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Article

Keywords: Marine Biota, Biogeochemistry, Geologic History, Total Weathering Rate, Ocean Productivity, Evolution of Marine Fauna

Posted Date: July 2nd, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-618748/v1>

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Weathering controls on the Phanerozoic phosphate cycle

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Although phosphate is an essential macronutrient for marine biota, critical to our understanding of marine productivity, biogeochemistry, and evolution, its long-timescale geologic history is poorly constrained. We constrain weathering-derived fluxes and seawater concentrations of phosphate throughout the Phanerozoic (541 Ma to present), by developing a model for the coupled, long-term biogeochemical cycles of phosphate, carbon, oxygen, and calcium. We find that the relative contribution of continental and seafloor weathering to the total weathering rate exerts a first-order control on ocean productivity, through a previously uninvestigated mechanism. Specifically, continental weathering is a source of the limiting nutrient phosphate, but seafloor weathering is not. As a result, times in Earth history in which seafloor weathering constitutes a large fraction of the total weathering rate (e.g., the early Paleozoic and Mesozoic), are also times in which phosphate delivery to the ocean is relatively low. A lower concentration of phosphate in seawater likely affected primary productivity, oceanic and atmospheric oxygen concentrations, with possible implications for the evolution

14 **of marine fauna over Earth history.**

15 By limiting marine primary productivity and organic carbon (C) burial over geologic
16 timescales, the long-term availability of phosphate (P) is a key determinant of atmospheric oxygen
17 and carbon dioxide levels (pO_2 and pCO_2 , respectively)¹⁻⁴, climate⁵, and marine faunal evolution
18 and diversity patterns⁶. On geologic timescales, the size of the marine P reservoir is set by a balance
19 between P supply from continental weathering and P loss, mostly by burial in sedimentary rocks⁷⁻⁹.
20 On timescales comparable to the mixing time of the ocean (thousands of years) the given long-term
21 marine P reservoir is distributed between the surface and deep ocean by a balance between P in-
22 corporation into newly fixed organic matter and P release during organic matter remineralization⁵.
23 The long-term source of P into the ocean is chemical weathering of continental silicate rocks⁸⁻¹⁰.
24 Seafloor weathering, on the other hand, is considered to be a minor sink of P¹¹⁻¹³. During seafloor
25 weathering, away from the spreading axis, low-temperature (generally 5–20°C) water circulates in
26 the highly porous upper oceanic crust¹⁴. Though the exact mechanism is unclear, porewater and
27 bulk-rock chemical analyses suggest that P is removed from seawater during off-axis water-rock
28 interactions, likely due to adsorption onto iron-(oxy)hydroxides in sediments, secondary apatite
29 precipitation, or microbial activity in the crust¹¹.

30 Both continental and seafloor weathering rates depend on temperature through the chemical
31 reaction kinetics¹⁵⁻¹⁸. Continental silicate weathering rates also depend on temperature through
32 changes in precipitation and runoff, which alter the water to rock ratio¹⁹⁻²¹. The temperature
33 dependence of both continental and seafloor weathering has led to suggestions of negative cli-

mate feedbacks^{17,22–27}. According to these feedbacks, at a given volcanic outgassing rate, CO₂ will accumulate in the atmosphere to a steady-state concentration at which the global-average temperature-dependent continental and seafloor weathering rates (which are equal to the rate of carbonate burial) exactly match the CO₂ outgassing rate. As continental weathering is also the source of the nutrients required for the production of organic matter, a similar feedback is suggested to exist between the temperature-dependent rate of continental P weathering and organic C burial^{23,28}. Since continental silicate weathering is a source of both calcium (Ca) and P and seafloor weathering is only a source of Ca and a minor sink of P, the relative proportion of seafloor weathering to the total weathering (seafloor + continental) has implications for the P balance. For example, a gradual increase in pO_2 over 1,500–500 Ma has been suggested to reflect a gradual increase in the relative proportion of continental weathering, shifting the balance between the inorganic and organic C burial sinks²⁹. The consequences for the Phanerozoic P cycle, to our knowledge, have not been fully explored.

