Constraining the climate and ocean pH of the early Earth with a geological carbon cycle model

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The early Earth’s environment is controversial. Climatic estimates range from hot to glacial, and inferred marine pH spans strongly alkaline to acidic. Better understanding of early climate and ocean chemistry would improve our knowledge of the origin of life and its coevolution with the environment. Here, we use a geological carbon cycle model with ocean chemistry to calculate self-consistent histories of climate and ocean pH. Our carbon cycle model includes an empirically justified temperature and pH dependence of seafloor weathering, allowing the relative importance of continental and seafloor weathering to be evaluated. We find that the Archean climate was likely temperate (0–50 °C) due to the combined negative feedbacks of continental and seafloor weathering. Ocean pH evolves monotonically from 6.6 to 7.0 at 4.0 Ga to 7.0 to 7.9 at the Archean–Proterozoic boundary, and to 7.9 to 8.1 at the Proterozoic–Phanerozoic boundary. This evolution is driven by the secular decline of pCO₂, which in turn is a consequence of increasing solar luminosity, but is moderated by carbonate alkalinity delivered from continental and seafloor weathering. Archean seafloor weathering may have been a comparable carbon sink to continental weathering, but is less dominant than previously assumed, and would not have induced global glaciation. We show how these conclusions are robust to a wide range of scenarios for continental growth, internal heat flow evolution and outgassing history, greenhouse gas abundances, and changes in the biotic enhancement of weathering.

Ocean pH is another important environmental parameter because it partitions carbon between the atmosphere and ocean and is thus linked to climate. Additionally, many biosynthetic pathways hypothesized to be important for the origin of life are strongly pH dependent (14–16), and so constraining the pH of the early ocean would inform their viability. Furthermore, bacterial biomineralization is favorable at higher environmental pH values because this allows cells to more easily attract cations through deprotonation (17). Arguably, low environmental pH values would be an obstacle to the evolution of advanced life due to biomineralization inhibition (18). Finally, many pO₂ proxies are pH dependent (19–21), and so understanding the history of pH would enable better quantification of the history of pO₂.

As with climate, debate surrounds empirical constraints on Archean ocean pH. Empirical constraints are scant and conflicting. Based on the scarcity of gypsum pseudomorphs before 1.8 Ga, Grotzinger and Kasting (22) argued that the Archean ocean pH was likely between 5.7 and 8.6. However, others note the presence of Archean gypsum as early as 3.5 Ga (23); its scarcity could be explained by low sulfate (24). Blättler et al. (24) interpreted Archean Ca isotopes to reflect high Ca/alkalinity ratios, which in turn would rule out high pH and high pCO₂ values. Friend et al. (25) argued for qualitatively neutral to weakly alkaline Archean ocean pH based on rare Earth element anomalies.

Constraining the climate and ocean chemistry of the early Earth is crucial for understanding the emergence of life, the subsequent coevolution of life and the environment, and as a point of reference for evaluating the habitability of terrestrial exoplanets. However, the surface temperature of the early Earth is debated. Oxygen isotopes in chert have low δ¹⁸O values in the Archean (1). If this isotope record reflects the temperature-dependent equilibrium fractionation of δ¹⁸O and δ¹⁷O between silicate and seawater, then this would imply mean surface temperatures around 70 ± 15 °C at 3.3 Ga (2). A hot early Earth is also supported by possible evidence for a low viscosity Archean ocean (3), and the thermostability of reconstructed ancestral proteins (4), including those purportedly reflective of Archean photic zone temperatures (5). Silicon isotopes in cherts have also been interpreted to infer 60–80 °C Archean seawater temperatures (6).

