

Two-step rise of atmospheric oxygen linked to the growth of continents

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Earth owes its oxygenated atmosphere to its unique claim on life, but how the atmosphere evolved from an initially oxygen-free state remains unresolved. The rise of atmospheric oxygen occurred in two stages: approximately 2.5 to 2.0 billion years ago during the Great Oxidation Event and roughly 2 billion years later during the Neoproterozoic Oxygenation Event. We propose that the formation of continents about 2.7 to 2.5 billion years ago, perhaps due to the initiation of plate tectonics, may have led to oxygenation by the following mechanisms. In the first stage, the change in composition of Earth's crust from iron- and magnesium-rich mafic rocks to feldspar- and quartz-rich felsic rocks could have caused a decrease in the oxidative efficiency of the Earth's surface, allowing atmospheric O₂ to rise. Over the next billion years, as carbon steadily accumulated on the continents, metamorphic and magmatic reactions within this growing continental carbon reservoir facilitated a gradual increase in the total long-term input of CO₂ to the ocean-atmosphere system. Given that O₂ is produced during organic carbon burial, the increased CO₂ input may have triggered a second rise in O₂. A two-step rise in atmospheric O₂ may therefore be a natural consequence of plate tectonics, continent formation and the growth of a crustal carbon reservoir.

Oxygen is a major element in all of the terrestrial planets in our Solar System. Yet, no planet besides Earth has an oxygenated atmosphere because oxygen is locked away as oxides in the rocky interiors of planets. Detrital uraninite and pyrite minerals, as well as mass-independent sulfur isotope fractionation, indicate that Earth's atmosphere was also initially free of O₂ (refs 1,2). Around 2.5 to 2.0 billion years ago (Ga), oxygen levels rose from <10⁻⁷–10⁻⁵ that of present atmospheric levels (PAL) to anywhere from 10⁻⁴–10⁻² PAL, corresponding to a relative increase of more than 10- to 10⁴-fold during a protracted transition known as the Great Oxidation Event (GOE)^{1–6} (Fig. 1a). Atmospheric oxygen levels remained at intermediate levels for another billion years, rising a second time in the Neoproterozoic Oxygenation Event (NOE) to the oxygenated levels (~0.2 atm) that characterize the Phanerozoic⁵. This latter rise in O₂ appears to coincide with the rise of complex life forms (animals) that require O₂ for respiration⁵.

How Earth's atmosphere became oxygenated is a fundamental question in the Earth sciences. The amount of molecular oxygen in the atmosphere is controlled by the sources of O₂ and the efficiency of the O₂ sinks⁷. Earth's current oxygenated atmosphere is the result of oxygenic photosynthesis but life alone, or even photosynthesis, does not guarantee an oxygenated atmosphere; oxygenic photosynthesis may have originated well before 2.7 Ga and thus before the GOE^{5,8–11}. One possibility is that photosynthetic production of O₂ could increase as a result of enhanced nutrient availability. This scenario has been invoked for the NOE¹². Alternatively, production of H₂ gas during volcanism, serpentinization, microbial processes or photodissociation of water followed by H₂ escape to space would oxidize the Earth's crust or interior. In turn, this would result in oxidation of volcanic gases, decreasing the efficiency of volcanism as an oxygen sink^{4,13,14}. It has also been suggested that an emergence of subaerial magmatism could lead to more oxidized volcanic gases as a result of auto-oxidation within ascending magmas¹⁵. However,

mantle redox appears not to have changed significantly over time^{16,17} and self-oxidation of volcanic gases is ultimately accompanied by reduction of Fe³⁺ in the magma itself, resulting in no net change in the redox state of erupted products.

Here, we suggest that the evolution of atmospheric O₂ is linked to continent formation and changes in the composition of continental crust-forming magmas from mafic to felsic around 2.5 Ga. The formation of felsic crust decreases the flux of mantle-derived reductants to the Earth's surface and atmosphere, which in turn allows atmospheric O₂ to accumulate. A second rise in atmospheric O₂ comes with the accumulation of carbon on the continents — once the continents were established, most carbon would have been deposited on continental margins, rather than returned to Earth's interior by subduction. Metamorphically and magmatically induced release of this growing continental carbon reservoir amplifies the background mantle contribution, increasing geologic inputs of CO₂ into the ocean-atmosphere system over time. Because net O₂ production is tied to production of CO₂, O₂ rises after sufficient amounts of carbon accumulate in the continents and geological sinks of O₂ attain their limit. Atmospheric evolution models of oxygen must operate on top of this geologic background.

Transition from mafic to felsic continental crust 2.7–2.5 Ga
Continents are regions of Earth's surface that ride high above the sea floor, near but not necessarily always above sea level. They can be mafic or felsic as the key to their high elevations is crustal thickness¹⁸. Direct determination of the growth of continents through time is difficult, so indirect geochemical methods are usually used. Zircons have become a popular tool for assessing continental growth because they form during magmatism and crustal reworking and because they are sufficiently enriched in U to enable geochronological analyses. Large, independent compilations of detrital zircon U–Pb ages show that zircons fall into distinct age clusters^{19,20} (Fig. 1b). In all

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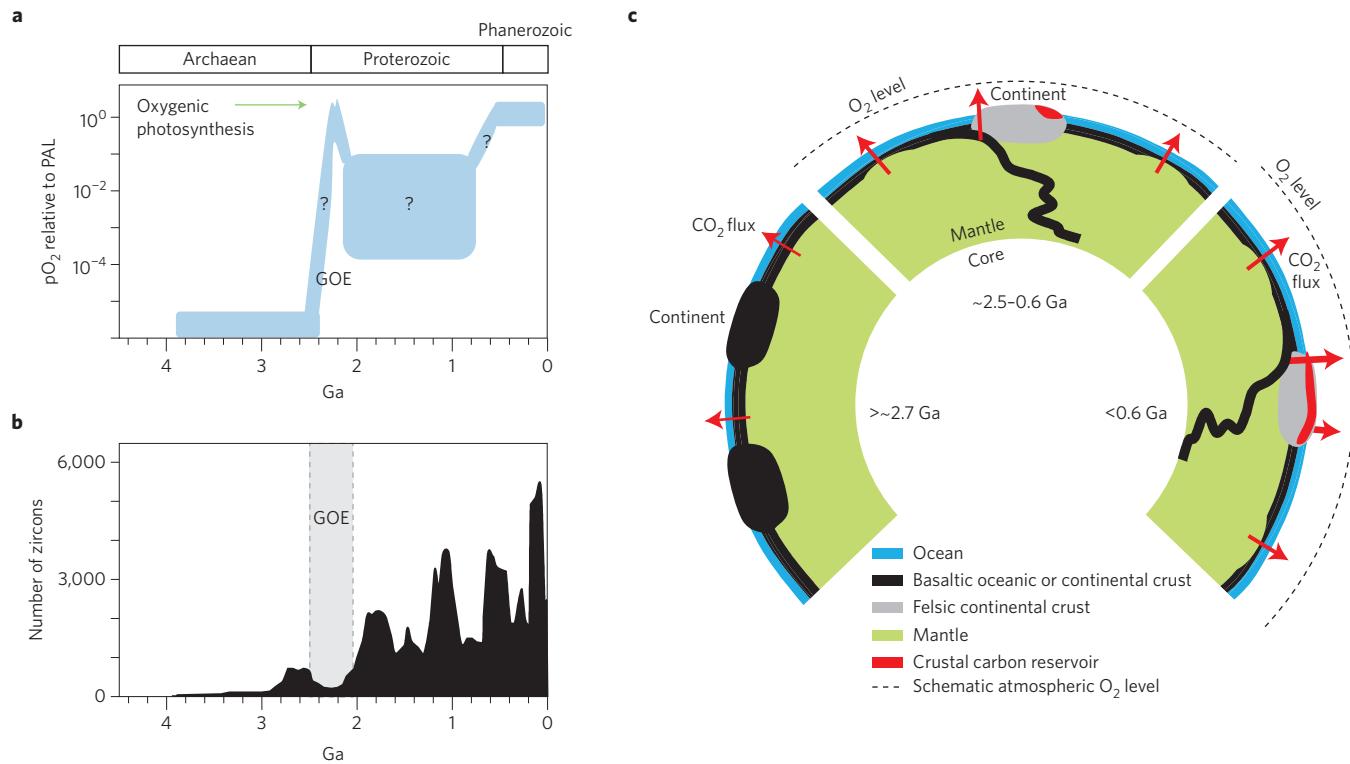


