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Redox regime shifts in microbially mediated biogeochemical cycles

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Abstract. Understanding how the Earth's biogeochemical cycles respond to environmental change is a prerequisite for the prediction and mitigation of the effects of anthropogenic perturbations. Microbial populations mediate key steps in these cycles, yet they are often crudely represented in biogeochemical models. Here, we show that microbial population dynamics can qualitatively affect the response of biogeochemical cycles to environmental change. Using simple and generic mathematical models, we find that nutrient limitations on microbial population growth can lead to regime shifts, in which the redox state of a biogeochemical cycle changes dramatically as the availability of a redox-controlling species, such as oxygen or acetate, crosses a threshold (a "tipping point"). These redox regime shifts occur in parameter ranges that are relevant to the present-day sulfur cycle in the natural environment and the present-day nitrogen cycle in eutrophic terrestrial environments. These shifts may also have relevance to iron cycling in the iron-containing Proterozoic and Archean oceans. We show that redox regime shifts also occur in models with physically realistic modifications, such as additional terms, chemical states, or microbial populations. Our work reveals a possible new mechanism by which regime shifts can occur in nutrient-cycling ecosystems and biogeochemical cycles, and highlights the importance of considering microbial population dynamics in models of biogeochemical cycles.

1 Introduction

Metabolic conversions mediated by microorganisms play a key role in the Earth's biogeochemical cycles (Falkowski et al., 2008; Madigan et al., 2009; Fenchel et al., 1998). For example, microbial nitrogen fixation contributes an estimated 100–200 Tg of nitrogen to the world's oceans annually (Karl et al., 2002), while the microbial decomposition of soil carbon exceeds the anthropogenic contribution of carbon dioxide to the atmosphere by an order of magnitude (Aguilos et al., 2013). Predicting the response of these cycles to environmental changes, including climate change, is a central current challenge in Earth system science (IPPC, 2013). However, mathematical models for global geochemical cycles often represent microbially mediated transformations as crude "black boxes" (Allison and Martiny, 2008): for example, microbial decomposition in soil is often represented as a first-order decay process (Todd-Brown et al., 2012; Westrich and Berner, 1984). Indeed, many of the models cited in the most recent IPCC report use linear representations of microbially mediated processes (IPPC, 2013). This simplified picture contrasts strongly with the wealth of data on microbial community diversity and functional complexity which is being generated by recent advances in high-throughput sequencing technology (Nikolaki and Tsiamis, 2013). There is thus an urgent need to re-evaluate the role of microbial population dynamics in biogeochemical models (Todd-Brown et al., 2012; Allison et al., 2010).

Here, we use simple mathematical models to show that microbial population dynamics can have important qualitative effects on the response of microbially mediated biogeochemical cycles to environmental change. Specifically, nu-

trient limitations on microbial population growth can lead to abrupt changes in redox state in response to a gradual change in an environmental parameter. Sharp transitions, often described as regime shifts, are known to occur in diverse systems in response to diverse stimuli; examples range from aquatic ecosystems in the leaves of carnivorous pitcher plants (Sirota et al., 2013) to large-scale shifts in terrestrial vegetation cover (Higgins and Scheiter, 2012). These shifts are usually attributed to specific features of the system structure (or "topology"; Scheffer et al., 2009). Our work suggests that, for biogeochemical cycles, nonlinear effects arising from microbial population dynamics can lead to sharp transitions between broadly oxidized and reduced system states, even for systems with simple topologies. We term this a "redox regime shift", i.e., a nonlinear transition in the predominant redox state of a biogeochemical cycle in response to a gradual change in an environmental stimulus. In some other studies, the term "regime shift" has been associated with bistability. Here, we use the term simply to describe a sharp response, without any implied bistability.

In a biogeochemical cycle, a chemical element is shuttled between its oxidized and reduced forms in a series of steps that may be biotically or abiotically mediated (Falkowski et al., 2008). Figure 1 illustrates simplified topologies of the iron, sulfur, carbon, and nitrogen cycles (Fig. 1a–d) (Falkowski et al., 2008; Fenchel et al., 1998; Galloway et al., 2004; Canfield et al., 2005). To encapsulate the basic topology of these cycles, we begin by considering a simplified two-state model (Fig. 1e), in which an oxidized form of a chemical element (here denoted s_o) is converted via microbial metabolism to a reduced form (s_r), which is recycled back to the oxidized form either by a second microbial metabolism or by an abiotic reaction. Although this model is topologically very simple, it reveals an important and nontrivial regime shifting behavior. Later in this paper we show that this behavior is preserved in more realistic models that include features such as spatial heterogeneity, multiple redox states, and explicit coupling to the environment.

A redox reaction in a biogeochemical cycle couples the oxidation/reduction of the element being cycled to the reduction/oxidation of another chemical species. For example, in the sulfur cycle, the microbial reduction of sulfate can be coupled to the oxidation of acetate (Rickard, 2012), while in the nitrogen cycle, the oxidation of ammonia can be coupled to the reduction of molecular oxygen (Fenchel et al., 1998). In this paper, in order to avoid confusion, we refer to the latter chemical species (in these examples acetate or oxygen) as the "auxiliary electron donor/acceptor". The auxiliary electron donor/acceptor may be supplied from some external source (e.g., oxygen from the atmosphere) or may be generated by another biogeochemical process (e.g., microbial decomposition producing acetate). Many different chemical species can act as auxiliary electron donors or acceptors; for example, acetate or hydrogen can function as the electron donor for reductive reactions, while nitrate or oxygen can function as the electron acceptor for oxidative reactions. The redox-shifting behavior which arises in our models is generic, independent of which chemical species performs the role of auxiliary electron donor/acceptor.