Alternatively, the trend in δ¹⁸O over Earth history has been interpreted as a change in the oxygen isotope composition of seawater (7), or hydrothermal alteration of the seafloor (8). Isotopic analyses using deuterium (9) and phosphates (10) report Archean surface temperatures <40 °C. Archean glacial deposits (ref. 11 and references therein) also suggest an early Earth with ice caps, or at least transient cool periods. A geological carbon cycle model of Sleep and Zahnle (12) predicts Archean and Hadean temperatures below 0 °C due to efficient seafloor weathering. Analyses combining general circulation model (GCM) outputs with a carbon cycle model predicts more moderate temperatures at 3.8 Ga (13). Resolving these conflicting interpretations would provide a better understanding of the conditions for the origin and early evolution of life.

Significance

The climate and ocean pH of the early Earth are important for understanding the origin and early evolution of life. However, estimates of early climate range from below freezing to over 70 °C, and ocean pH estimates span from strongly acidic to alkaline. To better constrain environmental conditions, we applied a self-consistent geological carbon cycle model to the last 4 billion years. The model predicts a temperate (0–50 °C) climate and circumneutral ocean pH throughout the Precambrian due to stabilizing feedbacks from continental and seafloor weathering. These environmental conditions under which life emerged and diversified were akin to the modern Earth. Similar stabilizing feedbacks on climate and ocean pH may operate on earthlike exoplanets, implying life elsewhere could emerge in comparable environments.

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Data deposition: The Python source code is available on Github (https://github.com/joshuakt/early-earth-carbon-cycle).

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Theoretical arguments for the evolution of ocean pH also disagree. By analogy with modern alkaline lakes, Kempe and Degens (26) argue for a pH 9–11 “soda ocean” on the early Earth, but mass balance challenges such an idea (27). Additionally, high pH oceans (>9.0) would shift the NH₃⇌NH₄⁺ aqueous equilibrium toward NH₄⁺, which would volatilize and fractionate nitrogen isotopes in a way that is not observed in marine sediments (28). The conventional view of the evolution of ocean pH is that the secular decline of pCO₂ over Earth history has driven an increase in ocean pH from acidic to modern slightly alkaline. For example, Haley and Bachan (29) modeled ocean chemistry over Earth history with prescribed pCO₂ and climate histories, and reported a monotonic pH evolution broadly consistent with this view. However, it has also been argued that seafloor weathering buffered ocean pH to near-modern values throughout Earth history (12).

On long timescales, both climate and ocean pH are controlled by the geological carbon cycle. The conventional view of the carbon cycle is that carbon outgassing into the atmosphere–ocean system is balanced by continental silicate weathering and subsequent marine carbonate formation (30, 31). The weathering of silicates is temperature and pCO₂ dependent, which provides a natural thermostat to buffer climate against changes in stellar luminosity and outgassing. This mechanism is widely believed to explain the relative stability of Earth’s climate despite a ∼30% increase in solar luminosity since 4.0 Ga (31).

A possible complimentary negative feedback to seafloor weathering is provided by seafloor weathering. Such weathering occurs when the seawater circulating in off-axis hydrothermal systems reacts with the surrounding basalt and releases cations, which then precipitate as carbonates in the pore space (32, 33). If the rate of basalt dissolution and pore-space carbonate precipitation depends on the carbon content of the atmosphere–ocean system via pCO₂, temperature, or pH, then seafloor weathering could provide an additional negative feedback (12).

The existence of a negative feedback to balance the carbon cycle on timescales of several hundred million years is unclear. With it, atmospheric CO₂ would be depleted, leading to a runaway icehouse, or would accumulate to excessive levels (34). However, the relative importance of continental and seafloor weathering in providing this negative feedback, and the overall effectiveness of these climate-stabilizing and pH-buffering feedbacks on the early Earth are unknown.

In this study, we apply a geological carbon cycle model with ocean chemistry to the entirety of Earth history. The inclusion of ocean carbon chemistry enables us to model the evolution of ocean pH and realistically capture the pH-dependent and temperature-dependent kinetics of seafloor weathering. This is a significant improvement on previous geological carbon cycle models (e.g., refs. 12 and 35) that omit ocean chemistry and instead adopt an arbitrary power-law dependence on pCO₂ for seafloor weathering, which, as we show, overestimates CO₂ drawdown on the early Earth. By coupling seafloor weathering to Earth’s climate and the geological carbon cycle, we calculate self-consistent histories of Earth’s climate and pH evolution, and evaluate the relative importance of continental and seafloor weathering through time. The pH evolution we calculate is therefore more robust than that of Haley and Bachan (29) because, unlike their model, we do not prescribe pCO₂ and temperature histories.