Here, to study the evolution of the Phanerozoic P cycle, we developed a model for the coupled, long-term biogeochemical cycles of P, C, O₂, and Ca (Fig. 1), and simulated the fluxes of these elements between the ocean-atmosphere and rock reservoirs in response to major geologic forcings. We account for the significant parameter and forcing uncertainties by drawing these from distributions that represent the uncertainty in their values (*Supplementary Information, SI*). We validated our model against geologic proxies for pCO_2 , the C isotopic composition ($\delta^{13}C$) of carbonate minerals, and the C content of altered oceanic crust (*Methods*). We propose an evolutionary trajectory of the P cycle, consistent with these and other observational constraints. Our results

suggest that the P weathering flux and marine concentration varied throughout the Phanerozoic in response long-term variations in continental weatherability.

Continental and seafloor weathering throughout the Phanerozoic

Our analysis suggests that during the early Paleozoic era, continental weathering rates were low and seafloor weathering rates were high, relative to their present-day values. The lower contribution of continental weathering-derived alkalinity influx to the ocean (out of the total weathering-derived alkalinity influx) stems from lower continental weatherability before the evolution of land plants. Land plants enhance continental weatherability in several ways, for example, by exuding organic acids and metal chelators, by increasing the surface area for weathering due to their extensive root systems, and by recirculating water through evapotranspiration. The lower weatherability results in a balance between the volcanic CO₂ source and the weathering CO₂ sink (comprised of CaCO₃ and organic C burial) at a higher global-average temperature (Extended Data Fig. 1). The higher temperature accelerates both continental and seafloor weathering. As continental weatherability was significantly lower than the present, seafloor weathering becomes the dominant source of alkalinity to the ocean (Fig. 2).

As land plants expanded, ~400 to 350 Ma, continental weatherability increased, and a balance between CO₂ inputs and outputs was reached at a lower surface temperature. This resulted in slower temperature-dependent kinetics of both seafloor and continental weathering, though continental weathering rates net increased due to the higher plant-related weatherability (Fig. 2). During

the assembly of the supercontinent Pangaea between ~ 306 and 237 Ma, the average annual precipitation over land is thought to have decreased to a mid-Triassic minimum lower than today (Extended Data Fig. 2), due to the difficulty of delivering moisture to inland regions³⁰. Lower precipitation results in lower weathering rates at a given temperature, requiring a higher temperature for seafloor and continental weathering rates to match the volcanic outgassing rates. As in the early Paleozoic, the higher temperature accelerates both continental and seafloor weathering. However, due to the low continental weatherability, in this case related to lower precipitation over land, seafloor weathering becomes the dominant source of alkalinity to the ocean (Fig. 2b). In contrast, during the breakup of Pangaea, which started at ~ 237 Ma, continental weathering rates increased and seafloor weathering decreased to present-day levels (Fig. 2).

Our proposed geologic history of seafloor weathering rates is consistent with observed changes in CO₂ content of the oceanic crust^{14,26,31,32}. During seafloor weathering reactions, Ca is leached from the basalts, increasing the Ca concentration in crustal pore fluids, and promoting CaCO₃ precipitation in veins and void fillings^{14,17,26,31}. The rate of C addition to altered oceanic crust, as inferred from its measured CO₂ content²⁶, is higher in the Mesozoic than over Cenozoic time (Fig. 2b markers; Supplementary Table S1). Measurements of ⁸⁷Sr/⁸⁶Sr in the crustal carbonate minerals suggest that the ~ 5 fold C enrichment in Mesozoic cores results not from longer accumulation times, but from faster temperature-dependent kinetics of seafloor weathering²⁶. Our model trajectory of seafloor weathering rates matches the available Mesozoic-Cenozoic observations, providing confidence in this trajectory over Phanerozoic time.

