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

Joshua Krissansen-Totton[a,b,1], Giada N. Arney[b,c,d], and David C. Catling[a,b]

[a]Department of Earth and Space Sciences, University of Washington, Seattle, WA 98195; [b]Virtual Planetary Laboratory Team, NASA Astrobiology Institute, Seattle, WA 98195; [c]Planetary Systems Laboratory, NASA Goddard Space Flight Center, Greenbelt, MD 20771; and [d]Sellers Exoplanet Environments Collaboration, NASA Goddard Space Flight Center, Greenbelt, MD 20771

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 $6.6^{+0.6}_{-0.4}$ (2σ) at 4.0 Ga to $7.0^{+0.7}_{-0.5}$ (2σ) at the Archean–Proterozoic boundary, and to $7.9^{+0.1}_{-0.2}$ (2σ) at the Proterozoic–Phanerozoic boundary. This evolution is driven by the secular decline of pCO_2, 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.

carbon cycle | paleoclimate | Precambrian | ocean pH | weathering

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 $\delta^{18}O$ values in the Archean (1). If this isotope record reflects the temperature-dependent equilibrium fractionation of ^{18}O and ^{16}O between silica 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 $\delta^{18}O$ 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. An analysis 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.

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 pO_2 proxies are pH dependent (19–21), and so understanding the history of pH would enable better quantification of the history of pO_2.

However, just 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 pCO_2 values. Friend et al. (25) argued for qualitatively circumneutral to weakly alkaline Archean ocean pH based on rare Earth element anomalies.

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.

EARTH, ATMOSPHERIC, AND PLANETARY SCIENCES

Theoretical arguments for the evolution of ocean pH also disagree. By analogy with modern alkaline lakes, Kempe and Degens (26) argued 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 NH_3–NH_4^+ aqueous equilibrium toward NH_3, 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 pCO_2 over Earth history has driven an increase in ocean pH from acidic to modern slightly alkaline. For example, Halevy and Bachan (29) modeled ocean chemistry over Earth history with prescribed pCO_2 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 pCO_2 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 continental 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 pCO_2, 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 million-year timescales is undisputed. Without it, atmospheric CO_2 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 pCO_2 for seafloor weathering which, as we show, overestimates CO_2 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 Halevy and Bachan (29) because, unlike their model, we do not prescribe pCO_2 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 pCO_2, pH, and temperature. Model outputs are compared with proxy data for pCO_2, temperature, and carbonate precipitation (*SI Appendix D*).

Continental silicate weathering is described by the following function:

$$F_{sil} = f_{bio} f_{land} F_{sil}^{mod} \left(\frac{pCO_2}{pCO_2^{mod}} \right)^{\alpha} \exp(\Delta T_S / T_e) \tag{1}$$

Here, f_{bio} is the biological enhancement of weathering (see below), f_{land} is the continental land fraction relative to modern, F_{sil}^{mod} is the modern continental silicate weathering flux (Tmol y^{-1}), $\Delta T_S = T_S - T_S^{mod}$ is the difference in global mean surface temperature, T_S, relative to preindustrial modern, T_S^{mod}. The exponent α is an empirical constant that determines the dependence of weathering on the partial pressure of carbon dioxide relative to modern, pCO_2/pCO_2^{mod}. An e-folding temperature, T_e, defines the temperature dependence of weathering. A similar expression for carbonate weathering is described in *SI Appendix A*.

The land fraction, f_{land}, and biological modifier, f_{bio}, 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_{bio} (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
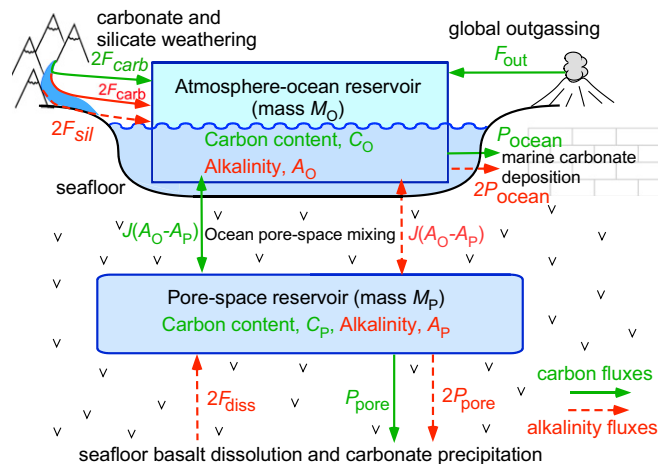