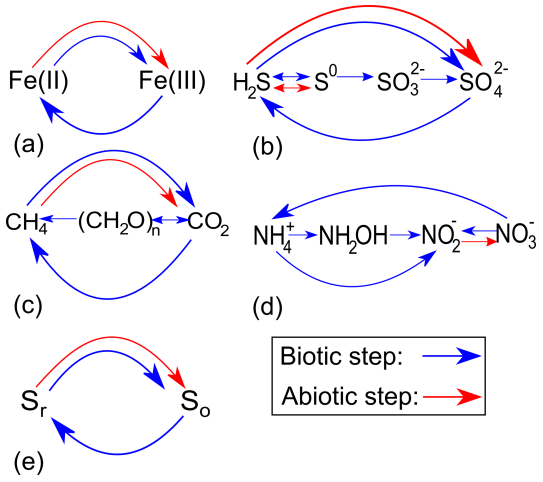

Figure 1. Schematic view of the biogeochemical redox cycles involving iron, sulfur, carbon, and nitrogen **(a–d)** (Falkowski et al., 2008; Fenchel et al., 1998; Galloway et al., 2004; Canfield et al., 2005), together with the model investigated in the first part of this work **(e)**. In all panels, oxidation reactions proceed to the right, and reduction reactions proceed to the left. Biologically catalyzed (metabolic) reactions are shown in blue, and abiotic reactions are shown in red. We note that abiotic reduction reactions are not shown, as these are minor reactions in the natural environment (but can be included in our model; see Sect. S1). We also note that many intermediate chemical states are not shown (particularly for the nitrogen and sulfur cycles) but inclusion of extra states does not affect our conclusions; see Supplement. In panel **(e)**, s_r and s_o represent the reduced and oxidized forms of the chemical element being cycled.

Crucially, if the auxiliary electron acceptor/donor is in short supply then its availability can control the rate of the redox reaction, and hence the flux of the biogeochemical cycle. Moreover, in natural environments, the availability of electron acceptors and donors is strongly dependent on the environmental conditions. For example, in aquatic ecosystems, the supply of oxygen depends on its solubility, which is temperature-dependent (Shaffer et al., 2009), and on the rate of photosynthesis (López-Urrutia et al., 2006), while the supply of acetate depends on the rate of microbial decomposition of organic matter, which can be drastically affected by factors like sewage effluent or phosphorus inflow from agricultural runoff (Conant et al., 2011).

Here, we show that changes in the supply of auxiliary electron acceptors or donors (such as oxygen or acetate) caused by environmental perturbations can have drastic effects on microbially mediated biogeochemical cycles. We first show that these perturbations can cause regime shifts in redox state for simple, spatially homogenous models. We then demon-

Table 1. Description of the notation used in the text.

Notation	Meaning
s_o	Concentration of the oxidized form of the chemical species being cycled
s_r	Concentration of the reduced form of the chemical species being cycled
n_{ro}	Population density of the oxidizing microbial population
n_{or}	Population density of the reducing microbial population

strate that the same phenomena can also occur in more realistic models which include features such as explicit supply of auxiliary electron acceptors or donors via microbial metabolism, intermediate redox states, and spatial heterogeneity (such that the nutrient supply is limited by transport processes). These regime shifts do not depend sensitively on the detailed structure of our equations or model, but instead result from the interplay between cyclic system topology and nonlinear microbial population growth requiring multiple nutrients. These redox regime shifts are predicted to occur in parameter ranges relevant to the natural sulfur and nitrogen cycles, and may also be relevant to iron cycling in the iron-containing ancient oceans.

2 Mathematical models for redox-cycling dynamics

Our aim is to predict the response of microbially mediated biogeochemical cycles to changes in the availability of auxiliary electron acceptors and donors, such as oxygen and acetate. We begin with a simple and generic "two-state" representation of a biogeochemical cycle; later we show that the same phenomena also occur in more complex models. In our two-state model (Fig. 1e), a chemical element is cycled between its oxidized and reduced forms, whose concentrations are denoted by s_o and s_r, respectively. The reduction step $s_o \rightarrow s_r$ (blue right-to-left arrow in Fig. 1e) is assumed to be biotic, i.e., mediated by microbial metabolism. This step requires an auxiliary electron donor, such as acetate. The oxidation step $s_r \rightarrow s_o$ may occur biotically or abiotically (indicated by the blue and red left-to-right arrows in Fig. 1e), and requires an auxiliary electron acceptor, such as oxygen. We have not included the possibility of an abiotic reduction reaction in our model because these are typically minor reactions at ambient temperatures in the natural environment (with the notable exception of the reaction of Fe(III) with sulfide; e.g., Canfield, 1989); further work could extend this model to include such reactions. It is important to note that, in reality, a given biogeochemical function may be performed by many coexisting microbial species (taxa); for example many different genetically distinct taxa can use acetate to reduce sulfate (Madigan et al., 2009). In our models, we group together all these "metabolically equivalent" taxa into a single effective population.

2.1 Fully biotic redox cycles

If both the oxidative and reductive steps in the redox cycle are mediated by microorganisms, the dynamics of our two-state model can be represented by the following set of differential equations (in which the dot represents a time rate of change):

$$\dot{n}_{or} = n_{or} G_{or}(s_o, n_{or}) - d n_{or}, \quad (1)$$

$$\dot{n}_{ro} = n_{ro} G_{ro}(s_r, n_{ro}) - d n_{ro}, \quad (2)$$

$$\dot{s}_r = \gamma \left[n_{or} G_{or} - n_{ro} G_{ro} \right] = -\dot{s_o}. \quad (3)$$

The variables in this dynamical system are n_{ro} and n_{or}, the population densities of the oxidizing and reducing microbial populations, respectively, and the concentrations s_o and s_r of the oxidized and reduced forms of the chemical species being cycled (Table 1 presents a key for this terminology). Equations (1) and (2) describe the microbial population dynamics; the reducing and oxidizing populations have growth rates $G_{or}(s_o, n_{or})$ and $G_{ro}(s_r, n_{ro})$, respectively, which depend not only explicitly on s_o and s_r but also implicitly on the concentrations of the auxiliary electron donor and acceptor, respectively. Both populations are assumed to be removed from the system at a constant rate d (e.g., due to viral predation and/or washout). Equation (3) describes changes in the substrate dynamics due to microbial consumption and production; here γ is a yield coefficient, which is assumed for simplicity to be the same for both reactions.

