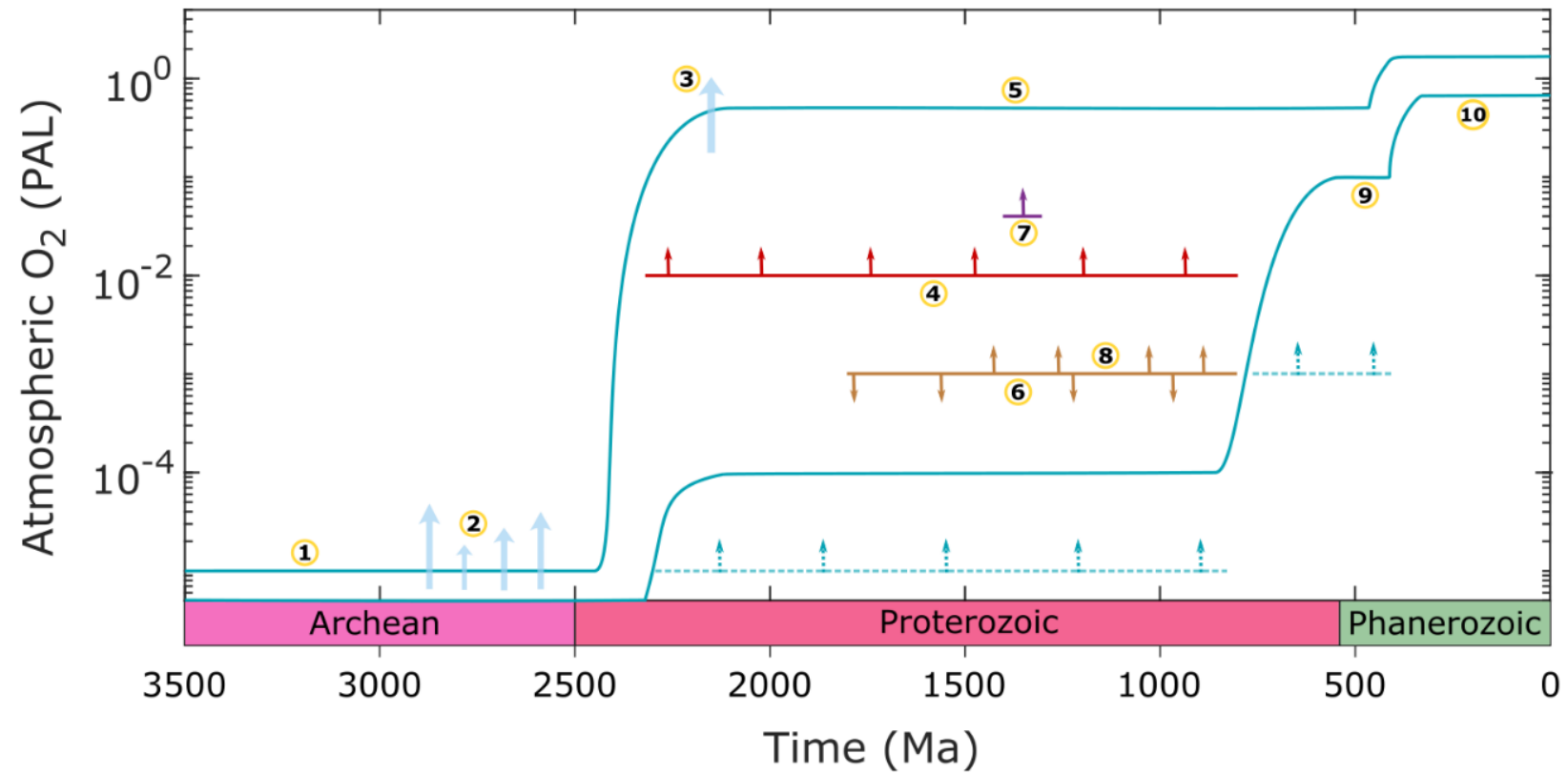


Figure 5.1 | Current ‘best guess’ atmospheric oxygen evolution over the last 3500 Myrs.

The solid blue lines represent the current view of atmospheric oxygen levels since 3500 Ma based on geological and geochemical evidence. The numbers denote: 1) MIF-S signals constraining O_2 to $<10^{-5}$ PAL (Farquhar, Bao and Thiemens, 2000; Pavlov and Kasting, 2002), 2) the blue arrows denoting possible ‘whiffs’ of O_2 (Anbar et al., 2007), 3) a rise in O_2 during the GOE with the arrow signifying a possible O_2 ‘overshoot’ associated with the Lomagundi C isotope excursion (Des Marais et al., 1992; Karhu and Holland, 1996; Bekker and Holland, 2012), 4) the appearance of terrestrial red beds and loss of detrital pyrite and uraninite (Holland, 2006), 5) an upper limit (of < 0.5 PAL) until ~ 420 Ma, based on geochemical water column redox data and allowing for modelling uncertainties (Canfield, 1998, 2014; Sperling et al., 2015), 6) minimal $\delta^{53}\text{Cr}$ fractionation implying $O_2 < 10^{-3}$ PAL (Planavsky et al., 2014), 7) RSE data indicating $O_2 > \sim 0.04$ PAL at 1400 Ma (Shuichang Zhang et al., 2016), 8) instances of significant $\delta^{53}\text{Cr}$ fractionation during the Mesoproterozoic ($O_2 > 10^{-3}$ PAL) (Gilleaudeau et al., 2016; Canfield et al., 2018), 9) likely minimum O_2 ($= > 10^{-1}$ PAL) required by late Ediacaran and Cambrian biota (Levin, 2003), (10) both upper and lower O_2 limits for the last 420 Myrs are based on the wildfire record from sedimentary charcoal abundance and modelling studies (Belcher and McElwain, 2008; Glasspool and Scott, 2010).

Although, the NOE is covered in more detail in Chapter 4, it is worth briefly mentioning that in the current ‘best guess’ figure, a minimum O_2 level of 10^{-1} PAL for the late Neoproterozoic and early Paleozoic (Fig. 5.1, #9) is commonly invoked, based on purported O_2 requirements by Ediacaran and Cambrian biota (Levin, 2003; Sperling

et al., 2015). However, experimental work suggests that some, less complex, animals could have survived, and even thrived, under O₂ levels as low as 5×10^{-3} to 4×10^{-2} PAL (Mills *et al.*, 2014), and the Cambrian was punctuated by extinction events and pulses in animal diversification (Peng, Babcock and Cooper, 2012; He *et al.*, 2019).

Here, we generate estimates of O₂ levels over the last 3400 Myrs by utilising an isotope mass balance technique, which incorporates geological data, such as the isotopic composition of sedimentary material and major tectonic changes (i.e. degassing and mountain building), to derive the source and sink fluxes in the geological oxygen cycle. This approach has been extensively employed in Phanerozoic modelling of O₂ (Garrels and Lerman, 1984; Berner, 1987, 2006a; Royer *et al.*, 2014; Krause *et al.*, 2018) and is extended in this paper to cover the Paleo-Archean through to the Present. Our expanded framework, named ARCHEOCARBSULF, builds upon a previous extension (named NEOCARBSULF) of the Phanerozoic GEOCARBSULF model (Berner, 2006a).

5.2. Methods

5.2.1. Model overview

The ARCHEOCARBSULF model is an extension of NEOCARBSULF and is solved in MATLAB, using an implicit, variable-order ODE method (Shampine and Reichelt, 1997). We retain the key updates to the NEOCARBSULF version, namely the introduction of an increasing crustal carbon inventory and recycling rate, following

Hayes and Waldbauer (2006), and the simplification of the equation for computing organic carbon (C_{org}) burial, following the work of Rothman *et al.* (2003).

5.2.2. Data updates

We expand the $\delta^{13}\text{C}$ record further back in time (see Fig. 5.2A) to use data from Havig *et al.* (2017) for the Archean through to the early Tonian, and from Saltzman and Thomas (2012) for the rest of the Neoproterozoic and Phanerozoic. The data were binned into 20 Myr bins and we applied a 20 Myr moving average with smoothing to eliminate variations over very short timescales. From this we obtained a $\pm 1\text{sd}$ for our Monte-Carlo analysis. During the Archean and early Proterozoic there are occasions where the -1sd $\delta^{13}\text{C}$ record displays deeply negative excursions, similar to the Shuram-Wonoka anomaly. During these occasions we cap the $\delta^{13}\text{C}$ values to be equal to that of the mantle input (-5‰), this prevents negative values for the -1sd of O_2 (neither the mean or $+1\text{sd}$ O_2 generated by the model returns negative values) at these points.

5.2.3. Reduced gases flux

We introduce into the model a flux of reduced gases, nominally H_2 , which acts as an additional O_2 sink with decreasing effectiveness over time (see Fig. 5.2B). These reduced gases (e.g. H_2 , CH_4 , H_2S etc.) would have outgassed from the mantle, and in the case of H_2 been produced anaerobically by the oxidation of ferrous Fe to ferric Fe (Kasting, 1993, 2013; Holland, 2002; Kump, 2008), forming an efficient sink for O_2 that would engulf O_2 source fluxes on the very early Earth.

In ARCHEOCARBSULF the formulation for the flux is as follows:

$$rgf = \{(0.85 \times 10^{17} \cdot e^{-0.001 \cdot t}) - 0.85 \times 10^{17}\} \cdot \left(\frac{1}{1 + e^{-3(\log_{10}(O_2mr) + 5)}} \right) \quad (5.1)$$

Where O_2mr is the ratio of O_2 at time (t) to O_2 at the present day.

The reduced gas flux is incorporated into the equation for calculating the O_2 reservoir:

$$\begin{aligned} \frac{d(O_2)}{dt} = & \left[F_{bg} + \left(\frac{15}{8} \cdot F_{bp} \right) \right] - (F_{wg\_y} + F_{wg\_a} + F_{mg}) \\ & - \left[\frac{15}{8} \cdot (F_{wp\_y} + F_{wp\_a} + F_{mp}) \right] - rgf \end{aligned} \quad (5.2)$$

Where: F_{bg} is the C_{org} burial flux; F_{bp} is the pyrite burial flux; F_{wg_y} and F_{wg_a} are the C_{org} weathering fluxes for the young and ancient reservoirs respectively; F_{mg} is the C_{org} degassing flux; F_{wp_y} and F_{wp_a} are the pyrite weathering fluxes for the young and ancient reservoirs respectively; and F_{mp} is the pyrite degassing flux.

Addition of the reduced gas flux to the model necessitates some modifications of the C_{org} weathering fluxes and the ocean-atmosphere carbon reservoir calculations, in order to maintain the present day O_2 cycle:

$$F_{wg\_y} = f\_R^{0.33} \cdot f\_A \cdot \{k_{wg} - (0.5 \cdot rgf)\} \cdot \left(\frac{\text{relative\_crustal\_carbon} \cdot G\_y}{G\_y} \right) \cdot ox\_weather \quad (5.3)$$

$$F_{wg\_a} = f\_R^{0.33} \cdot \{kwga - (0.5 \cdot rgf)\} \cdot \left(\frac{\text{relative\_crustal\_carbon} \cdot G\_a}{G\_a} \right) \cdot ox\_weather \quad (5.4)$$

$$\frac{d(CO_2)}{dt} = F_{wg\_y} + F_{wc\_y} + F_{wg\_a} + F_{wc\_a} + F_{mg} + F_{mc} - F_{bg} - F_{bc} + rgf \quad (5.5)$$

Where: f_R and f_A are the normalised parameters for mountain uplift and land area respectively; G_y and G_a are the young and ancient crustal C_{org} reservoirs; k_{wg} and $kwga$ are rate constants for young and ancient C_{org} weathering; $\text{relative\_crustal\_carbon}$ is the total crustal carbon normalised to present day, following Hayes and Waldbauer (2006); $ox\_weather$ is the oxidative feedback on C_{org} weathering; F_{wc_y} and F_{wc_a} are the young and ancient carbonate weathering fluxes; F_{mc} is the carbonate degassing flux; and F_{bc} is the carbonate burial flux.

5.2.4. Monte Carlo setup

In order to capture some of the uncertainty in the model parameterisation we ran a Monte-Carlo analysis of the ARCHEOCARBSULF model, where a number of variables are sampled from within defined limits, following a flat (instead of normal) distribution, at each timestep (see table 5.5). The key parameter for the Monte-Carlo analysis is the $\delta^{13}C$ record (see Fig. 5.2A) which will greatly influence the amount of

O₂ produced by way of C_{org} burial and is the only parameter for which there is geological data beyond the Mesoproterozoic.

For another important parameter: tectonic degassing (f_G), which can change the amount of O₂ consumption from both pyrite and C_{org} oxidation as well as the total carbon throughput, we assume a lower baseline at model initiation (3500 Ma – to allow for 100 Myrs of model spin-up) of 0.5x present-day levels, and an upper baseline of 2.5x present-day levels to encompass a range of possibilities with regards to Archean degassing. From 3500 Ma to 1000 Ma (after which we have modelling and/or geological data (Krause *et al.*, in review)) we apply a linear interpolation. Other important parameters such as: an increasing crustal carbon reservoir (Fig. 5.2C); and mountain uplift (Fig. 5.2E), which can affect the burial, degassing and weathering fluxes, and hence alter ARCHEOCARBSULF's O₂ predictions, are also sampled.

The ARCHEOCARBSULF model was run 2,000 times, instead of 10,000 times (e.g. Royer *et al.*, 2014), as previous modelling efforts (Krause *et al.*, in review) have shown that this is an adequate number of runs for the model to run to completion in this type of Monte-Carlo simulation, and for the number of parameters sampled.