Our approach remains agnostic on unresolved issues, such as the history of continental growth, internal heat flow, and the biological enhancement of weathering, because we include a broad range of values for these parameters. Our conclusions are therefore robust to uncertainties in Earth system evolution. We find that a hot early Earth is very unlikely, and pH should, on average, have monotonically increased since 4.0 Ga, buffered somewhat by continental and seafloor weathering.

Methods

The geological carbon cycle model builds on that described in Krissansen-Totton and Catling (36). Here, we summarize its key features, and additional details are provided in the SI Appendix. The Python source code is available on GitHub at github.com/joshuakt/early-earth-carbon-cycle.

We model the time evolution of the carbon cycle using two separate boxes representing the atmosphere–ocean system and the pore space in the seafloor (Fig. 1 and SI Appendix A). We track carbon and carbonate alkalinity fluxes into and between these boxes, and assume that the bulk ocean is in equilibrium with the atmosphere.

Many of the parameters in our model are uncertain, and so we adopt a range of values (SI Appendix, Table S1) based on spread in the literature rather than point estimates. Each parameter range was sampled uniformly, and the forward model was run 10,000 times to build distributions for model outputs such as pCO₂, pH, and temperature. Model outputs are compared with proxy data for pCO₂, temperature, and carbonate precipitation (SI Appendix D).

Continental silicate weathering is described by the following function:

$$f_{\text{land}} = f_{\text{land}}f_{\text{mod}}f_{\text{exp}}\left(\frac{\text{pCO}_2}{\text{pCO}_2^{\text{mod}}}\right)^{\alpha}\exp(\Delta\text{T}_{\text{e}}/T_{\text{e}})$$

Here, $f_{\text{land}}$ is the biological enhancement of weathering (see below), $f_{\text{mod}}$ is the modern continental land fraction relative to modern, $f_{\text{exp}}$ is the modern continental silicate weathering flux (Tmol y⁻¹), $\Delta\text{T}_{\text{e}} = T_{\text{e}} - T_{\text{e}}^{\text{mod}}$ is the difference in global mean surface temperature, $T_{\text{e}}$, relative to preindustrial modern, $T_{\text{e}}^{\text{mod}}$. The exponent $\alpha$ is an empirical constant that determines the dependence of weathering on the partial pressure of carbon dioxide relative to modern, $\text{pCO}_2/\text{pCO}_2^{\text{mod}}$. An $\alpha$-folding temperature, $T_{\alpha}$ defines the temperature dependence of weathering. A similar expression for carbonate weathering is described in SI Appendix A.

The land fraction, $f_{\text{land}}$, and biological modifier, $f_{\text{mod}}$, account for the growth of continents and the biological enhancement of continental weathering, respectively. We adopt a broad range of continental growth curves that encompasses literature estimates (Fig. 2A and SI Appendix A). For our nominal model, we assume Archean land fraction was anywhere between 10% and 75% of modern land fraction (Fig. 2A), but we also consider a no-land Archean endmember (Fig. 2B).

To account for the possible biological enhancement of weathering in the Phanerozoic due to vascular land plants, lichens, bryophytes, and ectomycorrhizal fungi, we adopt a broad range of histories for the biological enhancement of weathering, $f_{\text{mod}}$ (Fig. 2C). The lower end of this range is consistent with estimates of biotic enhancement of weathering from the literature (37–39).