The growth rate functions G_{or} and G_{ro} play a crucial role in the model. The microbial growth rate on a limiting nutrient is often described by a Monod function $vs/(K+s)$, where s is the nutrient concentration, v is the maximal growth rate, and K is the nutrient concentration at which the growth rate is half-maximal (Ingraham et al., 1983). While other, more complicated growth rate functions have been proposed (Button, 1985), the Monod form encapsulates the key fact that the growth rate is nutrient-dependent at low nutrient concentration but becomes saturated at high nutrient concentration. For a microbial population performing a redox reaction, the "nutrient" s is likely to be the chemical species being cycled, while the concentration of the auxiliary electron acceptor/donor can be implicitly included in the value of the maximal growth rate v.

Importantly, however, in the natural environment, the rate of microbial growth may be limited by other factors such as the availability of carbon or micronutrients, toxin or waste product formation at high densities, or simply competition for space (Hibbing et al., 2010). To account for this in a generic way, we multiply the Monod term by a population density-limitation factor $(1 - n/n_{max})$, where the parameter n_{max} sets a maximal population density. This type of logistic population density limitation is a convenient and commonly used way to encapsulate growth limitation by factors not explicitly included in the model (Marino et al., 2013; Jones and Lennon, 2010; Berry and Widder, 2014). To check the validity of this approach, we also simulated a model in which

population growth is instead explicitly limited by availability of an additional nutrient (e.g., carbon). These simulations gave qualitatively similar results to those presented here; see Supplement.

These considerations lead to simple forms for the microbial growth rates in our "two-state" model:

$$G_{\mathrm{or}} = \left[\frac{v_{\mathrm{or}} s_{\mathrm{o}}}{K_{\mathrm{or}} + s_{\mathrm{o}}}\right] \times \left[1 - \frac{n_{\mathrm{or}}}{n_{\mathrm{or,\,max}}}\right], \quad (4)$$

$$G_{\mathrm{ro}} = \left[\frac{v_{\mathrm{ro}} s_{\mathrm{r}}}{K_{\mathrm{ro}} + s_{\mathrm{r}}}\right] \times \left[1 - \frac{n_{\mathrm{ro}}}{n_{\mathrm{ro,\,max}}}\right], \quad (5)$$

in which the parameters are v_{or} and v_{ro}, the maximal growth rates for the reducing and oxidizing microorganisms, respectively; K_{or} and K_{ro}, the concentrations of the chemical species $\mathrm{s_o}$ or $\mathrm{s_r}$ at which the growth rate is half-maximal; and $n_{\mathrm{or,\,max}}$ and $n_{\mathrm{ro,\,max}}$, the maximal densities of the two populations. Importantly, the concentrations of the auxiliary electron donors and acceptors (e.g., acetate and oxygen) are implicit in the maximal growth rate parameters v_{or} and v_{ro}: we expect v_{or} to increase with the availability of the auxiliary electron donor, while v_{ro} will increase with the availability of the auxiliary electron acceptor. By including the auxiliary electron acceptor/donor concentrations as parameters controlling the maximal growth rates, we neglect the possibility that they may be depleted by utilization. This is, however, included in the more realistic versions of the model presented later in the paper.

2.2 Biotic–abiotic redox cycles

If the oxidation step in the redox cycle is instead abiotic, the model has only three variables: the population density of the reducing microbial population n_{or} and the concentrations of the oxidized and reduced forms of the chemical species being cycled, s_{o} and s_{r}. In this case, the dynamics of the microbial population n_{or} are still described by Eq. (1), but the chemical dynamics obey

$$\dot{s_{\mathrm{r}}} = -F(s_{\mathrm{r}}) + \gamma n_{\mathrm{or}} G_{\mathrm{or}} = -\dot{s_{\mathrm{o}}}. \quad (6)$$

Here, the abiotic oxidation rate is described by the function $F(s_{\mathrm{r}})$. Abiotic oxidation reactions can occur spontaneously (e.g., the abiotic oxidation of hydrogen sulfide; Goldhaber, 2003), or they can be catalyzed (e.g., some electron transfer processes on mineral surfaces; Schoonen and Strongin, 2005) or limited by transport processes (Roden, 2004). To account for these factors in a generic way, we assume a Michaelis–Menten form for $F(s_{\mathrm{r}})$ (Naidja and Huang, 2002):

$$F = \frac{v_{\mathrm{a}} s_{\mathrm{r}}}{K_{\mathrm{a}} + s_{\mathrm{r}}}, \quad (7)$$

where v_{a} is the maximal abiotic rate constant (which may implicitly depend on a catalyst concentration) and K_{a} is the concentration s_{r} at which the abiotic reaction rate is half-maximal. If K_{a} is large such that $K_{\mathrm{a}} \gg s_{\mathrm{r}}$, the reaction rate becomes linear in s_{r}, describing a spontaneous process.

2.3 Steady-state solutions

Analytical predictions for the steady-state population densities and the concentrations of the oxidized and reduced forms of the chemical species being cycled (s_{o} and s_{r}) can be obtained for both the fully biotic model (Eqs. 1–3) and the biotic–abiotic model (Eqs. 1 and 6). These are given in the Supplement, Sects. S1 and S2.

3 Regime shifts caused by population-density limitation

Our models allow us to investigate system-level responses to environmental change. We focus on environmental changes that affect the availability of auxiliary electron acceptors or donors, such as temperature-related changes in oxygen solubility (Shaffer et al., 2009), changes in photosynthesis rate, or changes in the abundance or rate of decomposition of organic matter (Conant et al., 2011). For the fully biotic cycle, the parameters v_{or} and v_{ro} are proxies for the availability of auxiliary electron donors and acceptors, respectively. For the biotic–abiotic cycle, the equivalent parameters are v_{or} and v_{a}. We quantify the response of the ecosystem to changes in auxiliary electron donor or acceptor abundance via the steady-state fraction of the oxidized chemical species, $s_{\mathrm{o}}/s_{\mathrm{tot}}$, which acts as a proxy for the global redox state of the system.

