

# Supplementary Information for: Weathering controls on the Phanerozoic phosphate cycle

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## Supplementary Methods

### Model development:

The mass balances of P and Ca in the ocean, C and O<sub>2</sub> in the ocean-atmosphere, and the sedimentary pools of organic matter (C<sub>org</sub>) and carbonate rocks are:

$$\frac{d}{dt}\mathbf{P} = F_{wP,ocean} - F_{borg,P} - F_{bap} - F_{bFeP} - F_{plume,P} - F_{off,P}, \quad (\text{S1})$$

$$\frac{d}{dt}\mathbf{C} = F_v + F_{wcarb} + F_{worg} - F_{bcarb} - F_{borg} - F_{borg,land}, \quad (\text{S2})$$

$$\frac{d}{dt}\mathbf{O}_2 = F_{borg} + F_{borg,land} - F_{worg} - F_{ored}, \quad (\text{S3})$$

$$\frac{d}{dt}\mathbf{Ca} = F_{wcarb} + F_{wsil} + F_{wsf} - F_{bcarb}, \quad (\text{S4})$$

$$\frac{d}{dt}\mathbf{C}_{org} = F_{borg} + F_{borg,land} - F_{worg} - F_{morg}, \quad (\text{S5})$$

$$\frac{d}{dt}\mathbf{CaCO}_3 = F_{bcarb} - F_{wcarb} - F_{mcarb}. \quad (\text{S6})$$

Reactive P enters the ocean from continental weathering ( $F_{wP,ocean}$ ), and is removed via organic P burial ( $F_{borg,P}$ ), apatite burial ( $F_{bap}$ ), adsorption onto iron oxides in the sediments ( $F_{bFeP}$ ) and in hydrothermal plumes ( $F_{plume,P}$ ), and removal during off-axis seafloor weathering reactions ( $F_{off,P}$ ). Carbon enters the ocean-atmosphere by volcanic outgassing ( $F_v$ ), which includes metamorphic, plume and mid-ocean-ridge fluxes, and from weathering of sedimentary rocks containing CaCO<sub>3</sub> and organic-matter ( $F_{wcarb}$  and  $F_{worg}$ , respectively). The major removal processes of C are inorganic C burial ( $F_{bcarb}$ ), marine organic C burial ( $F_{borg}$ ) and land-plant-derived organic matter burial ( $F_{borg,land}$ ). Oxygen is produced by the burial of organic C and consumed by oxidation of organic

C during weathering of organic matter-containing sedimentary rocks ( $F_{\text{worg}}$ ), and by oxidation of reduced volcanic gases such as  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CH}_4$  ( $F_{\text{ored}}$ ). The main source of Ca is continental weathering of carbonate and silicate rocks ( $F_{\text{wcarb}}$  and  $F_{\text{wsil}}$ , respectively). Furthermore, a significant amount of Ca enters the ocean from off-axis seafloor weathering reactions ( $F_{\text{wsf}}$ ). The main mechanism that removes Ca is carbonate mineral burial. Organic matter-containing sedimentary rocks are formed by the burial of marine and terrestrial organic matter, and are lost by weathering and metamorphism ( $F_{\text{morg}}$ ). Calcium carbonate-containing sedimentary rocks are formed by carbonate deposition (chemically- or biologically-driven), and lost by weathering and metamorphism ( $F_{\text{mcarb}}$ ). To simulate the evolution of the model variables through time, we adopted major geologic forcings over the Phanerozoic. The full set of forcings is shown in Extended Data Fig. 2, and described below. The full parameter ranges are presented in Supplementary Tables S2–S8.

### **Climate model:**

To relate mean global surface temperature ( $T$ ) to  $p\text{CO}_2$  and to the evolving solar luminosity and paleogeography, we adopt the following climate model:

$$T - T^0 = \Gamma \left( \frac{\ln(p\text{CO}_2/p\text{CO}_2^0)}{\ln(2)} - \frac{\text{age}}{\xi \times 187} \right) f_{\text{glac}} + \Delta T_{\text{geog}}. \quad (\text{S7})$$

Here,  $T^0 = 288$  K is the present-day global mean surface temperature, and  $\Gamma$  represents the temperature response to a doubling of  $p\text{CO}_2$  at present-day solar luminosity and paleogeography (it is divided by  $\ln(2)$  so that  $\Gamma$  has conventional units of Kelvins per  $\text{CO}_2$  doubling). In a simple black-

body system, doubling of  $p\text{CO}_2$  induces a radiative forcing of  $3.7 \text{ W m}^{-2}$ , which causes  $\sim 1.2 \text{ K}$  warming<sup>64</sup>. However, feedbacks such as cloud distributions and atmospheric moisture, cause a net amplification of this factor. The intergovernmental panel on climate change (IPCC) estimated  $\Gamma$  within the range  $1.5\text{--}4.5 \text{ K}$ , which is calculated based on the results of general circulation models (GCMs) that include only fast climate feedbacks<sup>63</sup>. However, paleo-climate data indicate that the Earth system climate sensitivity, which integrates fast and slow climate feedbacks, is potentially higher ( $\sim 4\text{--}8 \text{ K per CO}_2$  doubling)<sup>65,66</sup>.  $\Gamma$  was, therefore, sampled from a uniform distribution between  $1.5$  and  $8.0 \text{ K per CO}_2$  doubling.

The second term in the parentheses represents the linear response of the climate system to the short-wave solar luminosity forcing at preindustrial  $p\text{CO}_2$  and paleogeography. The solar luminosity term was derived as follows. The solar luminosity reduction that is needed to offset the “black box” radiative forcing of  $3.7 \text{ W m}^{-2}$  induced by a  $p\text{CO}_2$  doubling, is calculated by accounting for Earth’s geometry, and assuming a constant global albedo of  $0.3$ :

$$\frac{3.7[\text{Wm}^{-2}]}{1368[\text{Wm}^{-2}] \times (1 - 0.3)/4} = 0.0155 = 1.55\%. \quad (\text{S8})$$

Equation S8 indicates that in order to offset the  $p\text{CO}_2$  doubling, present-day solar luminosity ( $1368 \text{ W m}^{-2}$ ) should reduce by  $1.55\%$ . To estimate the age when solar luminosity was  $1.55\%$  lower, an equation from ref. 67 was used:

$$\frac{S(\text{age})}{S^0} = \frac{1}{1 + 2/5 (\text{age}/4750)}, \quad (\text{S9})$$

where  $S(\text{age})$  is the solar luminosity at  $\text{age}$  (Ma),  $S^0$  is the present-day solar luminosity, and  $\text{age} = 4570$  Ma is the age of the Sun. We substitute:  $0.9845 = 1/(1+2/5(\text{age}/4570))$ , and get that the age at which solar luminosity was reduced by 1.55% is 187 Ma. Hansen et al. (1997)<sup>68</sup> reported that the direct response of the climate system to solar forcing is likely lower than the response to forcing by  $p\text{CO}_2$ , because the solar forcing preferentially warms the stratosphere, which radiates back to space some of the incoming radiation. We, therefore, introduced a reduction factor  $\xi$  that was drawn from a uniform distribution between 1.0 and 1.5.

Models and proxy-based methods suggest that  $\Gamma$  likely evolved through the Phanerozoic. For example,  $\Gamma$  was likely higher during Earth's cold phases due to the sea-ice feedback, relative to warm phases<sup>66,69</sup>. To account for this effect a time-dependent, unitless variable  $f_{glac}$  was introduced.  $f_{glac}$  is drawn from a uniform distribution between 1 and 2 when there is evidence for long-lived glaciations in the late Paleozoic (330–260 Ma) and late Cenozoic (34 Ma to present), and is set to unity over the rest of the Phanerozoic (Extended Data Fig. 2).

$\Delta T_{geog}$  is a unitless, time-dependent factor that accounts for the effect of continental configuration, latitude and vegetation cover on surface albedo, and consequently, on average continental temperature. This factor is taken from Royer et al. (2014), who estimated  $\Delta T_{geog}$  by running the model of Godd ris et al. (2012) at different continental configurations, at preindustrial  $p\text{CO}_2$  and solar luminosity. The model of Godd ris et al. (2012) includes continental ice sheet growth during periods of long-lived glaciations, and the effect of vegetation on continental albedo. The warming trend in  $\Delta T_{geog}$  during the Paleozoic is related to the movement of the continents equatorward,

and to the reduction of the continental albedo in response to the expansion of land plants. The continental configuration and latitude during the Mesozoic (the assembly of the supercontinent Pangaea) is associated with net warming<sup>62,71</sup>.

### **Silicate weathering:**

The dependence of silicate weathering on temperature is thought to provide an important climate regulation feedback in the long-term C cycle<sup>22,23</sup>. Silicate weathering depends on temperature through the chemical reaction kinetics<sup>15,16</sup>. This dependency is often expressed as an Arrhenius term. The rate of continental silicate weathering additionally depends on temperature through changes in precipitation and runoff, which alter the water to rock ratio<sup>19,21</sup>. This relationship is usually expressed as a linear term, derived from GCM studies. We lumped these two effects into one exponential term that describes the temperature-enhancement of silicate weathering relative to the present day ( $f_W$ ):

$$f_W = e^{\left(\frac{\Delta E_{\text{sil}}}{R \times (T^0)^2}\right)(T - T^0)}, \quad (\text{S10})$$

where  $R$  is the gas constant ( $0.008314 \text{ kJ mol}^{-1} \text{ K}^{-1}$ ),  $T^0$  is the present-day temperature (K), and  $\Delta E_{\text{sil}}$  ( $\text{kJ mol}^{-1}$ ) is the activation energy for silicate weathering that includes both the effect of temperature on reaction kinetics and the effect of temperature on runoff (Supplementary Table S3).

Silicate weathering ( $F_{\text{wsil}}$ ;  $\text{Tmol Ca yr}^{-1}$ ) also depends on the direct effect of  $p\text{CO}_2$  on weath-

ering ( $f_{CO_2}$ ), the effect of paleogeography on runoff ( $f_{PG}$ ), the effect of uplift rates on weatherability ( $f_U$ ), the effect of vegetation on continental weatherability ( $f_E$ ), and the fraction of land area undergoing chemical weathering ( $f_A$ ):

$$F_{\text{wsil,Ca}} = F_{\text{wsil,Ca}}^0 \times f_W \times f_{CO_2} \times f_{PG} \times f_U \times f_E \times f_A, \quad (\text{S11})$$

where  $F_{\text{wsil}}^0$  (Tmol Ca yr<sup>-1</sup>) is the present day silicate weathering rate (Supplementary Table S3).

### **Carbonate weathering:**

Carbonate dissolution kinetics is rapid<sup>72,73</sup>, and therefore, the temperature-enhancement of carbonate weathering (relative to present day;  $f_{W_{carb}}$ ) is considered to be only through the thermodynamic effect of temperature on carbonate solubility (lower solubility at high temperature), and the effect of temperature on runoff. We adopt the following empirical relationship between temperature and carbonate weathering<sup>72,74</sup>:

$$f_{W_{carb}} = (1 + k_{Ca} \times (T - T^0)), \quad (\text{S12})$$

where  $k_{Ca}$  is a constant derived from an empirical correlations between temperature and carbonate weathering (Supplementary Table S3). We assume that carbonate weathering depends also on  $pCO_2$  ( $f_{CO_2}$ ), the effect of paleogeography on runoff ( $f_{PG}$ ), the effect of vegetation on continental weathering ( $f_E$ ), the fraction of land area undergoing chemical weathering ( $f_A$ ), and the fraction

of land area covered by carbonates ( $f_L$ ). The uplift term is discarded, assuming that carbonates undergo subsurface dissolution by groundwater, regardless of uplift<sup>28</sup>. The overall carbonate weathering term is:

$$F_{\text{wcarb}} = F_{\text{wcarb}}^0 \times \left( \frac{\text{CaCO}_3}{\text{CaCO}_3^0} \right) \times f_{\text{Wcarb}} \times f_{\text{CO}_2} \times f_{\text{PG}} \times f_E \times f_A \times f_L, \quad (\text{S13})$$

where  $F_{\text{wcarb}}^0$  (Tmol Ca yr<sup>-1</sup>) is the present day carbonate weathering rate (Supplementary Table S3), and  $\text{CaCO}_3/\text{CaCO}_3^0$  is the total pool of carbonates in sedimentary rocks normalized to the present day.