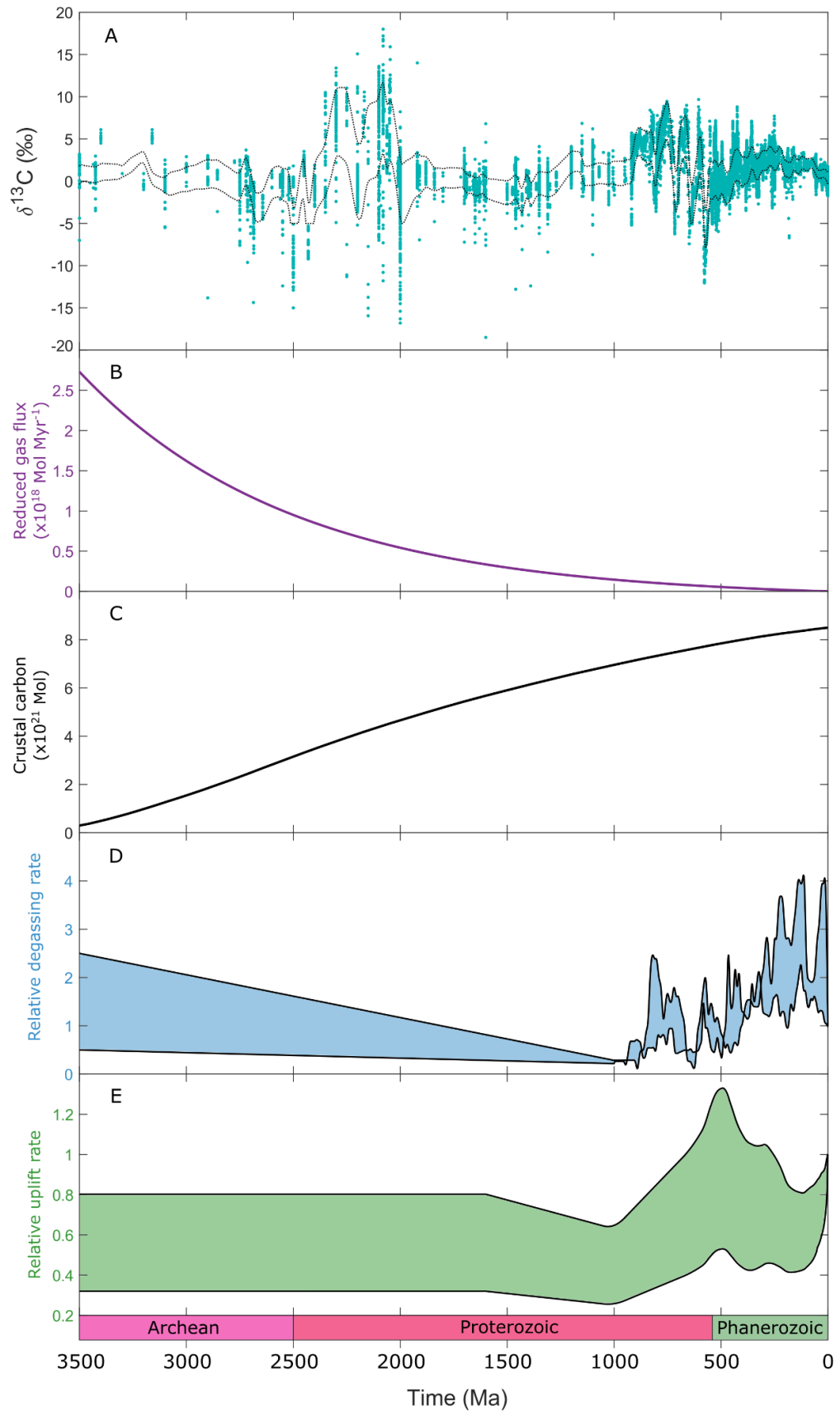


Figure 5.2 | Key updates to the ARCHEOCARBSULF model.

*A) A compilation of $\delta^{13}\text{C}$ through time (teal dots), with the black dotted line representing $\pm 1\text{sd}$ of a smoothed average of the data (see Methods). The data is taken from the compilations of Havig *et al.* (2017) and Saltzman and Thomas (2012) and references therein. B) A flux of reduced gas, modelled as H_2 , which acts as a further O_2 sink, is newly introduced to the model (see Methods for further details). C) An increase in the crustal carbon reservoir since 1500 Ma (Hayes and Waldbauer, 2006). D) Tectonic degassing, normalised to the present day, where the black boundaries represent the Monte Carlo sampling limits. E) Mountain uplift normalised to the present day, where the black boundaries represent the Monte Carlo sampling limits.*

5.3. Results

The model results are plotted in log (Fig. 5.3A) and linear form (Fig. 5.3B), to effectively highlight the absolute changes in magnitude of O_2 levels throughout the last 3400 Myrs. Our results suggest that O_2 in the Archean was very low ($<10^{-5}$ PAL), and briefly rose above 10^{-5} PAL near the Archean-Proterozoic boundary. At ~2420 we see a geologically rapid and spectacular rise in O_2 levels, from $\sim 3 \times 10^{-6}$ PAL to ~ 0.04 PAL in just 150 Myrs. Such high levels are short-lived however, as O_2 drops to $\sim 8.5 \times 10^{-4}$ PAL by 2190 Ma, before increasing again to ~ 0.07 PAL by 2075 Ma, coincident with the Lomagundi positive isotope excursion. Post-Lomagundi, O_2 levels crash once more to $\sim 4 \times 10^{-4}$ PAL. For the remainder of the Paleoproterozoic, through to ~920 Ma, O_2 levels rise slowly but non-monotonically, taking almost 1000 Myrs to increase by around an order of magnitude. The Neoproterozoic ushers in a period of extreme variability in O_2 (Krause *et al.*, in review) which is sustained until the Paleozoic Oxygenation Event at the end of the Ordovician (Krause *et al.*, 2018).

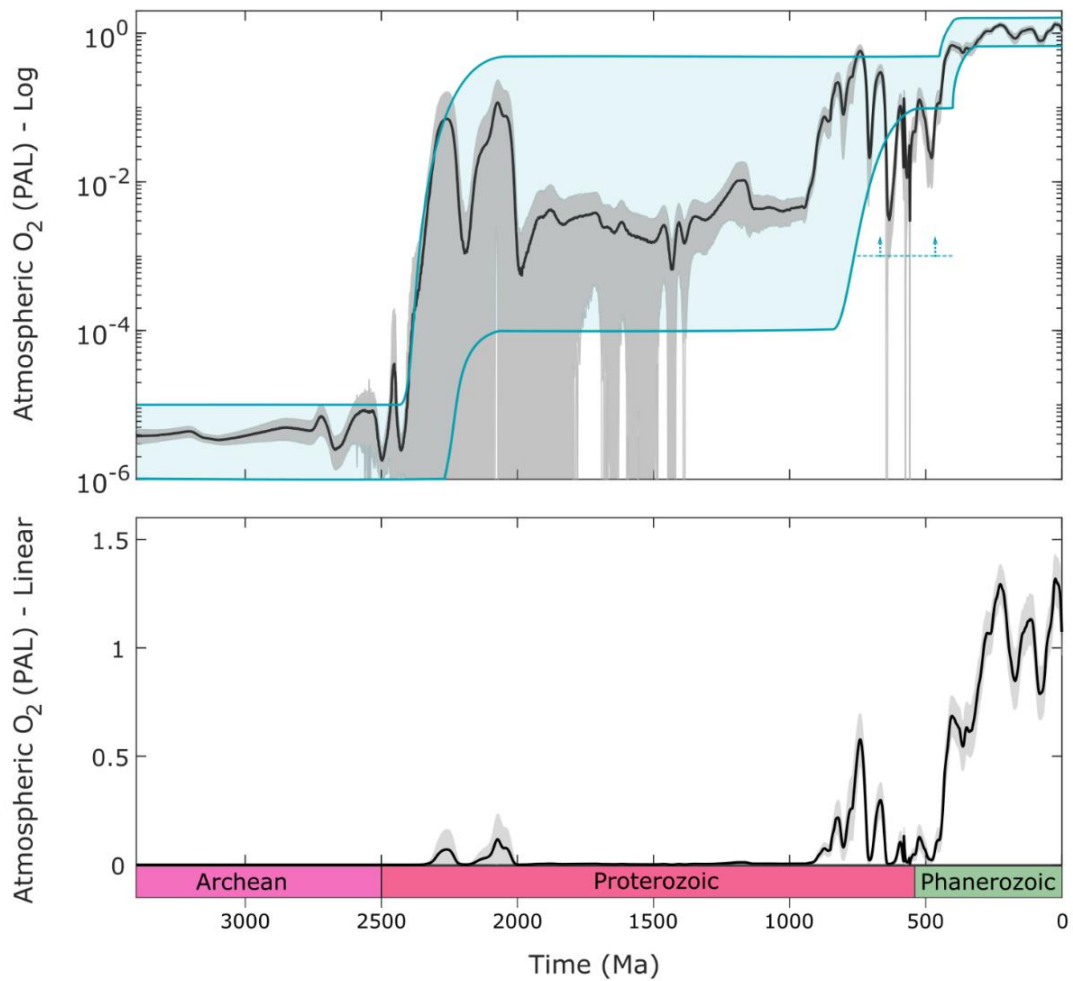


Figure 5.3 | A history of atmospheric O_2 from 3400 Ma to present.

A) Atmospheric oxygen results estimated from the ARCHEOCARBSULF model, plotted in log form, where the black line is the mean result of 2,000 model runs. The grey shaded band is the ± 1 sd, which may include very low values on occasion. The blue solid line and blue shaded area represent the prevailing view of O_2 evolution garnered from geochemical proxies, as shown in Fig. 5.1. B) The same results from panel A but plotted in linear form to highlight the magnitude of O_2 changes during the three oxygenation events.

5.4. Discussion

Our results are a good match to various geological and geochemical proxies which suggest a state change in the redox nature of the Earth in the early Paleoproterozoic. First, our Archean results are compatible with the proposed limit of 10^{-5} PAL due to the presence of the MIF-S signal in the rock record (Farquhar, Bao and Thiemens, 2000; Pavlov and Kasting, 2002), and consequently are well below the limits indicated by the retention of redox-sensitive detrital grains of pyrite, uraninite and siderite in fluvial sediments (Buick, 2008). It is possible that O_2 generated by the model should be below 10^{-6} PAL (Zahnle, Claire and Catling, 2006) prior to the GOE. This is possible to achieve by simply increasing the magnitude of the reduced gases flux, whose quantity is a significant unknown, at the model initiation. While ‘whiffs’ of O_2 have been suggested for the Archean (Anbar *et al.*, 2007; Scott *et al.*, 2008) they likely emanated from ocean O_2 oases (Olson, Kump and Kasting, 2013) which are local in nature. Generating these ‘whiffs’ probably requires the addition of short-term atmospheric chemistry to the model, thus they are not predicted by this version, which combines the ocean and atmosphere into a single, global reservoir.

ARCHEOCARBSULF predicts the first major rise in O_2 at ~2420 Ma, and the timing is broadly consistent with recent work on dating the Ongeluk Formation large igneous province (2426 ± 3 Ma), which is thought to be coeval with the GOE (Gumsley *et al.*, 2017). Additionally, work using triple oxygen isotopes suggest the formation of the mass-independent fractionation of O_2 (MIF-O) around the time of the GOE (Crockford *et al.*, 2019). The appearance of MIF-O infers that O_2 levels were high enough ($> 10^{-3}$

PAL) to create a stable ozone layer (e.g. Goldblatt, Lenton and Watson, 2006) and generally our results show that, aside from a couple of short-lived events after the Lomagundi and in the Mesoproterozoic, O_2 after the onset of the GOE remained above this threshold, in good agreement with both this proxy and with the absence of detrital siderite.

A pertinent question to ask of this model is one which has been debated within the isotope community for decades (e.g. Schidlowski, 1988), namely: why does O_2 rise through time when the $\delta^{13}C$ record has been relatively static over the course of Earth history? The answer, to a large extent, is that C_{org} burial rates are dependent on the total amount of carbon entering the ocean-atmosphere reservoir (i.e. the sum of all the carbon weathering and degassing fluxes), as well as the fraction of carbon subsequently leaving the ocean in organic form (f_{org}). The magnitude of the carbon fluxes at any point in time is limited by the amount of carbon in the crustal reservoirs, the sizes of which are imposed on the model to vary in line with prior modelling work (see Fig. 5.2C) suggesting a near exponential increase through time (Hayes and Waldbauer, 2006).

Large swings in f_{org} early in Earth's history then, are tempered by the low total carbon flux at that time, leading to smaller C_{org} burial rates and thus O_2 production than might otherwise be expected, particularly during the GOE and Lomagundi (Des Marais *et al.*, 1992; Karhu and Holland, 1996; Bekker and Holland, 2012) but also the Mesoproterozoic (Shuichang Zhang *et al.*, 2016; Daines, Mills and Lenton, 2017). Comparatively smaller changes in f_{org} throughout the Phanerozoic, on the other hand, are exacerbated by the high total carbon, resulting in modern day levels of O_2 .

Changes to O_2 sinks through time are also important, and the diminution of O_2 consumption through time has previously been offered as an explanation for the problem of rising O_2 but static f_{org} (Krissansen-Totton, Buick and Catling, 2015). The introduction of the reduced gases flux into ARCHEOCARBSULF (see Fig. 5.2B) serves to model the effect this may have on O_2 concentrations in the geologic past.

Without the reduced gas flux, ARCHEOCARBSULF predicts O_2 levels above, albeit not substantially so, the 10^{-5} PAL threshold, thereby underlying its importance – perhaps as much as the increasing crustal carbon inventory is – to Archean and Paleoproterozoic predictions. Furthermore, without the reduced gases, O_2 estimates for the Mesoproterozoic are of an order of magnitude higher (Krause *et al.*, in review), which are more in line with other modelling work (e.g. Daines, Mills and Lenton, 2017), than when this flux is included. Therefore, it is possible that the reduced gases flux was higher than is assumed in this model for the Archean, but also declines more rapidly, such that the flux is minimal before the onset of the Mesoproterozoic. This is an avenue of research worthy of further consideration.

The ARCHEOCARBSULF framework allows for the simultaneous estimation of CO_2 levels, temperature and seawater $\delta^{34}S$, which generally fall within observed ranges and help validate the model O_2 predictions (see Fig. 5.4), although there is a clear mismatch in $\delta^{34}S$ (Fig. 5.4C) during the Cryogenian, where the model predicts very low rates of pyrite burial. This discrepancy is driven by the model assumption that pyrite burial must scale with carbon burial to some extent, which may not hold true during the Cryogenian.