Phosphate weathering and concentration throughout the Phanerozoic

As continental weathering is a source of both alkalinity and P, whereas seafloor weathering is a source of alkalinity only, the variation in the relative importance of continental and seafloor weathering described above carries implications for the marine P budget. Our results (of 10^6 random parameter draws; Fig. 3) indicate that the high relative importance of seafloor weathering in the early Paleozoic (Fig. 3b) led to weathering-derived P fluxes and deep-ocean P concentrations that are both lower-than-present by a factor of ~ 3 . When land plants evolved (~ 400 – 350 Ma) and continental weatherability increased, weathering-derived P influxes and deep-ocean P concentrations increase in response to the higher relative importance of continental weathering. The low continental weatherability during the tenure of the supercontinent Pangaea (~ 306 – 237 Ma), caused by the difficulty of delivering moisture to the continental interior, results in lower weathering-derived P influxes and marine P concentrations. In contrast, since the onset of the breakup of Pangaea (~ 237 Ma) P delivery rates and deep-ocean concentrations increased toward their present-day values. Our predicted geologic history of the P cycle (weathering and organic C burial fluxes) differs from a recent prediction based on $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{13}\text{C}$ values in marine carbonates³³. We note, however, that the aforementioned prediction accounted neither for recognized changes in continental lithology as drivers of marine carbonate $^{87}\text{Sr}/^{86}\text{Sr}$ records, nor for recognized deviations in the C:P of buried organic matter from the “Redfield” ratio of 106:1.

Weathering-derived P influxes and the seawater P concentrations depend on assumptions about the temperature dependence of seafloor weathering rates. Assuming that seafloor weather-

ing rates are temperature-independent, only alkalinity influxes from continental weathering may respond to changes in CO₂ outgassing, through a change in the global average surface temperature. As continental weathering is also a source of P, in this case, higher CO₂ influxes translate directly to higher P influxes. For this reason, with temperature-independent seafloor weathering rates, the Paleozoic weathering-derived P influxes and deep-ocean P concentrations are higher than with temperature-dependent seafloor weathering, and they closely follow the temporal evolution of the CO₂ outgassing rate (dark red envelope; Fig. 3). Below, we argue that the limited observational constraints on the evolution of seawater P concentrations support temperature-dependent seafloor weathering.

To our knowledge, there is only a limited number of proxies for the marine P concentration. An increase in P/Fe ratios in iron-oxide-rich marine sediments, from a pre-Cretaceous average of 0.38 to a Cretaceous-Cenozoic average of 2.55, has been interpreted to reflect a change in the silica cycle, rather than an increase in the seawater P concentration⁴. Specifically, a decrease in the seawater silica concentration due to the expansion of siliceous phytoplankton (diatoms) was inferred to have reduced the competition with P for adsorption sites on the surface of iron oxides, resulting in enhanced P adsorption and higher P/Fe, without a major change in the seawater P concentration. However, the Phanerozoic silica cycle is poorly constrained³⁴, making estimates of Phanerozoic seawater silica concentrations uncertain. Moreover, diatom expansion is recorded only around 66 Ma^{35–37}, inconsistent with the observed timing of the increase in P/Fe. Instead, at least part of the P/Fe increase in sedimentary rocks may reflect the Triassic to Cretaceous increase in seawater P concentrations predicted by our model in response to the breakup of Pangaea (Fig.

3).

Indirect evidence for an increase in P availability through the Phanerozoic is suggested by the temporal succession of dominant phytoplankton taxa. The dominant phytoplankton taxa of the early Paleozoic were green algae and cyanobacteria^{35,36}. Dinoflagellates and coccolithophorids dominated in the Mesozoic and Paleogene, followed by the explosive diversification of diatoms during the Neogene^{35,36}. In cultures of modern representatives of these major groups, taxa from groups that emerged later in Earth history tend to prefer progressively more P-rich conditions³⁸, and tend to produce biomass richer in P³⁹⁻⁴¹. If these nutrient requirements and utilization patterns are conserved group-specific traits, they suggest that P availability increased over the Phanerozoic⁶.