Fig. 1. Schematic of carbon cycle model used in this study. Carbon fluxes (Tmol C y^{-1}) are denoted by solid green arrows, and alkalinity fluxes (Tmol eq y^{-1}) are denoted by red dashed arrows. The fluxes into/out of the atmosphere–ocean system are outgassing, F_{out}, silicate weathering, F_{sil}, carbonate weathering, F_{carb}, and marine carbonate precipitation, P_{ocean}. The fluxes into/out of the pore space are basalt dissolution, F_{diss}, and pore-space carbonate precipitation, P_{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 Ca^{2+}). A constant mixing flux, J (kg y^{-1}), exchanges carbon and alkalinity between the atmosphere–ocean system and pore space.
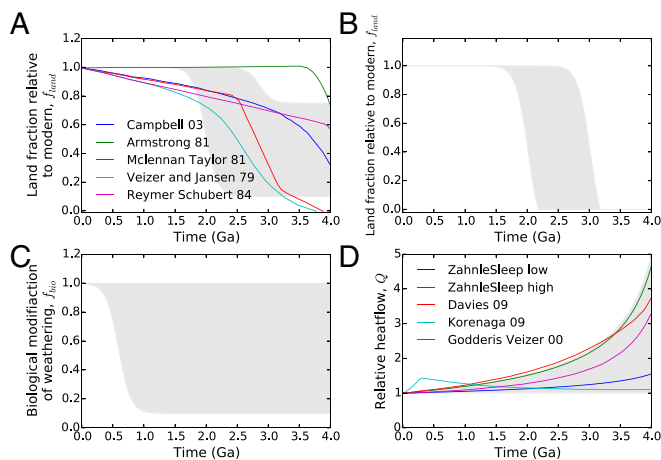
Fig. 2. Gray shaded regions are ranges assumed for selected model input parameters. (*A*) Range of continental growth curves assumed in our nominal model, f_{land}. Various literature estimates are plotted alongside the model growth curve (*SI Appendix A*). (*B*) Range of continental growth curves for an endmember of no Archean land; (*C*) range for biological enhancement of weathering histories, f_{bio}; and (*D*) range of internal heat flow histories, Q, compared with literature estimates (*SI Appendix A*).

data and fully coupled global climate models reveal a linear relationship between deep ocean temperature and surface climate (36). Equations relating pore-space temperature, deep ocean temperature, and sediment thickness are provided in *SI Appendix A*.

Carbon leaves the atmosphere–ocean system through carbonate precipitation in the ocean and pore space of the oceanic crust. At each time step, the carbon abundances and alkalinities are used to calculate the carbon speciation, atmospheric pCO_2, and saturation state assuming chemical equilibrium. Saturation states are then used to calculate carbonate precipitation fluxes (*SI Appendix A*). We allow calcium (Ca) abundance to evolve with alkalinity, effectively assuming no processes are affecting Ca abundances other than carbonate and silicate weathering, seafloor dissolution, and carbonate precipitation. The consequences of this simplification are explored in the sensitivity analysis in *SI Appendix C*. We do not track organic carbon burial because organic burial only constitutes 10–30% of total carbon burial for the vast majority of Earth history (40), and so the inorganic carbon cycle is the primary control.

The treatment of tectonic and interior processes is important for specifying outgassing and subduction flux histories. We avoid tracking crustal and mantle reservoirs because explicitly parameterizing how outgassing fluxes relate to crustal production and reservoirs assumes modern-style plate tectonics has operated throughout Earth history (e.g., ref. 12) and might not be valid. Evidence exists for Archean subduction in eclogitic diamonds (41) and sulfur mass-independent fractionation in ocean island basalts ostensibly derived from recycled Archean crust (42). However, other tectonic modes have been proposed for the early Earth such as heat-pipe volcanism (43), delamination and shallow convection (44), or a stagnant lid regime (45).

