Supplementary Information for
Geologic controls on phytoplankton elemental composition

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Sensitivities of elemental ratios to volcanic outgassing rates. To demonstrate the model sensitivity specifically to volcanic outgassing, we conducted additional model runs where the seafloor-spreading rate was enhanced and reduced by a factor of two. Both mid-ocean and subduction-zone volcanic fluxes are parameterized as linearly proportional to the spreading rates, and as these fluxes account for ~90% of all outgassing, a doubling/halving of the seafloor spreading rate is equivalent to almost a doubling/halving of the total volcanic outgassing rates. These simulations were conducted at 30 and 80 kJ mol⁻¹ activation energies for silicate weathering, a parameter that dictates the strength of the silicate-weathering thermostat.

Our results suggest that periods of rapid seafloor spreading are associated with elevated atmospheric CO₂ and temperature, and higher phosphate (P) concentrations. Furthermore, when the activation energy for silicate weathering is higher, temperatures are lower (i.e., the silicate-weathering thermostat is stronger). The ratios of C:P_{org} and N:P_{org}, therefore, are relatively higher in the simulations with higher volcanic outgassing and lower activation energy. The overall trend of decreasing C:P_{org} and N:P_{org} over the Phanerozoic is conserved at the different outgassing and activation energy extremes explored here, as is the finer structure in this overall decrease (Fig. S1). We note that the uncertainty in model C:P_{org} and N:P_{org} due to these different parameter values are shown in the uncertainty envelope presented in the main text (Fig. 2A, B).

Existing estimates of marine phosphate concentrations and fluxes. There are several model estimates of Phanerozoic seawater P concentrations and/or fluxes (1-6). Though differences among these estimates exist, these differences are relatively small over the last ~400 million years (Fig. S2). The main differences are in the early to middle Paleozoic, where our model consistently yields lower marine P concentrations than the other models (7). However, we note that with two exceptions (1, 6), the focus of the studies cited above was not the P cycle, and versions of the same model sometimes give divergent estimates (e.g., refs. 2 vs. 3; 4 vs. 5). This challenges any effort to identify and discuss the factors controlling these trajectories.

In one of the two studies that did focus on the P cycle, it was suggested that Paleozoic P weathering rates were higher than present by a factor of ~1.5 (1). This estimation is based on a highly simplified model that includes a temperature-dependent weathering equation, convolved with the GEOCARB temperature curve (8), and the evolution of surface area of crystalline rocks (9). However, this model included neither factors that affect continental weatherability, such as land plants and variations in paleogeography and uplift, nor seafloor weathering. Indeed, the authors noted that including the effect of land plant evolution on continental weathering would have resulted in an acceleration of P weathering fluxes during the Devonian. Without accounting for such variations in continental weatherability, we consider the derived P influxes to be uncertain.

In the second study to focus on the P cycle, the $^{87}$Sr/$^{86}$Sr values in marine carbonates were used to estimate marine P influxes (6). Though the marine P concentration is not reported, a Phanerozoic decrease in P influxes of approximately a factor of 1.5, suggests that seawater P concentrations should have decreased by a similar factor (Fig. S2B). However, we note that this model did not account for changes in continental lithology, uplift rates, and paleogeography as drivers of marine carbonate $^{87}$Sr/$^{86}$Sr records. Accounting for the evolution of $^{87}$Sr/$^{86}$Sr in continental crust, which was driven by temporal variations in these factors, the $^{87}$Sr/$^{86}$Sr of riverine inputs to the ocean varies substantially (10, 11). Any estimate of riverine elemental fluxes that does not account for such variations suffers from appreciable uncertainty.

To our knowledge, there are only two observational constraints on geologic marine P budgets (12, 13). In the first study, an overall increase in P concentrations in sedimentary rocks over time was detected (12). Although the resolution of the dataset does not allow identification of Phanerozoic patterns, the findings of that study are broadly consistent with our model results, i.e., P concentrations in seawater have increased with time. The second study includes a compilation of phosphorous to iron ratios (P/Fe) in iron-oxide-rich sediment (13). Two distinct stages were observed in the Phanerozoic portion of the P/Fe record: from the Cambrian to the Jurassic periods (541-145 Ma) the average P/Fe is 0.38, and from the Cretaceous period to the present day (145-0 Ma) the average P/Fe is 2.55 (Fig. S2A). The authors interpreted this pattern to emerge mostly from changes in the silica cycle related to the emergence of silicifying organisms, but we raise the
possibility that evolving marine P concentrations, as modeled here independently, may have contributed to the observed P/Fe pattern.

