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Key Points:

- Sulfur cycling drives phosphorus (P) release from modern anoxic sediments to overlying seawater
- In a high-sulfate, high-O₂ world, P regeneration stabilizes atmospheric O₂ on long timescales, but amplifies transient ocean anoxic events
- In a low-sulfate, low-O₂ world, P regeneration amplifies transient atmosphere oxygenation events

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A Double-Edged Sword: The Role of Sulfate in Anoxic Marine Phosphorus Cycling Through Earth History

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Abstract Modern anoxic marine sediments release phosphorus (P) to seawater, driving feedbacks at multiple timescales. On sub-Myr timescales, anoxic P regeneration amplifies ocean deoxygenation; on multi-Myr timescales, it stabilizes atmospheric O₂. Some authors have extended this thinking to the Precambrian: by analogy, widespread ocean anoxia would imply extensive P regeneration from sediments. However, this neglects the role of sulfate in P regeneration. While abundant in seawater today, sulfate was scarce in the Precambrian. Here a simple model is used to isolate the role of sulfate in anoxic P cycling. The model reproduces known feedbacks driven by anoxic P regeneration in a high-sulfate world, but shows muted P regeneration in low-sulfate, anoxic sediments. The transition between “limited” and “enhanced” P regeneration is thus controlled by sulfate. As a result, sulfate is a double-edged sword wielded by the anoxic P cycle: it can amplify oxygenation or deoxygenation depending on environmental context.

Plain Language Summary Phosphorus is a critical nutrient and its availability controls the rate of biological productivity in the ocean. Constraining phosphorus availability in seawater through time is thus of great interest to paleoceanographers. A key observation in recent years has been that ancient marine sediments from the Precambrian Era (prior to 541 million years ago) contain less phosphorus than younger sediments. Researchers disagree as to why this is, with proposed ideas falling into two main camps. One camp maintains that phosphorus burial was efficient in the Precambrian, meaning that phosphorus was quickly removed from seawater, creating a small ocean inventory and keeping sedimentary phosphorus levels low. Another camp suggests that Precambrian phosphorus burial was inefficient, causing sediments to have low phosphorus content, instead allowing phosphorus to accumulate to high levels in seawater. Here a simple model is used to reconcile these contrasting hypotheses. The model examines the effect of sulfate on phosphorus burial efficiency in anoxic sediments, finding that lower sulfate levels imply higher burial efficiency, and vice-versa. The contrasting hypotheses for Precambrian phosphorus burial can thus both potentially be accurate, and this exercise highlights the importance of constraining marine sulfate levels to know more about the ancient phosphorus cycle.

1. Introduction

Phosphorus (P) is the ultimate limiting nutrient for marine photosynthesis (Tyrrell, 1999). Earth historians have thus spent decades trying to reconstruct the evolution of the marine P reservoir. In lieu of multiple stable isotopes, most efforts use the P concentration of marine sediments—or specific sedimentary P phases (Ruttenberg, 1992; Thompson et al., 2019)—to gain insights into P burial during transient perturbations (e.g., OAE's; Handoh & Lenton, 2003; Mort et al., 2007; Kraal et al., 2010) or long-term secular evolution (e.g., Precambrian; Reinhard et al., 2017). A key observation emerging from this work is that Precambrian siliciclastic marine sediments have lower P contents than Phanerozoic equivalents (Reinhard et al., 2017). While this signal clearly represents low P burial, authors disagree as to why.

Some contend that the Precambrian marine P reservoir was smaller, due to either P scavenging by Fe minerals in an Fe-rich ocean (Bjerrum & Canfield, 2002; Derry, 2015; Laakso & Schrag, 2014; Reinhard et al., 2017) or limited P recycling (i.e., high organic burial efficiency; Kipp et al., 2021) in an oxidant-poor ocean (Kipp & Stüeken, 2017; Laakso & Schrag, 2018). In these scenarios for a smaller marine P reservoir—and thus less productive marine biosphere—diminished P burial on continental shelves reflects the proportionally smaller P export flux to sediments. Another way of framing these models is that P burial was efficient in the Precambrian.

Others, citing modern and Phanerozoic anoxic sediments as analogs (Ingall et al., 1993; Ingall & Jahnke, 1994), infer that Precambrian shales record inefficient P burial due to enhanced P recycling from anoxic sediments

(Alcott et al., 2019; Lenton et al., 2014; Poulton, 2017). In this scenario, P recycled from anoxic sediments back to seawater sustained higher-than-modern productivity. Thus, despite higher P export to continental shelves under a higher-productivity marine biosphere, most P was lost from these sediments during diagenesis.

These two views of anoxic P cycling, *limited P recycling* and *enhanced P recycling*, have quite different implications for the Precambrian Earth system. Here, a simple model is used to place these disparate scenarios on a single continuum. To do so, the role of sulfate in anoxic P cycling is considered. While prior modeling has used modern anoxic settings as analogs for the Precambrian ocean, that work has not accounted for shifts in marine sulfate concentration that have occurred. As sulfate directly and indirectly impacts P burial, this is a crucial variable to examine.

