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Pierre Maffre, Nicholas Swanson-hysell, Yves Godd ris. Limited Carbon Cycle Response to Increased Sulfide Weathering Due to Oxygen Feedback. *Geophysical Research Letters*, 2021, 48 (19), <10.1029/2021GL094589>. <hal-03412326>

HAL Id: hal-03412326

<https://hal.science/hal-03412326v1>

Submitted on 7 Aug 2022

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Geophysical Research Letters[®]

RESEARCH LETTER

10.1029/2021GL094589

Key Points:

- The effect of oxidative sulfide weathering on CO₂ is dependent on the coupled oxygen–carbon–sulfur cycles
- Due to feedbacks, an increase in sulfide weathering will switch from a transient C source to a C sink on geologically short timescales
- This behavior is robust for a large range of oxygen feedback strengths

Supporting Information:

Supporting Information may be found in the online version of this article.

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Citation:

Maffre, P., Swanson-Hysell, N. L., & Godd  ris, Y. (2021). Limited carbon cycle response to increased sulfide weathering due to oxygen feedback. *Geophysical Research Letters*, 48, e2021GL094589. <https://doi.org/10.1029/2021GL094589>

Received 28 MAY 2021

Accepted 12 SEP 2021

Limited Carbon Cycle Response to Increased Sulfide Weathering Due to Oxygen Feedback

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Abstract The chemical weathering of sulfide-bearing rocks can result in the dissolution of carbonate rocks leading to degassing of CO₂ to the atmosphere. While this process has been argued to be a significant geologic source of CO₂, it also perturbs the geological cycles of oxygen and sulfur, triggering a cascade of geochemical feedbacks. Using a numerical model of geochemical cycles and climate, we found that due to feedbacks on atmospheric oxygen associated with the organic carbon cycle, an increase of sulfide weathering leads to a limited source of CO₂ followed by a longer sink of CO₂. This result is due to the stoichiometry of sulfide weathering where more O₂ is consumed than CO₂ is released. If sulfide weathering increases progressively on a geological timescale, the duration of the carbon source is extended, but its magnitude is negligible before it becomes a carbon sink.

Plain Language Summary Earth's climate has changed through time from being warmer than today for millions of years to being colder than today for millions of years. Climate on Earth over these long time periods is set by the balance of carbon dioxide coming into the ocean and atmosphere and carbon dioxide going out. Knowing how big different sources of carbon dioxide to Earth's surface is important for understanding what has caused Earth's climate to change through time. While carbon dioxide coming out of volcanoes is usually thought to be the most important source, there are other sources. One such source is when the common mineral pyrite (sometimes known as "fools gold") gets exposed in mountains and rusts through exposure to oxygen. This process results in acid which dissolves other rocks that can release carbon. However, when pyrite rusts it consumes oxygen. At lower oxygen levels, organic carbon that is made through photosynthesis is more likely to be preserved and buried in sediments. As a result, the overall effect of pyrite weathering on carbon dioxide levels is limited and can actually cause them to go down by a small amount.

1. Introduction

On million-year timescales, the sources and sinks of CO₂ on Earth's surface need to be balanced (Berner & Caldeira, 1997). Volcanism and metamorphic outgassing are typically considered the main sources of CO₂ to the long-term carbon cycle. However, recent attention has been drawn to the CO₂ source associated with sulfuric acid produced by sulfide mineral weathering (e.g., pyrite) dissolving carbonate rocks (Blattmann et al., 2019; Emberson et al., 2018; K  lling et al., 2019; Shukla et al., 2018; Spence & Telmer, 2005; Torres et al., 2014, 2017). The sulfide oxidation flux has been reestimated at higher values than previously thought (Burke et al., 2018; Calmels et al., 2007) and is correlated to erosion rate (Bufe et al., 2021; Calmels et al., 2007; Hilton & West, 2020; Torres et al., 2016, 2017). This process could be important in the evolution of Earth's climate and is relevant in association with orogenies that uplift sulfide-bearing sedimentary lithologies. Torres et al. (2014) proposed that sulfide oxidation coupled to terrestrial carbonate dissolution could be a sustained carbon source, owing to the relatively long residence time of sulfate in the ocean (10–15 Myr). The authors argued that this process could be a missing source of CO₂ in the Cenozoic Era, accompanied by a decrease of atmospheric oxygen (as sulfide oxidation is a sink of O₂).

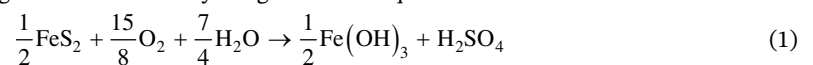
A modification of the sulfide oxidation flux would also modify the interrelated geochemical cycles of carbon, oxygen, and sulfur. The overall response of atmosphere–ocean geochemistry to a perturbation of sulfide oxidation therefore depends on the strength and timing of the different feedbacks in these geochemical cycles.