Global temperature and atmospheric CO₂ concentration is of great significance for early Earth habitability, given that the Sun's luminosity has increased with time, such that at 4700 Ma the solar output was ~70% of that at present day (Gough, 1981). Without the presence of greenhouse gases, the lower solar luminosity would have resulted in a frozen Earth during the Hadean and Archean, yet evidence for the presence of water-borne sedimentary processes (Lowe, 1980), and silicon and oxygen isotopes (e.g. Knauth and Lowe, 2003; Knauth, 2005; Robert and Chaussidon, 2006; Hren, Tice and Chamberlain, 2009; Blake, Chang and Lepland, 2010) point towards a temperate to hot early Earth.

Our CO₂ results (Fig. 5.4A) for the Archean and Proterozoic are in good agreement with other carbon cycle modelling (green band and dotted line) (Krissansen-Totton, Arney and Catling, 2018) and various proxies, and are consistent with the absence of siderite in paleosols, which implies an upper limit of 28,000 ppm CO₂ from 2.75 – 2.2 Ga (Rye, Kuo and Holland, 1995). CO₂ declines steadily across the course of the Archean through to the Neoproterozoic, from ~32,000 ppm at 3400 Ma to ~9,100 ppm at 1000 Ma, with increased variability over the last 1000 Myrs due to the higher resolution of input parameters after this time.

Our model CO₂ estimates result in temperate climatic conditions (see Fig. 5.4B) in the Archean to Neoproterozoic, with global average surface temperatures that are below the threshold required for the formation of glaciers, in line with evidence for glaciations in the Archean and Paleoproterozoic (Kirschvink *et al.*, 2000; Evans, 2003; Reddy and Evans, 2009; Gumsley *et al.*, 2017). There is no CH₄ cycle in ARCHEOCARBSULF, but due to the probable high Archean CH₄ levels there is the possibility that Archean temperatures were higher than those predicted by ARCHEOCARBSULF. Prior modelling work (Olson, Reinhard and Lyons, 2016)

suggests a limitation on Proterozoic CH₄ levels due to efficient microbial oxidation of CH₄, even at low oceanic sulfate concentrations, and consequently a possible revival of the Faint Young Sun paradox (Sagan and Mullen, 1972).

Nevertheless, our results suggest that the carbon cycle alone, without the influence of additional greenhouse gases, could generate a temperate climate on the early Earth. However, the temperature function used in ARCHEOCARBSULF is very simple and thus the model strongly regulates temperature, resulting in minimal deviation from the modern day value (Mills *et al.*, 2019). Therefore, the temperature output is no substitute for those obtained from GCMs.

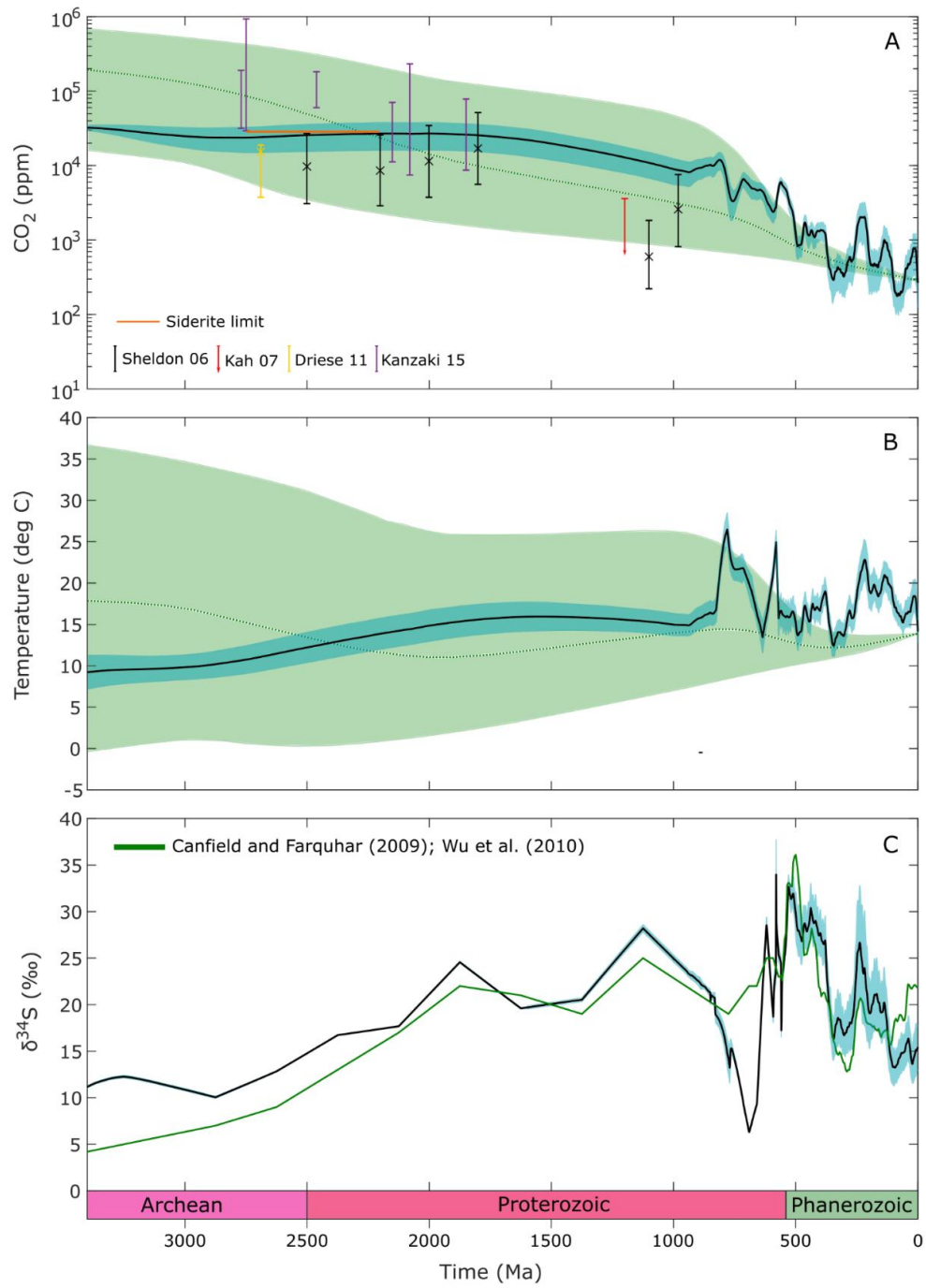


Figure 5.4 | Atmospheric CO_2 , temperature and $\delta^{34}\text{S}_{\text{sulf}}$ evolution over the last 3400 Myrs.

A) Atmospheric CO₂ results from 2,000 runs of ARCHEOCARBSULF are plotted, with the mean of all runs in black and the blue shaded band is the ± 1 sd. The results are compared to modelling conducted by Krissansen-Totton et al. (2018)(the green dotted line and green shaded band are the median and confidence intervals from their nominal model), the limit imposed by the absence of siderite (orange line)(Rye, Kuo and Holland, 1995) and various proxies (Sheldon, 2006; Kah and Riding, 2007; Driese et al., 2011; Kanzaki and Murakami, 2015). B) ARCHEOCARBSULF's temperature predictions (black line with a blue shaded band as per panel A) compared to other modelling work (Krissansen-Totton, Arney and Catling, 2018)(colours as per panel A). C) ARCHEOCARBSULF predictions for $\delta^{34}\text{S}$ (black line and blue shaded band), compared to geological data (green line)(Canfield and Farquhar, 2009; Wu et al., 2010).

Our results clearly show that the Earth experienced three oxygenation events in its history. It is possible that only the POE should be considered a true unidirectional step change, as O₂ levels are sustained at roughly modern day levels, whereas the GOE experiences an 'oxygen overshoot', and the NOE represents a period of O₂ volatility to match its climatic variability. As such, instead of centring our discussion on whether the oxygenation events could be regarded as true or stepwise 'events', we can undoubtedly point to three periods of O₂ stability.

5.5. Supplementary information

5.5.1. *Further model validation and sensitivity analyses*

In addition to the model outputs discussed in Fig. 5.4, ARCHEOCARBSULF can also predict changes to oceanic sulfate concentration over time (Fig. 5.5) which can then be compared to other estimates (Canfield and Farquhar, 2009; Algeo *et al.*, 2015). Our model shows good agreement with other work during the Archean (Canfield and Farquhar, 2009) and during the Phanerozoic (Algeo *et al.*, 2015), but is too low for much of the Proterozoic.

After the GOE, the increase in atmospheric oxygen would have increased the oxidative weathering of sulfide minerals, enhancing the flux of sulfate into the oceans (Cameron, 1982), but model sulfate concentrations do not rise until the mid-Neoproterozoic, and are significantly lower during the Mesoproterozoic than levels proposed (~ 1.5 to 4.5 mM) by some carbonate-associated sulfate data (Kah, Lyons and Frank, 2004).

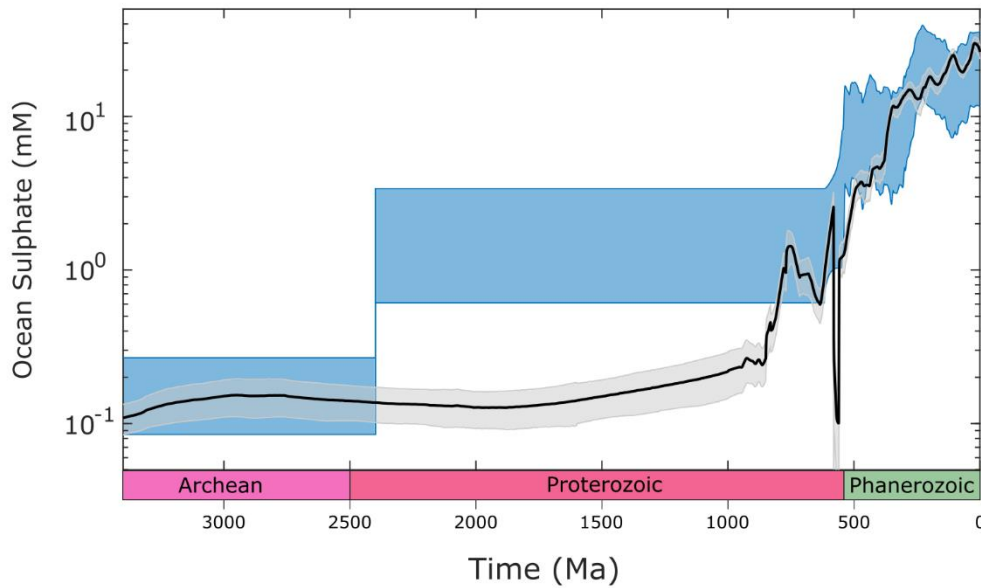


Figure 5.5 | Ocean sulfate predictions compared to other work.

The black line is the mean of 2,000 model runs and the grey window is the ± 1 sd of the runs. The blue window shows predicted sulfate levels from other modelling work (Canfield and Farquhar, 2009; Algeo et al., 2015).

There are three possible reasons for this disconnect between low model predictions, and the higher levels from other work: 1) weathering and/or degassing rates of crustal sulfur are too low; 2) burial rates of sulfur are too high; or 3) a combination of both. The weathering and degassing fluxes for both pyrite and gypsum are dependent on the sizes of their respective crustal reservoirs (see equations 5.19 – 5.24). The size of the total gypsum reservoir (i.e. the sum of young and ancient reservoirs) is small, compared to the size of the total pyrite reservoir (Fig. 5.6), meaning that if weathering/degassing rates need to be increased it would have to be from pyrite, rather than gypsum.

Weathering fluxes are greatly affected by the uplift rate (Fig. 5.2E) where we use a wide sampling range in our Monte Carlo analysis, however, for degassing fluxes which heavily rely on the normalised degassing rates (Fig. 5.2D) the sampling range is relatively narrow for much of the Proterozoic. A low normalised degassing rate would affect the size of the reduced sulfur (emanating from the ‘pyrite’ reservoir) degassing flux much more than the oxidised sulfur (from the ‘gypsum’ reservoir) flux, due to the size of the reservoirs, therefore it is possible that this is the source of the issue of low oceanic sulfate.

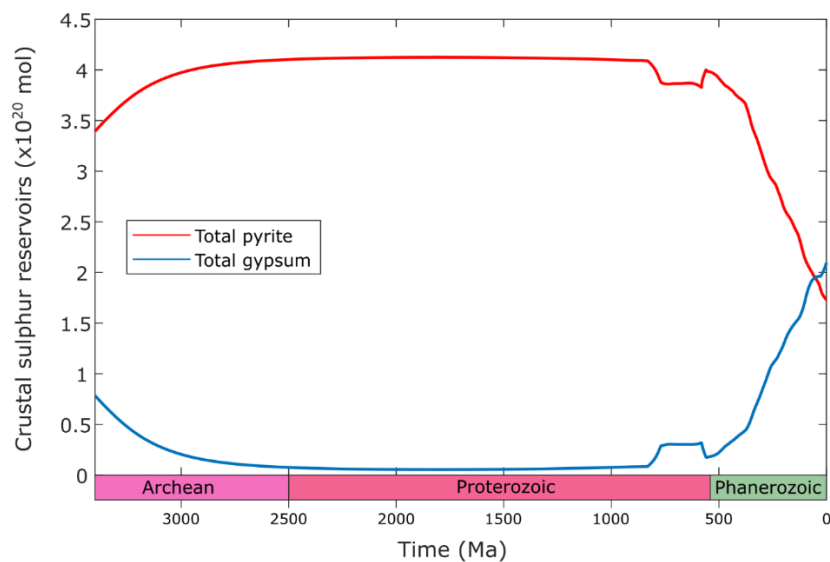


Figure 5.6 | ARCHEOCARBSULF predictions of total pyrite (red) and total gypsum (blue) over the last 3400 Myrs.

Our model predictions for f_{pyr} – the fraction of sulfur leaving the oceans as pyrite – are close to 1 for much of the Precambrian (Fig. 5.7), in line with other predictions (Canfield and Farquhar, 2009). This suggests that the model is obtaining the correct balance between pyrite burial and gypsum burial throughout the Precambrian. This

does not preclude the possibility that both pyrite and gypsum burial rates are too high, depleting the ocean of sulfate, however, in a somewhat circular fashion, the size of these two fluxes are dependent on ocean sulfate levels, therefore providing a limiting constraint on their magnitude.

