Review

THE ROYAL SOCIETY
PUBLISHING

On the use of models in understanding the rise of complex life

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Recently, several seemingly irreconcilably different models have been proposed for relationships between Earth system processes and the rise of complex life. These models provide very different scenarios of Proterozoic atmospheric oxygen and ocean nutrient levels, whether they constrained complex life, and of how the rise of complex life affected biogeochemical conditions. For non-modellers, it can be hard to evaluate which—if any—of the models and their results have more credence—hence this article. I briefly review relevant hypotheses, how models are being used to incarnate and sometimes test those hypotheses, and key principles of biogeochemical cycling models should embody. Then I critically review the use of biogeochemical models in: inferring key variables from proxies; reconstructing ancient biogeochemical cycling; and examining how complex life affected biogeochemical cycling. Problems are found in published model results purporting to demonstrate long-term stable states of very low Proterozoic atmospheric pO_2 and ocean P levels. I explain what they stem from and highlight key empirical uncertainties that need to be resolved. Then I suggest how models and data can be better combined to advance our scientific understanding of the relationship between Earth system processes and the rise of complex life.

1. Introduction

As complex and self-aware organisms, some of us are fascinated by the origin and rise of complex life—because it is a key part of our origins. As well as establishing when those origins were, and in what order things evolved, as scientists we are drawn to questions of causality: were those origins determined by intrinsic controls on biological evolution, by abiotic factors or by a more complex interplay between living and non-living parts of the Earth system? How did the rise of complex life in turn alter the Earth system? And how can we gain knowledge about any causal relationships, given the hundreds of millions of years that have passed since?

At the Discussion meeting behind this Theme Issue, Jochen Brocks asked: What is the role of models in understanding the rise of complex life? And how should non-modellers view their results? This review is an attempt to answer those queries. For non-modellers, models can be 'black boxes' playing an opaque role in gaining scientific knowledge. This can insulate models and modellers from critical scrutiny. Hence, this paper aims to expose and explore the ways in which models are being used to address the relationships between biogeochemical processes and the rise of complex life.

The broad time correlation between the rise of complex life and huge changes in the Earth system—including the carbon cycle and climate—during the Neoproterozoic Era has led many researchers to assume there is a causal connection between them. However, there are currently very different perspectives on the direction(s) of causality. One perspective argues that environmental constraints held back the evolution [1]—or rise to ecological prominence [2]—of complex life. An opposing perspective argues that complex life evolved and then it altered ecological and environmental conditions [3]. A coevolutionary feedback perspective combines elements of these two positions, arguing that complex life transformed ecology and biogeochemical cycling, feeding back into its subsequent evolution [4]. Other important perspectives recognize the challenging

evolutionary–developmental aspects of animal origins [5], and consider how unusual environmental–conditions may have triggered (rather than suppressed) their origin [6].

Modelling has been used to varying degrees to represent and sometimes to test different hypotheses for the relationship between complex life and Earth system processes. Predominantly, this has been biogeochemical modelling. Modelling of the ecological changes associated with the rise of complex life is less common. Modelling the physiology of early complex life is even rarer, and modelling the evolutionary dynamics of the rise of complex life has only been attempted in the generic spirit of evolutionary theory. Hence, this review focuses predominantly on biogeochemical modelling—but the forward look considers other approaches.

First, I briefly review relevant hypotheses concerning the relationships between the rise of complex life and Earth system processes, the different roles that models can play in understanding deep time and the key biogeochemical principles models should embody. Then I critically review published model approaches to inferring key environmental conditions from proxies; understanding Proterozoic biogeochemical cycling; and modelling how complex life altered biogeochemical conditions. I consider what all the current biogeochemical models may be missing. Then I suggest ways forward for modelling to help improve our understanding of the rise of complex life.

2. Relevant hypotheses

Complex life means more here than just animals (Metazoa). Currently, there is much interest in whether the late rise of algae to ecological prominence, detected in the biomarker record in the Cryogenian Period, was due to chronically limiting nutrient levels beforehand [7]. More prominently, it has long been argued [8] that a lack of oxygen held back the evolution—or at least the radiation—of animal life. Recently, it became apparent that oxygen levels would have to have been very low to have constrained the evolution or ecological expansion of sponges (the basal animals) [9] and several other (subsequently evolved) types of animal life [2]. One response to this has been to argue that Proterozoic atmospheric oxygen levels were in fact much lower than previously thought [1]. Another response has been to argue that oxygen constrained particular eco-physiological traits of animal life, if not its origin [10]. Yet another response has been to reject the role of oxygen as a constraint altogether [3]. Other candidate environmental constraints have occasionally been considered; for example, too much toxic hydrogen sulfide suppressing eukaryotes [11].

A different view is that the evolution of complex life was just intrinsically difficult and slow and its timing had nothing to do with environmental conditions or constraints. However, given that natural selection occurs, and given evidence of changes in environmental variables known to affect the physiology and ecology of animals, it seems odd to rule out some role for the environment in the evolution of complex life—even if the pertinent 'environment' is a localized and ecological context selecting some traits over others. Furthermore, highly differentiated animals with apoptosis (programmed cell death) pose their own evolutionary puzzle, as they represent a major evolutionary transition to a new level of selection [12]. Explaining such transitions remains a major subject of evolutionary enquiry. It generally needs special conditions in which between-group variation and selection outweighs within-group variation and selection [13]. One hypothesis is that extreme environmental conditions—in particular the 'snowball Earth' events—could have altered the selective environment in a way that favoured animal evolution [6].

Once they had evolved, complex life forms could affect ecology and biogeochemical cycling [3,4,14–16]. Several hypotheses have been proposed: by grazing on the smallest (cyanobacterial) phytoplankton cells, the first predatory protists (using phagocytosis) could have created a niche for larger (algal) phytoplankton cells, which in turn created a niche for larger predators, and so on—thus starting to create a size-structured community [16]. The advent of larger phytoplankton cells could have increased the efficiency of the biological pump (sinking of organic matter through the water column) [4]. The evolution of filter-feeding sponges, which filter out the smallest phytoplankton cells, could also have selected for larger (eukaryotic) algae and strengthened the biological pump [4]. When planktonic animals with through-guts and faecal pellets evolved, this could have further added to the efficiency of the biological pump [14]. Sessile benthic animals including sponges and 'rangeomorph' fronds could have concentrated resources where they were located on the sediments [17]. When mobile, burrowing, bioturbating animals evolved, they could have oxygenated the upper sediments, altering the cycling of phosphorus, carbon and sulfur and ultimately the oxygen content of the atmosphere [18,19].

3. Uses of models

Models are currently being used in several ways to probe potential causal relationships between Earth system processes and the rise of complex life. Biogeochemical models, in particular, are being used: to interpret proxy data; to explore how the ancient world could have worked; and to try to establish how it did work by testing hypotheses against data. There are two principal scientific targets for this modelling: to establish Proterozoic biogeochemical conditions and to quantify the potential effects of complex life on those conditions.

3.1. General considerations

A model should be as simple as possible but not too simple, following Einstein's advice. Hence, users of model results should always look critically at whether the underlying model is too simple or unnecessarily complex to address the question at hand. All models must obey some basic principles of consistency with well-established constraints—such as conservation of matter. In our focal context, a model may need to capture some of the spatial heterogeneity of biogeochemical conditions—but no more than necessary to accurately capture key process controls. Models should also be grounded in sound process representations, ideally ones that have empirical support, which, in this context, usually means from studies of contemporary or more recent Earth system processes. If a model contains ad hoc process representations, or representations that are clearly at odds with current scientific understanding, then its results should be questioned. We should ask how those results are sensitive to changing the process representations that we have doubts about. (This means performing a 'structural' sensitivity analysis where functional forms are varied, not just a more typical parameter sensitivity analysis where only parameter values are varied.) If the

modellers do not provide an answer, we should suspend judgement on whether their model is telling us anything meaningful or useful about the ancient world.

3.2. Inferring key variables from proxies
In almost all deep time cases, a model is necessary to convert a proxy measurement into an Earth system property (environmental parameter) of interest. For hypotheses surrounding the rise of complex life, key Earth system properties that we would like to know include: the oxygen content of the atmosphere, the redox state of the ocean, the levels of limiting nutrients in the ocean and the productivity of the biosphere. Sometimes, the role of models in proxy interpretation is well hidden—the presence of a model may not be mentioned at all—but there is always some model involved (however simple) whenever we are dealing with a 'proxy'—i.e. we do not have a direct measurement of our variable of interest. Sometimes, the absence of some proxy is used, via a model, to infer a constraint on a variable of interest—adding the familiar complication that 'absence of evidence is not evidence of absence'.