The calculations presented here demonstrate that both *limited P recycling* and *enhanced P recycling* can occur in anoxic marine systems, with the sulfate concentration acting as a switch between these two states. This model thus links the proposed mechanisms for limited Precambrian P burial, emphasizing the importance of constraining marine sulfate levels to better understand the P cycle in deep time. Furthermore, these findings suggest that changes in sedimentary P burial could have been driven by waxing and waning of the marine sulfate reservoir, as has recently been argued (Alcott et al., 2022; Kipp et al., 2020; Laakso et al., 2020).

2. Background

2.1. The Marine P Cycle

Phosphorus is predominantly delivered to seawater via continental weathering. Of this riverine flux, <50% is “reactive” bioavailable P (Ruttenberg, 2003); the remainder is particulate P that enters estuarine or marine sediments without participating in biological reactions.

Bioavailable P is consumed by primary producers in the photic zone, creating a phosphate minimum. Remineralization of biomass in the water column regenerates P, causing $[\text{PO}_4^{3-}]$ to increase with depth, that is, a “nutrient-type” profile (Broecker & Peng, 1982). Regeneration of P within the ocean ($\sim 1,200$ Tg/yr)—including both water column and sediment porewaters—vastly outweighs riverine input (~ 2 Tg/yr) (Schlesinger & Bernhardt, 2013). Thus, most marine productivity is sustained by nutrient recycling within the ocean.

The dominant source of P to typical marine sediments is export production—that is, biomass that escapes water column remineralization. In some settings, P adsorption to Fe-(oxyhydr)oxides is an additional source (Berner, 1973). Another minor source is detrital P that has not participated in biological cycling.

In sediments these P phases undergo chemical transformations, occasionally exchanging P (“sink switching”). Of initial importance are reactions liberating P from the phases that brought it to sediments. The most prevalent of these is organic matter remineralization, which releases P into porewaters. As will become important, remineralization can occur aerobically or anaerobically, in both cases liberating P. Another important reaction is Fe-(oxyhydr)oxide dissolution; in anoxic and sulfidic (“euxinic”) environments, Fe-(oxyhydr)oxides undergo reductive dissolution and the liberated Fe can form Fe-sulfides (Canfield, 1989). As P neither coprecipitates with nor adsorbs to Fe-sulfides (Krom & Berner, 1980), this can release P into porewaters and ultimately seawater (although P can become secondarily sequestered in Fe(II)-phosphates, for example, vivianite, März et al., 2018; see below).

On the flip side of P release to porewaters is sequestration in authigenic minerals. One pathway is adsorption to Fe-oxides in porewaters that sit above the redox threshold for Fe reduction. This can mean that P released lower in sediments is sequestered closer to the sediment-water interface. However, redox fluctuations can lead to dissolution of these phases, ultimately releasing P to seawater. Another pathway for P sequestration is authigenic apatite precipitation (Ruttenberg & Berner, 1993). On long timescales, apatite is more stable than organic-P or Fe-P phases, thus providing an important route for ultimate P burial in marine sediments. Phase-specific P analyses of recent (Ruttenberg, 1992) and Precambrian (Thompson et al., 2019) samples show that these phases (detrital apatite, authigenic apatite, Fe-bound P, organic-bound P) represent the major host phases for P in marine sediments and sedimentary rocks.

2.2. Redox Sensitivity of P Burial in Marine Sediments

Many of the processes described above are redox-sensitive. This begs the question: what is the net effect of redox on P burial in marine sediments? This question has received considerable attention since the 1990's, beginning with a study noting that C/P ratios in Paleozoic shales were higher in anoxic than oxic beds (Ingall et al., 1993). Subsequent work in modern settings similarly showed higher C/P in anoxic than oxic marine sediments (Ingall & Jahnke, 1994). Since then, a slew of studies has corroborated and expanded upon the finding that P is released from anoxic marine sediments (Algeo & Ingall, 2007; Anderson et al., 2001; Colman & Holland, 2000; Ingall & Jahnke, 1997; März et al., 2014; McManus et al., 1997; Mort et al., 2010; Rozan et al., 2002; Schenau et al., 2001).

Here it is important to unpack those observations: how do we know P is less efficiently buried in anoxic than oxic sediments? A useful datum to track is the C/P ratio, and specifically $C_{\text{org}}/P_{\text{tot}}$, where the numerator represents organic C, and the denominator total P. As organic matter is remineralized, P can be selectively liberated if P-rich molecules are more quickly degraded than P-poor components (Clark et al., 1998). This preference may itself be redox-sensitive, as aerobic remineralization appears to preserve $C_{\text{org}}/P_{\text{org}}$ (Anderson & Sarmiento, 1994), while anoxic sediments have high $C_{\text{org}}/P_{\text{org}}$ (Anderson et al., 2001). In any case, as P is released from biomass, $C_{\text{org}}/P_{\text{org}}$ can increase.

The $C_{\text{org}}/P_{\text{tot}}$ ratio depends on whether liberated P is retained in sediments or lost to seawater. If not retained in authigenic mineral phases, P will escape to overlying waters, driving $C_{\text{org}}/P_{\text{tot}}$ higher. High $C_{\text{org}}/P_{\text{tot}}$ in modern anoxic sediments (Algeo & Ingall, 2007) suggests that retention of P in authigenic phases is muted under anoxic conditions. As noted above, the most important early authigenic host phases for P are Fe minerals and authigenic apatite. So what inhibits P incorporation into these phases in modern anoxic sediments?

