

The Maintenance and Restoration of Habitable Conditions on Terrestrial Planets: from Snowball Earth to TRAPPIST-1

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Abstract

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This dissertation investigates how terrestrial planets sustain habitable conditions and recover from catastrophic perturbations, combining insights from Earth’s geologic record with the study of exoplanets. The first section examines Earth’s two “Snowball Earth” events in the Cryogenian period (720–635 Myr ago), when global ice cover persisted for millions to tens of millions of years. Using a numerical model of the geologic carbon cycle, **Chapter 2** shows how the mass and rapid deposition of post-Marinoan “cap carbonates” – carbonate layers that directly overlie glacial deposits – can be explained by a multi-stage process of syn-glacial seafloor weathering, post-glacial continental weathering, and slow ocean mixing. **Chapter 3** applies the same framework to show why the first glaciation (the “Sturtian”; ~56 Myr) lasted an order of magnitude longer than the second (the “Marinoan”; ~4 Myr), revealing how seafloor weathering and redox state modulated Earth’s recovery from snowball conditions. Together, these studies clarify the mechanisms by which Earth has repeatedly regained habitable climates after near-total glaciation. The second section extends this perspective to the TRAPPIST-1 exoplanet system, which contains seven terrestrial planets that are prime targets for atmospheric characterization. **Chapter 4** combines magma chemistry and knowledge of volcanism on Earth, Mars, and Io to demonstrate that volcanic outgassing could supply long-lived secondary atmospheres rich in water vapor on the TRAPPIST-1 planets, counteracting escape processes. These results provide new constraints on the processes that control atmospheric evolution and underscore the potential for habitable

conditions beyond the Solar System. Overall, this work advances the study of terrestrial planets as dynamic objects that can overcome barriers to habitability via a variety of processes.

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1. Introduction

1.1 Background

Terrestrial planets exhibit a remarkable diversity of chemical and physical properties. Starting in the solar system, we see that Venus, Earth, and Mars all formed from the same disk of gas and dust, but have wound up with very different present-day conditions: atmospheric surface pressure varies by a factor of $\sim 15,000$ across all three planets and average surface temperatures range from -60°C on Mars to 470°C on Venus (Catling & Kasting, 2017; pg. 332, 371). We also know that of these three planets, only Earth has supported a continuous record of life for over 3.5 billion years (Westall, 2025). Looking further afield, the catalogue of known exoplanets is rapidly growing, and we are only beginning to understand their true diversity (Cloutier, 2026). For example, observed exoplanets often orbit very close to their host star – closer than Mercury orbits the Sun – and exoplanets with an intermediate size between Earth and Neptune are very common (Fulton et al., 2017; Bean et al., 2021), for which there is no solar system analog. Why do terrestrial planets have such a diversity of conditions and what determines these outcomes? How can we place Earth, and the life that exists here, in the context of this larger set of terrestrial planets?

The evolution of a planet's chemical and physical conditions, and thus the range of possible outcomes, is governed by the interaction of its distinct chemical reservoirs, such as the atmosphere, hydrosphere, lithosphere, and biosphere. Through these interactions, matter and energy are exchanged via a variety of processes that shape the conditions on a planet's surface, including the atmospheric composition and surface temperature, characteristics that determine how suitable an environment is for life (see Catling & Kasting, 2017). These processes can combine to produce complex behavior, such as self-regulating geochemical cycles or stable surface conditions that result from powerful, but balanced, opposing chemical fluxes. The study of these interactions and the development of general insights is key for understanding the diversity of terrestrial planets in the galaxy, the history of the solar system, and the history of our planet.

This dissertation is dedicated to studying the processes by which planets can maintain and restore habitable surface conditions despite the many perturbations they face in their lifetime. Chapters 2 and 3 focus on the processes by which Earth has maintained its habitable conditions and restored them after being pushed into extreme “Snowball Earth” climate states in the past.

Chapter 4 develops a theoretical pathway for terrestrial exoplanets to maintain habitable atmospheres despite the harsh radiation environment that many of them are subject to.

1.2 Snowball Earth

The paradigmatic explanation for Earth's long-term habitability is that the geologic carbon cycle provides a negative feedback mechanism that stabilizes the surface temperature (Walker et al., 1981). In the idealized climate feedback, silicate weathering (the primary sink for atmospheric CO₂) accelerates when temperatures rise. So, if an external perturbation raises Earth's surface temperature, CO₂ is drawn down by the increased weathering, greenhouse warming weakens, and the surface temperature decreases, thereby stabilizing climate on the timescale of about one million years. This process works in reverse as well: if a perturbation lowers surface temperature, silicate weathering decreases and additional atmospheric CO₂ builds up from volcanic outgassing, thereby raising the surface temperature and once again stabilizing climate.

A climate feedback in the geologic carbon cycle must have been present throughout the Phanerozoic Eon to maintain mass balance (Berner & Caldeira, 1997), and its stabilizing effect can be observed in the temperature record (Arnscheidt & Rothman, 2022), but the mechanism is now known to be more complicated than originally proposed (François & Walker, 1992). Additional processes other than silicate weathering are now recognized for playing important but potentially conflicting roles in the climate feedback (see Coogan et al., 2026 for a recent review). These processes include seafloor weathering (Brady & Gíslason, 1997; Alt & Teagle, 1999; Coogan & Gillis, 2018), reverse weathering (Mackenzie & Garrels, 1966; Michalopoulos & Aller, 1995; Mackenzie & Kump, 1995), continental carbonate weathering (Gaillardet et al., 1999), and organic carbon weathering and preservation (Hilton et al., 2015; Soulet et al., 2021). Geologic and tectonic forcings, like the continental configuration and volcanism, also play a key role in setting the behavior of carbon cycle processes and thus the equilibrium temperature of the climate feedback. These forcings may play a dominant role during some periods in Earth history, which would limit or remove the climate-stabilizing effect altogether (e.g., Raymo & Ruddiman, 1992; Kump et al., 2000; Maher & Chamberlain, 2014; Krissansen-Totton & Catling, 2017; Macdonald et al., 2019; Gernon et al., 2021; Coogan & Dosso, 2022).

To disentangle these processes and evaluate the actual strength of the negative climate feedback, it is critical to observe the behavior of the geologic carbon cycle throughout Earth

history. For example, previous studies have illuminated the importance of seafloor weathering during the Archean Eon (Sleep & Zahnle, 2001; Krissansen-Totton et al., 2018). Others have proposed that reverse weathering plays a key role in the evolution of Precambrian climate (Isson & Planavsky, 2018; Krissansen-Totton & Catling, 2020). It has also been shown that shorter-term organic carbon cycling plays a key role in relation to Phanerozoic ice ages (Hülse & Ridgwell, 2025). These studies provide key context for the development of other aspects of the Earth system (e.g., the biosphere), they are critical for determining how processes in the climate feedback depend on Earth's surface conditions, and they show how the behavior of the feedback has changed over time.

Global glaciation events in Earth's past are ideal for studying the geologic carbon cycle climate feedback response to extreme temperature perturbations. During the so-called "Snowball Earth" events of the Cryogenian Period (720–635 Ma), Earth froze over twice for millions of years, which were some of the most dramatic climate events known in Earth history (Kirschvink, 1992; Hoffman et al., 1998). On one hand, the occurrence of such extreme climate perturbations indicates that the stabilizing climate feedback failed to keep Earth's surface in a habitable temperature range (i.e., above the freezing point of water). On the other hand, Earth's recovery from these events indicates that the climate feedback eventually succeeded by restoring habitable surface conditions after a catastrophic perturbation. Reconciling these two aspects of the geologic carbon cycle climate feedback in relation to the Snowball Earth events is a key goal in understanding the paradigmatic theory of Earth's continuous habitability, and it is the topic of Chapters 2 and 3.

Chapter 2 (Thomas & Catling, 2024) focuses on the dynamics of Snowball Earth termination and the restoration of habitable surface conditions via the geologic carbon cycle. Here, we address the formation of post-glacial "cap carbonates", which are thick layers of limestone or dolostone that sharply overlie Snowball glacial deposits, indicating an abrupt transition from a frozen climate to a hot, high CO₂ climate in the Snowball Earth aftermath. Despite being foundational to the Snowball Earth hypothesis, a comprehensive explanation of cap carbonate formation has been elusive for over three decades (see Yu et al., 2020). In this chapter, we propose that cap carbonates are formed in a three-stage mechanism that includes syn-glacial seafloor weathering, post-glacial continental weathering, and slow ocean mixing. This mechanism explains multiple cap carbonate characteristics, including their timescale of deposition, observed sedimentary structures, and geochemical tracers. By simulating this formation mechanism, we

constrain the evolution of Earth's climate (e.g., surface temperature, atmospheric CO₂, and ocean pH) and provide a predictive framework for Earth's surface chemistry at the end of Snowball Earth events.

Chapter 3 (Thomas et al., 2026) focuses on the processes that control the duration of the Snowball Earth events. Here we address the striking, but unexplained, 14-fold difference in duration between the first Snowball glaciation (the “Sturtian”; ~56 Myr) and the second (the “Marinoan”; ~4 Myr). We show that the difference can be explained by changes in seafloor weathering, which is the primary CO₂ sink during global glaciation and thus impacts the rate of atmospheric CO₂ buildup. From the geologic record, we find support that these changes were driven by evolving ocean chemistry related to Earth's surface oxygenation and seawater sulfate concentration, providing a new explanation for another fundamental aspect of the Snowball Earth hypothesis and showing how its key characteristics are controlled by processes in the geologic carbon cycle.

1.3 The TRAPPIST-1 exoplanets

Looking beyond Earth, we have yet to find evidence for any other mechanisms that similarly stabilize habitable planetary surface conditions. Mars had a brief window of early habitability, demonstrated by geologic evidence for past surface water (Fassett & Head, 2011), but has subsequently lost its atmosphere and become cold and dry (Haberle et al., 2001). It is possible that Venus had an early window of habitability where a liquid ocean condensed (Way & Del Genio, 2020), but today liquid water is not stable on the surface (Catling & Kasting, 2017; pg. 371). Modern Mars and Venus therefore cannot support a climate feedback like Earth's geologic carbon cycle because weathering and carbonate deposition both require persistent surface liquid water. Given the natural climate stabilization observed on Earth, and the lack of stabilization on Mars and Venus, what should we expect on terrestrial exoplanets?

Terrestrial exoplanets face unique barriers to maintaining stable, habitable, surface conditions. The most favorable exoplanet targets for atmospheric characterization via transit spectroscopy with the James Webb Space Telescope (JWST) are planets on close-in orbits around M stars. These planets are also extremely common, as M stars are about three quarters of the main sequence stars in the galaxy (Bochanski et al., 2010). The primary challenge to maintaining habitable conditions on these planets is the harsh radiation environment produced by the M stars.

Due to the close-in planetary orbit and the stellar properties, high-energy radiation and magnetic field interactions are expected to drive intense atmospheric escape, which could quickly remove any putative atmospheres that the orbiting planets may have (e.g., Gialluca et al., 2024). Given this challenge, is it possible for terrestrial planets orbiting M stars to support atmospheres at all, let alone habitable conditions?

Chapter 4 (Thomas et al., 2025) focuses on one process by which terrestrial planets orbiting M dwarfs could support atmospheres and habitable conditions in such a harsh radiation environment: volcanic outgassing. Present-day atmospheres on terrestrial planets in the solar system ultimately originated from volcanic outgassing, where volatiles from a planet's interior are released to the surface via the production and movement of magma. Here, we use knowledge of the solar system planets to assess whether volatile replenishment from volcanic outgassing could support stable atmospheres against the expected high rates of atmospheric escape on M dwarf planets. This chapter focuses on the TRAPPIST-1 exoplanet system, which has seven planets orbiting an M dwarf, three of which are in the habitable zone, and all of which are consistent with terrestrial composition (Agol et al., 2021). We place theoretical boundaries on the expected volcanic outgassing rates for these planets and demonstrate that this process may sustain atmospheres against escape. The results support continued JWST characterization and provide a framework for the interpretation of future observations.

1.4 Astrobiology relevancy statement

This thesis is directly relevant to astrobiology as outlined in the two most recent community strategy documents (NASA, 2015; National Academies of Sciences et al., 2019). The first recommendation of the 2019 document is to catalyze research on dynamic habitability – the idea that an environment may transition between habitable and uninhabitable states over different spatial and temporal scales. The overall topic of this thesis is within the scope of this recommendation. More explicitly, the six priority areas of astrobiology research defined in the 2015 document are:

1. Identifying abiotic sources of organic compounds
2. Synthesis and function of macromolecules in the origin of life
3. Early life and increasing complexity
4. Co-evolution of life and the physical environment

5. Identifying, exploring, and characterizing environments for habitability and biosignatures
6. Constructing habitable worlds

Chapters 2 and 3 focus on global “Snowball Earth” glaciation events where Earth was covered in ice sheets multiple times for millions of years. These events are among the largest known perturbations to Earth’s otherwise habitable conditions, and they occurred alongside pivotal changes that led to the modern world, including an increase in atmospheric O₂ by over an order of magnitude and eventually the first fossil animals visible to the naked eye. My work explores the co-evolution of Earth and life during these events, making these chapters directly relevant to points 3 and 4.

Chapter 4 focuses on terrestrial exoplanets that may host habitable conditions. Many of the potentially Earth-like worlds that are most amenable to atmospheric characterization orbit M stars (e.g., TRAPPIST-1), which create a harsh radiation environment that poses a challenge for planets to retain atmospheres and support habitable conditions. My work presents new pathways for overcoming this challenge to habitability and needed geologic context that guides observation, making this chapter directly relevant to points 5 and 6.

2. Three-stage formation of cap carbonates after Marinoan snowball glaciation consistent with depositional timescales and geochemistry

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Abstract

At least two global “Snowball Earth” glaciations occurred during the Neoproterozoic Era (1000–538.8 million years ago). Post-glacial surface environments during this time are recorded in cap carbonates: layers of limestone or dolostone that directly overlie glacial deposits. Postulated environmental conditions that created the cap carbonates lack consensus largely because single hypotheses fail to explain the cap carbonates’ global mass, depositional timescales, and geochemistry of parent waters. Here, we present a global geologic carbon cycle model before, during, and after the second glaciation (i.e. the Marinoan) that explains cap carbonate characteristics. We find a three-stage process for cap carbonate formation: (1) low-temperature seafloor weathering during glaciation generates deep-sea alkalinity; (2) vigorous post-glacial continental weathering supplies alkalinity to a carbonate-saturated freshwater layer, rapidly precipitating cap carbonates; (3) mixing of post-glacial meltwater with deep-sea alkalinity prolongs cap carbonate deposition. We suggest how future geochemical data and modeling refinements could further assess our hypothesis.

2.1 Introduction

Earth's Neoproterozoic Era (1 billion years ago to 538.8 million years ago) is marked by dramatic global climate change. Geologic evidence indicates two major glacial intervals where ice sheets reached low latitudes for millions of years (e.g., reviewed by Hoffman et al., 2017). These “snowball Earth” events (Kirschvink, 1992; Hoffman, 1998) are the Sturtian from 717 to 659 million years ago (Ma) and the Marinoan from ca 645 to 635 Ma. Together, these events bookend the Cryogenian Period (720–635 Ma).

The Cryogenian glacial intervals occurred alongside other global changes, including the appearance of the first large, complex organisms in Earth's history in the subsequent Ediacaran Period (Narbonne, 2005), an increase of atmospheric O₂ relative to low levels in the mid-Proterozoic (Planavsky et al., 2018), large excursions in the global carbon isotope record (Kaufman & Knoll, 1995), and the break-up of Rodinia and later assembly of Gondwana supercontinents (Cordani et al., 2003). All of these transitions occurred during or continued after the Cryogenian Period, which is only ~2% of Earth's 4.5-billion year history. Despite this temporal connection, the causes and the relationships between these global changes remain unclear.

Cap carbonates (CCs) probe Earth's surface environment during, and immediately after, the Cryogenian. CCs are layers of limestone or dolostone up to ~200 meters thick that sharply overlie Sturtian and Marinoan glacial deposits in over 50 locations on all major Neoproterozoic continents (reviewed by Yu et al., 2020). Carbonates record Earth's surface conditions because they are sensitive to the chemistry of the atmosphere and ocean from which they precipitate. Thus, the sharp distinction between the glacial deposits and CCs is interpreted as an abrupt shift in Earth's surface environment at the end of each Cryogenian glacial interval from cold, frozen conditions to hot conditions with a high partial pressure of atmospheric carbon dioxide, pCO₂ (Hoffman, 1998). In this scenario, continental weathering was inhibited during the glacial intervals, allowing volcanic CO₂ to accumulate in the atmosphere and provide enough greenhouse warming to overcome the high albedo of Earth's ice-covered surface, causing deglaciation. The post-glacial Earth then entered a high pCO₂ but low albedo state in which continental weathering produced cations and carbonate ions (i.e. alkalinity) that drove rapid carbonate deposition (Kirschvink, 1992; Hoffman, 1998).

The above explanation for CC deposition is broadly consistent with the geologic evidence, but a complete explanation must answer several key questions. First, was the alkalinity source

from continental weathering sufficient for the CCs? It is estimated that the global mass of the Marinoan CCs is over 10^{18} kg (Yu et al., 2020). Enough alkalinity to generate this much carbonate must be supplied after the glacial interval. Second, what was the timescale of CC deposition? The interpretation of sedimentary structures, the presence of paleomagnetic reversals, and radiometric dating yield conflicting estimates that have yet to be resolved (Table 2-1). Third, what were the physical and chemical properties of the water body from which the CCs precipitated? After the Marinoan glaciation, the post-glacial ocean was subject to a large influx of glacial meltwater, sea level rise, and transgression onto the land. The deposition of the CCs was likely influenced by these changing ocean conditions.

Many explanations for CC deposition have been proposed, but none are complete. As summarized in Yu et al. (2020), suggestions include oceanic overturn (Grotzinger & Knoll, 1995; Knoll et al., 1996), continental weathering (Hoffman et al., 2017; Hoffman & Schrag, 2002), gas hydrate destabilization (Kennedy et al., 2001; Kennedy et al., 2008), glacial meltwater plumes and subsequent ocean overturn (Shields, 2005), sediment starvation (Kennedy & Christie-Blick, 2011; Spence et al., 2016), microbial activity (Nédélec et al., 2007; Font et al., 2010), and calcareous loess (Retallack, 2011). Also summarized in Yu et al. (2020), these explanations all have unresolved deficiencies related to the physical and chemical conditions of the post-glacial ocean, the interpretation of the geologic evidence, and the predicted timescale of deposition.

Advances in our knowledge of the geologic carbon cycle and of Cryogenian conditions allow new tests of hypotheses for CC deposition.

Seafloor weathering has been recognized as a process in the geologic carbon cycle that has been important during some times in Earth's history. Seafloor weathering occurs when seawater circulating through oceanic crust at low-temperatures reacts with constituents of basaltic rock (e.g., volcanic glass, olivine, and plagioclase) to release alkalinity in the form of Ca ions (e.g. reviewed by Coogan & Gillis, 2018). Krissansen-Totton and Catling (2017) developed an empirically justified parameterization of seafloor weathering in a geologic carbon cycle model, and Krissansen-Totton et al. (2018) used this model to show that seafloor weathering may have been comparable in strength to continental weathering at some points in Earth's history. The role of seafloor weathering in CC deposition has not been assessed. Previous global geologic carbon cycle models applied to Cryogenian glacial intervals used theoretical rate parameterizations that have

Radiometric Dating				
Age	Measurement Location	Method	Geologic Formation	Reference
632.50 ± 0.48 Ma	5 meters above top of CC	U-Pb	Doushantuo Formation, China	Condon et al. (2005)
632.30 ± 5.9 Ma	0.9 meters above top of CC	Re-Os	Sheepbed Formation, Canada	Rooney et al. (2015)
635.23 ± 0.57 Ma	Within CC, 2.3 meters above base	U-Pb	Doushantuo Formation, China	Condon et al. (2005)
634.57 ± 0.88 Ma	Base of CC	U-Pb	Nantuo Diamictite, China	Zhou et al. (2019)
636.41 ± 0.45 Ma	1 meter below base of CC	U-Pb	Cottons Breccia, Tasmania	Calver et al. (2013)
635.21 ± 0.59 Ma	~30 meters below base of CC	U-Pb	Ghuab Formation, Namibia	Prave et al. (2016)
635.5 ± 1.2 Ma	~30 meters below base of CC	U-Pb	Ghaub Formation, Namibia	Hoffmann et al. (2004)
Paleomagnetism				
Depositional Timescale	Description	Geologic Formation		Reference
>1.25 Myr	5 polarity reversals in first 20 meters of CC	Mirassol d'Oeste Section, Brazil		Trindade et al. (2003)
>1.25 Myr	5 polarity reversals in first 20 meters of CC	Terconi Section, Brazil		Font et al. (2010)
>0.5 Myr	2 polarity reversals in first 9 meters of CC	Jebel Akhdar Section, Oman		Kilner et al. (2005)
>0.5 Myr	2 polarity reversals in first 12 meters of CC	Second Plain Section, Australia		Schmidt et al. (2009)
Sedimentology				
Depositional Timescale	Description	Geologic Formation		Review Reference
10 ³ -10 ⁴ yr	Rapid deglaciation and rapid deposition	Many		Hoffman et al. (2017)
>10 ⁵ yr	Slow deglaciation and slow deposition	Many		Spence et al. (2016)

Table 2-1: Estimates for the age and timescale of Marinoan cap carbonate deposition. To calculate depositional timescale from paleomagnetic data, we assume 1 reversal occurred every 250 kyr, consistent with the Miocene, Jurassic, and Cambrian (Font et al., 2010). The sedimentological lines of evidence are broad interpretations of many CC formations across the literature. CC cap carbonate.

proven inconsistent with recent experiments (Le Hir et al., 2008), or they omit low-temperature seafloor weathering (Penman & Rooney, 2019; Hood et al., 2022; Fang & Xu, 2022).

The Marinoan CCs were likely deposited in a stratified, post-glacial ocean. The large volume of glacial meltwater following deglaciation should have created a distinct layer on top of the existing ocean. It has been proposed that the dolostone components of the CCs precipitated out of this layer (Shields, 2005). This hypothesis is supported by geochemical measurements of the CCs, including $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{26}\text{Mg}$ in multiple formations (Liu et al., 2013, 2014, 2018) and a global analysis of Ca, Mg, Sr, and C isotopes (Ahm et al., 2019). A freshwater layer is consistent with 1D and 3D ocean models, which show that it could last for up to 10^5 years (Yang et al., 2017; Ramme & Marotzke, 2022). Thus, the evidence indicates that the meltwater layer must be considered in CC deposition; however, the previous global geologic carbon cycle models only consider whole-ocean chemistry.

Here, we investigate CC deposition with a geologic carbon cycle model that includes an empirically justified parameterization of seafloor weathering, explicit calculation of chemistry in the post-glacial meltwater layer, and other advances in our knowledge of both the geologic carbon cycle and Cryogenian conditions. Our model is applied to the Marinoan glaciation, but many aspects are likely applicable to the Sturtian and perhaps other glaciations. We identify a mechanism for Marinoan CC deposition that builds on previous explanations to answer the key questions mentioned above, and we find it is consistent with the global collection of CCs (See Supplementary Fig. S2-1).

2.2 Results

2.2.1 Climate evolution

We constructed a model for the evolution of the carbon content and marine alkalinity in Earth's atmosphere and ocean before, during, and after the Marinoan glaciation (Fig. 2-1). We use a box model that evolves according to the processes of the geologic carbon cycle, which include continental silicate and carbonate weathering, volcanism, carbonate deposition, and seafloor weathering. In order to capture the unique climates of a glaciation event, we configure the model to address 4 distinct phases: the background Neoproterozoic phase, the syn-glacial phase, the post-glacial stratified ocean phase, and the post-glacial well-mixed ocean phase.

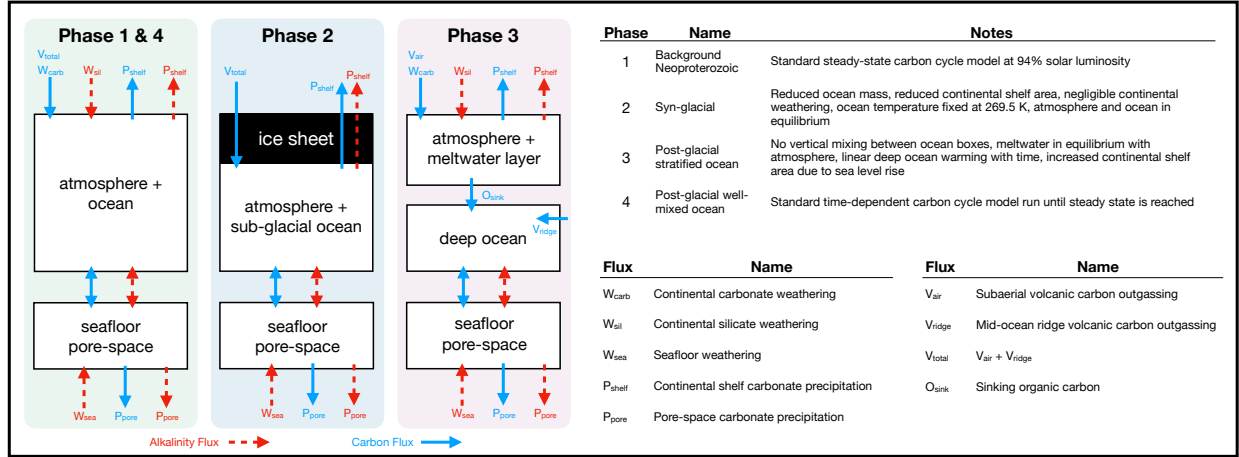


Figure 2-1: Schematic diagram of the box model used in this work, showing carbon (blue) and alkalinity (red) fluxes in the various model phases.

The basic model builds upon a previously data-validated model (Krissansen-Totton & Catling, 2017; Krissansen-Totton et al., 2018) and consists of two boxes: one box for the combined atmosphere-ocean and one box for water in the seafloor rock pore-space, where seafloor weathering takes place. In the post-glacial stratified ocean phase, another box is included to explicitly account for a glacial meltwater layer. After calculating the aqueous chemistry in each box, the model calculates climate variables (e.g., ocean pH, surface temperature, and pCO_2) and geologic processes (e.g., weathering rates, carbonate deposition rates). A complete description of these calculations is found in Methods and Supplementary Material.

Transitions between model phases are imposed. A rigorous treatment of the transitions would require calculations beyond the scope of this work such as the complex movement of ice sheets subject to the ice-albedo instability or changes in the 3D circulation of the ocean. Thus, model transitions are not explicitly calculated, but they are informed by the literature. We instead focus on the major environmental and chemical conditions within each model phase.

We sample uncertain model parameters within their plausible value ranges. We follow Krissansen-Totton and Catling (2017) and Krissansen-Totton et al. (2018) to sample the key uncertain parameters in the geologic carbon cycle model. We also introduce extra parameters related to the glaciation, such as the size of the ice sheets, the continental shelf area during glaciation, and the composition of glacial meltwater.

By modeling the glaciation event in 4 distinct phases, we generate results that are self-consistent across the full range of potential climate states. The nominal model evolution through all phases is shown in Figs. 2-2 and 2-3. The model is run 3000 times to derive median values and confidence intervals while sampling uncertain parameters.

The pre-glacial phase (Phase 1), given typical Neoproterozoic parameters, is characterized by a temperate or cool background climate. The 95% confidence interval for equilibrium atmospheric $p\text{CO}_2$ is 1.6×10^{-4} to 5.5×10^{-3} bar, yielding surface temperatures of 274.4–291.6 K, ocean pH of 7.6–8.4, and ocean calcite saturation state of 3.3–5.2, which is reasonable given uncertainty in marine Ca^{2+} concentration in the Neoproterozoic (e.g. Hill et al., 2000; Arp et al., 2001; Spear et al., 2014). In the median model evolution, $p\text{CO}_2$ is 5.9×10^{-4} bar and the ocean pH is 8.11, which is similar to the modern values of 4×10^{-4} bar and 8.1, respectively; however, the reduced solar luminosity allows for lower surface temperatures. The low surface temperature would leave Earth in a state that is potentially vulnerable to a snowball-causing climate perturbation.

During glaciation (Phase 2), $p\text{CO}_2$ steadily rises while seafloor weathering supplies alkalinity to the subglacial ocean. With ice sheets covering the land and a slow hydrologic cycle, we assume that continental weathering either stops completely or is fixed at a rate several orders of magnitude below modern, following Lan et al. (2022). Seafloor weathering continues though, and causes alkalinity in the sub-glacial ocean to reach up to $0.035 \text{ mol eq kg}^{-1}$, which is ~14 times higher than modern seawater ($2320 \text{ } \mu\text{mol eq kg}^{-1}$; Pilson, 2012, p. 131). The built-up alkalinity does not result in widespread carbonate precipitation because high CO_2 levels cause the ocean to be acidic, the ocean is cold, and the thick ice sheets eliminate most of the available shelf area for precipitation (though there is still some carbonate precipitation in the ocean crust). Thus, atmospheric $p\text{CO}_2$ steadily rises as CO_2 is supplied by subaerial and submarine outgassing. Note that we assume the atmosphere and ocean are in equilibrium despite widespread ice sheets, which is further justified in Methods.

We force the glaciation to end after 10 Myr, which is consistent with constraints on the duration of the Marinoan glaciation (see Hoffman et al., 2017, and references within). At the end of glaciation, $p\text{CO}_2$ is 0.13–0.35 bar, consistent with estimates of the required $p\text{CO}_2$ to cause global melting of 0.1–0.3 bar (Hoffman et al., 2017; Higgins & Schrag, 2003; Pierrehumbert, 2004). We

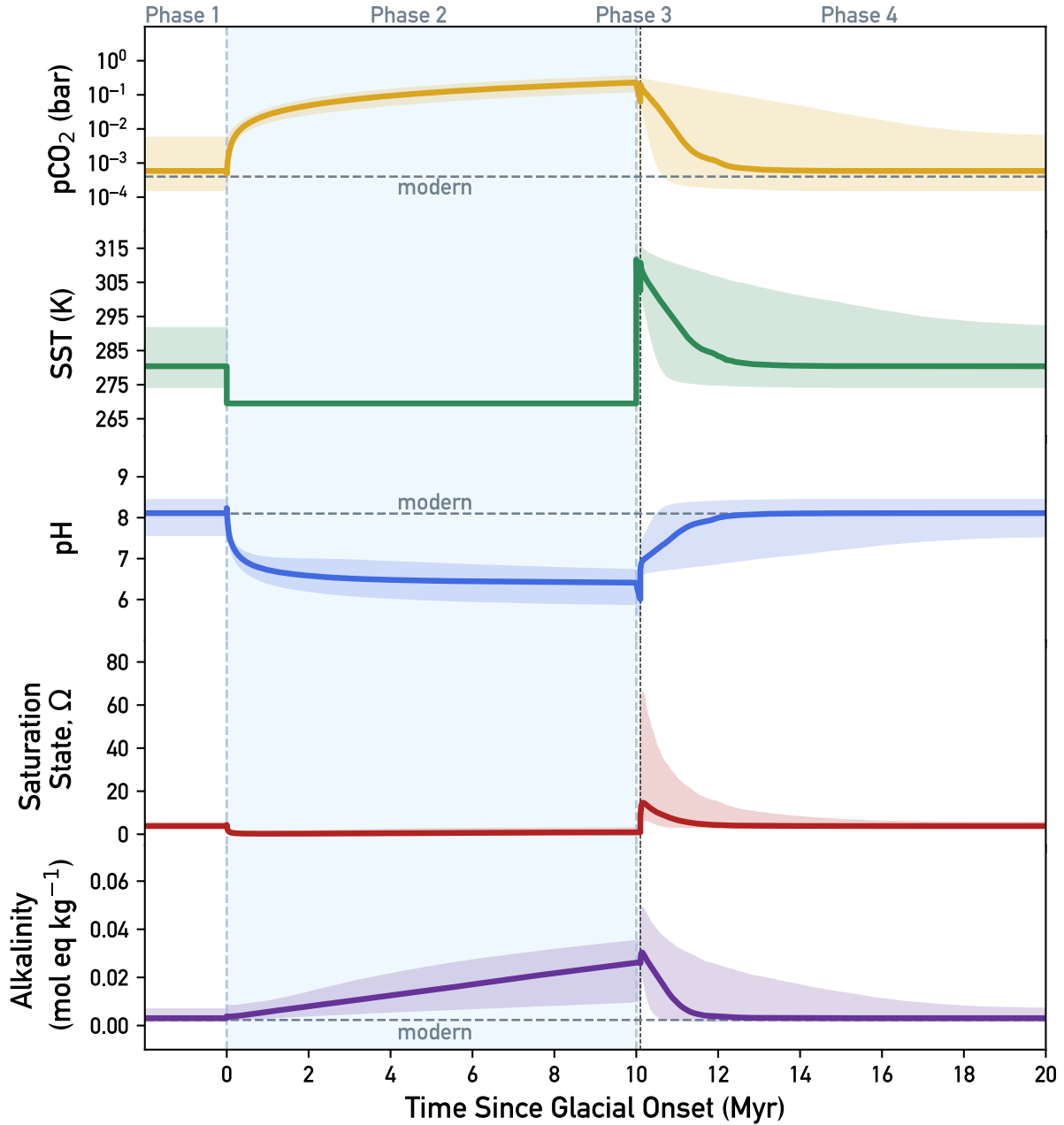


Figure 2-2: Climate evolution through all modeled phases noting that post-glacial Phase 3 is very compressed on a Myr timescale, so is expanded in Fig. 2-3. The shaded regions are the 95% confidence intervals and the solid lines are the median model runs with randomly sampled parameters. Glaciation was terminated after 10 Myr and the stratified ocean was terminated after 100 kyr ($t_{strat} = 10^5$ years). Vertical dashed lines indicate boundaries between model phases, noting the two close vertical lines at 10 Myr and 10.1 Myr bounding post-glacial stratified ocean Phase 3. Horizontal dashed lines show modern values noted in the main text.

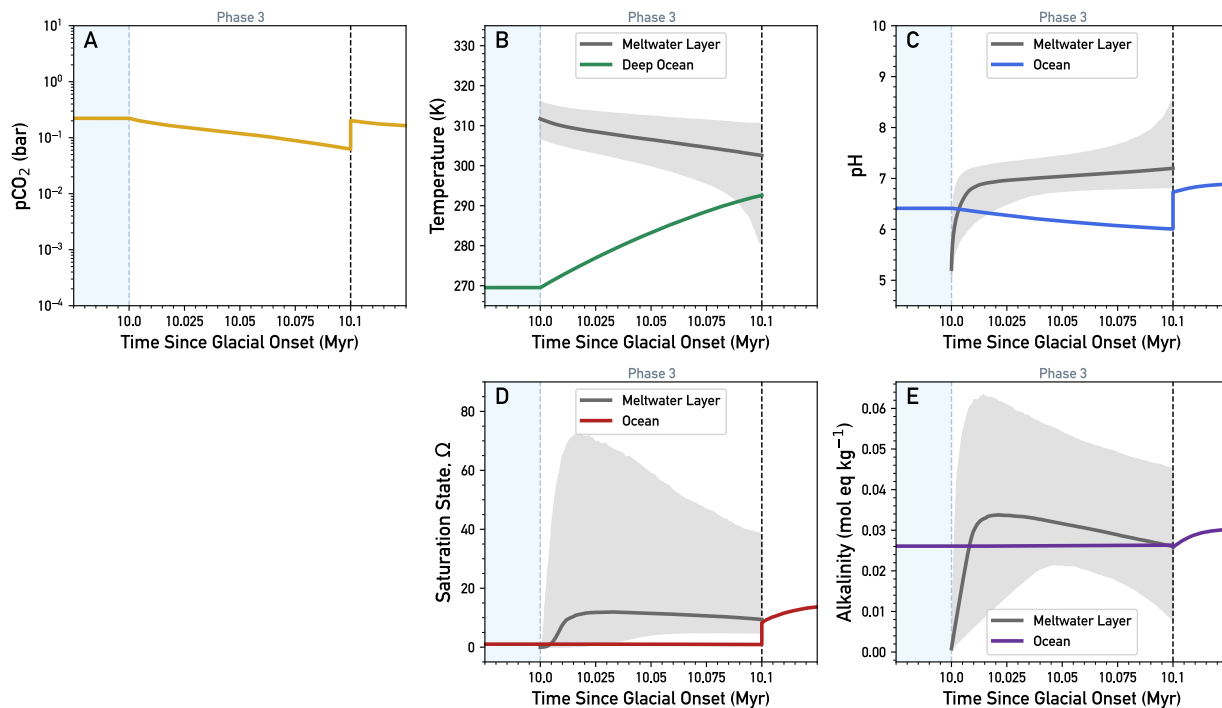


Figure 2-3: Climate evolution in the stratified ocean Phase 3 from Fig. 2-2. The shaded regions are the 95% confidence intervals and the solid lines are the median model runs with randomly sampled parameters. Post-glacial ocean stratification is assumed to last 100 kyr ($t_{strat} = 10^5$ years), indicated by the vertical dashed black line. **A** shows the evolution of atmospheric $p\text{CO}_2$. **B–E** show the evolution of parameters related to the post-glacial meltwater layer in gray and the underlying ocean in color. Following stratification, the two reservoirs are combined and averaged.

do not include the complicated process of ice sheet melting in our model, because we focus on the evolution of geochemical parameters.

In the post-glacial stratified ocean (Phase 3), continental weathering rapidly supplies alkalinity to the meltwater layer (Fig. 2-3E) and CC deposition begins. In the nominal model, we assume that the lifetime of the meltwater layer, t_{strat} , is 10^5 years, but we also consider a scenario with $t_{strat} = 10^4$ years (Supplementary Figs. S2-2 and S2-3). The equilibration of the meltwater layer with the high CO_2 atmosphere initially causes immediate and intense acidification. The acidification is then counteracted by alkalinity delivered from continental weathering in the hot, high CO_2 conditions. Alkalinity supplied to the meltwater layer can cause the calcium-carbonate saturation state to reach over 70 before carbonate deposition can remove alkalinity at the same rate

and balance the system. In the median model runs, carbonate deposition in the meltwater layer removes 0.04 and 0.16 bar CO₂ in the first 10⁴ and 10⁵ years of stratification, respectively.