3.3. Exploring how the world could have worked
Models are also used, more ambitiously, to help us think in a qualitatively and quantitatively consistent way about how the world *could* work—in this case, how the Earth system and its relationship with complex life could work. The 'Earth system' modelling challenge here is generally greater than the interpretation of proxy data, because it demands making an internally consistent model of the whole world, or at least pertinent aspects of it. The exercise can be insightful, in particular in limiting what may otherwise seem like a very large 'possibility space', because the act of building an internally consistent model usually significantly limits the range of behaviours and results it can exhibit. Making the model obey well-established constraints—such as closure of biogeochemical cycles and conservation of Earth's surface redox balance—can be critical in this (and in the next section, I outline some of these key principles). Nevertheless, exploring how the ancient world *could* have worked is not the same as establishing how it *did* work.

3.4. Testing hypotheses to establish how the world did work
To help to establish how the ancient world actually *did* work, we need to be able to test and falsify hypotheses for causal relationships. That means we need to use data from the time(s) in question to test our models against. Thus, we need to combine models of how the Earth could have worked with proxy data. This means modelling the link between variables of interest and available proxies, as well as modelling the controls on the variables of interest. Here, the role of the model is to incarnate (represent) mechanistic hypotheses, and make quantitative predictions from those hypotheses of variables that are detectable in the geologic record. Those 'testbed' data need to be independent from any data that are used to drive the model (to avoid circular reasoning), and for the comparison of model with data to be possible, the model has to predict observable proxy variable(s). There are numerous caveats here, not least that there are always a multitude of wrong models that can

successfully fit any given data. However, if the model cannot fit the data it pertains to predict, and we think the data are reliable, then, clearly, there is something wrong with the model and it can be said to be *falsified* (at least in some part). Increasing the number of independent data targets that we try to get the model to predict generally increases the chances of falsifying the model (lowers the success rate). However, here we must be wary of modellers making a model more complex as that just increases the potential field of successful but wrong models.

4. Key principles of biogeochemical cycling
To help readers evaluate models of Proterozoic conditions, and the potential effects of complex life on those conditions, it is important to review some basic principles of biogeochemical cycling.

4.1. Time-scale separation and material balances
Different key Earth system variables have different natural time scales (figure 1), and those time scales are separated in a way that can help us to understand Earth system functioning and simplify our modelling. For material variables like the oxygen content of the atmosphere–ocean or the phosphorus content of the ocean, it is standard to define a mean residence time for an atom or molecule in the reservoir—that is, the size of the reservoir divided by its input/output flux [20]. Response time scales in the presence of feedback can also be defined [20]. Over time scales comparable to or longer than the residence time, the inputs to and outputs from the reservoir must be in close balance, otherwise the constituent would build up indefinitely or disappear [20]. The time scale(s) we are interested in determine what processes we need to include in our models. Things that change much slower than our time scale(s) of interest can be treated as approximately constant (and excluded from our model). Things that change much faster than our time scale(s) of interest can be assumed to be close to 'steady state'—i.e. with inputs and outputs in balance (which does not mean they are constant). However, we must consider the processes setting that steady state and whether and how they (and the resulting steady state) change with the slower variables.

The origin and rise of complex life played out over hundreds of millions of years, after a preceding Proterozoic state that persisted for a billion years. Over these time scales, there could have been significant material exchanges between the crust and the mantle [21], which most models neglect, as well as approximately 500 Myr supercontinent (Wilson) cycles. Crucially, models must include the exchange of matter (including electrons/redox equivalents) with sedimentary rock reservoirs that are recycled by plate tectonics over approximately 100 Myr time scales. As Garrels and colleagues first showed in the 1970s, enforcing the conservation of key elements and electrons across sedimentary reservoirs and the ocean–atmosphere system provides a powerful constraint on models, enabling reconstruction of key variables such as CO_2 and O_2 consistent with major (C, S) isotope records [22–24].

The surface, fluid aspects of the Earth system—the oceans and atmosphere (including the biosphere) and different reservoirs of matter within them—generally have shorter time scales than sedimentary rocks. Today, sulfate in the ocean has a residence time of approximately 12 Myr, oxygen in
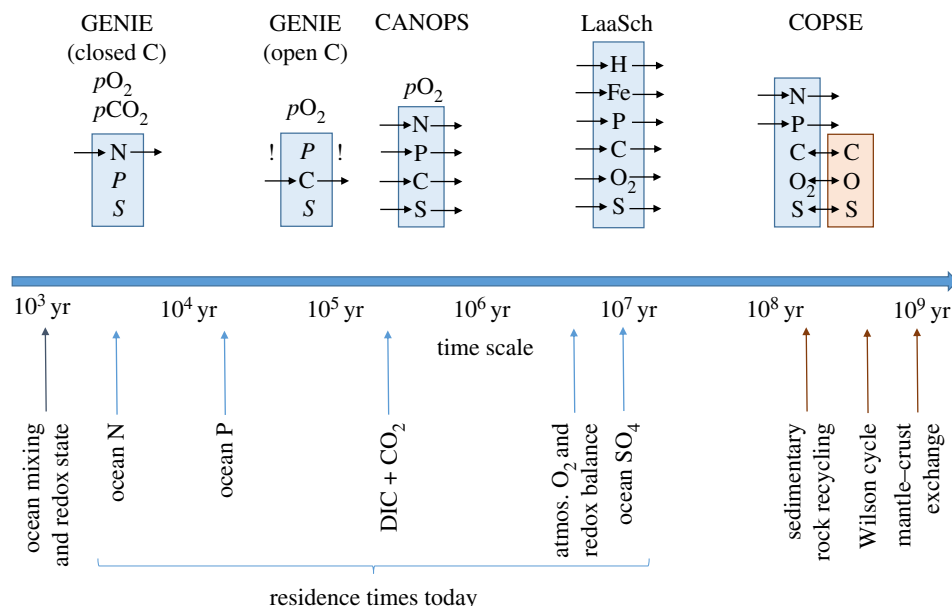
Figure 1. Time scales of key Earth system processes and of model applicability. Time scales of key processes (below the line) include residence times of several key variable reservoirs today (DIC, dissolved inorganic carbon); 'redox state' refers to the deep ocean redox state; 'redox balance' refers to the Earth surface redox balance. Models are positioned above the line according to their approximate (maximum) time scale of applicability, given their assumptions about which reservoirs are treated as constant (in italics). Note that inferences about much longer time scales than indicated have been made in some studies using CANOPS and LaaSch (discussed in the text). The major element cycles captured within the ocean–atmosphere of each model are listed inside the blue box, ordered fast to slow (from top to bottom) based on the present-day residence times. Incoming and outgoing arrows indicate an open system representation for a cycle. Double-headed arrows indicate exchange with sedimentary rock elemental reservoirs, which are indicated in a brown box. Two ways of running GENIE are indicated. Exclamation marks indicate a time-scale inconsistency (where a fast variable is treated as constant despite a slower variable being treated with an open system).

the atmosphere(–ocean–biosphere) approximately 6 Myr (with respect to exchange with the crust), carbon dioxide and dissolved inorganic carbon (DIC) in the ocean–atmosphere approximately 500 000 years, phosphorus in the ocean approximately 20 000 years and nitrogen in the ocean approximately 5000 years. The time-scale separation between variables means, for example, that today we can consider oxygen to be approximately constant over the time scales over which phosphorus varies, or conversely when considering time scales of variation in atmospheric oxygen, phosphorus must be close to steady state. However, in the Proterozoic, we should consider whether residence times were quite different, including whether some constituents had a shorter time scale than the approximately 1000 year ocean mixing time scale and, therefore, would have had heterogeneous distributions in the ocean [25].

4.2. Linking nutrients, carbon and oxygen

Nutrients are linked to oxygen via the limitation of primary production and the associated production and eventual burial of organic carbon, which represents the net source of oxygen—i.e. the net of oxygen production and consumption in respiration and other oxidative pathways. Today plants on land make a major contribution to organic carbon burial and net oxygen production [26], but in the Proterozoic, although there were photosynthetic microbial mats on land [27], they are generally assumed not to have contributed significantly to organic carbon burial. Hence, the focus has been on the controls on marine production of organic carbon, its sinking through the water column (the 'biological pump') and its preservation and burial in sediments.

A crucial notion is that the availability of one nutrient in the ocean ultimately limits the export (sinking) flux of new photosynthetic matter from the surface ocean. Today that nutrient is phosphorus, even though nitrogen may be proximately limiting (i.e. run out first)—because nitrogen levels adjust (on a shorter time scale) to variations in phosphorus levels through the stimulation or suppression of nitrogen fixation (and the action of denitrification) [28,29]. In the more anoxic Proterozoic–early Palaeozoic ocean, we need to consider whether elevated levels of denitrification made nitrogen more proximately limiting (i.e. phosphorus levels in the ocean could considerably exceed organisms' requirement for phosphorus) [25,30], and whether trace metals limited nitrogen fixation and thus primary production [31].

