

Proterozoic oxygen rise linked to shifting balance between seafloor and terrestrial weathering

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A shift toward higher atmospheric oxygen concentration during the late Proterozoic has been inferred from multiple indirect proxies and is seen by many as a prerequisite for the emergence of complex animal life. However, the mechanisms controlling the level of oxygen throughout the Proterozoic and its eventual rise remain uncertain. Here we use a simple biogeochemical model to show that the balance between long-term carbon removal fluxes via terrestrial silicate weathering and ocean crust alteration plays a key role in determining atmospheric oxygen concentration. This balance may be shifted by changes in terrestrial weatherability or in the generation rate of oceanic crust. As a result, the terrestrial chemical weathering flux may be permanently altered—contrasting with the conventional view that the global silicate weathering flux must adjust to equal the volcanic CO₂ degassing flux. Changes in chemical weathering flux in turn alter the long-term supply of phosphorus to the ocean, and therefore the flux of organic carbon burial, which is the long-term source of atmospheric oxygen. Hence we propose that increasing solar luminosity and a decrease in seafloor spreading rate over 1,500–500 Ma drove a gradual shift from seafloor weathering to terrestrial weathering, and a corresponding steady rise in atmospheric oxygen. Furthermore, increased terrestrial weatherability during the late Neoproterozoic may explain low temperature, increases in ocean phosphate, ocean sulfate, and atmospheric oxygen concentration at this time.

carbon cycle | biogeochemistry | Precambrian

Increases in ocean oxygen concentration during the Neoproterozoic Era are supported by evidence from iron speciation (1) and enrichments in molybdenum concentration (2). The atmospheric concentration of oxygen is also likely to have increased over this time, resulting in higher ocean sulfate concentration (3) and increased isotopic fractionation of chromium (4) and sedimentary sulphides (5). Oxygenation of the deep oceans at ~580 Ma is well defined by redox proxies (1, 6); however, the mechanisms controlling this change are uncertain. It is not clear if this required a rise in atmospheric oxygen (7) and, if so, whether this was relatively rapid or the result of a steady rise over the Proterozoic.

The major long-term source of atmospheric oxygen is the burial of organic carbon in sediments, and a drift toward more positive $\delta^{13}\text{C}$ values over the period 1,500–800 Ma (8) suggests a gradual rise in organic carbon burial and atmospheric O₂ (9). Extreme positive fractionation in $\delta^{13}\text{C}$ observed in parts of the late Neoproterozoic record may indicate periods of elevated organic carbon burial, although the signal is at least partially a consequence of the aftermath of global glaciations occurring at this time (10, 11).

Long-term control of ocean productivity, and ultimately of organic carbon burial rates, is linked to the concentration of the ultimate limiting nutrient phosphorus, which is supplied via chemical weathering on the continents. However, changes in chemical weathering fluxes are constrained in several existing biogeochemical models (12, 13), due to a simplified view of the carbon cycle wherein the rate of CO₂ removal via silicate weathering and carbonate deposition (plus any excess of organic

carbon burial over oxidative weathering) must equal the rate of volcanic CO₂ degassing over long timescales (14). This equality is maintained by negative feedback between CO₂ concentration, global temperature, and silicate weathering rates (15).

Assuming this model is correct, an increase in terrestrial “weatherability”—a dimensionless parameter describing the ease with which the terrestrial surface is weathered (16)—will cause an initial decrease in CO₂ concentration due to an increased silicate weathering flux. Over time, however, lower CO₂ and associated lower global temperatures and humidity will act to reduce chemical weathering rates until a balance is struck and the flux of silicate weathering returns to the amount required to balance CO₂ input from degassing (Fig. 1A). Thus, at steady state, a change in terrestrial weatherability (which may be caused by a more active land biota or exposure of more easily weathered silicate rocks at the surface) cannot alter the weathering flux but results in lower atmospheric CO₂ and a colder, drier global environment. This has important implications for atmospheric oxygen levels: Under the assumption that long-term phosphorus input to the ocean scales with global weathering rates, the marine burial flux of organic matter and therefore the atmospheric oxygen concentration at steady state should not be significantly altered by a change in weatherability (7, 17).