Figure 1 | Constraints on continental evolution. **a**, Estimated secular evolution of atmospheric pO_2 (relative to PAL). Blue represents the range of pO_2 based on various palaeo-redox and oxygen indicators¹. Oxygen rose ~2.5–2.0 Ga (in the GOE) and 0.7–0.5 Ga (in the NOE). Oxygenic photosynthesis occurred as early as 3.3 Ga. The question marks indicate that oxygen levels are uncertain. Data from ref. 1. **b**, Histogram of concordant U–Pb ages from our global compilation of detrital zircons. Data from refs 19,21. **c**, Trilogy of Earth’s history in terms of pO_2 . Before 2.7 Ga, Earth was characterized by stagnant-lid convection and continents were basaltic. At ~2.5 Ga, plate tectonics and subduction were initiated, shifting continental crust-forming magmatism to felsic compositions and decreasing the flux of mantle-derived reductants via magmatism. The carbon reservoir on continents builds up, increasing CO_2 inputs from crustal metamorphism, thereby leading to greater O_2 production.

compilations, the oldest prominent population of detrital zircons occurs between 2.8–2.4 Ga^{19,20}. An assessment of a recent zircon compilation from Cryogenian to recent sediments²¹ shows that zircons older than 2.8 Ga — an ~1.7 Gyr (billion year) interval — account for only ~1% of the global population, whereas zircons with ages between 2.8–2.4 Ga — only a 400 Myr (million year) interval — account for ~4% of the global population.

Clearly, the Earth experienced a fundamental change at ~2.8 Ga. One interpretation is that the zircons represent periods of enhanced continental crust formation, which would imply that the first continents formed 2.8–2.4 Ga, followed by episodic production of continents afterwards¹⁹. However, the presence of sediments dating back into the early Archaean indicates that land mass, and by implication continental crust, existed well before 2.8 Ga, yet it did not sufficiently produce zircons. Furthermore, the Nd isotopic composition of Archaean mantle suggests that large volumes of incompatible trace element-enriched crust, presumably continental crust, already existed by late Archaean times²². A second interpretation is that the zircon record is biased towards preservation, with zircon-poor time intervals corresponding to periods of enhanced continental erosion, destruction and recycling²³.

A third, simpler hypothesis is that the zircon record reflects the generation of distinct rock types^{21,24}. Felsic rocks (granodiorites to granites) are the only magmas that commonly saturate in zircon, basaltic rocks generally do not (Fig. 2a). Mafic magmas are initially under-saturated in zircon, allowing Zr contents of fractionating magmas to rise with increasing SiO_2 until saturation is reached, after which Zr declines by fractionation of zircon²⁵. The zircon record is therefore biased to felsic crust, which forms primarily in continental

arc or mature island arc systems (Fig. 2b), where hydrous magmas have undergone protracted crystal–liquid differentiation. Island arcs, large igneous provinces and oceanic crust are generally basaltic (Fig. 2b) and unlikely to generate appreciable zircon. The first major peak in zircon U–Pb ages between 2.8–2.4 Ga could therefore represent the first appearance of large volumes of felsic crust, not the first appearance of continents. An increase in the Rb/Sr ratio of juvenile crusts coincident with a decrease in transition metal concentrations of sediments and crustal rocks corroborates our suggestion^{26–29}. Thus, although continents certainly existed before 2.8 Ga, the lack of zircons before 2.8 Ga suggests that these continents were basaltic.

Special conditions are required to generate large volumes of felsic magmas. Felsic magmas typically represent only the last <10% of a basaltic magmatic parent³⁰ and thus require extreme crystal fractionation, but reaching these conditions requires significant amounts (wt%) of water dissolved in the parental magmas. Water not only expands the field over which silicic melts are stable during crystal fractionation, but also delays most of the latent heat of crystallization to near-solidus temperatures³¹. The latter effect prolongs the lifespan of magma bodies at the temperatures at which silicic magmas form, providing sufficient time for silicic liquids to segregate. Today, hydrous parental magmas are only widespread in subduction zones, where water from Earth’s surface is transported into the mantle through subduction of hydrated oceanic crust. There are no other mechanisms that return large amounts of water into the mantle, therefore a transition to felsic continents may have been associated with a transition from stagnant-lid convection, in which the Earth’s surface is not recycled, to a mobile-lid regime, analogous to plate tectonics today where oceanic plates subduct³².