Implications for the carbon and oxygen cycles

Predicted marine primary productivity (Tmol C yr^{-1}) tracks the dissolved surface P concentration (Fig. 4a, b), as primary productivity is calculated from the surface-ocean P concentration and the elemental composition of the primary producers (here assumed to be constant at the Redfield ratio; *SI*). Accordingly, early Paleozoic primary productivity is ~ 2.5 times lower than today (Fig. 4b). Though the burial of marine-derived organic C is proportional to marine primary productivity, early Paleozoic organic C burial is lower than today by only $\sim 30\%$ (Fig. 4c). This muted response to lower-than-present primary productivity is related to lower early Paleozoic $p\text{O}_2$ (Fig. 4e, f), which led to a higher marine organic C burial efficiency⁴². Lower early Paleozoic $p\text{O}_2$ stems from the absence of land plants and the associated terrestrial organic C burial flux (Fig. 4d), which has

C:P approximately an order of magnitude higher than marine organic C.

The $\delta^{13}\text{C}$ values of marine carbonate rocks are widely used to constrain the relative proportions of organic C and CaCO_3 burial^{30,43,44}. With the emergence of land plants, our model predicts a ~ 3 -fold increase in organic C burial, driven mostly by the onset of terrestrial organic C burial. Over the same period, inorganic C burial is predicted to increase by only a factor of ~ 2 (Extended Data Fig. 1). Nevertheless, model carbonate $\delta^{13}\text{C}$ values only modestly increase over this interval, consistent with the marine carbonate $\delta^{13}\text{C}$ record (Extended Data Fig. 1). The modest increase is due to the stabilizing effect of oxidative weathering of organic C-bearing sedimentary rocks (e.g., ref. 45), which delivers ^{13}C -depleted C to the oceans more rapidly upon the land plant-related $p\text{O}_2$ increase.

Our trajectory for deep-ocean O_2 concentrations is consistent with molybdenum isotope and iron-based proxies for deep-ocean O_2 concentrations, as well as with previous model estimates of atmospheric $p\text{O}_2$, which suggest a late Paleozoic increase in deep-ocean O_2 concentrations from a few tens μM to near-modern values^{46–49}.

Conclusions

We identify the relative importance of continental and seafloor weathering as a key factor in the marine P cycle and, through the effect of P on primary productivity, also the global C and O_2 cycles. Our analysis reveals two geologic events where a change in the relative importance of continental and seafloor weathering drove enhanced P delivery rates. The first event was the evolution of land

plants during the Devonian, which facilitated the uptake of nutrients from rocks. The second was the Mesozoic breakup of the supercontinent Pangaea, which resulted in an increase in precipitation over the continents. Both events increased continental weatherability, thereby increasing the relative importance of continental out of the total weathering, and enhancing the P supply to the ocean. Our biogeochemical model suggests that the enhanced P supply led to an increase in marine primary productivity, with possible implications for evolutionary trajectories of the biosphere over time.

Methods

Modern phosphate cycle

The long-term biogeochemical cycle of P involves a source from physical and chemical weathering of silicate rocks on land, mainly apatite, and oxidative weathering of organic matter in sedimentary rocks. A fraction of the weathered P is buried as terrestrial organic biomass, either on land or in marine environments, with much of the burial occurring in deltaic environments. However, most of the P is delivered to the ocean. The forms of P that enter the ocean are particulate and dissolved, organic, and inorganic. The riverine flux of particulate inorganic P into the sea is 0.23–0.65 Tmol P yr⁻¹ (refs. 9, 10, 50), the particulate organic P influx is 0.03–0.26 Tmol P yr⁻¹ (refs. 51, 52), and the total dissolved P (organic and inorganic) influx is 0.01–0.06 Tmol P yr⁻¹ (refs. 7, 9, 10, 53–55). Some of the P that enters the ocean, mostly the particulate P, is not bioavailable and is buried as detritus or iron oxide-bound P in shelf sediments^{9,10}. However, a fraction of

the initially unavailable P become bioavailable due to bacterial remineralization of the organic P, and/or release by reductive dissolution of the iron oxide-bound P. The flux of bioavailable P from continental weathering is loosely constrained due to the large uncertainty associated with the fraction of particulate P that becomes bioavailable, estimated to be 8–69%^{10,52,56–60}.