How much of the organic matter created in primary production sinks and reaches the sediments—i.e. the efficiency of the 'biological pump'—plays a crucial role in determining the ocean redox state and in setting ocean nutrient levels [4,16,25]. On the approximately 10^3 year time scale of ocean mixing, the amount and location of organic matter remineralization in the water column, together with the supply of oxygen from above, jointly determine the redox state of deeper waters. On the approximately 10^4 year time scale of balancing the phosphorus cycle, the phosphorus (and coupled nitrogen) concentration in the ocean must adjust until output to sediments matches input from rivers. For example, if, without complex life, the biological pump was less efficient (i.e. it was more difficult to get organic material to the bottom of the shelf seas and ocean and bury it), then (all else being equal) nutrient and productivity levels would need to have been higher to balance the phosphorus cycle [4,16]. Alternatively, if in a more anoxic ocean there were another efficient way of transferring phosphorus to the sediments—e.g. removal with iron minerals of mixed redox state such as vivianite—then a lower phosphorus concentration could have balanced the phosphorus cycle [32,33]. Either way, phosphorus concentration can be decoupled from phosphorus input/output.

The burial efficiency of organic matter in sediments and the $C:P$ stoichiometry of what is buried also affect phosphorus and atmospheric oxygen levels [34–36]. Today, most of the organic material that reaches the sediments is recycled (remineralized) back to the water column. There is a long-running debate about whether organic carbon is more efficiently remineralized under oxic versus anoxic bottom water conditions. Any difference is unclear under the high sedimentation rates of shallow ocean margins where greater than 80% of organic carbon is buried today, but preservation could be markedly more effective under anoxic conditions at the low sedimentation rates in the deep ocean [37]. Under today's oxic ocean conditions, phosphorus is more efficiently recycled than carbon leaving buried organic matter with a higher $(C:P)_{org}$ ratio than primary production, but phosphorus is often trapped in other forms in sediments—especially in authigenic calcium minerals (e.g. apatite), or adsorbed to the surface of iron oxide minerals, meaning the total sedimentary ratio of organic carbon to reactive phosphorus $(C_{org}:P_{react})$ can be lower than in primary production. The recycling of phosphorus from organic matter markedly increases under anoxic conditions, increasing $(C:P)_{org}$ burial ratios, phosphorus concentration, organic carbon burial and atmospheric oxygen [36]. However, if the evolution of complex life increased the efficiency of phosphorus preservation in sediments then this would have lowered phosphorus concentration, organic carbon production and burial and atmospheric oxygen [19].

4.3. Earth surface redox balance

If we tally up all the significant reduced and oxidized reservoirs in the ocean–atmosphere and their input and output fluxes, these must be near long-term balance—or Earth's surface redox state, including atmospheric oxygen levels, will change [23,24]. Today, organic carbon burial is balanced both by the oxidative weathering of ancient sedimentary organic carbon exposed on the continents and by the volcanic outgassing and subsequent oxidation of subducted organic carbon. The sulfur cycle also plays an important role in today's redox balance. In sediments, the electrons in organic carbon may be transferred to pyrite (FeS_2) before burial. Ancient pyrite exposed on the continents is rapidly oxidized and some pyrite sulfur is outgassed and oxidized. Carbon and sulfur also have large oxidized sedimentary reservoirs—carbonate and gypsum—which are deposited from the ocean, weathered on continents and the C and S they contain outgassed from volcanoes following subduction. Over geologic time, the fraction of carbon buried in organic (reduced) versus oxidized form may vary, as may the fraction of sulfur buried in pyrite (reduced) versus oxidized form. Changes in both burial fractions have affected Earth's surface redox state over Phanerozoic time [22,30], but (as will see) the situation was different in the Proterozoic. Furthermore, over Proterozoic time scales, net oxidation of iron in the Earth's crust, and hydrogen loss to space, could have significantly affected the Earth surface redox balance.

5. Alternative model interpretations of proxy data

Currently, major debates surround oxygen levels in the Proterozoic atmosphere and phosphorus, nitrogen and productivity levels in the Proterozoic ocean. This is partly because different models give very different inferences of key variables from the same proxy data. Summaries of the proxy data can be found in, for example, [25] (spanning Earth history) and [38] (spanning Neoproterozoic–Palaeozoic).

5.1. Atmospheric oxygen levels

There is currently no widely accepted, direct record of atmospheric oxygen levels prior to the Quaternary ice-core record. Measurements of gas inclusions in halite minerals have been suggested to record the ancient atmosphere [39], but can be contaminated with modern air [40]. Hence, attempts to derive a proxy for atmospheric oxygen rely on models. The absence of mass-independent fractionation of sulfur isotopes (MIF-S) since the Great Oxidation approximately 2.3 Ga indicates the continuous presence of an ozone layer and that the sulfate level in the ocean has remained sufficient to prevent any MIF-S signals being recorded. One-dimensional atmosphere models suggest the ozone layer starts to form at pO_2 approximately 10^{-5} PAL (present atmospheric level), although the total column depth of ozone is still an order of magnitude below present at pO_2 approximately 0.001 PAL [41]. The presence of mass-independent fractionation of oxygen ($\Delta^{17}O$) at times in the Proterozoic [42] indicates sufficient oxygen and ozone to initiate the required stratospheric photochemistry, which models suggest requires $pO_2 \geq 0.001$ PAL [41,43]. Other proxies for atmospheric oxygen rely on models of oxidation processes in weathering, transport or shallow ocean environments, which are complicated by the existence of gradients in oxygen concentration from the atmosphere to depth in weathering profiles or shelf seas, and by any presence of organic matter or other reductants.

Traditionally, steady-state model interpretations of data indicating oxidized iron retention at the top of rare ancient soil profiles (palaeosols) were used to set a lower limit on pO_2, given an assumed pCO_2—e.g. $pO_2 > 0.01$ PAL at 1.85 Ga (Flin Flon palaeosol) and at 1.1 Ga (Sturgeon Falls palaeosol) [44]. Some subsequent modelling has revised the 1.85 Ga constraint upwards to greater than 0.05 PAL [45]. Other mass balance modelling has given lower pCO_2 estimates requiring lower pO_2 to explain iron retention [46]. Iron retention in the 1.1 Ga Sturgeon Falls palaeosol has also been questioned, leaving the 1.1 Ga pO_2 inference uncertain [43]. The presence of any microbial mats, e.g. secreting organic acids that can cause iron loss, further complicates palaeosol interpretation [27]. More recently, kinetic modelling of abiotic or biotic manganese oxidation and associated chromium oxidation and isotope fractionation was used to argue that $pO_2 < 0.001$ PAL is necessary to explain a lack of positively fractionated $\delta^{53}Cr$ in marine ironstones and shales [1]. However, the modelling assumed equilibration of soil pore fluids with atmospheric pO_2, whereas more realistic one-dimensional (1D) modelling of shale weathering shows that the presence of ancient organic matter (kerogen) can readily drive entire weathering profiles anoxic up to pO_2 approximately 0.05 PAL [47]. Furthermore, new data have shown evidence of positively fractionated $\delta^{53}Cr$ in mid-Proterozoic shales [48] and carbonates [49]—illustrating that the previous absence of evidence should not have been taken as universal evidence of absence with which to infer pO_2 over greater than 1 Gyr. Instead, it seems likely that pO_2 varied over Proterozoic time. What remains unresolved is what minima it reached when positive $\delta^{53}Cr$ is absent,

and whether the overall pattern was of oxygenation events against a very low pO_2 baseline [50], or deoxygenation events against a higher pO_2 baseline.

Traditionally, the lack of detrital pyrite (or uraninite) in sediments after the Great Oxidation indicates exposure of these grains to sufficient oxygen in weathering or aquatic transport environments to fully oxidize them. Modelling of shale weathering profiles across observed ranges of erosion rates on the land surface predicts that the oxidation of pyrite in soils would be incomplete at $pO_2 < 0.1$ PAL [47]. Kinetic modelling of the dissolution of detrital pyrite (and uraninite) grains in solution equilibrated with atmospheric oxygen—e.g. during transport down rivers—indicates that $pO_2 > 0.05$ PAL would be required to completely dissolve them, especially for short river transport times [51]. This pO_2 limit would go up if the grains spend time in organic-rich riverine sediments—as seems likely for longer river transport times—because they are readily driven anoxic at low pO_2. These models all depend on poorly known pyrite oxidation kinetics at low pO_2, which have recently been revised faster [52], which will tend to shift the pO_2 lower limits downwards.