The dissolution of basalt in the seafloor is dependent on the spreading rate, pore-space pH, and pore-space temperature (SI Appendix A). This formulation is based on the validated parameterization in ref. 36. Pore-space temperatures are a function of climate and geothermal heat flow. Empirical

![Fig. 1. Schematic of carbon cycle model used in this study. Carbon fluxes (Tmol C yr⁻¹) are denoted by solid green arrows, and alkalinity fluxes (Tmol eq y⁻¹) are denoted by red dashed arrows. The fluxes into/out of the atmosphere–ocean system are outgassing, $F_\text{out}$, silicate weathering, $F_\text{sil}$, carbonate weathering, $F_\text{carb}$, and marine carbonate precipitation, $P_\text{carb}$. The fluxes into/out of the pore space are basalt dissolution, $F_\text{dis}$, and pore-space carbonate precipitation, $P_\text{pore}$. Alkalinity fluxes are multiplied by 2 because the uptake or release of one mole of carbon as carbonate is balanced by a cation with a 2⁺ charge (typically Ca²⁺). A constant mixing flux, $J_\text{in}$ (kg y⁻¹), exchanges carbon and alkalinity between the atmosphere–ocean system and pore space.](image-url)
Fig. S1 depicts the evolution of the solar luminosity, which is a critical parameter for our model. In this context, solar luminosity is parameterized in a way that allows us to investigate the effects of different scenarios on the Earth's climate.

The results show that the Earth's climate is highly sensitive to variations in solar luminosity. For instance, a slight increase in solar luminosity can lead to significant changes in the Earth's climate, such as changes in temperature and sea level.

Fig. S2 illustrates the role of continental weathering in the Earth's climate. Continental weathering is a major process that influences the Earth's climate by releasing greenhouse gases into the atmosphere.

In our model, we consider the effect of continental weathering on the Earth's climate. The results show that continental weathering plays a crucial role in regulating the Earth's climate. For example, a decrease in continental weathering can lead to a significant increase in the Earth's temperature.

Fig. S3 demonstrates the impact of oceanic processes on the Earth's climate. Oceanic processes, such as oceanic circulation and the exchange of gases between the atmosphere and the ocean, are critical for the Earth's climate.

Our model shows that oceanic processes have a significant impact on the Earth's climate. For instance, changes in oceanic circulation can lead to significant changes in the Earth's temperature and sea level.

In conclusion, our model provides valuable insights into the complex interactions between the Earth's climate and its various components. By considering the effects of different processes, we can better understand the Earth's climate and how it may change in the future.
Fig. 3. Nominal model outputs. Gray shaded regions represent 95% confidence intervals, and black lines are the median outputs. (A) Ocean pH with the 95% confidence interval from Halevy and Bachan (29) plotted with red dashed lines for comparison. Our model predicts a monotonic evolution of pH from slightly acidic values at 4.0 Ga to slightly alkaline modern values. (B) Atmospheric pCO₂ distribution at 4.0 Ga is shifted downward relative to modern values. (C) Global outgassing flux. (D) Mean surface temperature plotted alongside glacial and geochemical proxies from the literature. Our model predicts surface temperatures have been temperate throughout Earth history. (E) Continental silicate weathering flux. (F) Seafloor weathering flux plotted alongside flux estimates from Archean altered seafloor basalt. dep, deposit.

Fig. 5 shows model outputs where we have assumed 100 ppm Proterozoic methane and 1% Archean methane levels (SI Appendix E). The temperature changes are smaller than what might be expected if only methane levels were changing. This is because pCO₂ drops in response to the imposed temperature increase—pCO₂ must drop otherwise weathering sinks would exceed source fluxes. The pCO₂ distribution at 4.0 Ga is shifted downward relative to the nominal case with no other greenhouse cases, and ocean pH increases in response to this pCO₂ drop. Note that for parts of parameter space where CO₂/CH₄ ≥ 0.2 (50), our temperatures should be considered upper limits because a photochemical haze would form, cooling the climate (SI Appendix E).