Most of the bioavailable P, after being fixed in newly produced organic matter, settles to the sediments⁹. In the sediments, the organic matter undergoes remineralization and dissolved (bioavailable) P is released into the sediment porewater. From the sediment porewater, the dissolved P may either diffuse back into the ocean, precipitate as apatite [$\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{Cl}, \text{F})$], or adsorb onto iron-oxide particles, depending on the chemical composition and oxidation state of the porewater. The modern flux of organic C burial is between 4.5 and 18 Tmol C yr⁻¹. The molar ratio of C to P in buried organic matter, which depends on the degree of ocean anoxia, is between 237 and 250 (mol C mol P⁻¹). Thus, a total of 0.018–0.076 Tmol P yr⁻¹ is ultimately buried as organic P. The modern fluxes of P burial as apatite and iron oxide-sorbed P are 0.015–0.091 and 0.024–0.041 Tmol P yr⁻¹, respectively (see Supplementary Table S2).

In addition to the sedimentary P sinks described above, P is removed from the deep ocean by adsorption onto iron-oxide particles formed by oxidation of reduced iron emitted in hydrothermal plumes at mid-ocean ridges. The modern-day flux of P removed in this process is estimated at 0.004–0.008 Tmol P yr⁻¹. Furthermore, oceanic P is also removed by ridge-flank crustal reactions. It is unclear whether P is removed via adsorption onto iron (oxy)hydroxides in sediments, secondary apatite precipitation, or biological processes in the crust¹¹. The magnitude of this flux

in the present ocean is loosely constrained and is estimated at 0.007–0.028 Tmol P yr⁻¹ (Supplementary Table S2).

Model development and numerical solution

In order to decipher the evolutionary trajectory of P in response to different geologic forcings throughout the Phanerozoic, we develop a model for the coupled, long-term biogeochemical cycles of the P, C, O₂, and Ca, as well as total pools of sedimentary organic matter and carbonate rocks (Fig. 1). The model simulates the fluxes of these elements between the ocean-atmosphere and rock reservoirs, and computes the ocean carbonate system. Using the model, we simulated the evolution of the marine and sedimentary pools of these elements through the Phanerozoic by adopting some established forcings and parametrizations and introducing new parametrizations (*SI*).

To account for the uncertainties associated with the parameters and time-dependent forcings, we performed $\sim 10^6$ simulations. In these simulations, we randomly drew 34 parameters and 11 time-dependent factors from distributions that represent the uncertainty in their values (Supplementary Tables S2–S8 and Extended Data Fig. 2). We exclude simulations that yielded results out of allowable ranges of several present-day observables. The allowable ranges include $\pm 50\%$ preindustrial $p\text{CO}_2$ (μatm), $\pm 15\%$ of modern $p\text{O}_2$ (atm), $\pm 15\%$ of modern deep-ocean P concentration ($\mu\text{M P}$), $\pm 15\%$ of modern oceanic Ca concentration (mM Ca), $\pm 4\text{K}$ of modern global surface temperature, and 2σ around the mean of the C isotopic composition of carbonate minerals in modern marine sediments (‰) (Supplementary Table S9).

To test the sensitivity of the model prognostics to the different parameters, we varied each parameter (total 34) within its range, and recorded the deep-ocean P concentration at two time points, 0 and 500 Ma. The results are presented in Extended Data Fig. 3. We further tested the model prognostics' sensitivity to the different geologic forcings by applying each one of the forcings separately, together with the Phanerozoic evolution of solar luminosity, which was included in all model sensitivity simulations. The results are presented in Extended Data Figs. 4–5. The marine P concentration, which is the main prognostic of interest in this study, is sensitive to the parameters and forcings that affect the delivery of alkalinity and CO₂ to the ocean-atmosphere. The reason for this sensitivity is that the influxes of P to the ocean depend on the absolute rates and relative contributions of continental and seafloor weathering (i.e., sources of alkalinity), which are required to balance the outgassing source of CO₂ by a combination of carbonate and organic C burial. Thus, the parameters and forcings that affect the delivery of alkalinity and CO₂ to the ocean-atmosphere ultimately control the sources and major sinks of P.

