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Invited review

# COPSE reloaded: An improved model of biogeochemical cycling over Phanerozoic time

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ABSTRACT

The 'COPSE' (Carbon, Oxygen, Phosphorus, Sulphur and Evolution) biogeochemical model predicts the coupled histories and controls on atmospheric $O_2$, $CO_2$ and ocean composition over Phanerozoic time. The forwards modelling approach utilized in COPSE makes it a useful tool for testing mechanistic hypotheses against geochemical data and it has been extended and altered a number of times since being published in 2004. Here we undertake a wholesale revision of the model, incorporating: (1) elaboration and updating of the external forcing factors; (2) improved representation of existing processes, including plant effects on weathering and ocean anoxia; (3) inclusion of additional processes and tracers, including seafloor weathering, volcanic rock weathering and $^{87}Sr/^{86}Sr$; (4) updating of the present-day baseline fluxes; and (5) a more efficient and robust numerical scheme. A key aim is to explore how sensitive predictions of atmospheric $CO_2$, $O_2$ and ocean composition are to model updates and ongoing uncertainties. The revised model reasonably captures the long-term trends in Phanerozoic geochemical proxies for atmospheric $pCO_2$, $pO_2$, ocean $[SO_4]$, carbonate $\delta^{13}C$, sulphate $\delta^{34}S$ and carbonate $^{87}Sr/^{86}Sr$. It predicts a two-phase drawdown of atmospheric $CO_2$ with the rise of land plants and associated cooling phases in the Late Ordovician and Devonian-early Carboniferous, followed by broad peaks of atmospheric $CO_2$ and temperature in the Triassic and mid-Cretaceous – although some of the structure in the $CO_2$ proxy record is missed. The model robustly predicts a mid-Paleozoic oxygenation event due to the earliest land plants, with $O_2$ rising from ~5% to > 17% of the atmosphere and oxygenating the ocean. Thereafter, atmospheric $O_2$ is effectively regulated with remaining fluctuations being a Carboniferous–Permian $O_2$ peak ~26% linked to burial of terrestrial organic matter in coal swamps, a Triassic–Jurassic $O_2$ minimum ~21% linked to low uplift, a Cretaceous $O_2$ peak ~26% linked to high degassing and weathering fluxes, and a Cenozoic $O_2$ decline.

## 1. Introduction

How the composition of the atmosphere and the global biogeochemical cycling of major elements have changed over geologic time is a subject of broad inter-disciplinary interest. In particular atmospheric $CO_2$ and $O_2$ are 'master variables' of the Earth system that have been affected by both geological drivers and biological evolution (Lenton and Watson, 2011). Variations in atmospheric $CO_2$ are in turn a key contributor to long-term climate regulation (Walker et al., 1981), and variations in atmospheric $O_2$ have been linked to the evolution of aerobic life forms (Sperling et al., 2015a). The Phanerozoic is the best studied Eon with the most data. Yet despite numerous proxies to reconstruct past atmospheric $CO_2$ levels there are still lingering disagreements among those proxies and important gaps in the record especially before ~420 Ma (Royer, 2014). For past atmospheric $O_2$ levels there are only indirect constraints during parts of the Phanerozoic (Bergman et al., 2004). The best established constraint on $O_2$ is a lower limit of 15–17% from combustion experiments combined with the near continuous presence of fossil charcoal over the past ~420 Myr (Belcher and McElwain, 2008; Glasspool et al., 2004; Scott and Glaspool, 2006). A more uncertain upper limit on $O_2$ of 25–35% has been inferred from the sensitivity of fire frequency to increasing $O_2$ and the continuous presence of forests over the past ~370 Myr (Glasspool and Scott, 2010; Lenton and Watson, 2000b).

The limitations of the proxy record mean that models, combined with data, have a key role to play in trying to reconstruct past variations in atmospheric $CO_2$ and $O_2$. However, model predictions should not be confused with reality. In particular, inferences about the supposed

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effects of predicted variations in atmospheric $O_2$ on animal evolution (Berner et al., 2007; Falkowski et al., 2005; Graham et al., 1995; Graham et al., 2016) should be treated with caution, given that there are already several quite different model predictions of Phanerozoic $O_2$ variations (Mills et al., 2016). Before making such inferential leaps, the focus should be on which (if any) of the features in past $O_2$ (and $CO_2$) reconstructions are robust to model and data uncertainty.

The aim of this paper is therefore to try to better understand, mechanistically and quantitatively, the controls on atmospheric $CO_2$ and $O_2$ over Phanerozoic time, and to assess how sensitive predictions of these variables are to factors we are scientifically uncertain about. To undertake such an exercise we need to be clear about our scientific method and specifically the role we want a model to play in gaining knowledge (our epistemology). Hence we start by briefly reviewing existing approaches to modelling Phanerozoic biogeochemical cycling.

### *1.1. Review of existing modelling approaches*

All models of biogeochemical cycling over Phanerozoic timescales typically have some representation of sedimentary reservoirs (e.g. of carbon and sulphur in reduced and oxidised forms) coupled to much smaller ocean-atmosphere reservoirs (e.g. of carbon, oxygen and sulphate). However, there are two very different ways in which the models are used to try and gain knowledge; the inverse (data-driven) and forwards modelling approaches (Fig. 1).