In the post-glacial well-mixed ocean (Phase 4), alkalinity is supplied to the surface from the deep ocean, CC deposition continues, and a steady state climate is eventually recovered. As mentioned above, seafloor weathering causes alkalinity to build up in the sub-glacial ocean during Phase 2. During Phase 3, this alkalinity remains trapped in the deep ocean under the meltwater layer. It is not until Phase 4, when the meltwater layer mixes with the underlying ocean, that this alkalinity is delivered to the surface ocean and contributes to carbonate precipitation on continental shelves. Note that in our model construction, the meltwater layer and the underlying ocean are abruptly mixed in a single timestep, which causes the discontinuity seen in some climate variables. This transition was probably more gradual and localized in reality, but we expect the ultimate evolution of the climate variables to be the same. In Phase 4, CO₂ continues to be removed from the atmosphere on the timescale of the geologic carbon cycle, and the background Neoproterozoic steady state climate is generally recovered within 5 Myr of deglaciation.

2.2.2 Post-glacial carbonate deposition

Figures 2-4 and 2-5 show how carbonates are deposited after the glaciation event in the nominal model runs with $t_{strat} = 10^4$ and 10⁵ years. Confidence intervals are derived from the model runs in Figs. 2-2 and 2-3 and in Supplementary Figs. S2-2 and S2-3.

The carbonate deposition rate quickly rises in the first 10 kyr after deglaciation and reaches a maximum value 10 to 100 kyr after deglaciation (Fig. 2-4). For $t_{strat} = 10^4$ years, the median deposition rate peaks ~67 kyr after deglaciation, when the ocean is well-mixed (Phase 4). For $t_{strat} = 10^5$ years, the median deposition rate peaks ~25 kyr after deglaciation, when the ocean is still stratified (Phase 3). These results are due to the fact that the meltwater layer can reach a higher saturation state and faster deposition rate when it has a longer lifetime because more alkalinity can be delivered. When $t_{strat} = 10^5$ years, the second peak in deposition rate after the ocean mixes is probably unrealistic because it is due to the abrupt water mixing we impose in the model. In reality, the carbonate deposition rate would likely have been uniformly higher in the stratified ocean phase as the alkalinity from the deep ocean slowly mixed into the meltwater layer.

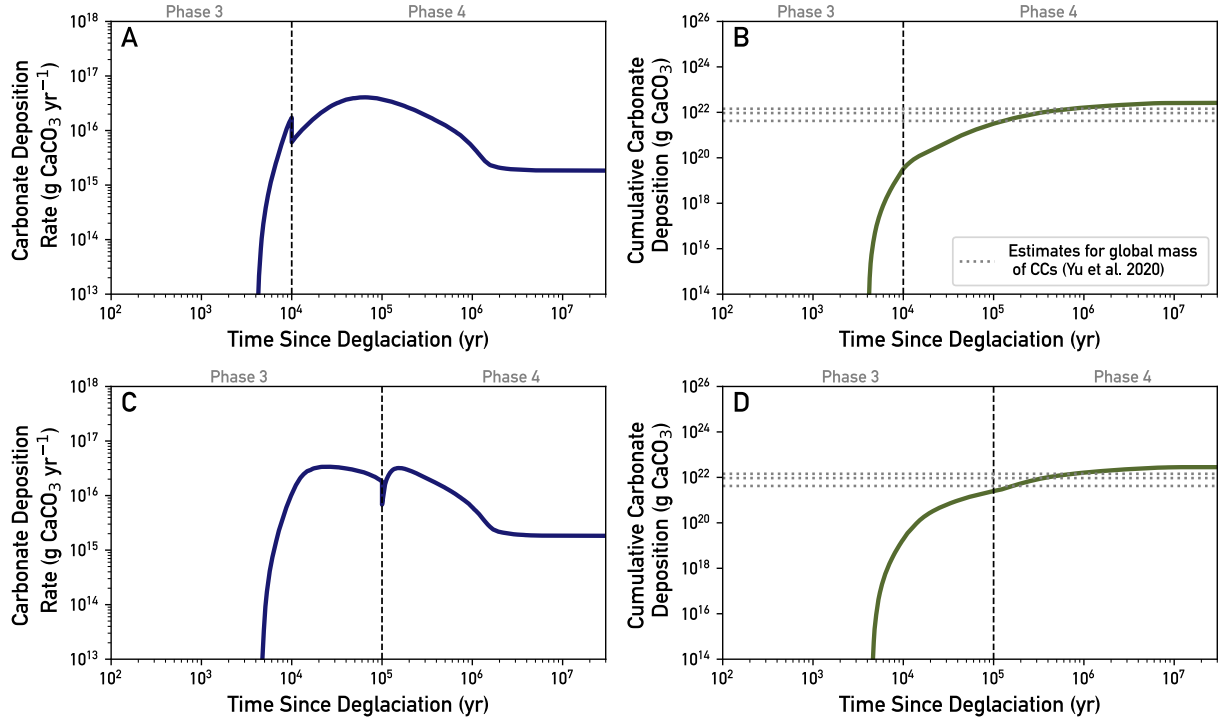


Figure 2-4: Carbonate deposition rate and cumulative carbonate deposition after deglaciation in terms of mass for different lifetimes of the stratified ocean. The end of the stratified ocean (Phase 3), t_{strat} , is indicated by the vertical dashed black lines. In **A** and **B**, $t_{strat} = 10^4$ years. In **C** and **D**, $t_{strat} = 10^5$ years. Horizontal dotted lines in **B** and **D** are minimum, median, and maximum estimates of the global mass of Marinoan cap carbonates from Yu et al. (2020): 4.2×10^{21} , 9.3×10^{21} , and 14.4×10^{21} g, respectively. The shaded regions are the 95% confidence intervals and the solid lines are the median model runs with randomly sampled parameters.

For context, post-glacial carbonate deposition peaks above 10^{17} g $\text{CaCO}_3 \text{ yr}^{-1}$, 2 orders of magnitude higher than modern carbonate deposition on continental shelves ($\sim 1.4 \times 10^{15}$ g $\text{CaCO}_3 \text{ yr}^{-1}$; Iglesias-Rodriguez et al., 2002). The post-glacial deposition rate is so high primarily because the saturation state in the meltwater layer reaches up to $\Omega = 70$, compared to $\Omega = 3\text{--}5$ at the surface of the modern ocean.

From the 95% confidence intervals for both values of t_{strat} , we predict that it took between 32 kyr and 591 kyr to produce the estimated minimum global mass of CCs (Fig. 2-4). In the median model runs, the time to deposit the CCs is 127 kyr and 162 kyr for $t_{strat} = 10^4$ and 10^5 yr, respectively. The timescales are similar despite differences in t_{strat} because the sources of alkalinity

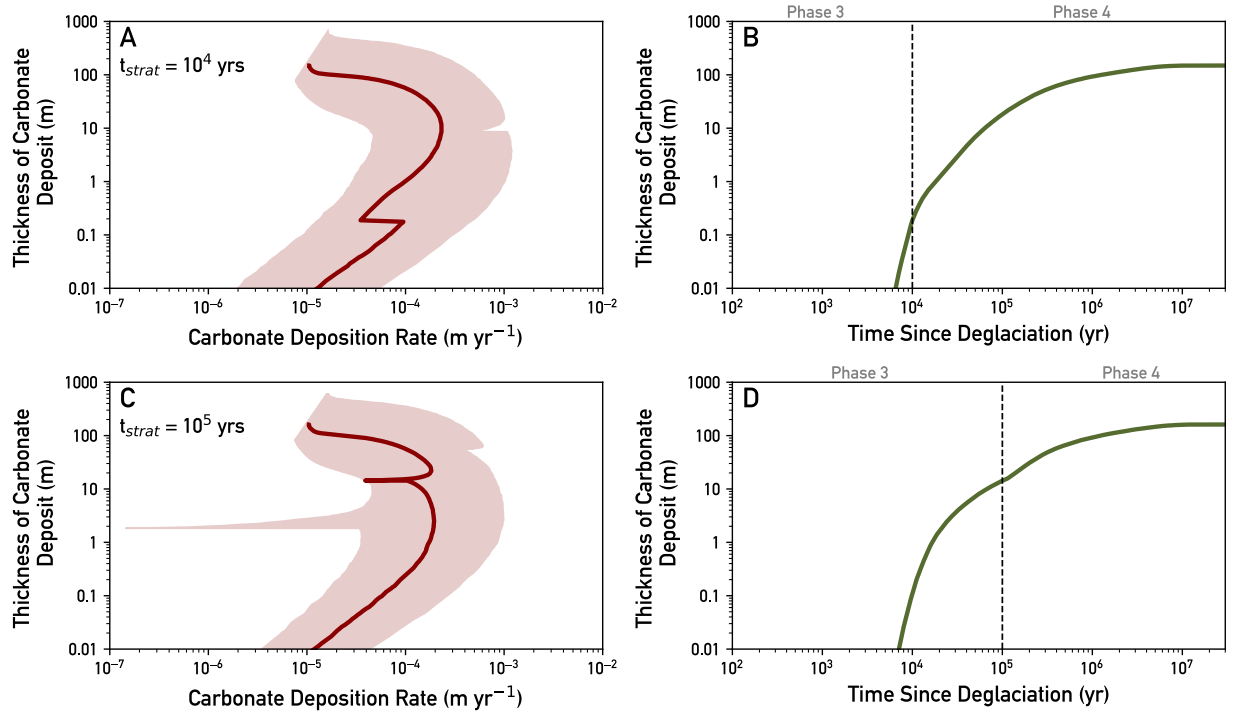


Figure 2-5: Carbonate deposition rate and cumulative carbonate deposition after deglaciation in terms of deposit thickness for different lifetimes of the stratified ocean. The end of the stratified ocean (Phase 3), t_{strat} , is indicated by the vertical dashed black line in **B** and **D**. In **A** and **B**, $t_{strat} = 10^4$ years. In **C** and **D**, $t_{strat} = 10^5$ years. The shaded regions are the 95% confidence intervals and the solid lines are the median model runs with randomly sampled parameters. Confidence intervals do not align in **A** and **C** because they are originally time-based but are converted into height-based here.

are the same: seafloor weathering during glaciation and continental weathering after glaciation. The alkalinity sources are the ultimate limiting factor for carbonate precipitation, and the timescale of deposition is set by the time it takes for them to saturate the whole ocean.

The proportion of the CCs deposited from the meltwater layer versus the well-mixed ocean depends on t_{strat} (Fig. 2-4). For $t_{strat} = 10^4$ years, the median total carbonate mass deposited in the meltwater layer is 3.3×10^{19} g, with 95% confidence interval of 3.3×10^{15} g to 1.4×10^{21} g. For $t_{strat} = 10^5$ years, the median is 2.5×10^{21} g and the 95% confidence interval is 3.2×10^{20} g to 9.4×10^{21} g. Most of the CCs are deposited after ocean mixing. Relative to the total carbonate mass

deposited in the first 5 Myr after deglaciation, 0.13% and 9.83% of the CCs were deposited in the meltwater layer in the median model runs with $t_{strat} = 10^4$ and 10^5 yr, respectively.

For more direct relevance to the geologic record, we convert the mass of carbonates into a deposit thickness (Fig. 2-5). For a rough comparison, we assume constant sedimentation rates and that the total carbonate mass is evenly spread over a surface area equal to 2 times the modern continental shelf area to account for post-glacial sea level rise (See Methods). This calculation is somewhat qualitative because the dynamics of the depositional environments on post- glacial Earth were complex and subject to regional variability (e.g. Creveling & Mitrovica, 2014; Irie et al., 2019). In the median model runs, the peak deposition rate in a globally averaged CC deposit occurs 10.8 m and 2.6 m upsection for $t_{strat} = 10^4$ and 10^5 yr, respectively. In the 95% confidence interval for $t_{strat} = 10^4$ years, < 0.001–8.12 m were deposited out of the meltwater layer. For $t_{strat} = 10^5$ years, the range is 1.84–53.68 m.

2.2.3 High-alkalinity meltwater scenario

In the nominal model results, carbonate deposition does not begin until at least ~1 kyr after deglaciation. In this depositional hiatus, continental weathering has not yet supplied enough alkalinity to raise the saturation state of the meltwater high enough for rapid carbonate precipitation. This occurs for two reasons: (1) we assume that the initial alkalinity of the glacial meltwater is low, estimated from modern glacial waters, and (2) we do not explicitly model the global deglaciation, where meltwater from continental ice sheets would have traversed rocky terrain before entering the ocean. In reality, as the Earth was deglaciating, the water from the continental ice sheets would have weathered some of the rock and probably caused the initial alkalinity of the meltwater to be higher than we nominally assume.

Coupled climate and ice-sheet models indicate that the deglaciation process lasted ~2 kyr, due to the ice-albedo instability (e.g. Hyde et al., 2000; Myrow et al., 2018). We use our silicate weathering parameterization to calculate the delivery of alkalinity from melting glaciers during these 2 kyr. We assume that $p\text{CO}_2$ is 0.1 bar and the surface temperature is 310 K during deglaciation. We fix the weatherability factor, $f_w = 1$, and then vary the empirical factors in their standard ranges. This results in a maximum alkalinity delivery rate of 4.73×10^{15} mol eq yr⁻¹ and a maximum meltwater alkalinity of 70,000 $\mu\text{mol eq kg}^{-1}$ when integrated over 2 kyr. This is 70–100 times higher than our previous meltwater alkalinity assumption of 700–1000 $\mu\text{mol eq kg}^{-1}$

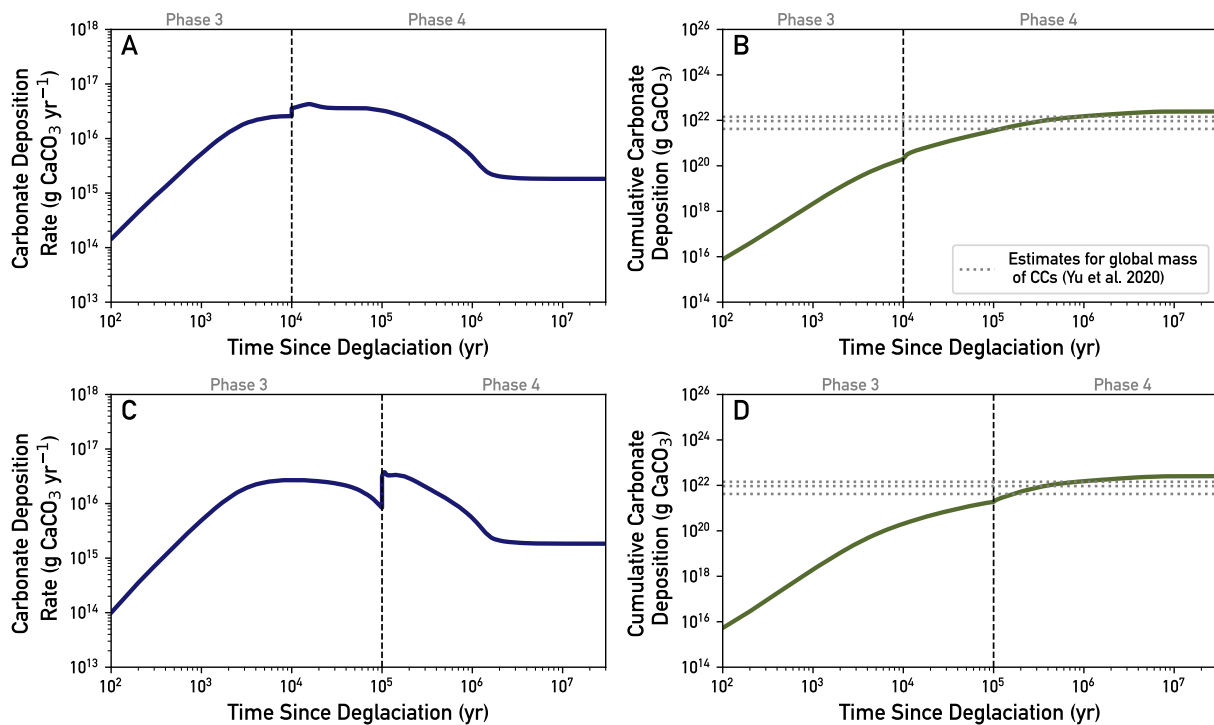


Figure 2-6: Post-glacial carbonate deposition by mass in the high-alkalinity melt- water scenario. The initial alkalinity of the meltwater in phase 3 is $70,000 \mu\text{mol eq kg}^{-1}$, compared to $700\text{--}1000 \mu\text{mol eq kg}^{-1}$ in the baseline case. The end of the stratified ocean (Phase 3), t_{strat} , is indicated by the vertical dashed black lines. In **A** and **B**, $t_{\text{strat}} = 10^4$ years. In **C** and **D**, $t_{\text{strat}} = 10^5$ years. Horizontal dotted lines in **B** and **D** are minimum, median, and maximum estimates of the global mass of Marinoan cap carbonates from Yu et al. (2020): 4.2×10^{21} , 9.3×10^{21} , and 14.4×10^{21} g, respectively. The shaded regions are the 95% confidence intervals and the solid lines are the median evolutions with randomly sampled parameters in 3000 model runs.

based on modern glacial meltwater. Moreover, the true value may be even higher because the land surface was likely highly weatherable after enduring millions of years of rock-grinding glacier movement. Here we test this scenario by running our model with the higher initial meltwater alkalinity of $70,000 \mu\text{mol eq kg}^{-1}$.

The meltwater layer rapidly saturates and carbonates begin precipitating immediately after deglaciation in this scenario (Fig. 2-6). Here, deposition starts 100 years after deglaciation, which is essentially instantaneous in our model, since 100 years is the minimum timestep in this phase. On the other hand, the total timescale of CC deposition is similar to the baseline case. This is

because the high-alkalinity melt-water scenario only adds alkalinity to the meltwater layer equivalent to 2 kyr of weathering, which is small relative to the 100 kyr timescale of full CC deposition in the baseline case.

Additionally, the meltwater layer is much less acidic in this scenario (Supplementary Fig. S2-4). In the baseline case, the pH of the meltwater layer starts at ~5 and then increases to ~7 after 100 kyr. In the high alkalinity scenario, however, the pH of the meltwater layer starts over 7 and reaches close to 10 in some cases. This is a consequence of inorganic carbon speciation: when all else is held equal, increased alkalinity causes increased pH.

2.2.4 Comparison to geologic evidence

Here we compare our model results to several lines of evidence in the Marinoan CCs, which refers to the combination of (1) the cap dolostones, which are uniform in character, ubiquitous, and sit directly on top of Marinoan glacial deposits, and (2) the overlying limestones, which are more variable in character and thickness, and sit on top of the dolostones. Our conclusions are therefore most applicable to the Marinoan glaciation. However, some results may generalize to the Sturtian glaciation, which has CCs with notable differences from the Marinoan, such as being often far thinner or absent and generally limestone, not dolostone.

Our results are consistent with the global mass and thickness of the Marinoan CCs. As shown in Fig. 2-4, we find that enough alkalinity is generated in the post-glacial aftermath to explain the estimated global mass of CCs. The alkalinity source is a combination of continental and seafloor weathering, described above. Considering deposit thickness, we find that the observed global average CC thickness, ~11 meters (Yu et al., 2020), is generally precipitated in under 200 kyr, while thicker sections can be deposited on longer timescales in model runs further from the median evolution (Fig. 2-5). This is consistent with the geologic record because there was likely significant regional variability in depositional environments (e.g. Creveling & Mitrovica, 2014; Irie et al., 2019) and some CCs are hundreds of meters thick, such as the Noonday Formation (e.g. Petterson et al., 2011).

The timescale of CC deposition is constrained by three general types of evidence that have not been reconciled: radiometric dating, paleomagnetism, and sedimentology (Table 2-1). Although useful for determining absolute ages, the radiometric dating measurements cannot give a statistically significant estimate for the timescale of CC deposition due to the measurement

uncertainty and scattered locations in different CCs. The presence of multiple paleomagnetic reversals in multiple sections is evidence for a depositional timescale on the order of 10^5 to 10^6 years, with uncertainty due to the unknown frequency of polarity reversals in the Neoproterozoic and the fidelity of the paleomagnetic data and their interpretations. Marinoan CCs also have unusual, heavily debated sedimentary structures. The standard Snowball hypothesis (Hoffman et al., 2017) suggests that features like giant wave ripples and sheet-crack cements are present in CCs as a result of rapid deglaciation, implying depositional timescales of $\sim 10^3$ to 10^4 years (e.g. Shields, 2005; Allen & Hoffman, 2005; Hoffman & Macdonald, 2010). However, these features have instead been interpreted as tepees and bedding expansion features that imply prolonged depositional timescales of $\geq 10^5$ years (e.g. Spence et al., 2016; Fairchild & Kennedy, 2007; Wallace et al., 2019).

Our results help reconcile the differing lines of evidence for the depositional timescale of the CCs.

First, we predict that the minimum global CC mass is deposited in 32 to 591 kyr in our nominal 95% confidence intervals. This result suggests that the global timescale of CC deposition was intermediate, with endmember scenarios for extremely rapid or prolonged deposition due to regional variability corresponding to model runs outside of the 95% confidence interval. So, we suggest that the sedimentary structures may reflect deposition on both short and long timescales. On one hand, deposition on timescales below 30 kyr may have occurred in regions with enhanced alkalinity delivery, where deposition can start as fast as 100 years after deglaciation (Fig. 2-6). On the other hand, deposition on timescales over 500 kyr can be reconciled by the fact that our modeled deposition rates remain higher than the baseline for over 2 Myr following deglaciation (Fig. 2-4). Considering the regional variability, it is likely that the overlying limestones in several sections experienced prolonged deposition in favorable environments—i.e., the Brazil, Oman, and Australian CCs—thus explaining the presence of the paleomagnetic reversals and some of the sedimentary structures.

Second, we predict that the peak carbonate deposition rate is achieved on timescales of 10^4 yrs after deglaciation (Figs. 2-4 and 2-6). We suggest that this can help reconcile evidence of both rapid and prolonged deposition. In our interpretation, the 10^3 – 10^4 yr timescale of CC deposition inferred from some of the sedimentary structures is an underestimate because it is assumed that the peak deposition rates lasted for the entirety of CC deposition. Perhaps some of the sedimentary

structures indeed indicate peak deposition rates, but they did not last for the entirety of CC deposition, creating other sedimentary structures and recording paleomagnetic reversals as a result of longer deposition. This idea is consistent with our model results and a recent analysis of the Svalbard Marinoan CC (Fairchild et al., 2023), which both indicate peak deposition rates occurring shortly after deglaciation and then declining over time. The record of peak deposition rates can be further analyzed by comparing the distribution of sedimentary structures with respect to height to our qualitative deposition rates as a function of height (Fig. 2-5).

Third, our results are consistent with the contact between glacial deposits and CCs. In all Marinoan sections, there is sharp contact between CC and glacial unit (e.g. Hoffman et al., 2017), suggesting that the CCs precipitated during and immediately after deglaciation, with no hiatus (e.g. Domack & Hoffman, 2011). In the high-alkalinity meltwater scenario (Fig. 2-6), we show that there is no depositional hiatus (i.e. no more than ~100 years). In the baseline scenario with low initial meltwater alkalinity (which is biased toward slow deposition relative to the high-alkalinity meltwater scenario), the hiatus only lasts ~1 to ~10 kyr, which may be consistent with the evidence depending on sedimentation rates. Our model does not explicitly treat the dynamics of the deglaciation with respect to changing meltwater volume, regional variability, and weathering rates, so the two model scenarios cannot distinguish between syn-deglacial or post-deglacial deposition, but they are consistent with the general lack of a depositional hiatus, which has been a longstanding problem for CC explanations involving post-glacial continental weathering as an alkalinity source (see Yu et al., 2020).

Our results are also consistent with the general stratigraphy of the Marinoan CCs. Our model shows that CC deposition in the meltwater layer (Phase 3) is caused by alkalinity supply during and immediately after deglaciation, which is consistent with the transgressive nature of the Marinoan cap dolostones, deposited as sea levels rose (Hoffman & Schrag, 2002). Subsequent CC deposition in the well-mixed ocean (Phase 4) is consistent with the more variable and prolonged deposition of the overlying limestones, as outlined in the “cap limestone” phase of Shields (2005); here we have shown it is valid in a global geochemical model.

Several lines of geochemical evidence probe Marinoan post-glacial ocean stratification. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in seawater is raised by continental weathering and lowered by hydrothermal input (e.g. Davis et al., 2003; Vance et al., 2009; Allègre et al., 2010). Several studies (Liu et al., 2013, 2014, 2018; Wei et al., 2019) have measured $^{87}\text{Sr}/^{86}\text{Sr}$ along CC sections and found that they

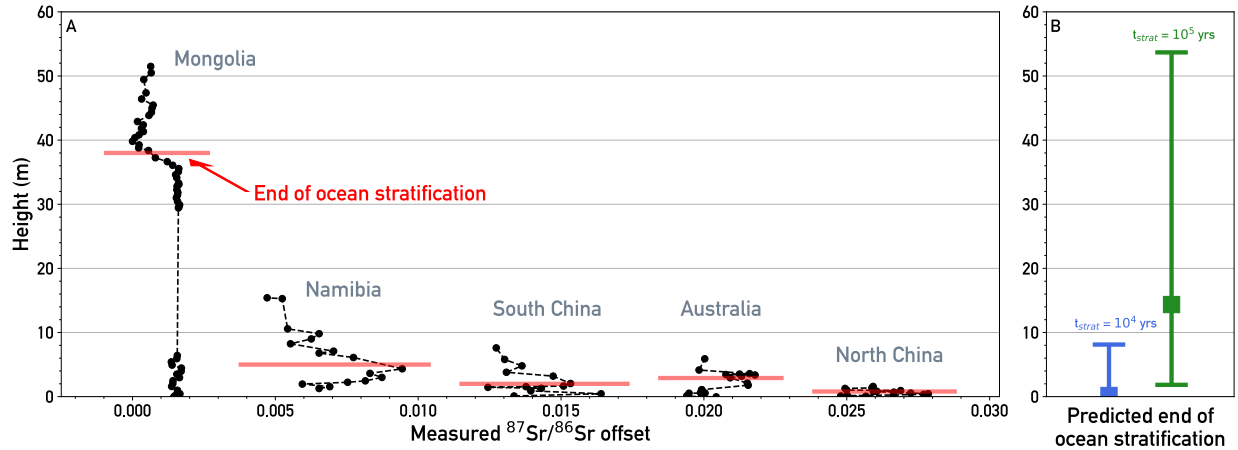


Figure 2-7: Comparison of measured strontium isotopes and model results for determining the end of post-glacial ocean stratification. **A** Measured $^{87}\text{Sr}/^{86}\text{Sr}$ offsets upsection in 5 cap carbonates. The red lines are the roughly inferred heights in the cap carbonate at which ocean stratification ends according to the mixing models of those who obtained and analyzed the data: Liu et al. (2014, 2018; Mongolia), Liu et al. (2013; Australia), and Wei et al. (2019; Namibia, South China, and North China). Below the red lines, the cap carbonates were precipitated out of mostly glacial meltwater with elevated, continentally influenced $^{87}\text{Sr}/^{86}\text{Sr}$. Above these lines, the cap carbonates were precipitated out of mostly ocean water with lower, hydro-thermally influenced $^{87}\text{Sr}/^{86}\text{Sr}$. **B** Model predictions for the height at which ocean stratification ends in the baseline scenario. These are effectively predictions for where the red lines should be. Results assuming $t_{\text{strat}} = 10^4$ years are on the left in blue, and assuming $t_{\text{strat}} = 10^5$ years are on the right in green. The filled squares are the median model predictions and the error bars are the 95% confidence interval corresponding to Fig. 2-5.

show a stepwise decrease from high to low values upsection, indicated by the red lines in Fig. 2-7a. This decrease suggests that (1) first, CCs precipitate out of a glacial meltwater layer with elevated $^{87}\text{Sr}/^{86}\text{Sr}$ due to massive continental weathering, and then (2) second, the CCs precipitate out of a well-mixed ocean which has a lower $^{87}\text{Sr}/^{86}\text{Sr}$ that is closer to the typical modern ocean value. Thus, the height at which this stepwise decrease occurs should reflect the point at which the post-glacial ocean becomes well-mixed. This interpretation is further supported by other Ca, Mg, and Sr isotope measurements (Ahm et al., 2019; Wei et al., 2019; Wang et al., 2023).

Our results are consistent with $^{87}\text{Sr}/^{86}\text{Sr}$ trends in CC sections. In Fig. 2-7b, we show our model results for the CC height at which ocean stratification ends. In the case with $t_{\text{strat}} = 10^4$ years, 0.18 meters of the CCs are deposited in the stratified ocean in the median model run; with $t_{\text{strat}} = 10^5$ years, this value increases to 14.36 meters. The 95% confidence intervals of these two cases incorporate the full range of Sr-inferred mixing heights. Our model is global, so it is likely that different places experienced different timescales of ocean stratification. For example, we would expect that the Mongolian deposit experienced 10^5 years or more of ocean stratification, the North China deposit experienced 10^4 years of ocean stratification or even less, and the Namibia, South China, and Australia deposits experienced an intermediate time between 10^4 and 10^5 years.

2.3 Discussion

In the above sections, we have presented a global model for the deposition of CCs after the Marinoan glaciation. This model is consistent with geologic evidence regarding the global mass and thickness of the CCs, the timescale of their deposition, and their deposition in a post-glacial stratified ocean. Our results could be summarized as the “Seafloor weathering-Continental weathering-Ocean Mixing (SCOM)” mechanism for CC deposition (Fig. 2-8).

The SCOM mechanism has 3 phases. First, seafloor weathering in high CO_2 , acidic conditions during the glaciation supplies alkalinity to the sub-glacial ocean. Second, intense continental weathering supplies alkalinity to the post-glacial meltwater layer and CCs begin precipitating. Third, the eventual mixing of the meltwater layer and the deep ocean supplies alkalinity to the surface and CCs continue precipitating.

The SCOM mechanism explains Marinoan CC deposition on a global scale and was likely subject to regional variability. For example, post-glacial sea level rise was likely highly regionally variable (e.g. Creveling & Mitrovica, 2014; Irie et al., 2019), runoff rates from continental weathering depend on regional topography, and the duration of ocean stratification likely depends on regionally varying currents. These important regional distinctions explain how individual CCs could deviate from our median model predictions, but even the most unique CCs are broadly consistent with our 95% confidence intervals. We therefore propose that Marinoan CC deposition on a global scale was primarily driven by the SCOM mechanism.

The SCOM mechanism draws from several previous hypotheses for CC deposition. In the plumeworld hypothesis (Shields, 2005), it was proposed that CCs rapidly precipitate out of a stable

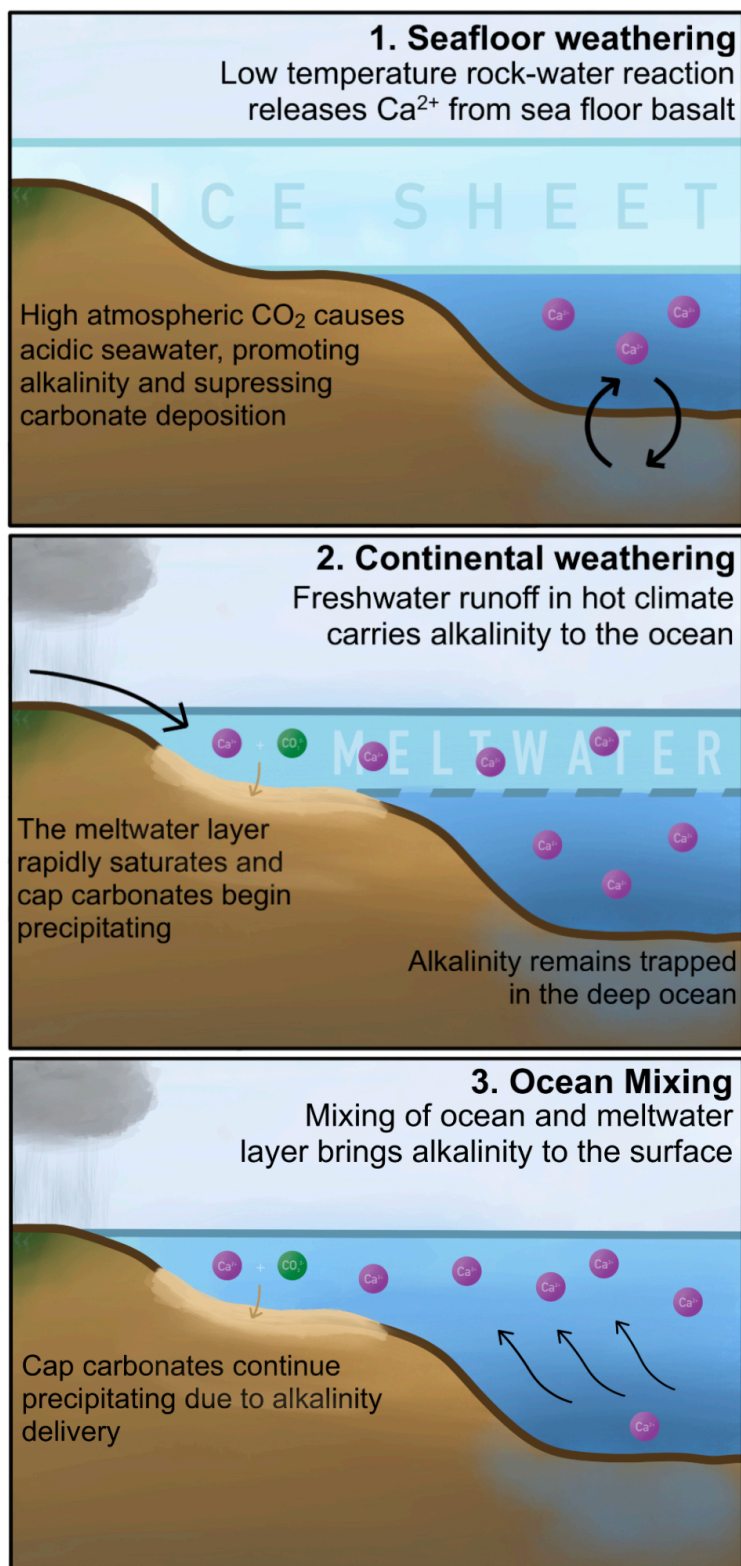


Figure 2-8: Schematic diagram of the “Seafloor weathering—Continental weathering—Ocean Mixing (SCOM)” mechanism for cap carbonate deposition.

glacial meltwater layer with alkalinity generated from a variety of sources. Many others have hypothesized that rapid continental weathering would have supplied the necessary alkalinity to the ocean to generate the CCs (e.g. Hoffman & Schrag, 2002; Higgins & Schrag, 2003). Deep ocean upwelling of alkalinity—derived from the degradation of organic matter, not seafloor weathering—has also been suggested (Grotzinger & Knoll, 1995; Knoll et al., 1996). While these hypotheses are plausible and have been extensively studied individually, they struggle to explain the timescale of deposition, the required alkalinity source, and other geologic evidence (Yu et al., 2020). With the SCOM mechanism, we self-consistently combine and refine these hypotheses to show that it is consistent with the geologic evidence on a global scale. The key improvements presented here include the previously unconsidered alkalinity source of seafloor weathering, the explicit calculation of aqueous chemistry in the glacial meltwater layer and subsequent mixed ocean, and the rigorous calculation of the geologic carbon cycle.

There are several caveats and limitations on the SCOM mechanism from both the geologic record and our modeling approach. First, transitions between phases are imposed in our model due to their complexity; for example, the deglacial transition would require a careful treatment of ice sheet dynamics and climate, and the ocean mixing transition would require GCM-like treatment of 3D ocean dynamics. We do, however, provide a sensitivity study to explore the effect of a prolonged deglaciation (Supplementary Section C2). In the most extreme endmember, this may increase the time required for CC deposition by up to 90 kyrs, but does not change our main conclusions. Further discussion of forcing model transitions and sensitivities are found in Supplementary Section C. Second, our model is global, and does not explicitly capture regional behavior, which is important for interpretation of individual CCs. Third, compilation of the global CC record is subject to variability in interpretation and measurement, which may cause biases (e.g., toward thicker CC sections than are actually present or toward over interpretation of paleomagnetic data). Future studies on the model transitions, the implications for regional behavior, and improved global interpretation of the CC record can improve or test the SCOM mechanism and are encouraged.

There are many other lines of geologic evidence that can be used to test the SCOM mechanism, including ocean pH proxies of boron isotopes (e.g. Kasemann et al., 2010) and rare Earth element distributions (Lin & Catling, 2024), styles of carbonate deposition within CCs, sedimentation rates and carbonate concentrations as a function of height within CCs, developing

proxies that probe alkalinity in the subglacial ocean, and more radioisotope dates from multiple CCs (preferably at the top and bottom of the same section). Additionally, comparisons to the record of Sturtian CCs may provide insights into how the two major Cryogenian glaciations differed (e.g., the effect of disparate glacial durations) and their implications on the evolution of Earth's surface. In this work we have shown that the SCOM mechanism is broadly consistent with the global characteristics of Marinoan CCs, but future studies making more detailed, regional comparisons to the above evidence are suggested.

2.4 Methods

We model the evolution of the carbon content and marine alkalinity in Earth's atmosphere and ocean as it is subject to processes of the geologic carbon cycle before, during, and after a global glaciation event. Our model is based on previous geologic carbon cycle models that have been rigorously validated against Earth's last 100 Myr and applied as far back as 4 Ga (Krissansen-Totton & Catling, 2017; Krissansen-Totton et al., 2018). In order to capture the unique climate of the Cryogenian glaciations, we modify the model accordingly and separate it into 4 distinct configurations (Fig. 2-1): the background Neoproterozoic phase, a syn-glacial phase, a post-glacial stratified ocean phase, and a post-glacial well-mixed ocean phase.

Key aspects of the model are described below. Additional information is in the Supplementary Material. The calculation of the baseline carbon cycle fluxes, aqueous chemistry, and climate is in Supplementary Section A. Calibration and benchmarking of the model against the modern and post-glacial Earth is in Supplementary Section B. Further description of transitions between model phases and a sensitivity study are in Supplementary Section C.