Here we investigate the effects of accounting for additional climate regulation via seafloor weathering on phosphorus input to the ocean and hence atmospheric oxygen. Carbonate precipitation in low-temperature, off-axis hydrothermal systems accounts for a carbon flux into the ocean crust of $\sim 0.5\text{--}3 \times 10^{12}$ mol/y (18–20), making it important for the long-term carbon cycle (21, 22). The degree to which the flux is affected by ocean and atmosphere carbon concentration is highly debated, and a direct link via pH has been ruled out (23). However, recent

Significance

We investigate the balance between two mechanisms that remove carbon from the atmosphere and oceans over long timescales—weathering of terrestrial silicates and alteration of the ocean floor. We show that this balance should strongly influence atmospheric oxygen concentration, since it dictates the delivery rate of the ultimate limiting nutrient phosphorus to the ocean. Increasing solar luminosity and declining seafloor spreading rates over Proterozoic time are expected to have shifted the balance of carbon removal toward terrestrial weathering. This leads to the prediction of a gradually increasing oxygen concentration over Proterozoic time, with transient higher oxygen concentration in the late Neoproterozoic.

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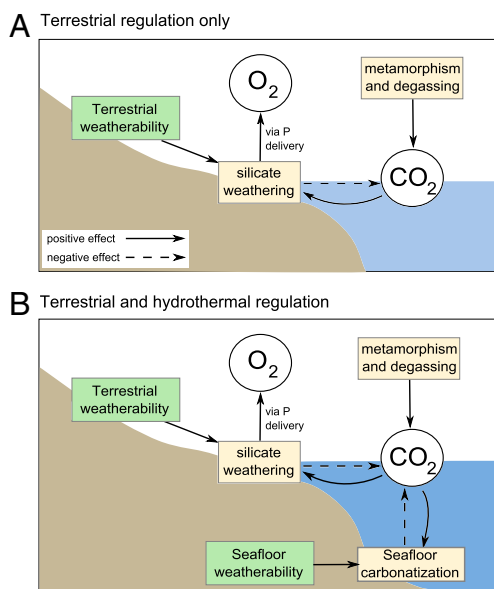


Fig. 1. Simplified long-term CO₂ feedbacks. Boxes show processes; ovals show hydrospheric constituents. Solid arrows show positive effect; dashed arrows show negative effect. (A) If terrestrial weathering is the only CO₂ regulator, the weathering flux must have the same steady state value regardless of weatherability. Increases in silicate weathering are nullified by pCO₂ falling. (B) Adding independent deep sea regulation allows for stable CO₂ under an altered silicate weathering flux, with stability maintained by a concurrent change in seafloor carbonatization rate. The balance dictates O₂ production, and may be shifted by enhancement of either process.

modeling of the differences between Mesozoic and Cenozoic drill cores (24) supports a dependency of the rate of seafloor weathering on crustal K-feldspar uptake, and on bottom water temperature (25).

Both of these mechanisms constitute an indirect negative feedback on CO₂ concentration. Indeed, Coogan and Gillis (24) conclude that during the late Mesozoic, the strength of the seafloor weathering–CO₂ feedback may have been of a similar magnitude to the feedback between CO₂ and terrestrial silicate weathering. In the present-day system, the rate of CO₂ removal via seafloor weathering is significantly smaller than the removal flux from terrestrial weathering [around 1/4 of the magnitude (26)]. However, the dependence of seafloor weathering on the mantle heat flux and ridge generation rate suggests a much more significant role in the Precambrian carbon balance (27), such that it was the primary sink for CO₂ in the Archean (28).

While all basalts contain phosphorus in fluorapatite, the localized alkalinity generation and carbonate precipitation during seafloor weathering does not generate a phosphorus source to seawater (29). Hydrothermal basalt alteration is a weak sink for phosphate in the present-day system (30) due to combination with ferric iron or carbonates (31). In contrast, phosphorus is released to solution during acidic terrestrial chemical weathering and can pass through the land and ocean ecosystems before reaching the seafloor. As a conservative estimate, and taking into account the weakening of phosphorus sinks in an anoxic and possibly high-alkalinity Precambrian ocean (32), we assume here there is no P flux associated with seafloor weathering.