Our generalized parameterizations for heat flow, spreading rates, and outgassing histories are described in *SI Appendix A*. Fig. 2*D* shows our assumed range of internal heat flow histories compared with estimates from the literature. Spreading rate is connected to crustal production via a power law, which spans endmember cases (*SI Appendix A*). These parameterizations provide an extremely broad range of heat flow, outgassing, and crustal production histories, and do not assume a fixed coupling between these variables.

We used a 1D radiative convective model (46) to create a grid of mean surface temperatures as a function of solar luminosity and pCO_2. The grid of temperature outputs was fitted with a 2D polynomial (*SI Appendix E*). We initially neglect other greenhouse gases besides CO_2 and H_2O, albedo changes, and assumed a constant total pressure over Earth history. However, later we consider these influences, such as including methane (CH_4) in the Precambrian. The evolution of solar luminosity is conventionally parameterized (47).

Our model has been demonstrated for the last 100 Ma against abundant proxy data (36) and it can broadly reproduce Sleep and Zahnle (12) if we replace our kinetic formulation of seafloor weathering with their simpler CO_2-dependent expression (*SI Appendix B*). Agreement with ref. 12 confirms that the omission of crustal and mantle reservoirs does not affect our conclusions.

Results

Fig. 3 shows the evolution of the geological carbon cycle over Earth history according to our nominal model. Here, we have used our kinetic parameterization of seafloor weathering rather than the arbitrary pCO_2 power law adopted in previous studies (*SI Appendixes A* and *B*). We have also assumed a range of continental growth curves (Fig. 2*A*), a range of Phanerozoic biological weathering enhancements (Fig. 2*C*), and a range of temperature dependencies of weathering from ref. 36. Proxies for surface temperature, atmospheric pCO_2, and seafloor weathering flux are plotted alongside model outputs for comparison (*SI Appendix D*). For all results, both 95% confidence intervals and median values are plotted for key carbon cycle outputs. Median values are calculated at each time step, and consequently their evolution does not necessarily resemble the most probable time evolution of carbon cycle variables. In practice, however, most individual model realizations tend to track the median, at least qualitatively (*SI Appendix A*).

We observe that modeled temperatures are relatively constant throughout Earth history, with Archean temperatures ranging from 271 to 314 K. The combination of continental and seafloor weathering efficiently buffers climate against changes in luminosity, outgassing, and biological evolution. This temperature history is broadly consistent with glacial constraints and recent isotope proxies (Fig. 3*D*). The continental weathering buffer dominates over the seafloor weathering buffer for most of Earth history, but in the Archean the two carbon sinks are comparable (*SI Appendix, Fig. S1*). Indeed, if seafloor weathering were artificially held constant, then continental weathering alone may be unable to efficiently buffer the climate of the early Earth—the temperature distribution at 4.0 Ga extends to 370 K, and the atmospheric pCO_2 distribution extends to 7 bar (*SI Appendix, Fig. S3*).

In our nominal model, the median Archean surface temperature is slightly higher than modern surface temperatures. If solar evolution were the only driver of the carbon cycle, then Archean temperatures would necessarily be cooler than modern temperatures; weathering feedbacks can mitigate this cooling but not produce warming. Warmer Archean climates are possible because elevated internal heat flow, lower continental land fraction, and lessened biological enhancement of weathering all act to warm to Precambrian climate. These three factors produce a comparable warming effect (*SI Appendix, Fig. S17A* and *Appendix C*), although the magnitude of each is highly uncertain and so temperate Archean temperatures cannot be uniquely attributed to any one variable.

Continental and seafloor weathering also buffer ocean pH against changes in luminosity and outgassing. Ocean pH increases monotonically over Earth history from 6.3–7.2 at 4.0 Ga, to 6.5–7.7 at 2.5 Ga, and to the modern value of 8.2. The broad range of parameterizations does not tightly constrain the history of atmospheric pCO_2, but the model pCO_2 outputs encompass paleosol proxies (Fig. 3*B*).