5.2. Deeper ocean redox state

Models can indicate how the ocean redox state varies with atmospheric pO_2, ocean nutrient levels and the nature of the biological pump, helping infer the ocean redox state from marine sediment proxies.

The most established redox proxy—iron speciation of sediments—is a localized proxy usually taken to directly indicate whether overlying waters were oxic, anoxic and sulfate-reducing (euxinic) or anoxic and iron-reducing (ferruginous). Models suggest that 'ferruginous' does not imply iron rich, but rather [Fe^{2+}] approximately 0.1 µM [25,53], and oxygen and nitrate rather than iron may dominate organic carbon remineralization [53]. A growing range of redox-sensitive trace metals with anoxic or euxinic sinks are also being used to try and get a 'global' proxy of ocean redox state. Different metals with different redox sensitivity can add information—for example, molybdenum (Mo) removal is specifically sensitive to euxinic (rather than ferruginous) conditions, whereas uranium (U) removal tracks anoxic conditions in general. Models are still required to estimate the global spatial extent of anoxic or euxinic bottom waters, and the results are typically sensitive to assumptions about kinetics, the present extent of anoxic bottom waters and other uncertain terms in the isotopic mass balance. They show that complete removal of redox-sensitive metals need not imply global anoxia or euxinia, with estimates of greater than 30–40% of Proterozoic seafloor anoxic and approximately 1–10% euxinic [54]. Consistent with this, basin transects and broader compilations of iron-speciation data indicate a spatially heterogeneous deeper ocean redox state at several Proterozoic times. This is supported by other redox proxies in very rare samples of the deep ocean, which indicate oxic bottom waters at some places and times [55,56]. To interpret such a spatially heterogeneous redox structure requires a spatially explicit model, and one model in particular has been used.

5.3. GENIE

'GENIE' is a coarse-resolution three-dimensional (3D) ocean model coupled to a two-dimensional (single layer) atmosphere and sea-ice, with marine C, P, S and optional N, biogeochemical cycling, designed to consider controls on ocean redox state, atmospheric pCO_2 and global temperature. GENIE's strengths include that it is fast for a 3D model and has data-assimilated modern biogeochemistry, which has been tested against multiple events in the geochemical record. It also captures some of the spatial variability in climate and has an optional weathering module. Key limitations include the lack of an open P cycle, limited iron-nutrient relationships and very limited resolving of shelf seas. Atmospheric pO_2 is prescribed and so, crucially, is ocean P content. GENIE can be run with a closed or open C cycle (figure 1)—i.e. with prescribed or interactive pCO_2. With an open C cycle, including interactive silicate weathering, GENIE can be integrated for up to a million years to achieve steady state of the inorganic carbon cycle. However, as ocean P content is prescribed, this leads to some time-scale inconsistency—e.g. organic carbon burial is prescribed, when in reality it responds interactively (and can affect pCO_2) over such time scales. Hence, we concentrate on closed O_2, C and P system applications of GENIE to interpret proxy data, and consider open N system responses. Later, we consider the inclusion of ecological dynamics, noting throughout that the lack of an open P cycle response limits what we can infer about dynamical responses over time scales $\geq 10^4$ year.

GENIE has been used to explore how ocean redox state depends on prescribed pO_2 [25,57], PO_4 [25,58] and the nature of the biological pump [25,59]. This suggests that spatial redox heterogeneity requires a finely poised global balance between atmospheric oxygen levels and ocean limiting nutrient levels, and is sensitive to the nature of the biological pump. Assuming a modern biological pump, it requires pO_2 : nutrient approximately 0.4 of today's ratio [25], consistent with other models. This can be achieved in very different ways. If Proterozoic $pO_2 \ll$ PAL then nutrients must have been chronically limiting, but if nutrients were near present ocean levels (POL) then pO_2 approximately 0.4 PAL is consistent with times of deeper ocean redox heterogeneity. Prototype inclusion of Fe–S cycling in such a mixed redox state ocean predicts [Fe^{2+}] approximately 0.1 µM with removal as pyrite in euxinic settings but iron oxide at the oxic–anoxic boundary [25].

GENIE further shows that at pO_2 : nutrient < 0.05 of today—under which deeper waters would be completely anoxic—surface waters of the ocean start to exhibit redox heterogeneity including 'oxygen oases' and anoxic areas (i.e. they cease to be equilibrated with the atmosphere) [25,57]. This makes other recent model attempts to infer very low pO_2 approximately 0.001 PAL from shallow ocean sediment redox proxies, e.g. approximately 1.85 Ga [60], problematic, because conceivably anoxic signatures, e.g. in Ce/Ce* [60] (or iron speciation), simply indicate anoxic areas caused by excess local reductant input. These may indicate less extreme $pO_2 < 0.05$ PAL or higher nutrient levels, noting that shallow shelf-sea locations are often enriched with nutrient runoff from land.

5.4. Ocean nutrient levels and productivity

Modelling was originally used to infer very low ocean [PO_4] from the phosphorus content of iron formations [61]. Subsequently, experiments showed that the results are highly sensitive to assumptions about the concentration of other

ions in seawater, notably silica [62,63]. Using plausible limits on [Si], revised estimates put mid-Proterozoic [PO$_4$] at or above POL and well above POL in the Neoproterozoic [64]. A more recent high-profile paper argues from the low bulk phosphorus content of shales that, prior to the Neoproterozoic, [PO$_4$] $\ll 1$ POL [33]. However, the argument that, because phosphorus burial was less, phosphorus concentration in the ocean must have been lower is logically flawed. Phosphorus burial is only directly informative of phosphorus input to the ocean (on time scales longer than the residence time), *not* phosphorus concentration. Instead, the authors construct a model (discussed below) in which a very efficient process of phosphorus removal is assumed to have been going on elsewhere, in unrecorded deep ocean settings, thus maintaining low [PO$_4$]. Without this assumption, they predict elevated [PO$_4$], and if we assume the biological pump was less efficient, much higher [PO$_4$] could be predicted. Hence, huge uncertainty currently surrounds Proterozoic [PO$_4$] levels. The application of phosphorus speciation to ancient sediments holds great potential to improve knowledge but will also need modelling to interpret it. The first data from approximately 1 Ga indicate efficient P removal with iron minerals in a low productivity, ferruginous ocean margin setting, but (C : P)$_{org}$ suggests that primary production was no more nutrient limited than today [65].

Ancient marine N cycling is hard to constrain even with data and models. The nitrogen isotope composition of shales should provide some information, but, unfortunately, the same δ^{15}N signature can be produced in different ways. In GENIE simulations of a mixed redox state Proterozoic ocean, abundant nitrogen fixation comprising approximately one-third of new production is predicted to balance intense regions of denitrification, and the deep ocean comprises small and rapidly turning over reservoirs of nitrate and ammonium in anoxic and oxic waters, respectively [25]. Consequently, [PO$_4$] is decoupled significantly above the nitrogen levels determining productivity and P burial in a more anoxic ocean—at around double the levels that would make it proximately limiting. Recent GENIE results suggest the decoupling of P above N could be even greater [66]. Extending such a spatial model to predict δ^{15}N distributions could provide a test of this scenario against available data.

Recently, a simple model has been used to try and infer gross primary productivity (GPP) from the triple oxygen isotope (Δ^{17}O) composition of sedimentary sulfate at particular times in the Proterozoic [42,67,68]. However, the problem is underconstrained, because Δ^{17}O depends jointly on pO$_2$, pCO$_2$ and GPP, with positive correlation between pO$_2$ and GPP. Hence, for example at approximately 1.4 Ga, both lower pO$_2$ approximately 0.001–0.01 PAL and GPP approximately 6% of today, and higher pO$_2$ approximately 0.01–0.1 PAL and GPP approximately 40% of today, are consistent with the same Δ^{17}O data [42]. Had the authors considered pO$_2 > 0.1$ PAL, their GPP inference would be higher again. The same issue pertains at other times of Δ^{17}O data, although around approximately 2 Ga, there is Δ^{17}O evidence that GPP declined [68] or pO$_2$ increased. Attempts to further constrain the solution space [43], by mechanistically tying the unknown variables together, depend on contestable models (that are discussed next). They risk circular reasoning—taking a model that ties low pO$_2$ and low nutrients together, taking different model-dependent inferences of low pO$_2$, and then (unsurprisingly) inferring from Δ^{17}O a low productivity, low nutrient, low pO$_2$ world.

6. Alternative models for global biogeochemical cycling

I now consider three recent models of global biogeochemical cycling, including oxygen and nutrient levels prior to and during the rise of complex life (figure 1). I compare and contrast these different models, explain why they come to quite different results, examine what (if any) testable predictions they make and thus try to establish which (if any) results we should trust. Table 1 summarizes and contrasts key process representations in the three models.