### **Sedimentary organic carbon weathering:**

Evidence for transport and burial of old, unoxidized organic matter in modern sediments suggests that oxidative weathering depends on  $p\text{O}_2$ <sup>75</sup>. The scaling factor of weathering rates of organic matter-bearing rocks on  $p\text{O}_2$  is:

$$f_O = (p\text{O}_2/p\text{O}_2^0)^{n_O}, \quad (\text{S14})$$

where  $p\text{O}_2^0$  (atm) is the modern  $p\text{O}_2$ , and  $n_O$  is a unitless exponent that describes the dependence of weathering rates on  $p\text{O}_2$  (Supplementary Table S3). Weathering of organic matter in sedimentary rocks ( $F_{\text{worg}}$ ; Tmol C yr<sup>-1</sup>) is also assumed to depend on the uplift term ( $f_U$ ), on the effect of paleogeography on runoff ( $f_{\text{PG}}$ ), assuming that more flushing of the organic matter by O<sub>2</sub>-containing water should increase weathering<sup>28</sup>, and on the land area undergoing chemical weathering ( $f_A$ ).

Land plants affect weathering rates through the production of organic acids, the release of respiratory  $\text{CO}_2$  in the soils, and the generation of a larger surface area for reaction. Only the latter of these matters for oxidative weathering of organic matter, and we consider land plants to play a lesser role in enhancement of organic matter weathering<sup>28</sup>. The overall weathering of organic C in sedimentary rock term is:

$$F_{\text{worg}} = F_{\text{worg}}^0 \times (C_{\text{org}}/C_{\text{org}}^0) \times f_O \times f_{PG} \times f_U \times f_A, \quad (\text{S15})$$

where  $F_{\text{worg}}^0$  is present-day kerogen weathering and  $C_{\text{org}}/C_{\text{org}}^0$  is the total, normalized-to-present day pool of sedimentary organic carbon. The value of  $F_{\text{worg}}^0$  is poorly constrained (2.5–22 Tmol  $\text{y}^{-1}$ , refs. 1, 76, 77). Therefore,  $F_{\text{worg}}^0$  was evaluated by solving the C-isotopic mass balance equation (Eq. S16) at a steady state to yield:

$$\delta^{13}\text{C} = \delta^{13}\text{C}_v - \varepsilon \frac{(F_{\text{worg}}^0 - F_{\text{borg}}^0 - F_{\text{borg,land}}^0)}{F_v^0}. \quad (\text{S16})$$

Here  $\delta^{13}\text{C}$  is the isotopic compositions of C in the ocean-atmosphere,  $\delta^{13}\text{C}_v$  is the isotopic compositions of  $\text{CO}_2$  emitted from volcanic outgassing, and  $\varepsilon$  is the average fractionation of C isotopes associated with photosynthesis on land and in the ocean at present-day levels of  $p\text{CO}_2$  and  $p\text{O}_2$ , respectively.  $F_{\text{borg}}^0$  and  $F_{\text{borg,land}}^0$  are present-day burial of organic C in the ocean and on land, respectively, and  $F_v^0$  is the present-day  $\text{CO}_2$  input from metamorphic and volcanic degassing. Re-

arranging Eq. S16 and solving for  $F_{\text{worg}}^0$ , we get:

$$F_{\text{worg}}^0 = \frac{F_v^0}{\varepsilon} (\delta^{13}\text{C}_v - \delta^{13}\text{C}) + F_{\text{borg}}^0 + F_{\text{borg,land}}^0. \quad (\text{S17})$$

### Seafloor weathering:

Seafloor weathering occurs as seawater circulates through the upper oceanic crust in low-temperature, off-axis hydrothermal systems. Basalt weathering is sensitive to temperature, and of interest to the model described in this study, it is a source of net alkalinity as it releases  $\text{Ca}^{2+}$  ions, some of which precipitate as  $\text{CaCO}_3$  in veins and void fillings<sup>26,78</sup> and some of which are injected into the ocean. Therefore, similar to continental weathering, seafloor weathering constitutes a feedback between the average temperature of circulating fluids, which is related to  $p\text{CO}_2$ , and the burial flux of  $\text{CaCO}_3$ <sup>17,27,79</sup>. We include an Arrhenius-style temperature dependence of seafloor basalt weathering:

$$f_{W_{sf}} = e^{\left(\frac{\Delta E_{\text{bas}}}{R \times (T_{\text{pore}}^0)^2}\right)} (aT \times (T - T^0)), \quad (\text{S18})$$

where  $f_{W_{sf}}$  is a unitless parameter representing the enhancement of seafloor weathering due to temperature relative to the present day (unitless),  $R$  is the gas constant,  $T_{\text{pore}}^0$  is the present-day, average porewater temperature (K),  $\Delta E_{\text{bas}}$  is the effective activation energy of basalt dissolution ( $\text{kJ mol}^{-1}$ ), and  $aT$  is a parameter that describes the relationship between the surface and porewater temperature<sup>79</sup>. The total rate of  $\text{Ca}^{2+}$  leaching due to seafloor weathering ( $F_{\text{wsf}}$ ) is further

scaled with seafloor spreading rate ( $f_{SF}$ ), assuming that faster seafloor spreading enhances the seafloor weathering rate by exposing fresh crust to weathering:

$$F_{wsf} = F_{wsf}^0 \times f_{Wsf} \times f_{SF}. \quad (\text{S19})$$

### **Estimation of the present-day flux of calcium into the ocean from seafloor weathering:**

Chemical fluxes associated with off-axis seafloor weathering reaction ( $F_{wsf}^0$ ) can be determined from the net changes in the Ca concentration ( $\Delta\text{CaO}$  in %wt) of the crust, combined with estimates of the total oceanic crust production rate. Subtracting the  $\text{CaCO}_3$ -associated Ca concentration from the total Ca concentration in the altered crust provides an estimate of the net loss of Ca from the basaltic crust<sup>78</sup>. Irrespective of whether this Ca precipitates in pores and veins in the altered crust or is injected into the ocean and precipitates to form carbonate sediments, it constitutes a sink of seawater DIC. We used  $\Delta\text{CaO}$  estimates from young and Cretaceous-age cores and ophiolites (Supplementary Table S3) to constrain the present-day Ca leaching flux. As Cretaceous bottom-water temperature is thought to have been  $\sim 10^\circ\text{C}$  warmer<sup>26</sup>, potentially increasing the rate of Ca leaching from oceanic crust (and associated C uptake), Cretaceous  $\Delta\text{CaO}$  estimates require correction to present-day temperatures in order to provide constraints on the present-day Ca leaching rate. All Cretaceous flux estimates that are presented in Supplementary Table S3 were normalized to the present day, assuming bottom-water temperature is  $10^\circ\text{C}$  lower today than in the Cretaceous.  $F_{wsf}^0$  was then drawn from a uniform distribution constrained by the available

observational estimates (Supplementary Table S3). Further details are in the table caption.

It is possible that some Ca loss from the crust is coupled to magnesium (Mg) gain, in which case the net alkalinity change is zero. However, CaCO<sub>3</sub> deposition in the crust would not be possible at a Ca:Mg exchange ratio of 1:1<sup>31</sup>. Furthermore, the Mg budget in off-axis circulation systems is highly uncertain. A compilation of the Mg concentration in fresh and altered oceanic crust shows instances of Mg loss, gain or little change (Supplementary Table S10 and reference therein). Fluids from near-axis hydrothermal systems are strongly depleted in Mg, suggesting Mg uptake by the crust during high-temperature water-rock interactions<sup>80</sup>. However, the effect of low-temperature, off-axis circulation on fluid chemistry is much more minor, in accordance with the inferences made on the basis of our crustal Mg concentration compilation. The large uncertainty associated with off-axial Mg fluxes has been attributed to the exchange of olivine in the fresh crust by Mg-bearing clays in the altered crust<sup>78</sup>.

### **The effect of $p\text{CO}_2$ on weathering:**

The direct effect of  $p\text{CO}_2$  on weathering, mostly through the effect of carbonic acid on soil pH and mineral dissolution rates, is of the form:

$$f_{CO_2} = ([\text{H}^+]_{\text{soil}}/[\text{H}^+]_{\text{soil}}^0)^{n_C}, \quad (\text{S20})$$

where  $[\text{H}^+]_{\text{soil}}$  is the proton concentration in the soil water, and  $n_C$  is an exponent that describes the dependence of weathering rates on soil water pH (Supplementary Table S3).  $[\text{H}^+]_{\text{soil}}^0$  is the proton concentration in preindustrial soil which is taken to be  $\sim 30 \times p\text{CO}_2^0$  (ref. 81).  $[\text{H}^+]_{\text{soil}}$  can be estimated by the following expression:  $[\text{H}^+]_{\text{soil}} \sim (p\text{CO}_{2,\text{soil}} \times K_H \times K_1)^{1/2}$ , where  $K_H$  is the Henry's Law constant for  $\text{CO}_2$ ,  $K_1$  is the carbonic acid first dissociation constant, and  $p\text{CO}_{2,\text{soil}}$  is the  $\text{CO}_2$  partial pressure in the soil pores.

The steady-state  $p\text{CO}_{2,\text{soil}}$  can be calculated following ref. 81, by defining total land productivity ( $\Pi$ ), a diffusive exchange coefficient between the atmosphere and the soil ( $k_{\text{soil}}$ ), and a fraction of the productivity released by the below-ground ecology as soil  $\text{CO}_2$  ( $f_{\text{root}}$ ). In an annually-averaged, approximate steady state, the flux of  $\text{CO}_2$  from the soil to the atmosphere balances its production in the soil:

$$k_{\text{soil}} \times (p\text{CO}_{2,\text{soil}} - p\text{CO}_2) = f_{\text{root}} \times \Pi. \quad (\text{S21})$$

The terms  $k_{\text{soil}}$  and  $f_{\text{root}}$  are assumed to be constants, and their ratio can be calculated based on present-day conditions:

$$f_{\text{root}}/k_{\text{soil}} = (p\text{CO}_{2,\text{soil}}^0 - p\text{CO}_2^0)/\Pi^0. \quad (\text{S22})$$

By combining Eqs. S21 and S22 the normalized  $p\text{CO}_{2,\text{soil}}$  relative to present day can be written as:

$$\left(\frac{p\text{CO}_{2,\text{soil}}}{p\text{CO}_{2,\text{soil}}^0}\right) = \left(\frac{\Pi}{\Pi^0}\right) \left(1 - \frac{p\text{CO}_2^0}{p\text{CO}_{2,\text{soil}}^0}\right) + \frac{p\text{CO}_2}{p\text{CO}_{2,\text{soil}}^0}. \quad (\text{S23})$$

Equation S23 indicates that prior to the evolution of land plants when  $\Pi = 0$ , soil  $\text{CO}_2$  was equal to  $p\text{CO}_2$ . With a fully-established terrestrial biosphere (i.e., today)  $p\text{CO}_{2,\text{soil}}^0 = 30 \times p\text{CO}_2^0$ . The evolving normalized soil respiration  $\Pi/\Pi^0$  is approximated in our model by the time-dependent forcing  $f_{\text{land}}$ , which reflects the colonization and expansion of terrestrial biomass (Extended Data Fig. 2). The total effect of  $p\text{CO}_2$  on weathering  $f_{\text{CO}_2} = \left(\frac{p\text{CO}_{2,\text{soil}}}{p\text{CO}_{2,\text{soil}}^0}\right)^{n_C/2}$  is written as:

$$f_{\text{CO}_2} = \left(f_{\text{plants}} \times \left(1 - \frac{p\text{CO}_2^0}{p\text{CO}_{2,\text{soil}}^0}\right) + \frac{p\text{CO}_2}{p\text{CO}_{2,\text{soil}}^0}\right)^{n_C/2}. \quad (\text{S24})$$

### **Tectonic uplift:**

Uplift due to tectonic processes exposes fresh rock to chemical weathering and enhances the delivery of dissolved nutrients and alkalinity into the ocean<sup>82</sup>. Following GEOCARB, enhancement of weathering fluxes due to continental uplift was scaled by a unitless, normalized to the present-day, time-dependent forcing factor ( $f_U$ ; Extended Data Fig. 2). This factor was derived by Berner & Kothavala (2001)<sup>83</sup> from a cubic fit to terrigenous sediment abundance data of Ronov (1993)<sup>84</sup>. This method is in agreement with the  $^{87}\text{Sr}/^{86}\text{Sr}$  method of estimation of tectonic uplift<sup>83</sup>.