Our main result is that, for both the fully biotic and the biotic–abiotic models, our model can undergo regime shifts: sharp changes in the predominant redox state of the system as the availability of auxiliary electron acceptors or electron donors (such as oxygen or acetate) crosses a critical threshold (Fig. 2). These regime shifts happen under circumstances where the total concentration of the chemical element being cycled ($s_{\mathrm{tot}} = s_{\mathrm{o}} + s_{\mathrm{r}}$) is high, such that $s_{\mathrm{tot}} \gg K_{\mathrm{or}}, K_{\mathrm{ro}}, K_{\mathrm{a}}$, implying that the microbial population density is limited by factors other than the availability of s_{o} or s_{r}. In contrast, for lower concentrations of the chemical element being cycled, $s_{\mathrm{tot}} < K_{\mathrm{or}}, K_{\mathrm{ro}}, K_{\mathrm{a}}$, the model predicts a more gradual change in system state as the availability of the auxiliary electron acceptor or donor varies.

Figure 2a and c show results for the fully biotic cycle model; in Fig. 2a, we vary the maximal reducer growth rate v_{or}, mimicking a change in auxiliary electron acceptor abundance, while in Fig. 2c we vary the maximal oxidizer growth rate v_{ro}, mimicking a change in auxiliary electron donor abundance. As expected, these perturbations lead to profound changes in the system's global redox state (as measured by the fraction of the oxidized chemical species s_{o}), from oxidized to reduced (Fig. 2a) or vice versa (Fig. 2c). Crucially, the sharpness of this transition increases as we increase the total abundance of the chemical species being cycled, s_{tot}. When s_{tot} is large enough to saturate the growth rates of the relevant microbial populations ($s_{\mathrm{tot}} \gg K_{\mathrm{or}}, K_{\mathrm{ro}}$), we obtain a "switch-like" response, which we term a redox regime shift.

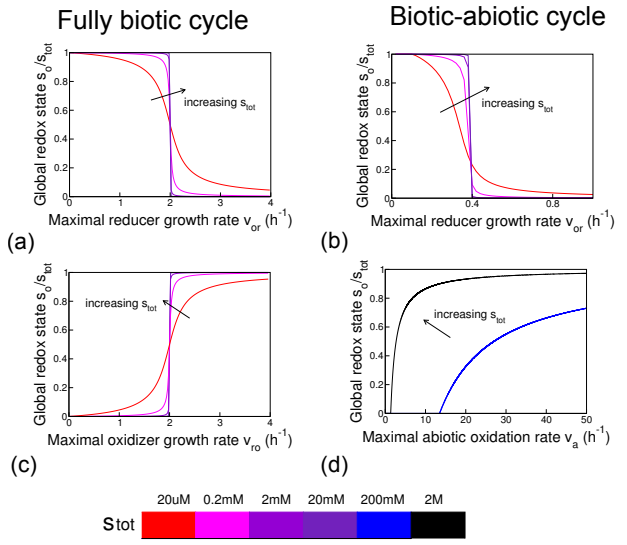

Figure 2. Redox regime shifts in model nutrient cycles. The global redox state, as measured by the oxidized fraction s_o/s_{tot}, predicted by the steady-state solution of the model equations for the fully biotic cycle (**a** and **c**, Eqs. 1–3) or the biotic–abiotic cycle (**b** and **d**, Eqs. 1, 2, and 6) is plotted as a function of parameters that form proxies for the degree of reductive or oxidative driving. v_{or} is taken as a proxy for electron donor (acetate) availability, and v_{ro} is taken as a proxy for electron acceptor (oxygen) availability. These parameters are, for reductive driving, the maximal growth rate of the reductive population, v_{or} (**a** and **b**, keeping v_{or} fixed at $2\,h^{-1}$ or $v_a = 0.2\,\mu M\,h^{-1}$), and, for oxidative driving, either the maximal growth rate of the oxidative population v_{ro} (**c**, keeping v_{ro} fixed at $2\,h^{-1}$) or the maximal abiotic oxidation rate v_a (**d**, also with $v_{ro} = 2\,h^{-1}$). The results show a shift between oxidized and reduced ecosystem states as a threshold in reductive or oxidative driving is crossed; the sharpness of this transition increases with the concentration of the chemical species being cycled, s_{tot} (shown in the color bar). The other parameters are $K_{or} = K_{ro} = K_a = 1\,\mu M$ (Ingvorsen et al., 1984), $n_{or,max} = n_{or,max} = 9 \times 10^7$ cells L^{-1}, $d = 0.1\,h^{-1}$, and $\gamma = 3 \times 10^{-8}$ μmoles cell^{-1} (Jin et al., 2013). The analytic forms for the steady-state solutions are given in Sect. S1.

For the fully biotic cycle, the model prediction is symmetric with respect to changes in v_{or} and v_{ro} (electron donor and acceptor; compare Fig. 2a and c). Consequently, it is the *ratio* of $v_{or}\,/\,v_{ro}$ (mimicking a change in the ratio of auxiliary electron donor/acceptor abundance) that drives the behavior of the model.

Figure 2b and d show equivalent results for the biotic–abiotic cycle model. In this case also, the model predicts regime shifts in response to both increasing auxiliary electron donor or acceptor availability (Fig. 2b and d, respectively), for large concentrations of the chemical species being cycled ($s_{tot} \gg K_{or}, K_{ro}, K_a$). However, in contrast to the situation for the fully biotic cycle, here the responses to changes in auxiliary electron acceptor and donor are qualitatively different in shape (compare Fig. 2b and d). This is because the biotic and abiotic reaction rates (the two terms in Eq. 6) have different functional dependences on s.