2.4.1 Phase 1: Background Neoproterozoic

The goal of phase 1 is to find the background climate in the Neoproterozoic era before any glaciation events occur. In this phase, there are two model reservoirs: one for the combined atmosphere and ocean, and one for water in the pore-space of the seafloor. The pore-space reservoir captures the chemistry of water circulating through the upper portion of the oceanic crust, which is important for investigating the impact of seafloor weathering. The time evolution of carbon chemistry in these reservoirs is described by the following set of equations:

$$\begin{aligned}
\frac{dC_o}{dt} &= \frac{1}{M_o} (-J(\text{DIC}_o - C_p) + V_{\text{total}} + W_{\text{carb}} - P_{\text{shelf}}), \\
\frac{dA_o}{dt} &= \frac{1}{M_o} (-J(A_o - A_p) + 2W_{\text{sil}} + 2W_{\text{carb}} - 2P_{\text{shelf}}), \\
\frac{dC_p}{dt} &= \frac{1}{M_p} (-J(C_p - \text{DIC}_o) - P_{\text{pore}}), \\
\frac{dA_p}{dt} &= \frac{1}{M_p} (-J(A_p - A_o) + 2W_{\text{sea}} - 2P_{\text{pore}}).
\end{aligned} \tag{2.1}$$

Here, C is the concentration of inorganic carbon with units mol C kg^{-1} and A is the carbonate alkalinity with units mol eq kg^{-1} where the subscript o and p indicate the ocean-atmosphere and pore-space reservoirs, respectively. C_p is equal to the dissolved inorganic carbon (DIC) of the pore-space. C_o is the sum of DIC in the ocean and the carbon content in the atmosphere, given by $C_o = \text{DIC}_o + \text{pCO}_2 \times s$, where s is a scaling factor equal to the total number of moles C per bar in the atmosphere divided by the mass of the ocean, $s = 1.8 \times 10^{20}/M_o$, and pCO_2 is in bar. We assume that the masses of the ocean and pore-space water are equal to their modern values, respectively given by $M_o = 1.35 \times 10^{21} \text{ kg}$ and $M_p = 1.35 \times 10^{19} \text{ kg}$ (Caldeira, 1995). J is the water mass flux between the deep ocean and pore-space, which has been estimated by balancing crustal heat fluxes: $J = 0.6\text{--}2 \times 10^{16} \text{ kg yr}^{-1}$ (Coogan & Gillis, 2018); this is equivalent to the entire ocean circulating through the pore space every 70 to 250 kyrs.

The remaining terms are fluxes of carbon (mol C yr^{-1}) and alkalinity (mol eq yr^{-1}) due to processes of the geologic carbon cycle: V_{total} is the sum of volcanic outgassing from subaerial and mid-ocean ridge sources, W_{carb} is continental carbonate weathering, W_{sil} is continental silicate weathering, W_{sea} is seafloor weathering, P_{shelf} is carbonate precipitation on the continental shelf, and P_{pore} is carbonate precipitation in the pore-space. Calculation of these fluxes is in Supplementary Section A.

2.4.2 Phase 2: Syn-glacial

Starting from the background Neoproterozoic climate, we impose a glaciation event. In the syn-glacial phase, we calculate the time-dependent evolution of the geologic carbon cycle until a threshold for deglaciation is reached. The equations in (1) are still the governing equations of this phase, but they are modified in several ways, described below.

With the presence of a large global ice sheet, sea level should fall significantly and the global mass of the liquid ocean should decrease. Hoffman et al. (2017) estimate ocean volume change during glaciation by summing continental and sea ice volumes under various dust accumulation rates and $p\text{CO}_2$ levels (Goodman & Strom, 2013; Benn et al., 2015). We explore the range of estimates and assume a decrease in ocean volume of 10% to 30% relative to the modern ocean. To calculate the immediate increase in dissolved species concentration from a shrinking ocean, we assume that no conservative cations (e.g., Ca^{2+}) are trapped in the ice during freezing. Thus, the ocean alkalinity and dissolved inorganic carbon increase relative to the background Neoproterozoic values by the same relative proportion that the ocean volume decreases.

The 2D and 3D ocean circulation models of Ashkenazy et al. (2013, 2014) show that the sub-glacial ocean should have had vigorous convective mixing under the ice cover, causing it to be isothermal and chemically well-mixed. Thus, we continue to use a single box in our model to represent the ocean. We assume that the syn-glacial ocean had a uniform and constant temperature of 269.5 K, regardless of $p\text{CO}_2$, which is indicated by ocean models with complete ice cover (Ashkenazy et al., 2013, 2014). This assumption is justified for scenarios with incomplete ice cover as well since global averaged surface temperatures are predicted to be below 269.5 K (Hoffman et al., 2017).

We nominally assume that the atmosphere and sub-glacial ocean were in equilibrium with respect to inorganic carbon speciation and aqueous chemistry during the glaciation. Several lines of evidence support this assumption: (1) It has been shown that atmosphere-ocean equilibrium with respect to CO_2 can be reached on million year time-scales with only 10^3 km^2 open ocean (Le Hir et al., 2008). Areas of open ocean likely exceeded this threshold via geothermal heat production and lava flows alone, as the modern area of emerged active hydrothermal systems ($1.5 \times 10^6 \text{ km}^2$) is 3 orders of magnitude greater than what is required for equilibration (Dessert et al., 2003). (2) Sedimentological evidence, oxygen isotopes, and sulfur isotopes of the Svalbard Marinoan glacial deposits indicate that ice sheets were sensitive to orbital forcing as $p\text{CO}_2$ rose, creating extensive patches of open water (Mitchell et al., 2021). (3) Geochemical measurements of carbon, nitrogen, and iron in the Nantuo Formation suggest there was aerobic nitrogen cycling in surface waters and swaths of open ocean at mid-latitudes during glaciation (Song, 2023). (4) Approximately 25% of global volcanic outgassing of CO_2 occurs at underwater mid-ocean ridges on the modern Earth (Catling & Kasting, 2017, p. 203). CO_2 bubbles from this volcanism would directly equilibrate

with the subglacial ocean regardless of ocean-atmosphere equilibrium. Combined, this evidence indicates that a chemically isolated atmosphere and ocean is unlikely.

In order to determine the minimum timestep for modeling this phase, we must estimate how long it takes for the atmosphere-ocean equilibrium to be reached. Le Hir et al. (2008) showed that only 3000 km³ of open ocean is required for full ocean CO₂ diffusion on the order of several millions of years. When combined with the efficient mixing of the subglacial ocean, it is reasonable to assume that equilibrium would be reached on timescales similar to the modern ocean. We conservatively assume equilibration takes 100 times longer than the modern time, and thus our minimum model timestep during this phase is 100,000 years.

During widespread ice sheet coverage on land, continental weathering rates are expected to have been significantly reduced or completely stopped. We nominally assume that there was no continental weathering during glaciation; however, we do test our model with the incorporation of low, constant weathering rates calculated in Lan et al. (2022). Their models estimate that the continental silicate weathering rate was $3.3\text{--}22 \times 10^8 \text{ mol eq yr}^{-1}$ and that the continental carbonate weathering rate was $8\text{--}18 \times 10^8 \text{ mol C yr}^{-1}$, both of which are several orders of magnitude lower than their modern rates of $\sim 8 \times 10^{12} \text{ mol eq yr}^{-1}$ (Moon et al., 2014) and $\sim 11 \times 10^{12} \text{ mol C yr}^{-1}$ (Hartmann et al., 2009), respectively. Our parameterization of seafloor weathering and pore-space carbonate deposition remains unchanged through this time period.

There should be few neritic environments for carbonate deposition in the syn-glacial ocean. Sea level is expected to have dropped by over 500 m during glaciation due to the size and extent of the ice sheets (Liu & Peltier, 2013), so the syn-glacial sea level should be too low to support carbonate deposition on continental shelves given that they are generally not deeper than 200 m on modern Earth. However, evidence has been found for syn-glacial carbonate deposition during the Sturtian glaciation (Hood et al., 2022), indicating that some carbonate depositional environments must have persisted through global glaciation, potentially on the continental slopes. This motivates us to allow carbonate deposition during glaciation. We continue to use the baseline parameterization to calculate the deposition rate, but we reduce the ratio of syn-glacial continental shelf area to modern ($A_{shelf}/A_{shelf}^{mod}$) to account for the decrease in depositional environments. On the modern Earth, the surface area of continental shelves is $3.22 \times 10^7 \text{ km}^2$ and of continental slopes is $1.96 \times 10^7 \text{ km}^2$ (Harris et al., 2014); the removal of continental shelves results in a 62%

decrease in depositional area. Thus, we explore a range of $A_{shelf} / A_{shelf}^{mod}$ values from 0.3 to 0.5 to simulate the elimination of deposition on continental shelf environments during glaciation.

2.4.3 Phase 3: Post-glacial stratified ocean

After the syn-glacial phase ends, the model transitions to the post-glacial stratified ocean phase. This phase is time-dependent and spans from the end of the glaciation until the ocean becomes well-mixed.

To account for the post-glacial ocean stratification, we alter the Neoproterozoic background model for atmosphere and ocean chemistry by splitting the whole-ocean box into two boxes: one box contains the atmosphere and meltwater layer, and the other contains the deep ocean. We follow Boudreau et al. (2019) to design the basic framework of the 2-box model. The time evolution of carbon chemistry is now described by the following set of equations:

$$\begin{aligned}
 \frac{dC_s}{dt} &= \frac{1}{M_s} (-K(DIC_s - C_d) + V_{air} + W_{carb} - P_{shelf} - O_{sink}), \\
 \frac{dA_s}{dt} &= \frac{1}{M_s} (-K(A_s - A_d) + 2W_{sil} + 2W_{carb} - 2P_{shelf}), \\
 \frac{dC_d}{dt} &= \frac{1}{M_d} (-K(C_d - DIC_s) - J(C_d - C_p) + V_{ridge} + O_{sink}), \\
 \frac{dA_d}{dt} &= \frac{1}{M_d} (-K(A_d - A_s) - J(A_d - A_p)), \\
 \frac{dC_p}{dt} &= \frac{1}{M_p} (-J(C_p - C_d) - P_{pore}), \\
 \frac{dA_p}{dt} &= \frac{1}{M_p} (-J(A_p - A_d) + 2W_{sea} - 2P_{pore}).
 \end{aligned} \tag{2.2}$$

The model now tracks carbon and alkalinity in three boxes: the surface ocean meltwater layer (s), the deep ocean (d), and the pore- space (p). C is still the concentration of inorganic carbon and A is still carbonate alkalinity. C_s contains the sum of the DIC in the surface ocean and the carbon in the atmosphere, $C_s = DIC_s + pCO_2 \times s$, and s is adjusted to reflect the mass of the surface ocean meltwater layer, $s = 1.8 \times 10^{20}/M_s$. J is the water mass flux between the deep ocean and pore-space, and is unchanged from the Neoproterozoic background configuration. K is the water mass flux between the surface and deep ocean. The volcanic outgassing flux is now split into a subaerial component (V_{air}) and mid-ocean ridge component (V_{ridge}), which are 75% and 25% of

the total volcanic flux, respectively (Catling & Kasting, 2017, p. 203). Finally, O_{sink} is the flux of sinking organic carbon from the surface to the deep ocean.

We assume that the deep ocean retains the same DIC and alkalinity as the final results from the sub-glacial ocean in phase 2. On the other hand, we must make assumptions about the initial chemical properties of the glacial meltwater. To determine the alkalinity, we use compositional measurements of modern glacial meltwater, compiled in Brown (2002). The compilation includes 22 different measurements of glacial meltwater from around the world, including both land and sea glaciers. The average alkalinity from the minimum and maximum bounds of these measurements is 700-1000 $\mu\text{mol eq kg}^{-1}$. We take this as the starting alkalinity for the post-glacial surface ocean. We then assume that the meltwater is immediately equilibrated with the atmosphere to calculate the DIC.

We assume the total post-glacial ocean mass is equal to the modern day ocean mass, as we did in phase 1. This assumption is justified because modern Earth's glaciers are responsible for only $\sim 2\%$ of the total water budget (Pilson, 2012), so even if they were completely melted in the post-glacial hothouse climate they would not significantly change the mass of the ocean. The mass of the meltwater layer is 10–30% of the global ocean mass, consistent with the ice volume in phase 2. The deep ocean makes up the rest of the total mass.

We assume the glacial meltwater layer remains chemically distinct from the deep ocean for a variable amount of time after deglaciation. We assume the stratification lasts for $t_{strat} = 10^4$ or 10^5 years, consistent with 1D and 3D models of the post-glacial ocean (Yang et al., 2017; Ramme & Marotzke, 2022). These models form the basis for the assumptions we make to simulate the post-glacial ocean. First, we nominally assume that there is no mixing between the meltwater layer and the deep ocean ($K = 0$) during stratification. Second, we assume that the meltwater layer is in thermal equilibrium with the surface, as the melting glacial water is quickly heated at the surface before sinking deeper into the layer. Third, we assume that the deep ocean temperature warms linearly during the time of stratification. As is shown in the models, the ocean eventually recovers to a well-mixed state with a surface temperature for which our baseline deep ocean temperature parameterization applies. Thus, the deep ocean temperature (T_d) evolution is described by

$$T_d = 269.5 + \frac{t}{t_{strat}} (a_{grad} T_s + b_{int} - 269.5), \quad (2.3)$$

where 269.5 K is the temperature of the sub-glacial ocean, t is the time after glaciation, and the term in the parenthesis is the difference between the deep ocean temperature calculated via the baseline parameterization and the sub-glacial ocean temperature.

The minimum timestep for this phase is set by the time it takes for chemical equilibrium to be reached between the meltwater layer and the atmosphere. We expect this to be shorter than the modern timescale for several reasons. First, the meltwater originates at the surface in small parcels as it melts. We expect that the meltwater should reach atmospheric equilibrium as soon as it is produced due to the high surface area to volume ratio of the parcels and their direct exposure to the atmosphere. Second, the meltwater layer contains only the upper portion of the ocean. Mixing at the surface is more vigorous than deep ocean mixing due to e.g. wind-driven perturbation and should lead to faster equilibration. This mixing is enhanced when paired with an estimated 22% increase in runoff relative to modern (Le Hir et al., 2009). Third, and most importantly, there is simply less water to equilibrate. The meltwater layer has a water mass that is 10-30% of the modern ocean. Combining these arguments, we indeed assume that equilibration in the meltwater layer is faster than in the modern ocean. We nominally assume this equilibration happens in 100 years, which is the minimum allowable timestep for phase 3.

We apply our baseline continental weathering parameterizations to the post-glacial environment. The post-glacial environment likely had a high CO₂ atmosphere, leading to high surface temperatures and a rapid hydrologic cycle. Le Hir et al. (2009) investigated the post-glacial climate using the FOAM General Circulation Model and the WITCH weathering model to estimate continental weathering rates as a function of pCO₂. As shown in Supplementary Section B, our standard continental weathering parameterization aligns with and encompasses the rates from the more detailed models in Le Hir et al. (2009). The spread in our derived rates is mainly a product of the weatherability factor, f_w , which was varied from 0.5 to 1.5. Narrowing this range can more closely align our predicted rates with those from Le Hir et al. (2009) but may not be justified given all the uncertain factors that determine f_w .

We apply the baseline carbonate deposition parameterization, which was originally developed for the Neoproterozoic pre- and post-glacial climates (Ridgwell et al., 2003). The post-glacial shelf area relative to modern is needed in order to apply this parameterization. In the post-glacial climate, the eustatic sea level should be higher in general due to total ice melting and thermal expansion (e.g. Ramme & Marotzke, 2022), but regional-scale sea level change is highly

variable (Creveling & Mitrovica, 2014). If all of the ice on modern Earth was melted, it would result in at least 60 m of global sea level rise (Frederikse et al., 2020). Sea level rise due to thermal expansion in the post-glacial hothouse climate is predicted to be up to 8 m (Ramme & Marotzke, 2022). Based on modern Earth’s hypsometry (Eakins & Sharman, 2012), a 70 m rise in sea level would cover about $1.5 \times 10^7 \text{ km}^2$ of land, which is equivalent to $\sim 50\%$ of the area of modern continental shelves (Harris et al., 2014). Using this as the basis for our calculation, post-glacial shelf area would have been 1.5 times larger than the modern area. Thus, we explore the range of values $A_{shelf} / A_{shelf}^{mod} = 1 - 2$.

We nominally assume that all carbonate precipitation chemistry is based on calcite and aragonite. Post- and syn-glacial snowball Earth carbonates are frequently dolomitic in composition; however, recent isotopic evidence suggests the cap carbonates were deposited as calcium carbonate and later altered to dolomite via marine diagenesis (Ahm et al., 2019). Furthermore, a similar modeling study (Hood et al., 2022) shows that the geochemical evolution of the ocean during and after the Sturtian glaciation is not sensitive to the difference in carbonate chemistries based on using calcite, magnesite, or dolomite as the representative carbonate mineral. Thus, we believe our assumption is justified for modeling the large-scale features of the geologic record such as the total mass and depositional timescale of the Cryogenian carbonates.

Because we have split the ocean box into surface and deep components, we now include an organic carbon export flux from the surface ocean to the deep ocean, following Boudreau et al. (2019). The modern global rate of organic carbon export is on the order of 100 Tmol yr^{-1} (Pilson, 2012). We expect carbon export in the post-glacial ocean to be greatly diminished for two reasons: (1) total biomass in the Precambrian era should have been less than in the modern day, and (2) the abrupt swings of temperature, ocean pH, and unfrozen ocean area should have exterminated a large portion of existing biomass. Nevertheless, we explore a range of values for carbon export in the post-glacial ocean: $O_{sink} = 50\text{--}200 \text{ Tmol yr}^{-1}$. We assume that all carbon exported from the surface is regenerated in the deep ocean.

2.4.4 Phase 4: Post-glacial well-mixed ocean

After the post-glacial stratified ocean phase is terminated, the model transitions to the post-glacial well-mixed ocean phase. This phase is time-dependent and spans from the end of the stratified ocean until the background climate state is recovered. The model configuration in phase 4 is almost

identical to phase 1. The only difference is the increase in assumed shelf area due to sea level rise, described in phase 3. Phase 4 is terminated when a steady state background climate is reached and the model run is complete.

2.5 Supplementary material

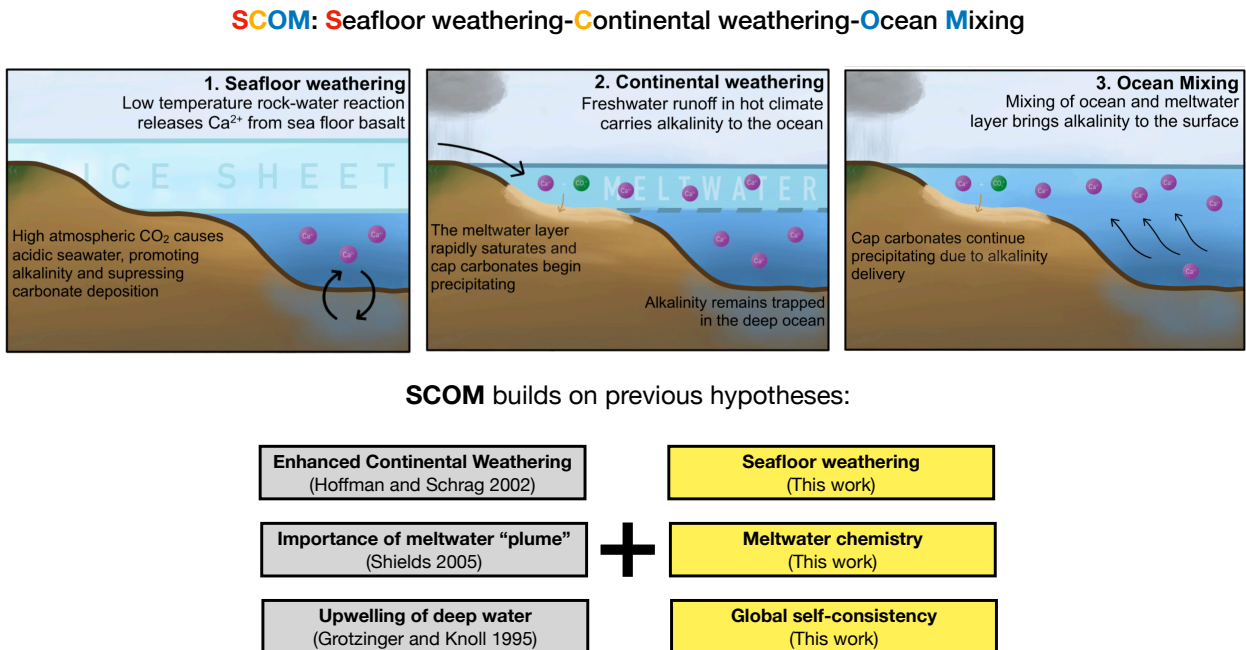


Figure S2-1: Summary of the SCOM mechanism and relationship to previous hypotheses.

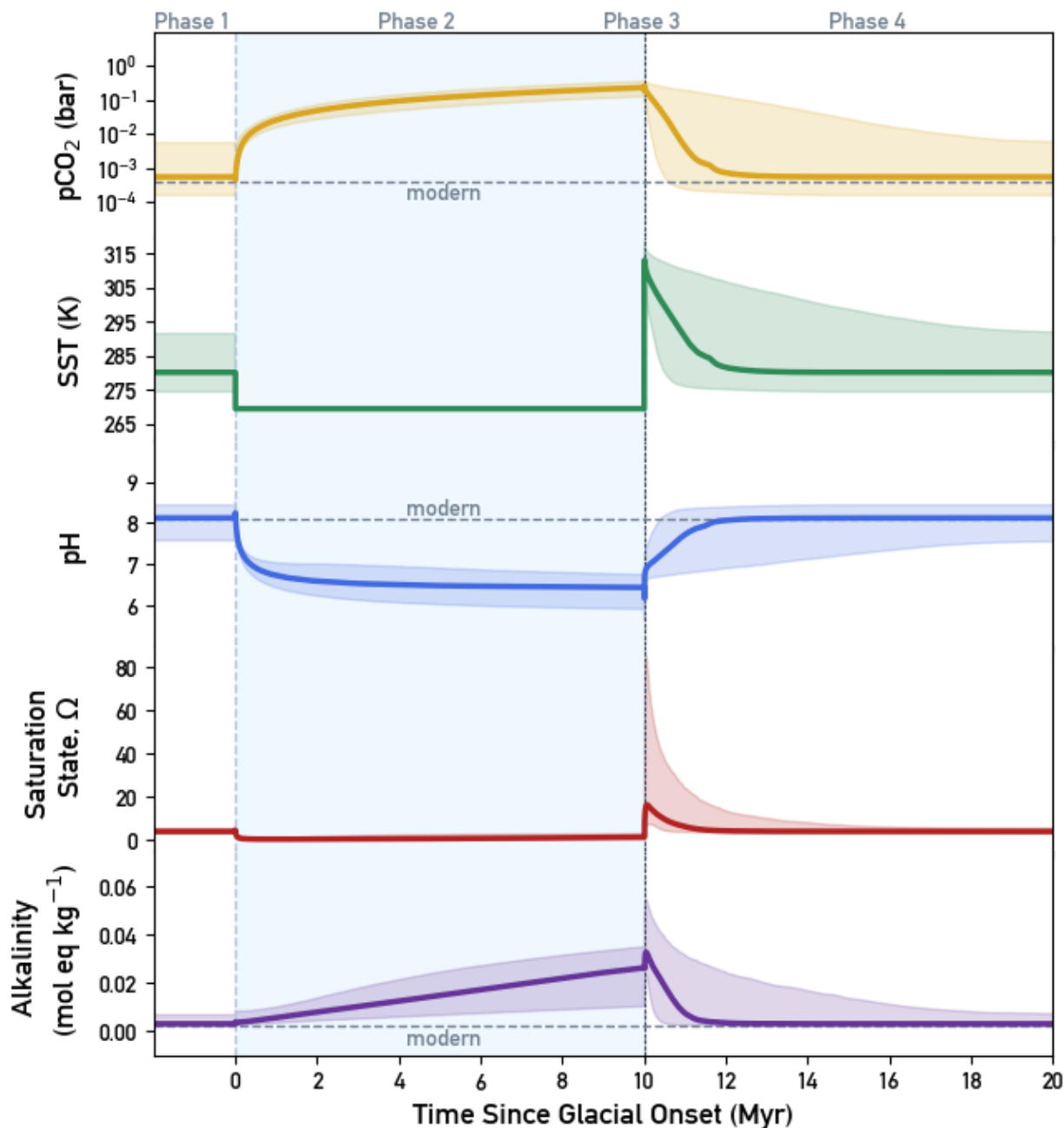


Figure S2-2: Climate evolution through all modeled phases with post-glacial meltwater layer duration of $t_{strat} = 10^4$ years. The shaded regions are the 95% confidence intervals and the solid lines are the medians of 3000 model runs with randomly sampled parameters. Glaciation was terminated after 10 Myr and the stratified ocean was terminated after 10 kyr ($t_{strat} = 10^4$ years). Vertical dashed lines indicate boundaries between model phases, noting the two close vertical lines at 10 Myr and 10.01 Myr bounding the post-glacial stratified ocean phase. See Figure S3 for a close-up on the post-glacial stratified ocean phase.

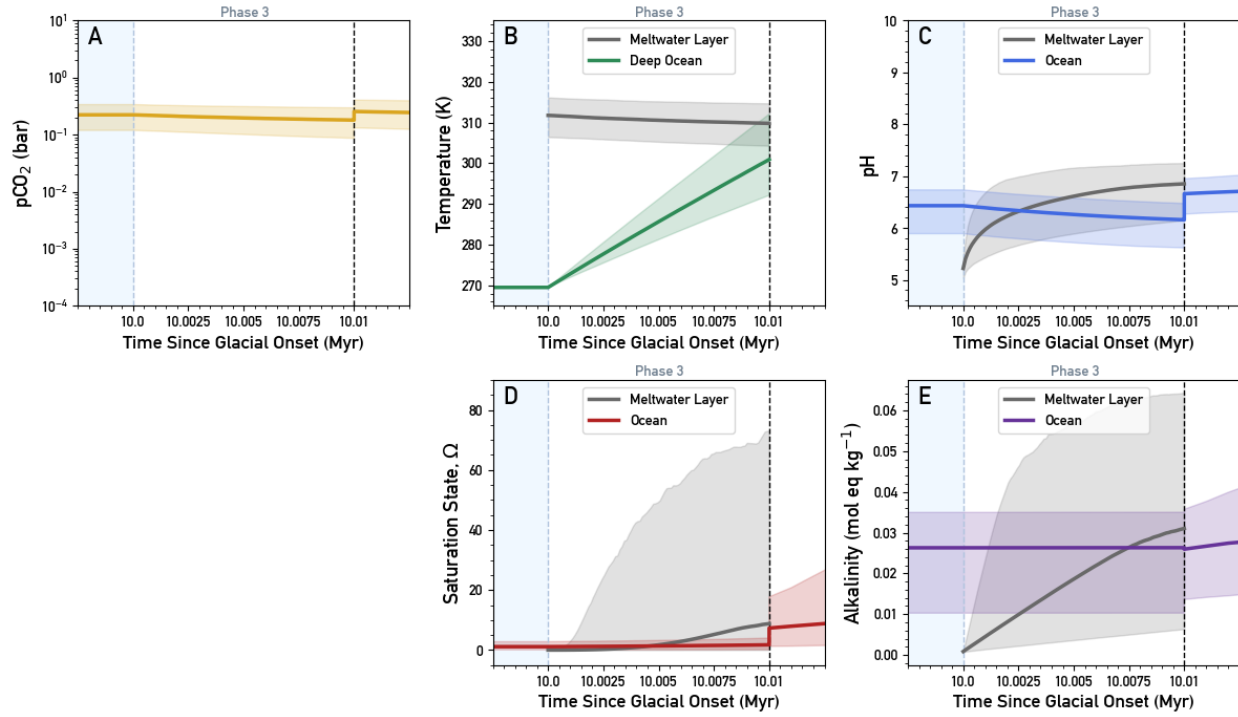


Figure S2-3: Climate evolution in the stratified ocean phase from Figure S2-2 with post-glacial meltwater layer duration of $t_{strat} = 10^4$ years. The shaded regions are the 95% confidence intervals and the solid lines are the medians of 3000 model runs with randomly sampled parameters. Post-glacial ocean stratification is assumed to last 10 kyr ($t_{strat} = 10^4$ years), indicated by the vertical dashed black line. Following stratification, the two reservoirs are combined and averaged.

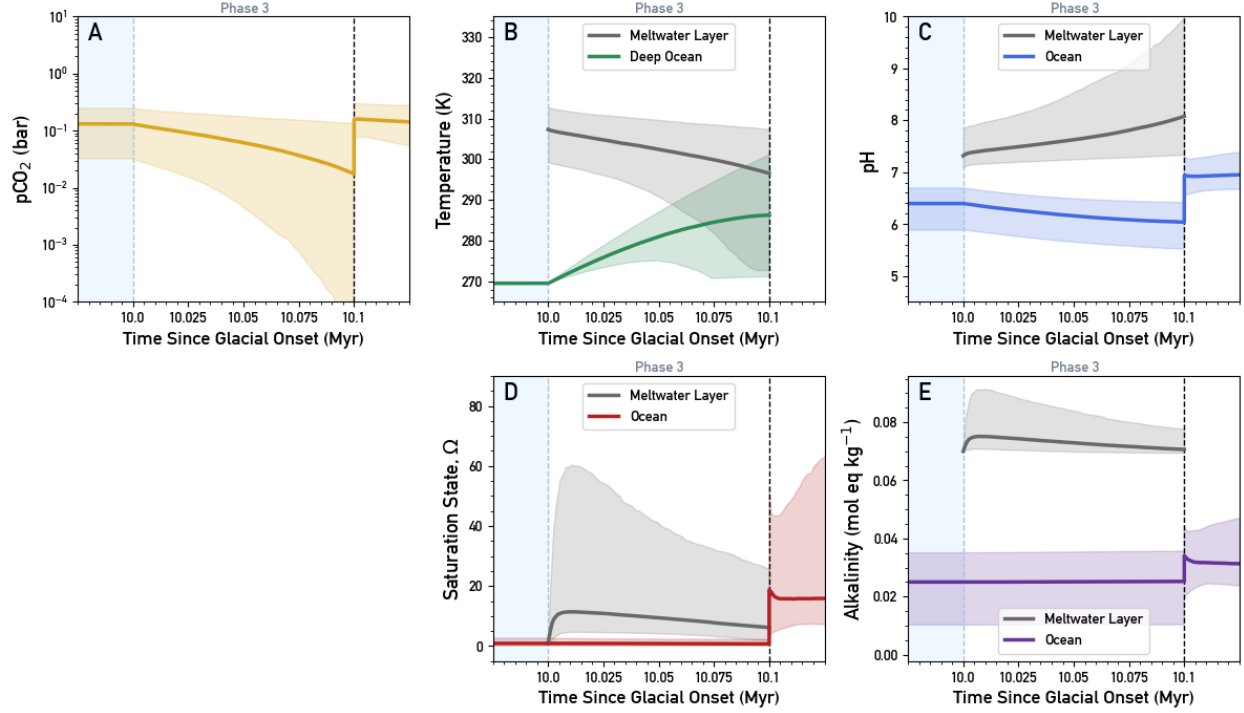


Figure S2-4: Climate evolution in the high-alkalinity meltwater scenario. The stratified ocean phase is shown with post-glacial meltwater layer duration of $t_{strat} = 10^5$ years. The initial alkalinity of the meltwater in phase 3 is 70,000 $\mu\text{mol eq kg}^{-1}$, compared to 700 - 1000 $\mu\text{mol eq kg}^{-1}$ in the baseline case. The shaded regions are the 95% confidence intervals and the solid lines are the medians of 3000 model runs with randomly sampled parameters. Post-glacial ocean stratification is assumed to last 100 kyr ($t_{strat} = 10^5$ years), indicated by the vertical dashed black line. Following stratification, the two reservoirs are combined and averaged.

2.5.1 Calculation of baseline carbon cycle fluxes, aqueous chemistry, and climate

These calculations follow Krissansen-Totton & Catling (2017) and Krissansen-Totton et al. (2018). Any modifications are indicated below.

2.5.1.1 Aqueous chemistry

With the carbon content and alkalinity of a given reservoir, we can calculate the other parameters of the carbon system that are used to determine fluxes and climate. To calculate the aqueous chemistry, we first define the dissolved inorganic carbon (DIC) and carbonate alkalinity (ALK):

$$\begin{aligned} \text{DIC} &= [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{CO}_{2,\text{aq}}], \\ \text{ALK} &= 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-]. \end{aligned} \quad (\text{S2.1})$$

We then calculate the rest of the aqueous chemistry with the following equations (Pilson, 2012):

$$[\text{CO}_{2,\text{aq}}] = p\text{CO}_2 H_{\text{CO}_2}, \quad (\text{S2.2})$$

$$[\text{HCO}_3^-] = \frac{[\text{CO}_{2,\text{aq}}] K_1^*}{[\text{H}^+]}, \quad (\text{S2.3})$$

$$[\text{CO}_3^{2-}] = \frac{[\text{HCO}_3^-] K_2^*}{[\text{H}^+]}, \quad (\text{S2.4})$$

$$\text{pH} = -\log_{10}([\text{H}^+]), \quad (\text{S2.5})$$

$$0 = \frac{\text{ALK}}{K_1^* K_2^*} \left(1 + \frac{s}{H_{\text{CO}_2}} \right) [\text{H}^+]^2 + \frac{(\text{ALK} - \text{C})}{K_2^*} [\text{H}^+] + (\text{ALK} - 2\text{C}), \quad (\text{S2.6})$$

where H_{CO_2} is the Henry's law constant of CO_2 , $[\text{CO}_{2,\text{aq}}]$ is the sum of the concentrations of dissolved CO_2 and H_2CO_3 , and K_1^* and K_2^* are the first and second apparent dissociation constants of carbonic acid, respectively. The derivation of equation S2.6 and the temperature-dependent values for the dissociation constants are found in Krissansen-Totton & Catling (2017). These equations are solved separately in each reservoir at each timestep. For reservoirs that are not in direct equilibrium with the atmosphere (i.e., the pore-space), $s = 0$.

The carbonate saturation states of the ocean and pore-space (Ω_o and Ω_p , respectively) are calculated via the equation

$$\Omega = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_{\text{sp}}(T)}, \quad (\text{S2.7})$$

where the concentrations and temperatures are taken individually from each reservoir. The expressions for the temperature dependent solubility product, $K_{sp}(T)$, are found in Krissansen-Totton & Catling (2017).

To calculate the calcium concentration in each reservoir, we assume that all changes in carbonate alkalinity are balanced by changes in calcium concentration:

$$[\text{Ca}^{2+}] = \frac{1}{2}(\text{ALK} - \text{ALK}_{\text{modern}}) + [\text{Ca}^{2+}]_{\text{modern}}. \quad (\text{S2.8})$$

This equation effectively assumes that all changes in alkalinity are due to changes in the calcium concentration and that no other processes affect the calcium concentration. We use the modern Earth as a reference point for this approach and assume that $[\text{Ca}^{2+}]_{\text{modern}} = 10.27 \text{ mmol kg}^{-1}$ (Pilson, 2012). $\text{ALK}_{\text{modern}}$ is calculated during model calibration so that the modern steady-state climate (e.g., surface temperature, pCO_2 , and ocean pH) is reproduced. This assumption has been tested and justified for the full Earth evolution (Krissansen-Totton et al., 2018), so it is suitable for calculating the background Neoproterozoic climate.

2.5.1.2 Air and water temperature

We assume that the solar luminosity in the Neoproterozoic era was 94% of the modern value (Gough, 1981). To calculate Earth's surface temperature (T_s) as a function of pCO_2 , we employ the extensively tested parameterization of a 1D radiative convective climate model used in Krissansen-Totton et al. (2018). We assume that the temperature of the ocean reservoir is equal to the atmospheric surface temperature. The temperature of the pore-space water is partially determined by the temperature of the water in the deep ocean that enters the crust. We use an empirical relationship derived in Krissansen-Totton & Catling (2017) to calculate the deep ocean temperature (T_d) as a function of T_s :

$$T_d = a_{\text{grad}}T_s + b_{\text{int}}, \quad (\text{S2.9})$$

where a_{grad} ranges from 0.8 to 1.4 and $b_{\text{int}} = 274.037 - a_{\text{grad}} \times 285 \text{ K}$ to ensure modern conditions are reproduced. The pore-space temperature, T_p , is related to T_d via another empirical relationship identified for the Cenozoic and Mesozoic: $T_p = T_d + 9 \text{ K}$ (Coogan & Dosso, 2015; Krissansen-Totton & Catling, 2017). We assume this relationship is true because Earth's internal heat flux is not expected to have changed substantially from the modern day to the Cryogenian (See Krissansen-Totton et al., 2018, their Figure 2D).

2.5.1.3 Volcanic outgassing

We assume that the source rate of CO₂ from volcanic outgassing is equal to the modern value, 6.5–10.5 Tmol yr⁻¹ (Catling & Kasting, 2017). This assumption is justified because interior evolution models indicate that Earth’s internal heat flux should not have changed substantially from the modern day to the Cryogenian (See Krissansen-Totton et al., 2018, their Figure 2D). Additionally, estimates of degassing rates based on global ridge reconstructions indicate that the degassing rate at 750 Ma should have been approximately equal to the modern value (See Mills et al., 2019, their Figure 9A).

2.5.1.4 Continental weathering

As derived in Walker et al. (1981), we express continental silicate weathering as

$$W_{sil} = f_w F_{sil}^{mod} \left(\frac{pCO_2}{pCO_2^{mod}} \right)^\alpha \exp \left(\frac{\Delta T_s}{T_e} \right). \quad (S2.10)$$

F_{sil}^{mod} is the modern continental silicate weathering flux (mol eq yr⁻¹), calculated by running the model for modern day conditions and assuming the system is in a steady-state. Agreement between the model value and modern estimates is shown in our modern Earth benchmark. The exponent α is an empirical constant that determines the weathering dependence on the model atmospheric pCO₂ value relative to the modern value (pCO_2^{mod}). $\Delta T_s = T_s - T_s^{mod}$ is the difference in the model global average surface temperature (T_s) and the preindustrial modern value ($T_s^{mod} = 285$ K), and T_e is the e-folding temperature that determines the temperature dependence of the weathering rate. We explore a range of values based on existing literature estimates for the empirical constants that determine the pCO₂ and temperature dependencies: $\alpha = 0.1 - 0.5$ and $T_e = 10 - 40$ K (Krissansen-Totton et al., 2018; Krissansen-Totton & Catling, 2017; Sleep & Zahnle, 2001; Volk, 1987; Walker et al., 1981). f_w is the continental weatherability factor, described below.