The results described above assume an Archean landmass fraction between 0.1 and 0.75 times the modern land fraction. Next, we consider the endmember scenario of zero Archean landmass. This is unrealistic because abundant evidence exists for Archean land (48). However, a zero land fraction case could represent a scenario where continental fraction is sufficiently small that continental silicate weathering becomes supply limited (e.g., ref. 49).

Fig. 4 shows model outputs for the zero land fraction case. When continental weathering drops to zero, seafloor weathering increases dramatically to balance the carbon cycle (Fig. 4*F*). This is largely a consequence of the temperature-dependent feedback of seafloor weathering. The climate warms by 10–15 K (Fig. 4*D*) before the temperature-dependent seafloor weathering flux is sufficiently large to balance the carbon cycle. Even in this extreme case, the median Archean temperature is ~305 K, and the upper end of the temperature distribution at 4 Ga only extends to ~328 K, excluding a "hot" Archean of 60–80 °C. Archean pCO_2 (and pH) are slightly higher (lower) in the zero land case, but the seafloor weathering feedback is still an effective buffer.

Finally, we investigated whether the inclusion of methane as a Precambrian greenhouse gas would substantially change our results.
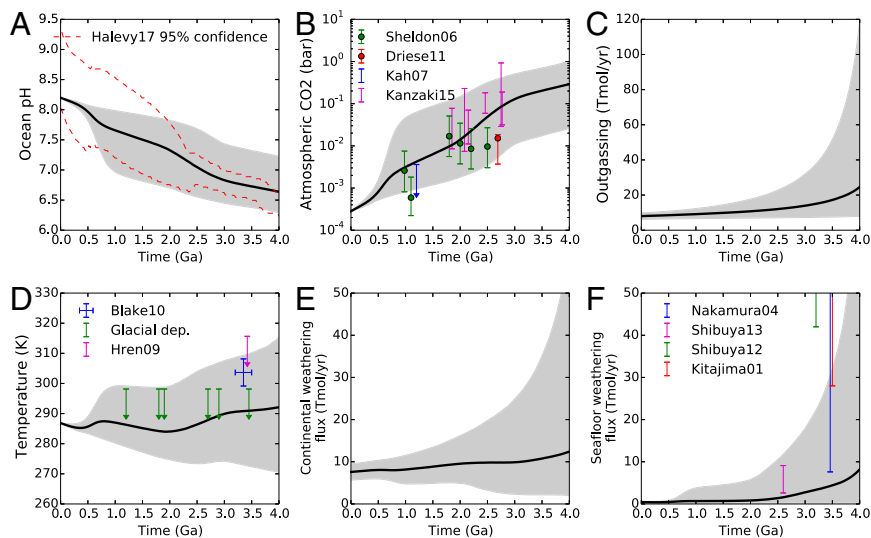
Fig. 3. Nominal model outputs. Gray shaded regions represent 95% confidence intervals, and black lines are the median outputs. (*A*) Ocean pH with the 95% confidence interval from Halevy and Bachan (29) plotted with red dashed lines for comparison. Our model predicts a monotonic evolution of pH from slightly acidic values at 4.0 Ga to slightly alkaline modern values. (*B*) Atmospheric pCO_2 plotted alongside proxies from the literature. (*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 pCO_2 drops in response to the imposed temperature increase—pCO_2 must drop otherwise weathering sinks would exceed source fluxes. The pCO_2 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 pCO_2 drop. Note that for parts of parameter space where $CO_2/CH_4 \gtrsim 0.2$ (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 when methane is included due to lower pCO_2, but there is still a monotonic evolution in pH over Earth history.

Discussion

Previously, Sleep and Zahnle (12) modeled the evolution of the geological carbon cycle over Earth history and reported the Hadean and Archean mean surface temperatures below 0 °C, unless atmospheric methane abundances were very high. In contrast, we find that Archean temperatures were likely temperate, regardless of methane abundances. This disparity can be ascribed to the differing treatments of seafloor weathering. Sleep and Zahnle (12) did not include ocean chemistry in their model (they effectively fix pH), and were thus forced to parameterize seafloor weathering using a power-law pCO_2 dependence with a fitted exponent. This parameterization overestimates the role of Archean seafloor weathering. Experiments with basalt dissolution reveal a weak pH dependence and a moderate temperature dependence, but no direct pCO_2 dependence (see discussion in ref. 36).