As discussed above, the presence of H_2S following microbial sulfate reduction (MSR) has important effects on P sink-switching. Dissolution of Fe-(oxyhydr)oxides and formation of authigenic Fe-sulfides can both liberate P to porewaters and eliminate potential binding sites. The availability of sulfate to fuel MSR—and generate H_2S —is thus critically important. Indeed, low-sulfate lakes retain P in anoxic sediments (Caraco et al., 1989). The reasons for this may include: diminished Fe-sulfide formation, enabling precipitation of authigenic Fe(II)-phosphates (Xiong et al., 2019), greater apatite authigenesis in non-euxinic conditions (Papadomanolaki et al., 2022), and limited organic remineralization due to muted sulfate reduction. Whatever the mechanism(s), sulfate affects whether P is released or retained by anoxic sediments.

This framework can be considered in the context of Earth history. For ~400 Myr (Lenton et al., 2017), $p\text{O}_2$ has remained within a factor ~2 of modern (0.21 bar). Under this oxygenated atmosphere, oxidative weathering delivers appreciable sulfate to the ocean, and the marine sulfate reservoir has remained large ($[\text{SO}_4^{2-}] = 3\text{--}30\text{ mM}$; Algeo et al., 2015) with a $\sim 10^7$ yr residence time (Claypool et al., 1980). In this regime, the seafloor is pervasively oxygenated; in localized settings with anoxic bottom waters, there is abundant sulfate to fuel MSR and drive P recycling from sediments to seawater.

In contrast, in Earth's early history, prior to the Great Oxidation Event (GOE), SO_4 was scarce in seawater ($[\text{SO}_4^{2-}] = \sim 3\text{ }\mu\text{M}$; Crowe et al., 2014). In such an ocean, sediments would have been anoxic, but lacking SO_4 to drive MSR. Thus, Archean sediments likely did not release P to overlying waters as in modern anoxic settings. The purpose of this modeling exercise is to isolate this effect of sulfate in anoxic sedimentary P cycling through Earth history.

3. Model

3.1. Model Architecture

A simple model is employed that distills elements of approaches taken by Van Cappellen and Ingall (1996), Tsandev and Slomp (2009), and Alcott et al. (2019). Detailed analyses of spatial heterogeneity, precise thresholds/coefficients for fluxes, and specific events in Earth history are beyond the scope of this exercise. Rather, the goal in utilizing a pared-down, one-box model here is to constrain the process of interest (sulfate-driven anoxic P cycling) in direction and magnitude.

The ocean is considered a single reservoir with inputs and outputs of phosphorus, sulfur, and oxygen, governed by the equations

$$\frac{d(P_{sw})}{dt} = J_{riv_P} - J_{oxic_P} - J_{anoxic_P} \quad (1)$$

$$\frac{d(SO_{4sw})}{dt} = J_{riv_SO4} + J_{phot_SO4} - J_{sulfide} - J_{evap_SO4} \quad (2)$$

$$\frac{d(O_{2sw-atm})}{dt} = J_{orgC_O2} + J_{sulfide_O2} - J_{O2_weathering} - J_{reduced_outgassing} \quad (3)$$

Rivers deliver P to the ocean (J_{riv_P}), which is buried in oxic (J_{oxic_P}) and anoxic (J_{anoxic_P}) sediments, with P_{sw} denoting the size of the marine P reservoir. Sulfate is likewise delivered to seawater by rivers (J_{riv_SO4}), and a term (J_{phot_SO4}) is included to represent atmospheric photolysis of volcanic SO_2 and/or photochemical sulfide oxidation (Hao et al., 2022), which may have been important in the Archean. Sulfur is buried as sulfide following MSR ($J_{sulfide}$) or as sulfate evaporites ($J_{sulfate_evap}$), with SO_{4sw} denoting the size of the marine sulfate reservoir. Since the atmosphere holds $\sim 10^2$ times more O_2 than the ocean, and equilibrates with the ocean on timescales (\sim yr) shorter than those considered here, the ocean-atmosphere system is the O_2 reservoir. Oxygen is produced via organic carbon (J_{orgC_O2}) and sulfide ($J_{sulfide_O2}$) burial, and consumed today principally via oxidative weathering ($J_{O2_weathering}$). An O_2 sink from reduced volcanic gases ($J_{reduced_outgassing}$) is included in the Archean.

The fluxes are calculated as follows. The fluxes J_{riv_P} , J_{phot_SO4} , and $J_{reduced_outgassing}$ are used to force the model, and values are thus designated for each run. P burial is partitioned

$$J_{oxic_P} = (1 - f_{anoxic}) \frac{J_{orgC_burial}}{CP_{Redfield}} \quad (4)$$

$$J_{anoxic_P} = (f_{anoxic}) \frac{J_{orgC_burial}}{CP_{anoxic}} \quad (5)$$

where $CP_{Redfield}$ is C_{org}/P_{org} of phytoplankton (106; Redfield, 1934), and CP_{anoxic} is C_{org}/P_{tot} of anoxic sediments. To capture the dependence on sulfate, CP_{anoxic} is calculated

$$CP_{anoxic} = CP_{anoxic_modern} \frac{SO_{4sw}}{k_{SO4} + SO_{4sw}} \quad (6)$$

where $CP_{anoxic_modern} = 4,000$ (Lenton et al., 2017). A Monod expression was utilized because it relates MSR rate to $[SO_4^{2-}]$ ($k_{SO4} = 100 \mu M$; Pallud & Van Cappellen, 2006). The extent of P regeneration from anoxic sediments is thus controlled by MSR, though both direct (P liberation from organic matter) and indirect (H_2S production) effects of MSR impact CP_{anoxic} . In any case, it is the CP_{anoxic} versus $[SO_4^{2-}]$ relationship (Figure 1c) that is of interest; k_{SO4} and CP_{anoxic_modern} can be varied (Boudreau & Westrich, 1984; Targaard et al., 2011), but the directionality of observed feedbacks remains the same (only the amplitude changes).