Importantly, the behavior of our model does not depend strongly on its other parameters. In particular, the total microbial population density is not important for the results of Fig. 2, as we show analytically in Sect. S3. For the fully biotic cycle, the steady-state solution of the model depends only on the ratio of the maximal population density parameters ($n_{ro,max}/n_{or,max}$) and not on the absolute values of the maximal population density $n_{ro,max}$ and $n_{or,max}$. Moreover the ratio $n_{ro,max}/n_{or,max}$ affects only the threshold point at which the regime shift happens, not the qualitative switching behavior (see Sect. S3 for more details). Thus we expect to see redox regime shifts across environments with very different microbial population densities, even for systems with very large microbial populations, and for those where the sizes of the oxidizing and reducing populations are different, as long as the microbial population density is ultimately limited by a factor other than the concentration of the chemical element being cycled. It is important to note, however, that the *timescale* over which the system responds to environmental change does depend on the population density; for large populations, the system responds more slowly. For the biotic–abiotic cycle, the mathematical results are slightly more complicated but the conclusions are broadly similar (see Sect. S3).

3.1 Regime shifts also occur in models with spatial heterogeneity and chemical sinks

The oxidation and reduction steps in natural microbial nutrient cycles are usually spatially separated (Fenchel et al., 1998). Extending our model, we find that our prediction of redox regime shifting behavior is robust to the inclusion of spatial separation between reductive and oxidative zones; indeed, the resulting transport limitation of chemical species s_o and s_r actually enhances the switching phenomenon (see Sect. S5).

In the natural environment, coupling between the different redox cycles shown in Fig. 1 may also be important. For example, sulfide reacts with iron ultimately to form pyrite, which represents a stable sink for iron and sulfide (Raiswell and Canfield, 2012). We find that our model still produces redox regime shifts when we include extra terms to simulate these sink effects (see Sect. S6).

3.2 Origin of the regime shifts

The redox regime shifts which we observe in our model arise from the interplay between nonlinear population growth, which can be limited by factors other than the chemical species being cycled, and the topology of the biogeochemical cycle. In our model, the global redox state is controlled by the balance between oxidative and reductive chemical fluxes. An increase in the availability of the auxiliary electron ac-

ceptor stimulates the oxidation reaction, resulting in an increase in concentration of the oxidized chemical species, s_o. If there were no other growth-limiting factor, this increase in s_o would stimulate the growth of the reducing microbial population, which consumes s_o; thus the global redox state would respond only gradually to changes in electron acceptor availability (and likewise for changes in the electron donor availability), as shown in Fig. 2 for small values of s_{tot} (red lines). However, the situation is different if the microbial population density is limited by other factors (such as carbon availability). In this case an increase in auxiliary electron acceptor availability increases s_o, but the reducer population cannot respond to this increase in s_o because it is already close to its maximal population density. Once the auxiliary electron acceptor supply crosses a critical threshold, the production rate of s_o exceeds the maximal consumption capacity of the reducer population and the system undergoes a regime shift to an oxidized state, as in Fig. 2 for large values of s_{tot} (blue lines). The same scenario holds in reverse for changes in the availability of the auxiliary electron donor; here, as electron donor availability increases, a redox regime shift from an oxidized to a reduced system state occurs.

4 Mapping to enzyme kinetics

Interestingly, the system-scale regime shifts that we observe in our biogeochemical models can be mapped directly onto a well-known molecular-scale phenomenon in intracellular biochemical signaling networks. In biological cells, responses to environmental signals are often mediated by phosphorylation–dephosphorylation cycles, in which a target enzyme is activated by addition of a phosphate group, and deactivated by removal of the phosphate group; the kinase and phosphatase enzymes mediating these reactions act in opposition to each other (Alberts et al., 2002). Phosphorylation–dephosphorylation cycles can exhibit "zero-order ultrasensitivity", in which they respond extremely sensitively to changes in the level of signal, because the enzymes have become saturated, decoupling the enzymatic conversion rates from the concentration of substrate (Goldbeter and Koshland, 1981). Although they act on very different length and timescales, biogeochemical cycles are topologically similar to phosphorylation–dephosphorylation cycles. In fact, one can show mathematically that our models, in the steady state, map exactly onto the classic Goldbeter–Koshland model for phosphorylation–dephosphorylation cycles (Goldbeter and Koshland, 1981), and that the regime shifts observed in our models are equivalent to the ultrasensitive signal responses predicted by this model (see Sect. S7). This raises the interesting possibility of mapping molecular-level dynamic phenomena onto biogeochemical models more generally – a direction that may prove fruitful in future work.

5 Redox regime shifts in a more realistic model

Thus far our investigation has focused on a rather simplified model for microbially mediated biogeochemical cycles. In this simple model, varying v_{ro} and v_{or} was assumed to be analogous to varying the availability of auxiliary electron acceptors (such as oxygen or nitrate) and electron donors (such as acetate or hydrogen), respectively. In reality, however, auxiliary electron acceptors or donors may be supplied, or utilized by, other biotic or abiotic processes, and thus we expect their concentrations to vary with the system dynamics. We now introduce a more ecologically realistic model in which the concentrations of the auxiliary electron acceptor/donor are explicitly represented, and allowed to vary. For this model, we find the same redox regime-shifting behavior as in the simple model described previously.