Continental carbonate weathering is expressed similarly as

$$W_{carb} = f_w F_{carb}^{mod} \left(\frac{pCO_2}{pCO_2^{mod}} \right)^\xi \exp \left(\frac{\Delta T_s}{T_e} \right). \quad (S2.11)$$

$F_{carb}^{mod} = 7 - 14$ Tmol C yr⁻¹ is the modern continental carbonate weathering flux, for which we explore the full range of values (Hartmann et al., 2009). The exponent ξ determines the carbonate weathering dependence on the model pCO₂ and is analogous to α in the continental silicate weathering parameterization. We similarly explore the range $\xi = 0.1 - 0.5$ (Berner, 2004).

A key free parameter in the model is f_w , the continental weatherability factor. The parameter f_w is multiplied with both the silicate and carbonate weathering rates to account for inherent uncertainties that arise when extrapolating back to the Precambrian. On one hand, landmasses with recently-rifted margins were probably concentrated at the equator throughout the Neoproterozoic as the supercontinent Rodinia broke up (Li et al., 2013). Some studies have argued that this should lead to enhanced continental weathering and a cooler background climate (e.g., Cox et al., 2016; Macdonald & Wordsworth, 2017; Rooney et al., 2014), but at least one carbon cycle model shows that it may have had little impact (Mills et al., 2019). On the other hand, the lack of widespread biology likely had an important and complex impact on weathering rates. Vegetation can impact weathering rates via several processes, including modifying groundwater hydrology, modifying the surface area of weatherable rocks, and modifying the water-rock contact time. Similarly, microorganisms alter the surface chemistry of weatherable rocks and potentially degrade them directly. Estimates for the biological enhancement due to weathering (i.e., biotic weathering rate divided by abiotic weathering rate) range from 0.1 to 8, with most experiments suggesting that organisms enhance weathering rather than slow it (See Wild et al., 2022, and references within). Because the processes described above are highly uncertain and may have offsetting effects, we group them together within the weatherability factor. We explore the range $f_w = 0.5 - 1.5$ and explicitly mention when we fix f_w at a discrete value.

2.5.1.5 Seafloor weathering

Seafloor weathering is the dissolution of basaltic ocean crust at low temperatures, away from mid-ocean ridges. Following Krissansen-Totton & Catling (2017), we model the rate of seafloor weathering as

$$W_{sea} = k_{sea} \left(\frac{[H^+]_p}{[H^+]_p^{\text{mod}}} \right)^\gamma \exp \left(\frac{-E_{bas}}{RT_{pore}} \right). \quad (\text{S2.12})$$

Here, k_{sea} is a proportionality constant that reproduces the modern flux when the model is calibrated to the modern climate system, where the modern flux is approximately $0.4 \text{ Tmol eq yr}^{-1}$ (Krissansen-Totton et al., 2018). $[H^+]_p$ is the model hydrogen ion molality in the pore-space and $[H^+]_p^{\text{mod}}$ is the modern value. E_{bas} is the effective activation energy of basalt dissolution and the exponent γ accounts for the pH dependence of seafloor weathering. We adopt the empirically-

derived ranges for these values from Krissansen-Totton & Catling (2017): $E_{\text{bas}} = 60 - 100 \text{ kJ mol}^{-1}$ and $\gamma = 0 - 0.5$.

We implicitly assume that other factors impacting seafloor weathering in the Neoproterozoic are negligible compared to changes in pore-space pH and temperature. For example, the seafloor weathering rate depends on geologic properties such as Earth's internal heat flux and the rate of seafloor spreading that provides fresh, weatherable basalt. As described in the above section on volcanic outgassing, interior evolution models and global ridge reconstructions indicate that these processes should not significantly impact the rate of seafloor weathering in the Neoproterozoic relative to modern (Krissansen-Totton et al., 2018; Mills et al., 2019).

2.5.1.6 Carbonate precipitation

On modern Earth, ocean carbonate precipitation and deposition occurs in the deep, open ocean (i.e., pelagic) and on the warmer, shallower continental shelves (i.e., neritic). Modern pelagic carbonate deposition is sourced by calcifying plankton, which did not arise until about 150 Ma, during the Jurassic period (Bernier, 2004). To our knowledge, there is no evidence for pelagic carbonates before this. Thus, we assume that carbonate deposition in the Neoproterozoic occurred only in neritic environments.

Following Ridgwell et al., (2003), we parameterize the rate of continental shelf carbonate deposition as:

$$P_{\text{shelf}} = k_{\text{shelf}} \frac{A_{\text{shelf}}}{A_{\text{shelf}}^{\text{mod}}} (\Omega_o - 1)^n, \quad (\text{S2.13})$$

where k_{shelf} is a proportionality constant that reproduces the modern flux when the model is calibrated to the modern climate system. $A_{\text{shelf}} / A_{\text{shelf}}^{\text{mod}}$ is the ratio of continental shelf area at the model time relative to the modern continental shelf area. We assume this ratio is 1 for the background Neoproterozoic climate. Ω_o is the calcite saturation state of the ocean, and n determines the dependence of carbonate precipitation on the saturation state. We explore a range of $n = 1.0 - 2.5$ to consider the precipitation of both calcite and aragonite (Opdyke & Wilkinson, 1993). Finally, when calibrating the model to the modern climate system, we include pelagic carbonate deposition to ensure steady state balance in the same way as Krissansen-Totton & Catling, (2017).

The pore-space carbonate precipitation rate is treated similarly to the continental shelf rate, but there is no dependence on area:

$$P_{pore} = k_{pore}(\Omega_p - 1)^n \quad (\text{S2.14})$$

where k_{pore} is a proportionality constant that reproduces the modern flux when the model is calibrated to the modern climate system.

2.5.2 Calibration and benchmarking against modern and post-glacial Earth

To calibrate many of the carbon and alkalinity fluxes, we must benchmark the model against the modern system. Following Krissansen-Totton & Catling (2017) and Krissansen-Totton et al. (2018), we assume that the system is in a steady state at modern day, and thus we can set all of the governing differential equations equal to zero. We then enforce the measured values of the modern outgassing rate, the modern continental carbonate weathering rate, the modern pore-space carbonate precipitation rate, and the ratio of seafloor weathering to pore-space carbonate precipitation. From this, we directly calculate the required modern values of seafloor weathering, continental silicate weathering, and ocean carbonate precipitation that balance the system. This approach is justified in Krissansen-Totton & Catling (2017) and Krissansen-Totton et al. (2018) because only the relative sizes of the carbon and alkalinity fluxes impact the calculation of observable values. A sample of model runs in the modern climate state compared to measured values is shown in Figure S2-5.

In phase 1, we run the model until a steady state is reached. We define a steady state as the point in the model evolution when CO_2 would change by less than 1% if its rate of change is projected 1 billion years into the future. Comparison to the WITCH weathering model (Le Hir et al., 2009) for post-glacial Earth is shown in Figure S2-6.

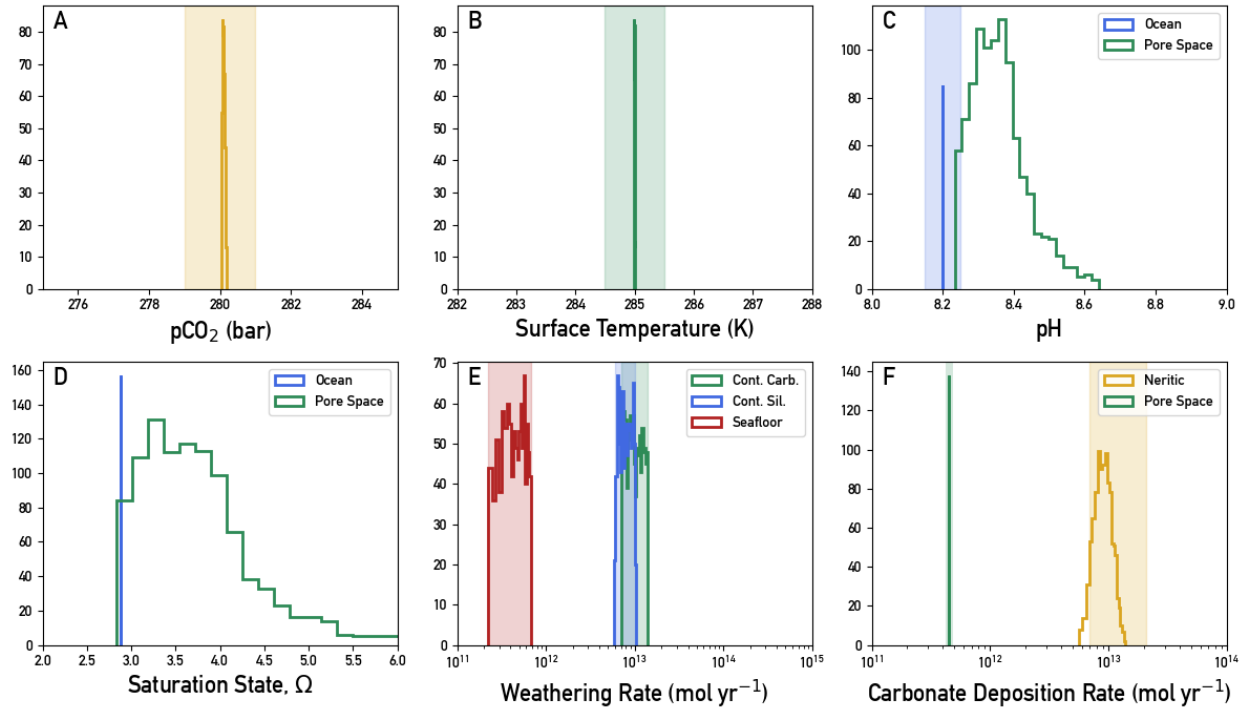


Figure S2-5: Model benchmark against the modern climate system. Histograms show the results for observable variables from 1000 model runs where uncertain parameters are sampled. The vertical shaded regions are the measured or assumed modern values. (A, B, C) We assume the pre-industrial modern climate had 280 ppm atmospheric CO₂, 285 K surface temperature, and 8.2 ocean pH. (D) The calcite and aragonite saturation states of the modern ocean vary from over 5 at the surface to below 0.5 in the deep ocean (Pilson, 2012). (E) Estimates of continental carbonate weathering rates are from Hartmann et al. (2009), continental silicate weathering rates are from Moon et al. (2014), and seafloor weathering rates are from Coogan & Gillis (2013) and Krissansen-Totton et al. (2018). (F) Estimates of neritic carbonate deposition rates are from Iglesias-Rodriguez et al. (2002) and pore-space deposition rates are from Gillis & Coogan (2011) and Krissansen-Totton et al. (2018).

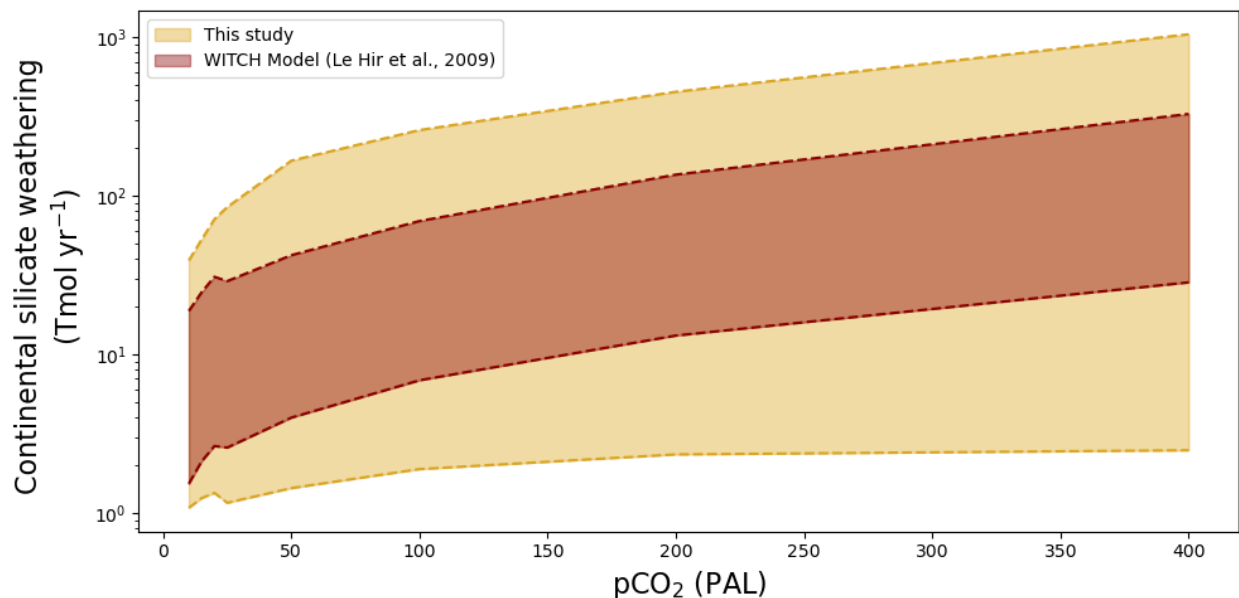


Figure S2-6: Post-glacial continental weathering rate predictions as a function of $p\text{CO}_2$ from this study versus Le Hir et al. (2009).

2.5.3 Model transitions

2.5.3.1 Glaciation

The initiation of the glaciation is instantaneous and forced in our model. Previous coupled climate and ice-sheet models indicate that the onset of global glaciation should be rapid, on the order of 2 kyr, due to the ice-albedo feedback (e.g., Hyde et al., 2000). This is below the typical ~ 1 Myr timescale on which the geologic carbon cycle impacts climate. Consistent with the purpose of this study, we do not model the evolution of climate and surface chemistry during this relatively short transition interval. Thus, we are effectively modeling this transition period within a single timestep.

2.5.3.2 Deglaciation and ocean stratification

When entering phase 3, we nominally assume that all ice sheets and glaciers melt instantaneously. This is consistent with the many positive feedbacks associated with melting (e.g., the ice-albedo instability) that cause predictions of rapid melting on the timescale of 2 kyr (Hoffman et al., 2017; Hyde et al., 2000). However, it is possible that melting was more prolonged than we nominally assume, on the order of 100 kyr (e.g. Fairchild et al., 2023).

Here we present a sensitivity study to evaluate how a prolonged deglaciation would impact our model results. To do this, we modify the phase 3 model configuration so that the mass of the meltwater layer (M_s) changes over time, due to the melting of ice sheets. To incorporate this in the model, we first have to modify the governing system of equations (Eqs 2.2 in main text) related to the meltwater layer. Previously, M_s was assumed to be constant and could be factored out in the differential equations. Now $M_s = M_s(t)$, so it cannot be factored out and must be differentiated via the chain rule. This accounts for the addition of new water into the meltwater layer as the glaciers melt, where we assume that the carbon concentration of the added water is determined by equilibration with the atmosphere and we assume that the alkalinity of the added water is the same as our nominal model scenario. The governing equations for carbon and alkalinity in the meltwater layer in phase 3 become

$$\begin{aligned}\frac{dC_s}{dt} &= \frac{1}{M_s(t)} \left(-K(\text{DIC}_s - C_d) + V_{air} + W_{carb} - P_{shelf} - O_{sink} \right) - C_s \frac{M'_s(t)}{M_s(t)}, \\ \frac{dA_s}{dt} &= \frac{1}{M_s(t)} \left(-K(A_s - A_d) + 2W_{sil} + 2W_{carb} - 2P_{shelf} \right) + (A_{melt} - A_s) \frac{M'_s(t)}{M_s(t)},\end{aligned}\tag{S2.15}$$

where $M'_s(t) = dM_s(t)/dt$ and A_{melt} is the alkalinity of the meltwater that is being added to the layer.

We now consider 2 scenarios for $M_s(t)$ in the prolonged deglaciation scenario. In both cases, we assume it takes 100 kyrs for all ice to melt to test the most extreme endmember. First, we consider a scenario where melting occurs linearly with time:

$$M_s(t) = M_s(t_{strat}) \left(0.1 + 0.9 \frac{t}{t_{strat}} \right),\tag{S2.16}$$

where $M_s(t_{strat})$ is the mass of the meltwater layer after deglaciation is complete, the same as we assume in the nominal model described in Methods. We assume the meltwater layer starts at 10% of its final mass and then linearly increases until the final mass is reached at the same time ocean stratification ends (100 kyrs). Second, we consider a scenario where melting occurs in 3 pulses:

$$\begin{aligned}M_s(t) &= M_s(t_{strat}) \left(0.1 + \frac{0.9/3}{1 + e^{-100(t/t_{strat}-0.25)}} + \frac{0.9/3}{1 + e^{-100(t/t_{strat}-0.5)}} \right. \\ &\quad \left. + \frac{0.9/3}{1 + e^{-100(t/t_{strat}-0.75)}} \right).\end{aligned}\tag{S2.17}$$

The above equation is the sum of 3 logistic functions that approximate stepwise increases in $M_s(t)$ at 25, 50, and 75 kyrs. We again assume that the meltwater layer starts at 10% of its final mass.

We also use the melt percentage ($M\% = M_s(t)/M_s(\text{final})$) to scale the continental weathering rates and sea surface temperature. First, we simply multiply the continental weathering rates by $M\%$ to approximate the reduction in weathering due to coverage of weatherable land by ice sheets and the slow hydrologic cycle. Second, our climate model does not take surface albedo as an input, so we approximate the changing albedo of the surface by using $M\%$ to linearly scale the surface temperature ($T_s(t)$) between the assumed snowball ocean temperature (269.5 K) and the result of the climate model ($T_{s,\text{clim}}(p\text{CO}_2)$):

$$T_s(t) = 269.5 + M\%(T_{s,\text{clim}}(p\text{CO}_2) - 269.5). \quad (\text{S2.18})$$

The results of the sensitivity study with linear glaciation are shown in Figures S2-7 and S2-8, and with pulsed deglaciation are shown in Figures S2-9 and S2-10. The mass of the meltwater layer can have a noticeable impact on the meltwater chemistry. This is especially visible for the pulsed deglaciation case where other climate variables reflect the stepwise increases in meltwater mass. This leads to differences in the rate of CC deposition. In the nominal model, the minimum global mass of CCs is deposited in 32 kyr to 591 kyr. In the linear deglaciation sensitivity study, the minimum global mass of CCs is deposited in 101 kyr to 682 kyr. In the pulsed deglaciation sensitivity study, the minimum global mass of CCs is deposited in 109 kyr to 618 kyr.

Prolonged deglaciation in the nominal sensitivity study increases the depositional timescale by up to 90 kyr. This is because of the reduced meltwater volume and the reduction in weathering rates and thus alkalinity delivery to the meltwater layer, which is required for CC deposition. However, the sensitivity study shown here is the "worst case" endmember scenario because (1) we assume a very long deglaciation time of 100 Myr (2) we assume weathering rates and surface temperature are reduced in direct proportion to the amount of deglaciation, which is likely an overestimate, (3) we assume that the added meltwater has very low alkalinity, and (4) we assume that none of the alkalinity from the deep ocean mixes into the meltwater layer, although this would likely occur given the smaller meltwater mass and lower flux to the ocean. If any of these assumptions are relaxed, the depositional timescale will likely approach our nominal model results. Additionally, because we were forced to make simple modifications to our existing weathering rates and climate model to approximate the partial coverage of ice sheets, a more detailed weathering study in the future would help to further investigate this topic.

2.5.3.3 Ocean mixing

When phase 3 ends, we assume that the ocean instantaneously overturns and becomes well-mixed. The ocean dynamics models predict that this process should be more gradual, with slow mixing that eventually overturns the ocean by the time t_{strat} is reached (Ramme & Marotzke, 2022; Yang et al., 2017). Thus, we implicitly overestimate the intensity of stratification for a given value of t_{strat} ; however, we test two values for t_{strat} to mitigate this. We maintain a simplified approach here to avoid additional model uncertainty during this transition and to focus on the more prominent geochemical trends during phase 3.

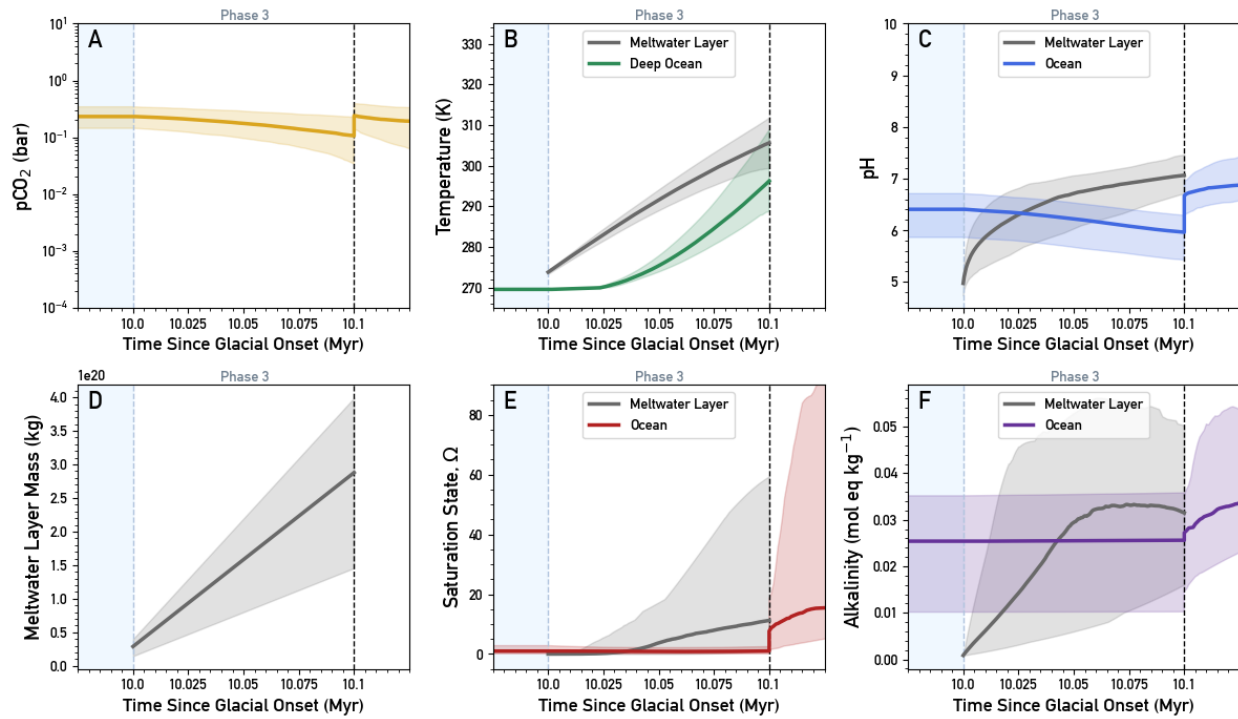


Figure S2-7: Climate evolution in sensitivity study with linear deglaciation. The shaded regions are the 95% confidence intervals and the solid lines are the medians of 3000 model runs with randomly sampled parameters.

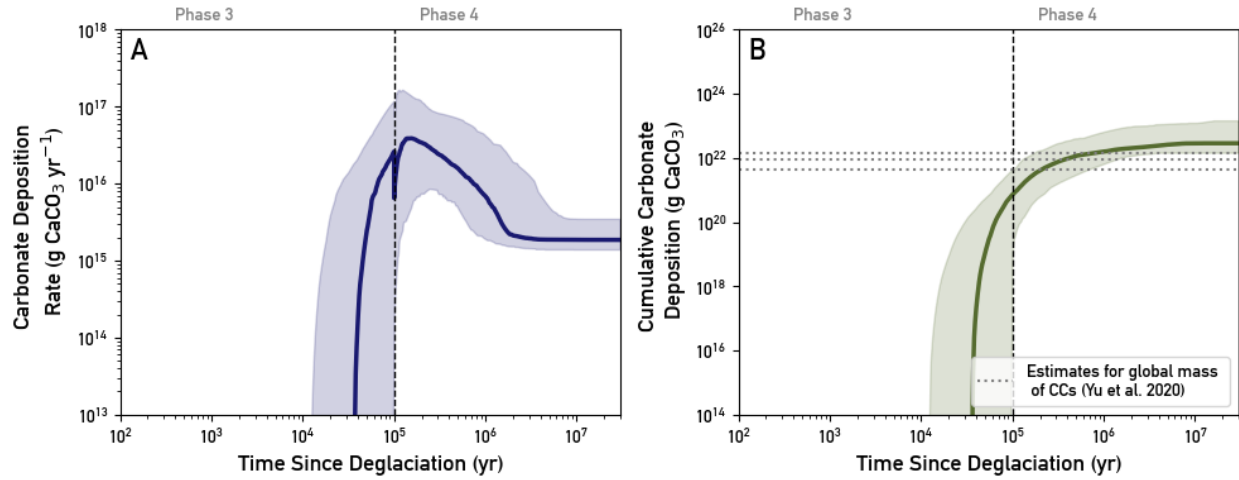


Figure S2-8: Carbonate deposition rate and cumulative carbonate deposition in the sensitivity study with linear deglaciation, corresponding to Figure S2-7. The shaded regions are the 95% confidence intervals and the solid lines are the median model runs with randomly sampled parameters.

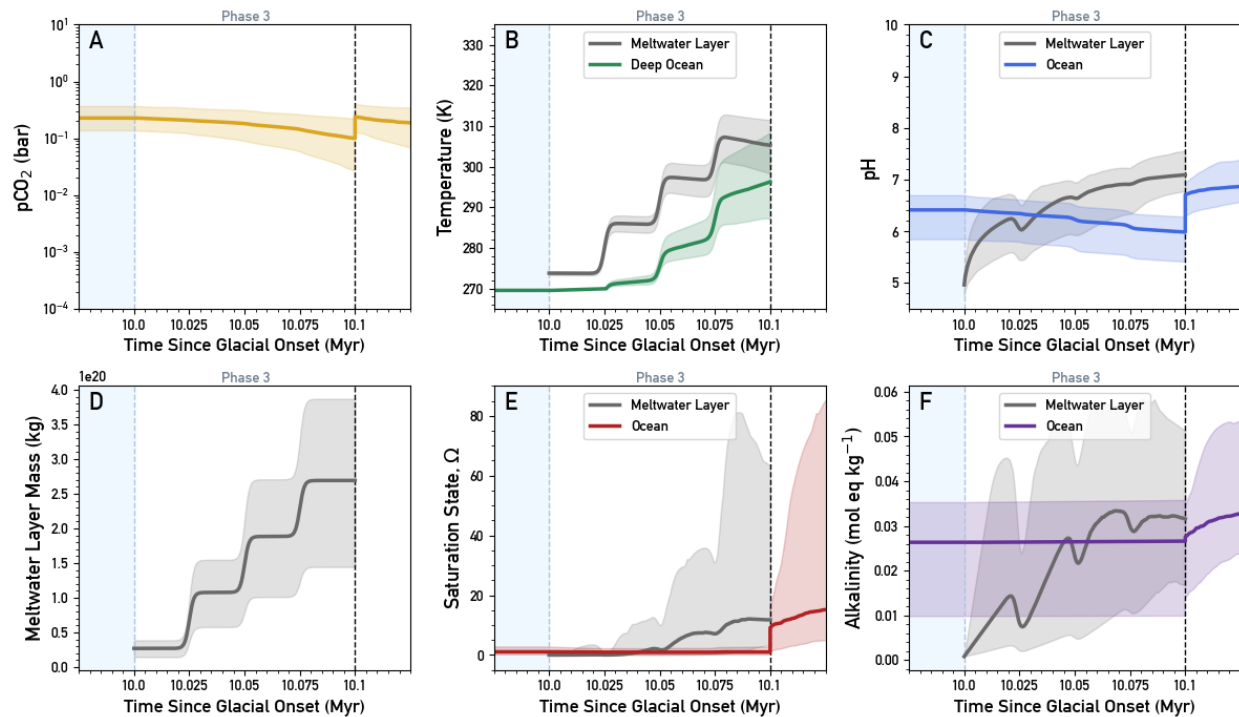


Figure S2-9: Climate evolution in sensitivity study with pulsed deglaciation. The shaded regions are the 95% confidence intervals and the solid lines are the medians of 3000 model runs with randomly sampled parameters.

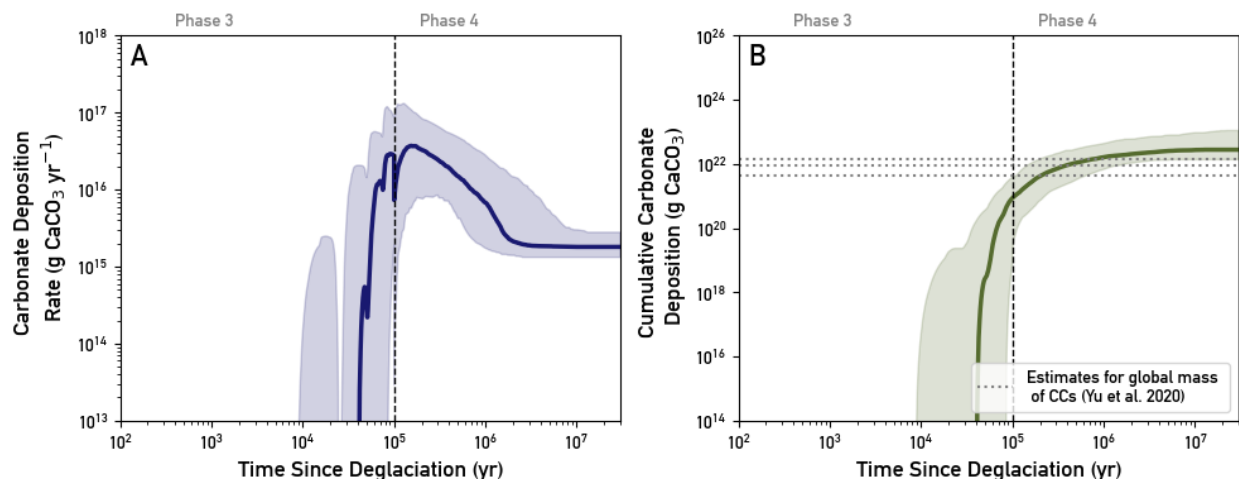


Figure S2-10: Carbonate deposition rate and cumulative carbonate deposition in the sensitivity study with pulsed deglaciation, corresponding to Figure S2-9. The shaded regions are the 95% confidence intervals and the solid lines are the median model runs with randomly sampled parameters.

2.6 Data availability and acknowledgements

The datasets corresponding to this study and code to reproduce all figures are available at Zenodo (<https://doi.org/10.5281/zenodo.12786460>). The GOOSE model code developed and used in this work is persistently available at Zenodo (<https://doi.org/10.5281/zenodo.12786460>) and on the lead author's GitHub (github.com/trentagon).

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3. Seafloor weathering can explain the disparate durations of Snowball glaciations

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Abstract

The Cryogenian Period (720–635 Ma) witnessed two Snowball Earth glaciations: the largest known perturbations to the geologic carbon cycle in Earth history. These two runaway ice-albedo catastrophes naturally test planetary climate stability and habitability. Geochronological data show that the Sturtian glaciation lasted 56 m.y., and the Marinoan was as short as 4 m.y., which is an unexplained difference previously attributed to changing volcanic outgassing rates and dust or ice albedo. Here, we propose that this difference in duration is instead due to changes in the extent of seafloor weathering, which was elevated during both glaciations by an acidic ocean under relatively high CO₂. By assuming modern volcanic outgassing rates and a conservative range of ice albedos, we find that seafloor weathering rates 25–53 times higher than modern are required to suppress atmospheric CO₂ and maintain glaciation for a 56 m.y. Sturtian glaciation, whereas <15 times higher than modern are required for a 4 m.y. Marinoan glaciation. Rates were plausibly enhanced further by reduced deep-sea sedimentation and low marine sulfate, which would have prevented hydrothermal anhydrite production and created more porous, weatherable oceanic crust. Geochemical data indicate low marine sulfate (<2 mM) during the Sturtian, which rebounded for the Marinoan (up to ~30 mM), and can account for the different seafloor weathering rates required by our model. Thus, our results suggest seafloor weathering and evolving ocean redox chemistry are critical for determining the duration of Snowball Earth glaciations.

3.1 Introduction

During the Cryogenian Period (720–635 Ma) ice sheets extended to low latitudes twice for millions of years (e.g., Macdonald et al., 2010; Rooney et al., 2015). These glaciations have been interpreted as Snowball climate states, caused by runaway ice-albedo feedback (Kirschvink, 1992; Hoffman et al., 1998). In the Snowball Earth scenario, with cold temperatures and extensive ice-cover, the hydrological cycle should have been limited and continental silicate weathering greatly reduced. After millions of years, the buildup of atmospheric CO₂ from volcanic outgassing should then produce an intense green-house effect and override the high ice albedo, causing deglaciation and rapid weathering of carbonates and silicates on land. Assuming similar albedos and volcanic outgassing rates, the two glaciations may be expected to have had similar durations. However, radiometric dating shows that the first glaciation, the Sturtian, lasted 56 m.y. (717–661 Ma; Macdonald et al., 2010; Rooney et al., 2020), whereas the second glaciation, the Marinoan, may have lasted only 4 m.y. (639–635 Ma; Tasistro-Hart et al., 2025).

The up to 14-fold duration difference in successive glaciations requires big differences in the geologic carbon cycle or surface radiative balance. The end of glaciation, and thus duration, is largely determined by greenhouse warming (presumably from CO₂), the albedo of surface ice and dust, and the radiative effects of clouds (Pierrehumbert et al., 2011). On one hand, explaining the shorter Marinoan duration is difficult, requiring a stochastic radiative perturbation to cause fast deglaciation (e.g., Lan et al., 2022). On the other hand, explaining the longer Sturtian duration is also difficult, requiring low CO₂ outgassing rates relative to the Marinoan to prolong glaciation (Dutkiewicz et al., 2024).

With continental silicate weathering greatly reduced during each glaciation, low-temperature seafloor weathering was likely the primary alkalinity source to the ocean that regulated atmospheric CO₂ (Le Hir et al., 2008; Thomas and Catling, 2024). Here, we hypothesize that redox-chemistry-driven changes in seafloor weathering caused the differing glacial durations. We test this hypothesis by simulating the evolution of the geologic carbon cycle during a Cryogenian Snowball Earth and statistically analyzing model parameters that result in 4 m.y., 15 m.y., and 56 m.y. glaciation.

3.2 Methods

We use a previously published model to simulate the geologic carbon cycle during a Snowball Earth event (Thomas and Catling, 2024). This model tracks the evolution of carbon and alkalinity in the atmosphere and ocean while calculating environmental variables such as surface temperature, ocean pH, and atmospheric pCO₂. These variables evolve with geologic carbon cycle processes: continental and seafloor weathering, carbonate precipitation, and volcanic outgassing. We simulate global glaciation assuming air-sea gas exchange (i.e., “soft” Snowball) using the Phase 2 configuration from Thomas and Catling (2024).

For a given model run, volcanic outgassing of CO₂ (V) is held constant in the range of modern-day uncertainty: 6.5–10.5 Tmol Cyr⁻¹ (Catling and Kasting, 2017, p. 203; see Supplementary Material for a sensitivity study). Seafloor weathering occurs when seawater dissolves oceanic crust at low temperatures away from mid-ocean ridges, releasing alkalinity (e.g., via Ca²⁺) into the pore-space and ocean. Higher alkalinity increases the ocean’s carbon storage and causes carbonate precipitation, lowering atmospheric pCO₂. Seafloor weathering is considered in detail in our model (see Thomas and Catling, 2024), and the charge-weighted alkalinity flux is (Tmol eq yr⁻¹):

$$W_{sea} = X_{sea} k_{sea} \left(\frac{[H^+]_p}{[H^+]_p^{mod}} \right)^\gamma \exp(-E_{bas}/RT_{pore}). \quad (3.1)$$

Here, k_{sea} is a constant calibrated to the modern flux ($W_{sea} \sim 0.4$ Tmol eq yr⁻¹; Coogan and Gillis, 2013), $[H^+]_p$ is the model hydrogen ion molality in the pore-space of the oceanic crust, $[H^+]_p^{mod}$ is the modern value, γ is the pH-dependence of the reaction (0 – 0.5; Gudbrandsson et al., 2011; Krissansen-Totton and Catling, 2017), E_{bas} is the energy of basalt dissolution (60 – 100 kJ mol⁻¹; Coogan and Dosso, 2015; Krissansen-Totton and Catling, 2017), R is the universal gas constant, T_{pore} is the model temperature of water in the pore-space, and X_{sea} is a multiplier to test the effect of enhanced seafloor weathering. Although empirically grounded, uncertainties remain in pore-water properties and their link to global seawater.