Under the operation of the two independent, climate-dependent sinks for CO₂ (Fig. 1B), the link between degassing rates and silicate weathering rates is weakened substantially. CO₂ degassing must now be balanced by a combination of terrestrial silicate weathering and seafloor weathering, plus any imbalance in the organic carbon cycle. In this system, a decrease in CO₂ concentration due to increasing terrestrial weatherability would reduce

both the terrestrial and deep ocean carbon sinks until the total carbon removal flux again equaled the degassing input. In the new stable state, the seafloor weathering flux is reduced below its initial value, and the terrestrial silicate weathering flux is increased permanently relative to the previous stable state. It is probable therefore that an increase in terrestrial weatherability would lead to a permanent increase in terrestrial chemical weathering fluxes, and therefore phosphorus supply to the ocean, while maintaining stability of the long-term carbon cycle. An increase in the weatherability of the ocean floor will similarly shift the balance in favor of seafloor weathering, reducing the terrestrial silicate weathering flux and phosphorus supply.

To quantitatively test the biogeochemical implications of changes in the CO₂ removal balance, a dynamical representation of the seafloor weathering process is added to a simplified version of the carbon oxygen phosphorus sulphur evolution (COPSE) Earth system model (13). COPSE combines the long-term carbon cycle from the GEOCARB (geochemical carbon cycle) model (33) with a model of ocean nutrient and atmospheric oxygen cycling (34, 35), to estimate paleoconcentrations of carbon dioxide, oxygen, and ocean sulfate (see *SI Text* for full model description). In the model, imbalances in the organic carbon cycle are self-limiting due to negative feedback that maintains stable oxygen levels over long timescales (i.e., dependency of oxidative weathering rates on the crustal inventory of organic carbon, and on atmospheric oxygen concentration). Thus, in our model, the organic carbon cycle may be driven by the inorganic cycle via weathering rates and nutrient input.

Following Sleep and Zahnle (27), seafloor weathering rate is linked to the global spreading rate, and the dependence on relative atmospheric CO₂ concentration (RCO₂) is denoted by a power law relationship: $sfw \propto (RCO_2)^\alpha$. The limited laboratory experiments of Brady and Gislason (25) point to a dependency of $\alpha = 0.23$, which is the only available data on the magnitude of this important parameter and is used as the model baseline. This is a very weak feedback; for example, rewriting the silicate weathering rate approximation used in the GEOCARB models (36) in this form gives a dependency of $(RCO_2)^{-1.15}$. Evidence for a strong seafloor weathering feedback in the Mesozoic (24) suggests that $\alpha = 0.23$ may be a low estimate.

Results and Discussion

We first investigate the model response to changes in external forcing factors—terrestrial weatherability (W, Fig. 2), seafloor spreading rate (Fig. 3), and the incoming solar flux (Fig. 4). We then use reconstructions of these forcings over 1,500–500 Ma to produce predictions for Proterozoic climate (Fig. 5). Figs. 2–4 show model steady states with other parameters fixed at values for 1,000 Ma and the initial size of the crustal inventories of buried carbon chosen based on an existing model (44).

The results confirm that a change in terrestrial weatherability (Fig. 2) can translate to a permanent change in the terrestrial chemical weathering fluxes by altering the balance of CO₂ sinks, and that oxygen concentration at steady state is extremely sensitive to this balance. This holds for all values of the seafloor weathering feedback strength, providing some feedback exists ($\alpha > 0$). Allowing changes in terrestrial weatherability (W) to affect oxidative weathering of organic matter (an O₂ sink) in addition to silicate and carbonate weathering weakens its effect on atmospheric O₂, but does not change its sign unless α is very small (see Fig. S1).

Changes in seafloor spreading rate (Fig. 3) have a more complex effect on oxygen concentration. Increasing the spreading rate shifts the carbon removal balance toward seafloor weathering as would be expected; however, it also increases the rate of CO₂ release from subduction zones, which results in higher rates of CO₂ removal via both pathways (due to a larger CO₂ source). So, while an increase in spreading rate always drives a decrease in the fraction of carbon