The term f_{anoxic} denotes the fraction of the seafloor overlain by anoxic waters. Here, organic C burial in oxic versus anoxic sediments linearly scales with f_{anoxic} (Equations 4 and 5). This is an over-simplification, as organic C export is higher on continental shelves, particularly in modern anoxic settings. However, neglecting this correlation means that if anything these calculations under-estimate the importance of CP_{anoxic} in driving feedbacks in the marine P cycle, because actual organic export to anoxic sediments is higher than considered. Following Lenton et al. (2017), f_{anoxic} is calculated

$$f_{anoxic} = \frac{1}{\exp(-k_{anox} * (k_U * \left(\left(\frac{P_{sw}}{P_{sw_modern}} \right) - \left(\frac{O_{2sw-atm}}{O_{2sw-atm_modern}} \right) \right))} \quad (7)$$

where k_{anox} sets the sharpness of the oxic-anoxic transition and (with k_U) the modern anoxic extent. Here, $k_{anox} = 12$ and $k_U = 0.5$ (Lenton et al., 2017, Figure 1a).

Marine net primary productivity (NPP) is proportional to the marine P reservoir

$$NPP = NPP_{modern} \left(\frac{P_{sw}}{P_{sw_modern}} \right) \quad (8)$$

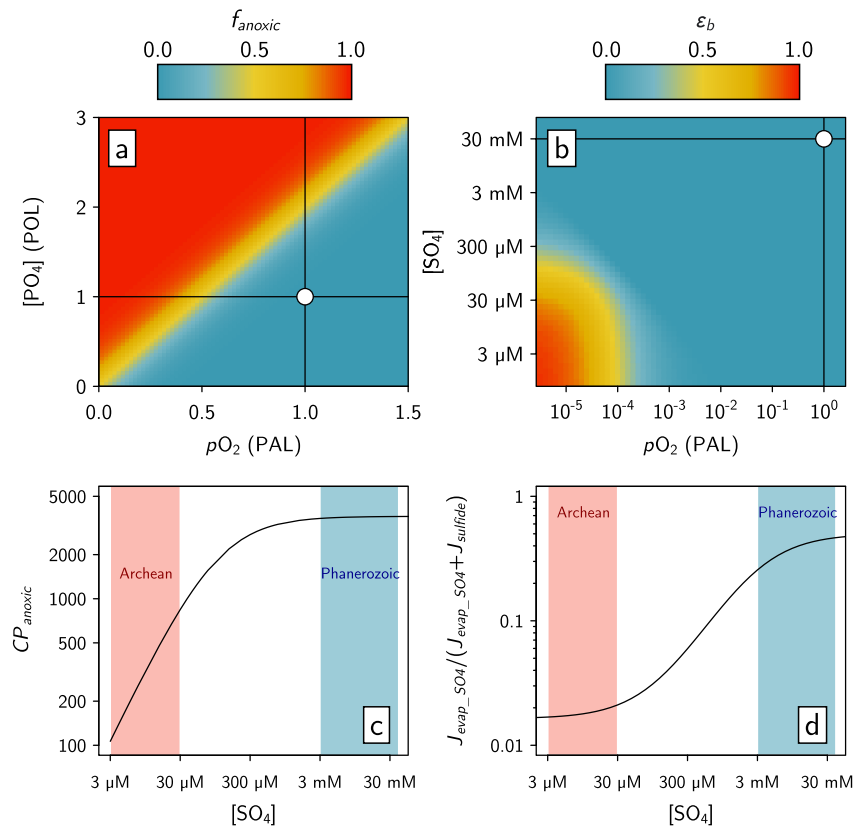


Figure 1. Parameterizations of (a) seafloor anoxia (f_{anoxic}), (b) organic burial efficiency (ϵ_b), (c) C_{org}/P_{tot} in anoxic sediments (CP_{anoxic}), and (d) sulfate evaporite burial ($J_{evap_SO4}/(J_{evap_SO4} + J_{sulfide})$). Equations are given in the text. PAL = present atmospheric level; POL = present oceanic level.

where NPP_{modern} is 4,000 Tmol C/yr (Field et al., 1998) and P_{sw_modern} is 2,900 Tmol (Ruttenberg, 2003). The assumption of P-limited productivity means that these simulations only apply to the Earth after the origin of oxygenic photosynthesis, when electron donors were no longer limiting (Canfield et al., 2006; Kharecha et al., 2005; Ward et al., 2019). The C reservoir of the ocean-atmosphere system is not tracked, as it is assumed that primary productivity is limited by P not C, and effects of changing pCO_2 are not considered here.