Model validation

In Extended Data Fig. 1, we compared our model output to a compilation of $\delta^{13}\text{C}$ values in marine carbonate rocks⁴⁴, which contains 43,972 samples. Data before the mid-Jurassic are derived mostly from shallow-water (platform), near-shore carbonates. Data from the Jurassic through the modern are derived mostly from CaCO₃ secreted by planktonic foraminifera and calcareous nannoplankton, which was extracted mainly from oceanic drill-cores. Overall, the envelope covering 90%

of the model $\delta^{13}\text{C}$ results is mostly within one standard deviation of a 10-million-year moving average of $\delta^{13}\text{C}$ values measured in marine carbonate rocks.

In Extended Data Fig. 1, we compared our model $p\text{CO}_2$ predictions to ~ 1240 newly calibrated proxy $p\text{CO}_2$ estimates derived from 112 studies of stomatal density in fossilized leaves, the $\delta^{13}\text{C}$ values in alkenones, liverworts and carbonate minerals in paleosols, and marine boron isotopes⁶¹. The uncertainty envelope on the proxy $p\text{CO}_2$ estimates (the 5th to 95th percentiles) includes the error associated with each proxy and age determination⁶¹. The overall pattern in the proxy records is of high $p\text{CO}_2$ (maximum probability between 1000 and 2000 ppm) during the early Devonian, a decline to present-day levels by ~ 320 Ma, a rise to high $p\text{CO}_2$ (maximum probability between 1000 and 2000 ppm) during the early Mesozoic, and then a decline to present-day levels⁶¹. This pattern is roughly captured by our model envelope over the time period covered by the proxy records. The model produces elevated $p\text{CO}_2$ (~ 1000 – $4,000$ ppm) during the early Devonian, low $p\text{CO}_2$ (~ 300 – 400 ppm) between ~ 350 and 252 Ma, higher early Mesozoic $p\text{CO}_2$ (~ 1000 – 3000 ppm) and a Cenozoic decline to present-day $p\text{CO}_2$ (Extended Data Fig. 1).

In Fig. 2b we compared the Ca flux from the altered oceanic crust, estimated from the bulk CO_2 content of oceanic crust at different ages and an assumption of a 1:1 molar ratio of Ca:C in the crustal carbonates that yielded the CO_2 , to the fluxes of Ca leaching from the oceanic crust obtained in our model. The bulk CO_2 content of the altered crust was obtained from Table 1 in Gillis & Coogan (2011)²⁶. We note that the parameterization of the Ca leaching fluxes in our model (SI) is unrelated to the observations of Gillis & Coogan (2011), making this comparison an

independent test of the predicted Ca fluxes. To convert from CO₂ (%wt) to C flux from the ocean into the crust (Tmol C yr⁻¹), which is approximately equivalent to the Ca flux from alteration of the oceanic crust, we used the following equation: $F_{\text{CO}_2} = \frac{\Delta\text{CO}_2}{MW_{\text{CO}_2}} \times d \times \rho \times R_{\text{SFS}}^0 \times f_{\text{SF}} \times 10 \times 10^{-12}$, where F_{CO_2} is the flux of CO₂ from the ocean into the crust (Tmol C yr⁻¹), ΔCO_2 is the inorganic C uptake by the oceanic crust (as measured, not including sediment) (%wt=g 100g⁻¹), d is the crust thickness (600 m), ρ is the density of the crust (2900 kg m⁻³), R_{SFS}^0 is the present-day rate of crust production ($3.45 \times 10^6 \text{ m}^2 \text{ yr}^{-1}$), MW_{CO_2} is the molecular weight of CO₂ (44 g mol⁻¹), f_{SF} is a unitless, time-dependent parameter that describes the enhancement in the rate of seafloor production, relative to the present day (unitless; *SI*; Extended Data Fig. 2), 10 is a multiplier to convert %wt units to 100g kg⁻¹, and 10⁻¹² is to convert mol to Tmol.