Thus, even with considerable warming from an additional greenhouse gas, the median temperature at 4.0 Ga is below 300 K, and the temperature distribution extends to 320 K, again excluding a hot Archean. SI Appendix, Fig. S7 shows the results for the most extreme case of no Archean land and high methane abundances. Even in this extreme scenario, the seafloor weathering flux successfully buffers the climate to a median 4.0 Ga value of ~310 K. Archean pH values are closer to circumneutral than the modern flux (SI Appendix, Fig. S12). The only way to produce Archean climates below 0 °C in our model is to assume the Archean outgassing flux was 1–5× lower than the modern flux (SI Appendix, Fig. S12). However, dramatically lowered Archean outgassing fluxes contradict known outgassing proxies and probably require both a stagnant lid tectonic regime and a mantle more reduced than zircon data suggest, which lowers the portion of outgassed CO₂ (SI Appendix C). Moreover, even when outgassing is low, frozen climates are not guaranteed (SI Appendix, Fig. S12).

Our model gives a monotonic evolution of ocean pH from 6.3–7.7 in the Archean (95% confidence), to 6.5–8.1 (95% confidence) in the Proterozoic, and increasing to 8.2 in the modern surface ocean. This history is broadly consistent with that of Halevy and Bachan (29) (Figs. 3 and 4). Halevy and Bachan (29) tracked Na, Cl, Mg, and K exchanges with continental and oceanic crust, and related these fluxes to the thermal evolution of the Earth. Minor constituents such as HS, NH₄, Fe²⁺, and SO₄²⁻ were also considered. However, they prescribe many features of the carbon cycle rather than apply a self-consistent model as we have done here. Specifically, they imposed pCO₂ to ensure near-modern temperatures throughout Earth history. Consequently, the explicit temperature dependence of both seafloor and continental weathering were omitted. Additionally, subduction and outgassing were assumed to be directly proportional, a limited range of heat flow histories were adopted, and continental silicate weathering was described using an overall pCO₂ power-law dependence with no allowance for changing land fraction or biogenic enhancement weathering. Thus, the uncertainty envelopes for the early Earth ocean pH are underestimated in ref. 29 as can be seen by their uncertainty diminishing further back in time. Good agreement with the results of ref. 29 confirms that the details of ocean chemistry...
are of secondary importance to pH evolution, and that the monotonic evolution of pH is instead driven by solar luminosity evolution, buffered by enhanced continental and seafloor weathering under high pCO$_2$ conditions. The two models also agree because the carbon cycle buffers to near-modern temperatures, allowing the constant temperature assumption of ref. 29, but there is no way of knowing the effectiveness of the buffer without a self-consistent model of the carbon cycle.

One caveat for our results is that the ocean chemistry is incomplete. Specifically, Ca abundances in the ocean and pore space are controlled entirely by alkalinity fluxes from continental and seafloor weathering. In reality, Ca abundances are modulated by other processes such as the hydrothermal exchange of Ca and Mg in the seafloor, dolomitization, and clay formation (51). To explore whether neglecting these processes would affect our results we conducted sensitivity tests with a large ensemble of Ca evolutions (SI Appendix C). High Archean Ca abundances might be expected to produce more acidic oceans because carbonate abundances are lower for the same saturation state. However, this effect is buffered by decreases in Ca and CO$_2$ activity coefficients (complexing), and so model outputs look very similar to our nominal model for a broad range of Ca abundance trajectories (SI Appendix, Fig. S9).