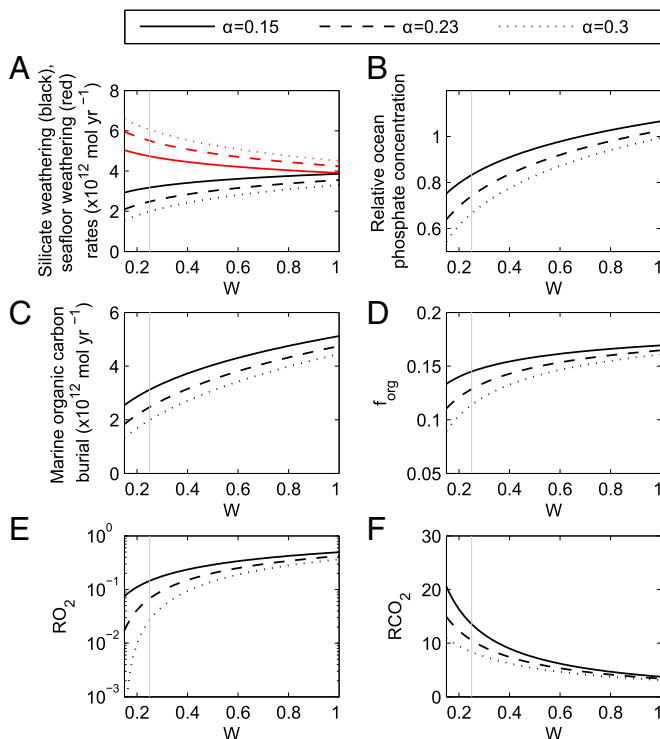


Fig. 2. Model steady states at 1,000 Ma as a function of terrestrial weatherability, W . Line type shows choices for the dependency of seafloor weathering rate on atmospheric CO_2 concentration. Rates of silicate and seafloor weathering (A), relative ocean phosphate concentration (B), organic carbon burial rate (C), the fraction of carbon buried organically (D), relative atmospheric oxygen (E), and CO_2 concentrations (F). Weatherability is defined as the global weathering flux that would be expected under present-day conditions, relative (i.e., normalized) to the present-day flux. Gray vertical line denotes best guess for W at 1,000 Ma. We assume a relative spreading rate and solar forcing of 1.83 (37) and 0.923 (38), respectively.

that is buried as organic matter (f_{org}), it only results in a significant oxygen decrease if the feedback strength is at least the value predicted by Brady and Gislason (25) ($\alpha \geq 0.23$). In COPSE, the rate of CO_2 degassing also depends on the carbon content of the crust, which has increased over time (44). Thus, considering steady states at 500 Ma shows a weaker link between spreading rate and oxygen concentration (Fig. S2); however, oxygen still decreases under an increase in spreading rate for $\alpha \geq 0.23$.

Altering the solar flux (S , Fig. 4) has a similar effect to changing the terrestrial weatherability, because terrestrial weathering rates are highly dependent on surface temperature. The difference is that while the weatherability parameter, W , is assumed to enhance silicate and carbonate weathering equally, the solar flux has a stronger effect on silicate weathering due to its assumed stronger temperature dependence (36). Carbonate weathering and deposition has no net effect on the carbon cycle but does release phosphate. This means that for low values of α , increasing the solar flux may result in a decreased rate of carbonate weathering at steady state (due to large decreases in CO_2 concentration), and a lower phosphate and hence O_2 concentration. For $\alpha \geq 0.23$, an increase in the solar flux produces a significant increase in steady state oxygen concentration. Some direct effect of surface temperature change on seafloor weathering rates is also expected, via deep water temperature, which is not considered in COPSE. However, the temperature dependence of terrestrial weathering fluxes is much stronger (25).

Model burial fluxes for phosphate have been modified to take into account the high concentration of dissolved silica in the

Precambrian, before the evolution of radiolarians and diatoms (45). In the baseline model used, the flux of iron-sorbed phosphorus burial is removed from COPSE following the assumption of extreme limitation under high silica (32). The model has also been run (see Figs. S3–S6) with further limitation of calcium-associated phosphorus burial, which may have occurred due to high alkalinity during the Precambrian (32). This results in higher concentrations of phosphate and oxygen for all scenarios. However, with a feedback strength of $\alpha \geq 0.23$, oxygen still decreases under an enhanced spreading rate and increases under an enhanced solar flux.

Because of the simplicity of our model, the results should be viewed as “pseudo”-steady states. The model does not include transfer between the mantle and the surface Earth system, or escape of hydrogen to space, and therefore does not represent a complete model of the oxygen cycle. However, the processes that we are interested in are not affected by these simplifications. Values for α outside of the range we have considered affect the model in a predictable way, shifting O_2 predictions further from the baseline ($\alpha = 0.23$) results.