6.1. CANOPS

'CANOPS' is a 1D ocean–atmosphere box model designed to consider controls on ocean nutrient and redox state [69,70] that has been used to explore how C, N, P and S cycling could have worked under different prescribed levels of atmospheric pO$_2$ [33,71]. CANOPS represents several key input and output fluxes from/to the lithosphere, but it does not represent key sedimentary reservoirs or their tectonic cycling. The modelling approach involves prescribing permissible distributions on a range of model boundary conditions (including pO$_2$), drawing many different instances of the model from those parameter distributions, and running those model variants to steady state for ocean reservoirs (if possible). Additional data-derived constraints may then be imposed on what is considered a permissible result. In ocean steady state, the input/output fluxes do not necessarily balance with respect to particular sedimentary reservoirs, nor do they necessarily achieve redox balance—instead an ad hoc flux is invoked to achieve that [71].

In one high-profile publication [33], CANOPS purportedly supports a 'stable low-oxygen world' in the Proterozoic with very low ocean nutrient levels. However, as pO$_2$ is prescribed (by the modellers), the first claim appears tautological. Several critical assumptions in the model's ocean process representation (table 1) determine that it produces a low nutrient ocean when low pO$_2$ is prescribed. Firstly, efficient abiotic removal of phosphorus is prescribed, nominally due to scavenging by iron minerals forming at the redox boundary of a largely anoxic water column (although Fe cycling is not represented). Secondly, the C : P stoichiometry of primary production is assumed to increase approximately threefold under low nutrient levels. Thirdly, organic C preservation is assumed to be more efficient under anoxic conditions [37]. The first assumption directly generates low P and productivity levels. The latter two assumptions dictate that when prescribed low pO$_2$ inevitably makes the ocean anoxic, in order to match the relatively low organic C content of Proterozoic shales, an anoxic ocean must have low P levels and productivity (because organic carbon creation and preservation are assumed more efficient). Hence, the model 'result' is wired into its assumptions. As the authors show [33], if the first assumption is dropped and there is no prescribed efficient scavenging of P, the response to prescribed low pO$_2$ is completely different, with higher than present P levels in the anoxic ocean supporting greater than present organic carbon burial, which would tend to cause pO$_2$ to rise.

In a subsequent paper [71], CANOPS purportedly manages to 'constrain global redox balance', support mid-Proterozoic 'severe P biolimitation' and find a role for the sulfur cycle in 'regulating atmospheric O$_2$ levels'. Here,

Table 1. Representation of key biogeochemical fluxes in three Proterozoic models.

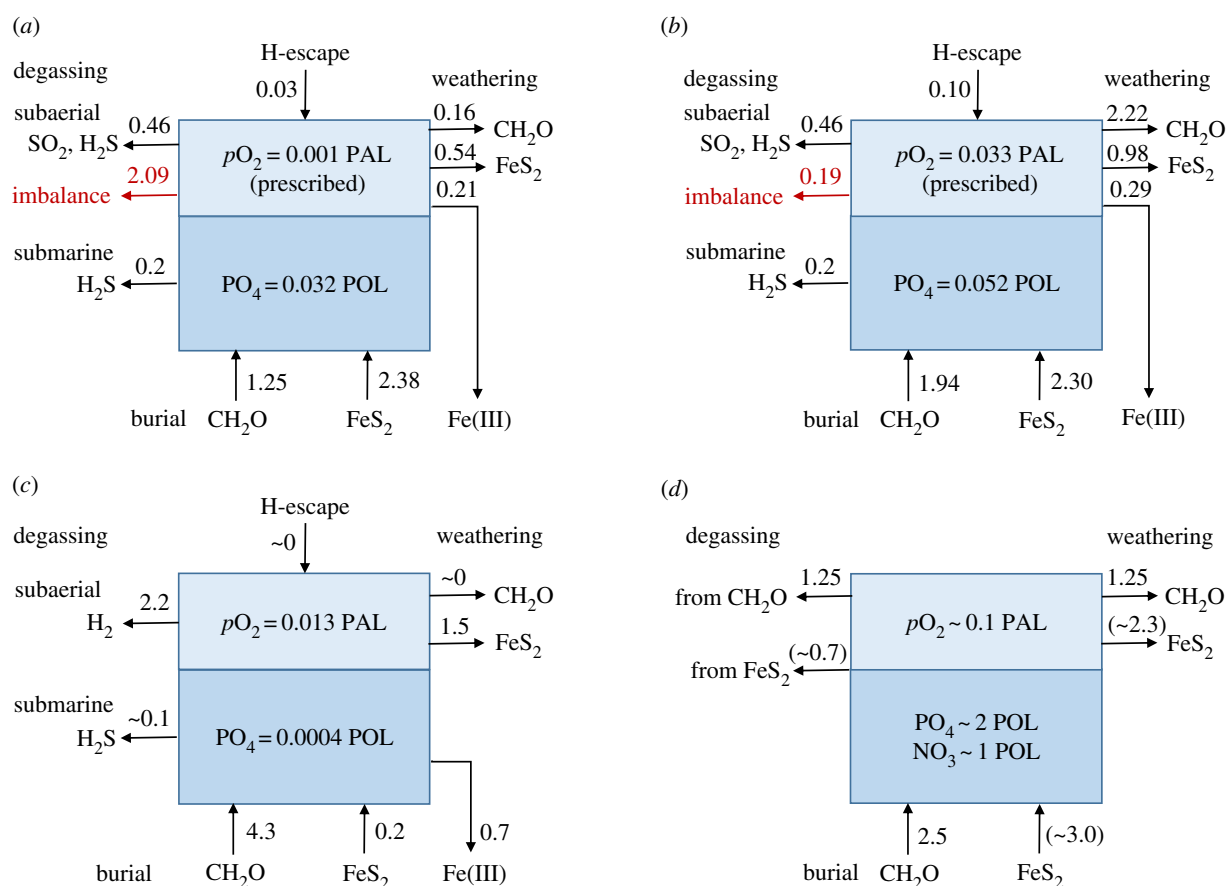| cycle process	model CANOPS	LaaSch	COPSE
nitrogen			
nitrogen fixation	compensates any N deficit	—	α (P-N/16)^2
denitrification (water)	f([NO$_3^-$],[O$_2$])	—	f(anoxia,N)
denitrification (sediment)	f([NO$_3^-$],[O$_2$],C$_{org}$)	—	f(N)
phosphorus			
P weathering	fixed flux: 0.18 Tmol P yr^{-1}	apatite (silicate) + oxidative	silicate + carbonate + oxidative
P bioavailability to ocean	= P weathering	0.33 → 1 as pO$_2$ 0.1 → 1 PAL (nominally Fe-mineral scavenging in estuaries)	= P weathering − P to land plants
P scavenging in ocean	α P upwelling * σ_{scav} parameter (0–1) (nominally by Fe-minerals)	α P (small flux)	—
Org-P burial	complex function, (C$_{org}$: P$_{org}$)$_{burial}$ increases with anoxia	P regeneration α f(O$_2$, (sedimentary oxic respiration + SO$_4$ reduction + Fe reduction))	α C$_{org}$ burial, (C$_{org}$: P$_{org}$)$_{burial}$ increases with anoxia (250 → 4000)
Ca–P (authigenic) burial	suppressed by anoxia		suppressed by anoxia
Fe–P burial	suppressed by anoxia		suppressed by anoxia
organic carbon			
C$_{org}$ degassing	—	(implicit in H$_2$ input)	α C$_{org}$ sedimentary reservoir
C$_{org}$ oxidative weathering	α pO$_2^{0.5}$	α pO$_2$	α pO$_2^{0.5}$, C$_{org}$ sedimentary reservoir
C$_{org}$ burial land plants	—	—	50% of today's total C$_{org}$ burial
export/new production	P-limited (Michaelis–Menten), C : P increases 106 → 400 as P decreases	P-limited (linear), C : P=106	N-limited, C : P = 117, N : P = 16
biological pump efficiency	remineralization = f(O$_2$,NO$_3$,SO$_4$,CH$_2$O)	remineralization = f(O$_2$,SO$_4$)	(constant)
C$_{org}$ burial efficiency	enhanced by anoxia	enhanced by anoxia	optional f(pO$_2$)
sulfur			(optional)
S degassing	0.7 Tmol S yr^{-1} (SO$_2$: H$_2$S = 9 : 1) subaerial + 0.1 Tmol S yr^{-1} (H$_2$S) submarine	0.07 Tmol S yr^{-1} (H$_2$S) submarine, (no subaerial)	reduced α pyrite reservoir, oxidized α gypsum reservoir
pyrite weathering	biotic≠f(O$_2$) + abiotic = f(O$_2$), complete oxidation pO$_2$ > 0.0035 PAL	0.8 Tmol S yr^{-1}, complete oxidation pO$_2$ > 10^{-7} PAL	α pyrite sedimentary reservoir (complete oxidation)
pyrite formation and burial	α sediment–water H$_2$S flux, burial efficiency suppressed by [O$_2$]	water column and sediment formation	α C$_{org}$ burial, [SO$_4$], (pO$_2$)$^{-1}$
gypsum weathering	constant α assumed initial gypsum reservoir, assumed erosion rate	2.8 Tmol S yr^{-1}	α gypsum reservoir
gypsum deposition	α [SO$_4$]	α [SO$_4$]	α [SO$_4$]
other O$_2$ terms			
H$_2$ input	—	2.2 Tmol O$_2$ eq yr^{-1}	—
hydrogen escape	α CH$_4$	f(H), diffusion limited	—
seafloor oxidation	—	α [O$_2$]$_d$	—
Fe^{2+} weathering	f(O$_2$), buried on land	α silicate weathering, all goes to ocean	—
Fe^{2+} hydrothermal	—	0.4 Tmol Fe yr^{-1}	—
Fe^{2+} ocean oxidation	—	α [O$_2$][Fe^{2+}], some buried as siderite	—