Thus, it is more likely that pyrite degassing is the root cause of the low ocean sulfate predictions for the Proterozoic. Proper tectonic modelling prior to 1000 Ma is required for more accurate estimates of model outputs in general, but, widening the sampling limits for normalised degassing may help to solve this problem in the interim.

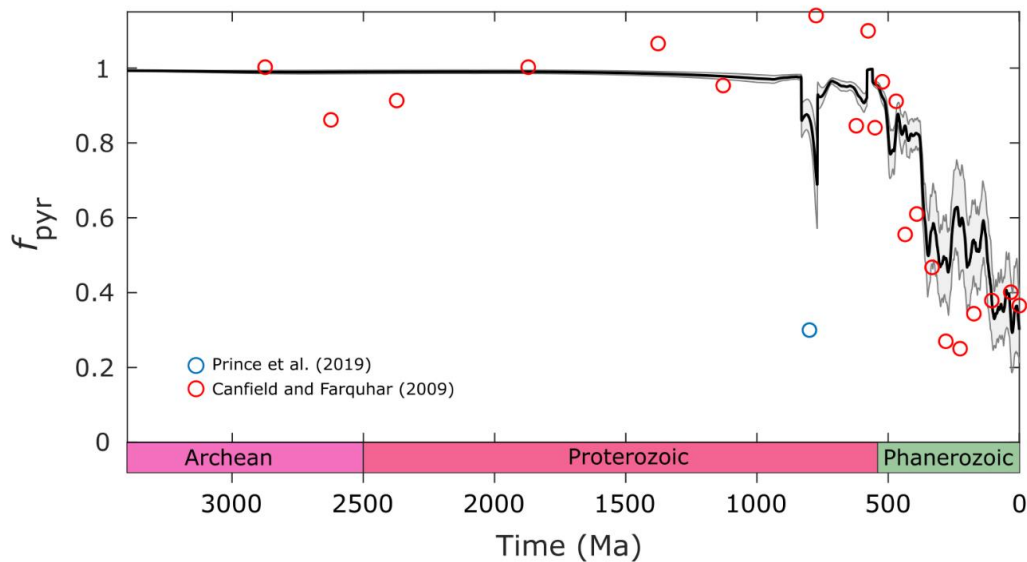


Figure 5.7 | The predicted fraction of sulfur leaving the ocean as pyrite.

The black line is the mean of 2,000 model runs, and the grey band is the ± 1 sd. The red circles and blue circle are predicted values from Canfield and Farquhar (2009) and Prince et al. (2019) respectively.

Plotting the progression of the crustal sulfur reservoirs (Fig. 5.6) also permits a validity check of the model, by comparing the results at the end of the model run with present-

day levels. The Precambrian crust is dominated by pyrite as expected (Canfield and Farquhar, 2009), and the Ediacaran-Cambrian boundary marks the start of a slow decline in pyrite and increase in gypsum, such that the total crustal pyrite achieves a value of $\sim 1.73 \times 10^{20}$ moles, and the total crustal gypsum of $\sim 2.10 \times 10^{20}$ moles at present-day, which are very close to actual values (Kump and Garrels, 1986).

Likewise, f_{pyr} model results can be checked against other work (Fig. 5.7) and are generally in good agreement throughout. There are some mismatches between ARCHEOCARBSULF's results and the data from Canfield and Farquhar (2009) in the Silurian and early Devonian, and again across the Permian to mid-Jurassic, where the model predicts a higher f_{pyr} , typically with a difference on the order of 0.2 – 0.3. Canfield and Farquhar (2009) calculate their f_{pyr} values from $\delta^{34}\text{S}$ data of both sulfates and sulfides, and an assumed constant $\delta^{34}\text{S}$ input into the oceans ($\delta^{34}\text{S}_{\text{in}}$) of 5‰ (see equation 5.51). However, as they acknowledge, the 5‰ value is based on recent Phanerozoic values and $\delta^{34}\text{S}_{\text{in}}$ may have varied through time (between $\sim 4\text{‰}$ and 12‰). The use of a lower $\delta^{34}\text{S}_{\text{in}}$ value during these periods would raise their f_{pyr} calculations to be closer to ARCHEOCARBSULF's results, so this is one possibility for the mismatch.

Alternatively, as ARCHEOCARBSULF uses equation (5.29) to calculate f_{pyr} , it is possible that for these timeframes the model is underestimating the gypsum burial flux. As the gypsum burial flux (equation 5.36) is highly dependent on oceanic sulfate concentrations through time, when concentrations are low, gypsum burial rates will also be relatively small. Although the mean of the model runs (black line in Fig. 5.5) plots within the $\pm 1\sigma$ uncertainty band (blue window in Fig. 5.5) for the Phanerozoic

(from Algeo *et al.* (2015)), it is on the low end of fluid inclusion estimates (Horita, Zimmermann and Holland, 2002; Lowenstein *et al.*, 2005), thus it is likely that there is not enough sulfur leaving the ocean as gypsum, and too much as pyrite during the Silurian and early Devonian, and the Permian to mid-Jurassic. This is also probably the case during the Tonian, where ARCHEOCARBSULF predicts a higher f_{pyr} than estimated from $\delta^{34}\text{S}$ data (Prince, Rainbird and Wing, 2019).

Two considerable alterations that have been made to the original GEOCARBSULF model through the course of this work are: the introduction of an increasing crustal carbon inventory; and an additional O_2 sink from reduced gases. As both alterations may have a significant impact upon O_2 estimates throughout time, it is prudent to conduct sensitivity analyses via further Monte Carlo sampling (see table 5.5).

Figure 5.8 shows the effect of varying the total crustal carbon reservoir by $\pm 50\%$. Apart from a brief excursion in the late Archean, and another in the early Paleoproterozoic, the mean O_2 from 2,000 runs when the crustal carbon is included in the Monte Carlo sampling (orange dashed line) is essentially the same as when it is not included (black line). As the sampling limits are $\pm 50\%$ of the value at each time point, this is not surprising, but it does suggest that, as with previous tests in Chapter 4, the number of model runs executed is sufficient to obtain the full spectrum of O_2 estimates.

The effect on the $+1\text{sd}$ is generally minimal, as the grey window, which reflects the inclusion of crustal carbon in the sampling, is not much higher than without it (blue window). Again, the major spread occurs during the late Archean and early Paleoproterozoic, suggesting that the model system is highly sensitive at these points

to variations in some of the parameters. The -1sd has more pronounced differences to the standard model run, returning very low, and sometimes negative O_2 values. This is because the crustal carbon inventory influences the total amount of carbon supplied to the ocean-atmosphere reservoir, from which C_{org} burial is derived (equation 5.31).

Thus, a high throughput of carbon to the ocean-atmosphere can buffer against low f_{org} values generated when $\delta^{13}\text{C}$ is negative and O_2 is much lower than PAL. However, this buffering capacity is significantly reduced when the crustal carbon inventory is low, hence the greater spread in O_2 estimates for the -1sd when the crustal carbon is included in the Monte Carlo sampling.

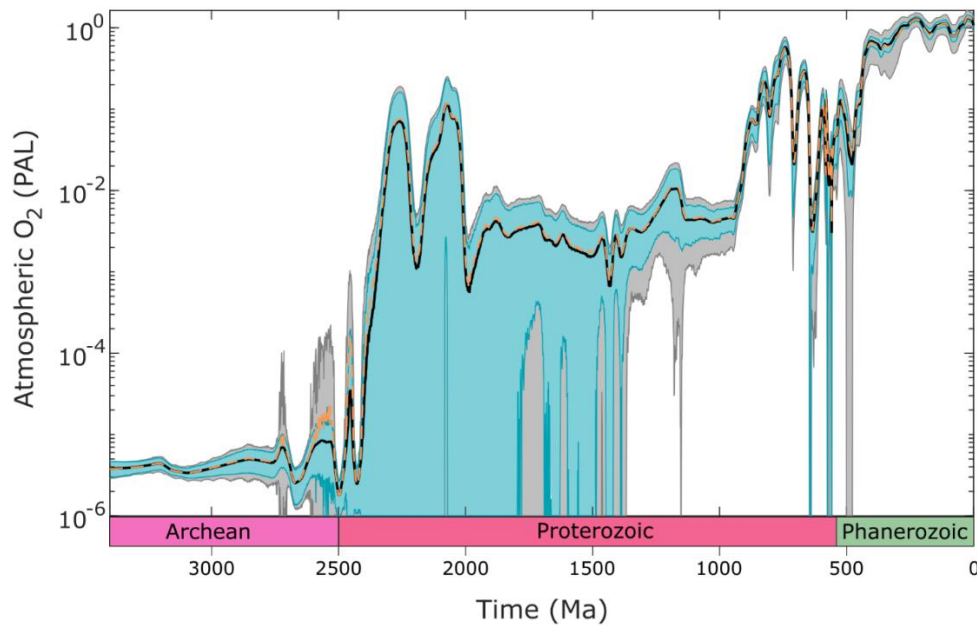


Figure 5.8 | Atmospheric O_2 sensitivity to total crustal carbon reservoir size.

The black line and blue window are the mean and $\pm 1\text{sd}$ from Figure 5.3. The orange dashed line and grey window are the mean and $\pm 1\text{sd}$ from 2,000 model runs where the total crustal carbon reservoir size has been included as a variable in the Monte Carlo sampling.

Figure 5.9 shows the effect of altering the reduced gases flux on ARCHEOCARBSULF's O_2 predictions. Instead of using a value of 0.85×10^{17} for two of the terms in equation 5.1, the Monte Carlo sampling limits use 0.35×10^{17} and 1.35×10^{17} to try and incorporate some of the uncertainty regarding the size of this flux, particularly during the Archean. Again, the mean of 2,000 runs with (orange dashed line) and without (black line) this additional variable in Monte Carlo sampling exhibits little difference, apart from the late Archean and early Paleoproterozoic. These time periods seem sensitive to any model changes, and this is likely due to the $\delta^{13}C$ record, where even the +1sd (see Fig. 5.2) is negative.

The effect on the ± 1 sd O_2 predictions is more evenly distributed than was the case for the crustal carbon sensitivity test, although there are occasions, such as during the Shuram-Wonoka anomaly, where the $\delta^{13}C$ record is very negative, and any increase in strength of the O_2 sinks can push the system into a depletion of O_2 in the atmosphere. The greater effect on the ± 1 sd estimates during the Archean to early Paleoproterozoic, compared to the rest of the Proterozoic and Phanerozoic is due to the exponential decay of the reduced gases flux (Fig. 5.2), where the flux for the standard model run is approximately 3x higher at the start of the Paleoproterozoic, compared to the start of the Mesoproterozoic.

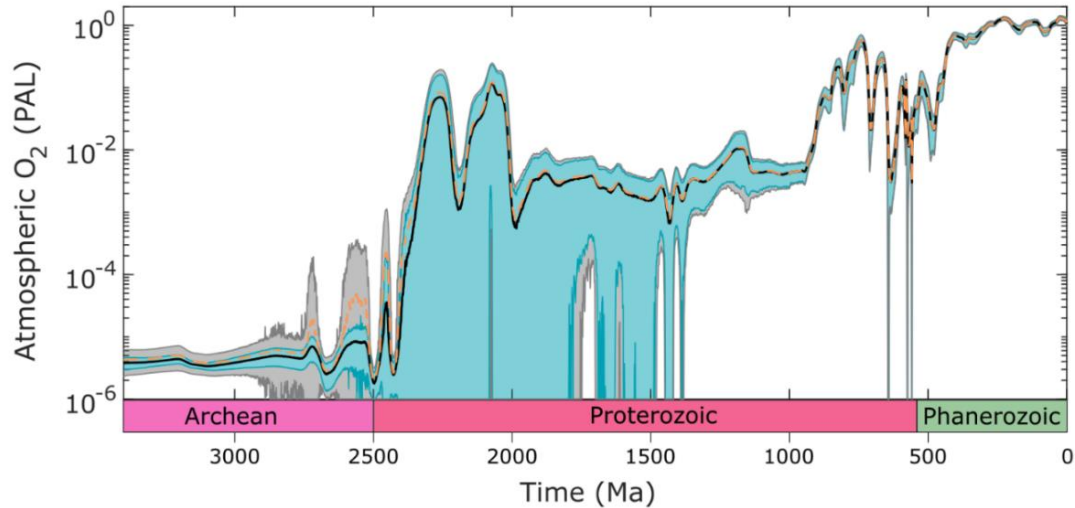


Figure 5.9 | Atmospheric O₂ sensitivity to the size of the reduced gases flux.

The black line and blue window are the mean and ± 1 sd from Figure 5.3. The orange dashed line and grey window are the mean and ± 1 sd from 2,000 model runs where the reduced gases flux size has been included as a variable in the Monte Carlo sampling.

As with Chapter 4, a number of fluxes generated by the model are plotted to check that ARCHEOCARBSULF returns present day values at the end of its run. In figure 5.10 the estimated C_{org} burial flux for the last 3400 Myrs is compared to modern day estimates used in other models. ARCHEOCARBSULF returns a mean present day burial rate of $\sim 6.62 \times 10^{18}$ Mol Myr⁻¹, which lies in the middle of other estimated present day rates of 5×10^{18} Mol Myr⁻¹ by Berner (1987) and 9×10^{18} Mol Myr⁻¹ in COPSE (Bergman, Lenton and Watson, 2004).