Fig. 5 shows model steady states at discrete time points between 1,500 Ma and 500 Ma for the case $\alpha = 0.23$. Results are plotted, where possible, against geological data. The choices for weatherability, W , reflect the uncertainty in the value of this parameter before the evolution of vascular plants in the Phanerozoic (46); the best guess of $W = 1/4$ (12) is shown in black. Declining spreading rate over the Proterozoic [taken from the model of Lowell and Keller (37) and shown as a gray dashed line in Fig. 5A] alongside an increasing solar flux [following Caldeira and Kasting (38) and shown as a gray dashed line in Fig. 5B]

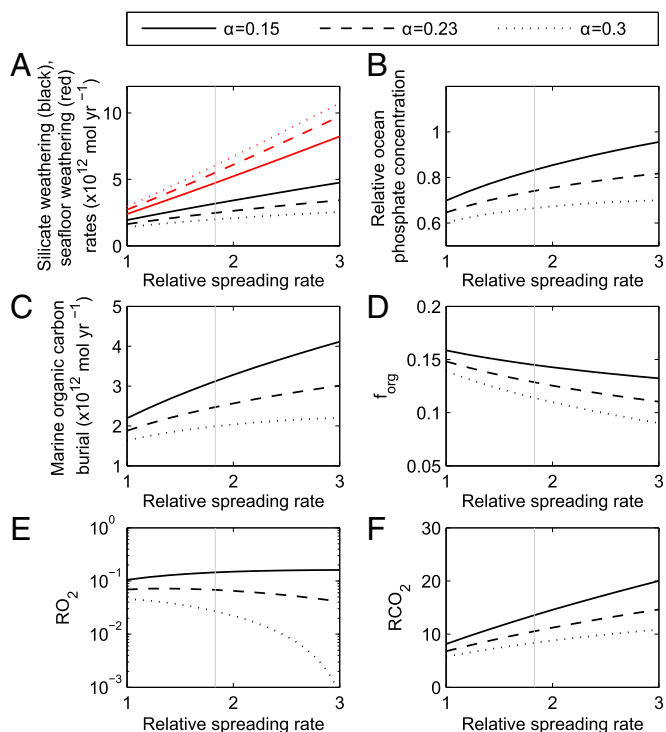


Fig. 3. Model steady states at 1,000 Ma as a function of relative seafloor spreading rate. Line type shows choices for the dependency of seafloor weathering rate on atmospheric CO_2 concentration. Rates of silicate and seafloor weathering (A), relative ocean phosphate concentration (B), organic carbon burial rate (C), the fraction of carbon buried organically (D), relative atmospheric oxygen (E), and CO_2 concentrations (F). Gray vertical line denotes assumed spreading rate at 1,000 Ma (37). We assume a terrestrial weatherability and solar forcing of 1/4 (12) and 0.923 (38), respectively.

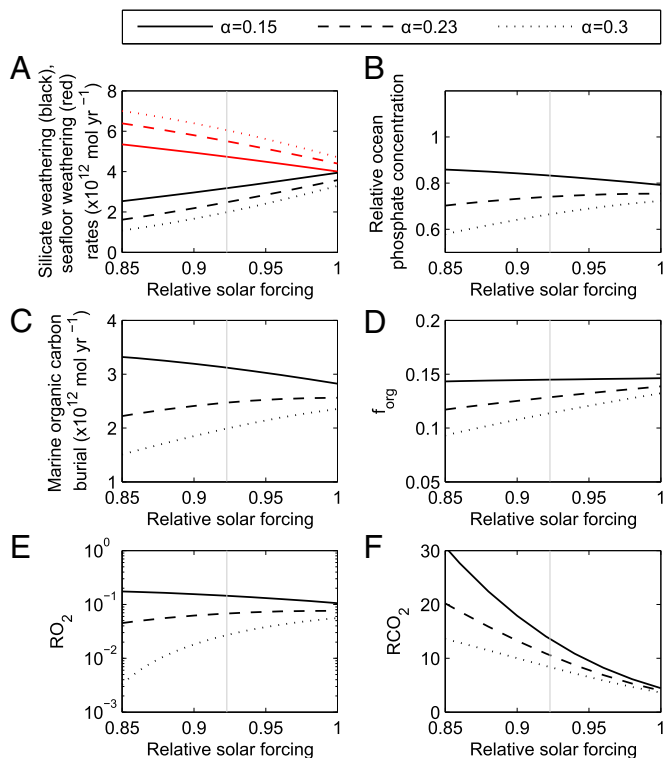


Fig. 4. Model steady states at 1,000 Ma as a function of relative solar flux. Line type shows choices for the dependency of seafloor weathering rate on atmospheric CO_2 concentration. Rates of silicate and seafloor weathering (A), relative ocean phosphate concentration (B), organic carbon burial rate (C), the fraction of carbon buried organically (D), relative atmospheric oxygen (E), and CO_2 concentrations (F). Gray vertical line denotes assumed solar flux at 1,000 Ma (38). We assume a relative terrestrial weatherability and spreading rate of 1/4 (12) and 1.83 (37), respectively.