The existence of a negative feedback stabilizing atmospheric CO₂ has been acknowledged for several decades, the so-called "weathering thermostat" of the climatic feedback on silicate weathering being presented

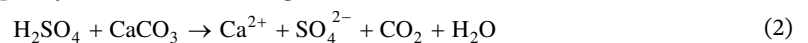
as the best candidate (Berner et al., 1983; Walker et al., 1981). Because of the short residence time of carbon in the ocean–atmosphere system (100 kyr), this feedback must operate within a few hundred thousand years (Berner & Caldeira, 1997). Despite large-scale orogenic activity over the Cenozoic, oxygen levels are estimated to be relatively stable, between 20% and 24% of atmosphere volume (Mills et al., 2016). The estimated range of variation since the Carboniferous is 15%–35% (Berner et al., 2003). This stability suggests the presence of a substantial negative feedback operating on atmospheric oxygen levels. Organic carbon burial in marine sediments is thought to prevent oxygen levels from getting too low, either through a reduction of O₂-dependent carbon oxidation during early diagenesis (Betts & Holland, 1991) or through enhanced productivity due to reduced phosphorus burial under anoxic conditions (Van Cappellen & Ingall, 1996). Land vegetation processes, including terrestrial wildfires, provide additional negative feedbacks (Lenton & Watson, 2000). The feedbacks on oceanic sulfate concentrations are not straight-forward. The formation of massive sulfate evaporites (e.g., gypsum, anhydrite) is more sensitive to the particular paleogeographic configurations that lead to restricted basins in arid environments than on sulfate concentrations. Nevertheless, precipitation of sulfide minerals through sulfate reduction likely depends on sulfate concentration (Canfield & Farquhar, 2009) and this may hold true for the precipitation of disseminated sulfate minerals as well. These processes would provide negative feedback that prevents unbounded drift. Hence, geochemical cycle models, such as COPSE (Lenton et al., 2018), generally assume those fluxes to be proportional to sulfate concentration.

Given the existence of these feedbacks, one cannot straightforwardly determine how CO₂ and climate would evolve in the million years following a perturbation of sulfide weathering. The present study addresses this question with a modeling approach. Using the coupled geochemical cycles/climate model GEOCLIM (Donnadieu et al., 2006; Godd ris & Donnadieu, 2019; Godd ris & Joachimski, 2004), we explore the sensitivity of transient climate evolution to an increase of sulfide weathering on million-year timescales.

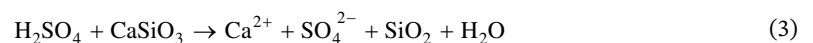
Sulfide oxidative weathering can be described by the generalized equation:



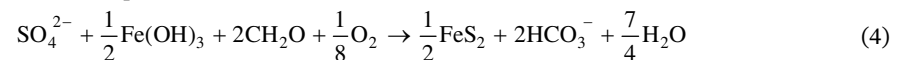
The released sulfuric acid typically dissolves surrounding carbonate minerals:



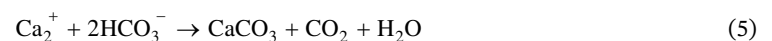
If not, it may alter the riverine or oceanic water alkalinity balance and carbonate precipitation, leading to the same budget. Alternatively, sulfuric acid might dissolve silicate minerals, the budget would then be different:



Eventually, the cycle is closed by sulfate reduction and sulfide precipitation in marine sediment that can be described by the generalized equation:



Followed by carbonate precipitation:



These last two processes balance the alkalinity and sulfur budgets, but not the carbon and oxygen ones. The burial of organic carbon produced by the biosphere finally close the budgets (expressed here with a stoichiometry comparable to previous equations):



2. Materials and Methods

2.1. Model

We used the global spatially resolved geochemical cycle model COMBINE that is a component of the GEOCLIM Earth system model (Donnadieu et al., 2006; Godd ris & Donnadieu, 2019; Godd ris &

Joachimski, 2004). The model code is available on Zenodo (<https://doi.org/10.5281/zenodo.5246622>). GEOCLIM simulates the cycles of geochemical species (including carbon, oxygen, alkalinity, and phosphorus) in ocean–atmosphere reservoirs that are discretized in 10 “boxes” (9 oceanic, 1 atmospheric) and is coupled to climate model results that are used to compute continental fluxes at the resolution of the climate model. GEOCLIM is designed for multimillion-year simulations while being fully dynamic (i.e., no steady-state assumption is made regarding the chemical species) and parameterizes fast processes, like ocean mixing and water column sedimentation. The coupled modeling of continental processes, climate, and ocean biogeochemistry enables the model to address the impact of increased sulfide weathering on the carbon cycle.

This study combines recent improvements of the GEOCLIM model and implements a simplified sulfur cycle. A more complete description of the model and the calibration procedure can be found in the Texts S1–S3.