In our nominal climate model, we did not include the effects of changing atmospheric pressure or albico changes. These effects are likely to be modest compared with the other sources of uncertainty in our model. Lower surface albico from a reduced Archean land fraction can contribute at most 5 W/m$^2$ of radiative forcing (52), which would cause only a few degrees of warming. Halving Archean total pressure—as has been suggested by paleoepressure proxies (53)—would cool the Earth by $\sim$5 K because of the loss of pressure broadening, thereby offsetting the lower land fraction (54). Changes in cloud cover could, in principle, induce larger warming, but the required conditions for $>$10 K warming are highly speculative (52). In any case, the effects of pressure changes and albico changes are unlikely to affect our conclusions because the temperature changes they induce will be compensated by pCO$_2$ variations to balance the carbon cycle. Sensitivity analyses where massive amounts of Archean warming are imposed (+30 K) still result in temperature surface temperatures because of this pCO$_2$ compensation (SI Appendix, Fig. S10). Although our model outputs are broadly consistent with paleo proxies and glacial constraints, some disagreement occurs with selected seafloor weathering proxies. Proxies for seafloor carbonate precipitation were estimated by using the average carbonate abundances in Archean oceanic crust, scaled by the model spreading rate at that time multiplied by an assumed carbonatization depth (SI Appendix D). Our modeled seafloor carbonate precipitation fluxes agree with that of Nakamura and Kato (55) and Shibuya et al. (56), but undershoot crustal carbonate abundances reported by Shibuya et al. (57) and Kitajima et al. (58). It is difficult to construct a balanced carbon cycle model with seafloor weathering fluxes in excess of 100 Tmol C/y as these latter two studies imply, and so the discrepancy may be because oceanic crust samples are not representative of global carbonatization flux, or because some of the carbonate is secondary. The only way to approach the carbonate abundances reported by Shibuya et al. (57) and Kitajima et al. (58) is to impose very high Archean outgassing (e.g., up to 60x the modern flux; SI Appendix, Fig. S11), but even then the fit is marginal. If high Archean crustal carbonate estimates were truly primary, then Archean outgassing would have been very high, and so Earth's internal heat flow would have decreased dramatically over Earth's history, contrary to Korenaga (59).

We conclude that current best knowledge of Earth's geologic carbon cycle precludes a hot Archean. Our results are insensitive to assumptions about ocean chemistry, internal evolution, and weathering parameterizations, so a hot early Earth would require some fundamental error in current understanding of the carbon cycle. Increasing the biotic enhancement of weathering by several orders of magnitude as proposed by Schwartzman (60) does not produce a hot Archean because this is mathematically equivalent to zeroing out the continental weathering flux (Fig. 4). In this case the temperature-dependent seafloor weathering feedback buffers the climate of the Earth to moderate temperatures (SI Appendix, Fig. S14). Dramatic temperature increases (or decreases) due to albedo changes also do not change our conclusions due to the buffering effect of the carbon cycle (see above). If both continental and seafloor weathering become supply limited (e.g., refs. 49 and 61), then temperatures could easily exceed 50 °C. However, in this case the carbon cycle would be out of balance, leading to excessive pCO$_2$ accumulation within a few hundred million years unless buffered by some other, unknown feedback.

Conclusions

The early Earth was probably temperate. Continental and seafloor weathering buffer Archean surface temperatures to 0–50 °C. This result holds for a broad range of assumptions about the evolution of internal heat flow, crustal production, spreading rates, and the biotic enhancement of continental weathering.
Even in extreme scenarios with negligible subaerial Archean land and high methane abundances, a hot Archean (>50 °C) is unlikely. Sub-0 °C climates are also unlikely unless the Archean outgassing flux was unrealistically lower than the modern flux. The seafloor weathering feedback is important, but less dominant than previously assumed. Consequently, the early Earth would not have been in a snowball state due to pCO2 drawdown from seafloor weathering. In principle, little to no methane is required to maintain a habitable surface climate, although methane should be expected in the anoxic Archean atmosphere once methanogenesis evolved (ref. 62, chap. 11).

Ignoring transient excursions, the pH of Earth's ocean has evolved monotonically from 6.6±0.4 at 4.0 Ga (2σ) to 7.0±0.5 at 2.5 Ga (2σ), and 8.2 in the modern ocean. This evolution is robust to assumptions about ocean chemistry, internal heat flow, and other carbon cycle parameterizations. Consequently, similar feedbacks may control ocean pH and climate on other Earthlike planets with basaltic seafloors and silicate continents, suggesting that life elsewhere could emerge in comparable environments to those on our early planet.

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