Organic C burial (J_{orgC_burial}) is calculated

$$J_{orgC_burial} = \epsilon_b(NPP) \quad (9)$$

where ϵ_b is organic carbon burial efficiency in marine sediments. Modern burial efficiency (ϵ_{b_modern}) of $\sim 0.7\%$ achieves steady state when utilizing literature estimates for other fluxes. This agrees with other estimates ($0.1\% < \epsilon_b < 1\%$; Holland, 1984; Hedges & Keil, 1995; Middelburg, 2019). Burial efficiency was likely higher in the oxidant-poor Precambrian ocean (perhaps 10's of percent; Katsev & Crowe, 2015; Kipp et al., 2021; Krissansen-Totton et al., 2021); this is captured by allowing ϵ_b to increase as a function of $[O_2]$ and $[SO_4^{2-}]$

$$\epsilon_b = \begin{cases} 1 - \text{resp}_{O_2} - \text{resp}_{SO_4} & \epsilon_b > \epsilon_{b_modern} \\ \epsilon_{b_modern} & \epsilon_b \leq \epsilon_{b_modern} \end{cases} \quad (10)$$

$$\text{resp}_{O_2} = \frac{O_{2_sw-atm}}{k_{O_2}(O_{2_sw-atm_modern}) + O_{2_sw-atm}} \quad (11)$$

$$\text{resp}_{SO_4} = \frac{SO_{4_sw}}{k_{SO_4} + SO_{4_sw}} \quad (12)$$

where Equations 11 and 12 are Monod expressions for aerobic respiration ($k_{O_2} = 10^{-4}$; Alcott et al., 2019) and MSR (as in Equation 6) (Figure 1b).

Riverine sulfate input ($J_{riv_SO_4}$) is calculated

$$J_{riv_SO_4} = J_{riv_SO_4_modern} \sqrt{\frac{O_{2_sw-atm}}{O_{2_sw-atm_modern}}} \quad (13)$$

reflecting a $pO_2^{0.5}$ relationship of oxidative weathering (Chang & Berner, 1999). Sulfur burial is calculated

$$J_{evap_SO_4} = J_{evap_SO_4_modern} \left(\frac{SO_{4_sw}}{k_{gypsum} + SO_{4_sw}} \right) \quad (14)$$

$$J_{sulfide} = J_{sulfide_modern} \left(\frac{SO_{4_sw}}{k_{SO_4} + SO_{4_sw}} \right) \quad (15)$$

where k_{gypsum} relates sulfate evaporite deposition to $[SO_4^{2-}]$. As sulfate evaporites are absent in the Archean, k_{gypsum} is tuned to give negligible $J_{evap_SO_4}$ at μM $[SO_4^{2-}]$ (Figure 1d). Sedimentary sulfide deposition follows MSR (Equation 6). These rate constants give sub-equal $J_{evap_SO_4}$ and $J_{sulfide}$ under modern conditions, while $J_{sulfide}$ dominates (>98%) under Archean conditions (Figure 1d).

Finally, O_2 source fluxes are calculated

$$J_{orgC_O_2} = J_{orgC_burial} \quad (16)$$

$$J_{sulfide_O_2} = 2 * J_{sulfide} \quad (17)$$

following the 1:1 O_2 :C stoichiometry of organic C burial and 2:1 O_2 :S stoichiometry of sulfide burial. Oxidative weathering is calculated

$$J_{O_2_weathering} = J_{O_2_weathering_modern} \sqrt{\frac{O_{2_sw-atm}}{O_{2_sw-atm_modern}}} \quad (18)$$

following Chang and Berner (1999).

3.2. Model Scenarios

The model was used to illustrate the response of the marine P cycle to three distinct perturbations. These scenarios do not precisely mimic any event; they are rather designed to use the principles of anoxic P cycling to model responses to different forcings.

3.2.1. Long-Term Negative Feedback on pO_2

The first scenario tests the long-term ($\sim 10^7$ yr) negative feedback that anoxic P recycling exerts on pO_2 (as in Van Cappellen & Ingall, 1996). Modern fluxes and reservoir sizes are utilized, and a 25% increase in O_2 sink is imposed. To test the effect of sulfate on the observed response, five iterations were run, spanning modern (30 mM) to Archean (<100 μM) sulfate.

3.2.2. Short-Term Positive Feedback on f_{anoxic}

The second scenario tests the short-term ($\sim 10^4$ yr) positive feedback that anoxic P recycling exerts on f_{anoxic} (as in Tsandev & Slomp, 2009). Modern fluxes and reservoir sizes are utilized, and a transient (100 kyr) 50% increase in J_{riv_P} is imposed. To test the effect of sulfate on the observed response, five iterations were run, spanning modern (30 mM) to Archean (<100 μM) sulfate.