GEOCLIM’s continental weathering module computes physical erosion, silicate, carbonate, petrogenic organic carbon and phosphorus weathering, and terrestrial organic carbon export. Surface bedrock is divided into six lithological classes, following Park et al. (2020), utilizing the data compilation of Hartmann and Moosdorf (2012). The erosion and silicate weathering components are similar to Park et al. (2020) but solve the equations dynamically instead of assuming a steady-state regolith. Terrestrial biospheric organic carbon export is an addition with respect to published versions of GEOCLIM and uses the formulation of Galy et al. (2015). Regarding petrogenic organic carbon and sulfide weathering, following recent studies that indicate a near linear relationship between those two fluxes and erosion rates (Calmels et al., 2007; Hilton et al., 2014), we considered them to be proportional to the modeled erosion rate, with prescribed organic matter content and C:S ratio. As a simplification, we assumed that sulfuric acid released by sulfide oxidation dissolves carbonate and silicate rocks, in addition to chemical weathering driven by carbonic acid, with the same carbonate/silicate flux ratio as for “carbonic” weathering.

The climate simulations used by the weathering module are the same as in Park et al. (2020). The GFDL CM2.0 General Circulation Model (Geophysical Fluid Dynamics Laboratory Coupled Model version 2.0, Delworth et al., 2006) was run, at 1, 2, and 4 times preindustrial CO₂ with other boundary conditions set to be constant at preindustrial values.

For the purpose of this study, a simplified sulfur cycle has been implemented in GEOCLIM. We assume that the only processes modifying the sulfur budget are the continental sulfide oxidation and the reduction of sulfate in marine sediments. All other fluxes (sulfur degassing, evaporite dissolution, and precipitation) are set at steady-state values. This simplification of the pathways is implemented given the difficulties in accurately representing evaporite precipitation with no explicit evaporitic basins.

The preservation of deposited organic carbon in marine sediments is mostly controlled by the local sedimentation rate. Organic carbon burial efficiency is modulated by O₂ and SO₄^{2−} concentrations, providing a negative feedback for those element cycles (Betts & Holland, 1991; Canfield & Farquhar, 2009; Hartnett et al., 1998). These processes are simulated using an early diagenesis module (Simon et al., 2007). It consists of a steady-state reactive-transport model calculating at each time step of GEOCLIM the amount of organic matter escaping oxidation such that it is buried in the sediment. Organic matter moves downward, at the sedimentation rate, through a bioturbated layer (starting at the surface of sediment), where it is oxidized by O₂, and through a “sulfate reduction layer,” where it is oxidized by SO₄^{2−}. H₂S generated by this process reacts with iron to form sulfide minerals (Equation 4). Oxidation rate is considered to be proportional to the concentration of organic matter in the sediment times the concentration of the oxidant (O₂ or SO₄^{2−}) in the local GEOCLIM ocean box. Hence, the oxidation flux F_{oxid} in a given layer is

$$F_{oxid} = \frac{F_{in}}{1 + w/kh[X]} \quad (7)$$

With F_{in} the incoming flux of C at the top of the layer, w the sedimentation rate, h the layer thickness, $[X]$ the concentration of the oxidant (O₂ or SO₄^{2−}), and k the rate constant.

The GEOCLIM model was calibrated to reproduce preindustrial conditions using modern fields of slope and lithology and climate fields from climate model runs at 1× CO₂, under the assumption of steady-state. While this assumption is questionable for long residence time species (S and O), it should be considered as a neutral hypothesis given the difficulties to estimate the current imbalance of the geochemical cycles

(e.g., Burke et al., 2018). Starting the numerical experiments at steady-state is preferable as otherwise the assumed nonsteady state trajectory will be superimposed on responses to an imposed increase in sulfide weathering.

2.2. Design of Perturbations

The perturbations we applied to the preindustrial steady-state consist of increasing by 50% the sulfide weathering flux, either instantaneously at $t = 0$ (abrupt perturbation) or progressively over 40 Myr (progressive perturbation). This perturbation is scaled to the “background” sulfide weathering, which means it evolves with climate evolution (with erosion being parameterized to be dependent on runoff rates in addition to slope). In other words, this perturbation is equivalent to increasing by 50% the amount of sulfides in surface rock exposures, without changing its organic carbon content. Two end-members concerning the fate of the additional sulfuric acid are presented here: additional dissolution of carbonate and additional dissolution of silicate, referred as “carbonate” and “silicate” sulfuric weathering perturbations. More scenarios are discussed in the Text S5 and Figures S4–S8.

2.3. Oxygen Feedback Sensitivity Experiments

We conducted additional experiments where we varied the strength of the oxygen feedback. In GEOCLIM, two simulated processes are responsible of this feedback: the O_2 -dependent oxidation of organic matter in marine sediment and the burial of phosphorus with organic matter. The C:P burial ratio depends on the degree of anoxicity (Van Cappellen & Ingall, 1994):

$$(C : P)_{burial} = \frac{(C : P)_{oxic} \cdot (C : P)_{anoxic}}{(1 - DOA) \cdot (C : P)_{anoxic} + DOA \cdot (C : P)_{oxic}} \quad (8)$$

In other words, the amount of P buried for a given amount of buried C varies linearly with the degree of anoxicity (DOA) between the two end-members.

The DOA represents the fraction of the basin that is anoxic. It varies from 1 (fully anoxic basin) to 0 (fully oxic basin). It only depends on local oxygen concentration, using the relation of Van Cappellen and Ingall (1994, polynomial fit of Figure 4a of their contribution). Roughly speaking, it linearly decreases from 1 for $[O_2] = 0 \text{ mol/m}^3$ to 0 for $[O_2] = 0.4 \text{ mol/m}^3$ (see Figure S1).