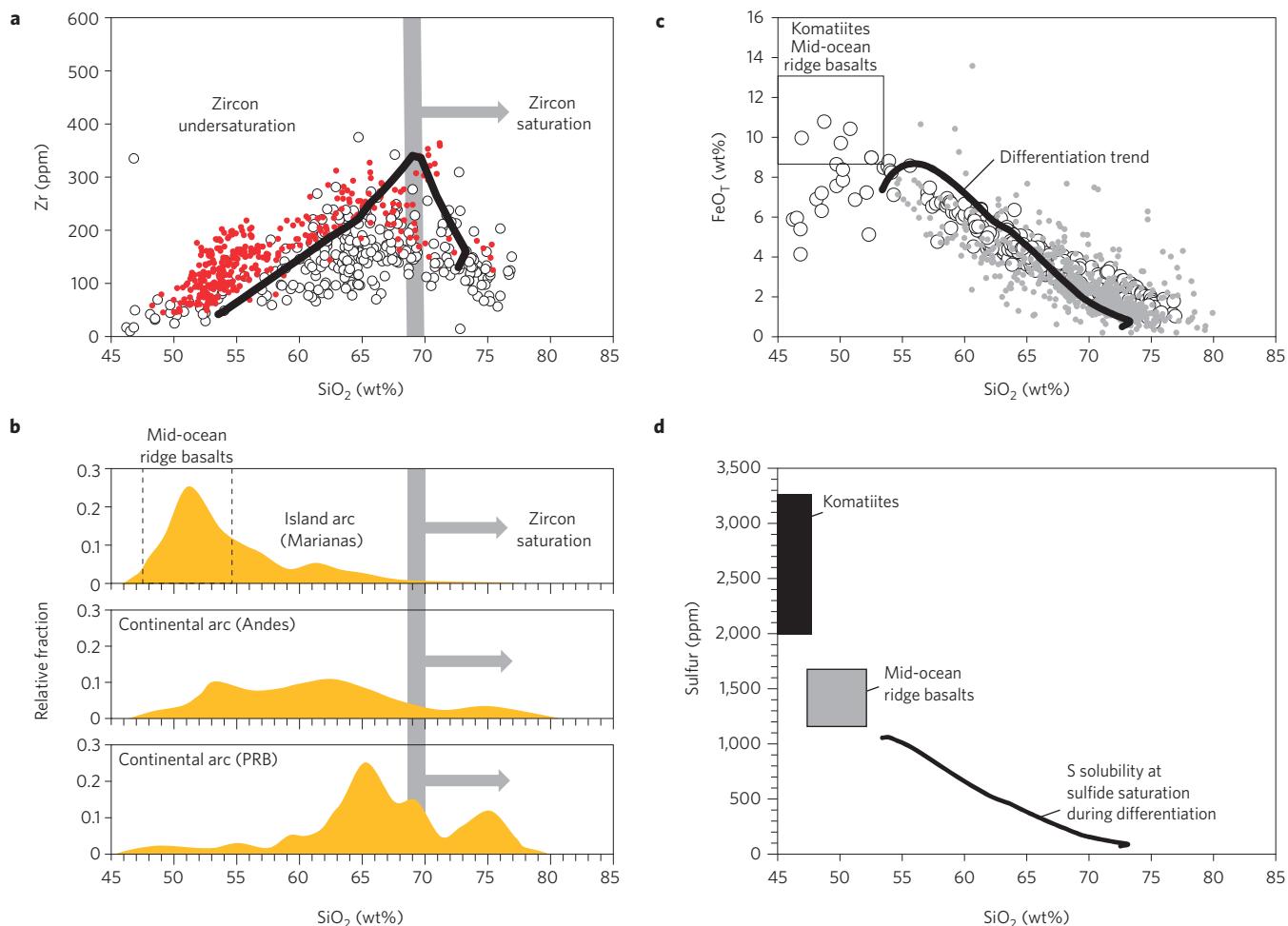


Figure 2 | Compositional systematics of magma differentiation. **a**, Bulk rock Zr (ppm) versus SiO_2 (wt% on volatile-free basis) for plutonic and volcanic rocks from the southern Andes (red) and the Cretaceous Peninsular Ranges batholith (PRB) in California, USA (white). The black line indicates the evolution of Zr during closed-system crystal-liquid segregation of a hydrous (4 wt% H_2O) basaltic andesite at 3 kbar pressure (oxygen fugacity buffered at the fayalite-magnetite-quartz buffer)⁵⁷. Zr increases initially because magmas are undersaturated in zircon, but at ~68–70 wt% SiO_2 , saturation in zircon is attained, causing Zr to decrease with progressive differentiation. The grey bar and arrow show that only silicic magmas generate zircon (basaltic magmas do not). Data from refs 57,58. **b**, Compositional range of mid-ocean ridge, island arc and continental arc volcanics⁵⁷. Only continental arcs are generally silicic enough to saturate zircon. **c**, Total FeO (FeO_T) versus SiO_2 for magmatic rocks from the Cretaceous PRB in California, USA⁵⁸ (white circles) and Archaean tonalites, trondjhemites and granodiorites (grey circles). Black line, the evolution of FeO_T during differentiation (the same differentiation path as in **a**), shows a substantial drop in total iron. **d**, Model evolution of sulfide (ppm) solubility at sulfide saturation versus SiO_2 using the S solubility model from ref. 59. S contents of komatiites and mid-ocean ridge basalts, assuming sulfide saturation in mantle source, are from ref. 36.

Alternatively, plate tectonics may have begun earlier in Earth's history, but geothermal gradients were too high prior to ~2.8 Ga to permit significant hydration of the oceanic lithosphere, minimizing transport of water into the mantle and preserving the mafic composition of the Earth's early crust. Whatever the cause, there was a fundamental change in the composition of the continents 2.8–2.4 Ga related to a change in global-scale dynamics of the Earth's interior.

First oxygenation linked to a decrease in crustal reductants

The transition from basaltic to felsic magmatism would have decreased the flux of mantle-derived reductants to the Earth's surface. The primary sinks of atmospheric oxygen are ferrous iron (Fe^{2+}) and sulfide (S^{2-}), the latter in the form of sulfide minerals and volcanic gas. Importantly, the amount of Fe^{2+} and S^{2-} available as an oxygen sink is lower in felsic rocks compared with mafic magmas. Depending on temperature and degree of differentiation, basalts typically have 8 to 12 wt% FeO_T (total Fe; ref. 33) of which ~90% is Fe^{2+} and hence oxidizable³⁴. Basalts typically have 1,200–3,000 ppm S^{2-} due to buffering by the presence of sulfide

minerals in the mantle³³. Although there is much less S than Fe in basalts, the oxidation of S^{2-} to S^{6-} in the form of SO_4^{2-} consumes eight electrons whereas oxidation of Fe^{2+} to Fe^{3+} consumes only one, so the reducing capacity of the sulfide component in basalts (sulfide to Fe oxidation capacity is ~0.8:1) is comparable to that of iron (arc-related basalts may have more total S due to higher amounts of SO_4^{2-} -species, but such highly oxidized basalts have not been shown to be important in the Archaean).

Felsic magmas, by contrast, are depleted in total iron by at least 80–90% relative to basalts (Fig. 2c), and most of this Fe is already in the oxidized ferric state³⁵. Thus, felsic rocks typically have much less than 10% of the reducing capacity of basalt. This depletion in Fe is caused by crystal fractionation of Fe-bearing phases, such as magnetite, amphibole and garnet. The depletion in Fe^{2+} in turn leads to a strong depletion in S^{2-} because sulfide solubility is controlled by complexation with Fe^{2+} in the melt³⁶ (Fig. 2d). Based on these solubility calculations, felsic magmas typically have <50 ppm sulfur in the form of S^{2-} compared with the 1,200–3,000 ppm S^{2-} in their parental basalts. Most of the 'missing' S and Fe is retained in deep