leads to a gradual weakening of the seafloor weathering carbon sink and a shift in the carbon removal balance toward terrestrial weathering. The result is a gradual increase over time in phosphorus delivery to the ocean and organic carbon burial, causing an increase in atmospheric oxygen over 1,500–500 Ma.

It is not absolutely certain that the global spreading rate has declined over time. One recent model (47) predicts a gradually increasing mantle heat flow and spreading rate over the Proterozoic. When incorporated into our model (Fig. S7), this significantly reduces the rate of oxygen increase. However, it is insufficient to reverse the O_2 rise, which is caused in this case by the increasing solar forcing.

High positive carbonate $\delta^{13}\text{C}$ observed across the Neoproterozoic and inferred high ocean phosphate, as well as low temperature associated with global glaciation, may be linked to a period of tectonically enhanced weatherability due to supercontinent breakup, unusually equatorial continental configuration, and the outpouring of large igneous provinces (48, 49). In our model, this would translate into a large increase in weatherability, perhaps to levels higher than the present day. The light green line in Fig. 5 shows $W = 2$ for the period 850–600 Ma. Note that O_2 and phosphorus increases in the model significantly predate current estimates for deep ocean oxygenation occurring around 635–580 Ma (50), although there is some evidence for rising O_2 throughout the breakup of Rodinia (1, 4).

Geologically forced increases in weatherability in the Neoproterozoic were likely transient, as the supercontinent Pangaea began to reform early in the Phanerozoic. This would be expected to cause oxygen concentration to drop in the Paleozoic after the

Neoproterozoic rise. Alternatively, if an expansion of land-based photosynthetic organisms occurred over the Proterozoic (51, 52), their enhancement of the terrestrial weathering process would be expected to cause a permanent shift toward higher weatherability and atmospheric O_2 .

Our model results for f_{org} (the fraction of carbon buried as organic matter) are consistently lower than the isotope-derived model it is compared with (8) (Fig. 5D). However, our model predictions for this fraction are largely dependent on the assumed present-day inorganic carbon fluxes in COPSE and the reduction in organic carbon burial due to the absence of land plants, which are both uncertain. Assuming extreme limitations on phosphate burial (32) (Fig. S6), our predicted f_{org} fits the isotope model (8) more closely. However, the present work is primarily concerned with the trends in this parameter rather than the absolute value. An alternative isotope model incorporates seafloor weathering as a carbon removal pathway (28) and produces similar f_{org} predictions to the current work. This requires