### **Land area undergoing chemical weathering and land area covered by carbonates:**

Land area ( $f_A$ ; relative to present-day land area) was adopted from Godd ris et al. (2012), that estimated this value from paleogeographic maps. The relative land area covered by carbonates ( $f_L$ ; relative to the present day) was adopted from Bluth and Kump (1991) that estimated it from the dataset of Ronov (1993)<sup>84</sup>.

### **The effect of volcanic vs. plutonic rock land cover on silicate weathering:**

River chemical data indicate that the weatherability of volcanic rocks, which currently constitute 30–35% of the total continental silicate weathering, is  $\sim 2$  times higher than the weatherability of plutonic silicate rocks<sup>19,86</sup>. Therefore, it is likely that changes in the relative land cover of volcanic vs. plutonic rocks may affect rates of  $p\text{CO}_2$  consumption through the Phanerozoic<sup>66,87</sup>. To account for this effect, following ref. 87, we include a time-dependent forcing  $f_{volc}$  that describes how changes in the proportion of volcanic rock affected continental weatherability throughout the Phanerozoic. This factor was derived from the  $^{87}\text{Sr}/^{86}\text{Sr}$  record and river chemical data (assuming a factor of 2 enhancement<sup>66,87,88</sup>). The relative fraction of volcanic rock is comparable to the data of Bluth and Kump (1991) for the last 120 Ma.

### **Paleogeography effect on global runoff:**

Runoff (precipitation minus evaporation) is a critical factor for mineral dissolution. The effect of the degree of supercontinentality and latitude on runoff was included in our model by applying a unitless parameter  $f_{PG}$ , which is normalized to present-day runoff. The time-dependent evolution of this parameter is computed from a GCM study that simulated the change in runoff as a function of paleogeography and latitude, at fixed present-day levels of  $\text{CO}_2$  and luminosity<sup>62,70</sup> (Extended Data Fig. 2). Briefly, the  $f_{PG}$  forcing is prescribed to account for the following sequence of events: the increase in  $f_{PG}$  during the early Phanerozoic is driven by the drift of the continents equatorward. As the continents drifted equatorward, the hydrological balance of evaporation and precipitation shifted in favor of precipitation and an increase in runoff and  $f_{PG}$  relative to the subtropical latitudes. At  $\sim 306$  Ma, the continents collided to form the supercontinent Pangaea. During the tenure of the supercontinent, the average annual precipitation over land is thought to have decreased due to the difficulty of delivering moisture to inland regions. Pangaea started to break up at  $\sim 237$  Ma, resulting in easier inland transport of moisture and an increase in runoff<sup>89–91</sup>.

### **Phosphate weathering:**

The P cycle involves input from continental weathering of P-bearing minerals, 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 into the ocean in the form of particulate and dissolved, organic, and inorganic P. Some of the P that enters the ocean, mostly the particulate P, is not bioavailable and is buried as detritus or iron-bound P in shelf sediments<sup>9,10</sup>. However, a fraction of the initially unavailable P becomes bioavailable in estuaries due to bacterial remineralization of the organic P, and/or release by reductive dissolution of the iron-bound P. Due to the large uncertainty regarding the fraction of the particulate P that becomes bioavailable<sup>9</sup>, the preindustrial fluxes of bioavailable, dissolved P into the ocean ( $F_{\text{wP,ocean}}^0$ ) is constrained using mass balance approaches, assuming that the input of bioavailable, dissolved P is equal to the total marine output ( $\sim 8.6 \times 10^{10}$ ; Supplementary Tables S2, S6). The flux of P into the ocean ( $F_{\text{wP,ocean}}$ ) is parameterized as follows:

$$F_{\text{wP,ocean}} = F_{\text{wP,ocean}}^0 \times \left( f_{\text{sil,p}} \times \frac{F_{\text{wsil}}}{F_{\text{wsil}}^0} + (1 - f_{\text{sil,p}}) \times \frac{F_{\text{wcarb}}}{F_{\text{wcarb}}^0} \right), \quad (\text{S25})$$

where  $f_{\text{sil,p}}$  is the fraction of weathered P that is delivered from silicate weathering, and the rest is delivered from carbonate weathering. Since the bioavailable P flux from oxidation of organic matter in shales is considered to be relatively minor ( $\sim 40\%$  of the particulate organic P flux of  $1 \times 10^{10}$  mol P yr<sup>-1</sup> is bioavailable<sup>10</sup>), the influence of  $p\text{O}_2$  on P weathering is neglected. As a result of this choice, the coupling of the P and O<sub>2</sub> cycles is exclusively through the dependence of the P sinks on  $p\text{O}_2$ .

## Phosphate cycling in the ocean:

The bioavailable, dissolved P is mostly consumed by marine phytoplankton in pelagic and deltaic environments during photosynthesis. Net primary productivity ( $F_{np,P}$ ; Tmol P yr<sup>-1</sup>) is assumed to be proportional to present-day primary productivity, and is limited by the concentration of bioavailable, dissolved P in the surface ocean ( $[P]_s$ ;  $\mu\text{M}$ )<sup>1,3</sup>:

$$F_{np,P} = k_{np} \times [P]_s, \quad (\text{S26})$$

where  $k_{np}$  is a normalization factor ( $k_{np} = F_{np,P}^0 / [P]_s^0$ ). Carbon-based primary productivity is calculated from the P-based primary productivity and the elemental composition of the primary producers ( $(C : P)_{pp}$ ), which is assumed to be constant at the Redfield ratio:

$$F_{np} = F_{np,P} \times (C : P)_{pp}. \quad (\text{S27})$$

Most of the organic matter produced in the photic zone is efficiently oxidized in the water column to reform dissolved inorganic C and other nutrients near the surface, and only around 10% is exported to the deep ocean (henceforth “export production”)<sup>92</sup>. Out of the exported organic matter, only about 1% is transported to the sediments<sup>93,94</sup>. In the sediments, the organic matter undergoes further remineralization and an even smaller fraction will ultimately be preserved in sedimentary rocks<sup>93,94</sup>. We formulate the concentration of organic matter in the surface ocean (0–100 m;  $P_{org,s}$ ; Tmol P), and in the deep ocean ( $P_{org,d}$ ; Tmol P), which includes the upper few

centimeters of the sediment, as follows:

$$\frac{d}{dt}P_{\text{org},s} = F_{\text{np},P} - k_{\text{sink}} \times (P_{\text{org},s}) - k_{\text{remin},s} \times (P_{\text{org},s}), \quad (\text{S28})$$

$$\frac{d}{dt}P_{\text{org},d} = F_{\text{ep},P} - k_{\text{b}} \times (P_{\text{org},d}) - k_{\text{remin},d} \times (P_{\text{org},d}) \times \left( \frac{O_{2,d}}{O_{2,d} + k_{ox}} \right), \quad (\text{S29})$$

where  $F_{\text{np},P}$  and  $F_{\text{ep},P}$  are P-based new production and export production respectively ( $\text{Tmol P yr}^{-1}$ ),  $k_{\text{sink}} \times (P_{\text{org},s})$  and  $k_{\text{b}} \times (P_{\text{org},d})$  are the fluxes of organic P from the surface ocean to the deep ocean, and from the deep ocean to the sediments, respectively ( $\text{Tmol P yr}^{-1}$ ). Remineralization in the surface ocean depends linearly on the organic matter concentration:  $k_{\text{remin},s} \times (P_{\text{org},s})$ , and the remineralization in the deep ocean depends also on the  $O_2$  concentration (expressed via Monod kinetics):  $k_{\text{remin},d} \times (P_{\text{org},d}) \times (O_{2,d}/(O_{2,d}+k_{ox}))$ , where  $O_{2,d}$  is the  $O_2$  concentration in the deep ocean, and  $k_{ox} = 0.1 \mu\text{M}$  is the half-saturation constant<sup>55,95</sup>. We note that the model results are insensitive to the choice of  $k_{ox}$  (Extended Data Fig. 3). As the processes of water-column and shallow-sediment remineralization are rapid relative to the geologic timescales of interest here, we solve for the fluxes of P-based export production and long-term burial of organic P in marine sediments ( $F_{\text{borg},P}$ ) at a steady state, by equating the right-hand-side of Eqs. S28 and S29 to zero. Assuming that most of the organic matter gets oxidized in the surface ocean and in the deep ocean, i.e.:  $k_{\text{sink}} \ll k_{\text{remin},s}$ ,  $k_{\text{b}} \ll k_{\text{remin},d} \left( \frac{O_{2,d}}{O_{2,d}+k_{ox}} \right)$ , and normalizing the export production and

burial fluxes to present-day rates, we get:

$$F_{\text{ep,P}} = F_{\text{ep,P}}^0 \times \left( \frac{F_{\text{np,P}}}{F_{\text{np,P}}^0} \right), \quad (\text{S30})$$

$$F_{\text{borg,P}} = F_{\text{borg,P}}^0 \times \left( \frac{F_{\text{ep,P}}}{F_{\text{ep,P}}^0} \right) \times \left( \frac{\text{O}_{2,\text{d}}^0}{\text{O}_{2,\text{d}}^0 + k_{\text{ox}}} \right) / \left( \frac{\text{O}_{2,\text{d}}}{\text{O}_{2,\text{d}} + k_{\text{ox}}} \right), \quad (\text{S31})$$

where  $F_{\text{ep,P}}^0$ , and  $F_{\text{borg,P}}^0$  are present-day export and burial of organic P (Supplementary Table S2).

### Phosphate cycling in the sediments:

Most of the bioavailable P settles to the sediments as organic matter<sup>9</sup>. In the sediments, the bioavailable P undergoes remineralization and dissolved P is released into the sediment porewater where it either precipitates as apatite  $[\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{Cl}, \text{F})]$ , or adsorbs onto iron-oxide particles, depending on the oxidation state of the porewater:

$$F_{\text{bap}} = F_{\text{bap}}^0 \times \left( F_{\text{borg,P}} / F_{\text{borg,P}}^0 \right), \quad (\text{S32})$$

$$F_{\text{bFeP}} = k_{\text{bFeP}} \times \frac{[\text{O}_2]_{\text{d}}}{[\text{O}_2]_{\text{d,max}}} \times \left( F_{\text{borg,P}} / F_{\text{borg,P}}^0 \right), \quad (\text{S33})$$

where  $F_{\text{bap}}^0$  is the present-day burial of apatite and  $k_{\text{bFeP}} = F_{\text{bFeP}}^0 / \frac{[\text{O}_2]_{\text{d}}^0}{[\text{O}_2]_{\text{d,max}}}$  is a normalization factor, derived from literature estimates (Supplementary Table S2).