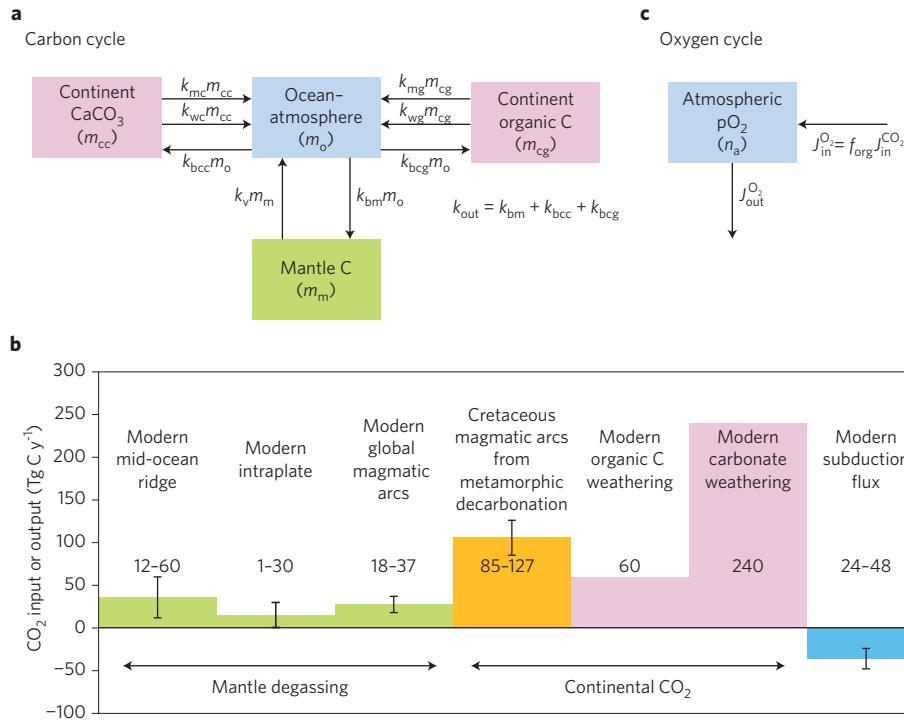


Figure 3 | Whole-Earth carbon and oxygen cycling. **a**, Simplified box model for carbon exchange between mantle, ocean-atmosphere and continents (k , rate constant; m , mass). m_{cc} , continent carbonate; m_{cg} , continent organic carbon; m_o , ocean-atmosphere carbon; m_m , mantle carbon; $k_{mc} m_{cc}$, metamorphism of continental carbonate; $k_{mg} m_{cg}$, metamorphism of continental organic carbon; $k_{wc} m_{cc}$, carbonate weathering; $k_{wg} m_{cg}$, oxidative weathering of organic carbon; $k_{bcc} m_o$, burial of carbonate on continental shelves; $k_{bg} m_o$, burial of organic carbon on continents; k_{m_m} , mantle degassing through all volcanoes; $k_{bm} m_o$, burial of organic carbon and carbonate in deep sea, which eventually subducts; k_{out} , total rate constant for carbon burial. Weathering contribution included here for completeness. **b**, Modern inputs or outputs of CO₂ (Tg carbon per year, for example, $\times 10^{12}$ g y⁻¹) into the ocean-atmosphere system from global mid-ocean ridge, intraplate and subduction zone volcanism^{41,60}, oxidative weathering of fossil organic carbon⁶¹, and weathering of continental carbonates (assuming an average organic C fraction f_{org} of 20%). Net output via subduction of sediments and carbonated oceanic crust⁴¹. Total CO₂ flux from global Cretaceous volcanic arcs (yellow), a time of pronounced continental arc activity, is shown for comparison⁴⁵. Error bars indicate maximum and minimum bounds. The numbers correspond to CO₂ inputs or outputs. **c**, Atmospheric pO₂ evolution. $J_{in}^{O_2}$, net production of O₂ via organic carbon burial; f_{org} , fraction of total carbon buried that is organic; $J_{in}^{CO_2}$, input of CO₂ into the ocean-atmosphere system minus that from carbonate and organic carbon weathering; $J_{out}^{O_2}$, loss of atmospheric O₂ via oxidation of Fe²⁺ and S²⁻ in volcanic gases and crust.

crustal cumulates that never make it to the surface, instead foundering back into the mantle, as evidenced by recent studies of chalcophile element systematics in continental crust and arc magmas³⁷. This decrease in S²⁻ concentration during the evolution of a basalt to a felsic magma translates into a >97% reduction in the magmatic flux of sulfide reductants dissolved in the magma or as volcanic gas (oxidized forms of S are not important as an oxygen sink). Given that felsic magmas represent no more than ~10% of the original parental magma, a conversion from basaltic to felsic magmatism results in an additional ~90% decrease in the continent-forming magmatic flux. Thus, this transition from basaltic to felsic magmatism would have resulted in a >99% decrease in the magmatic flux of reductants to the Earth's surface and atmosphere.

The effect on atmospheric O₂ levels can be described as follows. The rate of O₂ change in the atmosphere, dm_a/dt , where t represents time and m_a represents the mass of O₂ in the atmosphere, is equal to the sum of the photosynthetic production rate of O₂ ($J_{in}^{O_2}$) and the consumption or destruction of O₂, which at low O₂ levels scales linearly with the mass of O₂ in the atmosphere, that is, $k_{out} m_a$. The quantity k_{out} represents an effective global rate constant of oxidation, describing the efficiency of oxidation. It represents the inverse response time for O₂ drawdown or the effective residence time of O₂ in the atmosphere. In detail, k_{out} is the product of the total magmatic output rate (Q) of Fe²⁺ and S²⁻ multiplied by a factor that describes the probability (x) that Fe²⁺ and S²⁻ is actually oxidizable, that is, $k_{out} = xQ$. The quantity x depends on the actual mechanism

of oxidation. Reaction could occur directly with atmospheric O₂ or, more likely, through a series of oxidation-reduction steps that ultimately end in O₂ consumption or destruction. For example, oxidation of Fe²⁺ through reaction with water or other oxidants can result in H₂ gas, which then reacts with O₂ (or its photochemical derivatives) or is lost permanently to space^{13,14,38}. It is not critical to distinguish between these mechanisms because the factor x is meant to capture the net oxidation that ends with O₂ consumption.

The more important quantity is Q . On timescales of tens to hundreds of millions of years, atmospheric oxygen can be considered to be approximately at steady state, in which case atmospheric O₂ levels should scale with $J_{in}^{O_2}/k_{out}$ or $J_{in}^{O_2}/xQ$. Decreasing Q alone by 99% during the transition from mafic to felsic magmas can thus lead to a greater than 100-fold increase in steady-state atmospheric O₂ after 2.5 Ga. The predicted 100-fold rise in partial pressure of O₂ (pO₂) is consistent with observational constraints across the GOE, which is widely cited to be anywhere from 10- to 10⁴-fold¹⁻⁴, although a recent study based on Cr isotopes suggests a rise of $\leq 10^3$ -fold³⁹ (Fig. 1a). We note that nonlinear feedbacks involving atmospheric photochemistry, which are not included here, could amplify our predicted rise⁴⁰. We recognize that $J_{in}^{O_2}$ and x could change and that our model does not rule out other hypotheses for the GOE. Importantly, a fundamental change in the amount of Fe²⁺ and S²⁻ in crust-forming magmas must have a profound effect on atmospheric O₂. All other scenarios must operate on top of this shift in the flux of reductants to the Earth's surface during continent formation.