Specifically, we focus on an example in which acetate is the auxiliary electron donor and oxygen is the auxiliary electron acceptor. We suppose that acetate is produced by microbial decomposition of organic matter (long-chain organics such as lignin or cellulose; Rickard, 2012); we represent explicitly in the model not only the concentration of acetate but also the population density of the decomposer population. Likewise, we suppose that oxygen is generated by photosynthetic microorganisms; the model includes explicitly the dynamics of the photosynthesizer population as well as the oxygen concentration. External environmental inputs control the population dynamics of the decomposers and the photosynthesizers; these inputs are the organic matter concentration and the light intensity, respectively. Our model is shown schematically in Fig. 3a; we assume that oxidative and reductive processes occur in different spatial zones, represented by boxes and coupled by chemical transport of s_o and s_r. For simplicity, we consider transport only of the chemical species being cycled (s_o and s_r); allowing transport of oxygen/acetate would cause spatial shifting of the redox zones, which, although interesting, would be better investigated in a model with more detailed spatial resolution. In the model, the growth rate of the oxidizing microbial population (n_{ro}) is assumed to depend on the concentrations of both s_r and the auxiliary electron acceptor (i.e., oxygen), via a multiplicative Monod term, with explicit population density limitation, and the equivalent scenario holds for the reducer population. Multiplicative Monod kinetics is the most widely used method of modeling microbial growth limitation by multiple substrates (Moore et al., 2002; Jin and Bethke, 2005). However we note that Liebig's law of the minimum provides an alternative (Saito et al., 2008), which would not affect our qualitative results. Our model also includes a linear loss term for the auxiliary electron acceptors or donors, which represents competitive consumption by other populations. Full details and dynamical equations for this model are presented in Sect. S8.

Our simulations show that this model indeed undergoes redox regime shifts (Fig. 3b). In particular, the system re-

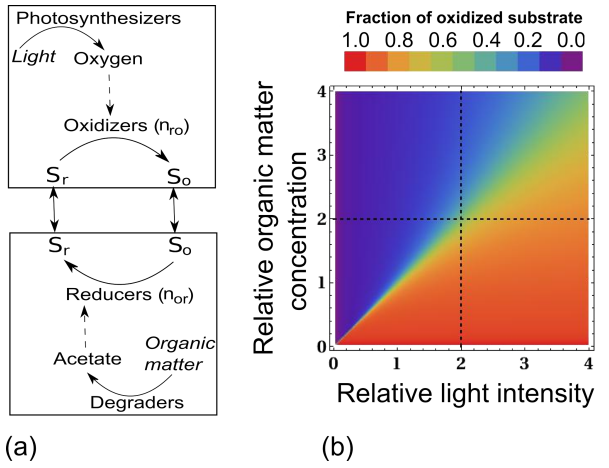

Figure 3. Redox regime shifts in a "complete ecosystem" model. **(a)** Illustration of the model. Oxidative and reductive processes take place in separate spatial zones, linked by chemical diffusion. The model explicitly represents the population dynamics of microbial photosynthesizers, decomposers, reducers, and oxidizers, and the chemical dynamics of oxygen, s_o, s_r, and acetate. Light intensity and organic matter availability are treated as control parameters. The dynamical equations corresponding to the model are presented in Sect. S8, Eqs. (S45)–(S54); these are integrated numerically to find the steady-state solution. Parameter values are also listed in the Supplement. **(b)** Steady-state solution of the model illustrated in **(a)**, obtained numerically, plotted as a function of the control parameters, light intensity (relative to the typical value 10 µE s^{-1} m^{-2}; Huisman et al., 2006) and organic matter concentration (relative to the typical value 100 mg cm^{-3}; Allison et al., 2010). The color represents the global redox state (see color key). The model shows redox regime shifts as the organic matter concentration is varied at fixed light intensity (vertical dashed line) or as the light intensity is varied at fixed organic matter concentration (horizontal dashed line).

dox state, as measured by the ratio s_o/s_{tot} (shown by color in Fig. 3b), changes sharply in response to changes in either organic matter availability (which stimulates the decomposer population and hence the reducer population), or to changes in light intensity (which stimulates the photosynthesizers and hence the oxidizer population). As organic matter availability increases at fixed light intensity (vertical dashed line in Fig. 3b), the redox state of the system changes sharply from oxidized to reduced (red to purple). Likewise, as the light intensity increases for fixed organic matter concentration (horizontal dashed line in Fig. 3b), the redox state also undergoes a regime shift, in this case from reduced (purple) to oxidized (red). We observe similar regime-shifting behavior in equivalent models where the oxidation step is abiotic (see Sect. S8). We have also shown that the qualitative behavior of the model is not dependent on the strength of the loss term representing competition for auxiliary electron acceptors/donors (see Sect. S10).

Since many natural redox cycles involve intermediate steps between the most oxidized and most reduced states (e.g., the nitrogen and sulfur cycles in Fig. 1), we have also simulated a version of the model which includes a redox state intermediate between s_o and s_r. This model also shows regime shifts between predominantly oxidized and predominantly reduced system states (see Sect. S9).

6 Conditions for redox regime shifts

Our analysis provides a clear set of criteria that need to be satisfied for redox regime shifts to occur. These are as follows:

1. The density of the redox-cycling microbial populations must ultimately be limited by a factor other than the concentration of the chemical element being cycled. This factor could be the concentration of another nutrient (see Sect. S4), or space limitation. It is important to note, however, that the population density need not be small; large populations are also predicted to show regime shifts, albeit with longer response times.

2. The total concentration of the element being cycled must be high enough to saturate the growth rates of the microbial reducers and oxidizers (or the abiotic oxidation reaction): $s_{tot} \gg K_{or}$, K_{ro}, K_a. This ensures that the growth of the redox-cycling populations will become saturated with respect to s, causing a switch-like response to changes in auxiliary electron acceptor or donor availability (as in Fig. 2).

3. The growth rates of the redox-cycling populations must be unsaturated with respect to the concentrations of the auxiliary electron acceptor and/or donor, so that the system responds to changes in auxiliary electron acceptor or donor availability.

7 Are redox regime shifts likely in the natural environment?

Thus far we have established our model, demonstrated that the predicted redox regime shift is robust as complications are introduced, and defined the conditions required for redox regime shifts to occur. We now assess whether these conditions are likely to be prevalent in the natural environment.

7.1 Condition 1: a factor exists that ultimately limits population density

In the natural environment, there are many possible limiting factors for microbial population density. Microbial growth requires sources not only of energy but also of carbon, nitrogen, phosphorus, sulfur, and other, trace biomass components (Madigan et al., 2009; Ingraham et al., 1983).