Figure 2. Earth surface redox (im)balance for the proposed Proterozoic states of different models. Arrows indicate fluxes in Tmol O_2 (equivalents) yr^{-1} (electrons flow in the opposite direction); PAL, present atmospheric level; POL, present ocean level; CH_2O, organic carbon; FeS_2, pyrite (but note the stoichiometry may differ); 'from' is used to indicate a source of electrons recognizing the gases/fluids will not be in that chemical form. (a) CANOPS 'low O_2' scenario reproduced from fig. 5a of [71] with unmodelled reductant input (Φ_{out}[Red]) indicated in red as redox 'imbalance'. (b) CANOPS 'high O_2' scenario reproduced from fig. 5b of [71]. (c) LaaSch 'low O_2' scenario reconstructed from [72] (note 'pyrite' burial flux actually has stoichiometry FeS). (d) COPSE example Proterozoic state from [47] assuming present-day marine organic carbon burial flux, and indicative S fluxes assuming the sedimentary S reservoir is dominated by pyrite (in brackets because the S cycle can then be excluded from the model and its redox balancing—see text).

independent but model-based estimates of [SO_4] approximately 0.1–1 mM are used to constrain subsets of permissible model solutions. The modellers show Earth's surface in redox balance by invoking an arbitrary balance term (Φ_{out}[Red] in fig. 5 of [71]—reproduced here as figure 2a,b with that flux labelled redox 'imbalance'). However, the failure to impose strict Earth surface redox balance within the model violates the assumption that pO_2 is fixed (stable) and the required balancing flux must be critically examined. Similarly, the lack of balanced sedimentary reservoirs should lead readers to question whether the purported model steady states and assumed pO_2 levels are sustainable in the long term. In the assumed 'low' pO_2 approximately 0.001 PAL case (figure 2a, reproducing fig. 5a of [71]), the required redox balance term is a large net removal of oxygen (approx. −2.1 Tmol O_2 eq yr^{-1}), which exceeds the sum of the resolved reduced matter input terms (approx. −1.6 Tmol O_2 eq yr^{-1}), or the uncertainty today in unresolved reduced matter input terms (−(0.8–1.4) Tmol O_2 eq yr^{-1}). Without this term (i.e. with the fluxes that are actually modelled), pO_2 would tend to rise. With an approximately 1.1 Tmol O_2 eq yr^{-1} input of reduced C gases required to balance the organic carbon cycle in the model (and consistent with today's unresolved reduced matter inputs), an approximately 1 Tmol O_2 eq yr^{-1} imbalance would remain, which can generate today's pO_2 reservoir in 37 Myr. This redox imbalance

(and the organic carbon cycle imbalance) largely disappears in CANOPS' 'high' pO_2 approximately 0.033 PAL case (figure 2b, reproducing fig. 5b of [71]).

The redox imbalance at pO_2 approximately 0.001 PAL exists because (in electron or oxygen equivalents) pyrite burial greatly exceeds sulfur oxidation, and organic carbon burial far exceeds organic carbon oxidation (plus iron oxidation) requiring a large unresolved input of H_2, CO, CH_4, Fe^{2+}. Pyrite oxidation is incomplete, at odds with the lack of detrital pyrite. The imbalance in the S cycle involves an excess of gypsum weathering and (implicit) degassing over (minimal) burial, which is unsustainable over Proterozoic time scales. There was gypsum deposition (for the first time) in the aftermath of the Great Oxidation, but the assumed initial model reservoir of $(50 \pm 25) \times 10^{18}$ mol would shrink on an approximately 100 Myr time scale (based on the modelled input/output imbalance). This would leave a crustal sulfur reservoir dominated by pyrite, invalidating the claim that sulfur cycling and especially pyrite burial played a role in regulating atmospheric O_2 over Proterozoic time scales (see below).

6.2. 'LaaSch'
Laakso & Schrag [72,73] have developed a simple box model—which I dub 'LaaSch'—to consider how atmospheric

oxygen could have been regulated at different levels over Earth history. LaaSch is an Earth surface model where outputs have to balance inputs for ocean–atmosphere reservoirs of material to be at steady state. Atmospheric pO$_2$ is an interactive variable (unlike in CANOPS) and predicting its stable level(s) is a key target of the model. In an early version of LaaSch, C, P, S and alkalinity cycling are included [73], with a subsequent version adding Fe and H cycling [72]. LaaSch does not include sedimentary reservoirs or their tectonic cycling. However, it does require that atmospheric pO$_2$ and the redox fluxes to/from the surface system adjust until redox balance is achieved. Again one should look at the predicted fluxes into and out from the sediments and consider whether they imply net transfers of C or S (or Fe) between sedimentary forms and whether those are consistent with observations or could be sustained over Proterozoic time scales greater than 100 Myr.

In its process representation (table 1), LaaSch makes critical assumptions—firstly that phosphorus is increasingly efficiently scavenged by iron minerals in rivers/estuaries as atmospheric pO$_2$ declines [73]. The shape of the functional response is arbitrarily chosen (and is changed markedly between studies [72,73]) in a way that generates alternative stable states for atmospheric pO$_2$ at approximately 1 PAL and approximately 0.1 PAL. The authors are explicit that 'the parametrization is tuned to give stability [of pO$_2$] at levels consistent with proxy records'. The reason a decline in P input with declining pO$_2$ is required is that LaaSch also assumes spectacularly efficient organic C transfer to sediments in an anoxic water column and very high preservation efficiency in anoxic sediments, which would otherwise tend to push pO$_2$ back towards modern levels. In a lower Proterozoic pO$_2$ steady state, LaaSch simulates only approximately 0.1% of modern primary production but greater than 70% of it being buried (whereas in today's world only approx. 0.1% is buried). Virtually no remineralization occurs in the model anoxic water column because it is assumed to only depend on O$_2$ (which is predicted absent) or SO$_4$ (which has a low predicted concentration), ignoring water column methanogenesis (or other oxidants). This is wrong and demonstrably incompatible with the geochemical record— for example, mid-Proterozoic euxinic shales require a productive biosphere and extensive sulfate reduction, and ignoring water column methanogenesis leads to erroneously low atmospheric methane levels, especially in the Late Archean where there is isotopic evidence for extensive marine methane cycling. The increase in organic carbon burial efficiency under anoxic conditions is also erroneously high because the model only considers the deep ocean, failing to recognize that greater than 80% of organic carbon burial occurs in shallow ocean margin sediments today [74], where the much higher sedimentation rates mask any difference between oxic and anoxic remineralization rates [37].