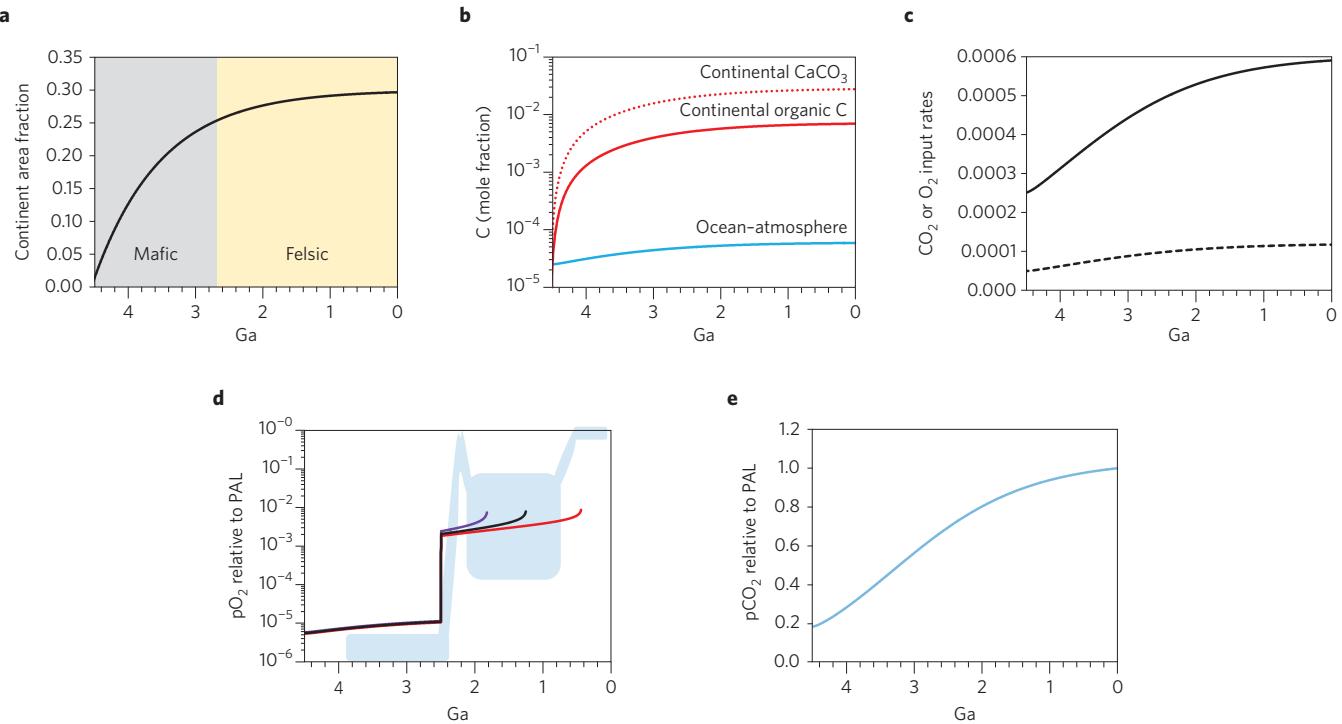


Figure 4 | Box modelling of carbon and oxygen. **a**, Cumulative continental growth curve used in our model. Continental crust-forming magmatism transforms from mafic to felsic at ~2.7–2.5 Ga. **b**, Accumulation of carbon in continental crust (as carbonates or organic C) and in the ocean-atmosphere system. Carbon content is normalized to the initial mass of C in whole mantle. **c**, Modelled CO₂ (solid line) and O₂ (dashed line) input rates (moles of CO₂ normalized to mass of C in the mantle per million years). **d**, Final model results for atmospheric pO₂ evolution relative to PAL. Prior to 2.7–2.5 Ga, Earth's O₂ levels were low because of high Fe- and S-bearing basalts. After 2.7–2.5 Ga, lower reductant flux associated with felsic magmatism allowed O₂ levels to rise. The second rise in O₂ is a runaway driven by increasing input of CO₂ into the atmosphere as a result of growing the continental carbon reservoir through time. This results in an increase in CO₂ and O₂ production. The blue region represents pO₂ estimates from Fig. 1a. The colours of the lines correspond to different kinetics of oxidation. **e**, Modelled rise of atmospheric pCO₂ relative to present day.

An important consequence of this transition in continental crust composition is that the magmatic flux of reductants associated with continent formation has no capacity to decrease any further, so a new, long-lived steady-state atmospheric O₂ level is established until another mechanism occurs, such as a change in the inputs of O₂ increase. Geologic observations indicate that after the GOE atmospheric O₂ levels did not rise significantly until a billion years later at the NOE⁵.

Continents as a growing carbon reservoir

To understand the second rise of O₂, we must turn to the whole-Earth carbon cycle. CO₂ slowly leaks out of the mantle through mid-ocean ridge, intraplate and subduction zone volcanism⁴¹ (Fig. 3a). Carbonate deposition and organic carbon burial remove CO₂ out of the exogenic (ocean-atmosphere) system, thereby modulating the carbon content of the exogenic system^{42–44}. However, over most of Earth's history, the majority of the carbon has been deposited on continental margins and a small fraction of carbon deposited in the deep ocean basins. Because continental margins do not subduct but ocean basins do, there is net accumulation of carbon at the Earth's surface in the form of organic and inorganic C stored on the continents^{45,46}.

Stored continental carbonates could be released by metamorphism of carbonates (CaCO₃ + SiO₂ = CaSiO₃ + CO₂) and organic carbon (2CH₂O + FeO = 2CO₂ + Fe₂O₃ + H₂), and by weathering of carbonates (H₂O + CO₂ + CaCO₃ = Ca²⁺ + 2HCO₃²⁻) and organic carbon (CH₂O + O₂ = CO₂ + H₂O). Crustal metamorphic contributions, for example, could occur during continental rifting, continental collisions and continental arc magmatism, the latter amplifying the contribution from the mantle wedge and subducting slab in

volcanic arcs^{45,47,48}. The data compilation in Fig. 3b shows that modern continental fluxes (metamorphism and weathering) are larger than mantle contributions. In addition, the modern subduction flux is less than the inputs to the exogenic system (mantle, metamorphism and weathering), requiring that there has been net storage of carbon at the Earth's surface.

A consequence of a growing continental carbon reservoir is that the continents become a growing source of carbon to the ocean-atmosphere system due to weathering and metamorphism of carbonates⁴⁵. To more quantitatively evaluate this effect, we perform a forward model of the growth of the crustal carbon reservoir by tracking the transport of carbon between the deep Earth and surface reservoirs (Fig. 3a). This is done by treating the efficiency of carbon transport between the mantle, continents and ocean basins in terms of effective rate constants equal to the inverse of plausible residence times of carbon in each reservoir (hundreds of millions of years for ocean basins and billions of years for the continents and mantle; see Methods). By further assuming that the global fraction of total carbon sequestered on continents scales with continental area (we adopt a progressive continental mass growth curve consistent with that inferred from the Nd isotope evolution of the mantle²²), we confirm that the growth of a continental carbon reservoir is indeed expected (Fig. 4). This growth facilitates an increase in total inputs of CO₂ into the exogenic system, which can be understood as follows. The flux of carbon into the exogenic system, $J_{in}^{CO_2}$, is the sum of metamorphism and volcanism (we have ignored carbonate and organic weathering because we assume those are balanced by reprecipitation of carbonate and organic carbon):

$$J_{in}^{CO_2} = k_{mc}m_c + k_{mg}m_{cg} + k_v m_v \quad (1)$$

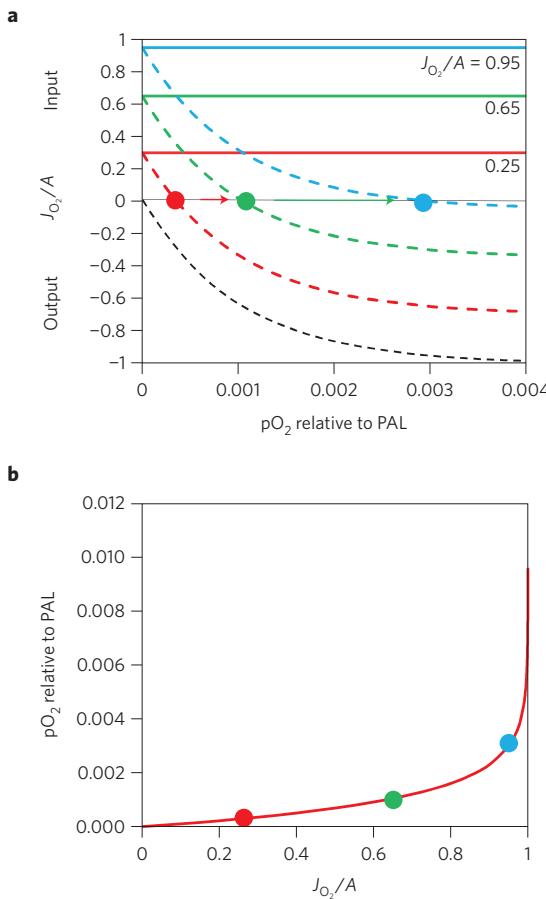


Figure 5 | O_2 inputs and outputs. **a**, Schematic diagram showing O_2 inputs, $J_{\text{in}}^{\text{O}_2}$, from total organic carbon burial (solid horizontal lines) and the behaviour of oxidative weathering outputs versus p_{O_2} (equation (4); black dashed line that plots negatively) versus the ratio between O_2 inputs and maximum oxidative weathering output, $J_{\text{in}}^{\text{O}_2}/A$ (see equations (4) and (5)). Other dashed lines represent the sum of the inputs $J_{\text{in}}^{\text{O}_2}$ and output function (black dashed line; equation (4)). Steady-state atmospheric O_2 (relative to PAL) is given when inputs and outputs are equal, that is, where the dashed lines intersect zero on the y axis. Coloured circles denote steady-state values. Steady-state oxygen levels increase when $J_{\text{in}}^{\text{O}_2}$ increases, but after some threshold, oxygen levels increase rapidly. **b**, Steady-state atmospheric oxygen (p_{O_2}) versus the ratio between O_2 inputs and maximum oxidative weathering output, $J_{\text{in}}^{\text{O}_2}/A$. Runaway occurs when inputs exceed threshold as in panel **a**. Coloured circles are the same as in **a**.