We ran the model 10,000 times with randomly sampled parameters in a standard configuration ($X_{sea} = 1$) and an enhanced seafloor weathering configuration (ESW; $X_{sea} = 1$ –5). Atmospheric pCO₂ required to cause deglaciation is 0.1–0.3 bar (see Wu et al., 2021, and references within), which incorporates uncertainty in surface albedo and cloud effects that are not in the model. Any model run with pCO₂ = 0.1–0.3 bar at 4 m.y., 15 m.y., or 56 m.y. is consistent

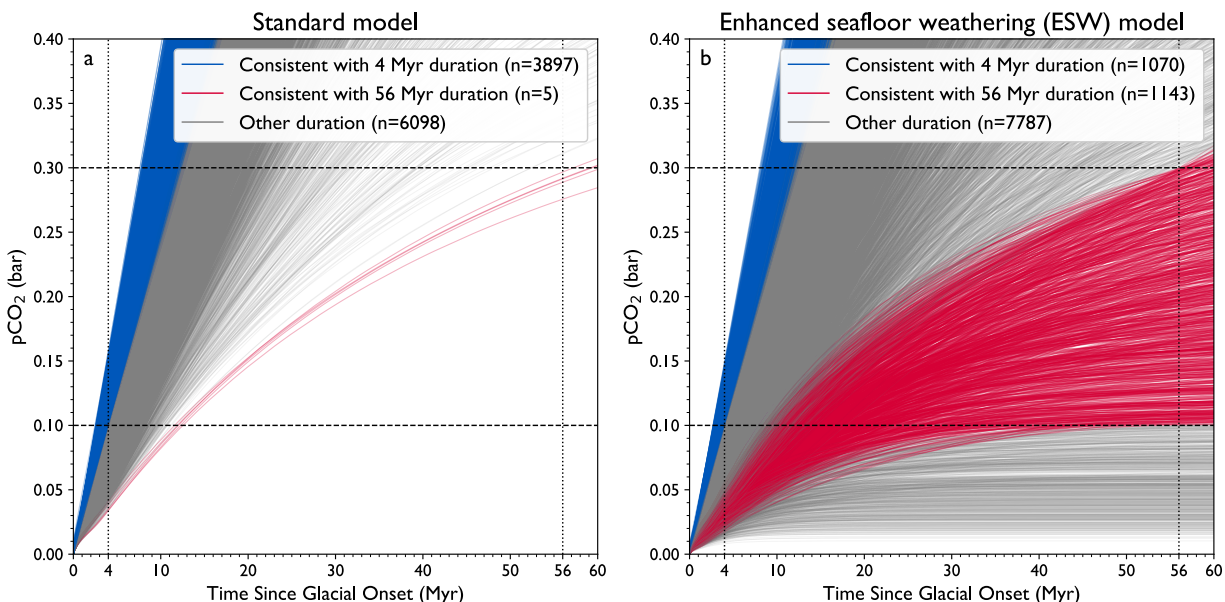


Figure 3-1: Evolution of atmospheric $p\text{CO}_2$ in 10,000 model runs with randomly sampled parameters in the (A) standard model and (B) enhanced seafloor weathering model, where a multiplicative factor (X_{sea}) increases seafloor weathering by a factor of 1–5. Vertical dotted lines show 4 m.y. and 56 m.y. glaciation. Horizontal dashed lines are the minimum and maximum atmospheric $p\text{CO}_2$ expected to cause deglaciation: 0.1–0.3 bar.

with that glacial duration and used to derive posterior distributions for model parameters. See the Supplementary Material for additional model parameter distributions, an example model evolution, and access to the source code and data.

3.3 Results

In our model runs, 56 m.y. glaciation is rarely generated without enhanced seafloor weathering (ESW), which prolongs glaciation by releasing alkalinity that drives carbonate deposition and CO_2 removal. In the standard model, only 0.05% of model runs are consistent with a 56 m.y. duration, whereas 39% are consistent with a 4 m.y. duration (Fig. 3-1A). Alternatively, when seafloor weathering is enhanced by a multiplicative factor ($X_{\text{sea}} = 1\text{--}5$), 11% of model runs are consistent with 4 m.y. and 56 m.y. durations, each (Fig. 3-1B). Additionally, 56 m.y. standard model runs do not achieve $p\text{CO}_2$ below 0.27 bar at the time of deglaciation, but deglaciation $p\text{CO}_2$ varies in the full range 0.1–0.3 bar in the ESW model. The 4 m.y. model runs do not achieve deglaciation $p\text{CO}_2$ above 0.16 bar in either scenario.

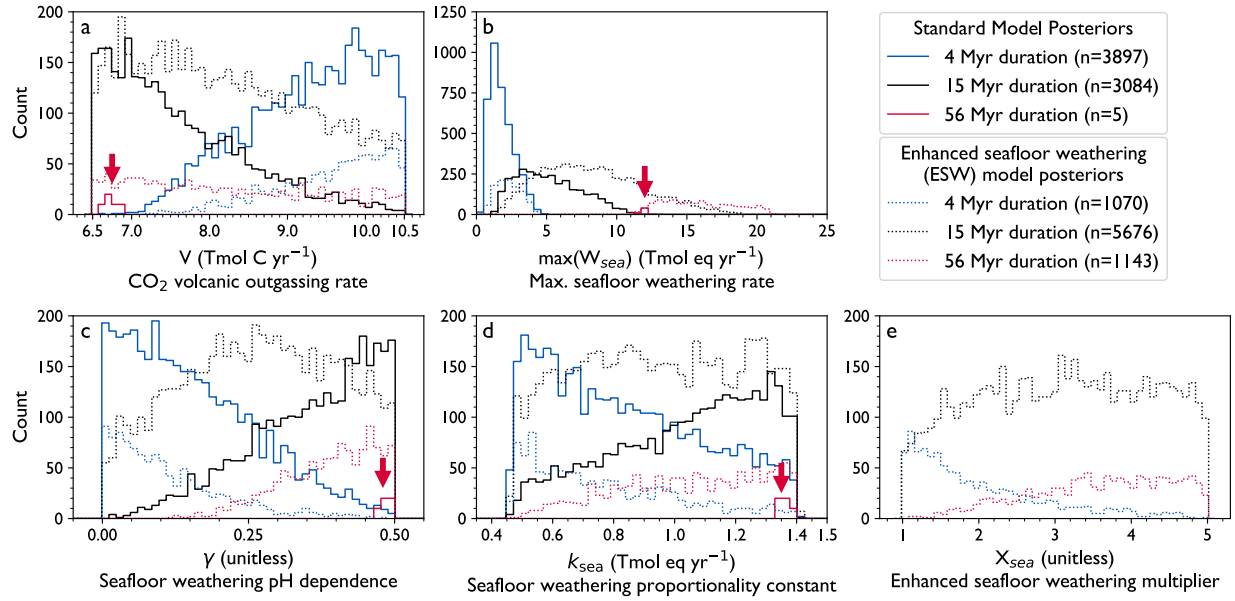


Figure 3-2: Posterior distributions for standard (solid lines) and enhanced seafloor weathering (ESW; dotted lines) model runs with glacial durations of 4 m.y., 15 m.y., and 56 m.y. Randomly sampled model inputs are (A) V , (C) γ , (D) k_{sea} , and (E) X_{sea} in the ESW model (but X_{sea} is fixed at 1 in the standard model). The maximum value of (B) W_{sea} is a model output for each run. Red arrows point to 56 m.y. standard model posteriors, which are enhanced tenfold for visibility.

If model parameters are kept within standard ranges, then 56 m.y. glaciation is only generated for a small set of volcanic outgassing and seafloor weathering parameters that are opposite to those required for 4 m.y. glaciation. In the standard model, 56 m.y. glaciation requires a low CO_2 outgassing rate (V ; Fig. 3-2A), high seafloor weathering pH-dependence (γ ; Fig. 3-2C), and a high seafloor weathering proportionality constant (k_{sea} ; Fig. 3-2D). Generating 4 m.y. glaciation requires the opposite parameters, with very little or no overlap in the distributions of V and γ .

If seafloor weathering is enhanced by a multiplicative factor ($X_{sea} = 1-5$), then 56 m.y. glaciation can be generated for a wider range of volcanic outgassing and seafloor weathering parameters that are consistent with 4 m.y. glaciation. In the ESW model, 56 m.y. glaciation can be reproduced by combining the full range of V (Fig. 3-2A) and k_{sea} (Fig. 3-2D), and more than half of the explored range for γ (Fig. 3-2C). This difference is explained by the seafloor weathering multiplier (X_{sea} ; Fig. 3-2E), which causes a maximum seafloor weathering rate (W_{sea}) up to two

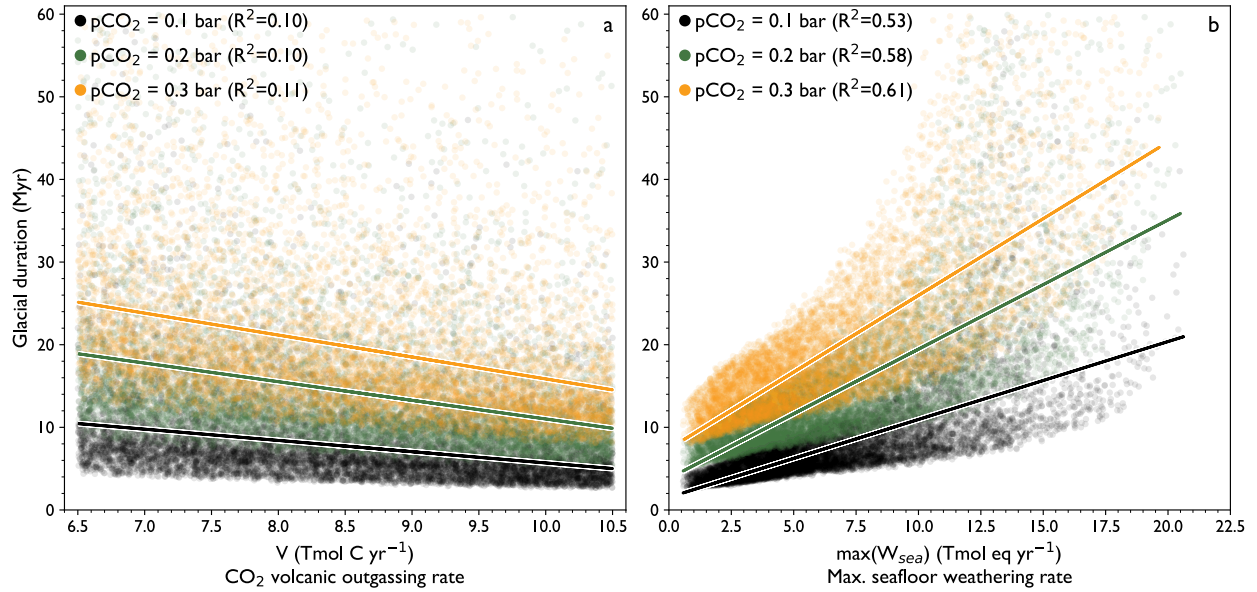


Figure 3-3: Glacial duration as a function of (A) V and (B) maximum W_{sea} for 10,000 enhanced seafloor weathering model runs. Glacial duration is the model time when atmospheric $p\text{CO}_2$ exceeds 0.1 (black), 0.2 (green), or 0.3 bar (orange). Lines of best fit are shown for each $p\text{CO}_2$ threshold, with R^2 values in the legend. Modern values: $V = 6.5\text{--}10.5 \text{ Tmol C yr}^{-1}$; $W_{sea} = \sim 0.4 \text{ Tmol eq yr}^{-1}$.

times higher than in standard 56 m.y. model runs (Fig. 3-2B). Moreover, parameter distributions for V , γ , and k_{sea} for 4 m.y. and 56 m.y. glaciation have significant overlap in the ESW model.

The seafloor weathering rate is a good predictor of glacial duration (Fig. 3-3). For varying $p\text{CO}_2$ deglaciation thresholds, the maximum W_{sea} correlates strongly with glacial duration (Fig. 3-3B), and 10–21 Tmol eq yr^{-1} is required to generate 56 m.y. glaciation (Fig. 3-2B). Such high W_{sea} is partially due to the acidic ocean under a high CO_2 atmosphere, but as shown in Figure 3-2B, alkalinity fluxes above 12 Tmol eq yr^{-1} can only be achieved when the seafloor weathering rate is enhanced by a multiplicative factor ($X_{sea} = 1\text{--}5$). In contrast, the volcanic outgassing rate correlates more weakly with glacial duration (Fig. 3-3A). Given that 4 m.y. and 56 m.y. glaciation occur in ESW model runs for a wide, overlapping range of CO_2 outgassing rates (Fig. 3-2A), enhancement of seafloor weathering due to X_{sea} alone can explain the glacial duration difference.

3.4 Discussion

Although the threshold of deglaciation is sensitive to albedo changes, it does not explain the long duration of the Sturtian glaciation, nor does reduced volcanic outgassing. Instead, our models require higher seafloor weathering rates and more CO₂ removal via carbonate precipitation during the 56 m.y. Sturtian than during the 4 m.y. Marinoan, with our proposed secular evolution shown in Figure 3-4. The glacial durations can be explained if seafloor weathering reaches a maximum of 10–21 Tmol eq yr⁻¹ during the Sturtian and 0–6 Tmol eq yr⁻¹ during the Marinoan, modeled with the multiplicative factor $X_{\text{sea}} = 1\text{--}5$ (Figs. 3-2A and 3-3); this begs the question: why do we expect such a difference in seafloor weathering rate?

The seafloor weathering rate is controlled by the fluid flux through seafloor basalt, which depends on the permeability structure of the oceanic crust. Presently, the fluid flux through off-axis oceanic crust is $0.6\text{--}2 \times 10^{16}$ kg yr⁻¹ (15%–50% of the river flux), which creates water-to-rock ratios of ~1500–4000 (Coogan and Gillis, 2018). Because low-permeability sediment accumulates on older crust, over 80% of the fluid flux (and most seafloor weathering) today occurs in <20-m.y.-old oceanic crust (Johnson and Pruis, 2003). However, Snowball ice sheets are expected to drastically reduce the sediment flux (Partin and Sadler, 2016), as is the lack of pelagic calcifiers, which would increase fluid flow in older crust.

Hydrothermal anhydrite (CaSO₄) formation reduces seafloor permeability and available basalt. In modern hydrothermal systems, $1.3\text{--}16 \times 10^{10}$ kg anhydrite is precipitated per year (Kleine et al., 2022), which lowers seafloor basalt porosity by a factor of 2.5–20 and forms a low-permeability layer (DePaolo et al., 2022), limiting available weatherable basalt by up to a factor of 10 (Sleep, 1991). Although 10%–60% of this anhydrite redissolves back into seawater over the ~200 m.y. lifetime of the oceanic crust (Kleine et al., 2022), most seafloor weathering occurs in <20-m.y.-old crust, which is largely clogged by anhydrite.

Hydrothermal anhydrite formation depends on the availability of seawater sulfate (SO₄), Ca, and Mg, and has been limited by sulfate throughout Earth history (Antonelli et al., 2017). The reactant Ca and SO₄ come from seawater, with additional Ca leached from hot basalt during seawater Mg exchange, so sulfate is the limiting factor when it is less abundant than seawater Ca + Mg. During the Cretaceous, reaction transport models predict a 26%–50% reduction in anhydrite production, and production at shallower depth, due to the low seawater sulfate (10 mM then versus 28 mM today; Fotherby et al., 2025).

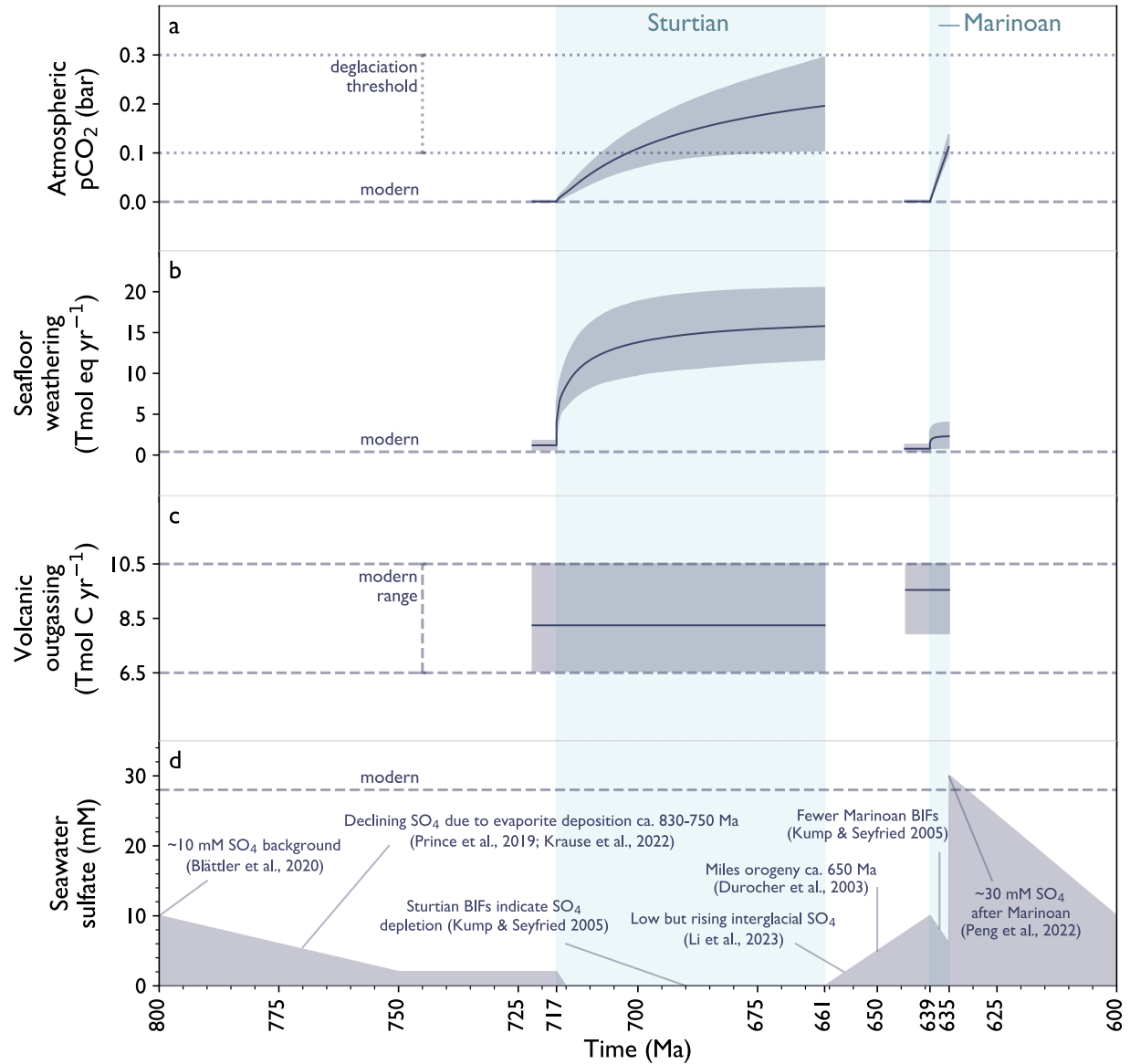


Figure 3-4: Secular evolution of the Cryogenian in the enhanced seafloor weathering (ESW) model. Solid lines are means, and envelopes are 95% confidence intervals from ESW model runs corresponding to Figure 3-2. Atmospheric $p\text{CO}_2$ (**A**) and seafloor weathering (**B**) are model results. Volcanic outgassing (**C**) is a model input; the step change is an artifact of combining the distributions in Figure 3-2A. Seawater sulfate (**D**) is not modeled explicitly in our model but implicitly in a weathering multiplier; here, it is estimated from literature (see main text). BIF—banded iron formation; blue regions—glaciation. Modern values: $p\text{CO}_2 = 0.00028$ bar; $W_{\text{sea}} = \sim 0.4$ Tmol eq yr^{-1} ; $V = 6.5\text{--}10.5$ Tmol C yr^{-1} ; $\text{SO}_4 = 28$ mM.

Stratigraphic and geochemical evidence indicate that marine sulfate concentrations declined during the Late Tonian, due to the deposition of giant sulfate evaporite deposits between ca. 830 Ma and 750 Ma, primarily in the Centralian Superbasin of Australia, which sequestered sulfate in continental basins (Prince et al., 2019; Krause et al., 2022). During the Sturtian, the presence of banded iron formations (BIFs) indicates near-complete removal of marine sulfate (Kump and Seyfried 2005; Cox et al., 2013). Sulfur isotopes in pyrite suggest seawater sulfate then rebounded leading up to the Marinoan (Li et al., 2023), consistent with the relative dearth of Marinoan BIFs. This may be due to an increase in sulfate weathering due to the ca. 650 Ma Miles Orogeny (also known as the Areyonga movement), which exhumed evaporites in the Centralian Superbasin (Durocher et al., 2003). In the immediate Marinoan aftermath, widespread barite (BaSO_4 ; Hoffman et al., 2017) in cap carbonates and sulfur isotopes (Peng et al., 2022) are consistent with near-modern marine SO_4 of ~ 30 mM or possibly higher.

We propose that low sulfate and limited anhydrite formation during the Sturtian increased seafloor weathering and prolonged glaciation. Consistent with the BIFs, seawater sulfate was low during the Sturtian due to anoxia and reduced continental weathering and continued microbial and hydrothermal consumption (Cox et al., 2013). As seawater sulfate declined, seafloor anhydrite formation slowed, and seafloor weathering increased. The 56 m.y. Sturtian duration is therefore a consequence of the following positive feedback: (1) seawater sulfate and sediment decreased, (2) seafloor weathering increased, (3) glaciation was prolonged by increased CO_2 removal via carbonate deposition, then back to (1). The magnitude of this effect on seafloor weathering may be a factor of 2.5–20 (see above), large enough to cause the difference required by our model. Consequentially, our model is consistent with evidence for Sturtian syn-glacial marine carbonate precipitation (Hood et al., 2022) and predicts that Sturtian ophiolites should be pervasively carbonatized (e.g., in the Arabian-Nubian Shield).

We propose that the shorter duration of the Marinoan suggests a threshold where higher seawater sulfate and/or slower sulfate consumption at the onset of the Marinoan did not enhance seafloor weathering enough to trigger the positive feedback, leading to deglaciation after only 4 m.y.

3.5 Conclusions

Our results indicate that the drastically disparate durations of the Sturtian and Marinoan Snowball Earth events can be explained by differences in seafloor weathering. Seafloor weathering drives CO₂ consumption via carbonate deposition and maintains a Sturtian-duration glaciation when the maximum alkalinity flux is 10–21 Tmol eq yr⁻¹, compared to 0–6 Tmol eq yr⁻¹ required for a Marinoan-duration glaciation. We propose that the difference in seafloor weathering was driven in part by marine sulfate: during the Sturtian, seawater sulfate was very low, which lead to less hydrothermal anhydrite production and highly porous, easily weathered seafloor basalt. In the Marinoan, higher seawater sulfate limited seafloor weathering and caused deglaciation before ocean anoxia and sulfate consumption prevailed. Overall, this work not only provides a new mechanism for maintaining Cryogenian glaciations, but also highlights critical planetary climate feedbacks linked to ocean chemistry and further connects global glaciation with atmosphere-ocean oxidation.

3.6 Supplementary material

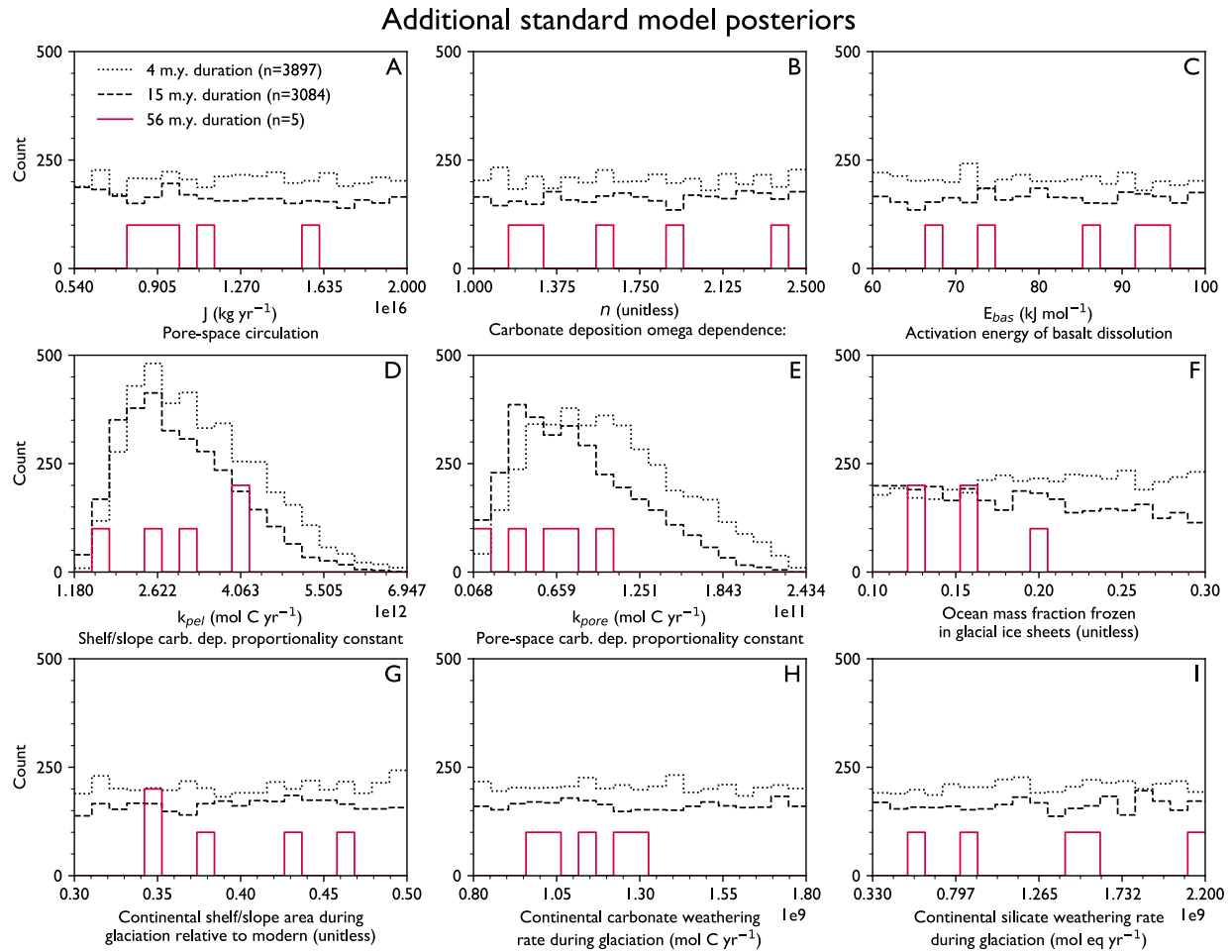


Figure S3-1: Additional posterior distributions for standard model runs with glacial durations of 4, 15, and 56 m.y. The 56 m.y. model posteriors (red) are enhanced by a factor of 100 for visibility. The distributions in panels D and E are approximately Gaussian instead of uniform because they are not directly sampled; rather, they are a downstream product of model calibration which depends on other uniformly randomly sampled parameters. Further description of parameters and their sampled ranges is found in Thomas and Catling (2024).

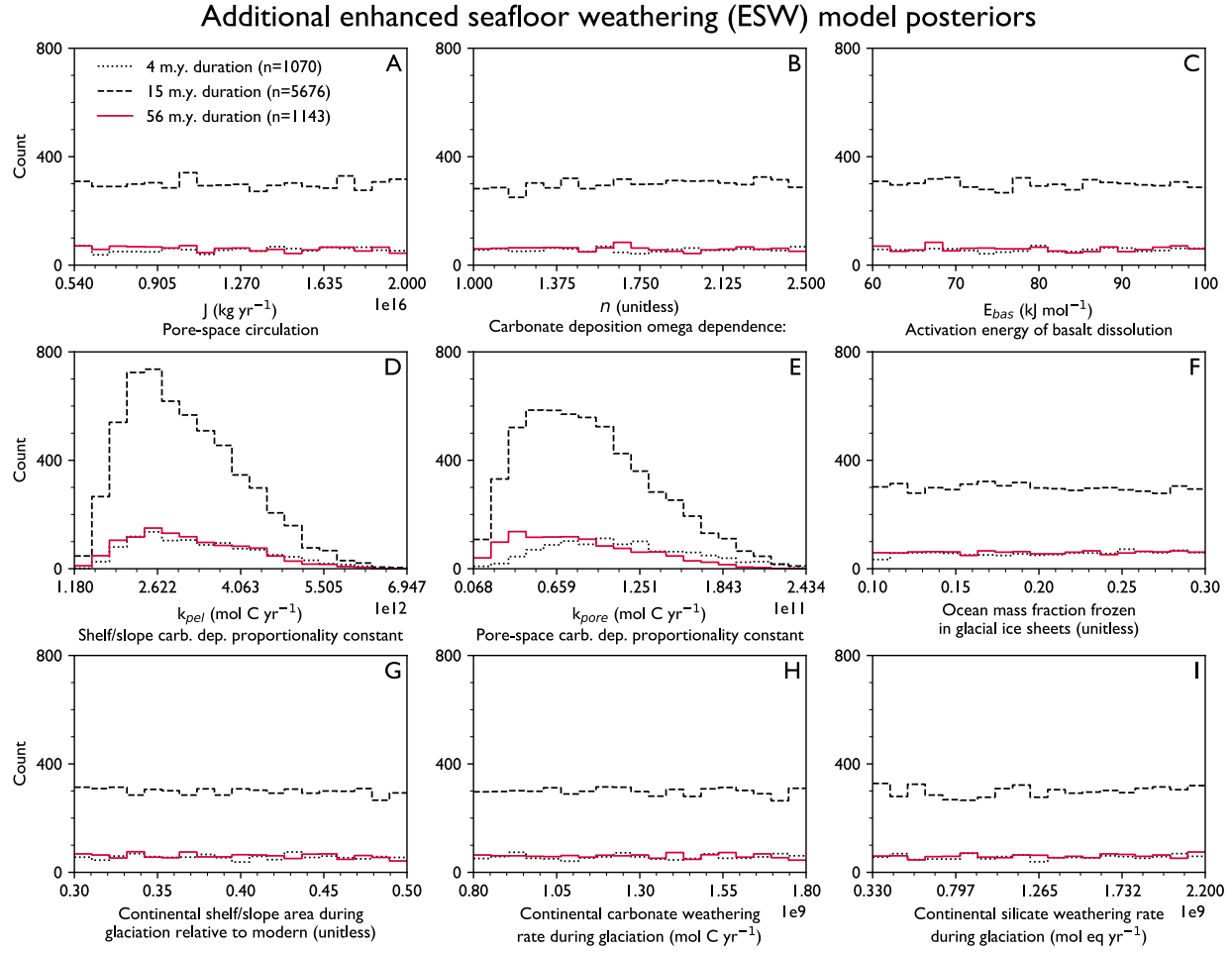


Figure S3-2: Additional posterior distributions for enhanced seafloor weathering (ESW) model runs with glacial durations of 4, 15, and 56 m.y. The distributions in panels **D** and **E** are approximately Gaussian instead of uniform because they are not directly sampled; rather, they are a downstream product of model calibration which depends on other uniformly randomly sampled parameters. Further description of parameters and their sampled ranges is found in Thomas and Catling (2024).

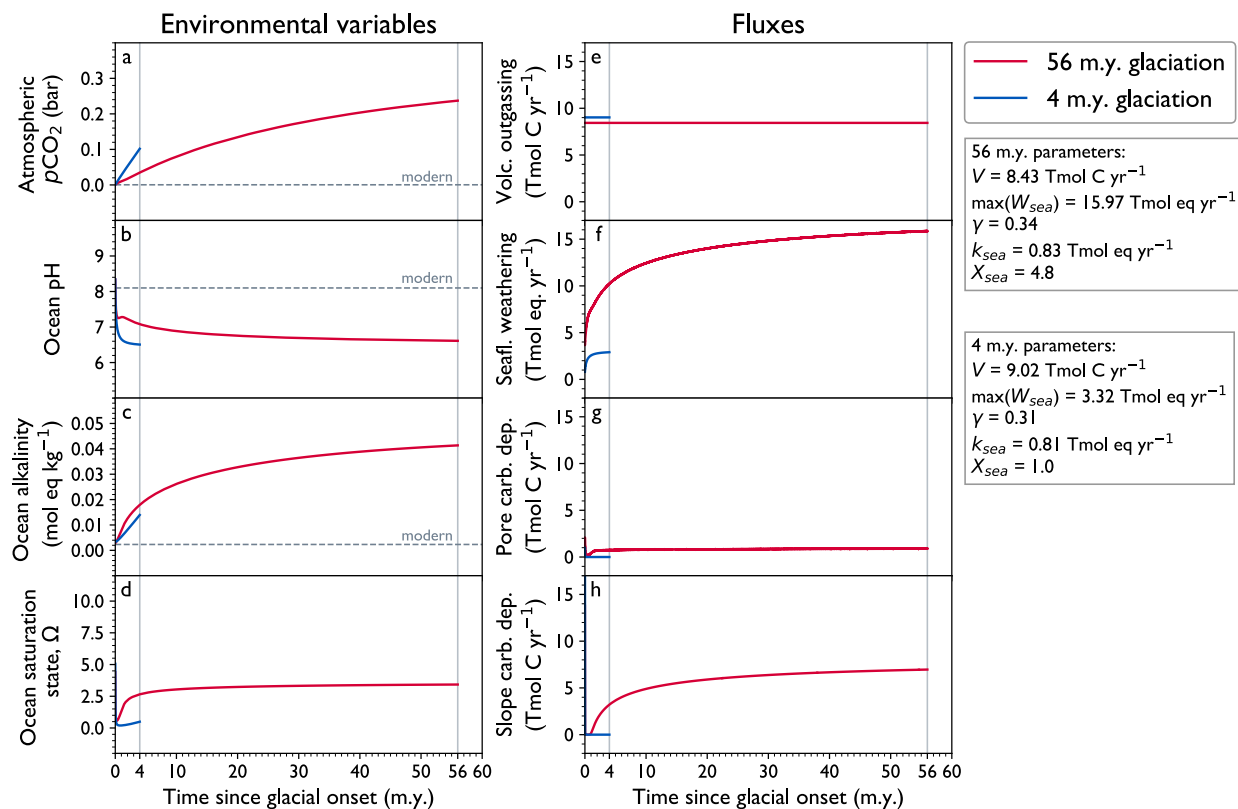


Figure S3-3: Representative model runs consistent with 4 and 56 m.y. glacial durations. Parameters used to generate these model runs are shown in the legend, with further description of parameters in Methods and Figures 2 and 3. **(a, b, c)** Horizontal dashed lines show modern Earth values ($p\text{CO}_2 = 0.00028 \text{ bar}$, $\text{pH} = 8.1$, $\text{alkalinity} = 0.00232 \text{ mol eq kg}^{-1}$; Pilson, 2012). **(d)** Ocean saturation state refers to calcium carbonate. Fluxes include **(e)** volcanic outgassing, **(f)** seafloor weathering, and carbonate deposition **(g)** in the oceanic crust pore-space and **(h)** on the continental shelf/slope.

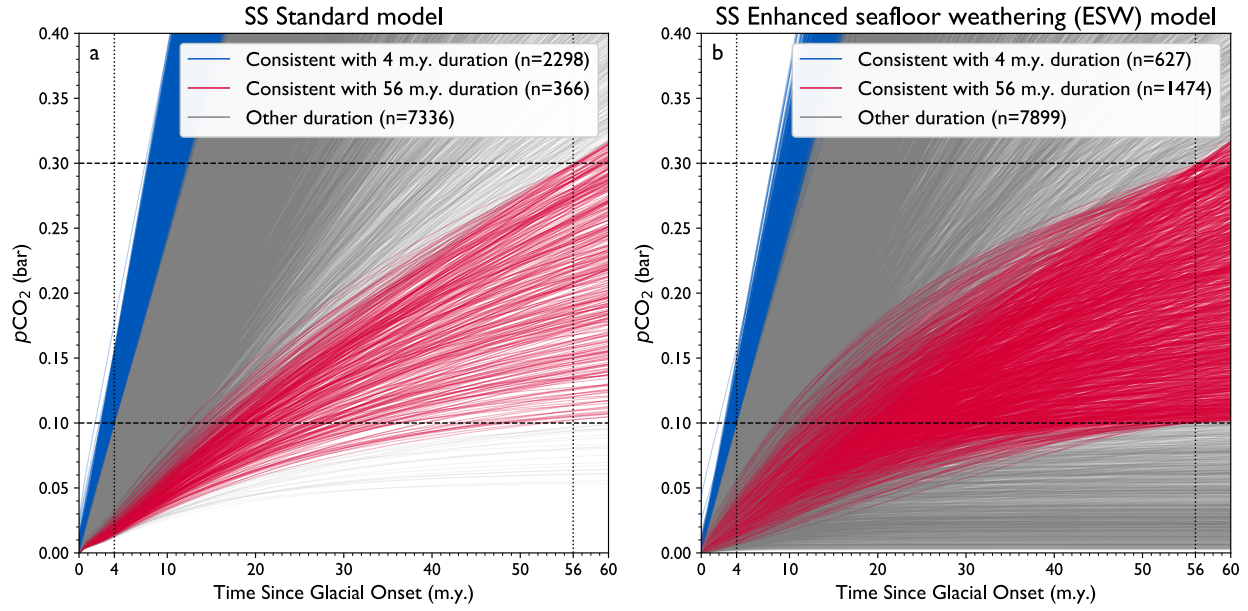


Figure S3-4: From the sensitivity study (SS) where $V = 3.5\text{-}10.5 \text{ Tmol C yr}^{-1}$: Evolution of atmospheric $p\text{CO}_2$ in 10,000 model runs with randomly sampled parameters in the (a) standard model and (b) enhanced seafloor weathering model, where a multiplicative factor (X_{sea}) increases seafloor weathering by a factor of 1-5. Vertical dotted lines show 4 and 56 m.y. glaciation. Horizontal dashed lines are the minimum and maximum atmospheric $p\text{CO}_2$ expected to cause deglaciation: 0.1-0.3 bar.

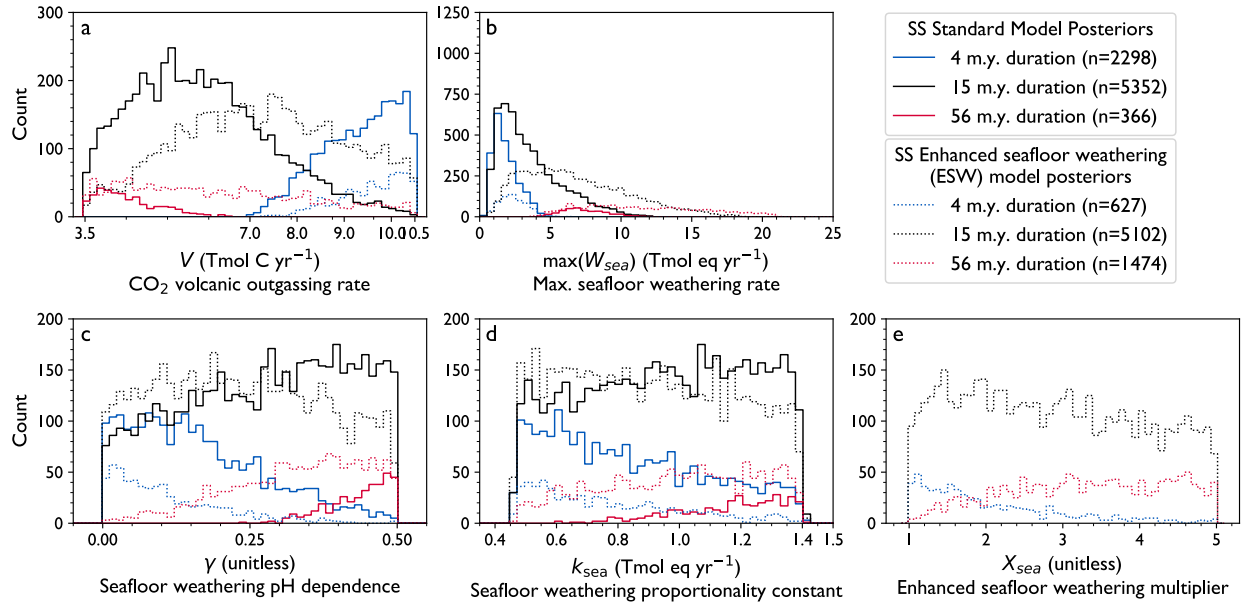


Figure S3-5: From the sensitivity study (SS) where $V = 3.5\text{-}10.5 \text{ Tmol C yr}^{-1}$: Posterior distributions for standard (solid lines) and enhanced seafloor weathering (ESW; dotted lines) model runs with glacial durations of 4, 15, and 56 m.y. Randomly sampled model inputs are (a) V , (c) γ , (d) k_{sea} , and (e) X_{sea} in the ESW model (but fixed at 1 in the standard model). The maximum value of (b) W_{sea} is a model output for each run.