The modelled 'low O$_2$' state (figure 2c) is predominantly stabilized by oxygen-sensitive iron oxidation in the water column, which would be expected to generate iron deposits and net oxidation of iron in the crust, whereas crustal iron oxidation appears to have mostly occurred during the 'Lomagundi' event 2.22–2.06 Ga [75] and Banded Iron Formations disappeared after approximately 1.8 Ga. This low pO$_2$ model solution also has gypsum dominating sulfur burial despite pyrite oxidation dominating sulfur input (and that is even true of the Archean 'anoxic' model solution, because

pyrite oxidation is erroneously assumed to be complete at pO$_2$ approx. 10^{-7} PAL). This implies a sulfur cycle imbalance with transfer of sulfur from pyrite to gypsum sedimentary reservoirs—and a corresponding carbon cycle imbalance with transfer of electrons from pyrite to the organic carbon sedimentary reservoir. Such a sulfur cycle imbalance is unsustainable over Proterozoic time scales, and is inconsistent with the sporadic nature of gypsum deposition in the Proterozoic and with evidence of widespread anoxic ocean conditions depositing extensive euxinic shales. Furthermore, it is well established from the δ^{13}C and δ^{34}S records and from models that do include sedimentary reservoirs that the major transfer of S from pyrite to gypsum (and corresponding transfer of electrons from pyrite to organic carbon) occurred in the Palaeozoic [22,30]. The simulated low pO$_2$ state also has minimal oxidative weathering of organic carbon, because that is wrongly [47] assumed to depend linearly on pO$_2$ (table 1). With considerable organic carbon burial, this implies massive growth of the sedimentary reservoir of organic carbon over Proterozoic time (figure 2c). This is a more appropriate scenario for prior to the Great Oxidation than after it [47]. The predicted organic fraction of carbon burial is considerably greater than today, implying higher δ^{13}C than the 0‰ observed (were it to be simulated). To counter this, the authors invoke an (un-simulated) isotopically heavy authigenic carbonate sink, but authigenic carbonate is typically isotopically light not heavy [76].

6.3. COPSE

My own efforts with colleagues extend the COPSE (Carbon, Oxygen, Phosphorus, Sulfur and Evolution) model, developed and tested for the Phanerozoic [30,77], back into Proterozoic time [47,78,79], both to try and understand how the Earth system could have worked and to test hypotheses to establish how it did work. COPSE is an Earth surface model that includes sedimentary rock reservoirs—following the tradition of Garrels, Berner and others. It has not (yet) included material or redox exchange with the mantle (or H loss to space). It maintains ocean–atmosphere redox balance and conserves matter and redox equivalents (electrons) in the total ocean–atmosphere–sediment system. COPSE includes C, O, P, S and N cycling (although some published work has removed the S cycle [47], for reasons explained below). Atmospheric pO$_2$ is interactive and predicting its stable level(s) is a key model target. COPSE predicts stable isotope records of carbon (δ^{13}C), sulfur (δ^{34}S) and strontium (^{87}Sr/^{86}Sr) to enable model testing against data. COPSE is forced by changing solar luminosity, changing tectonic factors (degassing, uplift/erosion) and changing biological factors.

Key process representations include a careful treatment of oxidative weathering (of C and S) based on running a detailed 1D weathering model over a realistic range of erosion rates [47]. This predicts that pyrite oxidation ceases to be complete below pO$_2$ approximately 0.1 PAL, and that organic carbon oxidation ceases at approximately 0.01 PAL and is particularly sensitive to varying pO$_2$ around approximately 0.1 PAL. COPSE includes the major contribution of land plants to organic carbon burial today, which when removed prior to the mid-Palaeozoic inevitably produces lower pO$_2$ and lower δ^{13}C approximately 0‰ (rather than approx. 2‰) consistent with data [30]. COPSE does not assume more efficient organic carbon burial under anoxic

conditions, but does include more efficient P recycling from organic matter under anoxic conditions, which is well established. It does not invoke more efficient P scavenging under lower pO_2, either in rivers/estuaries or in an anoxic water column. P fluxes are parametrized based on oxic or euxinic conditions with no special distinction of ferruginous P cycling—because, like the other models, it does not distinguish euxinic from ferruginous conditions. COPSE includes N cycling but has no distinction of ammonium from nitrate reservoirs, and does not predict $\delta^{15}N$. The efficiency of the biological pump is not varied. COPSE simulates a predominantly anoxic ocean in the early Palaeozoic and preceding Proterozoic, in which N and productivity levels are comparable to modern, but P levels are roughly double modern levels (required to support abundant N-fixation and a balanced N cycle).

Proterozoic COPSE simulations with a mostly anoxic ocean predict that pyrite burial dominates S removal and the pyrite sedimentary reservoir dominates the gypsum reservoir. Pyrite oxidation followed by pyrite burial has no net effect on Earth's redox state or atmospheric pO_2. Hence, in one Proterozoic study, the S cycle was assumed balanced and removed for simplicity [47]. This contrasts with the (implicitly) unbalanced sulfur cycles of CANOPS (net transfer from gypsum to pyrite) and LaaSch (net transfer from pyrite to gypsum). COPSE predicts stable Proterozoic atmospheric $pO_2 \sim 0.1$ PAL, with a lower limit of $pO_2 \sim 0.01$ PAL below which the Great Oxidation is reversed because organic carbon burial (electron removal) is insufficient to outweigh the input of reduced volcanic gases that are rapidly oxidized [47]. Incomplete oxidative weathering of organic carbon is the key oxygen regulator and it leads to the robust prediction of stable $\delta^{13}C$ approximately 0‰, consistent with the long-term record. In a Neoproterozoic study [79], driven by increasing degassing inferred from plate tectonic models, COPSE predicts a modest increase in pO_2 from approximately 0.2 to approximately 0.3 PAL and can reasonably match the $\delta^{34}S$ and $^{87}Sr/^{86}Sr$ records. Subsequent work with COPSE shows how large and persistent Neoproterozoic negative $\delta^{13}C$ excursions (notably the 'Shuram' event) can be maintained by gypsum evaporite weathering events following earlier sporadic deposition of gypsum [80].

6.4. Comparison and evaluation

As approaches to understanding how the Proterozoic world could have worked, the three models vary in the time scales they can be applied to (figure 1). CANOPS (as used thus far) is appropriate for making inferences about shorter time-scale variables than pO_2 [33], but inappropriate for considering pO_2 regulation or redox balance over 10+ Myr time scales [71]. LaaSch needs major modifications, after which it may be applied to pO_2 time scales, but not 100+ Myr sedimentary ones [72,73]. COPSE is applicable to pO_2 and sedimentary time scales but is missing longer time-scale exchanges with the mantle. The structural limitations of CANOPS and LaaSch lead them to predict long-term imbalances in redox [71] and/or crucial elemental cycles [71,72] that are at odds with data. CANOPS overall has better process representation than LaaSch, so if its time-scale limitations can be overcome (or more carefully considered in study design), it has greater potential.

As approaches to establishing how the Proterozoic world actually did work, COPSE makes testable predictions and has successfully simulated key records, notably $\delta^{13}C$. CANOPS qualitatively captures the low organic C content of shales, and LaaSch discuss the implications of their results for $\delta^{13}C$, but neither CANOPS nor LaaSch quantitatively predict proxy variables. Hence, they cannot test hypotheses (in any quantitative sense).

All of the models contain contestable process representations—although at least with COPSE these can (in principle) be falsified if the model fails to match proxy data. COPSE recognizes, while CANOPS and LaaSch ignore, the contribution of plants to today's organic carbon burial and oxygen balance. This necessarily generates lower Proterozoic–early Palaeozoic pO_2 in COPSE, whereas CANOPS and LaaSch invoke strong feedbacks to generate bi-stability including an alternative low pO_2 steady state. A third option would be that the rise of complex life itself altered pO_2. To achieve stable low pO_2, CANOPS assumes very effective P removal with iron minerals to the (anoxic) deep ocean floor, LaaSch assumes very efficient P removal in rivers/estuaries, but neither of these sedimentary environments tend to be preserved (making these assumptions untestable). COPSE assumes less efficient P removal with iron minerals under anoxic ocean conditions, which warrants revision. CANOPS and LaaSch also assume organic carbon burial efficiency increases markedly under anoxic conditions, whereas COPSE does not, and the empirical data on this have been widely debated [37].

7. Models linking complex life to biogeochemical cycling

There has been less work modelling causal links between complex life and biogeochemical cycling.

The hypothesis that the first predatory protists, by grazing on the smallest (cyanobacterial) phytoplankton cells, would have left nutrients underused and thus created a niche for larger (algal) phytoplankton cells [16] is based on adapting a classic model of size-structuring in marine communities [81]. The hypothesis that filter-feeding sponges, by predating the smallest phytoplankton cells, also selected for larger (eukaryotic) algae [4] follows the same logic—although how strong the selective effect of sponges is has yet to be modelled.

The same model [81] inspires the hypothesis that putative extreme Proterozoic nutrient limitation could have limited phytoplankton cell size and the expansion of eukaryotic algae [7]. Recent inclusion of a size-structured marine ecosystem in GENIE [82] confirms the original results [81] that prescribed nutrients limit cell size and trophic structure—for example, excluding zooplankton if $PO_4 < 0.1$ POL [82]. However, if GENIE had an open phosphorus cycle, the correspondingly weak biological pump and limited P supply to sediments should cause ocean $[PO_4]$ to rise and rebalance at a higher concentration. Furthermore, the most abundant algae in today's ocean are 1–3 μm diameter mixotrophs that prey upon cyanobacteria [83] and would not be excluded even at 1% of present ocean nutrient levels [82]. Hence, the hypothesis that lack of nutrients prevented the expansion of marine algae lacks support from current observations and models.