Less oxygen in seawater leads to less burial of phosphorus, leading to higher primary productivity via P upwelling, and more organic C burial.

This case is the reference oxygen feedback scenario (“ref”). To vary the strength of the oxygen feedback, we added or removed O_2 dependencies to several processes. We made the hydrothermal phosphorus sink (Wheat et al., 1996)—independent of oxygen in “reference” case—dependent to $[O_2]$ (case “feedback + 1”) or dependent to $[O_2]^2$ (case “feedback + 2”). We further made terrestrial biospheric organic carbon export dependent to $(pO_2)^{-0.5}$ (case “feedback + 3”) or to $(pO_2)^{-1}$ (case “feedback + 4”). To reduce the oxygen feedback strength, we imposed a constant DOA (case “feedback – 1”), independent of oxygen concentration. We further reduced the O_2 dependence in Equation 7 to $[O_2]^{0.5}$ (case “feedback – 2”). Finally, we removed the O_2 dependence in Equation 7, leaving no oxygen feedback in the model (case “no feedback”). These modifications serve as a way to modulate the overall oxygen feedback strength given that it has considerable uncertainty.

To quantify the strength of the oxygen feedback for each of those different scenarios, we computed the steady-state pO_2 after a 50% increase in petrogenic carbon weathering, everything else—including phosphorus weathering—unchanged. This “perturbed” steady-state pO_2 ranges from 0.44 to 0.68 PAL, the reference case being 0.56 PAL (see Text S4, Table S3, and Figure S2).

3. Results

3.1. Abrupt Perturbation

Starting from geochemical steady-state, we applied at $t = 0$ a step-function increase of sulfide weathering and carbonate dissolution by released sulfuric acid.