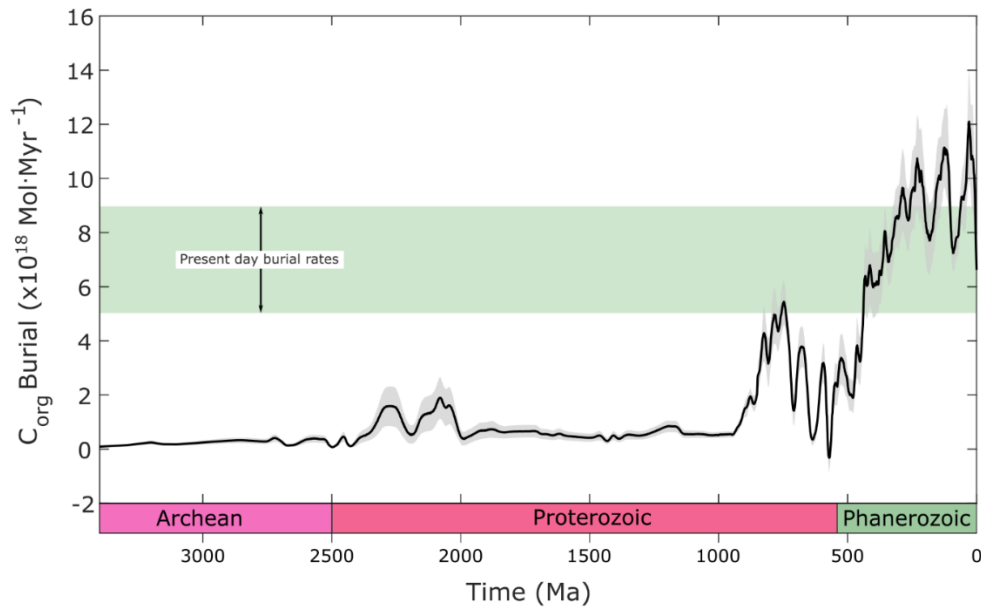


Figure 5.10 | Organic carbon burial rates for the last 3400 Myrs.

The black line is the mean of 2,000 model runs and the grey window is the ± 1 sd of the runs. The green window represents different estimates of present day burial rates (Berner, 1987; Bergman, Lenton and Watson, 2004).

Although the quantity of O_2 in the atmosphere has increased by more than five orders of magnitude from the Archean to the Present, this is not totally reflected in changes to the C_{org} burial flux, as the rate at 3400 Ma is $\sim 9.33 \times 10^{17} \text{ Mol Myr}^{-1}$ – only two orders of difference from the present day rate. Although pyrite burial is a key source of O_2 to the atmosphere, the model suggests that pyrite burial rates (see Fig. 5.11) have not significantly changed through time, thus O_2 sinks must have decreased in size from the Archean to the Present.

ARCHEOCARBSULF predicts mean pyrite burial rates of $\sim 1 \times 10^{18}$ Mol Myr⁻¹ at present day, which is slightly lower than the 1.2 to 1.7×10^{18} Mol Myr⁻¹ bounds of previous estimates (Berner, 1982; Hu and Cai, 2011), although the +1sd does finish between these values. As the model correctly predicts present day O₂ levels at the end of its run, this suggests that there is a slight imbalance between C_{org} and pyrite burial rates, and that ARCHEOCARBSULF's C_{org} burial rates should be slightly lower, and pyrite slightly higher for present day.

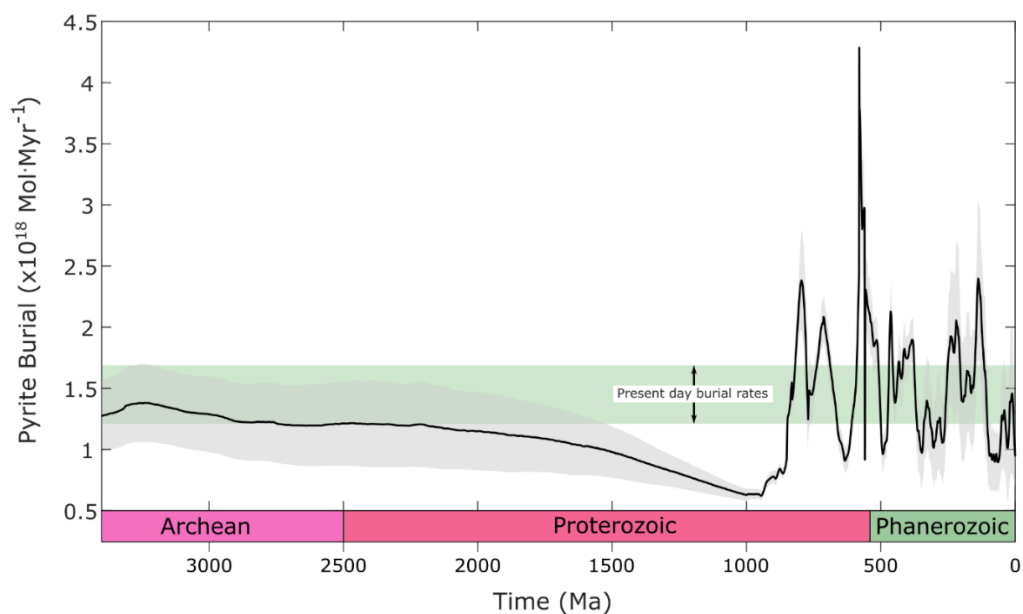


Figure 5.11 | Pyrite burial rates for the last 3400 Myrs.

The black line is the mean of 2,000 model runs and the grey window is the ± 1 sd of the runs. The green window represents different estimates of present day burial rates (Berner, 1982; Hu and Cai, 2011).

Finally, the silicate weathering flux from ARCHEOCARBSULF (figure 5.12) is plotted. As mentioned previously in Chapter 4, there is a strong relationship between relative degassing rates (f_G) through time with silicate weathering rates, whereby

increased rates would have increased the concentration of CO₂, temperature and thus silicate weathering. This explains the lack of variance in silicate weathering rates prior to the Neoproterozoic, yet ARCHEOCARBSULF starts its model run with a f_G upper bound of 2.5x present day levels (see Fig. 5.2) and therefore should at least affect the $\pm 1\text{sd}$ of the weathering rates for the Archean. This does not seem to be the case, and is likely due to the total amount of continental land mass being much lower during the Archean (Hawkesworth, Cawood and Dhuime, 2016), which would cap the amount of material available for weathering.

The mean silicate weathering flux at the end of the model runs is 5.82×10^{18} Mol Myr⁻¹ which is a bit lower than the 6.7×10^{18} Mol Myr⁻¹ value used by Berner in the original GEOCARB model (Berner, 1991), leading to slightly higher ‘present day’ (i.e. pre-industrial) CO₂ of ~296ppm. However, the present day temperature calculated by the model is ~14.5° so this suggests a disconnect between temperature, CO₂ and silicate weathering at present day in the model, which may be due to the high solar luminosity (W_s) value used to return reasonable CO₂ and temperature values for the early Earth. Regardless, the general good fit of the model results with various proxies and present day values suggests that the model is robust.

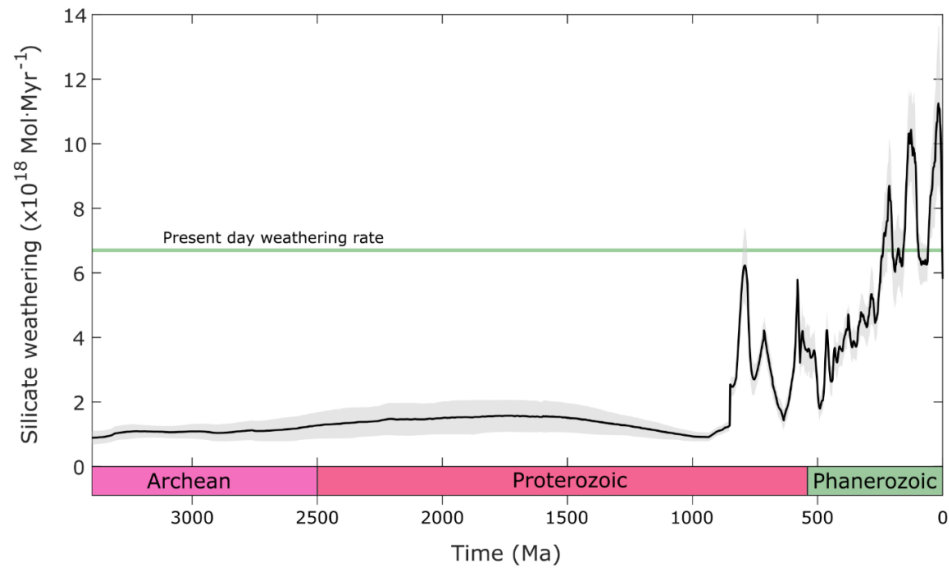


Figure 5.12 | Silicate weathering rates for the last 3400 Myrs.

The black line is the mean of 2,000 model runs and the grey window is the ± 1 sd of the runs. The green line is the original GEOCARB weathering rate for the present day (Berner, 1991).

5.5.2. Full model parameters

For the following tables, where we mention GEOCARBSULF as a source, we mean the final values as used in the 2009 (Berner, 2009) paper, some of which are unchanged from, for example, GEOCARB II (Berner, 1994).

Table 5.1: Present day parameters used in ARCHEOCARBSULF

Parameter	Algebraic Representation	Value	Source
Atmosphere and ocean CO ₂	A0	3.193x10 ¹⁸ mol	COPSE (Bergman, Lenton and Watson, 2004)
Atmosphere and ocean O ₂	O0	3.8x10 ¹⁹ mol	GEOCARBSULF (Berner, 2009)
Atmosphere and ocean sulfate	OA_S_0	3.8x10 ¹⁹ mol	GEOCARBSULF
Young buried pyrite sulfur	<i>Pyr_0</i>	12.8571x10 ¹⁸ mol	GEOCARBSULFOR (Krause <i>et al.</i> , 2018)
Young buried gypsum sulfur	<i>Gyp_0</i>	100x10 ¹⁸ mol	GEOCARBSULFOR
Temperature	<i>temp_0</i>	288 K	
Silicate weathering	<i>F_ws_0</i>	6.67x10 ¹⁸ mol myr ⁻¹	GEOCARBSULF
Young carbonate weathering	<i>F_wc_y0</i>	11.35x10 ¹⁸ mol C myr ⁻¹	GEOCARBSULFOR
Total crustal carbon	<i>crustal_carbon_0</i>	8500x10 ¹⁸ mol	Hayes and Waldbauer (2006)
Dissolved organic carbon pool	<i>DOC_0</i>	1.2566 x10 ¹⁷ mol	This study

Table 5.2: Constant parameters used in ARCHEOCARBSULF

Parameter	Algebraic Representation	Value	Source
Normalised activation energy for silicates	ACT_{si}	0.09 K^{-1}	GEOCARBSULF
Normalised activation energy for carbonates	ACT_{carb}	0.087 K^{-1}	GEOCARBSULF
Effect of solar insolation on temperature	Ws	25.6°	This study
Proportion of plants fertilised by increasing CO_2	$FERT$	0.4	GEOCARBSULF
Curve fitting parameter for effect of O_2 on $\delta^{13}\text{C}$ fractionation	J	4	GEOCARBSULF
Young pyrite weathering rate constant*	k_{wp}	$4.8 \times 10^{17} \text{ myr}^{-1}$	This study
Young gypsum weathering rate constant*	k_{wgyp}	$4.7 \times 10^{17} \text{ myr}^{-1}$	This study
Young C_{org} weathering rate constant	k_{wg}	0.02 myr^{-1}	This study
Young carbonate weathering rate constant	k_{wc}	0.02 myr^{-1}	This study
Ancient pyrite weathering rate constant	$kwpa$	0.0011 myr^{-1}	This study
Ancient gypsum weathering rate constant	$kwgypa$	0.0023 my^{-1}	This study
Ancient C_{org} weathering rate constant	$kwga$	0.00055 my^{-1}	This study
Ancient carbonate weathering rate constant	$kwca$	0.0005 my^{-1}	This study
Ancient pyrite degassing rate constant	$kmpa$	0.0011 my^{-1}	This study
Ancient gypsum degassing rate constant	$kmgypa$	0.0023 my^{-1}	This study

Ancient C _{org} degassing rate constant	<i>kmga</i>	0.00129 my ⁻¹	This study
Ancient carbonate degassing rate constant	<i>kmca</i>	0.00125 my ⁻¹	This study
Pyrite burial rate constant*	<i>k_bp</i>	1.45x10 ¹⁸ my ⁻¹	This study
Gypsum burial rate constant*	<i>k_bgyp</i>	2.32x10 ¹⁸ my ⁻¹	This study
Pyrite young to ancient flux rate constant	<i>k_p_ya</i>	0.01 my ⁻¹	GEOCARBSULFOR
Gypsum young to ancient flux rate constant	<i>k_gyp_ya</i>	0.01 my ⁻¹	GEOCARBSULFOR
C _{org} young to ancient flux rate constant	<i>k_g_ya</i>	0.018 my ⁻¹	GEOCARBSULFOR
Carbonate young to ancient flux rate constant	<i>k_c_ya</i>	0.018 my ⁻¹	GEOCARBSULFOR
A pulse of gypsum weathering	<i>S_pulse</i>	5 (baseline)	This study, see also table 5.5
A pulse of pyrite burial	<i>Pyr_pulse</i>	5 (baseline)	This study, see also table 5.5
A pulse of gypsum deposition	<i>Evap_pulse</i>	7 (baseline)	This study, see also table 5.5
Average isotopic composition of all crustal carbon	<i>delta_in</i>	-5‰	Holser <i>et al.</i> (1988)
Oceanic fraction of atmosphere and ocean CO ₂	<i>ocfrac</i>	0.98386	This study
Response of global mean temperature to atmospheric CO ₂ greenhouse effect	<i>gamma</i>	3	Royer <i>et al.</i> (2014)

* The values for these parameters are so much larger as they are multiplied by normalized reservoirs, instead of a reservoir at time (t).