The change from a CO_2-dependent parameterization to a temperature-dependent parameterization means the seafloor weathering feedback better stabilizes climate against increasing luminosity. For a purely temperature-dependent weathering feedback, decreasing luminosity does not change climate, as the weathering flux must remain constant to maintain carbon cycle balance. Instead, CO_2 adjusts upwards to maintain the same temperature at lower insolation. In contrast, for a purely CO_2-dependent weathering feedback, a decrease in solar luminosity will result in a temperature decrease (see also *SI Appendix B*). In short, the pH-dependent and temperature-dependent seafloor weathering parameterization we apply stabilizes climate and prevents a globally glaciated early Earth. This result is broadly consistent with a single time point at 3.8 Ga that calculated equilibrium surface temperatures using a GCM and geological carbon cycle model (13).

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 CO_2 (*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, NH_3, Fe^{2+}, and SO_4^{2-} 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 pCO_2 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 pCO_2 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
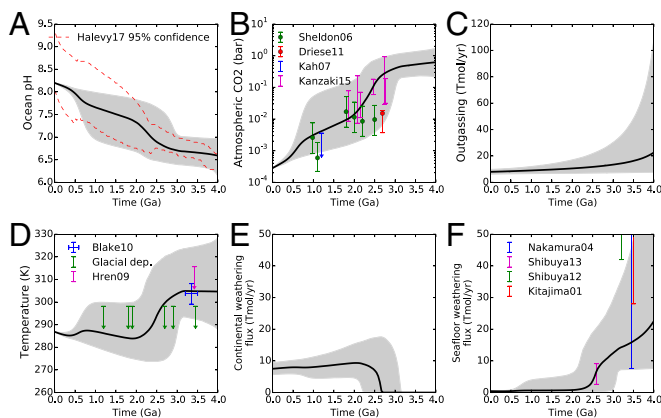
Fig. 4. No Archean land endmember scenario. Panels *A–F*, lines, and, shadings are the same as in Fig. 3. (*E*) Continental weathering drops to zero in the Archean, but (*F*) seafloor weathering increases due to its temperature dependence to balance the carbon cycle. This causes an increase in surface temperature in the Archean, (*D*) but conditions are still temperate throughout Earth history. The evolution of (*A*) ocean pH and (*B*) pCO₂ are similar to the nominal model. dep, deposit.

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 pCO₂ 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_3^{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 albedo changes. These effects are likely to be modest compared with the other sources of uncertainty in our model. Lower surface albedo from a reduced Archean land fraction can contribute at most 5 W/m² of radiative forcing (52), which would cause only a few degrees of warming. Halving Archean total pressure—as has been suggested by paleopressure proxies (53)—would cool the Earth by ~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 albedo changes are unlikely to affect our conclusions because the temperature changes they induce will be compensated by pCO₂ variations to balance the carbon cycle. Sensitivity analyses where massive amounts of Archean warming are imposed (+30 K) still result in temperate surface temperatures because of this pCO₂ compensation (*SI Appendix*, Fig. S10).

Although our model outputs are broadly consistent with paleosol 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 those 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 60× 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 pCO₂ 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.
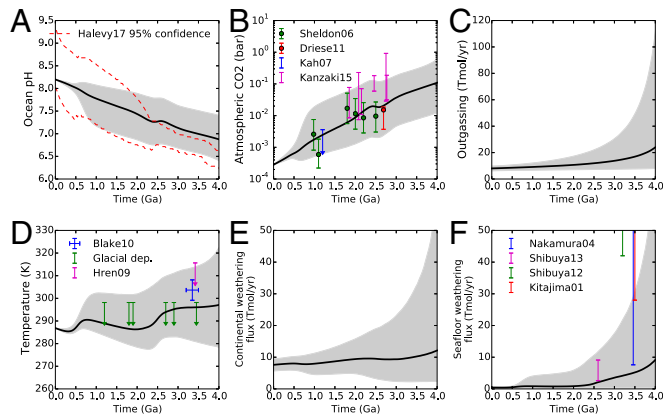
<div style="text-align: right">EARTH, ATMOSPHERIC, AND PLANETARY SCIENCES</div>