For redox-cycling microbial populations, the redox reaction provides an energy source, but cannot satisfy all the requirements for formation of biomass. It is thus almost inevitable that growth is ultimately limited by the availability of biomass components rather than the redox species. Indeed, carbon limitation is common in microbial soil/sediment communities (Demoling et al., 2007), while in ocean communities nitrogen or phosphorus is often growth-limiting (Mills et al., 2008).

7.2 Condition 2: high concentration of the chemical element being cycled

Our second condition states that $s_{tot} \gg K_{or}, K_{ro}$ (i.e., the oxidizer/reducer growth rate must be saturated with respect to s_r or s_o). To assess whether this condition is fulfilled in the natural environment, we surveyed measured values of the half-saturation constants K_{or} or K_{ro} for redox-cycling microorganisms reported in the literature, and compared these values with typical concentrations of the chemical species being cycled, in various environmental settings. The results of this survey are shown in Table 2. For sulfur-cycling organisms, these data suggest that the concentration of the chemical species being cycled can exceed the half-saturation constant of the relevant microbial populations, $s_{tot} \gg K_{or}, K_{ro}$. For example, marine sulfate reducers are generally not limited by sulfate, because sulfate is highly abundant (indeed it is the second most abundant anion in the oceans; Goldhaber, 2003). For nitrogen-cycling organisms these data suggest that redox regime shifts are unlikely to occur in "typical" nitrogen-cycling environments, such as the open ocean. However, there are many examples where anthropogenic influences such as agricultural runoff can lead to very high concentrations of nitrate such as lakes or groundwater aquifers. For example, groundwater sources often contain in excess of 400 µM nitrate. Data on the proportion of groundwater bodies across the EU in 2003 with a mean nitrate concentration in excess of 400 µM reported 80 % in Spain, 50 % in the UK, 36 % in Germany, 34 % in France, and 32 % in Italy (Rivett et al., 2008). Such high nitrate levels exceed the relevant half-saturation constant of 10 µM, and for this reason, we would expect redox regime shifts in the nitrogen cycle to occur in eutrophic terrestrial ecosystems.

In contrast, our data survey suggests that redox regime shifts are unlikely to be associated with carbon cycles, because the typical half-saturation constant for methanogenesis is large relative to typical environmental concentrations of acetate.

For the iron cycle, our survey suggests that redox regime shifts are unlikely in modern-day environments, but may have occurred in the past. While modern oceanic concentrations of dissolved Fe^{2+} ions are low, the ancient oceans may have contained high concentrations of Fe^{2+} (≈ 1 mM), suggesting that redox regime shifts could have occurred in the comparatively iron-rich Archean or Proterozoic iron cycles (Canfield, 1998).

7.3 Condition 3: low auxiliary electron acceptor or donor availability

Condition 3 states that, for biotic redox reactions, the concentration of the auxiliary electron donor or acceptor must be low enough that changes in their availability affect the growth rate of the microbial reducers/oxidizers (i.e., the oxidative and reductive microbial metabolic reactions must be unsaturated with respect to the auxiliary electron acceptor/donor).

Biotic reduction processes often take place in the presence of strong competition for auxiliary electron donor, for example, sulfate-reducing microorganisms typically compete with methanogens for acetate (Muyzer and Stams, 2008). The concentration of acetate in freshwater sediments is typically about 1 µM (Roden and Wetzel, 2003) but can be as high as 100 µM (Burdige, 2002). This compares to approximate half-saturation constants for growth with respect to acetate of 70 µM for sulfate reduction and 12 µM for methanogenesis (Roden and Wetzel, 2003; Ingvorsen et al., 1984), suggesting that indeed these reactions are very likely to be unsaturated with respect to acetate.

For oxidative processes, oxygen is the most widely used auxiliary electron acceptor. The supply of oxygen is expected to be rate-limiting for growth in oxygen-poor environments (which are becoming more common in the coastal oceans; Diaz and Rosenberg, 2008). The half-saturation constant with respect to oxygen for bacterial sulfide oxidation is 1–20 µM (Klok et al., 2012; González-Sánchez and Revah, 2007), and while the concentration of oxygen in oxygen-saturated (i.e., fully aerated) water is 0.3 mM (Kamyshny et al., 2011), significant competition for oxygen means that the concentration is much lower in many environments (Shaffer et al., 2009). It is interesting to note that oxygen concentrations were also low in the Proterozoic and Archean oceans (Canfield, 1998).

Taken together, this analysis suggests that the redox regime shifts predicted by our model are likely to be relevant in the present-day natural environment, with respect to the sulfur and nitrogen cycles, and may also have played a role in iron cycling in the iron-containing Proterozoic and Archean oceans.

7.4 What perturbations might cause redox regime shifts?

How likely are the changes in auxiliary electron acceptor/donor concentrations that could trigger redox regime shifts in biogeochemical cycles? Focusing on oxygen as the most significant natural auxiliary electron acceptor, oxygen concentrations in oceans or inland water bodies can be affected by temperature changes (for example, a 4.8 °C global

Table 2. Typical values for the half saturation constants K_{or} or K_{ro} for microbial growth, for various nutrient-cycling organisms, compared to typical values for the concentrations of the relevant nutrients in marine environments. All values are given rounded to an order of magnitude.