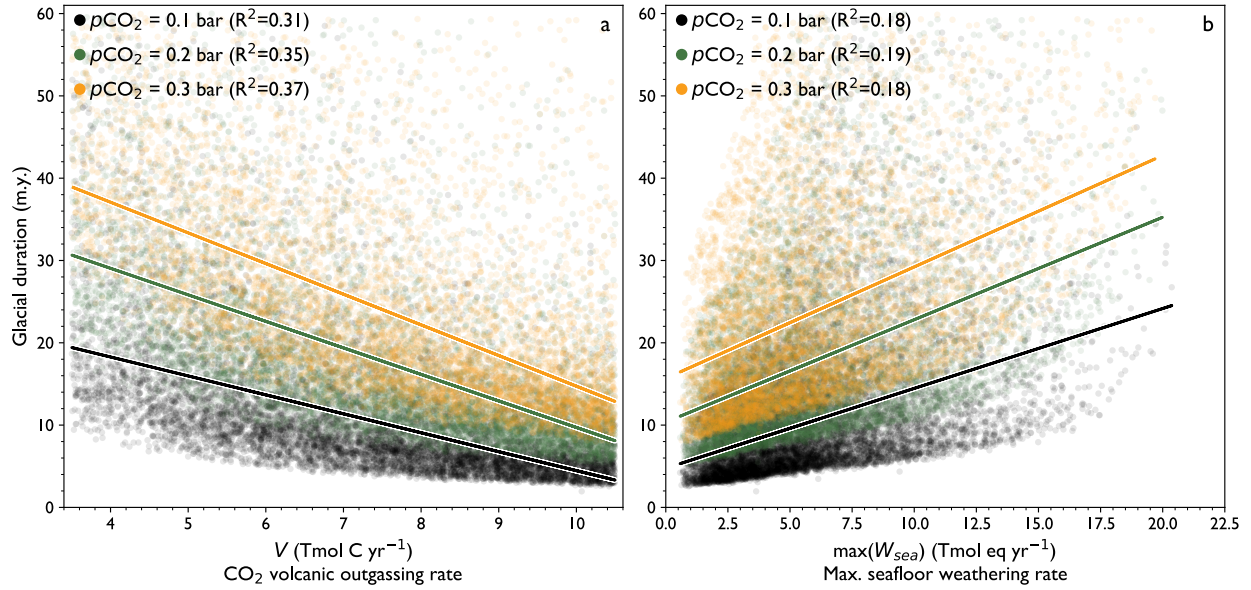


Figure S3-6: From the sensitivity study (SS) where $V = 3.5\text{--}10.5$ Tmol C yr $^{-1}$: Glacial duration as a function of (a) V and (b) maximum W_{sea} for 10,000 enhanced seafloor weathering model runs. Glacial duration is the model time when atmospheric $p\text{CO}_2$ exceeds 0.1 (black), 0.2 (green), or 0.3 bar (orange). Lines of best fit are shown for each $p\text{CO}_2$ threshold, with R^2 values in the legend. Modern values: $W_{sea} = \sim 0.4$ Tmol eq yr $^{-1}$.

3.6.1 Sensitivity study: volcanic outgassing rate

For a given model run in the main text, volcanic outgassing of CO₂ (V) is held constant in the range of modern-day uncertainty: 6.5-10.5 Tmol C yr⁻¹ (Catling and Kasting, 2017, p. 203). In Tasistro-Hart et al. (2025), the simpler analytical model of Arnscheidt and Rothman (2020) is used to study the duration of Snowball glaciations. The lower bound on V in this study is 3.5 Tmol C yr⁻¹, taken from the compilation of modern volcanic outgassing rates in Isson et al. (2020). Here we explore the effect of the lower bound on V by performing the same analysis presented in the main text, but exploring V in the range: 3.5-10.5 Tmol C yr⁻¹. Model runs in this sensitivity study are denoted SS.

Extending the lower bound on V makes the Sturtian slightly easier to produce and the Marinoan harder to produce (Fig S3-4). A 56 m.y. glaciation is reproduced 3.6% of the time in the SS standard model (0.5% in main text) and 15% of the time in the SS enhanced seafloor weathering (ESW) model (11% in the main text). A 4 m.y. glaciation is reproduced 23% of the time in the SS standard model (39% in the main text) and 6.3% in the SS ESW model (11% in the main text). This is a straightforward consequence of lowering V , which results in slower atmospheric CO₂ buildup and longer glaciation.

Four m.y. glaciation is impossible to reproduce in our model for values of V below 6.5 Tmol C yr⁻¹ (Fig. S3-5). So, although the Sturtian is slightly easier to reproduce with lower V , it is incompatible with the duration of the Marinoan. Therefore, if V was below 6.5 Tmol C yr⁻¹ during the Sturtian, it would have had to increase afterward to reproduce the Marinoan. The Marinoan distributions in Figure S3-5 are largely unchanged from main text Figure 3-2. Sturtian distributions show an expected preference for the lowest possible V and the max seafloor weathering rate distributions are wider, but still higher than the Marinoan distributions. Figure S3-6 is also largely unchanged from main text Figure 3-3, but there is more scatter in Fig S3-6b because of the larger range of V .

Ultimately, this sensitivity study further justifies the range of V explored in the main text. If V is taken to be lower than 6.5 Tmol C yr⁻¹, then the Marinoan becomes impossible to reproduce in our model and a change in volcanic outgassing rate between the two glaciations is required. This demonstrates the alternative scenario that is described in the main text (e.g., Dutkiewicz et al., 2024), further strengthening the purpose of the main text: to propose a new hypothesis for the differing glacial durations where the volcanic outgassing rate does not change between the two

glaciations. The range of V explored in the main text is where parameter distributions for the two glaciations overlap, which is the focus of our study. We conclude that extending the lower bound on the volcanic outgassing rate in this sensitivity study does not change any of our main text conclusions.

3.7 Data availability and acknowledgements

The Python source code used in this work is publicly available at the lead author's GitHub page (<https://github.com/trentagon>). The data used to generate all figures and analysis are available at Zenodo (<https://doi.org/10.5281/zenodo.17567191>).

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4. Statistical Geochemical Constraints on Present-day Water Outgassing as a Source of Secondary Atmospheres on the TRAPPIST-1 Exoplanets

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Abstract

The TRAPPIST-1 planetary system is observationally favorable for studying if planets orbiting M stars can retain atmospheres and host habitable conditions. Recent JWST secondary eclipse observations of TRAPPIST-1 c rule out a thick CO₂ atmosphere but do not rule out atmospheric water vapor or its photochemical product, oxygen. Given the high expected escape rate, maintenance of atmospheric water vapor would require a present-day water source, such as volcanic outgassing. Here, we simulate water outgassing on the TRAPPIST-1 planets over a broad phase space that is based on solar system terrestrial bodies. We then apply two filters based on observation and geochemistry that narrow this phase space and constrain the plausible outgassing scenarios. For all seven TRAPPIST-1 planets, we find that the water outgassing rate is most likely $\sim 0.03\times$ Earth's but has upper limits of $\sim 8\times$ Earth's. The allowed range also implies low, Mars-like magma emplacement rates and relatively dry, Earth-like mantles, although mantle water mass fractions up to 1 wt% are possible. We also present scenarios with magma emplacement rates similar to Mars, Earth, and Io, resulting in different preferred mantle water content and outgassing rates. We find that water outgassing rates are potentially high enough to balance water escape rates, providing a theoretical pathway for the TRAPPIST-1 planets to maintain surface water or water-vapor-containing atmospheres over long timescales. The bounds on outgassing rates and interior properties can be used in atmospheric chemistry and escape models to contextualize future observations of the TRAPPIST-1 planets, and may be applicable to other terrestrial exoplanets.

4.1 Introduction

The TRAPPIST-1 planetary system is a natural laboratory for studying habitability. This ultracool M dwarf star harbors seven transiting, terrestrial-sized planets, which span orbital distances interior to, within, and beyond the star’s habitable zone (Gillon et al., 2017). Most of the planets are remarkably similar to Earth in mass and radius but have a consistently lower density than the terrestrial planets in our solar system (Agol et al., 2021). Initial observations with the Hubble Space Telescope ruled out H₂-dominated primary atmospheres for the first six planets from the star (De Wit et al., 2016, 2018). M dwarf stars are $\sim 3/4$ of the stars in the galaxy (Bochanski et al., 2010), so the potential habitability of the TRAPPIST-1 planets may be indicative of potentially habitable worlds elsewhere. To that end, it is critical to understand whether planets orbiting ultracool dwarf stars can sustain secondary, outgassed atmospheres and host habitable surface conditions (e.g., Shields et al., 2016; Meadows et al., 2018; Krissansen-Totton et al., 2024). We now have the opportunity to investigate these possibilities by observing and characterizing the TRAPPIST-1 planets.

Recent JWST observations have placed constraints on the presence and nature of atmospheres on the TRAPPIST-1 planets, with no atmosphere or tenuous atmospheres being the most favored explanations, although some denser atmospheres may still be consistent with the data. Secondary eclipse observations have been made for the two innermost planets, TRAPPIST-1 b and c (Greene et al., 2023; Zieba et al., 2023). For TRAPPIST-1 b, Greene et al. (2023) concluded that the 15 μm secondary eclipse measurement is most consistent with an airless rock. In contrast, clear-sky and cloudy Venus-like atmospheres, and O₂-dominated atmospheres with more than 0.5 bar CO₂, were ruled out at over 6 σ (Greene et al., 2023), and atmospheres >0.3 bar with at least 100 ppm CO₂ were ruled out at 3 σ (Ih et al., 2023). However, a dense atmosphere may not be completely ruled out, as a preliminary combined analysis of JWST 15 μm and 12.8 μm secondary eclipse observations appears to be consistent with models of both an airless, fresh ultramafic surface—possibly indicative of active volcanism—or possibly a dense CO₂ atmosphere with a photochemical, haze-induced temperature inversion (Ducrot et al., 2025).

For TRAPPIST-1 c, the Zieba et al. (2023) 15 μm secondary eclipse measurement is also consistent with a range of airless and atmospheric scenarios. They found that the best fits to the data were for models with an airless rock or a thin (e.g., 0.1 bar) O₂–CO₂ atmosphere. They also found that Venus-like atmospheres of ≥ 10 bar, and O₂–CO₂ atmospheres of >1 bar surface pressure

with more than 1000 ppm CO₂, were ruled out at $>2.6\sigma$. Lincowski et al. (2023) expanded the compositional range of model atmospheres, finding that atmospheres that contain water vapor are also consistent with the data to within 1.7σ – 1.8σ , including a 0.1 bar O₂, 100 ppm CO₂, 10% water vapor atmosphere, or a ≤ 3 bar steam atmosphere. Transmission spectroscopy of TRAPPIST-1 b, which would be complementary to the secondary eclipse observations, has yet to yield the sensitivity needed for molecular detection in a secondary atmosphere, due to the challenges of removing stellar contamination from the spectra (Lim et al., 2023). For the rest of the TRAPPIST-1 planets, which are likely too cool to have observable mid-infrared secondary eclipses, initial JWST transmission spectroscopy has been obtained, and these data are still under analysis (Lafreniere, 2017; Lim et al., 2021; Stevenson et al., 2021; Lafreniere, 2022). So, whether or not these planets have secondary atmospheres is still unconstrained.

If the putative present-day atmospheric water on the TRAPPIST-1 planets is the result of delivery during planet formation and subsequent loss over time, then a large initial water endowment is required for any to remain today (e.g., over 50 Earth oceans would be required on the three inner planets; Gialluca et al., 2024). The large initial water endowment is required because water in the atmosphere would have been subject to intense atmospheric escape driven by the high luminosity and radiation from the host star during the lifetime of the system. Specific processes that would drive ocean and atmospheric escape include the long-lived super-luminous pre-main-sequence phase (Luger & Barnes, 2015; Bolmont et al., 2016; Gialluca et al., 2024), the high baseline stellar X-ray and ultraviolet (XUV) flux and stellar wind during the main sequence (Bourrier et al., 2017; Dong et al., 2018; Gialluca et al., 2024), and frequent stellar flares throughout the lifetime of the star (Amaral et al., 2022). If even traces of water vapor are confirmed in the atmosphere of TRAPPIST-1 c, it is important to know where this water came from and how it could have survived this intense atmospheric escape.

Alternatively, instead of originating from a large initial endowment, any current water in the atmospheres of the TRAPPIST-1 planets could be supplied by continuous outgassing from the planets' interiors. This is especially true for simulations of more tenuous 0.1bar O₂ atmospheres with greenhouse gases such as water vapor, that produce better fits to the observations of the two innermost planets (Ih et al., 2023; Lincowski et al., 2023; Gillon et al., 2025, in preparation). These tenuous atmospheres are likely to have short (less than a million year) lifetimes against atmospheric loss (Dong et al., 2018), and so must be continuously replenished to persist to present

day. These atmospheres also provide poor day–night heat transport, potentially resulting in freezing nightside temperatures that condense and trap water vapor (Lincowski et al., 2023).

Consequently, outgassed water on the TRAPPIST-1 planets would have important implications for their atmospheric evolution and habitability. On Earth, water vapor is the primary constituent of volcanic gases (Catling & Kasting, 2017), so it is reasonable to explore how water could be outgassed on the TRAPPIST-1 planets, given that their densities are consistent with terrestrial composition (Agol et al. 2021). If water is stored in the planets’ interiors before being outgassed to the atmosphere, then the outgassing bottleneck decreases the availability of water vapor for atmospheric escape during the lifetime of the system. This process would help to preserve the planetary water reservoir and extend the availability of water vapor in the planetary atmosphere (e.g., Moore & Cowan, 2020). Moreover, for the habitable zone planets, if the water outgassing rate is high enough, it could balance atmospheric escape (Dong et al., 2018; Gialluca et al., 2024) and create steady-state surface water that is potentially long-lived.

Given that the TRAPPIST-1 planets have densities typically 5%–10% lower than similarly sized solar system terrestrial planets (Agol et al., 2021), higher water outgassing rates than Earth’s might be expected. The low densities could be partially explained by a high interior water content, which may contribute to water-rich magmas and enhance water outgassing. Ultimately, if atmospheric water exists on the TRAPPIST-1 planets, it must come from either (1) an initial water endowment that was lost over time, or (2) continuous replenishment from a source like volcanic outgassing, or a combination of both.

The goal of this paper is to explore the likelihood of water outgassing as a potential source for present-day water on the TRAPPIST-1 planets by addressing the following question: what are plausible bounds on the present-day water outgassing rate? To address this question, we develop a modeling approach to statistically search a broad parameter space of possible present-day scenarios on the TRAPPIST-1 planets given their unconstrained geological properties. This model can help in the interpretation of atmospheric observations of the TRAPPIST-1 planets by identifying which scenarios are not only consistent with the observational data, but are also consistent with geochemical constraints based on solar system knowledge. If the TRAPPIST-1 planets are found to have no significant exterior water, the model also sets constraints on outgassing that may be applicable to observations of other planetary systems in the future. This

approach is complementary to planetary evolution models, which yield valuable insights but may be less suited to exploring the broad phase space of present-day possibilities.

4.2 Methods

To estimate plausible outgassing rates on the seven TRAPPIST-1 planets, we first develop a theoretical outgassing model that explores a large parameter space, then we filter these results to identify the most plausible outgassing ranges by considering observational, empirical, and theoretical constraints on the TRAPPIST-1 planets.

4.2.1 Theoretical model

In this section, we describe the theoretical model used to estimate modern rates of water outgassing on the TRAPPIST-1 planets, summarized in Figure 4-1. Our model is simpler in comparison to fully coupled atmosphere-interior evolution models (e.g., Krissansen-Totton & Fortney, 2022), but this design choice allows us to efficiently explore a large parameter space of possible present-day scenarios and generate statistical inferences. First, we estimate how much water could reasonably be stored in the interior of the TRAPPIST-1 planets based on theoretical studies that are informed by the mineralogy of solar system planets. Second, we describe an interior melting model that we use to determine how much water could be dissolved in interior magmas. Third, we estimate the rate at which magma is generated in the interior and delivered to the surface (i.e., the magma emplacement rate). Fourth, we estimate water outgassing rates on the TRAPPIST-1 planets using an equilibrium magmatic outgassing model that calculates the partitioning of gases (including water vapor) between the atmosphere and surface magma.

4.2.1.1 Interior water content

In our model, we consider mantle-derived magmas as the ultimate source for outgassed water on the TRAPPIST-1 planets. Once mantle water is sourced to the exterior, it may be recycled between the surface and crust, but this does not provide additional water and, thus, does not help replenish water lost to space on long timescales. Therefore, we must know the mantle water mass fraction, $m_{H_2O}^{mantle}$, to begin our calculation. The value of $m_{H_2O}^{mantle}$ for the TRAPPIST-1 planets is unknown, and indirect constraints on this value, via, e.g., density, are subject to degeneracies in the internal structure and composition (Agol et al., 2021), which will be discussed later. For these reasons, we

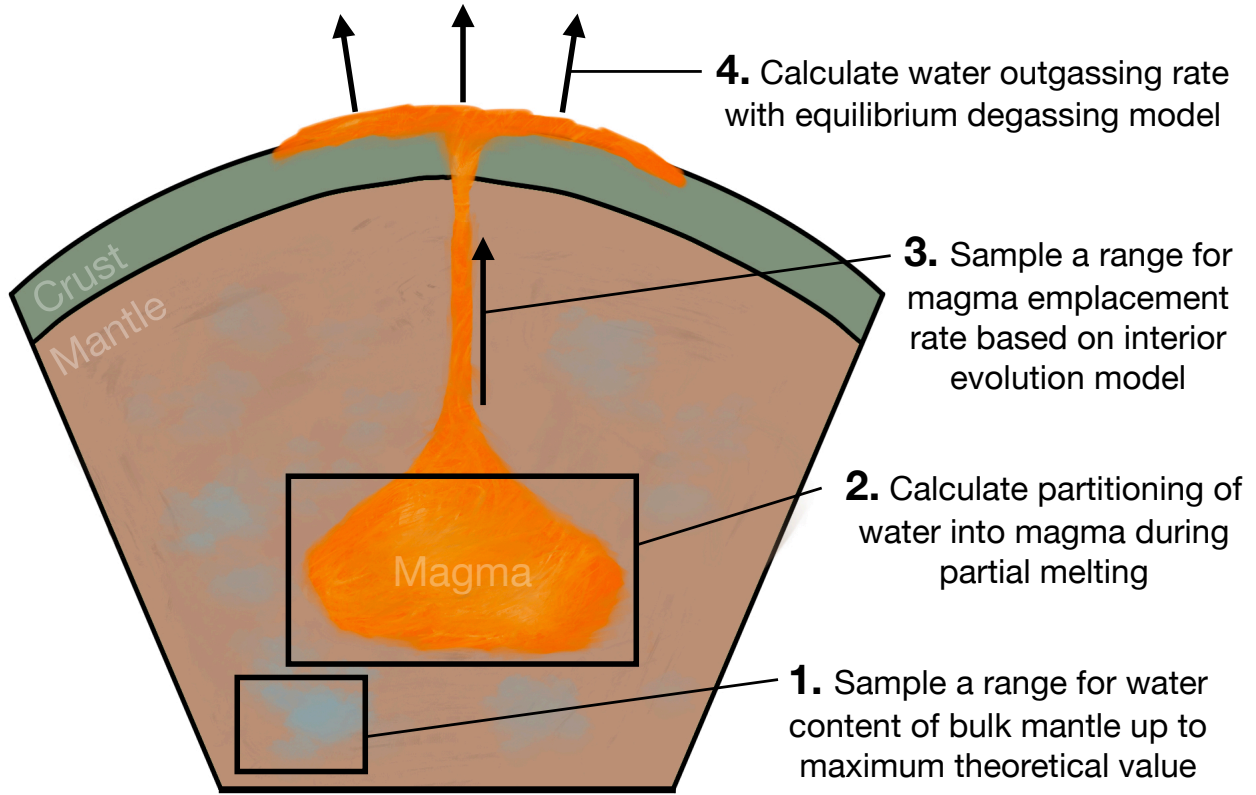


Figure 4-1: Schematic diagram of steps in the theoretical model. Further description of key parameters, sampled ranges, and calculation procedures is found in Methods.

rely on theoretical studies, informed by Earth’s properties, to estimate a plausible range of $m_{H_2O}^{mantle}$, including maxima for mantle water storage.

To construct models of the TRAPPIST-1 planets, which have densities comparable to, but slightly lower than Earth’s, we first consider the amount and mode of water storage in Earth’s mantle. Earth’s mantle contains $m_{H_2O}^{mantle} = 0.049\text{--}0.24$ wt% water (Ohtani, 2021), which is stored in a combination of hydrous minerals and nominally anhydrous minerals (NAMs; e.g., reviewed by Ohtani, 2015, 2021). Hydrous minerals can store over 10 wt% water by incorporating OH or H₂O directly in their crystal structure (see Tables 1 and 2 in Ohtani, 2015, and references within). Examples include serpentine, brucite, and numerous high-pressure “alphabet phase” Mg-silicate minerals. On the other hand, NAMs rarely exceed 1 wt% water, and store water by incorporating OH groups as impurities in the gaps of their crystal structure. Examples include olivine, wadsleyite, ringwoodite, and perovskite. Despite the superior water storage capacity of hydrous minerals, Earth’s deep mantle water is mostly stored in NAMs because hydrous minerals are

typically unstable at the high temperatures and pressures found deep in the interior (Bolfan-Casanova, 2005). However, differences in size, composition, and interior structure could allow other planets to have different proportions of these water-bearing minerals, and thus higher or lower $m_{H_2O}^{mantle}$ than Earth.

If we consider the multilayered terrestrial planetary interior model of Shah et al. (2021), we can constrain the maximum possible $m_{H_2O}^{mantle}$ for the TRAPPIST-1 planets to ~ 3 wt%. Shah et al. (2021) accounted for mantle hydration via both hydrous minerals and NAMs, including olivine polymorphs, brucite, perovskite, and post-perovskite, using available experimental data or molecular dynamics simulations when available. They found that the maximum capacity for total internal water storage on terrestrial planets is 6 wt%. However, most of this water is predicted to be stored within iron hydride in the core where it is unlikely to contribute to surface degassing. Shah et al. (2021) found that $m_{H_2O}^{mantle}$ is maximized when planets have high interior magnesium concentration relative to iron. For the masses of the TRAPPIST-1 planets, assuming they are magnesium-rich, the upper limit on mantle water mass as a fraction of total planet mass is ~ 2 wt% (Shah et al. 2021, Figure 7, top-middle panel). Scaling this according to the mass of the mantle, which is as low as 65% of the total planet mass for the corresponding magnesium abundance (Shah et al. 2021; see their Figure 2), results in an upper limit $m_{H_2O}^{mantle}$ of ~ 3 wt%.

Alternatively, Guimond et al. (2023) considered water storage only in NAMs, and estimated a more conservative upper limit on interior water storage of 1 wt%. Whereas Shah et al. (2021) assumed a fixed mineralogy within idealized terrestrial planet mantles, Guimond et al. (2023) specified bulk oxide content (e.g., MgO, SiO₂, and FeO) and used a thermodynamic model to calculate how these oxides speciate into different mineral phases. Importantly, Guimond et al. (2023) only considered water storage in NAMs. They did not include hydrous mineral phases or storage in the core. Guimond et al. (2023) found that terrestrial planets should not exceed a total water mass fraction (including core mass) of 0.2 wt% from mantle water storage alone, regardless of planet mass or compositional parameters (see their Figure 5). Converting the total water mass fraction into $m_{H_2O}^{mantle}$ assuming a large core mass fraction of 80 wt% (i.e., larger than Mercury's 65 wt%, which is the largest in the solar system; Charlier & Namur 2019) yields the maximum $m_{H_2O}^{mantle}$ of 1 wt%.

The interior water mass fractions of the TRAPPIST-1 planets are unlikely to be constrained through mass and radius observations (even though both have been precisely measured to within

~5% accuracy; Agol et al., 2021), highlighting the need for theoretical constraints. A surface water or ice layer has a more negative contribution to planet bulk density than the equivalent mass of H and O dissolved in interior silicates (e.g., Dorn & Lichtenberg 2021; Luo et al. 2024), which prevents us from extrapolating estimates of bulk water mass fraction from one reservoir to another. Furthermore, the size of each planetary water reservoir (e.g., core, mantle, exterior) is unknown. For example, it is possible that these planets do not have cores at all, which would immediately explain the low observed densities without the need for any additional low-density water (Agol et al., 2021). Taken together, the above degeneracies and uncertainties regarding the TRAPPIST-1 planets' observed densities are precisely why theoretical constraints based on known geochemistry are required.

Given that the observations do not strongly constrain the $m_{H_2O}^{mantle}$ values, we use the above theoretical studies to generate a plausible range for $m_{H_2O}^{mantle}$ on the TRAPPIST-1 planets. We assume that the maximum value of $m_{H_2O}^{mantle}$ is 1 wt% in the nominal model configuration, but we also test maximum values of 0.5 wt% and 3 wt% to assess model sensitivity. We assume that the minimum $m_{H_2O}^{mantle}$ is 0.01 wt% to account for a scenario in which the TRAPPIST-1 planets are relatively dry. These values bracket the Earth's $m_{H_2O}^{mantle} = 0.049\text{--}0.24$ wt% (Ohtani 2021). In summary, we initially explore the broad range $m_{H_2O}^{mantle} = 0.01\text{--}3$ wt% for the TRAPPIST-1 planets.

4.2.1.2 Magma water content

Assuming the above range of estimates for $m_{H_2O}^{mantle}$, we now calculate the corresponding water content of the interior magmas for the TRAPPIST-1 planets by considering the diversity of Earth's mantle-derived magmas and the processes that produce them. Magmas can have higher water content than the mantle minerals from which they are derived, as water preferentially partitions into magma during partial melting (Ni et al., 2016). Earth's magmas that are produced by subduction processes, giving rise to island arc basalts or continental margin basalts, typically have the highest water fractions due to the recycling of liquid water from the surface (Sigurdsson et al., 2015, Ch. 7). For the TRAPPIST-1 planets, we base our calculations on the mantle-derived magmas because they are the net source of water to the surface and atmosphere, whereas recycling processes (if present) are only responsible for the partitioning of water once it is at the surface or atmosphere. Therefore, we focus on the melting processes that generate Earth's mantle-derived mid-ocean ridge basalts (MORBs) and ocean island basalts. These magmas typically have H₂O

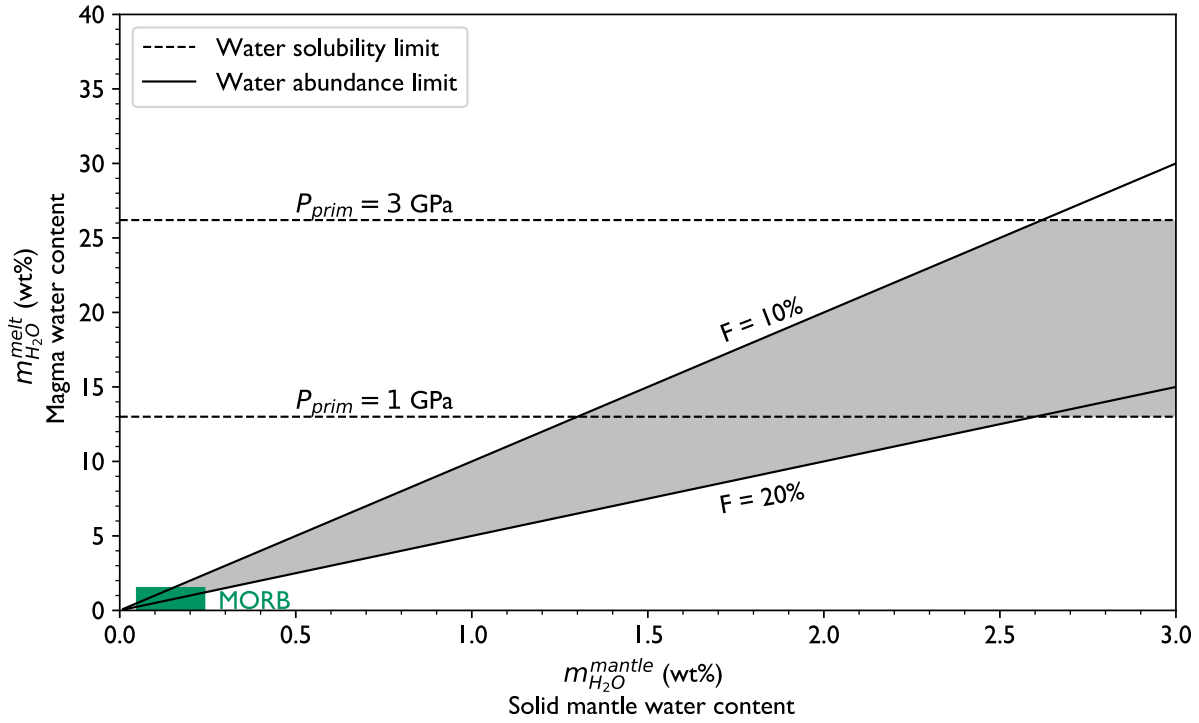


Figure 4-2: Water concentration in melt ($m_{H_2O}^{melt}$) as a function of bulk mantle water content ($m_{H_2O}^{mantle}$) considering water saturation and fractional melting. The dashed lines are the solubility-limited H_2O content of the magma under the maximum and minimum values of primary magma pressure, $P_{prim} = 1$ and 3 GPa. The black solid lines are the abundance-limited H_2O content of the magma assuming fractional melting under the maximum and minimum values of melt fraction, $F = 10$ and 20%. For a given $m_{H_2O}^{mantle}$, F , and P_{prim} , the true value of $m_{H_2O}^{melt}$ is the minimum from water saturation or fractional melting. The gray shaded region is the range of possible values allowed based on this procedure. The green shaded region labeled “MORB” shows the range for mid-ocean ridge basalt magma water content (0.1–1.5 wt%; Sigurdsson et al., 2015) and Earth’s mantle water concentration (0.049–0.24 wt%; Ohtani, 2021).

concentration of 0.1–1.5 wt% due to preferential water incorporation in the melt (Sigurdsson et al., 2015), up to $\sim 30\times$ Earth’s bulk mantle water content (Ohtani 2021).

The water content in the melt, $m_{H_2O}^{melt}$, can be limited by either the amount of water in the melting rocks (water abundance limit) or by the pressure-dependent ability of water to dissolve in the magma (water solubility limit). The value of $m_{H_2O}^{melt}$ is then given by the minimum value

	Nominal Range	Notes and References
Mantle water mass fraction, $m_{H_2O}^{mantle}$	0.01-1 wt%	See main text
Melt fraction, F	10%-20%	Based on MORBs ^b
Pressure of primary magma formation, P_{prim}	1-3 GPa	Based on MORBs ^b
Temperature of magma, T	873-1973 K	Based on Earth magmas ^c
Surface pressure, P_{surf}	0.001-100 bar ^a	Broad TRAPPIST-1 planet range
CO ₂ content of magma, $m_{CO_2}^{melt}$	$10^{-5} - 10^{-2}$ ^a	Based on Earth magmas ^d
Oxygen fugacity of magma, f_{O_2}	FMQ-4 to FMQ+5 ^a	Based on solar system observations ^e

Table 4-1: Outgassing model parameters.

^a Denotes this parameter was sampled uniformly in log space. All others were sampled uniformly in linear space.

^b See section on magma water content for further description. MORB = mid-ocean ridge basalt. The following references and corresponding parameter ranges were compiled in Wogan et al. (2020).

^c Coldest rhyolite magma to hottest komatiite magma (Huppert et al., 1984).

^d Approximate mass fraction range in Earth magma (Wallace, 2005, 2015; Anderson & Poland, 2017; Voyer et al., 2019).

^e Most reducing Martian meteorite to most oxidized Earth magma (Stamper et al., 2014; Catling & Kasting, 2017, p. 363).

calculated in these two limits. In the water abundance limit, we use the fractional melt model of Grott et al. (2011), which is based on known magma chemistry on Earth, and which Grott et al. (2011) applied to Mars. Following their Equation (6), $m_{H_2O}^{melt}$ as a function of $m_{H_2O}^{mantle}$ is given by

$$m_{H_2O}^{melt} = \frac{m_{H_2O}^{mantle}}{F} [1 - (1 - F)^{1/D}], \quad (4.1)$$

where F is the percentage of the mantle rocks that melt (i.e., local melt fraction), typically assumed to be 10%–20% for MORBs (e.g., Bolfan-Casanova, 2005), and D is the partitioning coefficient for water. D is defined as the concentration of water remaining in the rocks divided by the concentration of water that dissolves in magma, so lower D means more water in the magma. We assume $D = 0.01$ (Katz et al. 2003), but it can be as low as 0.001 in some cases (Aubaud et al. 2004); however, for either value of D , the term $(1 - F)^{1/D}$ in Equation (4.1) is $\ll 1$ for the range of

local melt fractions we assume. So, $m_{H_2O}^{melt}$ is primarily a function of the first term in Equation (4.1), $m_{H_2O}^{melt}/F$. We assume that the water concentration is homogeneous within the mantle water reservoir.

In the water solubility limit, we use a model that is similarly based on known magma chemistry on Earth and was previously applied to Mars (Katz et al., 2003; Grott et al., 2011). The pressure-dependent saturation concentration of H₂O in the melt is given by

$$m_{H_2O}^{melt} = \chi_1 P_{prim}^{\xi} + \chi_2 P_{prim}, \quad (4.2)$$

where $\chi_1 = 12 \text{ wt\% GPa}^{-\xi}$, $\chi_2 = 1 \text{ wt\% GPa}^{-1}$, and $\xi = 0.6$ are empirical constants. P_{prim} is the pressure at which the primary magma is produced in the planet's interior, typically 1–3 GPa for MORBs on Earth (Sigurdsson et al., 2015). The water concentration in the melt is then taken as the minimum concentration calculated from the water abundance limit (Equation (4.1)) or water saturation limit (Equation (4.2)). This relationship is shown in Figure 4-2, and the parameter ranges we explore are shown in Table 4-1.

4.2.1.3 Magma emplacement rate

We now calculate the volumetric magma emplacement rate, Q (km³ yr⁻¹), on the TRAPPIST-1 planets. Magma emplacement, the volcanic deposition of magma on the planet's surface, is driven by interior heat sources on a planet, including leftover heat from formation, radioactive decay, and tidal heating (e.g., Schubert et al., 2001). The magnitude of these internal heat sources depends on a planet's mass and age, among many other parameters. Given that the TRAPPIST-1 planets are 0.306–1.443 Earth masses (Agol et al., 2021), and the age of the system is 7.6 ± 2.2 Gyr (Burgasser & Mamajek, 2017), there is a wide range of possible internal heat values and corresponding magma emplacement rates. Further uncertainty is introduced due to our lack of constraints on the planets' interior compositions and structures.

Earth, Mars, and Io are known to have significantly different interior heat sources and planetary processes, and studies of these bodies have yielded a diverse range of magma emplacement rates (see Lourenço et al., 2018, and references within) that may provide useful benchmarks when considering the TRAPPIST-1 planets. Earth has plate tectonics, with most magma generated at plate boundaries. Mars is ~10% of Earth's mass, has stagnant lid tectonics, and is far less volcanically active. Io is ~1% of Earth's mass, yet it is more volcanically active because it is heated by tidal interactions with Jupiter. These three bodies have estimated magma

emplacement rates of $Q_{\text{MARS}} = 0.06 \pm 0.3 \text{ km}^3 \text{ yr}^{-1}$ (Hu & Thomas, 2022; Thomas et al., 2023), $Q_{\text{EARTH}} = 30 \pm 4 \text{ km}^3 \text{ yr}^{-1}$ (Crisp, 1984), and an upper limit of $Q_{\text{IO}} = 413 \text{ km}^3 \text{ yr}^{-1}$ (Breuer et al., 2022) assuming magma density of 2900 kg m^{-3} , consistent with MORBs (Sigurdsson et al., 2015) in all three cases.

To account for as many plausible scenarios as possible, we sample a range of values for magma emplacement rate (Q) for the TRAPPIST-1 planets with an upper limit of $8500 \text{ km}^3 \text{ yr}^{-1}$ set by Krissansen-Totton & Fortney (2022), which is an order of magnitude higher than Io's, and lower limits of $0.01 \text{ km}^3 \text{ yr}^{-1}$, which is lower than modern Mars but on the same order of magnitude (Table 4-2). Krissansen-Totton & Fortney (2022) used a planetary evolution model to estimate the modern-day magma emplacement rates on the TRAPPIST-1 planets over a wide range of model parameters and evolutionary scenarios. Their interior thermal evolution is calculated considering radioactive decay, heat from the core, convective and advective heat transport to the surface, and the impact of overlying rock on the melt boundary. Tidal heating is implicitly included by exploring a large range of initial radionuclide abundances, from $1/3x$ to $30x$ Earth's initial endowment. Barr et al. (2018) reported that TRAPPIST-1 b and c may experience a sustained tidal heat flux of up to 4.01 and 1.62 W m^{-1} , respectively, while Dobos et al. (2019) found lower tidal heat fluxes of 1.97 and 1.04 W m^{-1} . These upper limits on tidal heat flux are comparable to or less than Io (up to 4 W m^{-1} ; Breuer et al., 2022), and our parameter sweep easily encompasses them, as we explore Q values over an order of magnitude larger than Io's for both TRAPPIST-1 b and c. Tidal heating is not expected to be significant on the other planets (i.e., $<0.4 \text{ W m}^{-1}$; Dobos et al., 2019), yet the maximum explored Q values all exceed Io's. On the other hand, it is possible that the TRAPPIST-1 planets are effectively geologically dead, like Mars, due to cooling over their long lifetimes.