Fig. 5. Default continental growth range with imposed 100 ppm methane in the Proterozoic and 1% methane in the Archean. Panels *A–F*, lines, and, shadings are the same as in Fig. 3. (*D*) Temperature increases sharply in the Archean due to methane, but by less than what would be expected if pCO₂ were unchanged. In practice, there is a compensating decrease in atmospheric pCO₂, (*B*) which must occur to balance the carbon cycle. Otherwise temperatures would be too high and weathering sinks would exceed outgassing sources. Because pCO₂ is lower, Archean pH values are closer to circumneutral (*A*). dep, deposit.

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 pCO_2 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 $6.6^{+0.6}_{-0.4}$ at 4.0 Ga (2σ) to $7.0^{+0.7}_{-0.5}$ 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.

1. Knauth LP (2005) Temperature and salinity history of the Precambrian ocean: Implications for the course of microbial evolution. *Palaeogeogr Palaeoclimatol Palaeoecol* 219:53–69.
2. Knauth LP, Lowe DR (2003) High Archean climatic temperature inferred from oxygen isotope geochemistry of cherts in the 3.5 Ga Swaziland Supergroup, South Africa. *Geol Soc Am Bull* 115:566–580.
3. Fralick P, Carter JE (2011) Neoarchean deep marine paleotemperature: Evidence from turbidite successions. *Precambrian Res* 191:78–84.
4. Gaucher EA, Govindarajan S, Ganesh OK (2008) Palaeotemperature trend for Precambrian life inferred from resurrected proteins. *Nature* 451:704–707.
5. Garcia AK, Schopf JW, Yokobori SI, Akanuma S, Yamagishi A (2017) Reconstructed ancestral enzymes suggest long-term cooling of Earth's photic zone since the Archean. *Proc Natl Acad Sci USA* 114:4619–4624.
6. Robert F, Chaussidon M (2006) A palaeotemperature curve for the Precambrian oceans based on silicon isotopes in cherts. *Nature* 443:969–972.
7. Kasting JF, et al. (2006) Paleoclimates, ocean depth, and the oxygen isotopic composition of seawater. *Earth Planet Sci Lett* 252:82–93.
8. van den Boorn SH, van Bergen MJ, Nijman W, Vroon PZ (2007) Dual role of seawater and hydrothermal fluids in early Archean chert formation: Evidence from silicon isotopes. *Geology* 35:939–942.
9. Hren MT, Tice MM, Chamberlain CP (2009) Oxygen and hydrogen isotope evidence for a temperate climate 3.42 billion years ago. *Nature* 462:205–208.
10. Blake RE, Chang SJ, Lepland A (2010) Phosphate oxygen isotopic evidence for a temperate and biologically active Archaean ocean. *Nature* 464:1029–1032.
11. de Wit MJ, Furnes H (2016) 3.5-Ga hydrothermal fields and diamictites in the Barberton Greenstone Belt-Paleoarchean crust in cold environments. *Sci Adv* 2:e1500368.
12. Sleep NH, Zahnle K (2001) Carbon dioxide cycling and implications for climate on ancient Earth. *J Geophys Res Planets* 106:1373–1399.
13. Charnay B, Hir GL, Fluteau F, Forget F, Catling DC (2017) A warm or a cold early Earth? New insights from a 3-D climate-carbon model. *Earth Planet Sci Lett* 474:97–109.
14. Keller MA, Kampjut D, Harrison SA, Ralser M (2017) Sulfate radicals enable a nonenzymatic Krebs cycle precursor. *Nat Ecol Evol* 1:83.
15. Dora Tang TY, et al. (2014) Fatty acid membrane assembly on coacervate microdroplets as a step towards a hybrid protocell model. *Nat Chem* 6:527–533.
16. Powner MW, Sutherland JD, Szostak JW (2010) Chemoselective multicomponent one-pot assembly of purine precursors in water. *J Am Chem Soc* 132:16677–16688.