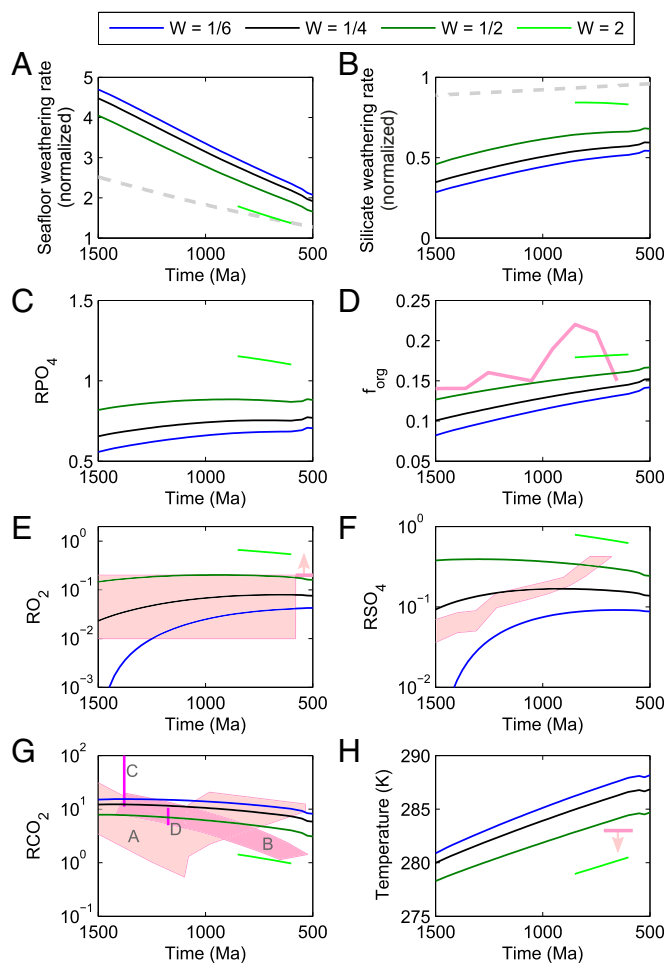


Fig. 5. Model steady states at discrete time points for 1,500–500 Ma for $\alpha = 0.23$. Line color denotes relative weatherability of the continents, W . Relative spreading rate (37) shown as dashed gray line in A; relative solar forcing (38) shown as dashed gray line in B. Geological constraints are shown in pink. Plotted are normalized rates of seafloor (A) and silicate (B) weathering; relative ocean phosphate concentration (C); the fraction of carbon buried organically (D); relative atmospheric oxygen concentration (E) against the constraints from refs. 6 and 39; relative ocean sulfate concentration (F) against ref. 3; relative CO_2 concentration (G) against data from ref. 9 (A), ref. 40, (B), ref. 41 (C), and ref. 42 (D); and global average surface temperature (H) shown with expected low temperature during the Neoproterozoic glacial period (43).

that seafloor weathering imparts a negative carbon isotope fractionation, which has been challenged by recent data (53).

Modeled temperature for >1,000 Ma is much lower than the absence of glaciation in the geologic record would suggest. Our model is, however, consistent with the evidence for modest CO₂ concentrations at this time (9, 42). A possible solution is that methane—a greenhouse gas not included in our model—was at a higher concentration under low Proterozoic oxygen concentrations (54), and would have boosted global temperature. We would expect higher surface temperature to shift the carbon removal balance toward silicate weathering, thus increasing oxygen concentration. However, high methane concentration would also increase the oxygen sink due to photochemical reaction between O₂ and CH₄ (55).

The results here show that enhancements of the continental weathering process may result in permanent changes in phosphorus supply to the ocean, which in turn influences organic carbon burial and ultimately atmospheric oxygen concentration. Hence we propose that planetary oxygenation during the Proterozoic may have depended on speeding up the terrestrial side of the carbon cycle, shifting the balance away from deep sea carbon removal.

Our model prediction of rising O₂ over the Proterozoic requires the dependence of seafloor weathering rate on CO₂ concentration to be at least as strong as the results of Brady and Gislason (25) suggest (i.e., $\alpha \geq 0.23$). The conclusions of Coogan and Gillis (24) point toward a stronger relationship, but, assuming a weak relationship of $\alpha \leq 0.15$, the O₂ response to changes in spreading rate and solar forcing is reversed (Figs. 3 and 4) and our model would predict a gradual fall in O₂ over the Proterozoic. The argument presented here is largely theoretical. Further

observational work to establish the changing rate of carbon uptake by the oceanic crust, and its power as a feedback mechanism, will clearly be important in determining the history of atmospheric oxygen.

Methods

Transfer of carbon from the hydrosphere to the crust via seafloor weathering follows Sleep and Zahnle (27) and the formulation of other fluxes in COPSE:

$$sfw = k_{sfw} \left(\frac{dA}{dt} \right) (RCO_2)^\alpha, \quad [1]$$

where $\frac{dA}{dt}$ is the relative spreading rate, RCO₂ denotes the relative concentration of CO₂ in the atmosphere, and $k_{sfw} = 1.75 \times 10^{12}$ mol/y is the assumed present-day rate, taken between current estimates (18–20). We follow ref. 27 in letting α express the dependency of hydrothermal carbonization on ocean CO₂. The seafloor weathering flux is added to COPSE as a transfer of carbon from the combined ocean/atmosphere reservoir to the buried carbonate reservoir. Other minor alterations are made to the COPSE model to make it more applicable to the Precambrian and to improve robustness to temperature and oxygen concentration outside the Phanerozoic window. See *SI Text* for list of modifications and full model equations.

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