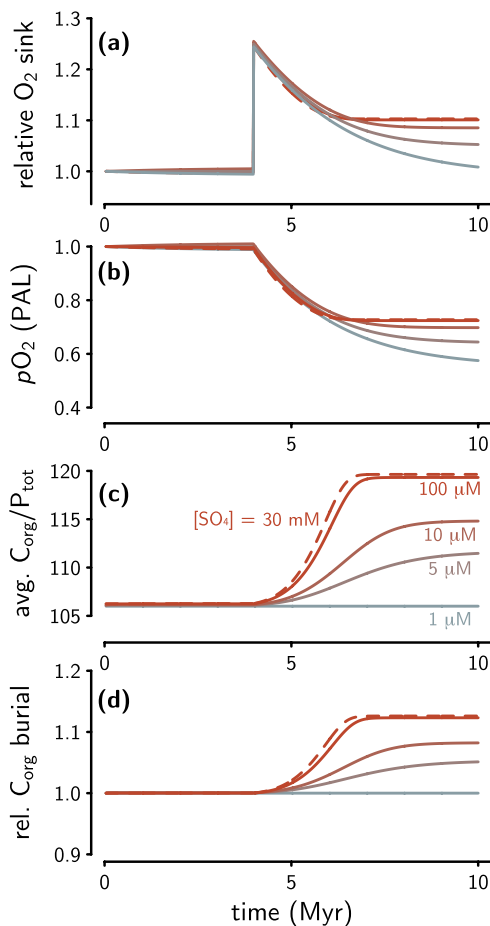


Figure 2. Long-term negative feedback on pO_2 . An instantaneous increase in O_2 sink (a) is compensated by diminished oxidative weathering. The pO_2 decrease is smaller with high sulfate (b) due to enhanced C_{org} burial (d) following enhanced P recycling (c).

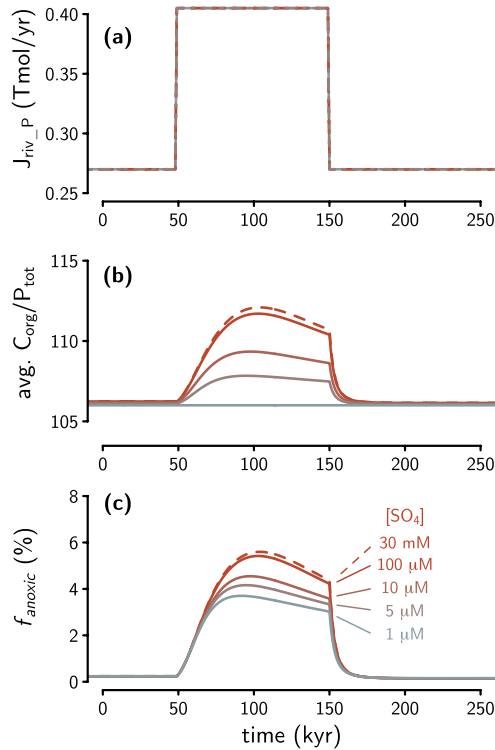


Figure 3. Short-term positive feedback during ocean anoxic event. A transient increase in J_{riv_P} (a) causes growth of the P reservoir, heightened productivity, and expansion of anoxia (c). When sulfate is abundant, this increases the average C_{org}/P_{tot} of marine sediments (b), thus recycling more P to seawater and amplifying the event; amplification is not observed when sulfate is scarce.

3.2.3. Short-Term Positive Feedback on pO_2

The third scenario tests the short term ($\sim 10^4$ yr) positive feedback that anoxic P recycling exerts on pO_2 in the pre-GOE world. Archean sulfate ($\sim 3 \mu\text{M}$) and oxygen ($< 10^{-6}$ PAL) levels are used, with P_{sw} starting at 1% of modern. J_{riv_P} is set equal to modern (Hao et al., 2020), $J_{reduced_outgassing} = 43.1$ Tmol/yr (Kipp et al., 2021), and $J_{photSO_4} = 0.5$ Tmol/yr (Holland, 2002).

Two mechanisms are tested. In the first, a transient (50 kyr) 40%–50% increase in J_{riv_P} is imposed. In the second, a transient (50 kyr) 4–7x increase in $J_{phot_SO_4}$ is imposed. To test the effect of sulfate on the observed response for each mechanism, two iterations were run, one with $CP_{anoxic} = CP_{Redfield}$ (negating anoxic P recycling), and one with CP_{anoxic} calculated via Equation 6.

4. Results and Discussion

4.1. High- O_2 World: Negative Feedback on pO_2 on 10^7 yr Timescales

In the first test, the spike in O_2 sink is followed by a decrease in oxidative weathering due to falling pO_2 (Figures 2a and 2b). However, pO_2 decreases less when sulfate is abundant. This is because O_2 production via C_{org} burial is enhanced (Figure 2d). This is driven by the increase in f_{anoxic} , which increases the average C_{org}/P_{tot} of marine sediments (Figure 2c); the larger resulting marine P reservoir drives higher productivity and C_{org} burial. Thus, enhanced P recycling from anoxic marine sediments (in the presence of sulfate) buffers the Earth system against large pO_2 swings on 10^7 yr timescales (Van Cappellen & Ingall, 1996). The time required to reach the new steady state (~ 5 Myr) is dictated by the ocean-atmosphere O_2 residence time (~ 1 Myr); 5 residence times are required to come within 1% of the new steady state.

4.2. High- O_2 World: Positive Feedback on f_{anoxic} on 10^4 yr Timescales

In the second test, the transient increase in J_{riv_P} (Figure 3a) causes growth of the P reservoir, which increases NPP and f_{anox} (i.e., an AOE). However, when sulfate is abundant, the expansion of anoxic seafloor area causes more deposition of high C_{org}/P_{tot} sediments. The average C_{org}/P_{tot} of all marine sediments thus increases (i.e., enhanced P recycling; Figure 3b). This P recycling amplifies the event, causing a higher f_{anox} peak (Figure 3c). This matches the mechanism of Tsandev and Slomp (2009).