17. Konhauser K, Riding R (2012) Bacterial biomineralization. *Fundamentals of Geobiology* (Wiley–Blackwell, Hoboken, NJ), pp 105–130.
18. Knoll AH (2003) Biomineralization and evolutionary history. *Rev Mineral Geochem* 54:329–356.
19. Liu X, et al. (2016) Tracing Earth's O2 evolution using Zn/Fe ratios in marine carbonates. *Geochem Persp Let* 2:24–34.
20. Garvin J, Buick R, Anbar AD, Arnold GL, Kaufman AJ (2009) Isotopic evidence for an aerobic nitrogen cycle in the latest Archean. *Science* 323:1045–1048.
21. Planavsky NJ, et al. (2014) Earth history. Low mid-Proterozoic atmospheric oxygen levels and the delayed rise of animals. *Science* 346:635–638.
22. Grotzinger JP, Kasting JF (1993) New constraints on Precambrian ocean composition. *J Geol* 101:235–243.
23. Buick R, Dunlop J (1990) Evaporitic sediments of early Archaean age from the Warrawoona Group, North Pole, Western Australia. *Sedimentology* 37:247–277.
24. Blättler C, et al. (2017) Constraints on ocean carbonate chemistry and pCO2 in the Archaean and Palaeoproterozoic. *Nat Geosci* 10:41–45.
25. Friend CR, Nutman AP, Bennett VC, Norman M (2008) Seawater-like trace element signatures (REE+ Y) of Eoarchaean chemical sedimentary rocks from southern West Greenland, and their corruption during high-grade metamorphism. *Contrib Mineral Petrol* 155:229–246.
26. Kempe S, Degens ET (1985) An early soda ocean? *Chem Geol* 53:95–108.
27. Sleep NH, Zahnle K, Neuhoff PS (2001) Initiation of clement surface conditions on the earliest Earth. *Proc Natl Acad Sci USA* 98:3666–3672.
28. Stüeken E, Buick R, Schauer A (2015) Nitrogen isotope evidence for alkaline lakes on late Archean continents. *Earth Planet Sci Lett* 411:1–10.
29. Halevy I, Bachan A (2017) The geologic history of seawater pH. *Science* 355:1069–1071.
30. Berner RA (2004) *The Phanerozoic Carbon Cycle: CO2 and O2* (Oxford Univ Press, New York).
31. Walker JC, Hays P, Kasting JF (1981) A negative feedback mechanism for the long-term stabilization of Earth's surface temperature. *J Geophys Res Oceans* 86:9776–9782.
32. Brady PV, Gíslason SR (1997) Seafloor weathering controls on atmospheric CO2 and global climate. *Geochim Cosmochim Acta* 61:965–973.
33. Coogan LA, Dosso SE (2015) Alteration of ocean crust provides a strong temperature dependent feedback on the geological carbon cycle and is a primary driver of the Sr-isotopic composition of seawater. *Earth Planet Sci Lett* 415:38–46.
34. Berner RA, Caldeira K (1997) The need for mass balance and feedback in the geochemical carbon cycle. *Geology* 25:955–956.
35. Franck S, Kossacki KJ, von Bloh W, Bounama C (2002) Long-term evolution of the global carbon cycle: Historic minimum of global surface temperature at present. *Tellus B Chem Phys Meterol* 54:325–343.
36. Krissansen-Totton J, Catling DC (2017) Constraining climate sensitivity and continental versus seafloor weathering using an inverse geological carbon cycle model. *Nat Commun* 8:15423.
37. Taylor L, Banwart S, Leake J, Beerling DJ (2011) Modeling the evolutionary rise of ectomycorrhiza on sub-surface weathering environments and the geochemical carbon cycle. *Am J Sci* 311:369–403.
38. Moulton KL, West J, Berner RA (2000) Solute flux and mineral mass balance approaches to the quantification of plant effects on silicate weathering. *Am J Sci* 300:539–570.