**The effect of phosphate burial efficiency on marine phosphate concentrations.** The long-term biogeochemical cycle of P is predominantly controlled by a source from chemical weathering of silicate rocks on land and a sink through burial of P in sedimentary rocks. Most sedimentation of P from the ocean is in the form of organic matter. In the sediments, the organic matter is remineralized, releasing dissolved P into the sediment porewater. This released P then either precipitates as apatite, adsorbs onto Fe(III) oxide and oxyhydroxide particles, or diffuses back into the water column.

Evidence suggests that the P burial efficiency strongly depends on the seawater O$_2$ concentration through several processes. On one hand, organic P burial is enhanced under anoxic conditions, as a smaller fraction of the organic matter gets oxidized in the water column and sediments (14). On the other hand, organic and inorganic P burial may be elevated under aerobic conditions due to a combination of preferential P storage by aerobic microorganisms and sorption of P released during remineralization onto Fe(III) oxides and oxyhydroxides (15). These processes, which affect the marine P budget, are included in our model (7).

Periods of high marine calcium concentrations may be characterized by more efficient burial as apatite of P released from organic matter (16). Although this process was not included in our model, an overall decrease in Ca concentrations from the Paleozoic to the present (17) suggests a decrease also in apatite burial. Thus, this process could have resulted in even lower Paleozoic seawater P concentrations, making our estimated seawater P trajectory conservative.

**The effect of off-axis seafloor weathering on phosphate concentrations and phytoplankton elemental composition.** Off-axis crustal reactions are suggested to be a sink for oceanic dissolved P. During these reactions P is removed via adsorption onto Fe(III) oxides and oxyhydroxides in the altered crust and overlying sediments, secondary apatite precipitation or biological processes in the crust (18). Recently, it has been suggested that under anoxic conditions, in the absence of Fe(III) oxide and oxyhydroxide traps, seafloor weathering is not a P sink, and that it may even be a source of P (19). This process may be significant in the early Paleozoic when studies suggest that the deep oceans were anoxic (20, 21). To account for this possibility, we conducted additional model simulations, where (a) seafloor weathering is not a sink for P throughout the entire Phanerozoic, (b) seafloor weathering is not a sink for P during the early Paleozoic, and (c) seafloor weathering is a source of P, similar to continental weathering, during the early Paleozoic.

When off-axis systems are not a P sink throughout the entire Phanerozoic, the P curve maintains its shape, though it is slightly elevated above our original P trajectory (Fig. S3B, compare solid- and dotted-black lines). When off-axis systems are not a P sink only during the Paleozoic, Paleozoic P concentrations are higher than the default simulations, but are still lower than present-day concentrations (Fig. S3B, dashed-red lines). On the other hand, when off-axis systems are a P source, Paleozoic P concentrations are close to present-day concentrations (between 0.4 and 0.6 µM P, Fig. S3B, dashed-blue lines). Of the three parameterizations of the dependence of C:N:P$_{org}$ on the abiotic environment, only the field-based P-dependent parameterization shows results that differ qualitatively from the trajectory that we consider most probable (Fig. S3E, F).
Fig. S1. The sensitivity of elemental ratios to volcanic outgassing rates. (A) Global temperature (K), (B) surface-ocean P concentrations (µM P). (C) C:Porg and (D) N:Porg (molar ratio) calculated using the temperature-dependent, field-based parameterization (22). (E) C:Porg and (F) N:Porg calculated using the P-dependent, field-based parameterization (23). (G) C:Porg and (H) N:Porg calculated using the temperature- and P-dependent, lab-based parameterization (24). Solid lines refer to default seafloor spreading rates, dashed lines refer to double the default seafloor spreading rates, and dotted lines refer to half the default seafloor spreading rates. Simulations were conducted with an activation energy for silicate dissolution of 30 and 80 kJ mol⁻¹ (black and red lines, respectively).
Fig. S2. Existing estimates of marine phosphate concentrations and fluxes. (A) Right y-axis: P/Fe ratio in sedimentary rocks (13). Left y-axis: seawater P concentrations (2, 3, 5, 7, 25). (B) Right y-axis: P influxes (1, 6). Left y-axis: P concentrations (7). All concentrations and fluxes are normalized to present-day values (i.e., unitless).
Fig. S3. The effect of off-axis seafloor weathering on phosphate concentrations and phytoplankton elemental composition. Comparison between (A) global temperature (K), and (B) surface-ocean P concentration (µM P) obtained in model simulations in which off-axis seafloor weathering is a P sink (default model simulations, black-solid lines), simulation without seafloor weathering acting as a P sink throughout the entire Phanerozoic (dotted-black lines), simulations without seafloor weathering acting as a P sink only in the early Paleozoic (dashed-red lines), and simulations in which seafloor weathering is a P source during the early Paleozoic (dashed-blue lines). (C-H) C:Porg and N:Porg (molar ratio) calculated as in Fig. S1.
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