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Acknowledgements: We thank the Interuniversity Institute for Marine Sciences in Eilat for hosting S.S. **Author Contributions:** S.S. and I.H. conceived the study, developed and analyzed the model, and wrote the paper. **Competing Interests statement:** The authors declare that they have no competing financial interests. **Data availability:** Supplementary Information is available for this paper. The model code is available with the *SI*. **Correspondence:** Correspondence and requests for materials should be addressed to: shlomit.sharoni@weizmann.ac.il (S.S.); itay.halevy@weizmann.ac.il (I.H.).

Figures

Figure 1: Model scheme. The long-term cycling of P, C, O_2 , Ca, and the sedimentary pools of organic matter (C_{org}) and carbonate rocks ($CaCO_3$). $F_{wP,ocean}$ is the continental weathering flux of P to the ocean, F_{bap} , F_{bFeP} , are P burial fluxes as apatite and iron oxide-sorbed P, respectively, and $F_{plume,P}$, $F_{off,P}$ are the fluxes of inorganic P that is removed by adsorption to iron oxides in hydrothermal plumes, and by off-axis seafloor reactions, respectively. F_{borg} and $F_{borg,land}$ are marine and terrestrial organic matter burial fluxes, respectively. F_v is the CO_2 input from metamorphic and volcanic degassing, and F_{wcarb} and F_{worg} are C weathering fluxes from carbonates and organic matter in sedimentary rocks, respectively. F_{bcarb} is carbonate burial. F_{morg} , F_{mcarb} , F_{ored} are fluxes associated with metamorphism of organic matter-bearing and $CaCO_3$ -bearing rocks, and oxidation of reduced gases, respectively. F_{wsil} and F_{wsf} are the Ca input flux from continental silicate and off-axis seafloor weathering, respectively.

Figure 2: Continental and seafloor weathering throughout the Phanerozoic. Results of $\sim 10^6$ default model simulations (frequency in color contours) where we draw 34 input parameters and 11 time-dependent forcings from probability distributions that represent uncertainty in their values. **(a)** Continental and **(b)** seafloor weathering rates (Tmol Ca yr⁻¹). Markers and error bars represent the inorganic C uptake by the oceanic crust, calculated from the CO₂ content of oceanic drill cores (see Supplementary Table S1). Assuming a 1:1 molar ratio of Ca:C, these fluxes are equivalent to the source of Ca from seafloor weathering reactions. The higher CO₂ contents of the upper crust in the Atlantic Ocean than in the Pacific Ocean, at any given age, are interpreted to reflect the incorporation of recrystallized sedimentary CaCO₃ into the slow-spreading Atlantic crust²⁶.

Figure 3: Phanerozoic phosphate weathering rates and deep-ocean concentrations. Comparison between (a) the P influx to the ocean from continental weathering ($Tmol P yr^{-1}$), and (b) the P concentration in the deep ocean ($\mu M P$) obtained in $\sim 10^6$ default model simulations (same as in Fig. 2, frequency in color contours), in which seafloor weathering rates depend on temperature, and simulation results obtained with temperature-independent seafloor weathering rates (5th to 95th percentiles delineated in dark red).

Figure 4: Effects of the proposed Phanerozoic evolution of the phosphate cycle on the carbon and oxygen cycles. All panels show the results of $\sim 10^6$ default model simulations (same as in Fig. 2, frequency in color contours). **(a)** Phosphate concentration in the surface ocean ($\mu\text{M P}$), **(b)** carbon-based primary productivity (Tmol C yr^{-1}), **(c)** marine organic C burial (Tmol C yr^{-1}), **(d)** terrestrial organic C burial (Tmol C yr^{-1}), **(e)** atmospheric $p\text{O}_2$ (atm), and **(f)** deep-ocean O_2 concentration ($\mu\text{M O}_2$).