Table 5.3: Time dependent parameters used in ARCHEOCARBSULF

Parameter	Algebraic Representation	Source	Notes
Total land area	f_A	Hawkesworth <i>et al.</i> (2016); Royer <i>et al.</i>	Time array
Fraction of land area experiencing chemical weathering	f_{AW}	Royer <i>et al.</i>	Time array
Global river runoff	f_D	Royer <i>et al.</i>	Time array
Effect of change in paleogeography on temperature	$GEOG$	Godd�ris <i>et al.</i> (2017); Royer <i>et al.</i>	Time array
Proportion of land area underlain by carbonates	f_L	Royer <i>et al.</i>	Time array
Degassing rate due to tectonics / seafloor spreading rate*	f_G or f_{SR}	This study; Merdith <i>et al.</i> (2019)	Time array
Ocean $\delta^{13}C$ carbonate record	δ_{OA_C}	Krissansen-Totton <i>et al.</i> (2015); Saltzman and Thomas (2012)	Time array

Dependence of weathering rate on soil biological activity due to land plants	f_E	GEOCARBSULF	0-80 Ma $f_E = 1$ 130-350 Ma $f_E = 0.875$ 380-470 Ma $f_E = 0.25$ 635-850 Ma $f_E = 0.1$ 850-3400 Ma $f_E = 0.05$ Linear interpolation between 80-130 Ma, 350-380 Ma and 470-635 Ma
Mean land elevation	f_R	Hay <i>et al.</i> (2006)	Time array
Dependence of degassing rate on relative proportions of carbonates on shallow platforms or deep ocean	f_C	GEOCARBSULF	150-3400 Ma $f_C = 0.75$ 0-150 Ma is a time dependent equation, see equation (5.6)
Temperature controlled runoff factor	RUN	GEOCARBSULF	0-40 Ma, 260-340 Ma, 635-649 Ma and 659-717 Ma: $RUN = 0.045$ All other time: $RUN = 0.025$
Effect of changes to CO ₂ on carbonate and silicate weathering	f_{CO2}	GEOCARBSULF	0-350 Ma: $f_{CO2} = VAS$ 380-3400 Ma: $f_{CO2} = NOVAS$ Linear interpolation between 350-380 Ma - see equations (5.11 – 5.16)

A scaling factor for enhanced gypsum weathering during the Shuram-Wonoka anomaly	<i>S_scaling</i>	This study / Shields <i>et al.</i> (2019)	0-559 and 581-3400 Ma: <i>S_scaling</i> = 1 560-580 Ma: <i>S_scaling</i> = <i>S_pulse</i> Linear interpolation between 559-560 and 580-581 Ma
A scaling factor for enhanced pyrite burial during the Shuram-Wonoka anomaly	<i>Pyr_scaling</i>	This study / Shields <i>et al.</i>	0-559 and 581-3400 Ma: <i>Pyr_scaling</i> = 1 560-580 Ma: <i>Pyr_scaling</i> = <i>Pyr_pulse</i> Linear interpolation between 559-560 and 580-581 Ma
A scaling factor for enhanced gypsum deposition in the Tonian period	<i>Evap_scaling</i>	This study / Shields <i>et al.</i>	0-769 and 831-3400 Ma: <i>Evap_scaling</i> = 1 770-830 Ma: <i>Evap_scaling</i> = <i>Evap_pulse</i> Linear interpolation between 559-560 and 580-581 Ma
Evolution of the Earth's crustal carbon content	<i>crustal_carbon</i>	Hayes and Waldbauer	Time array
Sulfur isotope fractionation	<i>alpha_S</i>	Canfield and Farquhar (2009); Wu <i>et al.</i> (2010)	Time array

* Both of these terms are used throughout the literature, but in GEOCARBSULF they are treated as the same thing.

For all time arrays we apply interpolation between data points.

Table 5.4: Starting reservoir sizes of ARCHEOCARBSULF

Parameter	Algebraic Representation	Value	Source
Ocean and atmosphere sulfur	OA_S	38×10^{18} mol	GEOCARBSULF
Young pyrite	Pyr_y	20×10^{18} mol	GEOCARBSULFOR
Ancient pyrite	Pyr_a	260×10^{18} mol	GEOCARBSULFOR
Young gypsum	Gyp_y	50×10^{18} mol	GEOCARBSULFOR
Ancient gypsum	Gyp_a	50×10^{18} mol	GEOCARBSULFOR
Young C_{org}	G_y	302.5×10^{18} mol	This study
Ancient C_{org}	G_a	1072.5×10^{18} mol	This study
Young carbonate	C_y	1072.5×10^{18} mol	This study
Ancient carbonate	C_a	3802.5×10^{18} mol	This study

Table 5.5: Monte-Carlo simulation parameters

Parameter	Algebraic Form	Lower Limit	Upper Limit	Non Monte-Carlo Value
Ocean $\delta^{13}\text{C}$ carbonate record	delta_OA_C	Smoothed average – 1sd	Smoothed average + 1sd	Smoothed average
Degassing rate due to tectonics / seafloor spreading*	f_G	Normalised degassing at subduction zones only	Normalised degassing at rift margins only	Normalised degassing at subduction zones only
Mean land elevation	f_R	Normalisation to Pleistocene deposition values	Normalisation to Miocene deposition values	Normalisation to Miocene deposition values
Proportion of land area underlain by carbonates	f_L	Time array – 0.5	Time array + 0.5	Time array
Fraction of land area experiencing chemical weathering	f_{AW}	Time array – 0.5	Time array + 0.5	Time array

Global river runoff	f_D	Time array – 0.5	Time array + 0.5	Time array
A scaling factor for enhanced gypsum weathering during the Shuram-Wonoka anomaly	S_{scaling}	5	30	5
A scaling factor for enhanced pyrite burial during the Shuram-Wonoka anomaly	Pyr_{scaling}	5	30	5
A scaling factor for enhanced gypsum deposition in the Tonian period	$Evap_{\text{scaling}}$	4	10	7
Increasing crustal carbon reservoir	$crustal\_carbon$	Time array – 50%	Time array + 50%	Time array
Reduced gases flux (see equation 5.1 for more information)	rgf	0.35×10^{17}	1.35×10^{17}	0.85×10^{17}

*For model initiation at 3500 Ma, the upper limit is set to be 2.5x present day rates, and the lower limit is 0.5x present day rates, with both limits declining via linear interpolation to their values at 1000 Ma as set in NEOCARBSULF

5.5.3. Full model equations

The full set of equations for the model, apart from equations 5.1 – 5.5 are documented below. The majority of the equations are from NEOCARBSULF. Those equations with the hash symbol (#) have a function in the model that effectively sets the value returned as zero if the model would otherwise calculate this flux as a negative value – see Chapter 4 for further details. The letter ‘*t*’ represents time and model run time is 3500 Myrs, to allow for 100 Myrs of spin-up time.

Table 5.6: Flux and parameter equations

f_{C} for $t < 150$ Ma:	$f_{\text{C}} = 0.75 + \left[\left(\frac{0.25}{150} \right) \cdot (150 + t) \right]$	[5.6]
Ratio of CO ₂ relative to PAL:	$\text{RCO}_2 = \frac{\text{CO}_2(t)}{\text{A0}}$	[5.7]
Ratio of O ₂ relative to present day:	$\text{O}_{2\text{mr}} = \frac{\text{O}_2(t)}{\text{O0}}$	[5.8]
CO ₂ effect on carbonate and silicate weathering:	$\text{VAS} = \left(\frac{2 \cdot \text{RCO}_2}{1 + \text{RCO}_2} \right)^{\text{FERT}}$ $\text{NOVAS} = \text{RCO}_2^{0.5}$	[5.9]

Global average temperature:	$temp = \left(gamma \cdot \left(\frac{\ln RCO_2}{\ln 2} \right) \right) - \left(Ws \cdot \frac{t}{-model\ run\ time} \right) + GEOG + temp_0$	[5.10]
Temperature effect on silicate weathering:	$f_{Tsi} = e^{(ACT_{si} \cdot [temp - temp_0])} \cdot \{1 + [RUN \cdot (temp - temp_0)]\}^{0.65}$	[5.11]
Temperature and CO ₂ effect on silicate weathering:	$f_{Bsi} = f_{Tsi} \cdot f_{CO2}$	[5.12]
Temperature effect on carbonate weathering:	$f_{Tcarb} = 1 + [ACT_{carb} \cdot (temp - temp_0)]$	[5.13]
Temperature and CO ₂ effect on carbonate weathering:	$f_{BBcarb} = f_{Tcarb} \cdot f_{CO2}$	[5.14]
[#] Oxygen dependency for C _{org} weathering:	$ox\_weather = O_2 mr^{0.5}$	[5.15]
Total crustal carbon normalised to present day:	$relative\_crustal\_carbon = \frac{crustal\_carbon(t)}{crustal\_carbon_0}$	[5.16]
Weathering of young carbonate:	$F_{wc\_y} = f_{BBcarb} \cdot f_L \cdot f_A \cdot f_D \cdot f_E \cdot k_{wc} \cdot relative\_crustal\_carbon \cdot C_y \cdot f_R^{0.9}$	[5.17]
Weathering of ancient carbonate:	$F_{wc\_a} = f_{BBcarb} \cdot f_L \cdot f_A \cdot f_D \cdot f_E \cdot kwca \cdot relative\_crustal\_carbon \cdot C_a \cdot f_R^{0.9}$	[5.18]
Weathering of young pyrite:	$F_{wp\_y} = \frac{F_{ws}}{F_{ws_0}} \cdot new\_kwp \cdot \frac{Pyr\_y(t)}{Pyr_0}$	[5.19]

Weathering of ancient pyrite:	$F_{wp\_a} = f_{R^{0.33}} \cdot kwpa \cdot Pyr\_a(t)$	[5.20]
Weathering of young gypsum:	$F_{wgyp\_y} = \frac{F_{wc\_y}}{F_{wc\_y0}} \cdot new\_kwgyp \cdot \frac{Gyp\_y(t)}{Gyp\_0} \cdot S\_scaling$	[5.21]
Weathering of ancient gypsum:	$F_{wgyp\_a} = f_A \cdot f_D \cdot kwgypa \cdot Gyp\_a(t) \cdot S\_scaling$	[5.22]
Degassing of ancient pyrite:	$F_{mp} = f_{SR} \cdot kmpa \cdot Pyr\_a(t)$	[5.23]
Degassing of ancient gypsum:	$F_{ms} = f_{SR} \cdot kmgypa \cdot Gyp\_a(t)$	[5.24]
[#] Degassing of ancient C _{org} :	$F_{mg} = f_{SR} \cdot kmga \cdot relative\_crustal\_carbon \cdot G\_a$	[5.25]
Degassing of ancient carbonate:	$F_{mc} = f_{SR} \cdot f_C \cdot kmca \cdot relative\_crustal\_carbon \cdot C\_a$	[5.26]
[#] Fractionation of $\delta^{13}C$:	$alpha\_C = 27 + [J \cdot (O_{2mr} - 1)]$	[5.27]
All carbon associated fluxes into the atmosphere-ocean:	$F_{total\_c} = F_{wc\_y} + F_{wc\_a} + F_{wg\_y} + F_{wg\_a} + F_{mc} + F_{mg}$	[5.28]
Fraction of the total sulfur leaving the ocean as pyrite (burial flux approach):	$f_{pyr} = \frac{F_{bp}}{F_{bp} + F_{bgyp}}$	[5.29]
Fraction of the atmosphere-ocean carbon pool that will leave as C _{org}	$f_{org} = \frac{delta\_OA\_C - delta\_in}{alpha\_C}$	[5.30]

Burial of C_{org}	$F_{bg} = f_{org} \cdot F_{total\_c}$	[5.31]
Burial of carbonate:	$F_{bc} = F_{ws} + F_{wc\_y} + F_{wc\_a}$	[5.32]
Oxygen dependency for pyrite burial:	$fox = 2 \cdot \left(\frac{1}{1 + e^{-5(-O_2mr + 1)}} \right)$	[5.33]
Normalised dissolved C_{org} pool	$norm\_DOC = \frac{\left(\frac{CO_2(t) \cdot ocfrac}{25} \right)}{DOC_0}$	[5.34]
Burial of pyrite:	$F_{bp} = k_{bp} \cdot \frac{OA\_S(t)}{OA\_S_0} \cdot fox \cdot norm\_DOC \cdot Pyr\_scaling$	[5.35]
Burial of gypsum:	$F_{bgyp} = k_{bgyp} \cdot \frac{OA\_S(t)}{OA\_S_0} \cdot Evap\_scaling$	[5.36]
Young to ancient pyrite flux:	$F_{ya\_p} = k_{p\_ya} \cdot Pyr\_y(t)$	[5.37]
Young to ancient gypsum flux:	$F_{ya\_gyp} = k_{gyp\_ya} \cdot Gyp\_y(t)$	[5.38]
Young to ancient C_{org} flux:	$F_{ya\_g} = k_{g\_ya} \cdot G\_y(t)$	[5.39]
Young to ancient carbonate flux:	$F_{ya\_c} = k_{c\_ya} \cdot C\_y(t)$	[5.40]
Silicate weathering:	$F_{ws} = fBsi \cdot (f_{AW} \cdot f_A \cdot f_D)^{0.65} \cdot f_R^{0.33} \cdot f_E \cdot F_{ws\_0}$	[5.41]

Table 5.7: Reservoir equations

Ocean and atmosphere sulfur:	$\frac{d(OA\_S)}{dt} = F_{wp\_y} + F_{wgyp\_y} + F_{wp\_a} + F_{wgyp\_a} + F_{mp} + F_{ms} - F_{bp} - F_{bgyp}$	[5.42]
Young pyrite:	$\frac{d(Pyr\_y)}{dt} = F_{bp} - F_{wp\_y} - F_{ya\_p}$	[5.43]
Ancient pyrite:	$\frac{d(Pyr\_a)}{dt} = F_{ya\_p} - F_{wp\_a} - F_{mp}$	[5.44]
Young gypsum:	$\frac{d(Gyp\_y)}{dt} = F_{bgyp} - F_{wgyp\_y} - F_{ya\_gyp}$	[5.45]
Ancient gypsum:	$\frac{d(Gyp\_a)}{dt} = F_{ya\_gyp} - F_{wgyp\_a} - F_{ms}$	[5.46]
Young C _{org} :	$\frac{d(G\_y)}{dt} = F_{bg} - F_{wg\_y} - F_{ya\_g}$	[5.47]
Ancient C _{org} :	$\frac{d(G\_a)}{dt} = F_{ya\_g} - F_{wg\_a} - F_{mg}$	[5.48]
Young carbonate:	$\frac{d(C\_y)}{dt} = F_{bc} - F_{wc\_y} - F_{ya\_c}$	[5.49]
Ancient carbonate:	$\frac{d(C\_a)}{dt} = F_{ya\_c} - F_{wc\_a} - F_{mc}$	[5.50]

Table 5.8: Non-model equations

Fraction of the total sulfur leaving the ocean as pyrite (isotope approach) (Canfield and Farquhar, 2009):	$f_{pyr} = \frac{\delta^{34}S_{in} - \delta^{34}S_{sulfate}}{\delta^{34}S_{sulfide} - \delta^{34}S_{sulfate}}$	[5.51]

6. Conclusions

In this chapter I summarise the main findings of this thesis before then detailing further work that could be conducted, either by using derivatives of the GEOCARBSULF model, or by using the results from this thesis as parameter inputs for other, more complex, models to investigate other possible constraints on habitability.