39. Arthur M, Fahey T (1993) Controls on soil solution chemistry in a subalpine forest in north-central Colorado. *Soil Sci Soc Am J* 57:1122–1130.
40. Krissansen-Totton J, Buick R, Catling DC (2015) A statistical analysis of the carbon isotope record from the Archean to Phanerozoic and implications for the rise of oxygen. *Am J Sci* 315:275–316.
41. Shirey SB, Richardson SH (2011) Start of the Wilson cycle at 3 Ga shown by diamonds from subcontinental mantle. *Science* 333:434–436.
42. Delavault H, Chauvel C, Thomassot E, Devey CW, Dazas B (2016) Sulfur and lead isotopic evidence of relic Archean sediments in the Pitcairn mantle plume. *Proc Natl Acad Sci USA* 113:12952–12956.
43. Moore WB, Webb AAG (2013) Heat-pipe Earth. *Nature* 501:501–505.
44. Foley SF, Buhre S, Jacob DE (2003) Evolution of the Archaean crust by delamination and shallow subduction. *Nature* 421:249–252.
45. Debaille V, et al. (2013) Stagnant-lid tectonics in early Earth revealed by 142 Nd variations in late Archean rocks. *Earth Planet Sci Lett* 373:83–92.
46. Kopparapu RK, et al. (2013) Habitable zones around main-sequence stars: New estimates. *Astrophys J* 765:131.
47. Gough D (1981) Solar interior structure and luminosity variations. *Sol Phys* 74:21–34.
48. Sleep NH (2010) The Hadean-Archaean environment. *Cold Spring Harb Perspect Biol* 2:a002527.
49. Foley BJ (2015) The role of plate tectonic-climate coupling and exposed land area in the development of habitable climates on rocky planets. *Astrophys J* 812:36.
50. Trainer MG, et al. (2006) Organic haze on Titan and the early Earth. *Proc Natl Acad Sci USA* 103:18035–18042.
51. Higgins JA, Schrag DP (2015) The Mg isotopic composition of Cenozoic seawater–Evidence for a link between Mg-clays, seawater Mg/Ca, and climate. *Earth Planet Sci Lett* 416:73–81.
52. Goldblatt C, Zahnle K (2010) Clouds and the faint young sun paradox. *Clim Past Discuss* 6:1163–1207.
53. Som SM, et al. (2016) Earth's air pressure 2.7 billion years ago constrained to less than half of modern levels. *Nat Geosci* 9:448–451.
54. Goldblatt C, et al. (2009) Nitrogen-enhanced greenhouse warming on early Earth. *Nat Geosci* 2:891–896.
55. Nakamura K, Kato Y (2004) Carbonatization of oceanic crust by the seafloor hydrothermal activity and its significance as a CO 2 sink in the early Archean. *Geochim Cosmochim Acta* 68:4595–4618.
56. Shibuya T, et al. (2013) Decrease of seawater CO 2 concentration in the late Archean: An implication from 2.6 Ga seafloor hydrothermal alteration. *Precambrian Res* 236:59–64.
57. Shibuya T, et al. (2012) Depth variation of carbon and oxygen isotopes of calcites in Archean altered upperoceanic crust: Implications for the CO 2 flux from ocean to oceanic crust in the Archean. *Earth Planet Sci Lett* 321:64–73.
58. Kitajima K, Maruyama S, Utsunomiya S, Liou J (2001) Seafloor hydrothermal alteration at an Archaean mid-ocean ridge. *J Metamorph Geol* 19:583–599.
59. Korenaga J (2008) Plate tectonics, flood basalts and the evolution of Earth's oceans. *Terra Nova* 20:419–439.
60. Schwartzman D (2002) *Life, Temperature, and the Earth: The Self-Organizing Biosphere* (Columbia Univ Press, New York).
61. Abbot DS, Cowan NB, Ciesla FJ (2012) Indication of insensitivity of planetary weathering behavior and habitable zone to surface land fraction. *Astrophys J* 756:178.
62. Catling DC, Kasting JF (2017) *Atmospheric Evolution on Inhabited and Lifeless Worlds* (Cambridge Univ Press, Cambridge, UK).