## Phosphate removal in hydrothermal processes:

Phosphate in the deep ocean is removed by adsorption onto iron-oxide particles formed by oxidation of  $\text{Fe}^{2+}$  emitted from hydrothermal plumes at mid-ocean ridges. Hydrothermal plume activity in mid-ocean ridges is proportional to the seafloor spreading rate<sup>96</sup>. It is, therefore, expected that an increase in mid-ocean ridge activity will lead to an increase in the formation rate of plume-related iron-(oxy)hydroxides and the associated scavenging of P from the ocean<sup>10</sup>. The extent of P removal is also related to the concentration of P in seawater<sup>97</sup>. Based on the above arguments we parameterize loss of P due to hydrothermal plumes in the following way:

$$F_{\text{plume,P}} = F_{\text{plume,P}}^0 \times f_{SF} \times (P/P^0), \quad (\text{S34})$$

where  $f_{SF}$  is the seafloor spreading rate, and  $P/P^0$  is the normalized P concentration. Estimates for global P removal in plumes are  $0.4 - 0.8 \times 10^{10} \text{ mol P yr}^{-1}$  (Supplementary Table S2).

Near-axial crustal reactions are thought to remove less than 1% of the riverine input<sup>11</sup>, and we neglect them. On the other hand, ridge-flank, off-axial crustal reactions are suggested to be more significant. It is unclear whether P is removed via adsorption onto iron-(oxy)hydroxides in sediments, secondary apatite precipitation or biological processes in the crust<sup>11</sup>. We assume that removal of P in off-axial reactions scales linearly with the P concentration, and with the seafloor

spreading rate:

$$F_{\text{off,P}} = F_{\text{off,P}}^0 \times f_{SF} \times (P/P^0), \quad (\text{S35})$$

where  $F_{\text{off,P}}^0$  is the present-day removal rate of P in off-axial hydrothermal systems.

To quantify  $F_{\text{off,P}}^0$ , we conducted an exponential regression of the porewater P concentration and porewater temperature data from ref. 98 (Fig. 4 in ref. 98, high quality data only, as assessed by the author) of the form  $[P]_{\text{pore}} = a \times \exp(b \times T_{\text{pore}})$ . To calculate the present-day flux from the porewater data, we used the following Eq.:

$$F_{\text{off,P}}^0 = \frac{H}{\Delta T \times c_p} \times ([P]_d - a \times \exp(b \times T_{\text{pore}})), \quad (\text{S36})$$

where  $H = 6.7$  (TW) is the mean heat flux that drives circulation in off-axial systems,  $\Delta T = 12.5$  the mean temperature difference between bottom-water and crust porewater,  $c_p = 4000$  ( $\text{J g}^{-1} \text{K}^{-1}$ ) is the heat capacity of seawater,  $[P]_d = 2.3 \mu\text{M}$  is P concentration in the deep ocean,  $a = 2.4$  and  $b = -0.04$  are the fit coefficient means, and  $T_{\text{pore}}$  ( $^{\circ}\text{C}$ ) is the average porewater temperature. The resulting  $F_{\text{off,P}}^0 = 0.56 \times 10^{10} \text{ mol P yr}^{-1}$  is within the present-day range of  $0.4 - 2.8 \times 10^{10} \text{ mol P yr}^{-1}$  (Supplementary Table S2).

## Coupling of the carbon, oxygen and phosphorus cycles:

Despite the meridional variability in the elemental composition of the organic matter in the surface ocean<sup>99</sup>, global observations indicate that the elemental composition of the organic matter between 400 and 4000 m depth is similar to the global average Redfield ratio<sup>100</sup>. These observations suggest that the surface variability is averaged out in the deep ocean, probably due to mixing<sup>101</sup>, and overall there is no preferential remineralization of P during water-column remineralization. We, therefore, assume that the ratio of the C:P<sub>org</sub> that rains into the deep ocean and reaches the sediment is equal to the surface ratio.

The burial flux of organic C ( $F_{\text{borg}}$ ) is coupled to that of organic P via the organic matter C to P burial ratio ( $(C : P)_{\text{borg}}$ ):

$$F_{\text{borg}} = (C : P)_{\text{borg}} \times F_{\text{borg,P}}. \quad (\text{S37})$$

$(C : P)_{\text{borg}}$  is governed by deep-ocean O<sub>2</sub> concentrations. When enough O<sub>2</sub> is available, bacteria in the sediment accumulate P as polyphosphates (the additional effect of O<sub>2</sub> on the P sink due to adsorption onto iron oxides is described above). Once O<sub>2</sub> is depleted, the bacteria utilize the polyphosphates as an energy source, which is eventually released as dissolved inorganic P from the sediment<sup>2</sup>. This redox-dependent burial of organic C relative to P is parameterized in the following

way<sup>2,102</sup>:

$$(C : P)_{\text{borg}} = \frac{(C : P)_{\text{oxic}}(C : P)_{\text{anoxic}}}{\left(\frac{[O_2]_d}{[O_2]_{d,max}}\right)(C : P)_{\text{anoxic}} + \left(1 - \frac{[O_2]_d}{[O_2]_{max}}\right)(C : P)_{\text{oxic}}}, \quad (\text{S38})$$

where  $(C : P)_{\text{oxic}}$  and  $(C : P)_{\text{anoxic}}$  are the ratios of organic matter C:P in the sediment under fully oxic and anoxic conditions, respectively,  $[O_2]_d$  is the  $O_2$  concentration in deep ocean in the present day, and  $[O_2]_{d,max} = 190 \mu\text{M}$  is the  $O_2$  concentration in the deep ocean under fully oxidized conditions<sup>55,95</sup>.

### **Deep-ocean oxygen concentration:**

The major source of the deep water in the modern ocean is surface water that sinks at the high latitudes. Once water leaves the surface ocean and communication with the atmosphere ceases,  $O_2$  is consumed by remineralization of organic matter. The rate at which  $O_2$  is consumed depends on the amount of the organic matter exported from the surface ocean, and the stoichiometry by which it is consumed. Export production is determined by the ability of the primary producers to utilize nutrients delivered from the deep to the surface ocean. At the high latitudes, the efficiency of the biological pump is relatively low, possibly due to iron or light limitation, or due to high grazing pressure<sup>103</sup>. We assume that the efficiency of the biological pump to utilize nutrients in the high

latitudes is constant through time. Therefore, the  $O_2$  concentration in the deep ocean is:

$$O_{2,d} = O_{2,h}^0 \times \left( \frac{pO_2}{pO_2^0} \right) - R_{O_2:P} \times (Eff \times [P]_d). \quad (S39)$$

$O_{2,h}^0 = 300 \mu\text{M}$  is the present-day average  $O_2$  concentration in the high latitude surface water,  $pO_2/pO_2^0$  is the  $pO_2$  normalized to the present day,  $R_{O_2:P} = 1.4$  is the oxygen demand per P released (respiration quota)<sup>100,104</sup>,  $[P]_d$  is the deep ocean P concentration ( $\mu\text{M}$ ), and  $Eff = 40\%$  is the biological pump efficiency<sup>103</sup>. The efficiency of the biological pump, which is defined as the in-situ productivity divided by the potential productivity<sup>103</sup>, is calculated in the following way:  $Eff = ([P]_d - [P]_h)/[P]_d$ , where  $[P]_h = 1.4$ , and  $[P]_d = 2.3$  are the present-day P concentrations in the high-latitude surface ocean, and in the deep ocean, respectively ( $\mu\text{M}$ ).

### **Weathering enhancement due to land plant evolution:**

The timeline for the evolution of land plants, as suggested from fossil evidence, was likely as follows. The first non-vascular plants (bryophytes, mosses, and lichen) emerged during the mid Ordovician period ( $\sim 460$  Ma). Between the late Silurian and early Devonian ( $\sim 420$ – $400$  Ma), the colonization and diversification of gymnosperms began. However, gymnosperms likely reached their full potential in terms of height, complexity, diversity, and continental coverage, only in the late Devonian ( $\sim 350$  Ma)<sup>105,106</sup>. In the early Cretaceous ( $\sim 130$  Ma), fossils and pollen assemblages of angiosperms (flowering plants) appeared, and by the end of the Cretaceous angiosperms were highly abundant and globally distributed<sup>107,108</sup>.

This sequence of events likely affected continental weatherability, because vascular land plants accelerate nutrient leaching, as their extensive root system increases fluid infiltration and the surface area that is exposed to weathering. Furthermore, the activity of their roots and symbiotic fungi releases acids and chelators that facilitate the scavenging of nutrients from the soil. Lastly, in dense forests evapotranspiration enhances rainfall and mineral dissolution<sup>106,109</sup>. The efficiency of these processes depends on the properties of the vegetation and its spatial coverage.

A unitless normalized factor  $f_E$  was introduced to account for the contribution of different types of vegetation and their spatial coverage to continental weatherability. Several uncertainties exist in the effect of land plants on continental weatherability: (a) the efficiency of weatherability enhancement by non-vascular land plants<sup>110–114</sup>, (b) whether angiosperms are more effective enhancers of weathering than the preexisting gymnosperms<sup>28,81,109,115</sup>, and (c) the exact timing of emergence and diversification of different land plant groups. To account for these uncertainties  $f_E$  was drawn from a uniform distribution at any given time, where the boundaries of the uniform distribution change over time to account for the evolution of land plants described above (Extended Data Fig. 2).

### **Burial of terrestrial organic matter:**

Land plants also affect the C, O<sub>2</sub>, and P cycles, by providing a new burial flux of organic matter. Over geologic timescales, large-scale ecosystem productivity, and the burial of organic matter may be limited by the availability of P<sup>116,117</sup>. The burial of terrestrial organic C ( $F_{\text{borg,land}}$ ) is formulated

in the following way:

$$F_{\text{borg,land}} = F_{\text{borg,land}}^0 \times f_{\text{cland}} \times \left( F_{\text{wP,ocean}} / F_{\text{wP,ocean}}^0 \right) \times f_{\text{ire}}, \quad (\text{S40})$$

where  $F_{\text{borg,land}}^0$  (Tmol C yr<sup>-1</sup>) is the present-day burial of terrestrial organic C (Supplementary Table S2),  $(F_{\text{wP,ocean}} / F_{\text{wP,ocean}}^0)$  is the normalized to present-day P weathering flux, and  $f_{\text{cland}}$  is a unitless, normalized, time-dependent parameter that accounts for the colonization and expansion of terrestrial biomass. There are uncertainties in the onset and initial magnitude of organic C burial on land. For example, it is unclear whether the early, non vascular land plants already contributed to terrestrial organic C burial at ~460 Ma, or whether burial of terrestrial biomass was mainly enhanced when vascular land plants evolved (~400 Ma)<sup>118</sup>. To account for these uncertainties  $f_{\text{cland}}$  was drawn from a uniform distribution at any given time, where the boundaries of the uniform distribution evolve over time (Extended Data Fig. 2).  $f_{\text{ire}}$  is a unitless parameter that accounts for the reduction of land biomass burial at high  $p\text{O}_2$  due a higher probability of forest fires (see the section below).

### **Reduction in terrestrial organic carbon burial due to the fire feedback**

Classical experiments on paper stripe ignitions are commonly used to “cap” Phanerozoic  $p\text{O}_2$  levels. These experiments have shown that at  $p\text{O}_2$  greater than approximately 0.3 atm plant biomass would ignite and burn so readily, that it would prevent the regeneration of forests<sup>119</sup>. Similar

experiments with natural plant materials, such as pine needles, have shown similar results, with a higher ceiling of 0.35 atm<sup>120</sup>. Following refs. 121, 122, we assume that the probability for ignition increases linearly with  $pO_2$ . Therefore, an increase in  $pO_2$  suppresses terrestrial biomass burial:

$$ignit = \max(586.2 \times pO_2 - 122, 0), \quad (S41)$$

$$f_{fire} = \min\left(\frac{k_{fire}}{k_{fire} - 1 + ignit}, 1\right). \quad (S42)$$

$k_{fire}$  corresponds to the strength of the fire feedback. For example, a  $pO_2$  increase of 10% would suppresses burial of land biomass by 10% if  $k_{fire} = 100$  and by 80% if  $k_{fire} = 3^{49,121,122}$ . We note that the model results are insensitive to the choice of  $k_{fire}$ .