where m_c is the mass of carbonate in the continents, m_{cg} is the mass of organic C in the continents, m_m is the mass of carbon in the mantle, k_{mc} is the efficiency of metamorphism of continental carbonates, k_{mg} is the efficiency of metamorphism of continental organic C and k_v is the efficiency of mantle degassing through all volcanoes (see Methods). Given that the mantle m_m is nearly an infinite reservoir relative to all surface reservoirs, an increase in the continental carbon reservoir $m_c + m_{\text{cg}}$ must lead to an increase in $J_{\text{in}}^{\text{CO}_2}$, consistent with a similar concept first recognized by Holland⁴⁶ (Figs 4b,c).

Second oxygenation linked to non-steady state carbon cycle

On long timescales, the total inputs of carbon into the ocean–atmosphere system is balanced by total carbon burial of which a fraction (f_{org}) is organic carbon and equates with O_2 production (Fig. 3c). A growing carbonate reservoir on the continents and the associated increase in the ocean–atmosphere carbon reservoir will influence the long-term evolution of atmospheric O_2 . Because the response times for CO_2 removal from the ocean–atmosphere are ~ 100 kyr

(kyr, thousand year; ref. 49), the ocean–atmosphere is at quasi-steady state on $>\text{Myr}$ timescales even though the continental and mantle carbon reservoirs are not. The production of O_2 ($J_{\text{in}}^{\text{O}_2}$) is tied to the increase in global carbon inputs to the ocean–atmosphere system (see Methods):

$$J_{\text{in}}^{\text{O}_2} = f_{\text{org}} J_{\text{in}}^{\text{CO}_2} \quad (2)$$

where $J_{\text{in}}^{\text{CO}_2}$ is the sum of the metamorphic and mantle inputs because weathering of carbonates and organic carbon as well as carbonate and organic carbon precipitation are balanced on long timescales^{7,50}. Although equation (2) shows that variations in f_{org} can control O_2 production, the carbon isotopic composition of carbonates on 100–Myr timescales has remained relatively constant since 3 Ga, indicating that f_{org} has remained at ~ 0.2 for most of Earth's history⁵¹. Thus, the absolute input of carbon $J_{\text{in}}^{\text{CO}_2}$ is the primary driver of O_2 production on long timescales whereas variations in f_{org} seem to be of secondary importance.

Atmospheric O_2 also depends on the nature of the O_2 sink. We assume that the rate of oxygen consumption ($J_{\text{out}}^{\text{O}_2}$) is proportional to atmospheric O_2 content (n_a), such that $J_{\text{out}}^{\text{O}_2} = \lambda n_a$, where λ is the global average rate constant of oxidation of ferrous iron and sulfide in the crust. On long timescales ($>\text{Myr}$), when net atmospheric inputs and outputs of O_2 balance ($J_{\text{in}}^{\text{O}_2} = J_{\text{out}}^{\text{O}_2}$), atmospheric O_2 content scales linearly with net CO_2 inputs into the ocean–atmosphere and inversely with the efficiency of crustal oxidation:

$$n_a = f_{\text{org}} J_{\text{in}}^{\text{CO}_2} / \lambda \quad (3)$$

For constant oxidative weathering efficiency, atmospheric O_2 scales linearly with growth of the continental carbonate reservoir. Equation (3) suggests that oxidative weathering rates can grow indefinitely if $J_{\text{in}}^{\text{CO}_2}$ grows, but this is clearly unrealistic at high O_2 levels because chemical weathering is limited by the rate at which fresh, unoxidized substrate is exposed by erosion. To capture a linear relationship of oxidative weathering at low O_2 and the insensitivity to O_2 at high O_2 (dashed lines in Fig. 5a), we use an exponential function (a more complicated model is not justified at this point):

$$J_{\text{out}}^{\text{O}_2} = A(1 - e^{-\phi n_a}) \quad (4)$$

where $J_{\text{out}}^{\text{O}_2}$ is the net output of O_2 from the atmosphere, ϕ is the inverse of the characteristic O_2 level in the atmosphere over which oxidative weathering rate decays by $1/e$, and A is a constant describing the maximum oxidative weathering rate (that is, when n_a becomes very large). Steady state atmospheric O_2 is then given by:

$$n_a = \frac{1}{\phi} \ln \left(\frac{1}{1 - ((f_{\text{org}} J_{\text{in}}^{\text{CO}_2})/A)} \right) \quad (5)$$

When $J_{\text{in}}^{\text{CO}_2}$ is small (crustal carbon reservoir is small), atmospheric O_2 levels must be low. Atmospheric O_2 initially grows slowly with the crustal carbon reservoir (Fig. 5b), but when O_2 production reaches threshold (for example, $f_{\text{org}} J_{\text{in}}^{\text{CO}_2} = A$), atmospheric O_2 grows exponentially (Fig. 5b). Thus, we predict a long period of relatively small increases in O_2 , consistent with Kanzaki and Murakami⁶, followed by a runaway rise of O_2 when CO_2 inputs into the ocean–atmosphere, and hence the mass of continental carbon, reach threshold values (Fig. 4d). We note that Holland⁴⁶ also recognized that a rise in atmospheric O_2 is a necessary outcome of a growing continental carbonate reservoir, but he invoked this mechanism for the GOE. Although we cannot predict exactly when the rise in O_2 occurred nor the exact rate of O_2 increase, due to uncertainties in the kinetics of weathering and

growth rate of continents, what is clear is that carbonate accumulation and storage occurs after continents have grown, hence a source-driven rise in O₂ occurs later in Earth's history than suggested by Holland. The magnitude and nature of our modelled second rise in O₂ thus predicts an event analogous to the NOE (Fig. 1b), ushering the Earth system into the oxygenated state of the Phanerozoic.

Implications of whole-Earth carbon and oxygen cycling

We suggest that the production of continents, and particularly felsic continental crust, naturally leads to a two-step rise in atmospheric oxygen. The first step is due to a decrease in crustal and volcanic reductants when continents became felsic, and the second step is due to progressive accumulation of near-surface carbon reservoirs, which enhance geological CO₂ inputs through metamorphic and magmatic decarbonation of near-surface carbon. These enhanced geologic CO₂ inputs increase total organic carbon burial and thus net oxygen production (Fig. 1c). The long-term secular evolution of atmospheric O₂ is tied to the dynamic evolution of the Earth's mantle, manifested in the growth of continents, which in turn controls the composition of the crust and the long-term evolution of the whole-Earth carbon cycle.