While CANOPS assumes the biological pump has got less efficient since the mid-Proterozoic, LaaSch assumes it has got much less efficient and COPSE assumes no change in efficiency, other models have begun to examine the effects of postulated increases in the efficiency of the biological pump [4,14]. Effects on ocean redox structure have been considered independently of effects on phosphorus levels, but over greater than 10^4 yr time scales, these effects should be consistently combined [4,16].

Three-dimensional GENIE simulations of effects on redox structure for a prescribed ocean nutrient inventory show that, without an effective biological pump, diffusion of organic matter concentrates oxygen demand in intermediate waters just below the surface ocean, generating the most intense anoxia there [25]. This could have left the deep ocean oxygenated by ventilation from high-latitude surface waters, owing to little or no oxygen demand from organic matter—assuming $pO_2 > 0.001$ PAL and 20 Sv ventilation sufficient to outweigh abiotic reductant input from mid-ocean ridges [25]. An inefficient biological pump also makes it harder to drive the deeper parts of shelf seas anoxic. As the biological pump becomes more efficient, this shifts oxygen demand to deeper waters and sediments, making it easier to drive deep shelves and the deep ocean anoxic, but making it harder to drive (near) surface waters anoxic.

However, the effect of changes in the biological pump on ocean P inventory (over approx. 10^4 yr time scales) and hence total oxygen demand in the water column works in the opposite direction. Simple calculations suggest that going from cyanobacterial to algal cells causes a roughly 10-fold increase in sinking terminal velocity and a 2.5-fold increase in material reaching the sediments [84]. A less efficient biological pump requires higher limiting nutrient levels in order to balance the P cycle, and an increase in pump efficiency tends to lower those nutrient levels, thus lowering total oxygen demand in the water column. Simple modelling of the net effect [85] supports earlier suppositions [4,16] that the change in nutrient inventory dominates—with a weaker pump P levels are higher and, therefore, deep anoxia more intense. As the pump strengthens, this tends to lower ocean P levels and the propensity for anoxia. The (much) longer time-scale effects on organic C burial and atmospheric pO_2 may work in the opposite direction again: if C_{org}/P_{react} burial ratios decline with ocean oxygenation, this will cause pO_2 to decline, ultimately reinstating anoxia, and creating the potential for long-time-scale oscillations [86,87]. Other modelling predicts that an increase in biological pump efficiency lowered atmospheric pCO_2 and might have contributed to triggering snowball Earth events [88].

Models have yet to simulate the impact of sessile benthic animals including sponges and 'rangeomorph' fronds concentrating resources where they were located on the sediments [17]. However, models have begun to consider proposed impacts of mobile, burrowing, bioturbating animals on biogeochemical cycling [18,19]. Including in COPSE the idea that, by oxygenating the upper sediments, bioturbating animals increase the retention of phosphorus and lower the $(C/P)_{org}$ burial ratio leads to a decline and then stabilization of atmospheric pO_2, consistent with evidence of ocean deoxygenation in the Late Cambrian–Ordovician [19]. The assumed timing of significant increase in bioturbation depth has been critiqued and argued to be much later in the Palaeozoic [89]. However, a subsequent version of COPSE showed that an early, nonlinear impact of shallow burrowing on C, S and P sediment cycling provides a better fit to $\delta^{13}C$, $\delta^{34}S$ and ocean redox data than a late impact [90]. Alongside this simple box modelling, detailed 1D reaction–transport sediment modelling has provided some support that bioturbation lowers C_{org}/P_{react} burial ratios [91]. There is clearly scope for more detailed process modelling of this kind to generate further insight into effects of bioturbation on P-speciation.

8. Ways forward

There is considerable scope for improved Proterozoic biogeochemical modelling. Better models of weathering, transport and sedimentary environments can improve understanding and interpretation of proxies. Models of global biogeochemical cycling need to be built on well-established principles, incorporating appropriate reservoirs and processes for the time scales they pertain to address—which for considerations of atmospheric oxygen regulation means enforcing Earth's surface redox balance and including sedimentary reservoirs. Biogeochemical models should predict proxy data targets to be testable and adding proxy targets has the potential to constrain model results—for example, COPSE could predict $\Delta^{17}O$ and better predict P-speciation. Once an appropriate model structure and link to data is established, a key unsolved challenge is to establish whether and how atmospheric oxygen could be regulated at $pO_2 \sim 0.001$ PAL. Predicting long-term fluctuations in pO_2 and nutrient levels is also a key target, which will require reconstruction of tectonic drivers and representation of how they affect climate and weathering.

Biogeochemical modelling should also explore a wider 'possibility space' of process assumptions. Most existing models assume phosphorus is the ultimate limiting nutrient, although COPSE and GENIE find nitrogen much more proximately limiting when anoxia is widespread, suggesting that possible trace metal limitation of nitrogen fixation deserves consideration [31]. Current models also assume that marine phytoplankton dominated global primary production in the Proterozoic, but if we take seriously existing predictions of much lower phytoplankton productivity [33,71,72,84,92], then modelling should consider whether microbial mats at the bottom of shelf seas, in freshwaters and/or on land [27] could have contributed significantly to global productivity. More complete Earth system modelling, including other potentially important factors for complex life, notably climate and the occurrence of 'snowball Earth' events, would also add insight and constrain results.

The possibility of significant feedback between biogeochemical conditions and the rise of complex life invites approaches that go beyond biogeochemical modelling. Trait-based physiological and ecological modelling could capture the environmental constraints on particular types of complex life, and coupling this to biogeochemical modelling could capture resultant feedbacks. For example, models of the physiological constraints on sponge pumping metabolism [93] and its hydrodynamics [94] could be coupled to models of its effects on phytoplankton community size structure and biogeochemical cycling. Size-structured modelling of phytoplankton community dynamics [81,82] could be extended to model the effects of different cell sizes, faecal pellets, zooplankton vertical migration, etc., on the biological pump [95–97], and resultant biogeochemical feedbacks. This

more comprehensive approach would offer new opportunities for testing hypotheses against empirical data. For example, the combination of molecular phylogenetics and relaxed molecular clocks calibrated on minimum ages from fossils can provide timing estimates for the origin of particular traits (e.g. animal guts). Models that can map from these traits to their biogeochemical consequences, including observable proxies, then give the potential to test and refine those age estimates.

9. Summary and implications

Some of the disagreements between existing models of atmospheric oxygen and ocean nutrient levels associated with the rise of complex life are the result of applying conceptual frameworks designed for a shorter range of time scales to longer time scales and questions, which demand the consideration of additional processes and balances. Some are due to disagreement over uncertain process representations, and some are due to clear flaws in process representation in some models.

Considering these model limitations, I conclude that Proterozoic atmospheric pO_2 varying in the range approximately 0.01–0.4 PAL is mechanistically plausible and could be consistent with available proxies, depending on the timing of pO_2 variations. No consistent model of biogeochemical cycling yet shows how pO_2 could be regulated at less than or equal to 0.001 PAL over long time scales, and it is not clear from model interpretations that any proxy demands such low levels, if we recognize that reductant inputs can create disequilibrium anoxic conditions in near-surface environments. However, this does not rule out that such conditions occurred and it should inspire further modelling to see if and how they could occur. Meanwhile, given current estimates of their minimum oxygen requirements, it is unclear that the evolution of stem group animals, sponges or simple bilaterian animals was prevented by lack of oxygen. However, the same reductant input that can create local anoxia and anoxic proxy signatures would clearly pose a problem for animals in those local environments. Furthermore, it remains possible that insufficient pO_2 and/ or unstable redox conditions restricted the later rise of more oxygen-demanding animal traits and modes of life.

A very wide range of stable Proterozoic phosphorus levels and associated productivity could be consistent with available phosphorus burial data, depending on contestable and largely untested model assumptions. Furthermore, phosphorus levels could have been several times above the Redfield ratio to proximately limiting nitrogen levels in a largely anoxic ocean. The lower atmospheric pO_2, the lower the limiting nutrient level consistent with times of heterogeneous ocean redox structure, but Earth surface redox balance requires a marine organic carbon burial flux of comparable order of magnitude to today. This makes it crucial to resolve the efficiency of the biological pump prior to complex life and the efficiency of organic carbon remineralization in a more anoxic ocean. Until we have more P-speciation data and models tested against them, the jury should remain out on Proterozoic nutrient levels. Currently, there is no decisive support for nutrient limitation of algae prior to the Cryogenian, leaving the apparently late rise of algae to ecological prominence as an unsolved puzzle.

The effects of complex life on biogeochemical cycling remain wide open for exploration, with current models suggesting that they could be substantial.

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