### **Collision- and subduction-related metamorphism of carbonates and organic carbon:**

Carbonate and organic C may be lost from sedimentary rocks via subduction- and collision-related metamorphism. During subduction, part of the C deposited as  $CaCO_3$  and as organic matter is volatilized upon heating of the subducting plate (decarbonation). Pelagic  $CaCO_3$  and sedimentary organic C that are not subducted accumulate in accretionary prisms. The formation of accretionary prisms and their possible uplift during the closure of ocean basins, as well as the uplift of carbonate platforms during continental collision, lead to collision-related metamorphic decarbonation<sup>123</sup>. We approximate that the total metamorphism fluxes are linearly proportional to the total pools of  $CaCO_3$  and  $C_{org}$ , and to the seafloor spreading rate. We additionally scaled the subduction-related

flux of  $\text{CaCO}_3$  decarbonation by a unitless time-dependent factor that accounts for the effect of the evolution of pelagic calcifiers on  $\text{CaCO}_3$  subduction ( $f_C$ ):

$$F_{\text{mcarb}} = F_{\text{mcarb}}^0 \times f_{SF} \times f_C \times (\text{CaCO}_3/\text{CaCO}_3^0), \quad (\text{S43})$$

$$F_{\text{morg}} = F_{\text{morg}}^0 \times f_{SF} \times (C_{\text{org}}/C_{\text{org}}^0). \quad (\text{S44})$$

Here  $F_{\text{mcarb}}^0$  and  $F_{\text{morg}}^0$  are the present-day estimates of total metamorphism of carbonate and organic carbon in sedimentary rock, respectively (Supplementary Table S6).

### **Volcanic and metamorphic outgassing:**

Volcanic outgassing occurs at mid-ocean ridges (MOR), subduction zones, and mantle plumes. We parameterize the total volcanic outgassing rate ( $F_v$ ) as follows:

$$F_v = F_{\text{vmor}} + F_{\text{vplume}} + F_{\text{varc}}, \quad (\text{S45})$$

where  $F_{\text{vmor}}$ ,  $F_{\text{vplume}}$  and  $F_{\text{varc}}$  are  $\text{CO}_2$  influxes in MOR, intraplate plumes, and arc settings, respectively. We scale MOR outgassing rates by the seafloor spreading rates ( $f_{SF}$ ), and hold the plume outgassing rate constant:

$$F_{\text{vmor}} = F_{\text{vmor}}^0 \times f_{SF}, \quad (\text{S46})$$

$$F_{\text{vplume}} = F_{\text{vplume}}^0, \quad (\text{S47})$$

where  $F_{\text{vmor}}^0$  and  $F_{\text{vplume}}^0$  are the present day MOR and plume volcanic outgassing rates, respectively. To parameterize arc volcanism we first divided it into its sources: the total  $\text{CO}_2$  outgassing at arc settings is derived from the mantle ( $f_{\text{varc,m}}$ ), from volatilization of subducted  $\text{CaCO}_3$  ( $f_{\text{varc,carb}}$ ), and from volatilization of subducted sedimentary organic matter ( $f_{\text{varc,org}}$ ). Each source carries a distinct isotopic signature, and is influenced by different processes. The mantle-sourced arc volcanism is proportional to the seafloor spreading rates, while the carbonates and sedimentary organic rock sources are proportional to their metamorphic rates ( $F_{\text{mcarb}}/F_{\text{mcarb}}^0$  and  $F_{\text{morg}}/F_{\text{morg}}^0$ , respectively), which are themselves proportional to the seafloor spreading rate:

$$F_{\text{varc}} = F_{\text{varc}}^0 (f_{\text{varc,m}} \times f_{SF} + f_{\text{varc,carb}} \times (F_{\text{mcarb}}/F_{\text{mcarb}}^0) + f_{\text{varc,org}} \times (F_{\text{morg}}/F_{\text{morg}}^0)), \quad (\text{S48})$$

where  $F_{\text{varc}}^0$  is the present day  $\text{CO}_2$  outgassing rates at arc settings, which includes point-source, diffuse, and metamorphic outgassing. There are several estimates of the point-source component, fewer estimates of the diffuse component, and no direct estimates of the metamorphic component at a global level (Supplementary Table S4). Previous studies have suggested that metamorphic  $\text{CO}_2$  outgassing is approximately equal to volcanic outgassing at arcs (the sum of point-source and diffusive volcanism)<sup>123,124</sup>. Therefore, to include the metamorphic fluxes, we multiplied the total volcanic arc estimates (point-source and diffuse) by a normal distribution with  $\mu = 2$ , and  $\sigma = 0.5$ .

The mean values of the MOR, arc (volcanic + metamorphic) and plume outgassing rates, according to our literature compilation, are 1.6, 5.4 and 0.9 Tmol C yr<sup>-1</sup>, respectively (Supplementary Table S4). The average sum is 7.9 Tmol C yr<sup>-1</sup>, which is within the range obtained by

long-timescale mass balance approaches of 6–11 Tmol C yr<sup>-1</sup> (refs. 23, 125).

The origin of the CO<sub>2</sub> in arc settings (i.e.,  $f_{\text{varc,m}}$ ,  $f_{\text{varc,carb}}$  and  $f_{\text{varc,org}}$ ), and the isotopic signature of global volcanic gases ( $\delta^{13}\text{C}_v$ ), were estimated from global data compilations of the C isotopic compositions and the CO<sub>2</sub>/<sup>3</sup>He ratio of volcanic arcs<sup>126,127</sup>, by solving the following equations:

$$1 = f_{\text{varc,m}} + f_{\text{varc,carb}} + f_{\text{varc,org}}, \quad (\text{S49})$$

$$\delta^{13}\text{C}_s = \delta^{13}\text{C}_m \times f_{\text{varc,m}} + \delta^{13}\text{C}_{\text{carb}} \times f_{\text{varc,carb}} + \delta^{13}\text{C}_{\text{org}} \times f_{\text{varc,org}}, \quad (\text{S50})$$

$$\frac{1}{[\text{CO}_2/^3\text{He}]_s} = \frac{f_{\text{varc,m}}}{[\text{CO}_2/^3\text{He}]_m} + \frac{f_{\text{varc,carb}}}{[\text{CO}_2/^3\text{He}]_{\text{carb}}} + \frac{f_{\text{varc,org}}}{[\text{CO}_2/^3\text{He}]_{\text{org}}}, \quad (\text{S51})$$

where  $\delta^{13}\text{C}_s$  and  $[\text{CO}_2/^3\text{He}]_s$  are the measured C isotope composition and the CO<sub>2</sub>/<sup>3</sup>He ratio in arc volcanic gases from different volcanoes around the globe (Supplementary Table S5<sup>126,127</sup>),  $\delta^{13}\text{C}_m = -6\text{‰}$ ,  $\delta^{13}\text{C}_{\text{carb}} = 0\text{‰}$ , and  $\delta^{13}\text{C}_{\text{org}} = -30\text{‰}$  are the average C isotopic composition of the mantle, carbonates and organic carbon in sedimentary rocks, respectively, and  $[\text{CO}_2/^3\text{He}]_m = 1.5 \times 10^9$ ,  $[\text{CO}_2/^3\text{He}]_{\text{carb}} = 1.0 \times 10^{13}$  and  $[\text{CO}_2/^3\text{He}]_{\text{org}} = 1.0 \times 10^{13}$  are the average CO<sub>2</sub>/<sup>3</sup>He composition of the mantle, carbonates and organic carbon in sedimentary rocks, respectively<sup>127,128</sup>. To extrapolate  $f_{\text{varc,m}}$ ,  $f_{\text{varc,carb}}$ ,  $f_{\text{varc,org}}$  and  $\delta^{13}\text{C}_v$  from the different volcanoes to a global flux, these values were weighted by the relative contribution of the volcano to the total CO<sub>2</sub> volcanic outgassing (Table S3 in ref. 126). The median fractions of carbonate-derived, organic-matter-derived, and mantle CO<sub>2</sub> are 0.79, 0.10 and 0.11, respectively (Supplementary Table S5). The resulting  $\delta^{13}\text{C}_v = -4\text{‰}$  is heavier than the C isotopic composition of the mantle ( $-6\text{‰}$ ), but is

within the range of  $-3.8$  to  $4.6\text{‰}$  estimated by Mason et al. (2017) for the mean global C isotope ratio of volcanic gases.

### **Oxidation of reduced gases:**

Reduced gases emitted from volcanoes, mainly  $\text{H}_2$ ,  $\text{CH}_4$  and  $\text{CO}$ , are relatively rapidly oxidized in the atmosphere. The influx of reduced gases comes from volatilization of subducted organic matter, and from mantle-related reduced gas influxes from arc, mid-ocean ridges and plume volcanism.

The flux of reduced gases is proportional to these inputs, and to oxygen concentration:

$$F_{\text{ored}} = F_{\text{ored}}^0 \times (f_{\text{oarc,org}} \times (F_{\text{morg}}/F_{\text{morg}}^0) + f_{\text{oplume}} + (1 - f_{\text{oarc,org}} - f_{\text{oplume}}) \times f_{SF}) \times \left( \frac{p\text{O}_2/p\text{O}_2^0}{p\text{O}_2/p\text{O}_2^0 + k_{\text{ored}}} \right), \quad (\text{S52})$$

where  $F_{\text{ored}}^0$  is the total, present day rate of oxidation of reduced gases, and  $f_{\text{oarc,org}}$ ,  $f_{\text{oplume}}$  and  $1 - f_{\text{oarc,org}} - f_{\text{oplume}}$  are the fraction of  $F_{\text{ored}}^0$  related to organic C subduction, plume, and mantle-related arc and MOR volcanism, respectively, and  $k_{\text{ored}}$  is the the half-saturation constant for reduced gases oxidation (Supplementary Table S5).

### **The effect of the evolution of pelagic calcification of carbonate subduction:**

In the present-day ocean  $\text{CaCO}_3$  burial mostly occurs on the continental shelf, in the open ocean on the elevated flanks of MOR, and in veins and void fillings in the oceanic crust during seafloor weathering<sup>24</sup>. It is probable that before pelagic calcification evolved ( $\sim 150$  Ma), the open-ocean component was of lesser importance or even negligible. As a result, it is probable that less  $\text{CaCO}_3$  underwent subduction, and that the arc-related volcanism due to decarbonation of  $\text{CaCO}_3$  was, therefore, reduced. To account for this possibility, we used a dimensionless, time-dependent factor  $f_C$ , which describes the effect of pelagic calcification on  $\text{CaCO}_3$  metamorphism. Previous studies<sup>28</sup> have suggested an increase in  $f_C$  from 0.75 prior to 150 Ma to unity at the present day. To account for uncertainty in the values of  $f_C$  over time, we adopt the suggested time-dependent value as the mean of a normal distribution from which we draw  $f_C$ . Prior to 150 Ma we assign  $2\sigma$  of  $\pm 0.25$  of the mean. From 150 Ma to the present day,  $2\sigma$  decreases linearly from 0.25 to 0 (Extended Data Fig. 2).