4.2.1.4 Equilibrium magmatic outgassing

To complete our calculation of water outgassing rates, we calculate the expected outgassing from a magma parcel as it rises to the surface and equilibrates with the atmosphere. We make this calculation with the equilibrium magma outgassing chemistry model of Wogan et al. (2020). This model was developed for mantle-sourced volcanoes and will de-gas what is exsolved from the magma (i.e., what is above the saturation pressure). This model solves for gas-gas and gas-melt equilibrium in the C–O–H system, including H_2O , CO_2 , H_2 , CO , and CH_4 . It has been validated

	b	c	d	e	f	g	h
Max. magma emplacement rate, Q [km ³ yr ⁻¹]	8500	5840	1230	2159	2130	2344	1230 ^a
Received XUV flux, F_{XUV} [erg s ⁻¹ cm ⁻²]	2935.13	1564.87	788.455	456.452	263.598	178.116	102.035
Energy-limited H escape rate, Φ_H [10 ¹² kg yr ⁻¹]	57.3	30.5	19.2	9.90	5.58	3.74	2.60

Table 4-2: TRAPPIST-1 model planet parameters. Q values are from Krissansen-Totton & Fortney (2022). F_{XUV} values are from Becker et al. (2020). See the main text for description of Φ_H .

^a No estimate is provided for TRAPPIST-1 h in Krissansen-Totton & Fortney (2022), so the upper limit is assumed to be the same as TRAPPIST-1 d due to their similar masses.

against the outgassing models of Gaillard & Scaillet (2014), Liggins et al. (2020), and Ortenzi et al. (2020).

We follow Wogan et al. (2020) and assume values for input parameters based on the variety of conditions in the solar system, shown in Table 4-1. The inputs for this model are the magma temperature (T), the pressure at the surface (P_{surf}), the magma water content ($m_{\text{H}_2\text{O}}^{\text{melt}}$), the magma CO₂ content ($m_{\text{CO}_2}^{\text{melt}}$), and the magma oxygen fugacity (f_{O_2}). The outputs are the gas production rates (q_i) for each species i in moles of gas per kg of magma.

Finally, the outgassing rate of any species i to the atmosphere (F_i) is then, following Wogan et al. (2020):

$$F_i = q_i \times Q \times \rho_{\text{mag}}, \quad (4.3)$$

where we assume $\rho_{\text{mag}} = 2900 \text{ kg m}^{-3}$ is the density of the magma, consistent with Earth's oceanic crust (Sigurdsson et al., 2015), and F_i is in units of moles yr⁻¹.

4.2.2 Filters

After applying the theoretical model to the TRAPPIST-1 planets and exploring a large parameter space, we narrow the space of plausible model results by applying two filters based on current observational and plausible geochemical constraints.

4.2.2.1 H_2 escape filter

With this filter, we use the constraint that telescope observations and atmospheric models find no evidence for large, H_2 -dominated atmospheres on the TRAPPIST-1 planets (Moran et al., 2018; De Wit et al., 2018; Wakeford et al., 2019; Hori & Ogihara, 2020; Turbet et al., 2020a) to identify model results with allowable H_2 outgassing rates. To be consistent with the lack of observed H_2 -dominated atmospheres, H_2 must either not be the dominant outgassed species, or if it is, then its outgassing rate cannot exceed its atmospheric escape rate; otherwise, H_2 would build up in the atmosphere. For all of our model runs, we predict both the rate of H_2O and H_2 outgassing, because we consider the equilibrium chemistry of the C–O–H system (Wogan et al., 2020). We then apply our filter to eliminate any model run where the H_2 is the dominant outgassed species (by number of moles, not mass) and the H_2 outgassing rate is higher than the estimated H_2 escape rate (calculated below).

For our escape calculations, we assume that hydrogen escape is energy-limited, which allows us to keep as many plausible scenarios as possible. Energy-limited escape is the theoretical upper limit on hydrogen escape, as it assumes the limiting factor is the XUV radiation from the star (e.g., see Catling & Kasting 2017). We calculate the energy-limited escape rate of hydrogen (Φ_H) on the TRAPPIST-1 planets according to Chassefière (1996) and Luger & Barnes (2015):

$$\Phi_H = \frac{\epsilon_{XUV} F_{XUV} r_p}{4GM_p K_{tide} m_H}, \quad (4.4)$$

where ϵ_{XUV} is the escape efficiency factor equal to the portion of XUV radiation that contributes to escape, assumed to be 0.3, which is the upper end of what is expected in hydrogen-rich atmospheres (Chassefière, 1996; Wordsworth & Pierrehumbert, 2013). F_{XUV} is the received XUV flux for each planet from Becker et al. (2020), shown in Table 4-2. The variables r_p and M_p are the radius and mass of the planet, respectively, from Agol et al. (2021). G is the gravitational constant. K_{tide} is a tidal correction term assumed to be 1 for simplicity. The mass of hydrogen is m_H . The hydrogen escape rates from this equation for the TRAPPIST-1 planets are shown in Table 4-2.

4.2.2.2 Evolutionary filter

With this filter, we identify the most plausible scenarios by requiring that the TRAPPIST-1 planets do not exceed the 1 wt% upper limit on $m_{H_2O}^{mantle}$ (see Section 2.1.1) throughout their history. We

do this by extrapolating our estimated modern water outgassing rate values ($F_{\text{H}_2\text{O}}$) back in time, adding the outgassed water back into the mantle, and then calculating the value of $m_{\text{H}_2\text{O}}^{\text{mantle}}$ over the history of the planets.

When extrapolating the outgassing rate and mantle water storage capacity back in time, we are forced to make several assumptions about water partitioning and recycling to simplify our approach. First, we assume that there is no recycling of water from the exterior back into the mantle (e.g., via plate tectonics), consistent with the rest of our model calculations and the lack of evidence for subduction on rocky bodies other than Earth (Stern et al., 2018). Second, we assume that the TRAPPIST-1 planets have not had 10–100 km deep surface oceans (Earth’s ocean is ~ 3.6 km average depth) that result in the 0.1–1 GPa overburden pressure required to suppress volcanic outgassing for the majority of their history (given Earth-like gravity and ocean crust composition; Krissansen-Totton et al., 2021). Third, we assume that the maximum mantle water content is always 1 wt%, although internal water storage changes over time as the planets cool (e.g., Dong et al., 2021). However, the 1 wt% upper limit is still valid since it is the maximum possible water storage, not the specific water storage over time for each planet. Fourth, we assume that $F_{\text{H}_2\text{O}}$ is constant throughout the planets’ histories, and equal to our calculation of the modern value. In reality, it is likely that $F_{\text{H}_2\text{O}}$ would have been higher in the past due to the early planet having a higher internal heat flux from formation and radionuclide decay.

We made the above assumptions so that the evolutionary filter is as permissive as possible, opting to keep model runs instead of eliminating them given our lack of constraints on the history of the TRAPPIST-1 planets. Thus, changing the above assumptions would generally make this filter stricter. For example, if we instead assumed that $F_{\text{H}_2\text{O}}$ was higher in the past, it would mean more water must be added back into the mantle in the past, the 1 wt% upper limit is more likely to be violated, and more model runs would be eliminated. Past water recycling would likely cause higher $F_{\text{H}_2\text{O}}$ in the past as well, leading to the same effect as above. However, this effect may be partially offset because the ingassed water would simultaneously be removed from the mantle as we extrapolate back in time. This filter would also be stricter if we modeled changing mantle water capacity over time instead of setting a maximum mantle water content. This change would result in a lower mantle water content limit and more model runs eliminated for violating it. Our assumption of the ocean overburden pressure has the opposite effect, as it would result in lower outgassing rates in the past, which would eliminate fewer model runs than with our current

assumption. These assumptions are therefore offsetting, but show that we are being as permissive as possible while maintaining model simplicity.

To calculate the mantle water mass fraction over time for each planet, $m_{H_2O}^{mantle}(t)$, we use conservation of mass to derive the following equation:

$$m_{H_2O}^{mantle}(t) = \frac{M_{mantle}(0)m_{H_2O}^{mantle}(0) + F_{H_2O}t}{M_{mantle}(0) + F_{H_2O}t}, \quad (4.5)$$

where t is the time before present, with $t = 0$ denoting the present day, so $M_{mantle}(0)$ is the modern mass of the mantle and $M_{mantle}(t) = M_{mantle}(0) + F_{H_2O}t$. For each model run, for each planet, we can invert Equation (4.5) to derive a maximum allowable water outgassing rate, $F_{H_2O}^{max}$, such that the 1 wt% upper limit on $m_{H_2O}^{mantle}$ is not exceeded throughout the planet's history:

$$F_{H_2O}^{max} = \frac{M_{mantle}(0)[0.01 - m_{H_2O}^{mantle}(0)]}{0.99 \times t}, \quad (4.6)$$

where we have substituted $0.01 = 1 \text{ wt\%}$ for $m_{H_2O}^{mantle}(t)$.

To eliminate the fewest possible scenarios, we choose values for the age of the system and the core mass fraction that maximize $F_{H_2O}^{max}$. First, M_{mantle} is calculated assuming a small core mass fraction of 18 wt%, consistent with other interior modeling studies of TRAPPIST-1 (e.g., Agol et al., 2021). Second, we use the minimum age of the TRAPPIST-1 system, 5.4 Gyr (Burgasser & Mamajek, 2017), as the largest value for t . For TRAPPIST-1 c, these parameter values result in $F_{H_2O}^{max}$ values up to $1.2 \times 10^{13} \text{ kg yr}^{-1}$ depending on $m_{H_2O}^{mantle}$ in a given model run. In contrast, selecting the median age of the system (7.6 Gyr) and an Earth-like core mass fraction (32.5 wt%) would result in $F_{H_2O}^{max}$ values up to $7 \times 10^{12} \text{ kg yr}^{-1}$, which would make this filter stricter.

4.3 Results

Here we describe the results of experiments that explore a broad range of parameters for the seven TRAPPIST-1 planets to generate plausible ranges for planetary water content, magma emplacement rates, and outgassing rates for water and other key gases. We then provide results for specific TRAPPIST-1 c test cases with fixed magma emplacement rates corresponding to those on Mars, Earth, and Io.

TRAPPIST-1 c parameter distributions and correlations with varying maximum mantle water content

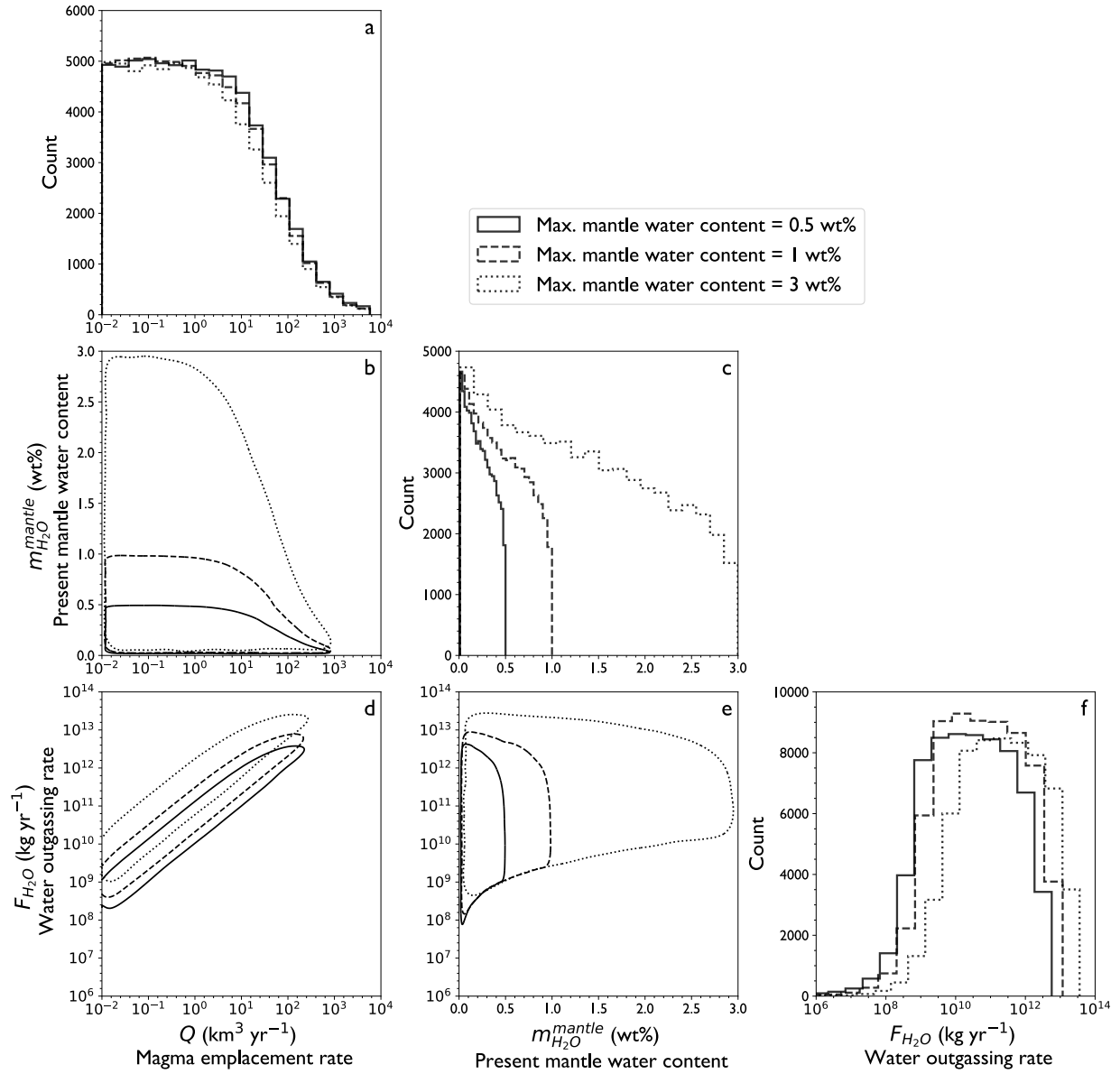


Figure 4-3: Parameter distributions and correlations with varying maximum mantle water content for TRAPPIST-1 c. Plots are derived from 100,000 model runs where the full parameter sweep is executed, then the two filters are applied to eliminate model runs, described in Section 4.2.2. Panels (a), (c), and (f): posterior parameter distributions. Panels (b), (d), and (e): parameter correlations. The contours contain 95% of the model runs, which are homogeneously distributed within.

4.3.1 Parameter correlations and sensitivity to filters

We first ran our model 100,000 times with Monte Carlo sampling to explore the plausible ranges for mantle water content, magma emplacement, and outgassing for the TRAPPIST-1 planets. Here, we sampled the full parameter ranges in Table 4-1, with the volumetric magma emplacement rate (Q) uniformly sampled in base 10 log space within upper limits given in Table 4-2. We then applied both of the filters described in Section 4.2.2 to remove cases that violated observational and geochemical constraints. This process is similar across the seven planets because most of the explored parameter ranges are the same, except for Q , which is different for each planet because it depends on mass and radius. Planetary mass and radius also factor into calculation of the energy-limited H_2 escape rate filter, and the mantle mass and mantle water content in the evolutionary filter. We also tested two additional scenarios where the maximum mantle water content is 0.5 wt% and 3 wt%, as opposed to the nominal 1 wt%. These results thus represent all of the allowed scenarios on the TRAPPIST-1 planets according to our modeling framework.

Figure 3 shows the posterior distributions and correlations of the mantle water content ($m_{H_2O}^{mantle}$), magma emplacement rate (Q), and water outgassing rate (F_{H_2O}) for TRAPPIST-1 c, revealing intrinsic relationships between these parameters and the impact of the two filters on the allowed phase space. First, we consider the nominal model scenario where the maximum mantle water content is 1 wt%. Figure 4-3(b) shows the envelope of constraints imposed by the evolutionary filter, where only lower outgassing rates, and thus lower Q , are possible for a planet with a very wet mantle at present day (as higher rates would imply mantle water contents higher than 1 wt% in the past). Higher Q values are thus only permitted for drier present interiors. Figure 4-3(d) shows that Q strongly correlates with F_{H_2O} , which is expected because it is a multiplicative factor, and thus, F_{H_2O} is directly proportional to Q (Equation (4.3)). Additionally, the H_2 escape filter eliminates model runs with high Q because higher Q values increase F_{H_2} , which cannot be higher than the energy-limited H_2 escape rate in order to be consistent with observational constraints. Figure 4-3(e) also shows constraints from the evolutionary filter, with a lower upper boundary on F_{H_2O} when present $m_{H_2O}^{mantle}$ is higher—again because Q must be lower when mantle water content is high. Although Figure 4-3 shows correlations for TRAPPIST-1 c only, we find that these behaviors broadly hold for all of the TRAPPIST-1 planets.

Figure 4-3 also shows that our model results are only slightly sensitive to varying the theoretical maximum mantle water content, partially because the evolutionary filter eliminates

model runs with high present mantle water content, motivating us to use the nominal 1 wt% upper limit going forward. The maximum and median water outgassing rates are 3x and 3.8x higher, respectively, when the maximum mantle water content is 3 wt% compared to 1 wt%; this difference is small relative to the ~ 6 orders of magnitude that the water outgassing rate distributions span (Figure 4-3(f)). The evolutionary filter, which was modified to reflect the varying maximum mantle water content, partially explains this behavior, because it is more likely to eliminate scenarios with present mantle water content close to the theoretical maximum. Therefore, the impact of lowering the theoretical maximum is buffered because model runs near the theoretical maximum are already eliminated.

In the 1 wt% upper limit model runs, the two filters combine to eliminate 29%–37% of model runs across the seven TRAPPIST-1 planets, where the vast majority are eliminated by the evolutionary filter. On one hand, the H₂-escape filter only eliminates $\sim 1\%$ of model runs, showing that H₂ outgassing rates are unlikely to exceed the energy-limited H₂ escape rates in the broad parameter space we searched. On the other hand, the evolutionary filter eliminates up to 37% of model runs, showing that many plausible parameter combinations for the modern-day TRAPPIST-1 planets are inconsistent with even the most permissive of evolutionary considerations.

4.3.2 Posterior distributions for mantle water content, magma emplacement, and outgassing on the TRAPPIST-1 planets

Figure 4-4 shows the posterior distributions for all seven TRAPPIST-1 planets for model parameters and outgassing rates after the Monte Carlo sampling and application of the two filters. Figure 4-4(a) shows that low magma emplacement rates are more likely for all TRAPPIST-1 planets. The median magma emplacement rate for TRAPPIST-1 c is $0.8 \text{ km}^3 \text{ yr}^{-1}$, which is 2 orders of magnitude lower than Earth's and indicates Mars-like magma emplacement is more likely. Additionally, the distributions are approximately uniform below $1 \text{ km}^3 \text{ yr}^{-1}$, suggesting that all values below this threshold are equally likely. The count density drops off steeply for high values of Q , where there is only a 13.5% chance that a model run will have Q higher than Earth and a 1.96% chance it will have Q higher than Io. Finally, the distributions for TRAPPIST-1 d (green line) and h (pink line) are shifted toward lower values relative to the other planets because they have lower masses, and thus, lower upper limits on Q , compared to the rest of the planets.

TRAPPIST-1 posterior distributions in all plausible scenarios

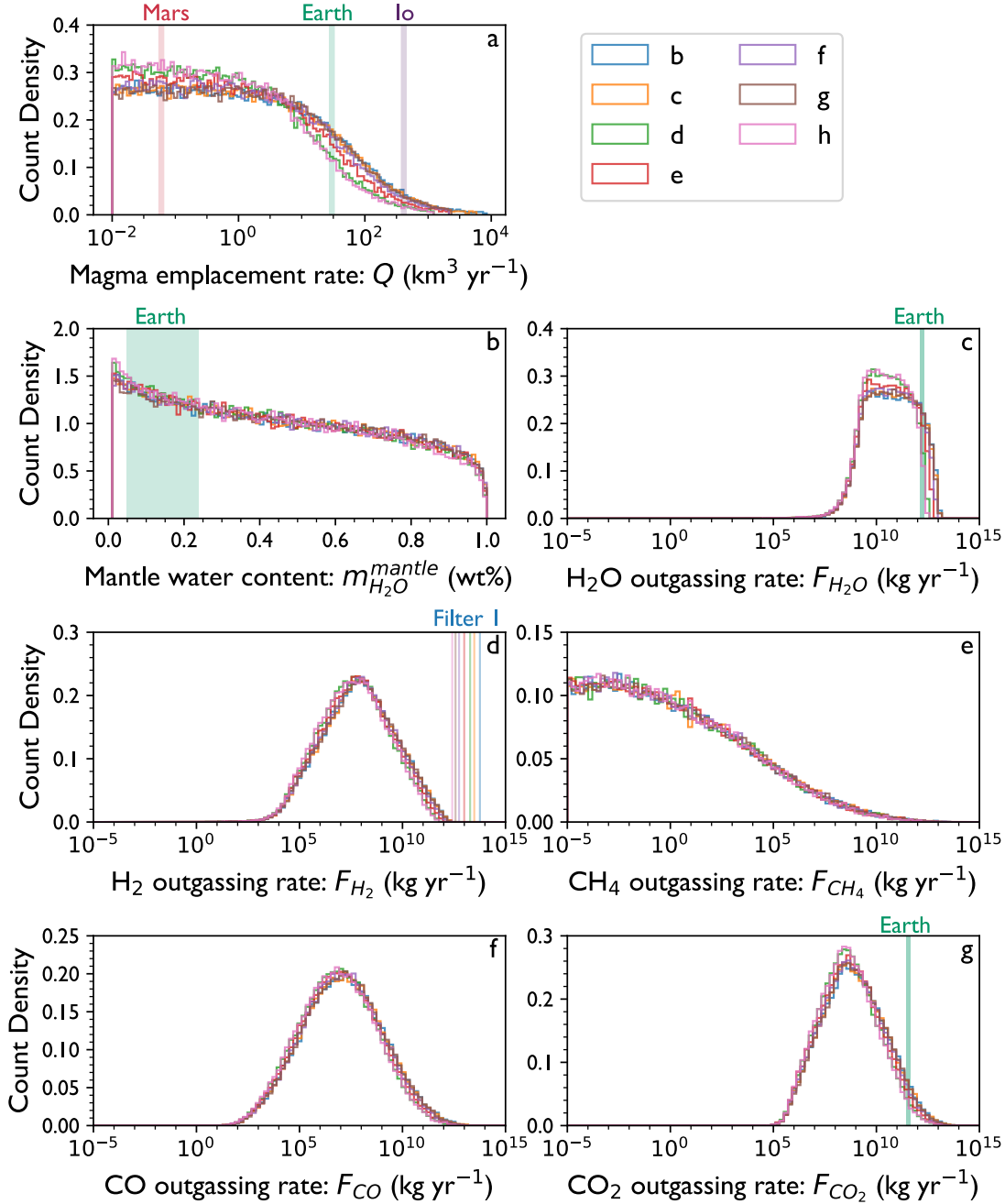


Figure 4-4: Posterior distributions of model values for all TRAPPIST-1 planets in all plausible model scenarios. Plausible model scenarios are derived by first executing the full parameter sweep and then applying empirical and theoretical filters to eliminate model runs, described in Section 4.2.2. The most likely scenario on the TRAPPIST-1 planets is that they have (a) low magma emplacement rates, (b) present mantle water content consistent with Earth or lower (although wetter mantles are possible), and (c) a water outgassing rate lower than Earth's (although it can be

up to an order of magnitude higher). Vertical bars are values from the solar system or filter application. Panel (a): Q for Mars, Earth, and Io are 0.06, 30, and 413 km³ yr⁻¹, respectively (Section 4.2.1.3). Panel (b): Earth $m_{H_2O}^{mantle}$ is 0.049–0.24 wt% (Ohtani, 2021). Panels (c) and (g): Earth’s H₂O and CO₂ outgassing rates are 1.35×10^{12} – 2.07×10^{12} kg yr⁻¹ and 2.86×10^{11} – 4.62×10^{11} kg yr⁻¹, respectively (Catling & Kasting, 2017). Panel (d): energy-limited H₂ escape rates from filter 1 (Section 4.2.2).

Figure 4-4(b) shows a preference toward the low end of the explored range for mantle water content, although values throughout the entire range are plausible for all TRAPPIST-1 planets. For example, the median mantle water content for TRAPPIST-1 c is 0.42 wt%, and the most frequent values are those at or below Earth’s range of estimates (0.049–0.24 wt%; Ohtani, 2021). Although there is a preference for lower values, there are still many model scenarios with wetter mantles, as the count density does not go to zero until the very top of the explored range is reached. There are currently no measurements of the mantle water content on Mars or Io to compare to.

Despite having mantle water contents comparable to or even higher than Earth’s, Figure 4-4(c) shows that the water outgassing rates for the TRAPPIST-1 planets are likely less than Earth’s. The outgassing rates follow an approximate log-normal distribution centered an order of magnitude below Earth’s value, but with upper limits that exceed it. For example, the median value for TRAPPIST-1 c is 5×10^{10} kg yr⁻¹, which is over an order of magnitude below Earth’s value of $\sim 2 \times 10^{12}$ kg yr⁻¹. This disparity is likely because (1) Earth’s water outgassing rate is enhanced by recycling of surface water during plate-tectonics-induced subduction processes, and (2) we sample uniform priors for, e.g., magma emplacement rate with much of the distribution below Earth’s value. In comparison, our calculations only assume mantle-derived magmas that are not impacted by subduction and transport of surface water. The modeled upper limits on water outgassing are 2.0 – 12.4×10^{12} kg yr⁻¹, which, at the higher end, are an order of magnitude higher than Earth’s value. Once again, the distributions for TRAPPIST-1 d and h are shifted toward lower or intermediate values of water outgassing rate because they have lower masses, lower upper limits on Q , and thus lower upper limits on F_{H_2O} compared to the rest of the planets.

Figures 4-4(d)–(g) show the outgassing rates of other gases that are self-consistently calculated in our model along with the water outgassing rate. The H₂, CO, and CO₂ outgassing rates follow approximate log-normal distributions that are shifted toward lower values relative to

TRAPPIST-1 c posterior distributions with fixed magma emplacement rates

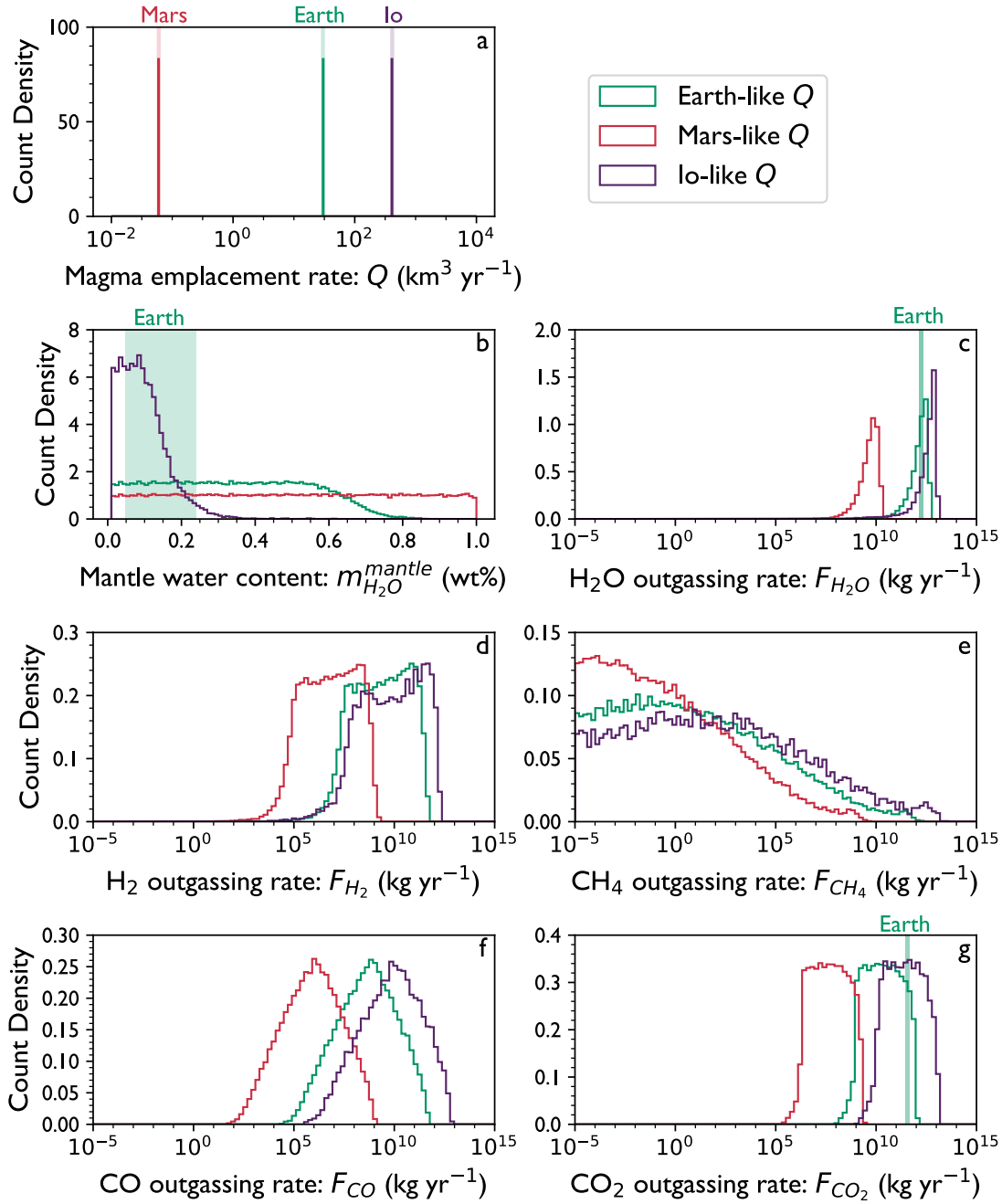


Figure 4-5: Posterior distributions of model values for TRAPPIST-1 c in plausible model scenarios with fixed magma emplacement rates based on those of Earth, Mars, and Io. Plausible model scenarios are derived by first executing the full parameter sweep but with Q fixed to one of the solar system values, then applying empirical and theoretical filters to eliminate model runs that violate known empirical and theoretical constraints, as described in Section 4.2.2. In this case, we

apply the filters using the mass and radius of TRAPPIST-1 c as a representative case. Vertical bars are values from the solar system. Panel (a): Q for Mars, Earth, and Io are 0.06, 30, and 413 km³ yr⁻¹, respectively (Section 4.2.1.3). Panel (b): Earth $m_{H_2O}^{mantle}$ is 0.049–0.24 wt% (Ohtani, 2021). Panels (c) and (g): Earth’s H₂O and CO₂ outgassing rates are 1.35×10^{12} – 2.07×10^{12} kg yr⁻¹ and 2.86×10^{11} – 4.62×10^{11} kg yr⁻¹, respectively (Catling & Kasting, 2017).

the water outgassing rate. The CO₂ outgassing rate is most frequently lower than Earth’s, because, although the explored CO₂ magma concentration is consistent with what is found on Earth, Q is preferred to be lower than Earth’s value in the corresponding posterior distribution in Figure 4-4(a). The CH₄ outgassing rate is much lower than all of the others because it requires a very reduced magma (i.e., low oxygen fugacity) to be the dominant species. Posterior distributions of other model parameters are omitted here because they did not change significantly from their flat prior distributions, but are shown in Appendix 4A. Posterior distributions in flux units are shown in Appendix 4B.

4.3.3 Solar system cases: Earth, Mars, and Io

While the above simulations showed the broad parameter sweep of allowable cases, we also explored the range of possible outcomes for specific cases with fixed magma emplacement rates (Q) spanning known values for solar system bodies (see Section 4.2.1.3). Figure 4-5 shows the results of running our model 100,000 times while Monte Carlo sampling the parameter ranges in Table 4-1, with Q fixed at representative values for Earth, Mars, and Io (Section 4.2.1.3), and then applying both of the filters described in Section 4.2.2. We show the results of applying this treatment to TRAPPIST-1 c as a representative scenario, noting that, in reality, the magma emplacement rate should scale with planet mass. Because the magma emplacement rates are fixed, they no longer incorporate each planet’s mass and radius, which will now only factor into calculation of the filters.

The three fixed Q values, and the filters, strongly constrain the inferred $m_{H_2O}^{mantle}$ and F_{H_2O} in these model runs (Figures 4-5(b) and (c)). With a highly volcanic, Io-like Q , TRAPPIST-1 c would likely have $m_{H_2O}^{mantle}$ at or less than that of Earth but F_{H_2O} over an order of magnitude larger than Earth. On the other hand, if TRAPPIST-1 c is volcanically dead and has a low, Mars-like Q , then there are no constraints on $m_{H_2O}^{mantle}$ within its sampled range, as all values are equally likely,

and $F_{\text{H}_2\text{O}}$ would be consistently orders of magnitude lower than Earth’s water outgassing rate. The Earth-like Q case provides a middle scenario that favors high $F_{\text{H}_2\text{O}}$ but many possible values of $m_{\text{H}_2\text{O}}^{\text{mantle}}$ below 0.6 wt%. The median values of $F_{\text{H}_2\text{O}}$ for TRAPPIST-1 c with Io-like, Earth-like, and Mars-like Q are 4.6, 1.7, and $0.005 \times 10^{12} \text{ kg yr}^{-1}$, respectively.

The outgassing rates for the additional molecules considered here are proportional to Q (Figures 4-5(d)–(g)), where an Io-like Q causes higher outgassing rates for all species relative to a Mars-like Q . The H_2 , CO , and CO_2 outgassing rates follow approximately log-normal distributions that are offset from each other based on the difference in Q . The CH_4 outgassing rate skews toward low values in all cases, but the offset based on Q is still present. Posterior distributions of other model parameters in these solar system test cases are omitted here because they did not change significantly from their flat prior distributions, but are shown in Appendix 4A. Posterior distributions in flux units are shown in Appendix 4B.

4.4 Discussion

We explored a comprehensive and broad parameter space to place plausible boundaries on outgassing rates for water and other key gases for the TRAPPIST-1 planets to support interpretation of data from upcoming observations of these worlds, and others. Although our explored parameter space covers a wide range of chemical and physical conditions, we constrained this space by using observational evidence for a lack of H_2 -dominated atmospheres (H_2 -escape filter) and theoretical limits on the maximum mantle water mass fraction over time (evolutionary filter).

Our results indicate that drier mantles are preferred within the broader explored range of mantle water content ($m_{\text{H}_2\text{O}}^{\text{mantle}} = 0\text{--}1 \text{ wt}\%$; Figure 4-4(b)). This arises due to our assumption that the TRAPPIST-1 planets have terrestrial interiors with mantle water contents that remain below a 1 wt% upper limit throughout the $\geq 5.4 \text{ Gyr}$ age of the TRAPPIST-1 system (Burgasser & Mamajek, 2017). The preference for lower $m_{\text{H}_2\text{O}}^{\text{mantle}}$ values is more consistent with Earth’s mantle water content (0.049–0.24 wt%; Ohtani, 2021). Although higher $m_{\text{H}_2\text{O}}^{\text{mantle}}$ values are still possible, there is no known terrestrial analog for comparison.

Our model results for magma emplacement rates also indicate that the TRAPPIST-1 planets are currently more likely to have low-to-no volcanic activity. Higher volcanic activity is disfavored, as it often implies past mantle water content over the 1 wt% upper limit. For all seven

planets, the posterior distributions for magma emplacement rates (Q) skew toward the low end of their allowed ranges, disfavoring rates that may be associated with high tidal heat fluxes (Figure 4-4(a)). For example, 86.5% of plausible model runs for TRAPPIST-1 c have Q below Earth's value ($30 \text{ km}^3 \text{ yr}^{-1}$; Crisp, 1984), and 52.5% are below $1 \text{ km}^3 \text{ yr}^{-1}$, indicating that extremely low, Mars-like rates of volcanism are the most likely. Conceptually, extremely low volcanic activity on the TRAPPIST-1 planets would be consistent with the fact that they are Earth-sized, and at least ~ 1 Gyr older than the comparable solar system bodies, so there has been more time for their planetary interiors to cool.

Our results indicate that the water outgassing rates on the TRAPPIST-1 planets are more likely to be lower than Earth's, but the plausible range also includes outgassing rates that are an order of magnitude higher than Earth's. Lower outgassing rates are more likely for two reasons: (1) we consider mantle- derived magmas in this study, which have lower water content than magmas derived from the recycling of surface material, like arc magmas on Earth, which acquire high water content due to subduction of hydrated oceanic crust, and (2) the highest modeled water outgassing rates are removed by the requirement that the TRAPPIST-1 planets' mantle water content cannot exceed a 1 wt% upper limit during the history of the system. This results in, for example, a median water outgassing rate for TRAPPIST-1 c of $5 \times 10^{10} \text{ kg yr}^{-1}$ ($\sim 0.03 \times$ Earth's). That being said, high water outgassing rates up to $1.2 \times 10^{13} \text{ kg yr}^{-1}$ ($\sim 8 \times$ Earth's) can be achieved for a broad range of mantle water contents if the TRAPPIST-1 planets have high magma emplacement rates (Figure 4-3).

Water is most frequently the dominant outgassed species in our model results and indicates that if secondary atmospheres are present, they will likely be dominated by water and/or its photochemical byproducts. However, there are still model scenarios where CO_2 , CO, and H_2 outgassing rates exceed water outgassing rates. The outgassing rate distributions and self-consistent scenarios can be used in future modeling studies to explore possible secondary atmospheres consistent with outgassing. Our calculated outgassing rates are provided in a repository and available as fluxes in $\text{mol s}^{-1} \text{ m}^{-2}$ units in Appendix 4B (Figures 4B-1 and 4B-2).