Most previous studies following Garrels and Lerman (1981, 1984), and including the GEOCARB family of models (Berner, 1991, 1994, 2006a; Berner and Kothavala, 2001), have taken the inverse (data-driven) modelling approach (Fig. 1a). Whilst some models are driven by rock abundance data (Berner and Canfield, 1989), most are driven by isotopic data, notably the $\delta^{13}C$ and $\delta^{34}S$ records and a set of associated assumptions about how they are related to key processes (burial of organic carbon and pyrite sulphur, respectively). This leaves the only remaining data to test the model against as the uncertain proxies for $CO_2$ (Royer, 2014), and the even sparser and more uncertain constraints on $O_2$. Furthermore it is unclear how strongly reconstructing $CO_2$ constrains past $O_2$ variations (or vice versa). Such isotope-driven models are sensitive to the chosen $\delta^{13}C$ and $\delta^{34}S$ input data, particularly in their predictions of atmospheric $O_2$ (Mills et al., 2016), yet these isotope records are imperfectly known with considerable regional variations superimposed on an underlying global signal. Isotope-driven model predictions, particularly of $O_2$, are also sensitive to assumptions made about the carbon and sulphur isotope mass balances, to the extent that they are unable to produce plausible reconstructions of atmospheric $O_2$ without assuming sensitivity of C and S isotope fractionation to $O_2$, which provides stabilising negative feedback (Berner et al., 2000; Lasaga, 1989). Isotope-driven models have also typically had to assume 'rapid recycling' of deposited sediments, whereby sedimentary rock reservoirs are divided into 'young' (rapidly recycled) and 'old' components – with the young sedimentary reservoirs assumed to be comparable in size to the ocean-atmosphere reservoirs of C and S, and the old reservoirs typically assumed to be much larger and constant in size.

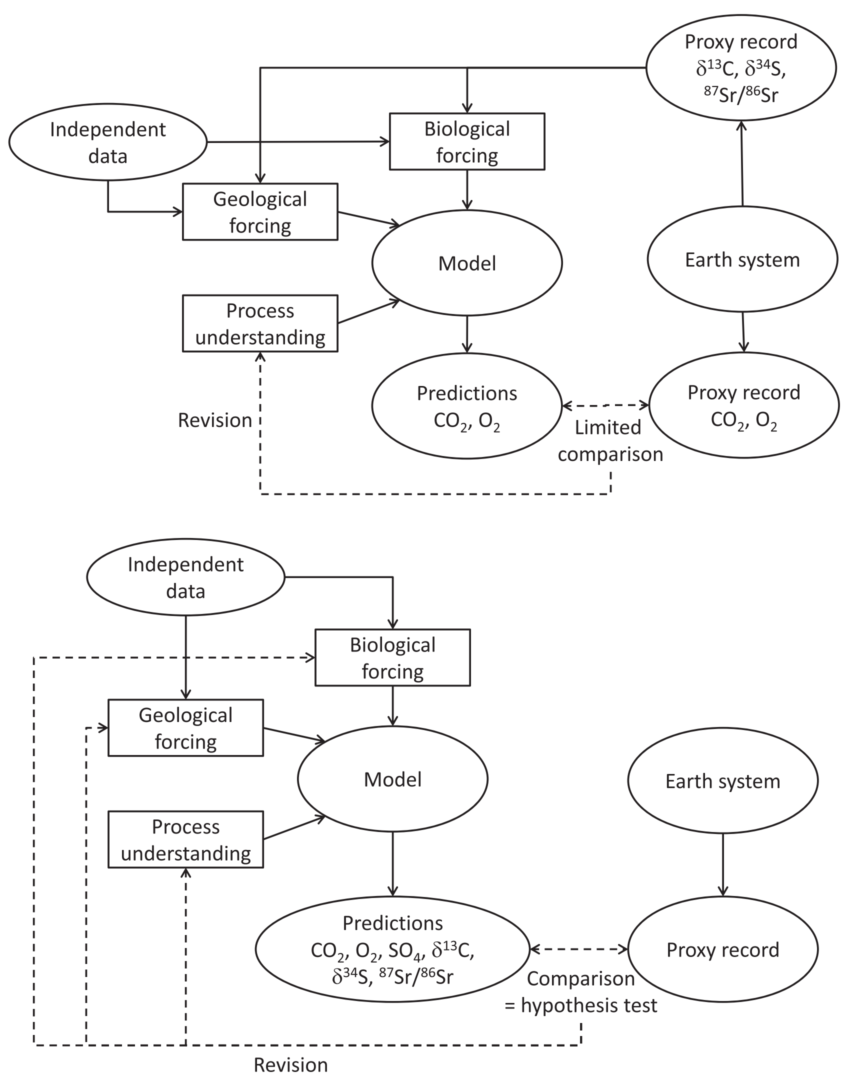


**Fig. 1.** Different approaches to modelling Phanerozoic biogeochemical cycling: (a) inverse modelling approach (b) forwards modelling approach (pursued herein).