### **Seafloor spreading rates:**

The rate of seafloor spreading is equal to the rate of plate subduction<sup>129</sup> and therefore controls the release of volcanic  $\text{CO}_2$  in both mid-ocean ridges and subduction zones. As a result, times of rapid seafloor spreading are commonly considered to be associated with elevated  $p\text{CO}_2$ <sup>23</sup>. Alternatively, high seafloor spreading rates have been suggested to enhance the rate of seafloor weathering

reactions, by exposing young oceanic crust to chemical weathering thereby drawing down  $\text{CO}_2$  by carbonate mineral precipitation in the altered oceanic crust<sup>14,17,27</sup>. Though the balance between the increased sources and sinks of  $\text{CO}_2$  due to faster seafloor spreading is uncertain, in most Earth-system evolution models faster spreading is considered an increased source of  $\text{CO}_2$ <sup>23,49,122</sup>. Concurrent with the increase in the delivery of  $\text{CO}_2$ , is an enhancement in the weathering rate of the oceanic crust<sup>17,23,122</sup>. We account for these processes with a unitless seafloor spreading factor between zero and unity ( $f_{SF}$ ; Extended Data Fig. 2), which is based on inversion of sea-level data to constrain seafloor spreading rates<sup>130</sup>. This correlation comes about because an increase in the total volume of the mid-ocean ridges, which displaces seawater upwards, accompanies faster seafloor spreading. To account for uncertainty in the value of  $f_{SF}$ , we draw it from a normal distribution with a time-dependent mean based on the sea-level inversion data, as described above, and  $2\sigma$  uncertainty of  $\pm 0.25$  of the mean (Extended Data Fig. 2).

### **Ocean carbonate chemistry:**

Atmospheric  $\text{CO}_2$  and the carbonate ion ( $\text{CO}_3^{2-}$ ) concentration, which governs the saturation state of  $\text{CaCO}_3$ , are calculated at each time step by solving the oceanic carbonate system. Two model prognostics are used in the calculation: (i) the amount of C in the whole ocean-atmosphere (Eq. S2), which is approximately equal to the total dissolved inorganic carbon pool ( $\text{DIC} = \text{CO}_2(\text{aq}) + \text{HCO}_3^- + \text{CO}_3^{2-}$ ), and (ii) the  $\text{Ca}^{2+}$  concentration (Eq. S4), from which total alkalinity (TA) can be derived:  $\text{TA} = \text{RAlk} + 2 \times [\text{Ca}^{2+}]$ , where  $\text{RAlk} = -18.2 \text{ mM}$  is calculated

on the basis of the present-day seawater alkalinity (2.4 mM) and  $\text{Ca}^{2+}$  concentration (10.3 mM).

Carbonate chemistry dictates that:

$$\text{DIC} = [\text{CO}_2(\text{aq})] \times \left( 1 + \frac{K_1}{[\text{H}^+]} + \frac{K_1 \times K_2}{[\text{H}^+]^2} \right), \quad (\text{S53})$$

$$\text{TA} = [\text{CO}_2(\text{aq})] \times \left( \frac{K_1}{[\text{H}^+]} + 2 \times \frac{K_1 \times K_2}{[\text{H}^+]^2} \right) + \frac{K_W}{[\text{H}^+]} - [\text{H}^+], \quad (\text{S54})$$

where,  $K_1$  and  $K_2$  are the stoichiometric first and second carbonic acid dissociation constants in seawater, and  $K_W$  is the stoichiometric water dissociation constant in seawater (Supplementary Table S7). Combining Eqs. S53 and S54 yields:

$$\text{DIC} \left( \frac{K_1}{[\text{H}^+]} + 2 \times \frac{K_1 \times K_2}{[\text{H}^+]^2} \right) = \left( \text{TA} - \frac{K_W}{[\text{H}^+]} + [\text{H}^+] \right) \left( 1 + \frac{K_1}{[\text{H}^+]} + \frac{K_1 \times K_2}{[\text{H}^+]^2} \right), \quad (\text{S55})$$

which is an equation of fifth order in  $[\text{H}^+]$ . Rearranging Eq. S55 we get:

$$0 = a \times [\text{H}^+]^5 + b \times [\text{H}^+]^4 + c \times [\text{H}^+]^3 + d \times [\text{H}^+]^2 + e, \quad (\text{S56})$$

where:

$$a = 1, \quad (\text{S57})$$

$$b = \text{TA} + K_1, \quad (\text{S58})$$

$$c = K_1 \times \text{TA} - K_W + K_1 \times K_2 - K_1 \times \text{DIC}, \quad (\text{S59})$$

$$d = K_1 \times K_2 \times \text{TA} - K_W \times K_1 - 2 \times K_1 \times K_2 \times \text{DIC}, \quad (\text{S60})$$

$$e = -K_W \times K_1 \times K_2. \quad (\text{S61})$$

Equation S56 has only one real, positive root that can be calculated by solving Eqs. S57–S61.

Once  $[\text{H}^+]$  is determined,  $p\text{CO}_2$  and  $[\text{CO}_3^{2-}]$  can be calculated ( $K_H$  is the Henry's Law constant for  $\text{CO}_2$  in seawater; Supplementary Table S7):

$$p\text{CO}_{2,\text{atm}} = \frac{\text{DIC}}{K_H \left( 1 + \frac{K_1}{[\text{H}^+]} + \frac{K_1 \times K_2}{[\text{H}^+]^2} \right)}, \quad (\text{S62})$$

$$[\text{CO}_3^{2-}] = \frac{p\text{CO}_{2,\text{atm}} \times K_H \times K_1 \times K_2}{[\text{H}^+]^2}. \quad (\text{S63})$$

### Calcite precipitation:

The flux of  $\text{CaCO}_3$  burial (chemically- or biologically-driven) was calculated from the  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  concentrations (the latter of which is calculated from carbonate speciation, as detailed

above):

$$\Omega = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_{sp}}, \quad (\text{S64})$$

$$F_{\text{bcarb}} = \begin{cases} k_{bc} (\Omega - 1) & \Omega > 1 \\ 0 & \Omega \leq 1 \end{cases}, \quad (\text{S65})$$

where  $\Omega$  is the calcite saturation state of the ocean,  $K_{sp}$  is the calcite solubility product constant in seawater (Supplementary Table S7), and  $k_{bc}$  is a scaling coefficient that is calculated from the modern calcite burial flux and the modern saturation state ( $k_{bc} = \frac{F_{\text{bcarb}}^0}{\Omega^0 - 1}$ ). We neglect dissolution of calcite, as on the timescales of interest,  $\text{CaCO}_3$  dissolution simply leads to an ocean that is near saturation, therefore, if  $\Omega < 1$  the calcite burial flux is set to zero.

## Carbon isotope calculations:

To calculate the C-isotopic compositions of  $\text{CaCO}_3$  ( $\delta^{13}\text{C}_{\text{carb}}$ ), organic matter in sedimentary rocks ( $\delta^{13}\text{C}_{\text{org}}$ ), and C in the ocean-atmosphere ( $\delta^{13}\text{C}$ ), the following equations are used:

$$\frac{d}{dt}(\delta^{13}\text{C}_{\text{org}} \times C_{\text{org}}) = F_{\text{borg}} (\delta^{13}\text{C}_{\text{aq}} - \varepsilon_m) + F_{\text{borg,land}} (\delta^{13}\text{C}_{\text{atm}} - \varepsilon_l) \quad (\text{S66})$$

$$- (F_{\text{worg}} + F_{\text{morg}}) \delta^{13}\text{C}_{\text{org}} \quad (\text{S67})$$

$$\frac{d}{dt}(\delta^{13}\text{C}_{\text{carb}} \times C_{\text{carb}}) = F_{\text{bcarb}} (\delta^{13}\text{C} + 1) - (F_{\text{wcarb}} + F_{\text{mcarb}}) \delta^{13}\text{C}_{\text{carb}}, \quad (\text{S68})$$

$$\begin{aligned} \frac{d}{dt}(\delta^{13}\text{C} \times C) &= F_v \times \delta^{13}\text{C}_v + F_{\text{wcarb}} \times \delta^{13}\text{C}_{\text{carb}} + F_{\text{worg}} \times \delta^{13}\text{C}_{\text{org}} \\ &- F_{\text{bcarb}} (\delta^{13}\text{C} + 1) - F_{\text{borg}} (\delta^{13}\text{C}_{\text{aq}} - \varepsilon_m) \\ &- F_{\text{borg,land}} (\delta^{13}\text{C}_{\text{atm}} - \varepsilon_l). \end{aligned} \quad (\text{S69})$$

Here  $C_{\text{org}}$ ,  $C_{\text{carb}}$  and  $C$ , are pools of organic C and carbonate in sedimentary rocks, and C in the ocean atmosphere, respectively,  $F_{\text{borg}}$ ,  $F_{\text{borg,land}}$  are burial of organic matter in the ocean and on land, respectively,  $F_{\text{worg}}$ ,  $F_{\text{morg}}$  are weathering and metamorphism of organic C in sedimentary rocks, respectively, and  $F_{\text{wcarb}}$ ,  $F_{\text{mcarb}}$ ,  $F_{\text{bcarb}}$  are weathering, metamorphism and burial of carbonates, respectively.  $\delta^{13}\text{C}_v = -4\text{‰}$  is the average C isotopic composition of volcanic gases<sup>126</sup>. Carbonate minerals are assumed to be slightly fractionated with respect to dissolved inorganic carbon, by 1.0‰ ( $\delta^{13}\text{C}_{\text{carb}} = \delta^{13}\text{C} + 1$ )<sup>131</sup>.

On the basis of previous experimental and theoretical studies, changes in  $p\text{CO}_2$  and  $p\text{O}_2$

affect the fractionation factors between organic matter and inorganic C via reservoir effects and competition for the RuBisCO active sites<sup>132,133</sup>. We adopt parameterizations from previous studies<sup>83,122</sup>, which account for these effects on the average C isotopic fractionation associated with fixation of inorganic C to form land-derived and marine organic matter ( $\varepsilon_l$  and  $\varepsilon_m$ , respectively):

$$\varepsilon_m = \varepsilon_m^0 + \frac{J_{CO_2}}{\sqrt{\frac{pCO_{2,atm}}{pCO_{2,atm}^0}}} + J_{O_2} \left( \frac{pO_2}{pO_2^0} - 1 \right), \quad (S70)$$

$$\varepsilon_l = \varepsilon_l^0 + J_{O_2} \left( \frac{pO_2}{pO_2^0} - 1 \right). \quad (S71)$$

Here  $J_{CO_2}$ ,  $J_{O_2}$  are factors that describe the dependence of the C isotopic fractionation on  $pCO_2$  and  $pO_2$ , which were derived from experimental and theoretical constraints, and were drawn from normal distributions with  $\mu = -9$ ,  $\sigma = 3$ , and  $\mu = 5$ ,  $\sigma = 2.5$  respectively<sup>122,133–136</sup>.  $\varepsilon_m^0$  and  $\varepsilon_l^0$  refer to the present day fractionations, which were derived by mass balance calculations (Supplementary Table S6). The overall C isotopic composition of marine-derived organic matter is:  $\delta^{13}C_{org} = \delta^{13}C_{aq} - \varepsilon_m$ , where  $\delta^{13}C_{aq}$  is the C isotopic composition of aqueous  $CO_2$ . The C isotopic composition of land-derived organic matter is:  $\delta^{13}C_{org} = \delta^{13}C_{atm} - \varepsilon_l$ , where  $\delta^{13}C_{atm}$  is the C isotopic composition of atmospheric  $CO_2$ .

We include a temperature-dependent C isotope fractionation between atmospheric  $CO_2$ , marine  $HCO_3^-$ , and marine  $CO_2(aq)$ <sup>137</sup>. Carbon-isotope mass balance dictates:  $q \times C \times \delta^{13}C + (1 - q) \times C \times \delta^{13}C_o = C \times \delta^{13}C$ , where  $\delta^{13}C_o$  is the C isotopic composition of  $HCO_3^-$ , and  $q$  is the

fraction of moles of C in the atmosphere out of the total moles of C in the ocean-atmosphere (Supplementary Table S6). Using this isotopic mass balance and the temperature-dependent equilibrium fractionations of C isotopes in the carbonate system<sup>137</sup> we get ( $T$  is the mean global surface temperature):

$$\delta^{13}\text{C}_{\text{atm}} = \delta^{13}\text{C} + (q - 1) \times (9483/T - 23.89\text{‰}), \quad (\text{S72})$$

$$\delta^{13}\text{C}_{\text{o}} = \delta^{13}\text{C} + q \times (9483/T - 23.89\text{‰}), \quad (\text{S73})$$

$$\delta^{13}\text{C}_{\text{aq}} = \delta^{13}\text{C}_{\text{o}} - 9866/T + 24.12\text{‰}. \quad (\text{S74})$$

## Supplementary Tables:

Table S1: **Global rates of carbon uptake into the upper oceanic crust.** Crustal CO<sub>2</sub> wt% data from Table 1 of Gillis and Coogan (2011) were used to calculate the global rates of C uptake into altered oceanic crust (see *Methods*).