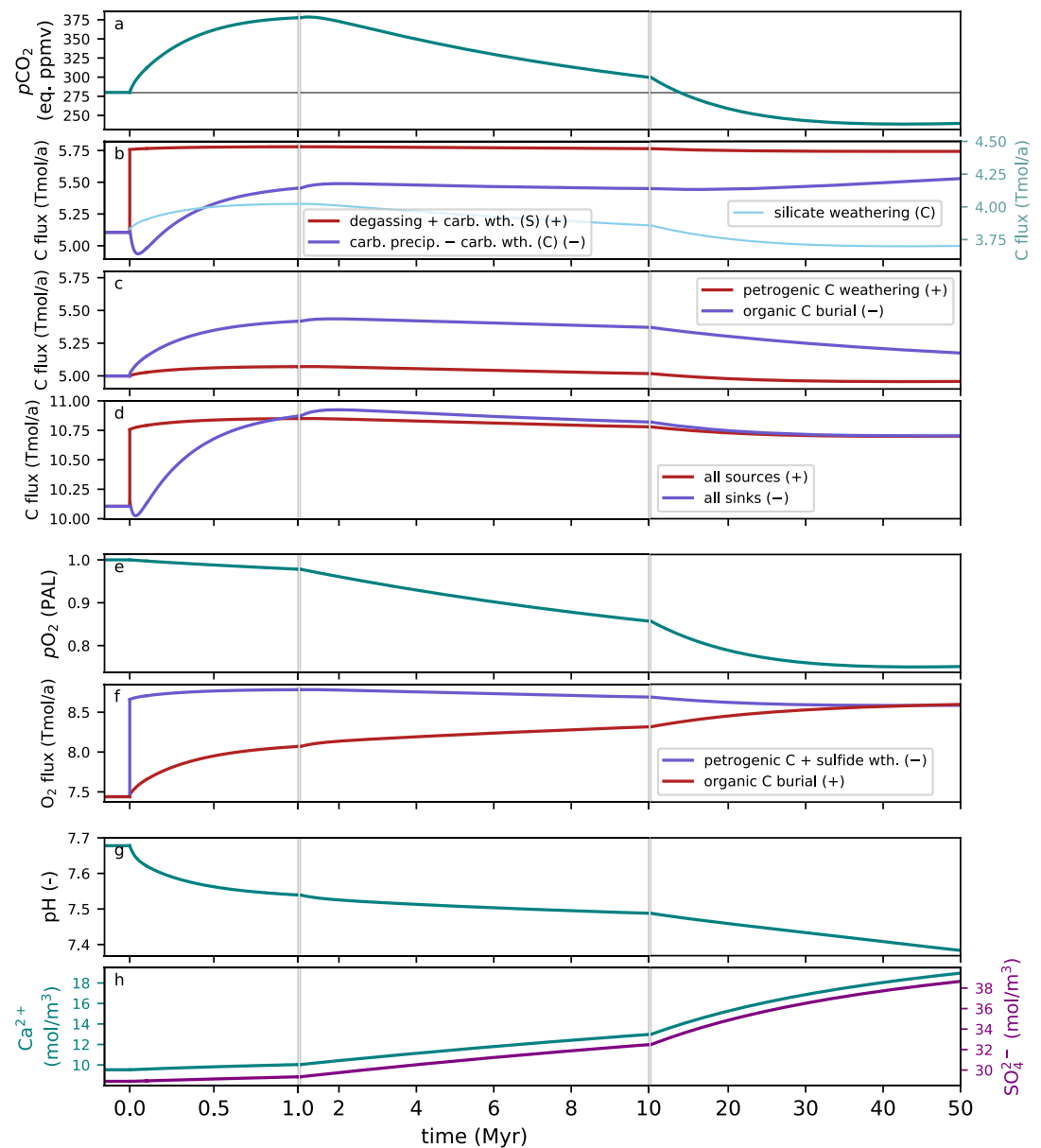


Figure 1. Time evolution of major ocean–atmosphere chemical species and fluxes following an “abrupt carbonate sulfuric weathering” perturbation applied at $t = 0$ and sustained. Fluxes are shown as their absolute value with a positive source indicated with a (+) in the legend and a negative sink indicated with a (–). (a) Atmospheric partial pressure of CO_2 , expressed in equivalent ppmv (theoretical mixing ratio if all other gases amounts were kept unchanged). (b) Inorganic carbon fluxes (left axis) and silicate weathering flux (right axis). (c) Organic carbon fluxes. (d) Sum of carbon sources and sinks. (e) Atmospheric partial pressure of O_2 , expressed relatively to present one (PAL). (f) Oxygen fluxes. (g) Mean ocean pH. (h) Mean ocean calcium (left axis) and sulfate (right axis) concentration. “wth” is the abbreviation of “weathering.” When ambiguous, weathering by carbonic or sulfuric acid is specified by C or S (respectively). In panels (b) and (h), the left and right y axes have the same scale.

The immediate response is an increase of atmospheric CO_2 (Figure 1a) because of the direct CO_2 release. This excess CO_2 causes a rapid drop of oceanic pH (Figure 1g) of 0.1, leading to a reduction of carbonate precipitation (Figure 1b) tempering the atmospheric CO_2 rise by storing dissolved inorganic carbon in the ocean.

The main negative feedback, in terms of amplitude, arises from the organic carbon cycle (Figure 1c). On the timescale of 1 Myr, the rise of temperature leads to lower oxygen solubility in seawater and, more

importantly, higher phosphorus delivery through weathering (see Figures S3 and S10), both increasing organic carbon burial flux by 0.42 Tmol/year. The silicate weathering flux also contributes to the CO₂ draw-down, but by a smaller amount — 0.22 Tmol/year in the same time interval (Figure 1b). These two fluxes stabilize $p\text{CO}_2$ at ~380 eq ppm.

On longer timescales (1–10 Myr), the progressive decline of $p\text{O}_2$ consumed by sulfide oxidation results in an increase of DOA in the ocean. Consequently, the preservation of organic C in sediment and the C:P ratio of the buried organic matter both increase. Higher primary productivity (given enhanced phosphorus availability, see Figure S3) and burial efficiency maintain the high organic carbon burial, consuming atmospheric CO₂. As a result, $p\text{CO}_2$ drops below its initial value around 14 Myr, long before the atmospheric oxygen level stabilizes (around 35 Myr, Figure 1f).

The sulfur cycle stays imbalanced by 0.1 Tmol/year after 50 Myr of run (see Figures 1h and S5). There are several reasons for this result. First, the modeled sulfur cycle residence time is significantly longer than the oxygen one (30 Myr vs. 5 Myr). Second, the sulfur negative feedback is not linear. The main control on sulfate reduction is the amount of organic carbon buried (Raiswell & Berner, 1986). Therefore, as organic carbon burial increases in the first couple of million years of simulation, so does sulfate reduction (see Figure S5). The ratio of organic C versus S burial fluxes into the marine sediments stays roughly constant during the phase of increasing organic carbon burial. Yet, the achievement of steady-state of all cycles requires a different C:S burial ratio. Steady-state is reached when organic carbon burial has increased by 16%, which buffers the oxygen perturbation, and sulfate reduction has increased by 50%, which buffers the sulfate perturbation. Accordingly, the C:S burial ratio progressively decreases in order to reach steady-state. To achieve this multicycle steady-state (including sulfur), the calculated oceanic sulfate must rise significantly given its weak control on the C:S burial ratio. An accelerated equilibrium simulation shows that sulfate concentration must increase up to 43.3 mol/m³ to balance the perturbation. Given that the sulfur cycle is imbalanced at 50 Myr of run, it would take approximately another 50 Myr to achieve steady-state.

In the last 20 Myr of simulation, oxygen and sulfur cycles are nearly at steady-state, while accommodating the long-term drift of the sulfur cycle (Figure 1). Atmospheric $p\text{O}_2$ decreases to 0.75 PAL for organic carbon burial to balance the oxygen sink (Figures 1e and 1f). Because sulfide weathering still exceeds sulfate reduction, the resulting net O₂ sink is compensated by an organic C burial flux higher than the sum of petrogenic C oxidation, carbonate sulfuric weathering, and sulfate reduction C fluxes. These coupled processes result in a net C sink, that is compensated by a reduced silicate weathering flux, itself controlled by lower than preindustrial atmospheric CO₂ (239 eq ppm, corresponding to a global cooling of 0.45°C, see Figures 1a and 1d). Eventually, when the sulfur cycle reaches steady-state, atmospheric CO₂ will return to its initial value, since only a perturbation of the inorganic carbon cycle is able to modify the steady-state CO₂.