Extended Data Figures

Extended Data Figure 1: Results of $\sim 10^6$ default model simulations (as in Fig. 2, frequency in color contours). (a) Temperature (K), (b) CaCO_3 burial rate (Tmol C yr^{-1}), and (c) oxidative weathering rate (Tmol C yr^{-1}). (d) Comparison between model $\delta^{13}\text{C}$ predictions and a compilation of $\delta^{13}\text{C}$ values in marine carbonate rocks. The median of the model predictions of the $\delta^{13}\text{C}$ (‰, PDB) is shown by a black dashed line and the 5th to 95th percentiles of the results are presented as a gray envelope. The carbonate $\delta^{13}\text{C}$ compilation⁴⁴ is shown in light blue markers. A 10-Myr moving average through the $\delta^{13}\text{C}$ compilation (cyan line) is shown with 1 σ (blue lines) and 2 σ (red lines) uncertainty. (e) Comparison between model $p\text{CO}_2$ predictions and proxy $p\text{CO}_2$ data. The model predictions of atmospheric $p\text{CO}_2$ (ppm) are presented as color contours. Proxy reconstructions of $p\text{CO}_2$ are shown in the gray envelope (representing the 5th to 95th percentiles), and the solid black line is the most probable value⁶¹.

Extended Data Figure 2: Time-dependent geologic forcings. (a) The effect of paleogeography on runoff throughout the Phanerozoic (f_{PG}). (b) The seafloor spreading rate (f_{SF}). (c) The effect of continental configuration, latitude and vegetation cover on surface albedo, and consequently, on average continental temperature (ΔT_{geog}). ΔT_{geog} is drawn from a normal distribution, where the mean was adopted from Goddris et al. (2012)⁶², and the standard deviation was adopted from the range of climate predictions associated with the CMIP5 models⁶³. (d) A time-dependent forcing that accounts for the enhancement of the climate sensitivity during cold periods (f_{glac}). f_{glac} is drawn from a uniform distribution between unity and two when there is evidence for long-lived glaciations, and is set to unity over the rest of the Phanerozoic. (e) Weathering enhancement due to land-plant evolution (f_E). (f) A time-dependent forcing that represents the colonization and expansion of terrestrial biomass (f_{cland}). f_E and f_{cland} were drawn from uniform distributions at any given time, where the boundaries of the uniform distribution change over time to account for the evolution of land plants described in the *SI*. (g) Uplift (f_U). (h) Land area (f_A). (i) The fraction of land area covered by carbonates (f_L). (j) The effect of volcanic vs. plutonic land cover on continental weatherability (f_{volc}). (k) The effect of the evolution of pelagic calcifiers on CaCO_3 subduction (f_C). All the time-dependent variables are unitless, and normalized to the present day. Unless mentioned otherwise, all the time-dependent variables were drawn from normal distributions marked by the frequency contours. For more information see *SI*.

Extended Data Figure 3: The sensitivity of deep-ocean phosphate concentration to the model parameters. In each simulation we varied a single parameter (total 34) within its range of values, and recorded the deep-ocean P concentration at two time points, 0 and 500 Ma. For the parameter definitions, see *SI*.

Extended Data Figure 4: The sensitivity of model prognostics to the time-dependent geologic forcings. In each model simulation we applied each one of the forcings separately (total 11), together with the Phanerozoic evolution of solar luminosity. **(a)** The P concentration in the deep ocean ($\mu\text{M P}$), **(b)** atmospheric $p\text{O}_2$ (atm), **(c)** atmospheric $p\text{CO}_2$ (ppm), **(d)** the $\delta^{13}\text{C}$ (‰, PDB), **(e)** temperature (K), and **(f)** Ca concentration in seawater (mM Ca). For the definitions of the time-dependent forcings, see Extended Data Fig. 2 and *SI*.

Extended Data Figure 5: The sensitivity of model prognostics to the time-dependent geologic forcings. As in Extended Data Fig. 4.

Supplementary Files

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