6.1. Main findings and discussion

This work has resolved a long-standing issue in the geochemical community, namely: why do isotope mass balance approaches, such as the GEOCARBSULF model (Berner, 2006a) predict high, modern-like levels of atmospheric O₂ during the early Paleozoic, when increasingly geochemical proxies suggest widespread ocean anoxia was prevalent until at least the end of the Cambrian (e.g. Sperling et al., 2015), but possibly until the start of the Devonian (e.g. Dahl et al., 2010)?

It was found that the answer to this question lies in GEOCARBSULF's simplified treatment of sulfur isotope fractionation, wherein even moderately low O₂ levels (<10% atm) are unattainable because when O₂ decreases to this threshold, the sulfur isotope fractionation – imparted by sulfate reduction – calculated by GEOCARBSULF is also low. Yet, low sulfur isotope fractionation in the model produces pyrite burial rates at least an order of magnitude higher than those at present-day, leading to high O₂ generation.

Reconfiguration of the sulfur cycle, using a ‘forwards’ modelling approach, instead of isotope inversion, leads to the prediction of low O₂ in the early Paleozoic,

with a step change to modern-like levels starting at the end of the Ordovician. Crucially, additional results from this model, such as $\delta^{34}\text{S}$ predictions, are compatible with the observed record. Although this is not the first piece of work to postulate a Paleozoic Oxygenation Event (POE), coincident with the evolution and spread of land plants (e.g. Dahl *et al.*, 2010; Lenton *et al.*, 2016), it is the first to provide detailed, quantitative support for this theory, based on direct geochemical evidence from the geological record.

Resolution of this disagreement between the GEOCARBSULF model and the geochemical proxies allowed for the extension of the model further back in time, to investigate the Neoproterozoic Oxygenation Event (Och and Shields-Zhou, 2012) and provide, for the first time, a quantitative estimate of O_2 through the Neoproterozoic.

The results suggest that the Neoproterozoic was a highly dynamic period of time, with O_2 oscillating between very low ($\leq \sim 1\%$ PAL) and moderately high ($\sim 60\%$ PAL) values, which is in general agreement with marine geochemical proxies that indicate fluctuating deep ocean redox conditions (e.g. Sahoo *et al.*, 2016). A possible hypothesis, which is worthy of further investigation is: Would O_2 levels have continued to rapidly (on geologic timescales) switch between the extreme values predicted by NEOCARBSULF, if it were not for the stabilising influence of the evolution of land plants or a resiliently oxygenated ocean?

Any answers to this hypothesis are not possible with this model but may be derived by a model with more complex ocean chemistry. As the Neoproterozoic likely witnessed the evolution of multicellular life (Knoll and Nowak, 2017), it is possible that fluctuating oxygen levels during this Era promoted metazoan innovations (e.g.

Wood and Erwin, 2018) but the absolute link between oxygen and the dawn of animals remains uncertain.

Finally, the model was extended further back, into the Archean, to investigate atmospheric O₂ levels during the GOE, and whether the ‘oxygen overshoot’ associated with the Lomagundi positive isotope excursion was really equivalent to modern-day levels of oxygen as postulated (Lyons, Reinhard and Planavsky, 2014).

Prior to the GOE, the model predicts O₂ levels to be $<10^{-5}$ PAL, which is in agreement with the mass-independent fractionation of sulfur (MIF-S) isotopes found in the rock record (Farquhar, Bao and Thiemens, 2000; Pavlov and Kasting, 2002). However, this is dependent on the input of reduced gases, and subsequent O₂ consumption, which is not well defined, thus the predicted O₂ levels are only semi-quantitative. The whole Earth system nature of the model, and in particular the combination of a single ocean-atmosphere reservoir, means that any ‘whiffs’ of O₂ in the Archean are hard to identify, although there is a temporary rise, pre-GOE, to levels slightly above those constrained by the MIF-S signal.

Importantly, the GOE which initiates at ~2420 Ma in our results, reaches approximately the same O₂ level at its maxima as the Lomagundi event does (~0.04 PAL and ~0.07 PAL respectively), with O₂ experiencing a similar level of decline post both events. This poses the intriguing question of whether the GOE should encompass the Lomagundi excursion, or whether they should be regarded as discrete events. What is clear, however, is that in broad terms, the GOE-Lomagundi does represent a stepwise oxygenation of the atmosphere, but our approach argues that O₂ levels during this time were still comparatively low, and not close to modern-day levels.

All three iterations of the model are, of course, dependent on a wide variety of geological and other modelling data in order to function. However, for many of the normalised parameters (e.g. degassing rates), the data available extends only as far back as the beginning of the Neoproterozoic, if that, with the exception of uplift rates, which are available for the Mesoproterozoic. Hence, as mentioned in Chapter 5, much of this data is unchanging for the Archean and early to mid-Proterozoic, or as is the case with the land area parameter, is a best guess based on modelling of crustal volume and thickness changes over time (Hawkesworth, Cawood and Dhuime, 2016) and therefore lacks the finesse of the sediment reconstruction work of Ronov (e.g. 1994).

The $\delta^{13}\text{C}$ record is of higher resolution, but still contains large gaps, necessitating more coarse binning and smoothing of the data than is ultimately desirable. This can greatly affect the organic carbon burial rates predicted by the model, and thus O_2 . Hence, not only the treatment of the $\delta^{13}\text{C}$ data, but also whether the data itself represents a truly primary signal are important topics for consideration, with regards to how accurately these O_2 results may reflect past conditions. Thus, pre-1000 Ma the atmospheric O_2 results have a greater uncertainty, which can be seen in the larger $\pm 1\text{sd}$ range in figure 5.3. Additionally, prior to the Neoproterozoic, temporal variations in O_2 are broad, and missing the finer details of the Neoproterozoic and Phanerozoic versions of the model. This also applies to other model outputs, such as CO_2 and temperature, which are both highly dependent on the normalised parameters, rather than the $\delta^{13}\text{C}$ record.

There are a number of things not included in this work (or are only lightly touched on) such as: using the paired $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{13}\text{C}_{\text{carb}}$, and $\delta^{34}\text{S}_{\text{pyr}}$ and $\delta^{34}\text{S}_{\text{sulf}}$ records to generate values for isotopic fractionation, instead of using O_2 -dependent equations or alternative (i.e. COPSE) formulations; and investigating the effect non-steady state carbon cycle dynamics may have on C_{org} burial rates, and thus O_2 production. These are important topics to consider and are discussed further in sections 6.2.2. and 6.2.3.

Overall though, despite the uncertainties with some of the data, it can be said that: by analysing the carbon and sulphur isotope records, alongside tectonic evolution, this work identifies three oxygenation events in Earth's history, two of which (the GOE and the POE) represented unidirectional stepwise changes in O_2 levels, with the remaining Neoproterozoic Oxygenation Event representing a chaotic regime change in atmospheric oxygen levels.

6.2. Future modelling work

6.2.1. GEOCARBSULF data updates

As previously described, the model requires data in order to run. Therefore, the previous section on model limitations leads directly into an idea for future work. It is hoped that as the body of work, both geological and modelling, on the various parameters grows in the future, with the possibility that oft neglected periods of time are investigated, GEOCARBSULF can be periodically revisited and updated. The aim would be to change the broad nature of pre-Neoproterozoic O_2 results into a high-resolution version. To that end, there is also the possibility that in the future more may be known about any relationship between sulphur isotope fractionation and O_2 , and

thus the isotope mass balance approach for the sulphur cycle can be reimplemented, though this may be addressed by using both $\delta^{34}\text{S}_{\text{pyr}}$ and $\delta^{34}\text{S}_{\text{sulf}}$ records (see section 6.2.2.).

6.2.2. *Isotopes and isotopic fractionation in GEOCARBSULF*

Carbon and sulfur isotopes and the extent of their fractionation have played a central part throughout this thesis, but the focus has predominately been on the $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{34}\text{S}_{\text{sulf}}$ records rather than the $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{34}\text{S}_{\text{pyr}}$. Yet, these records may be of use in GEOCARBSULF and its derivatives, either as a model driver, or as another geological archive that model results could be compared against.

Carbon

The final version of GEOCARBSULF by Berner (2009) employed the use of an O_2 -dependent equation to calculate the isotopic fractionation of carbon, whereas earlier versions of the model (e.g. Berner, 2006a) used the data of Hayes *et al.* (1999). The equation was based on laboratory work, where two types of vascular plants, and one algal species, were grown under a variety of conditions in order to determine the effect of O_2 and CO_2 concentrations on isotopic fractionation (Berner *et al.*, 2000). The equation uses the parameter, J , to fit a curve to the laboratory data, where $J = 2.5$ (Berner *et al.*, 2000) or $J = 3$ (Berner, 2001). Following further work involving both plant growth experiments and the extraction of C isotopes from Late Paleozoic – Mesozoic plant fossils, J was revised to $J = 4$ and this value has been used throughout this thesis (Beerling *et al.*, 2002; Berner, 2009). However, this J value may not accurately represent $\delta^{13}\text{C}$ fractionation generated by Precambrian photosynthesisers,

thus future work should include a range of J values in Monte Carlo model simulations, as although varying this parameter has minimal effect on O_2 predictions for the mid-Paleozoic (see Fig. 3.6), this may not be true for the Precambrian.

Additionally, there is an assumption in Chapters 4 and 5 that δ_{in} – the combined isotopic composition of mantle and riverine derived carbon entering the ocean-atmosphere reservoir – has remained static at -5‰ (Holser *et al.*, 1988). This value may change over time, particularly on shorter timescales when a greater proportion of inorganic versus organic carbon weathering (or vice versa) may take place (Krissansen-Totton, Buick and Catling, 2015), but is difficult to derive in the Precambrian without the detailed reconstructions of paleo sedimentary area by the likes of Bluth and Kump (1991). Nevertheless, a range of values could be used in the Monte Carlo simulation, to create a wider window of uncertainty with the model results.

Also, the $\delta^{13}C$ fractionation generated by the equation used throughout this work could be an explicit model output and compared to the fractionation implied by a statistical analysis of $\delta^{13}C$ data (Krissansen-Totton, Buick and Catling, 2015), to test whether the equation captures the general trend of changes in $\delta^{13}C$ fractionation through time, and as it is also possible for the model to generate a predicted $\delta^{13}C_{org}$ record, this too could be compared to geologic data.

Regardless of whether the $\delta^{13}C$ fractionation equation provides results which are in reasonable agreement with the geologic data or not, the paired records of $\delta^{13}C_{org}$ and

$\delta^{13}\text{C}_{\text{carb}}$ could instead be used in the model to perhaps more accurately derive the fraction of carbon buried in the organic form (f_{org}), as per equation (6.1):

$$f_{\text{org}} = \frac{\delta^{13}\text{C}_{\text{in}} - \delta^{13}\text{C}_{\text{carb}}}{\delta^{13}\text{C}_{\text{org}} - \delta^{13}\text{C}_{\text{carb}}} \quad (6.1)$$

Simple carbon cycle modelling by Kump and Arthur (1999) has shown that $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{13}\text{C}_{\text{carb}}$ can exhibit different responses and response times to various system perturbations (e.g. increased riverine phosphorus delivery to the oceans, or changes to CO_2 concentrations), which may not be entirely encapsulated by the O_2 -dependent fractionation equation, particularly during times of rapid and large changes to the carbon cycle, such as the Paleocene-Eocene Thermal Maximum. The paired data records would reflect changes to the Earth system, without requiring any assumptions with regards to the relative contributions of the various changes to the value of $\delta^{13}\text{C}$ fractionation through time.

It is difficult to predict what overall effect using the paired $\delta^{13}\text{C}$ records might have on atmospheric O_2 concentrations. During periods of reduced $\delta^{13}\text{C}$ fractionation (i.e. when $\delta^{13}\text{C}_{\text{org}} - \delta^{13}\text{C}_{\text{carb}}$ in equation (6.1) trends towards more positive values) f_{org} also increases. If the total amount of carbon buried remained constant, then an increase in f_{org} would result rather simply in an increase in C_{org} burial (Kump and Arthur, 1999), however, the actual C_{org} burial flux is also dependent on the total carbon throughput, which in Chapters 4 and 5 is not isotope dependent, and is variable. Furthermore, although burial fluxes seem to have a greater control over O_2 levels in the Phanerozoic (S. Zhang *et al.*, 2018), the sink fluxes also help to regulate atmospheric O_2 thus the

model needs to be run, and outputs assessed in order to fully disentangle the effect(s) including both $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{13}\text{C}_{\text{carb}}$ records would have on GEOCARBSULF.

One final alternative would be to follow the lead of Kump and Arthur (1999) and use an expression which describes the relationship between CO_2 levels and marine phosphate concentrations with $\delta^{13}\text{C}$ fractionation. Using this approach would assume that the CO_2 record generated by GEOCARBSULF is reasonable, and would require experimentation with phosphate concentrations as this (and bioavailable P in particular) will have changed through time (e.g. Poulton, 2017), but may provide some valuable insights regardless.