3.2. Progressive Perturbation

This abrupt perturbation experiment is helpful to understand the processes, but a more realistic sulfide weathering perturbation would occur gradually. We conducted a second experiment where we linearly increase the sulfide weathering (rigorously, the amount of sulfide in exhumed rocks) over 40 million years, up to the same value of +50%. Given that the onset of this perturbation occurs on a similar timescale to that of the oxygen feedback, the global warming associated with it is virtually nonexistent (+15.5 eq ppm of CO₂ corresponding to 0.15°C of warming), and the CO₂ drops below the initial level at 35 Myr instead of 13.7 Myr (Figure 2a, orange curves).

3.3. Silicate Dissolution

We consider here the second scenario where the additional sulfuric acid released by the sulfide weathering perturbation dissolves “new” silicate minerals (Equation 3). In that scenario, sulfuric acid is neutralized without additional source of carbon, so the atmospheric CO₂ continually decreases, because of the organic C-dependent oxygen feedback, to a much lower value than in the “carbonate” scenario (110 eq ppm of CO₂, 2.6°C of cooling, Figure 2a, blue curves). Atmospheric O₂ also stabilizes at lower value (0.55 PAL, Figure 2b), because of both reduced phosphorus weathering and higher seawater oxygen solubility in colder

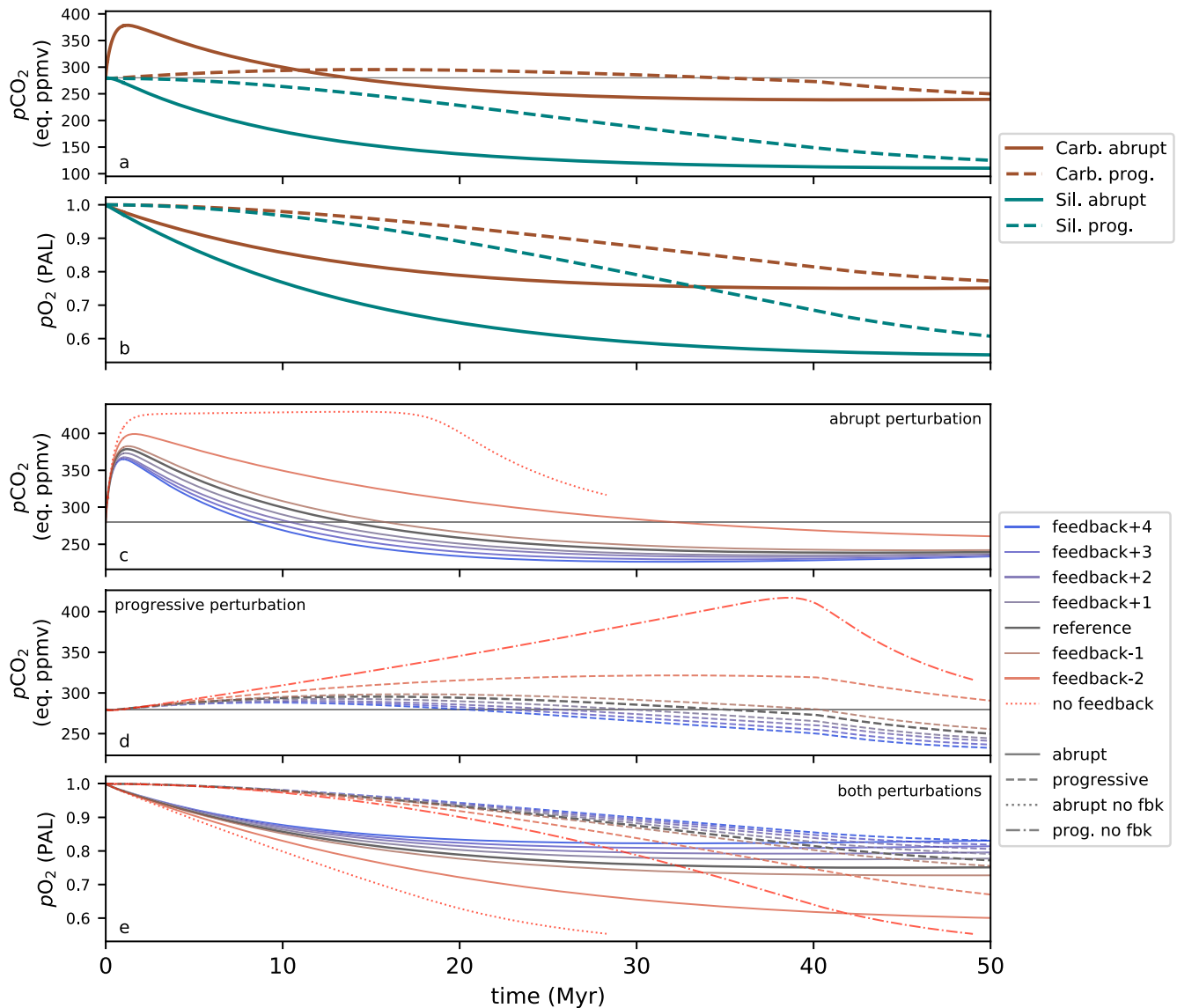


Figure 2. Time evolution of atmospheric CO₂ (a, c, and d) and O₂ (b and e) for different simulation setups. (a, b) “Carbonate” or “silicate sulfidic weathering” perturbation, abrupt or progressive over 40 Myr; (c–e) “carbonate sulfidic weathering” perturbation, abrupt (c, e) or progressive (d, e) with different strengths of O₂ feedback. The same color codes are applied in (a) and (b), and in (c)–(e). The units of pCO₂ and pO₂ are the same as in Figure 1.

climate. Considering a progressive perturbation rather than an abrupt one only delays the stabilization of the oxygen and carbon cycles (Figures 2a and 2b, blue curves).

3.4. Effect of Oxygen Feedback

Because the oxygen feedback is responsible for sulfide weathering perturbation to switch from a net source to a net sink of C, we investigated the sensitivity of our simulations to that feedback’s strength. We repeated this experiment of “carbonate sulfidic weathering” perturbation with different oxygen feedback strengths (see Section 2 and Text S4).

In the carbonate sulfidic weathering abrupt perturbation experiment, despite a relatively large scatter of pO₂ level at “steady-state” (0.6–0.83 PAL, Figure 2e), the CO₂ peak and its timing is a robust feature, with maximum pCO₂ of 365–400 eq ppm, reached at 1–1.6 Myr (Figure 2c). Only if all oxygen feedbacks are removed can the sulfide perturbation generate a sustained source of carbon, maintaining high CO₂ level

for tens of million years. However, in that theoretical experiment, CO₂ eventually declines near 17 Myr because the epicontinental waters below the photic zone becomes fully anoxic (O₂ concentration lower than 8 mmol/m³) and organic particles are no longer efficiently remineralized in the water column, which increases the organic carbon burial flux. At 28 Myr, oxygen mass balance can no longer be satisfied because the organic carbon oxidation during early diagenesis (made independent of O₂ concentration in this scenario) exceeds the amount of oxygen available in the basin.