Our model makes important, falsifiable predictions. As stated above, it implicitly predicts that total CO₂ inputs increase gradually over time due to the growing contribution from decarbonation of continental carbonates. From our model, it follows that the total amount of carbon in the ocean–atmosphere should also increase with time, and if partitioning of CO₂ between oceans and atmospheres is similar to today, atmospheric partial pressure of CO₂ (pCO₂) is also predicted to have increased gradually with time (Fig. 4e). Rising pCO₂ runs counter to arguments for higher pCO₂ during the Archaean and Proterozoic compared with the Phanerozoic; higher pCO₂ or other greenhouse gas equivalent in the Archaean compared with the Phanerozoic seems necessary to compensate for the lower luminosity of the Sun early in Earth's history — the 'faint young sun paradox'^{52,53}. Although this apparent inconsistency could invalidate our model from the onset, our simple model does not account for secular changes in ocean pH, silicate weathering kinetics or feedbacks with temperature and the hydrologic cycle. For example, silicate weathering kinetics were probably sluggish in the Archaean due to the lack of significant land biota, thereby permitting higher pCO₂ than our simple models predict, even if carbon fluxing into the exogenic system was low. Indeed, Tajika⁵⁴ has shown that high pCO₂ can be sustained with low CO₂ inputs if solar luminosity is low and the temperature effects of weathering are considered. Alternatively, the possibility that other greenhouse gases played a more important role than CO₂ should be considered. Because there are no direct ways to measure past pCO₂ levels, there is still debate over how high pCO₂ was in the Archaean and Proterozoic^{55,56}.

In summary, we suggest that oxygenated atmospheres are a natural consequence of having a hydrosphere, photosynthetic life and plate tectonics — characteristics that only Earth appears to have in our Solar System. Even in a dynamic planet like Earth, the whole-Earth carbon cycle has never been at steady state. This means that other processes commonly invoked to drive or influence atmospheric composition, such as nutrient availability, mountain building, the evolution of land plants and so forth, all operate on top of the baseline defined by the deep Earth and evolving crustal reservoirs of carbon. The evolution of atmospheric oxygen on billion-year timescales is tied to the availability and fate of carbon in the deep Earth and crust. Thus, the evolution of Earth's climate must also be tied to the non-steady state nature of the Earth's whole carbon cycle. Exactly how they are linked remains an open question, but any future work must build on the framework of whole-Earth cycling.

Methods

Methods and any associated references are available in the online version of the paper.

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Author contributions

C.-T. A. L. conceived the idea, developed the models and wrote the manuscript. L.Y.Y provided conceptual insight into box modelling and atmospheric chemistry. N.R.M provided insight into zircon data and general geology. Y.Y. and K.O. provided insight into global carbon cycle modelling. A.L. provided insight into mantle dynamics. All authors contributed to editing the manuscript and validating the models.

Additional information

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Competing financial interests

The authors declare no competing financial interests.

Methods

Because we are interested in long timescales (>1 Myr), we model the whole-Earth carbon cycle with three reservoirs: the mantle (m_m), the ocean-atmosphere (m_o) and the continents, the latter of which we subdivide into oxidized (m_{cc} , CaCO_3) and reduced carbon (m_{cg} , organic C) reservoirs following Berner⁷. In the ocean-atmosphere system, we assume all C is oxidized (carbonate, bicarbonate, carbonic acid or CO_2), but is deposited in the oceans and continental margins as organic C and carbonate, the rates of carbonate sequestration being dictated by silicate weathering. We assume that the fraction of organic C, f_{org} , is the same globally. Any C being deposited into the oceans is ultimately subducted. Once subducted, all C is treated as carbonate because upper mantle oxygen fugacities dictate that most of the C released from volcanoes is in the form of CO_2 . In detail, the subduction flux of carbon is complicated: some fraction is remobilized back out of volcanic arcs and the rest returned to the deep mantle. We do not worry about these details and ascribe, as a variable, an effective rate constant for removal of ocean/atmosphere C to the deep mantle to capture all of these processes. For volcanism, we lump all juvenile endogenic inputs (mid-ocean ridge, intraplate and the mantle component of arc volcanoes) of C to the exogenic system. Any recycled components in arc volcanoes represent short-circuiting, so there is no need to account for them. We ignore the contribution from large igneous provinces because they are too short-lived for the timescales of interest.

The change in mass of carbon, m , in the different reservoirs is given by:

$$\frac{dm_o}{dt} = k_v m_m + k_{mg} m_{cg} + k_{mc} m_{cc} - k_{out} m_o \quad (6)$$

$$\frac{dm_{cg}}{dt} = k_{bg} m_o - k_{mg} m_{cg} \quad (7)$$

$$\frac{dm_{cc}}{dt} = k_{bc} m_o - k_{mc} m_{cc} \quad (8)$$

$$\frac{dm_m}{dt} = k_{bm} m_o - k_v m_m \quad (9)$$

where k represents the kinetic rate constant (s^{-1}) describing the efficiency or probability of transfer between reservoirs, that is, k_v is the input of mantle CO_2 through ridges and volcanic arcs (excluding degassing of crustal carbonates, which we include in the continental metamorphism); k_{bm} is total carbon (carbonate and organic C) burial in the deep ocean and transfer to the mantle; k_{mg} is organic C burial on continental margins; k_{bc} is carbonate burial on continental margins associated with silicate weathering; k_{mc} represents decarbonation of carbonates from the continents via metamorphism or continental-type magmatism (for example, $\text{CaCO}_3 + \text{SiO}_2 = \text{CaSiO}_3 + \text{CO}_2$); k_{mg} represents production of CO_2 from organic C in continents via metamorphism or continental-type magmatism; and k_{out} is the sum of all carbon outputs from the ocean-atmosphere system, for example, $k_{out} = k_{bm} + k_{bg} + k_{bc}$, due to silicate weathering and organic carbon burial. We assume that carbonate weathering ($\text{CO}_2 + \text{H}_2\text{O} + \text{CaCO}_3 = \text{Ca}^{2+} + 2\text{HCO}_3^-$) followed by precipitation of carbonate does not affect atmospheric CO_2 , that is, carbonate deposition associated with silicate weathering is equal to total carbonate burial minus that of carbonate weathering. We also assume that oxidative weathering of organic C ($\text{CH}_2\text{O} + \text{O}_2 = \text{CO}_2 + \text{H}_2\text{O}$) is balanced by organic C deposition.

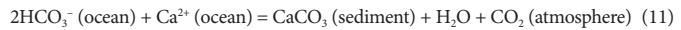
In reality, the kinetic rate constants are not constant. For example, weathering rates should depend on pCO_2 , temperature and so on. In order to illustrate a simple concept, however, we hold k constant and approximate C exchange between reservoirs with effective residence times. The inverse of k has units of time and represents the response time of the system to a particular process. In linear systems, the response time can also be thought of as a residence time. We assume response times for mantle degassing ($1/k_m$) to be ~4 Gyr, burial of total carbon ($1/k_{out}$) to be ~0.1 Myr, and metamorphic decarbonation of crustal carbonates ($1/k_{mc}$) and metamorphism of fossil organic carbon ($1/k_{mg}$) to both be ~100 Myr. The fraction of carbon deposited in ocean basins and eventually subducted is by definition, $X_{ocean} = k_m/k_{out}$. We define the organic C fraction as f_{org} . We assume that over long timescales f_{org} is constant at ~20% and that the metamorphosing proportions of carbonate and organic C on the continents are the same. The rate at which organic C is deposited on continents is thus given by $k_{bg} = f_{org}(1 - aX_{ocean})k_{out}$, and carbonate deposition on continents by $k_{bc} = (1 - aX_{ocean})k_{out}$, where a is a constant describing the ratio of total carbon burial versus area fraction of continents. We assume that continents reached an area equivalent to ~30% of the Earth's surface by the Phanerozoic and that 90% of the carbon is deposited on continents, so that a is taken to be 3.