Sulphur

There was a test conducted (see section 3.6.1.) to see if using the paired $\delta^{34}\text{S}_{\text{pyr}}$ and $\delta^{34}\text{S}_{\text{sulf}}$ records, instead of the O_2 -dependent equation for $\delta^{34}\text{S}$ fractionation in the original GEOCARBSULF model, would produce low O_2 in the early Paleozoic. However, using the $\delta^{34}\text{S}_{\text{sulf}}$ data from Berner (2006a) and the $\delta^{34}\text{S}$ fractionation data of Wu *et al.* (2010) produces very high O_2 (~35% atm) in the early Paleozoic and negative (or barely above 0% atm depending on model initialisation conditions) O_2 in the Mesozoic. While using both the $\delta^{34}\text{S}_{\text{sulf}}$ data and the $\delta^{34}\text{S}$ fractionation data of Wu *et al.* (2010) produces O_2 levels that are not so egregiously high (due to lower $\delta^{34}\text{S}_{\text{sulf}}$ values), they remain above the threshold dictated by widespread ocean anoxia (~10.4% atm) in the early Paleozoic; the Mesozoic drop to near 0% atm remains.

It is likely that the high O_2 in the early Paleozoic is a result of low $\delta^{34}S$ fractionation (<30‰ prior to 510 Ma), which would lead to significant pyrite burial (see Fig. 3.2), while very low O_2 in the Mesozoic is due to near-modern $\delta^{34}S$ fractionation (~40‰ compared to ~46‰) and therefore a reduction in pyrite burial, at a time when the contribution to O_2 levels from the carbon cycle is also in decline (Berner, 2009; Wu *et al.*, 2010; Saltzman and Thomas, 2012). It is possible that the problem with the sulfur cycle's contributions to O_2 levels in the original GEOCARBSULF model lie, not only with the O_2 -dependent $\delta^{34}S$ fractionation equation, but also with the constraints put upon the sulfur cycle by having the oceanic sulphate reservoir in steady state, and the ancient gypsum and pyrite reservoirs as constant in size through time.

A prudent first step for future work would be to follow the approach used in Chapters 4 and 5 for C_{org} burial, and calculate pyrite burial by multiplying f_{pyr} – the fraction of sulfur leaving the ocean as pyrite – which uses the $\delta^{34}S_{pyr}$ and $\delta^{34}S_{sulf}$ records (see equation 3.65) by the total throughput of sulfur. This could reduce any undue controls the constant ancient reservoir sizes may have on the isotopic composition of these reservoirs, which then go on to affect the size of the pyrite burial flux (see equation 2.49). If this change helps GEOCARBSULF to predict atmospheric O_2 levels which are in good agreement with geochemical proxies, then this version of the model, using the $\delta^{34}S_{pyr}$ and $\delta^{34}S_{sulf}$ records instead of the forwards modelling of the sulfur cycle in GEOCARBSULFOR, could be used to investigate the Precambrian.

For the Neoproterozoic, multiple sulfur isotope data have shown that in the aftermath of the Marinoan the oceanic sulfate reservoir was not in steady state, and was heavily

depleted due to an increase in pyrite burial (Sansjofre *et al.*, 2016). This idea of a non-steady state may help to explain the f_{pyr} ratios >1 that are thought to have occurred throughout the Proterozoic (Canfield and Farquhar, 2009), which are only attainable, following equation (3.65), if $\delta^{34}\text{S}_{\text{pyr}}$ is: a positive value; greater than the isotopic composition of the mantle; but lower than $\delta^{34}\text{S}_{\text{sulf}}$. Therefore, it is also important to change the gypsum burial equation from the steady state approach employed in the original GEOCARBSULF (equation 2.50), to the non-steady state version in GEOCARBSULFOR (equation 3.6), otherwise the model may not be able to reproduce the drawdown in oceanic sulfate during the Neoproterozoic, as suggested by the isotopes (Sansjofre *et al.*, 2016).

6.2.3. Non-steady state carbon cycle dynamics in GEOCARBSULF

Another avenue of future research involving the GEOCARBSULF model would be to investigate non-steady state mechanisms in the carbon cycle. This idea has been explored to a certain extent in Chapters 4 and 5, as the total carbon throughput to the ocean-atmosphere reservoir in the model now increases through time, thus the canonical view (see e.g. Bachan and Kump (2015) for a description of this) that large positive $\delta^{13}\text{C}$ excursions directly correspond to huge increases in the amount of C_{org} being buried (and hence an increase in O_2 production) does not hold absolutely true. However, if one were to instead assume that there is mass conservation of carbon in the system, as per the original GEOCARBSULF, other dynamics could be explored.

Bachan and Kump (2015) investigated the idea that the oxidation of a large reservoir of siderite provided the ocean-atmosphere reservoir with enough dissolved inorganic

carbon (DIC) to fuel large amounts of C_{org} production (and subsequent burial) as implied by the extremely positive $\delta^{13}C$ excursion ($>8\text{‰}$) during the Lomagundi Event. As O_2 levels rose above the threshold required for the oxidation of siderite, this led to an influx of DIC to the ocean-atmosphere, more C_{org} burial, more O_2 production and consequently more siderite oxidation in a positive feedback loop (Bachan and Kump, 2015). However, the higher levels of O_2 in the atmosphere would have also oxidised terrestrial sulfides and iron silicates, eventually leading to iron being drawn down in forms (e.g. pyrite) other than siderite, and thus the siderite reservoir would ultimately become exhausted (Bachan and Kump, 2015).

It would be interesting to see what effect an extra, mass-limited, reservoir of carbonate would have on O_2 levels in GEOCARBSULF for the Lomagundi Event and other periods of positive $\delta^{13}C$ excursions, such as in the early Neoproterozoic (Saltzman and Thomas, 2012). In the interim, as a simple thought experiment: the average $\delta^{13}C$ signature of Archean and Proterozoic siderite deposits is -0.9‰ , roughly 4‰ greater than the average mantle input (Holser *et al.*, 1988; Bachan and Kump, 2015). Assuming that $\delta^{13}C_{carb} = 10\text{‰}$, the $\delta^{13}C$ fractionation ranges between -25 to -29‰ ($\pm 2\text{‰}$ from the present day average (Berner, 2009)), and that the total carbon throughput $= 2.5 \times 10^{19}$, the organic carbon burial flux can be calculated for a range of $\delta^{13}C_{in}$ values, from an average mantle isotopic composition (-5‰), to an average siderite isotopic composition (-0.9‰), or higher. As can be seen in figure 6.1, the amount of C_{org} burial that might take place is very dependent on the isotopic composition of the carbon inputs to the ocean-atmosphere, and a switch from average mantle to average siderite isotopic composition, using the experimental values mentioned above, can result in almost a 30% decrease in the burial flux. Figure 6.1

also shows that the burial flux is also highly dependent on the $\delta^{13}\text{C}$ fractionation, thus it is worth exploring this further in the GEOCARBSULF framework, using both the paired $\delta^{13}\text{C}$ carbonate and organic records, as well as using the O_2 -dependent fractionation equation.

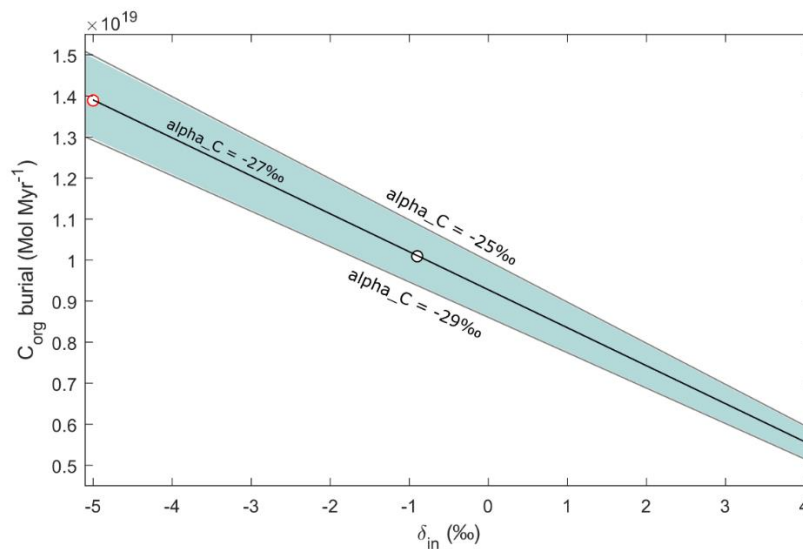


Figure 6.1 | Organic carbon burial as a function of changing the isotopic composition of inputs to the ocean-atmosphere.

The black line represents a $\delta^{13}\text{C}$ fractionation of -27‰ with the blue banded region representing $\delta^{13}\text{C}$ fractionation that is $\pm 2\text{‰}$ from this value. The red circle highlights the amount of C_{org} burial that might take place when $\delta_{\text{in}} = -5\text{‰}$, whereas the black dot represents C_{org} burial when $\delta_{\text{in}} = -0.9\text{‰}$.

As well as non-steady state dynamics with regards to the inorganic side of the carbon cycle, there were likely periods during Earth history – the Shuram-Wonoka anomaly for example – when the C_{org} part of the cycle was in non-steady state (Rothman *et al.*, 2003). The large oscillations in $\delta^{13}\text{C}_{\text{carb}}$ values in the Neoproterozoic (Saltzman and Thomas, 2012) are proposed to be as a result of a large reservoir of dissolved organic carbon (DOC) which equilibrates slowly compared to any changes to its input and

output fluxes, thus leading to similarly slow variations in the $\delta^{13}\text{C}_{\text{org}}$ record, compared to more rapid and substantial variations in the $\delta^{13}\text{C}_{\text{carb}}$ record (Rothman *et al.*, 2003).

This approach could potentially be incorporated into GEOCARBSULF. Using figure 6.2 as a guide to this approach, instead of calculating the outputs δ_1 and δ_2 from reservoirs 1 and 2 (DIC and DOC respectively), the $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ records could replace δ_1 and δ_2 to instead be used as inputs to reservoirs 1 and 2. This could help to back calculate what the original isotopic composition of these reservoirs, with differing residence times, might have been at each time step. The newly calculated original isotopic composition of the DIC and DOC reservoirs could then be used as new records for calculating f_{org} through time.

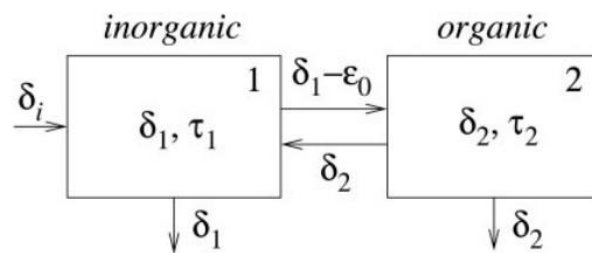


Figure 6.2 | A simple carbon cycle model with DIC and DOC reservoirs.

The inorganic reservoir has inputs from volcanism/weathering and remineralisation of organic carbon, and outputs due to photosynthesis and carbonate burial, with different isotopic signatures. The organic reservoir receives carbon via photosynthesis and has outputs due to organic carbon burial and remineralisation. Each reservoir has a different residence time for carbon. Taken from Rothman et al. (2003).

6.2.4. *GEOCARBSULF's ocean-atmosphere reservoir*

Finally, one last update to the GEOCARBSULF model could be a splitting of the ocean-atmosphere reservoir into two distinct boxes, with the possibility of further splitting the ocean box into sub-reservoirs (representing, for example, the deep ocean, open surficial seawater etc.). This may help to identify any global ocean oxygenation events (e.g. Sahoo *et al.*, 2016), or transient pulses of oxygenation (e.g. Anbar *et al.*, 2007; Olson, Kump and Kasting, 2013), but will at least allow a better comparison with most geochemical proxies, which are often marine in nature.

6.2.5. *Ozone levels in the Neoproterozoic-Paleozoic*

The oxygen output from NEOCARBSULF could be input into a more complex model, such as the NCAR Community Earth System Model (Danabasoglu *et al.*, 2020) or the 1D Atmos model (e.g. Zahnle, Claire and Catling, 2006), to predict what ozone levels might have been like at different points during the Neoproterozoic. Results from NEOCARBSULF suggest that oxygen levels exceeded the minimum levels required by Cambrian-like metazoans (10% PAL) as early as 875 million years ago and were as high as 60% PAL around 750 million years ago. However, it appears that animals of appreciable size did not evolve until later (Knoll and Nowak, 2017), and therefore it is possible that factors other than oxygen levels stalled the evolution of animals. A hypothesis that could be tested is whether the geologically rapid shifts in oxygen levels during the Neoproterozoic, and particularly low levels (<1% PAL) towards the end of and immediately after the Marinoan glaciation (~640 to ~620 Ma) slowed the build-up, or entirely reduced, ozone levels in the atmosphere. Low oxygen and ozone levels would have allowed significant amounts of UV radiation, which is damaging to DNA,

to continue to reach the Earth's surface. Recent work has shown there to be a considerable difference in the amount of UV shielding with oxygen concentrations of 1% PAL compared to 0.1% PAL (Arney et al., 2016). Although water can attenuate UV radiation, it is still transparent to UV rays to a certain depth, dependent on a variety of environmental factors (Häder et al., 2011). Consequently, high UV fluxes to the Earth's surface may have rendered shallow marine environments inhospitable and disrupted photosynthetic organisms and the biogeochemical cycling of nutrients, as well as preventing the colonisation of the land by plants.

6.3. Final remarks

This thesis provides a modelled reconstruction of the evolution of atmospheric oxygen for the last 3400 Myrs of Earth history and investigates some of the links between it and the evolution of life. Although it has not been explored earlier in this thesis, the findings do lead to some thoughts regarding the search for other habitable planets. Oxygenic photosynthesis may have evolved by 3 Ga, however, O₂ levels detectable by spectroscopic techniques may not have arisen until more than a billion years later. Thus, non-complex life may be abundant in the Universe but is difficult to detect, and/or oxygen on its own is not an ideal gas for investigating biosignatures.

However, in the search for *complex* life elsewhere in the Universe, this work does provide some possible constraints: if the evolution of land plants did lead to the generation of modern-like O₂ levels, paving the way for the appearance of terrestrial fauna, it required over 4 Gyrs for the land plants to materialise. This, then, may rule out relatively young planets and, if it was specifically terrestrial plants, rather than marine photosynthesisers or some other process (e.g. internal feedbacks in long-term

geochemical cycles: Alcott, Mills and Poulton, 2019), we may be able to eliminate ‘waterworlds’ from our search parameters, when it comes to looking for extra-terrestrial macroscopic life

7. References

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