Site	Age (Ma)	$\Delta\text{CO}_2$ wt%	$f_{SF}$	$F_{\text{CO}_2}$ (Tmol C yr <sup>-1</sup> )	Ref.
396B (Atlantic)	13.6	0.8±0.2	1.07	1.2±0.3	26
562 (Atlantic)	17	1.9±0.3	1.08	2.8±0.4	26
556 (Atlantic)	31	2.0±0.3	1.13	3.1±0.5	26
543A (Atlantic)	81	2.1±0.5	1.57	4.5±1.1	26
417A	120	3.9±0.2	1.60	8.7±0.4	31
417D		4.2±0.2			
418A (Atlantic)		4.0±0.2			
504B (Pacific)	6.8	0.2±0.1	1.04	0.3±0.1	14
896A (Pacific)	6.8	0.5±0.2	1.04	0.7±0.3	14
597C (Pacific)	28	0.4±0.1	1.15	0.6±0.2	26
1244F (Pacific)	48	0.5±0.2	1.22	0.8±0.3	26
843B (Pacific)	98	2.4±0.7	1.70	5.6±1.6	14
595B (Pacific)	140	1.9±0.3	1.45	3.7±0.6	26
801C (Pacific)	167	2.6±0.8	1.48	5.2±1.6	32

**Table S2: Literature estimates of present-day phosphate fluxes and C:P ratios in organic matter.**

Parameter (units)	Value	Ref.	Parameter (units)	Value (score)	Ref.
$F_{\text{bap}}^0$ (Tmol P yr <sup>-1</sup> )	0.015 <sup>a</sup>	7	$F_{\text{borg,land}}^0$ (Tmol C yr <sup>-1</sup> )	4.3 <sup>a</sup>	141
	0.091 <sup>a</sup>	57		3.6 <sup>b</sup>	142
	0.035 <sup>a</sup>	138		7.9 <sup>c</sup>	143
	0.080 <sup>a</sup>	139		6.6 <sup>b**</sup>	144
	0.035 <sup>b</sup>	140			
$F_{\text{plume,P}}^0$ (Tmol P yr <sup>-1</sup> )	0.004 <sup>a</sup>	145	$F_{\text{borg}}^0$ (Tmol C yr <sup>-1</sup> )	6.2 <sup>a***</sup>	141
	0.008 <sup>a</sup>	11		4.5 <sup>b</sup>	142
	0.004 <sup>a</sup>	54		18.3 <sup>b***</sup>	144
$F_{\text{np,P}}^0$ (Tmol P yr <sup>-1</sup> )	27.2 <sup>b</sup>	9	(C : P) <sub>pp</sub> (molar C/P)	125 <sup>a</sup>	147
	38.7 <sup>b</sup>	10		117 <sup>a</sup>	148
	35.0 <sup>b</sup>	146		146 <sup>a</sup>	99
	38.7 <sup>c</sup>	143		114 <sup>a*****</sup>	149
$F_{\text{off,P}}^0$ (Tmol P yr <sup>-1</sup> )	0.007 <sup>a</sup>	11	(C : P) <sub>borg</sub> (molar C/P)	250 <sup>a</sup>	7
	0.028 <sup>a</sup>	12		226 <sup>a</sup>	150
	0.006 <sup>b*</sup>	This study		235 <sup>a</sup>	151
			237 <sup>c</sup>	143	
$F_{\text{bFeP}}^0$ (Tmol P yr <sup>-1</sup> )	0.040 <sup>a</sup>	57	(C : P) <sub>anoxic</sub> (molar C/P)	3900 <sup>a</sup>	151
	0.023 <sup>a</sup>	138		1100 <sup>a</sup>	102
$f_{\text{sil,p}}$	0.8 <sup>c</sup>	152	(C : P) <sub>oxic</sub> (molar C/P)	150 <sup>a</sup>	151

Estimates are based on (a) empirical observations, (b) literature review with updates, and (c) model.

\*Based on data from ref. 98 (see *SI*).

\*\*Burdige (2005) assumed a total organic C burial rate of 25 Tmol C yr<sup>-1</sup> (Table 5)<sup>144</sup>. Out of this flux, 20 Tmol yr<sup>-1</sup> is buried in continental margin sediments, where a third of the organic C buried on the continental margins is land-derived, and 5 Tmol yr<sup>-1</sup> of the organic carbon is buried in deep-sea sediment.

\*\*\*Assuming that 50% of the “terrestrial” deltaic shelf sediment is of a marine origin<sup>142</sup>.

\*\*\*\* Based on a literature review of phytoplankton elemental composition in lab cultures. For parameter definitions, see *SI*.

**Table S3: Literature estimates of weathering parameters.**

Parameter (units)	Value (range)		Parameter (units)	Value (range)	Ref.
$E_{\text{sil}}$ (kJ mol <sup>-1</sup> )	59–63 <sup>a</sup>	153	$E_{\text{bas}}$ (kJ mol <sup>-1</sup> )	110 <sup>a</sup>	16
	51 <sup>a</sup>	154		120 <sup>a</sup>	19
	18–55 <sup>a</sup>	86		24–86 <sup>a</sup>	21
	50–80 <sup>a</sup>	155		88 <sup>a</sup>	27
	14–24 <sup>a</sup>	156		85–99 <sup>a</sup>	18
	20 <sup>b</sup>	157		39–45 <sup>a</sup>	158
			53–97 <sup>b</sup>	157	
			65 <sup>c</sup>	15	
			41–65 <sup>c</sup>	17	
$F_{\text{wcarb}}^0$ (Tmol Ca yr <sup>-1</sup> )	12.5 <sup>d</sup>	159	$F_{\text{wsil}}^0$ (Tmol Ca yr <sup>-1</sup> )	5.9 <sup>d</sup>	159
	12.4 <sup>d</sup>	23		5.9 <sup>d</sup>	23
	12.3 <sup>d</sup>	86		5.8 <sup>d</sup>	86
	7.3 <sup>e</sup>	160		6.4 <sup>e</sup>	76
	8.6 <sup>e</sup>	76		5.6 <sup>e</sup>	160
	7.3 <sup>e</sup>	161		6.2 <sup>e</sup>	161
$F_{\text{wsf}}^0$ (Tmol Ca yr <sup>-1</sup> )	0.4 <sup>*</sup>	162	$n_C$ (unitless)	0.50 <sup>b</sup>	28
	0.9 <sup>*</sup>	14, 163		0.45 <sup>a</sup>	167
	2.0 <sup>*</sup>	164		0.33 <sup>b</sup>	157
	0.3–0.9 <sup>**</sup>	165			
	0.7–2.0 <sup>**</sup>	31			
	0.5–1.4 <sup>***</sup>	166			
	78				
$n_O$ (unitless)	0.5–1.0 <sup>a</sup>	168	$a_T$ (unitless)	0.8–1.4 <sup>f</sup>	157
$k_{Ca}$ (unitless)	0.05–0.09 <sup>a</sup>	72, 74			
	0.02–0.08 <sup>b</sup>	62			

Estimates are based on (a) empirical observations, (b) a model, (c) lab dissolution experiments, (d) river chemical data, (e) a functional relationship between rock weathering rates of specific lithological classes and lithological maps, and (f) literature review with updates. For parameter definitions, see *SI*.

Estimates of the present-day Ca fluxes from off-axial system ( $F_{\text{wsf}}^0$ ) are based on changes in the CaO wt% content of \*Hole 504 (6.8 Ma), \*\*Holes 417/418 (120 Ma), and \*\*\* the Troodos ophiolite (91.6 Ma). Flux calculations were made assuming a Cenozoic crustal production rate of  $3.45 \times 10^6 \text{ m}^2 \text{ yr}^{-1}$ , an average crustal thickness of  $\sim 600 \text{ m}$ , and a crustal density of  $2900 \text{ kg m}^{-3}$ . Cretaceous cores and ophiolites were normalized to present-day temperature and seafloor spreading rates (if Cretaceous Ca leaching rates were reported as a flux). See *SI* for further details.

Table S4: **Literature estimates of present-day volcanic outgassing fluxes.**

Flux (Tmol C yr <sup>-1</sup> )	Value (mean)	Ref.	Flux (Tmol C yr <sup>-1</sup> )	Value (mean)	Ref.
$F_{\text{vmor}}^0$	0.5 <sup>a</sup>	169	$F_{\text{varc,point}}^0$	0.3 <sup>e</sup>	189
	0.7 <sup>a</sup>	170		1.5 <sup>e</sup>	190
	1.3 <sup>a</sup>	171		1.1 <sup>e</sup>	191
	0.8 <sup>a</sup>	172		1.2 <sup>e</sup>	192
	1.3 <sup>a</sup>	173		1.9 <sup>e</sup>	193
	1.4 <sup>a</sup>	174		1.5 <sup>f</sup>	183
	4.4 <sup>a</sup>	175		2.2 <sup>f</sup>	127
	11.0 <sup>a*</sup>	176		2.5 <sup>f</sup>	182
	15.0 <sup>a*</sup>	177		3.1 <sup>f</sup>	194
	0.7 <sup>b</sup>	178		0.7 <sup>g</sup>	195
	0.9 <sup>b</sup>	179		1.1 <sup>g</sup>	196
	1.3 <sup>b</sup>	180		1.8 <sup>g</sup>	170
	1.3 <sup>b</sup>	181		2.0 <sup>h</sup>	197
	2.2 <sup>b</sup>	182			
	1.5 <sup>b</sup>	183			
	1.5 <sup>b</sup>	184			
	2.1 <sup>b</sup>	185			
	2.2 <sup>b</sup>	186			
	4.2 <sup>b</sup>	187			
	0.7 <sup>c</sup>	80			
1.3 <sup>d</sup>	188				
$F_{\text{vplume}}^0$	0.03 <sup>e</sup>	191	$F_{\text{varc,diffuse}}^0$	2.3 <sup>e</sup>	191
	0.10 <sup>e</sup>	191		1.9 <sup>e</sup>	174
	1.60 <sup>f</sup>	182			
	0.82 <sup>g</sup>	195			
	1.80 <sup>i</sup>	183			

Volcanic outgassing rates (Tmol C yr<sup>-1</sup>) were estimated from: (a) crustal production rates multiplied by the crustal C content, (b) CO<sub>2</sub>/<sup>3</sup>He in mid-ocean ridge basalt glasses and fluids, (c) hydrothermal fluid composition and flux, (d) CO<sub>2</sub>/<sup>3</sup>He in plumes, (e) C/S in volcanic gases and the volcanic S flux, (f) CO<sub>2</sub>/<sup>3</sup>He in volcanic gases and the <sup>3</sup>He flux, (g) flux measurements, (h) polonium-210 emissions, and (i) magma production rates of plume volcanoes multiplied by the magmatic C content. \*2 $\sigma$  outlier. For parameter definitions, see *SI*.