In general, the carbon sequestration timescale is short compared to the timescales for volcanic degassing and metamorphism, that is, $k_{out} \gg k_v, k_{mc}$ and k_{mg} . Thus, on long timescales, the total carbon content in the ocean-atmosphere is at steady state, $dm_o/dt \sim 0$, so that net input of CO_2 into the ocean-atmosphere ($J_{in}^{\text{CO}_2} = k_v m_m + k_{mg} m_{cg} + k_{mc} m_{cc}$) equals the total carbon burial, $k_{out} m_o$. It follows that:

$$m_o = \frac{k_v m_m + k_{mg} m_{cg} + k_{mc} m_{cc}}{k_{out}} \quad (10)$$

If the residence time of C in the mantle is billions of years, then, as an approximation, the mass of C in the mantle (m_m) is relatively constant and the mass of C in the ocean-atmosphere system (m_o) increases if mantle degassing efficiency (k_v) increases, if the mass of C in the continental reservoir ($m_{cg} + m_{cc}$) increases, or if the efficiency of carbonate and organic C metamorphism increases. Although the ocean-atmosphere is in steady state, the continental and mantle reservoirs are not because of their much longer response times. Because there is net accumulation of carbon on the continents ($m_{cg} + m_{cc}$ increase with time), the carbon in the ocean-atmosphere system (m_o) must also increase from inspection of equation (10). This is where our model differs from that of Berner⁷, who assumed that the total carbon content of the Earth surface system was constant in the Phanerozoic such that mantle inputs are balanced by subduction outputs.

From equation (10), we can estimate the amount of CO_2 in the atmosphere. The atmosphere is assumed to equilibrate instantaneously with the ocean. Following the work by Kump and Arthur⁵⁰, partitioning of C between the ocean and atmosphere is controlled by:



where the equilibrium constant is given by:

$$K = \frac{M_{\text{Ca}} M_{\text{HCO}_3^-}}{\text{pCO}_2} \quad (12)$$

and the top two terms represent the mass of Ca and HCO_3^- in the ocean and pCO_2 is the partial pressure of CO_2 in the atmosphere. As a first approximation, we assume M_{Ca} is constant and that the pH of the oceans remains constant on long timescales, so that nearly all of the carbon in the ocean is HCO_3^- . Then, we can normalize the CO_2 content of the atmosphere (m_a) to the present day as follows⁵⁰:

$$m_a(t) = \left(\frac{m_o(t)}{m_o(0)} \right)^2 m_a(0) \quad (13)$$

where $m_o(t)$ is the carbon content in the ocean at time t in the past, $m_o(0)$ is the present carbon content of the ocean and $m_a(0)$ is the present day carbon content of the atmosphere. Whereas the ocean-atmosphere responds instantaneously on the long timescales we are interested in, the residence times of C in the mantle and in the continental crust are on the order of hundreds of million years to billion years, so the C content in these reservoirs are not at steady state. Consequently, the composition of the ocean-atmosphere directly reflects the distribution of C in the mantle and continents.

The mass of continental crust (M_{cc}) through time is modelled with the following equation:

$$\frac{dM_{cc}}{dt} = P(t) - k_{re} M_{cc} \quad (14)$$

where the first term is juvenile crust production rate and the second term is the loss of continental crust via erosion, subduction of sediments and other processes; k_{re} is the recycling rate constant, which we take to correspond to a ~1 Gyr residence time. We assume that the thickness of continental crust is constant, so the above equation equates with the areal production of continental crust. We assume for simplicity that the fraction of carbon deposited on the continents ($1 - X_{\text{ocean}}$) scales linearly with continental area fraction on Earth. Clearly, the distribution of carbonate deposition is far more complicated but the results are not that sensitive to the exact functional relationship of crustal growth. The crustal growth curve through time is unknown, but there is general consensus that most of the mass of continental crust had formed by mid-Proterozoic times, so we tuned our crustal growth model accordingly. The exact nature of the crustal growth curve is not essential. Had we assumed constant mass of continents with time, we would arrive at the same qualitative result.

To model oxygen in the atmosphere, we again assume that the atmosphere responds instantaneously on the long timescales of interest so that long-term inputs and outputs are roughly balanced. Production of O_2 is from photosynthesis, specifically the net leakage of organic carbon from the ocean-atmosphere system by geologic burial ($\text{CO}_2 + \text{H}_2\text{O} = \text{CH}_2\text{O} + \text{O}_2$). Thus, from equation (6), the net O_2 production rate on long timescales is equal to the CO_2 inputs from metamorphism and mantle degassing multiplied by f_{org} :

$$J_{in}^{\text{O}_2} = f_{org} J_{in}^{\text{CO}_2} = f_{org} k_{out} m_o = f_{org} (k_v m_m + k_{mg} m_{cg} + k_{mc} m_{cc}) \quad (15)$$

We have assumed here that weathering of organic C from the continents is balanced by organic C deposition and thus plays no role in atmospheric O_2 . Only the O_2 produced by reduction of atmospheric CO_2 derived from metamorphism of carbonates, metamorphism of organic carbon, and mantle degassing is relevant. It can be seen in equation (15) that the flux of O_2 depends on mass of carbon (m) in the different long-term reservoirs. Consumption of O_2 is from oxidation of ferrous iron and sulfide in the continental crust or sulfide species in volcanic gases, and depends on the amount of O_2 in the atmosphere (n_a) as well as the amount

of oxidizable components in the crust forming magmas and continental crust. In the text, we entertained briefly a linear relationship between oxidation rate and atmospheric O₂. However, at high O₂ contents, oxidative weathering is likely to be transport-limited rather than limited by availability of O₂. The following functional form captures this behaviour:

$$J_{\text{out}}^{\text{O}_2} = A(1 - e^{-\phi n_a}) \quad (16)$$

where $J_{\text{out}}^{\text{O}_2}$ is the net removal of O₂ via oxidative weathering of the crust (Fe²⁺ and S²⁻), ϕ is the inverse of the characteristic O₂ content in the atmosphere (n_a) over which oxidative weathering rate decays and A is a constant describing the maximum oxidative weathering rate of the continental crust, for example, when n_a is large. Setting equations (15) and (16) equal yields an equation for atmospheric O₂ as a function of the ratio between oxygen production and oxidative weathering kinetics, see equation 5. When $f_{\text{org}}^{\text{CO}_2}$ approaches A , n_a grows super-exponentially, resulting in runaway.

To couple the oxygen and carbon models, we normalized all C and O₂ values to the initial mass of carbon in the mantle so that all reservoir masses are

reported relative to initial C mass of the mantle. We assume that the whole mantle participates in convection and that the initial concentration of C in the mantle is 50 ppm by weight⁴¹, giving $\sim 17 \times 10^{21}$ moles of C in the mantle. Present day O₂ mass (4.1×10^{19} moles of O₂, assuming 21% O₂ in the atmosphere by volume) in the atmosphere is scaled according to the mass of C in the mantle, that is, the present day molar ratio of atmospheric O₂ to total C in the mantle is ~ 0.0024 . To implement the model, we forced the model to match present day O₂ levels (PAL) after 4.5 Gyr of Earth history. We then adopted a value of ϕ equivalent to 0.001 PAL, which is a measure of the O₂ level over which oxidative weathering efficiency decays by e-fold (equation (5)). This value was chosen to reflect O₂ levels in the Proterozoic. We chose different values for maximum oxidative weathering rate A . From 2.5 Ga to the present, we used a value close to oxygen production rates of the Phanerozoic. Prior to 2.5 Ga, we assume A is greater by a factor of 100 to simulate the effects of a fundamental decrease in Fe and S content of the crust. Given all the uncertainties, it is important to recognize that our goal is not to model exactly the behaviour of O₂ through time, especially since the accuracy of atmospheric O₂ evolution curves is poorly constrained. Our goal is only to evaluate whether a two-step rise in O₂ is a natural consequence of plate tectonics and the formation of continents.