All other sensitivity experiments show a drop of CO₂ below preindustrial level, occurring between 8 and 16 Myr, except for the “feedback – 2” case where the CO₂ decrease is much slower than the others.

In the case of a progressive perturbation, the CO₂ peak remains negligible (Figure 2d) while a similar persistent lower CO₂ is achieved after the sulfide weathering ceases to increase, with the exception of the “feedback – 2” and “no feedback” cases.

4. Discussion and Conclusion

4.1. Robustness of Oxygen Feedback Modeling

The strength and timing of the oxygen feedback is the key element controlling the CO₂ evolution in our experiments. Several mechanisms have been suggested to explain the negative feedback needed for the oxygen cycle, and their representation in GEOCLIM relies on empirical parameterizations.

Based on observed correlations between organic C content in marine sediment, sedimentation rate, and dissolved O₂ concentration, Betts and Holland (1991) found that the feedback provided by O₂-dependent organic C preservation in sediment would alone yield an atmospheric *p*O₂ of 0.1 atm (i.e., 0.48 PAL) for a 50% increase in oxidative weathering, in their “maximum slope” (i.e., maximum feedback strength) case. This value is close to our “feedback – 1” scenario (0.51 PAL, see Table S3), where O₂-dependent organic C preservation is the only feedback.

Other ocean-based feedbacks involved the removal of oceanic phosphorus with organic matter, adsorbed on iron hydroxides and calcium-bound, all providing a negative feedback; denitrification, on the other hand, provides a positive feedback (Lenton & Watson, 2000). In GEOCLIM (“reference” scenario), these feedbacks are parameterized with the degree of anoxicity, without explicit representation of iron speciation, nor organic matter and Ca binding. The nitrogen cycle and potential nitrogen-limitation on primary productivity is also ignored. Considering only the oceanic P-based feedbacks, Van Cappellen and Ingall (1996) found that *p*O₂ would drop down to 0.59 PAL after a 50% increase of oxidative weathering through uplift (the additional P delivered by enhanced continental weathering caused by uplift being delayed in their model). This *p*O₂ decrease is smaller than in our “reference” scenario.

Lenton and Watson (2000) argued that considering all these feedbacks together is needed to be consistent with the evidence of geologic oxygen stability. They also discussed land-based oxygen feedbacks, though more to explain the upper bound of oxygen variations. Land-based feedbacks are absent in the GEOCLIM “reference” scenario, we added a *p*O₂ dependence of terrestrial biospheric organic C export in scenarios “feedback + 3” and “feedback + 4.”

Given that the oxygen feedback in GEOCLIM “reference” is weaker than the literature estimates, the “high CO₂” scenarios (“feedback – 2” and “feedback – 1”) are unlikely, and the ones with lower CO₂ than “reference” are more probable.