Nutrient cycle	Reaction	Organism	K_{or} or K_{ro}	Concentration range
Sulfur	$H_2S \rightarrow SO_4^{2-}$	*Thiothrix* or *Thiobacillus*	1 µM (Canfield et al., 2005)	$0.1\,\mu M \leq [H_2S] \leq 100\,\mu M$ (Goldhaber, 2003)
	$SO_4^{2-} \rightarrow H_2S$	*Desulfovibrio*	1 µM (Ingvorsen and Jorgensen, 1984; Tarpgaard et al., 2011)	$0.1\,\mu M \leq [SO_4^{2-}] \leq 10\,mM$ (Goldhaber, 2003)
Iron	$Fe^{2+} \rightarrow Fe^{3+}$	*Thiobacillus ferrooxidans*	1 mM (Wichlacz and Unz, 1985)	$1\,pM \leq [Fe^{2+}] \leq 100\,\mu M$ (Landing and Bruland, 1987; Canfield et al., 1993)
	Fe(III) oxide $\rightarrow Fe^{2+}$	*Shewanella putrefaciens*	1 mM (Bonneville et al., 2004)	$0.1\,\mu M \leq$ [Fe(III) oxide] $\leq 10\,mM$ (Thamdrup and Canfield, 1996; Canfield et al., 1993)
Carbon	$CH_4 \rightarrow CO_2$	*Methylocystis*	0.1 µM (Baani and Liesack, 2008)	$1\,nM \leq [CH_4] \leq 100\,\mu M$ (Reeburgh, 2007)
	$CH_3CO_2^- \rightarrow CH_4$	*Methanosarcina*	1 mM (Dale et al., 2006)	$0.1\,\mu M \leq [CH_3CO_2^-] \leq 100\,\mu M$ (Burdige, 2002)
Nitrogen	$NH_4^+ \rightarrow NO_3^-$	*Nitrosomonas*	1 µM (Koper et al., 2010)	$0.01\,\mu M < [NH_4^+] \leq 100\,\mu M$ (Rees et al., 2006; Blackburn et al., 1993)
	$NO_3^- \rightarrow NO_2^-$	*Flavobacterium*	10 µM (Betlach and Tiedje, 1981)	$0.01\,\mu M < [NO_3^-] \leq 10\,\mu M$ (Rees et al., 2006; Blackburn et al., 1993)

temperature increase has been predicted to cause a 68 % reduction in the mean oceanic oxygen concentration; Shaffer et al., 2009) and by perturbations which affect the balance between photosynthesis and oxygenic respiration, such as eutrophication (which can lead to drastic increases of biomass, generating "oxygen minimum zones"; Diaz and Rosenberg, 2008). Furthermore, over Phanerozoic time, pO_2 varied between 15 and 37 %, which represents a variation large enough to generate redox regime shifts (Berner, 1999). Further work could parameterize our model to investigate whether a redox regime shift is possible within the range of published values for atmospheric oxygen and oceanic iron and sulfate on the early Earth, taking into account the evidence for the progressive changes in these parameters through geologic time from the Paleoproterozoic to the Phanerozoic.

The availability of auxiliary electron donors (such as acetate, lactate, or hydrogen) is expected to be altered by changes in the rate of organic matter degradation, which has been predicted to increase with temperature (Conant et al., 2011), and is also sensitive to changes in the abundance of organic matter due to sewage or phosphorus influx (Todd-Brown et al., 2012). Changes in electron donor availability could also arise due to competition effects, such as reductive degradation of pollutants (Beaudet et al., 1998), or perturbations in other biogeochemical cycles. This raises the interesting possibility that a redox regime shift in one biogeochemical cycle could trigger shifts in others, due to changes in the level of competition for auxiliary electron donors.

Furthermore, it is possible that redox regime shifts could occur in response to changes in the inflow rates of auxiliary electron donors and acceptors, instead of changes in the growth rates of the microbial populations within the environment that supply them. It is highly likely that such a system would produce redox regime shifts in response to variation in these fixed input rates. For example, future models could look at whether seasonal temperature-induced mixing effects can generate redox regime shifts.

8 Discussion

Microbial populations are key mediators of the Earth's biogeochemical cycles (Falkowski et al., 2008). Our work shows that microbial population dynamics can have important consequences for the response of biogeochemical cycles to environmental changes. Under circumstances where the microbial population density is limited by factors other than the concentration of the chemical being cycled (e.g., by the concentration of another limiting nutrient), our models predict that redox-cycling systems can undergo regime shifts in their predominant redox state in response to small changes in the availability of auxiliary electron acceptors or donors (such as oxygen and acetate), which drive the oxidative and reductive redox-cycling reactions, respectively. These regime

shifts arise from the interplay between the nonlinearity of microbial population dynamics, multiple nutrient limitation, and the cyclic system topology. Diverse environmental perturbations are expected to affect the availability of auxiliary electron acceptors and donors, including temperature-mediated changes in oxygen solubility and changes in organic matter abundance due to eutrophication, suggesting that these redox regime shifts may be common in the natural environment.

Regime shifts are a well-known phenomenon in many ecosystems (Scheffer et al., 2009), including microbial ecosystems (Bürgmann et al., 2011). They are known to occur in biogeochemical cycles (Blodau and Knorr, 2006) and have played an important role in the Earth's history – a notable example being the transition to an oxic atmosphere around 2.3 Ga (Lenton and Watson, 2011). Our work suggests a new mechanism by which regime shifts may occur in microbially mediated biogeochemical cycles. This mechanism is identified here in a very simple and generic model but also shown to exist in more realistic models. Further work could extend our models to include detailed spatial or temporal dynamics and/or additional environmental variables such as temperature or pH.

Our analysis also predicts clear criteria for the conditions under which redox regime shifts should be expected. By analyzing parameter values for a range of natural environments, we show that these criteria are likely to be satisfied for the natural sulfur and nitrogen cycles. This phenomenon may also be relevant for iron cycling in the Archean or Proterozoic oceans, due to their much lower oxygen concentrations and potentially much higher concentrations of iron than present-day oceans. Indeed, redox regime shifts may even help to explain changes in the Earth's biogeochemical cycles associated with mass extinction events, such as the rise in ocean sulfide levels during the end-Permian extinction event (251 Ma), which is believed to have poisoned the oceans and killed as much as 90 % of all macroscopic species on Earth (Benton and Twitchett, 2003). More generally, our work reveals that microbial population dynamics can lead to qualitative changes in the behavior of biogeochemical cycles, with significant system-level consequences. Better understanding of microbial population dynamics is vital for accurate prediction of the effects of anthropogenic changes on the Earth's systems, both on small and large scales.

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