**Table S5: The origin of the CO<sub>2</sub> in arc settings.**

Arc	$\delta^{13}\text{C}_s$	$\text{C}/^3\text{He}_s$	$f_{\text{varc},m}$	$f_{\text{varc},\text{carb}}$	$f_{\text{varc},\text{org}}$	$W \times 10^4$	Arc	$\delta^{13}\text{C}_s$	$\text{C}/^3\text{He}_s$	$f_{\text{varc},m}$	$f_{\text{varc},\text{carb}}$	$f_{\text{varc},\text{org}}$	$W \times 10^4$
K.- K.*	-11	11	0.14	0.50	0.36	15	Antilles	-5.9	349	0.00	0.80	0.20	146
	-12	36	0.04	0.57	0.39	15		-3.3	90	0.02	0.88	0.11	146
	-5.7	23	0.07	0.76	0.18	15		-2.9	43	0.03	0.87	0.09	146
	-9.9	13	0.12	0.58	0.31	15		-3.1	11	0.13	0.79	0.08	146
	-7.2	99	0.01	0.75	0.24	15		-3.0	13	0.12	0.81	0.08	146
Japan	-4.4	10	0.15	0.73	0.12	508	Andes	-7.6	15	0.1	0.67	0.23	3045
	-7.9	13	0.11	0.65	0.24	508		-4.9	12	0.13	0.73	0.14	3045
	-6.1	8	0.19	0.65	0.17	508		-9.5	31	0.05	0.64	0.31	3045
	-5.5	6	0.24	0.63	0.14	508		-6.8	19	0.08	0.71	0.21	3045
	-1.3	24	0.06	0.91	0.03	508		-8.2	17	0.09	0.66	0.26	3045
	-5.6	8	0.19	0.66	0.15	508		-6.9	17	0.09	0.7	0.21	3045
	-3.9	17	0.09	0.8	0.11	508		-7.7	40	0.04	0.71	0.25	3045
	-4.9	28	0.05	0.79	0.15	508		-2.5	9	0.16	0.79	0.05	3045
Kermadec	-8.7	28	0.05	0.67	0.28	565	P.N. Guinea	-2.6	11	0.13	0.81	0.06	4925
	-2.0	36	0.04	0.9	0.06	565		-2.8	11	0.13	0.80	0.07	4925
	-10	8	0.19	0.5	0.31	565							
C. America	-6.3	6	0.25	0.59	0.16	705	Indonesia	-3.9	14	0.11	0.78	0.11	92
	-3.9	6	0.24	0.68	0.08	705		-3.9	13	0.12	0.77	0.11	92
	-2.8	11	0.13	0.8	0.07	705		-4.4	15	0.1	0.77	0.13	92
	-2.8	18	0.08	0.84	0.08	705		-1.7	39	0.04	0.91	0.05	92
	-6.9	20	0.08	0.71	0.21	705		-3.7	13	0.12	0.78	0.1	92
	-3	29	0.05	0.86	0.09	705		-2.9	13	0.11	0.81	0.07	92
	-1.9	12	0.12	0.84	0.04	705		-1.7	8	0.19	0.79	0.02	92
	-2.5	20	0.07	0.86	0.07	705		-3.3	8	0.19	0.73	0.07	92
	-1.3	19	0.08	0.89	0.03	705		-1.2	78	0.02	0.94	0.04	92
	-3.3	23	0.07	0.84	0.1	705		-3.2	5	0.27	0.68	0.05	92
	-2.9	14	0.11	0.82	0.08	705		-3.6	8	0.18	0.74	0.08	92
	-2.9	32	0.05	0.86	0.09	705		-4.8	6	0.25	0.64	0.11	92
	-2.4	17	0.09	0.88	0.07	705							
	-2.5	33	0.04	0.86	0.07	705							
	-2.6	27	0.06	0.87	0.08	705							
	-2.8	16	0.09	0.83	0.07	705							
	-1.5	23	0.07	0.9	0.04	705							
-3.3	18	0.08	0.82	0.09	705								
-3.4	14	0.1	0.8	0.09	705								
-6.0	14	0.11	0.71	0.18	705								
-2.3	27	0.06	0.88	0.07	705								
-4.1	12	0.12	0.77	0.11	705								

The origin of the CO<sub>2</sub> in arc settings (i.e.,  $f_{\text{varc},m}$ ,  $f_{\text{varc},\text{carb}}$  and  $f_{\text{varc},\text{org}}$ ) was estimated from global data compilations of the C isotopic compositions and the CO<sub>2</sub>/<sup>3</sup>He ratio of volcanic arcs<sup>126,127</sup>, by solving equations S49 to S51 (SI). To extrapolate  $f_{\text{varc},m}$ ,  $f_{\text{varc},\text{carb}}$ , and  $f_{\text{varc},\text{org}}$  from the individual volcanoes to a global flux, these values were weighted by the relative contribution of the volcano to the total CO<sub>2</sub> volcanic outgassing:  $W = f_{\text{CO}_2}(\text{arc})/f_{\text{CO}_2}(\text{total})$ , where  $f_{\text{CO}_2}(\text{arc})$  is the CO<sub>2</sub> flux in a specific arc,  $f_{\text{CO}_2}(\text{total})$  is the total CO<sub>2</sub> degassing in arc volcanism (from Table S3 in ref. 126). \*K.- K. for Kuril - Kamchatka. For parameter definitions, see SI.

**Table S6: Parameters constrained by mass balance.**

Mass balance equation
$F_{\text{worg}}^0 = \frac{F_v^0}{\varepsilon} (\delta^{13}\text{C}_v - \delta^{13}\text{C}) + F_{\text{borg}}^0 + F_{\text{borg,land}}^0$
$F_{\text{wP,ocean}}^0 = F_{\text{borg,P}}^0 + F_{\text{bap}}^0 + F_{\text{bFeP}}^0 + F_{\text{plume,P}}^0 + F_{\text{off,P}}^0$
$F_{\text{bcarb}}^0 = F_{\text{wcarb}}^0 + F_{\text{wsil}}^0 + F_{\text{wsf}}^0$
$F_{\text{mcarb}}^0 = F_{\text{bcarb}}^0 - F_{\text{wcarb}}^0$
$F_{\text{morg}}^0 = F_{\text{borg,land}}^0 + F_{\text{borg}}^0 - F_{\text{worg}}^0$
$F_{\text{ored}}^0 = F_{\text{morg}}^0$
$f_{\text{oarc,org}} = \frac{f_{\text{varc,org}} \times F_{\text{varc}}^0}{F_{\text{vmor}}^0 + F_{\text{vplume}}^0 + F_{\text{varc}}^0 (f_{\text{varc,m}} + f_{\text{varc,org}})}$
$f_{\text{oplume}} = \frac{F_{\text{vplume}}^0}{F_{\text{vmor}}^0 + F_{\text{vplume}}^0 + F_{\text{varc}}^0 (f_{\text{varc,m}} + f_{\text{varc,org}})}$
$\varepsilon_m^0 = -(\delta^{13}\text{C}_{\text{org}}(\text{marine}) - \delta^{13}\text{C}_{\text{aq}}^0 + J_{\text{CO}_2})$
$\varepsilon_l^0 = -(\delta^{13}\text{C}_{\text{org}}(\text{land}) - \delta^{13}\text{C}_{\text{atm}}^0)$
$q = \frac{p_{\text{CO}_2} \times V_{\text{atm}}}{R \times T} / C$

$\delta^{13}\text{C}_{\text{org}}(\text{marine})$  and  $\delta^{13}\text{C}_{\text{org}}(\text{land})$  were drawn from normal distributions with  $\mu = -22.5$ ,  $\sigma = 5^{198}$ , and  $\mu = -30$ ,  $\sigma = 5$ , respectively<sup>44, 137, 199</sup>. For the development of these equations, see *SI*.

**Table S7: Model constants.**

Parameter (units)	Value	Ref.
$K_H$ (mol L <sup>-1</sup> atm <sup>-1</sup> )	10 <sup>-1.42</sup>	131
$K_W$ (mol <sup>2</sup> L <sup>-2</sup> )	10 <sup>-13.63</sup>	131
$K_1$ (mol L <sup>-1</sup> )	10 <sup>-5.95</sup>	131
$K_2$ (mol L <sup>-1</sup> )	10 <sup>-9.10</sup>	131
$K_{SP}$ (mol <sup>2</sup> L <sup>-2</sup> )	10 <sup>-6.36</sup>	131
$\delta^{13}\text{C}_{\text{aq}}^0$ (‰)	-7.5	137
$\delta^{13}\text{C}_{\text{atm}}^0$ (‰)	-6.4	137
$\delta^{13}\text{C}_m$ (‰)	-6.0	200, 201
$V_o$ (L)	1.4 × 10 <sup>21</sup>	
$V_{\text{atm}}^*$ (L)	5.6 × 10 <sup>21</sup>	
$V_d$ (L)	1.3 × 10 <sup>21</sup>	

$K$ s at T = 15°C and salinity = 35 PSU.

\*Assuming 75% of the atmosphere's mass is within 11 km of the Earth's surface.

**Table S8: Present-day pool sizes and phosphate concentration.**

Symbol	Definition	Present-day values
$P^0$	Phosphate pool in the ocean (Tmol P)	$3.00 \times 10^3$
$C^0$	Carbon pool in the ocean-atmosphere (Tmol C)	$3.02 \times 10^6$
$O_2^0$	Oxygen pool in the ocean-atmosphere (Tmol $O_2$ )	$3.80 \times 10^7$
$Ca^0$	Calcium pool in the ocean (Tmol C)	$1.48 \times 10^7$
$C_{org}^0$	Carbon pool in sedimentary organic rocks (Tmol C)	$1.25 \times 10^9$
$CaCO_3^0$	Carbon pool in $CaCO_3$ (Tmol C)	$5.00 \times 10^9$
$[P]_s^0$	Phosphate concentration in the surface ocean ( $\mu M$ P)	0.5
$[P]_d^0$	Phosphate concentration in the deep ocean ( $\mu M$ P)	2.3

**Table S9: Criteria for successful model runs.**

Parameter	Criterion	Allowable range
$pCO_2^0$	$\pm 50\%$ preindustrial $pCO_2$ (ppm)	300( $\pm 50\%$ )
$pO_2^0$	$\pm 15\%$ of modern $pO_2$ (atm)	0.21( $\pm 15\%$ )
$[P]_d^0$	$\pm 15\%$ of modern P concentration in the deep ocean ( $\mu M$ P)	2.3( $\pm 15\%$ )
$[Ca]^0$	$\pm 15\%$ of modern Ca concentration in the ocean (mM Ca)	10.3( $\pm 15\%$ )
$T^0$	$\pm 4K$ of modern global surface temperature (K)	284–292
$\delta^{13}C^0$	$2\sigma$ range of C-isotopic composition of carbonate minerals in modern marine sediments ( $\%$ )	-1.0–2.5

**Table S10: Literature estimates of calcium and magnesium exchange fluxes from seafloor weathering in off-axial systems based on changes in the CaO/MgO wt% content of oceanic crust.**

Site (Age)	$J_{Mg}$ (Tmol Mg $yr^{-1}$ )	$J_{Ca}$ (Tmol Ca $yr^{-1}$ )	Ref.
Hole 504 (6.8 Ma)	-0.36	0.43	162
Hole 504 (6.8 Ma)	-0.82	0.90	14, 163
Hole 504 (6.8 Ma)	0.10	1.97	164
Holes 417/418 (120 Ma)	0.03	1.60	165
Holes 417/418 (120 Ma)	0.92	3.59	31
The Troodos ophiolite (91.6 Ma)	-0.50*	2.50*	166
The Troodos ophiolite (91.6 Ma)	-0.30*	1.79*	78

Positive values indicate flux from the crust into seawater. Mg and Ca flux ( $J_{Mg}$  and  $J_{Ca}$ , respectively) calculations were made assuming a Cenozoic crustal production rate of  $3.45 \times 10^6$   $m^2$   $yr^{-1}$ , an average crustal thickness of  $\sim 600$  m, and a crustal density of  $2900$   $kg$   $m^{-3}$ . \*In the Troodos ophiolite, average crustal thickness is  $\sim 200$  m<sup>26,166</sup>.

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