4.2. Simplification of Sulfur Cycle

Sulfide burial is interpreted to be dependent on sulfate concentration (Canfield & Farquhar, 2009). However, how oceanic sulfate concentration controls sulfide burial is poorly known making it difficult to confidently parameterize. The much longer time required for sulfate reduction to balance sulfide weathering, compared to oxygen stabilization time, is another key element of the CO₂ evolution in our experiments, because of the stoichiometry of –15/8 O₂ for +1 CO₂ (Equations 1 and 2). Two arguments support this long sulfur balancing time: the long residence time of the “reduced” sulfur subcycle (30 Myr) compared to oxygen (5.1 Myr), and the consistent C:S ratio observed in sediments (Berner & Raiswell, 1983; Kurtz et al., 2003) suggesting a

weak control of sulfate concentration on this ratio; a ratio that needs to be modified in order for sulfur cycle to be balanced in our experiments.

It may be argued that the actual sulfur residence time is shorter because of the “evaporitic” subcycle, whose fluxes should respond to sulfate perturbations, and could potentially affect long-term climate (Shields & Mills, 2021). Considering an evaporitic sulfate weathering flux of 1.5 Tmol/year (Burke et al., 2018) would reduce the residence time of sulfur to 14 Myr. However, increasing evaporitic sulfate precipitation in response to sulfate and calcium concentration rise would not change the $O_2:CO_2$ stoichiometry, and the main effect is to further delay the rise of oceanic sulfate concentration needed for balancing the “reduced” sulfur subcycle. This would act in favor of an even more pronounced and longer CO_2 sink resulting from an increase in sulfide weathering.

4.3. Sulfide Weathering and Petrogenic Organic Carbon Weathering

Investigating the effect of an increase of sulfide weathering alone is a rather theoretical study. In Earth history, sulfide weathering is likely to have varied concomitantly with petrogenic organic carbon weathering, as sulfides are dominantly found in organic-rich sedimentary rocks. Both of their weathering rates have been shown to increase quasi-linearly with erosion rate (Calmels et al., 2007; Hilton et al., 2014). Decoupling of petrogenic organic carbon and sulfide weathering fluxes is still possible, by exhuming rocks with a lower C:S ratio than Earth surface average. Additionally, uplift and erosion influence on carbon fluxes is not restricted to sulfide and organic carbon weathering given concurrent changes in silicate weathering (Hilton & West, 2020), and uplift also affects ocean–atmosphere circulation, indirectly modifying weathering rates (Maffre, Ladant, Donnadiou, et al., 2018; Maffre, Ladant, Moquet, et al., 2018).

Nevertheless, a proportional increase of sulfide and petrogenic organic carbon weathering (presented in Text S5 and Figure S9) has a different impact. With an unchanged C:S ratio of global weathering fluxes, the rise of organic carbon burial and associate sulfate reduction fluxes caused by oxygen decline balances both oxygen and sulfur cycle in roughly the same time. This switches the ratio of $-15/8 O_2$ for $+1 CO_2$ toward a $-2 : +2$ ratio. Hence, CO_2 only undergoes a relaxation toward its preperturbation value instead of dropping below that value.

4.4. Consequences for Paleoclimatic Evolution

Sulfide oxidation linked to carbonate weathering is a source of CO_2 , but it is also a sink of O_2 , resulting in additional organic carbon burial and removal of CO_2 . Because of its larger effect on oxygen, an increase of sulfide weathering alone is, on the long term, a sink of CO_2 . Its source effect is either limited in time for a rapid perturbation or limited in amplitude for a progressive perturbation. This sink would be further enhanced if evaporite sulfate precipitation delays the rise of oceanic SO_4^{2-} , or if part of the additional sulfuric acid dissolves “new” silicates (i.e., silicates that would not have been dissolved by carbonic acid otherwise). The magnitude of such potential additional silicate weathering, however, is largely unknown. It is relevant for actively erosive environments, where “carbonic” silicate weathering is limited by kinetics rather than by the amount of exposed minerals, and therefore, less likely to be reduced by mineral consumption by enhanced “sulfuric” weathering.

Our findings suggest that sulfide weathering can not be solely interpreted as a missing source of carbon. Rather through the effects of oxygen and carbon cycle feedbacks it can instead be a sink. While there are significant uncertainties on the strength of the oxygen feedback, if there is a feedback on atmospheric oxygen levels through the carbon cycle, the decrease in atmospheric oxygen levels resulting from sulfide weathering will result in enhanced organic carbon burial that is a sink of carbon dioxide. This result highlights the need to consider the cascading biogeochemical effects of a process such as sulfide weathering. While reconstructing the forcing of long-term climate change remains a major challenge, the subdued effect of sulfide weathering on the carbon cycle emphasizes the relative importance of CO_2 outgassing and silicate weathering.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

All code associated with this study is archived on Zenodo (<https://doi.org/10.5281/zenodo.5246622>; doi:10.5281/zenodo.5246622).

Acknowledgments

Project research was supported by NSF Frontier Research in Earth Sciences (FRES) grant 1925990. The authors thank Daniel Stolper and members of the FRES project team for fruitful discussions. We thank the two anonymous reviewers whose constructive input improved the manuscript.

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