4.3. Low- O_2 World: Positive Feedback on pO_2 on 10^4 yr Timescales

In the third test, two scenarios are considered. In the first (Figures 4a and 4b), a transient increase in J_{riv_P} causes growth of the P reservoir, which increases NPP, C_{org} burial, and O_2 production. If the O_2 source flux overwhelms the O_2 sink from reduced volcanic gases, O_2 accumulates in the atmosphere and initiates oxidative weathering. This mechanism of heightened O_2 production from an increase in P delivery has been postulated as a driver of “whiffs” of oxygen in the late Archean (e.g., Meixnerová et al., 2021), and also ultimately of the GOE (e.g., Hao et al., 2020).

The increase in O_2 production occurs without enhanced P recycling, evidenced by model runs where $CP_{anoxic} = 106$ throughout (solid blue lines; Figures 4a and 4b). However, when allowing for enhanced P recycling (i.e., high CP_{anoxic}), the increase in O_2 production is amplified. This is because the sulfate reservoir grows once oxidative weathering begins. In the case of a “whiff” event (where O_2 does not accumulate to appreciable levels), this effect modestly increases O_2 production (Figure 4a). When the forcing is larger, enhanced P recycling can cross a threshold where positive feedback (O_2 production \rightarrow oxidative weathering \rightarrow sulfate delivery \rightarrow P recycling \rightarrow O_2 production) causes O_2 to rapidly accumulate toward levels that are buffered by oxidative weathering, not reduced gases (i.e., the GOE; Figure 4b). This rapid timescale ($\sim 10^5$ yr) of atmospheric oxygenation is consistent with

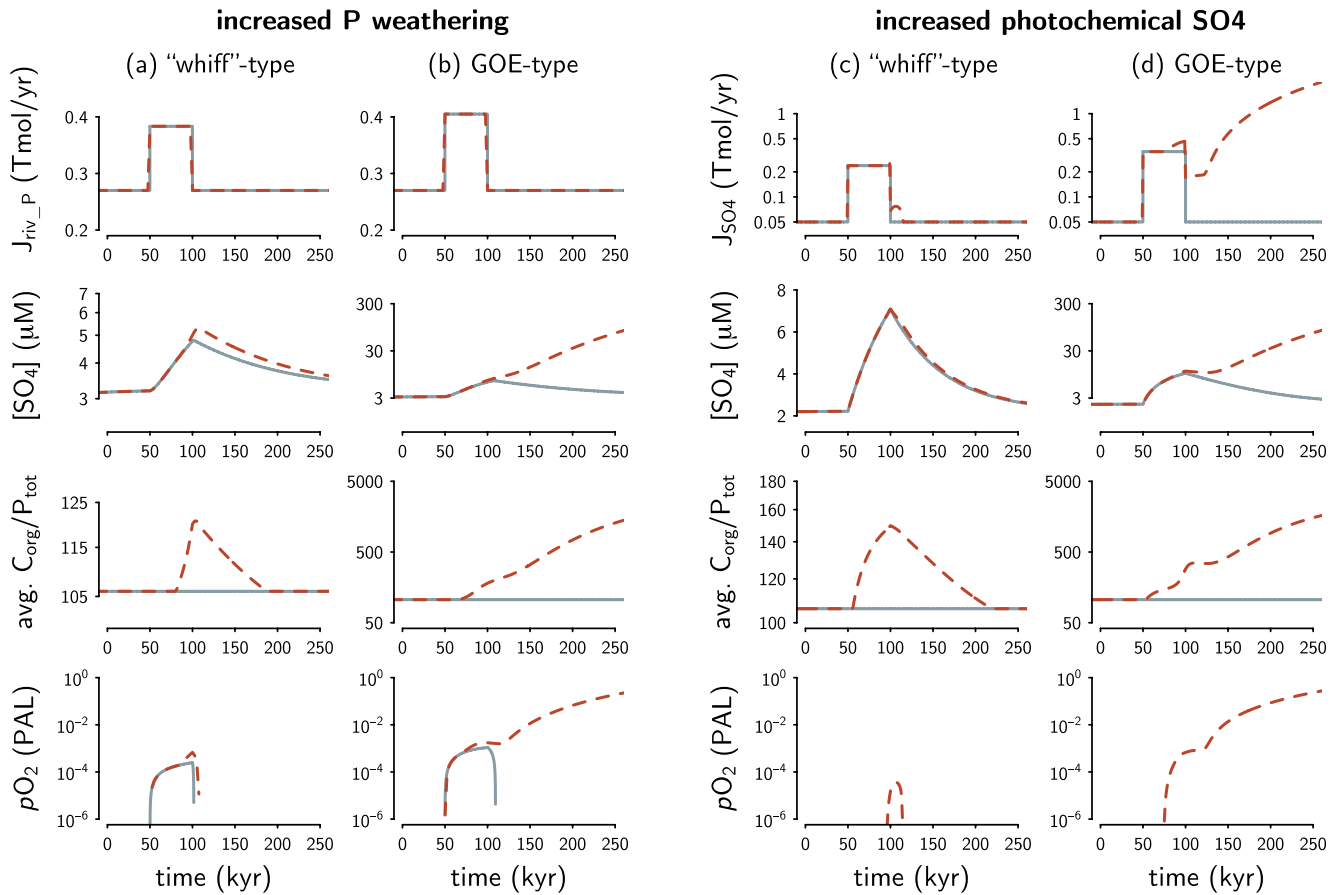


Figure 4. Short-term positive feedback during atmosphere oxygenation events. Two mechanisms are shown: increasing P weathering and SO_4 outgassing/photochemical oxidation. For each mechanism, a small forcing results in a transient O_2 pulse (“whiff”-type event; (a), (c)), while a larger forcing can cross a threshold where atmospheric O_2 accumulates (GOE-type event; (b), (d)). In all cases, SO_4 -mediated P recycling promotes productivity and O_2 production. The resulting O_2 accumulation initiates SO_4 input via oxidative weathering, amplifying the event (unless $\text{CP}_{\text{anoxic}}$ is held constant; solid blue lines).

theoretical (Goldblatt et al., 2006; Ward et al., 2016) and observational work (Luo et al., 2016) suggesting rapid O_2 accumulation once production exceeded volcanic sinks. In other words, this suggests that the onset of significant P recycling could have accelerated the GOE (Alcott et al., 2022).

In the second scenario, a more indirect pathway is tested. This follows work proposing a role of sulfate delivery from photochemically oxidized volcanic SO_2 (Olson et al., 2019) and crustal sulfides (Hao et al., 2022) in Archean oxygenation events. In these tests, increasing $J_{\text{phot_SO}_4}$ causes enhanced P recycling (unless $\text{CP}_{\text{anoxic}}$ is held at 106), which stimulates O_2 production. As in the tests above, O_2 accumulation initiates sulfate supply via oxidative weathering, amplifying the oxygenation event. This demonstrates that abiotic, anoxic sulfate delivery to the ocean can initiate oxygenation events by stimulating P recycling.

4.4. A Double-Edged Sword

The tests above demonstrate that sulfate is a double-edged sword wielded by the anoxic P cycle. In the Phanerozoic, sulfate sustains MSR in anoxic sediments, which releases P to porewaters and inhibits authigenic P burial. Phanerozoic sulfate therefore drives enhanced anoxic P recycling, stimulating export production and concomitant respiration, amplifying *deoxygenation* events on sub-Myr timescales (Figure 3).

Conversely, in the Archean, sulfate scarcity meant that in anoxic settings, P was buried efficiently; that is, there was limited P recycling. Processes that delivered more sulfate to the ocean (e.g., oxidative weathering, subaerial volcanism) would have enabled P recycling, thus stimulating productivity. In contrast to the Phanerozoic, the

already-anoxic ocean was not much affected by elevated respiration, while the anoxic atmosphere was strongly affected by the increased O₂ production. Thus, Archean sulfate amplifies sub-Myr oxygenation events (Figure 4).

5. Conclusions

Since Earth attained a large marine sulfate reservoir, there has been stabilization of atmospheric O₂ by the negative feedback in Figure 2 (as originally suggested by Van Cappellen & Ingall, 1996). During transient perturbations, though, the expansion of marine anoxia has been amplified by enhanced P recycling (Figure 3), as suggested by several authors (e.g., Handoh & Lenton, 2003; Tsandev & Slomp, 2009).

Prior to the GOE, the dearth of seawater sulfate means that enhanced P recycling cannot have operated. Instead, P was buried efficiently. As oxidative weathering began and marine sulfate levels first rose, increases in P recycling would have stimulated O₂ production, perhaps propagating “whiffs” of atmospheric O₂ (Figure 4; Anbar et al., 2007; Koehler et al., 2018). Interestingly, if the McRae “whiff” and similar events were indeed stimulated by P and/or sulfate delivery following LIP volcanism (Meixnerová et al., 2021), it would imply that the same forcing (Figures 3a and 4a) has different biogeochemical impacts as a function of sulfate/oxygen status (amplify oxygenation in Archean; amplify deoxygenation in Phanerozoic). Eventually, the sulfate reservoir became sufficient to enable vigorous P recycling, culminating in the GOE (Alcott et al., 2022).

It is unclear whether marine sulfate levels dropped sufficiently low in the Proterozoic to again enter a limited P recycling regime. This lack of clarity stems from both the poor understanding of Proterozoic seawater sulfate levels and the imprecise knowledge of the threshold at which the anoxic P cycle switches from “limited” to “enhanced” recycling. If P recycling was limited in the mid-Proterozoic, another increase in marine sulfate in the Neoproterozoic may have contributed to increased sedimentary P burial and surface oxygenation (Laakso et al., 2020).

In sum, this model demonstrates the critical role that sulfate plays in setting the behavior of the P cycle in anoxic marine systems. These findings speak not only to the evolution of Earth environments, but also to the controls on nutrient cycling on other habitable planetary bodies in our Solar System and beyond (Lingam & Loeb, 2018), as well as to the role of sulfate in amplifying human-induced ocean anoxia (Watson et al., 2017).

Data Availability Statement

No data were generated in this study. All equations used to generate the figures are provided in the main text. The R code used to execute these calculations is available at <https://doi.org/10.5281/zenodo.6603990>.

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