4.4.1 Comparison to other models of water outgassing and planetary evolution

We have grounded our modeling approach in present-day observational constraints and knowledge of the solar system to statistically search a broad parameter space of possible present-day scenarios

on the TRAPPIST-1 planets. Given the lack of constraints on the geological properties of these planets, a huge variety of present-day interior scenarios is possible. With our modeling approach, we can easily test a wide range of these present-day scenarios and provide information that informs observations. This approach is complemented by planetary evolution models, which consider the history of the system when predicting the present state. Many previous evolutionary models have investigated similar topics for the TRAPPIST-1 planets specifically (e.g., Bourrier et al., 2017; Barth et al., 2021; Krissansen-Totton & Fortney, 2022) and terrestrial planets orbiting M stars broadly (e.g., Moore & Cowan, 2020; Moore et al., 2023, 2024), which represent a sample of the many possible trajectories of the system. We do consider the evolution of the TRAPPIST-1 planets with our evolutionary filter (discussed below); however, the main strength of our modeling approach is the flexible statistical method we have used to search a broad parameter space of present-day properties.

We have constructed our evolutionary filter to be simple and permissive so that it is consistent with the lack of constraints on the history of the system. Given the lack of data, evolutionary models are forced into assumptions about the planets’ pasts that, while reasonable, may not be true. For example, the only data constraining the interiors of the TRAPPIST-1 planets are the observed mass and radius (Grimm et al., 2018; Agol et al., 2021), and estimates of elemental abundances based on the local stellar composition (e.g., Fe/Mg; Unterborn et al., 2018). Others have estimated interior properties from these data (e.g., Agol et al., 2021), but there are many interior scenarios consistent with the data at present-day, and it is highly uncertain how many of these interior properties would have changed in the past. Therefore, we have taken the simplest approach when designing the evolutionary filter so that a wide variety of reasonable scenarios is not ruled out. As described in Section 4.2, our evolutionary assumptions are as permissive as possible while maintaining simplicity: (1) water outgassing is constant, (2) there is no water recycling or regassing, (3) there are no large oceans that can suppress outgassing, and (4) the maximum mantle water content is constant.

Our resultant distributions of water and methane outgassing rates encompass previous estimates that make a variety of different assumptions, highlighting how our approach has established reasonable statistical boundaries on these values. The whole-planet evolutionary model of Krissansen-Totton & Fortney (2022) estimates that the modern water outgassing rate across all TRAPPIST-1 planets does not exceed $\sim 10^{12}$ kg yr⁻¹, and Moore & Cowan (2020) estimated that

peak water outgassing for Earth-like planets around M stars is $\sim 7.7 \times 10^{12} \text{ kg yr}^{-1}$, but occurs within the first billion years of the system. Both of these water outgassing rates are within our calculated boundaries, but were obtained using more detailed evolutionary models with different assumptions; for example, both models assume some form of plate tectonics occurred and that interior mineralogy is broadly similar to Earth. Additionally, our calculated methane outgassing rates are consistent with a previous application of the magma degassing model (Wogan et al., 2020), where the distribution of methane outgassing rates for Earth-like Q in Figure 4-5(e) is directly comparable to Wogan et al. (2020) Figure 4(d).

The 1 wt% upper limit on mantle water content we explore is geochemically plausible, but it is much higher than the mantle water content derived from current magma ocean models. The 1 wt% water content in the TRAPPIST-1 planets' mantles converts to up to ~ 50 Earth oceans depending on planet size and core mass fraction. Our model does not address how water is incorporated into the mantle during formation, but previous models that calculate the partitioning of water in planet interiors have not obtained the high mantle water content we test here. For example, Barth et al. (2021) found that up to five Earth oceans can be sequestered in the mantles of the outer TRAPPIST-1 planets. Moore et al. (2023) found that up to six Earth oceans can be sequestered in Earth-mass planet mantles, but possibly up to the saturation limit of 12 Earth oceans for extreme parameters given their assumed mineralogy. Other studies assume up to 12–15 Earth oceans of storage in terrestrial planet mantles is possible based on present-day Earth's mantle water capacity (Cowan & Abbot, 2014; Komacek & Abbot, 2016). Future theoretical and observational work that explores mechanisms for obtaining the theoretical maximum water content will thus bear on our model results going forward. However, the highest water outgassing rates in our models occur for lower water mantle water content, so the effect on water outgassing may be minimal.

4.4.2 Constraints on internal structure and composition of the TRAPPIST-1 planets

Our model's predicted relationship between lower mantle water content and higher outgassing rates provides a mechanistic explanation for the possible distribution of mass between the inner TRAPPIST-1 planets' (b, c, and d) atmospheres and interiors. If there is exterior water on the inner planets, it will most likely be in the vapor phase as an atmosphere (Turbet et al., 2019, 2020b; Agol et al., 2021). To match the observed total planetary density, the low density of the atmosphere would have to be offset by a denser solid planet, when compared to an atmosphere-free case. One

way to achieve the denser solid body is for the planetary interior, including the mantle, to have a lower water content with more high-density nominally anhydrous minerals. This argument applies in reverse too, where if there is a tenuous water-vapor-containing atmosphere, or none at all, the solid planet would have to be relatively less dense and could thus have a higher interior water content with more low-density hydrous minerals. These scenarios are consistent with our results, as the denser modeled scenarios with low mantle water content have the highest magma emplacement rate and highest water outgassing rates, which could theoretically support the thicker water-vapor-containing atmosphere against atmospheric escape. Applying this argument in reverse, we also find that a lower density mantle with the highest mantle water content would have lower magma emplacement rates and lower water outgassing rates, which would be consistent with a tenuous or no water-vapor-containing atmosphere.

Our results also strongly disfavor present-day Io-like volcanism on the TRAPPIST-1 planets, suggesting that the tidal or induction heating required to maintain these high levels of volcanism may not currently be present. This result is inconsistent with some existing model predictions (Kislyakova et al., 2017; Barr et al., 2018). For example, Barr et al., (2018) used an interior thermal model to predict that TRAPPIST-1 b has high volcanic activity with an interior heat flux twice as high as Io. According to our results, magma emplacement rates greater than or equal to Io's occur in only 1.8% of model scenarios. In these model scenarios, we predict that the high magma emplacement rates lead to the highest possible water outgassing rate (see Figure 4-5 with Io-like Q). Therefore, future constraints on the water outgassing rate for the TRAPPIST-1 planets via measurement of atmospheric water abundance have the potential to also constrain Q (via the correlation in Figure 4-3(b)), and thus may have implications for the degree of tidal or induction heating on the TRAPPIST-1 planets.

4.4.3 Outgassing as a source of atmospheres for the TRAPPIST-1 planets

The outgassing rates of water and the other gases provided here can be coupled with estimates of atmospheric escape to assess the presence and observability of water in the TRAPPIST-1 planet atmospheres.

We find that the predicted water outgassing rates in our plausible model scenarios can likely balance atmospheric escape, and could support stable water-vapor-containing atmospheres on the TRAPPIST-1 planets. For TRAPPIST-1 b, the closest planet to the parent star with the highest

stellar-radiation-driven escape rates, we compare our modeled water outgassing rates to the modeled water escape rates of Krissansen-Totton & Fortney (2022) and Gialluca et al. (2024). At 1 billion yr after planet formation, both studies predict a median water escape rate of $\sim 1.8 \times 10^{10}$ kg yr⁻¹, which decreases with time. This value is well below our upper limit for water outgassing of 1.2×10^{13} kg yr⁻¹. Therefore, our modeled outgassing rates are potentially high enough to balance the water escape rates on TRAPPIST-1 b and the other planets, indicating that steady-state water containing atmospheres are possible. Future studies are needed to further evaluate and characterize these steady states by coupling the outgassing rates provided here to atmospheric chemistry and escape models.

In fact, the higher plausible H₂O outgassing rates could produce significant atmospheres, or form oceans, on the temperate TRAPPIST-1 planets. The upper limit on the H₂O outgassing rate for TRAPPIST-1 c is 1.2×10^{13} kg yr⁻¹, producing ~ 50 Earth oceans of degassed water over the minimum 5.4 Gyr age of the system. This amount of water can likely survive atmospheric escape (Gialluca et al., 2024) and could theoretically be responsible for surface water accumulation on the habitable zone planets.

Moreover, the predicted higher CO₂ outgassing rates could also contribute to high-pressure CO₂ atmospheres. Note that 2% of our model runs for TRAPPIST-1 c have a CO₂ outgassing rate over 10^{12} kg yr⁻¹. When extrapolated to the minimum age of the system, this would result in an atmosphere with hundreds of bars of CO₂ if no escape or recycling processes are considered. Deriving an upper limit on CO₂ escape would provide further constraints on the models that would preclude excessive, and unobserved (Greene et al., 2023; Zieba et al., 2023) CO₂ build up.

4.4.4 Implications for current and future observations of TRAPPIST-1

Our results do not preclude water vapor in the atmosphere of TRAPPIST-1 c, and suggest its plausibility. As described in Section 4.1, the secondary eclipse observation of TRAPPIST-1 c is consistent with several water-vapor-containing atmospheres (Lincowski et al., 2023; Zieba et al., 2023). Our modeled outgassing rates can plausibly balance the high atmospheric escape rates on TRAPPIST-1 c, so this cannot be used as a basis to rule out the presence of a water-vapor-containing atmosphere and eliminate the scenarios presented in Lincowski et al. (2023). Instead, additional observations will be needed to further discriminate between possible atmospheric scenarios.

For the TRAPPIST-1 habitable zone planets, a large sustained water outgassing rate throughout their evolution may permit habitability, even after early water loss. Significant water loss is expected in the TRAPPIST-1 system from high radiation during and after the pre-main-sequence phase (e.g., Birky et al., 2021; Gialluca et al., 2024), which can be augmented by intense stellar flares throughout the star’s lifetime (e.g., Yamashiki et al., 2019; Amaral et al., 2022). However, even early loss of any surface volatile inventory could be offset by outgassed water from the interior that accumulates on the surface over time. In this scenario, early catastrophic loss of an M dwarf planet’s ocean and/or atmosphere does not necessarily preclude later habitability, and this could increase the chances that the TRAPPIST-1 habitable zone planets are indeed habitable (e.g., Moore & Cowan, 2020; Krissansen-Totton et al., 2024).

Our results also demonstrate that observations of TRAPPIST-1 planetary atmospheres could provide insight into interior processes. If the water outgassing rate can be constrained via water vapor detection on any of the TRAPPIST-1 planets, it will help narrow the allowed space of parameters tested here. If an upper limit on atmospheric water vapor is obtained on, e.g., TRAPPIST-1 c, it can be paired with atmospheric chemistry models to calculate the escape rate of water vapor from the potential atmosphere. We can then determine the upper limit on the water outgassing rate by requiring it not exceed the predicted escape rate. This will narrow the allowed parameter space for qualities of TRAPPIST-1 c, such as Q and $m_{H_2O}^{mantle}$ and may be generalized to the other planets if initial water endowments are assumed to be comparable.

4.4.5 Implications for other terrestrial exoplanets

Our results should apply for a wide variety of terrestrial exoplanets if they have broadly similar conditions to the TRAPPIST-1 planets. In our theoretical model, information specific only to TRAPPIST-1 includes the estimated magma emplacement rates from evolutionary models (Krissansen-Totton & Fortney, 2022), which depend on planet masses and radii. TRAPPIST-1 specific information includes the XUV flux for the H₂-escape filter, but this filter had little impact on the allowed parameter space compared to the evolutionary filter, which uses the age of the TRAPPIST-1 system. Therefore, our model results should apply to terrestrial exoplanets with comparable mass, radius, and age to the TRAPPIST-1 planets. More detailed calculations are necessary to determine the extent to which outgassing could support secondary atmospheres against intense atmospheric escape, but our results suggest that present-day outgassing of

atmospheric volatiles could play a role on, e.g., LHS 3844b (Kreidberg et al., 2019), GJ 1252b (Crossfield et al., 2022), Gl 486b (Mansfield et al., 2024), the LTT 1445 system (Winters et al., 2022), and the L 98-59 system (Cloutier et al., 2019). In some cases, tenuous atmospheres are only ruled out because they are not expected to survive intense atmospheric escape rates over extended periods of time (Kreidberg et al., 2019; Mansfield et al., 2024). Our results suggest that tenuous atmospheres could be supported by present-day outgassing, even in the presence of high escape rates. Thus, present-day tenuous atmospheres should not be ruled out solely on the basis that high escape rates acting over the life of the star would have likely removed an early atmosphere or ocean.

4.5 Conclusions

We explored a broad phase space of possible present-day water outgassing scenarios on the TRAPPIST-1 planets using observational constraints and theoretical maxima on mantle water content. Our results indicate that if the TRAPPIST-1 planets are terrestrial analogs with a core and mantle, they most likely have (1) low, Mars-like magma emplacement rates, (2) low, Earth-like mantle water mass fractions (although water mass fractions up to 1 wt% are still plausible), and (3) water outgassing rates $\sim 0.03\times$ Earth's (but rates up to $\sim 8\times$ higher than Earth's are not ruled out). If the TRAPPIST-1 planets have Mars-like magma emplacement rates, their mantle water content is unconstrained, and they are likely to have low water outgassing rates ($\sim 0.004\times$ Earth). If they have Io-like magma emplacement rates, their mantle water content is expected to be at or below Earth's, and they likely have high water outgassing rates (up to $\sim 7\times$ Earth).

Our plausible ranges of outgassing rates for water and other species can be used to help interpret ongoing observations of the TRAPPIST-1 planets, and our results have implications for future observational and theoretical studies of the TRAPPIST-1 system. Our results indicate high, Io-like volcanism driven by tidal heating is unlikely on the TRAPPIST-1 planets at present day. However, our results include plausible water outgassing rates that could balance the high atmospheric escape rates driven by the parent star, and support water-vapor-containing atmospheres on all of the TRAPPIST-1 planets. These model results, combined with atmospheric observations, could potentially constrain interior characteristics and processes. If a thick water-vapor-containing atmosphere is found on any of the planets, it increases the likelihood of a drier mantle with a high magma emplacement rate; if a tenuous or no water-vapor-containing

atmosphere is detected, it increases the likelihood of a wetter mantle with a low magma emplacement rate. Future work can further assess potential steady-state water-vapor-containing atmospheres by coupling the outgassing rates provided here to models of photochemistry and atmospheric escape. Our model results are likely applicable to other terrestrial exoplanets with similar mass, radius, and age to the TRAPPIST-1 planets. Ultimately, our results provide a theoretical model that supports the plausibility of habitable zone surface oceans and even tenuous atmospheres on M dwarf terrestrial exoplanets, despite the early superluminous phase of their host star, and their ongoing high rates of atmospheric escape.

4.6 Appendix 4A: Additional posterior distributions

Figures 4A-1 and 4A-2 show posterior distributions for other model parameters (described in Table 4-1) that are omitted from the main text because they do not change much from their uniform prior distributions. Figure 4A-1 shows the additional posterior distributions after Monte Carlo sampling all model parameters 100,000 times, with Q uniformly sampled in base 10 log space within upper limits given in Table 4-2. As demonstrated by the flat or near-flat parameter distributions, the filters do not place strong constraints on these model parameters. This indicates that they are less important for determining outgassing rates than the parameters referenced in the main text (magma emplacement rate and mantle water content).

Figure 4A-2 shows model parameter posterior distributions where the model is Monte Carlo sampled 100,000 times but with Q fixed to values based on solar system observations. These parameter distributions are flat or near-flat with the exceptions of the magma oxygen fugacity (Figure 4A-2(b)) and the magma melt fraction (Figure 4A-2(c)). The magma oxygen fugacity displays a slight preference for low values (i.e., more reduced magma) with Io-like and Earth-like magma emplacement rates. This slight preference is a result of the evolutionary filter, which generally eliminates model runs with high water outgassing rates. With a very reduced magma, the magma water content will be lower (because H_2O is favored in oxidized magmas), which leads to model runs with lower water outgassing rates that are not eliminated by the evolutionary filter. The melt fraction also displays a slight preference for high values with Io-like and Earth-like magma emplacement rates. This is also a consequence of the evolutionary filter, because high melt fractions result in lower magma water content and thus lower water outgassing rates. Both of these

effects are second-order compared to the parameters in the main text and thus only appear as slight deviations from uniform distributions in these specific cases.

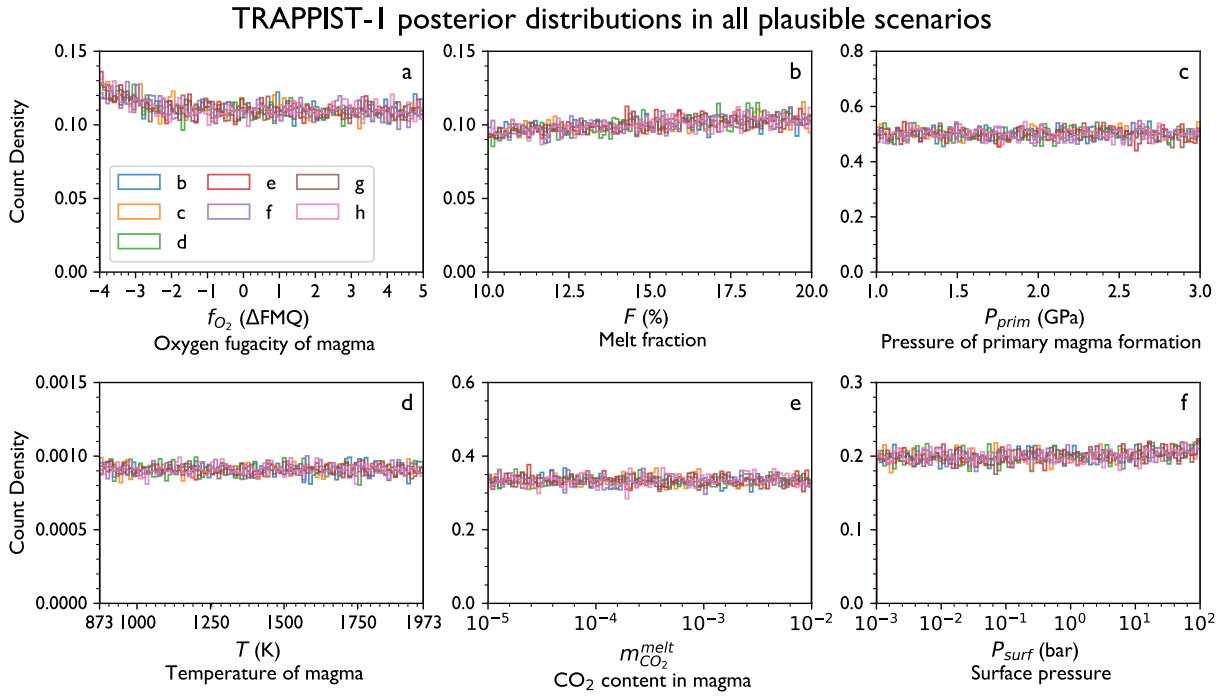


Figure 4A-1: Additional posterior distributions of model values for all TRAPPIST-1 planets in all plausible model scenarios. Plausible model scenarios are derived by first executing the full parameter sweep and then applying empirical and theoretical filters to eliminate model runs, described in Section 4.2.2.

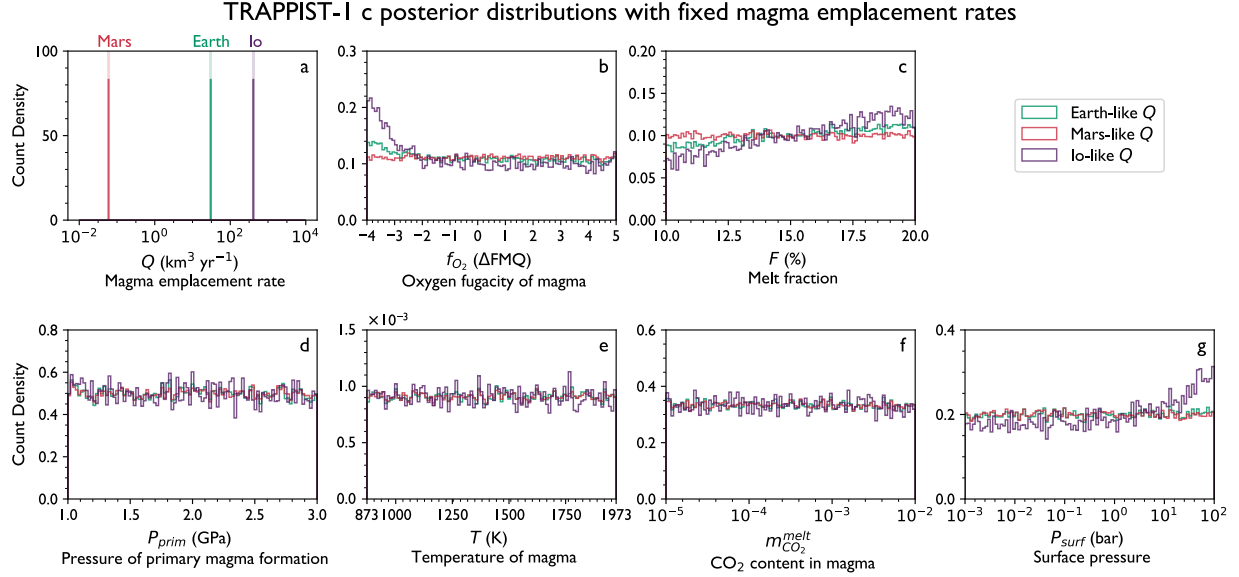


Figure 4A-2: Additional posterior distributions of model values for TRAPPIST-1 c in plausible model scenarios with fixed magma emplacement rates based on those of Earth, Mars, and Io. Plausible model scenarios are derived by first executing the full parameter sweep but with Q fixed to one of the solar system values, then applying empirical and theoretical filters to eliminate model runs that violate known empirical and theoretical constraints, as described in Section 4.2.2. In this case, we apply the filters using the mass and radius of TRAPPIST-1 c as a representative case. Panel (a): vertical bars are ground truth values of Q from the solar system: Mars, Earth, and Io are 0.05 , 31 , and $413 \text{ km}^3 \text{ yr}^{-1}$, respectively (Section 4.2.1.3).

4.7 Appendix 4B: Outgassing flux in $\text{mol s}^{-1} \text{ m}^{-2}$

Figures 4B-1 and 4B-2 show the posterior distributions for outgassing fluxes in units $\text{mol s}^{-1} \text{ m}^{-2}$, which are provided for compatibility and ease of use in future photochemical modeling studies. The distributions in Figure 4B-1 correspond directly to those in Figure 4-4. The distributions in Figure 4B-2 correspond directly to those in Figure 4-5. Planet radius values are taken from Agol et al. (2021).

TRAPPIST-I posterior distributions in all plausible scenarios

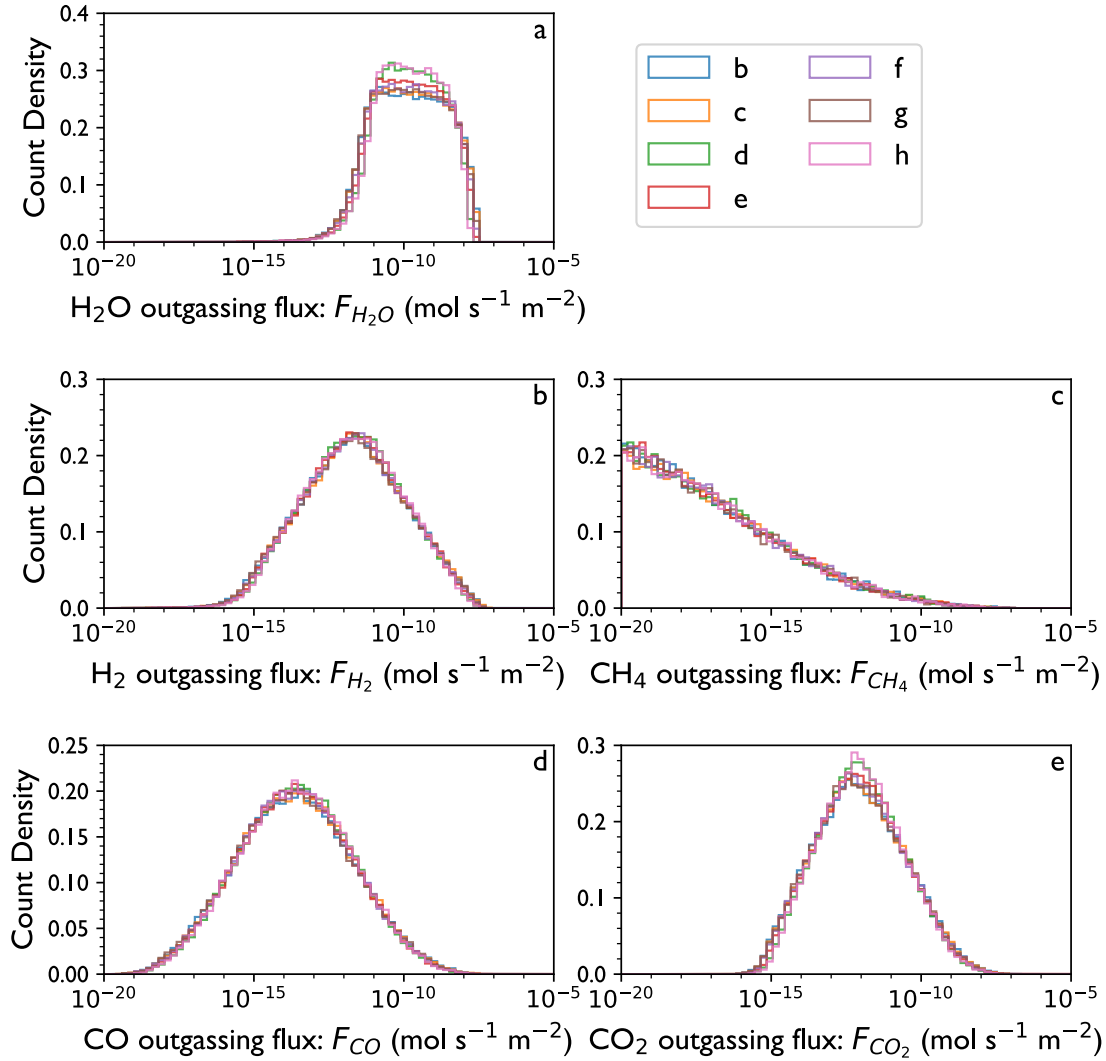


Figure 4B-1: Posterior distributions of outgassing fluxes in $\text{mol s}^{-1} \text{m}^{-2}$ units for all TRAPPIST-1 planets in all plausible model scenarios. Plausible model scenarios are derived by first executing the full parameter sweep and then applying empirical and theoretical filters to eliminate model runs, described in Section 4.2.2.

TRAPPIST-1 c posterior distributions with fixed magma emplacement rates

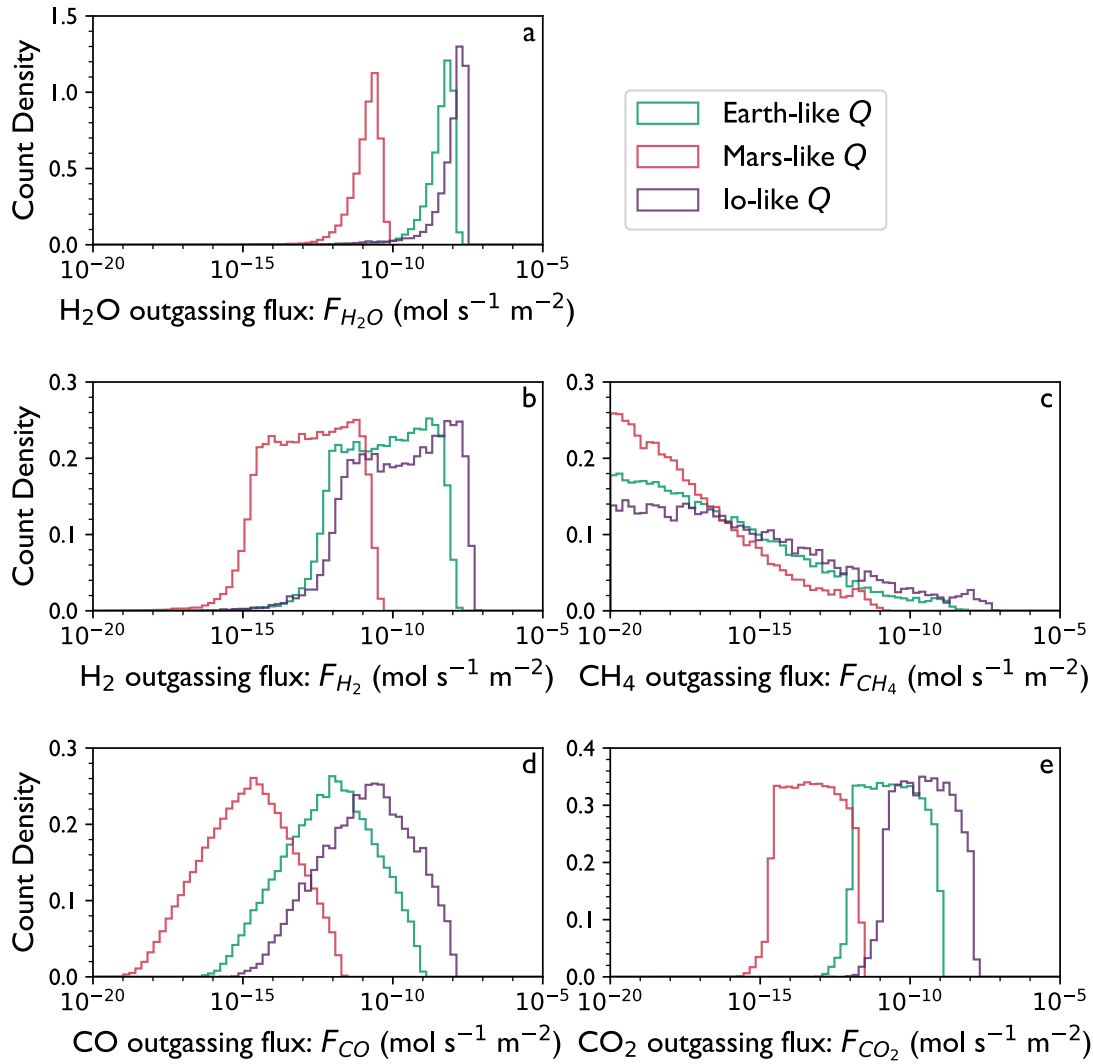


Figure 4B-2: Posterior distributions of outgassing fluxes in $\text{mol s}^{-1} \text{m}^{-2}$ for TRAPPIST-1 c in plausible model scenarios with fixed magma emplacement rates based on those of Earth, Mars, and Io. Plausible model scenarios are derived by first executing the full parameter sweep but with Q fixed to one of the solar system values, then applying empirical and theoretical filters to eliminate model runs that violate known empirical and theoretical constraints, as described in Section 4.2.2. In this case, we apply the filters using the mass and radius of TRAPPIST-1 c as a representative case. The value of Q for Mars, Earth, and Io is 0.05, 31, and 413 $\text{km}^3 \text{yr}^{-1}$, respectively (Section 2.1.3).

4.8 Data availability and acknowledgements

The Python source code and data in this work are publicly available at GitHub (<https://github.com/trentagon/trout>) and Zenodo (doi:10.5281/zenodo.15345251).

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5. Conclusions

The goal of this dissertation is to elucidate the processes by which planets maintain or restore habitable surface conditions despite the many perturbations they face in their lifetime. Chapters 2 and 3 have shown how Earth's geologic carbon cycle plays a key role in maintaining and restoring habitable conditions despite catastrophic perturbations. Chapter 4 has shown how terrestrial exoplanets orbiting M stars may overcome the intense atmospheric escape they face via supply of volatiles from volcanic outgassing. The work presented here demonstrates that planets are dynamic systems with a wide range of processes that impact their ability to support habitable surface conditions.

In Chapter 2, we proposed a new mechanism to explain the formation of the enigmatic “cap carbonates”, which probe the termination and immediate aftermath of the Cryogenian Snowball Earth events. By applying our model of the geologic carbon cycle to the second glaciation event (i.e., the Marinoan), we found a three-stage process responsible for cap carbonate formation. This process generates the conditions required to form the estimated global mass of the cap carbonates first through syn-glacial seafloor weathering, then post-glacial continental weathering, and finally slow ocean mixing. This process helps resolve longstanding controversies over the timescale of cap carbonate formation, the source of their chemical ingredients, and the properties of the water from which they precipitated. In a broader sense, we have quantitatively described the process by which the geologic carbon cycle stabilizes Earth's surface conditions when faced with extreme climate events.

Suggested future work in this area includes devising additional tests of the proposed mechanism via comparison to the geologic record and calculating the regionally varying implications of the proposed mechanism for cap carbonate formation. For example, proxies that probe the alkalinity of the syn-glacial ocean and the extension of the modeling framework to predict the evolution of the ocean's Sr isotope ratio may be particularly powerful for testing this hypothesis. Another fruitful avenue may be to investigate the differences in this mechanism when operating during the Sturtian glaciation instead of the Marinoan. Finally, this study was done when the duration of the Marinoan glaciation was constrained to 3-15 Myr; however, a recent measurement has constrained the duration to 4 Myr (Tasistro-Hart et al., 2025), so a follow-on study that incorporates this new measurement would be valuable.

In Chapter 3, we proposed that a difference in the seafloor weathering rate could explain the 14-fold duration difference between the two Cryogenian Snowball Earth events. Seafloor weathering – and subsequent deposition of carbonates – is the primary CO₂ sink when Earth is frozen over, but its influence on the Snowball duration had not yet been investigated. Using our model of the geologic carbon cycle, we showed that the long duration (56 Myr) of the Sturtian glaciation could be maintained if the rate of seafloor weathering was ~20-50x higher than modern, while the 4 Myr Marinoan glaciation requires a seafloor weathering rate <15x modern. Overall, our work shows that seafloor weathering has a strong enough influence on the global carbon cycle to explain the difference in duration.

A natural follow-up question, though, is why were the seafloor weathering rates different during the two glaciations? To answer this, we proposed that the seafloor weathering rate is related to the sulfate concentration in the ocean, which was changing throughout the Cryogenian. The seawater sulfate concentration limits the amount of anhydrite that forms in the ocean crust, which restricts fluid flow and may limit the seafloor weathering rate. Therefore, the duration of Snowball Earth events, and the timing of Earth system recovery after a catastrophic perturbation, may be driven by a new connection between the geologic carbon cycle and the chemical composition of the ocean.

There are now at least four clear hypotheses for the cause of the duration difference of the Cryogenian Snowball Earth events. They are (1) a change in the rate of seafloor weathering (this work), (2) a change in the rate of volcanic outgassing of CO₂ (Dutkiewicz et al., 2024), (3) a change in continental silicate weathering under ice sheets (Kadoya & Daswani, 2026), and (4) that the Sturtian glaciation was actually many discrete glaciations rather than one continuous event (Minsky et al., 2026). A recent measurement found a mantle-like Sr isotope ratio in a Sturtian cap carbonate, indicating that the sub-glacial Sturtian ocean was strongly influenced by hydrothermal circulation and seafloor weathering rather than continental weathering (Macdonald et al., 2025), which favors the hypothesis that we put forward in Chapter 3. However, this measurement is not definitive, and future work should continue analyzing the geologic record in search of the best way to test these competing hypotheses.

In Chapter 4, we placed constraints on the expected volatile outgassing rates on the TRAPPIST-1 planets, with an emphasis on water. We derived these constraints by developing a theoretical model of volcanic outgassing and exploring a broad phase space based on the solar

system terrestrial bodies. We found that, on average, the expected outgassing rates on the TRAPPIST-1 planets are $\sim 0.03\times$ Earth's, but the upper limit across these planets is $\sim 8\times$ Earth's. When compared to other studies of atmospheric escape in the TRAPPIST-1 system, we find that volcanic outgassing could plausibly support steady-state atmospheres despite the current harsh radiation environment. This work therefore provides a theoretical pathway for the maintenance of habitable conditions on the TRAPPIST-1 habitable zone exoplanets that motivates future telescope observation.

Chapter 4 provides a strong theoretical basis for assessing the nature, origin, and persistence of putative atmospheres on the TRAPPIST-1 planets, as it provides key constraints on the likelihood that volcanic outgassing can balance atmospheric escape. The constraints from Chapter 4 are currently being incorporated in a coupled model to determine the likelihood and observability of such a balance (Gialluca et al., accepted). They have also been used as a benchmark for additional evolutionary studies of the TRAPPIST-1 planets (Chen et al., 2025) and motivation to continue searching for atmospheres on these planets with the James Webb Space Telescope (Berardo et al., 2026). We hope to see future work incorporate our constraints into the variety of models and techniques used to study the TRAPPIST-1 planets and understand their potential to host habitable conditions.

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Appendix A: The atmospheric evolution of Mars

From 2018-2023, I pursued additional research under the supervision of Renyu Hu at NASA's Jet Propulsion Laboratory. This work resulted in three published papers:

- Adams, D., Scheucher, M., Hu, R., Ehlmann, B. L., Thomas, T. B., Wordsworth, R., Scheller, E., Lillis, R., Smith, K., Rauer, H. & Yung, Y. L. Episodic warm climates on early Mars primed by crustal hydration. *Nat. Geosci.* 1–7 (2025) doi:10.1038/s41561-024-01626-8.
- Hu, R. & Thomas, T. B. A nitrogen-rich atmosphere on ancient Mars consistent with isotopic evolution models. *Nat. Geosci.* **15**, 106–111 (2022) doi: 10.1038/s41561-021-00886-y
- Thomas, T. B., Hu, R. & Lo, D. Y. Constraints on the Size and Composition of the Ancient Martian Atmosphere from Coupled CO₂–N₂–Ar Isotopic Evolution Models. *Planet. Sci. J.* **4**, 41 (2023) doi: 10.3847/PSJ/acb924

Abstract

We created and applied atmospheric evolution models that combine atmospheric escape, volcanism, and surface interactions to reconstruct Mars's atmospheric history (Fig. A1). Geologic evidence overwhelmingly shows that liquid water flowed on Mars's surface 3-4 billion years ago, yet the size and composition of the ancient atmosphere that supported this water has remained a mystery. By integrating multiple planetary processes that impact the isotopic composition of the atmosphere, we placed new constraints on ancient Mars's atmosphere. To start, we compared our model to atmospheric and geochemical observations via Bayesian inversion to show, for the first time, that N₂ was likely a major component of the ancient atmosphere but has been subsequently lost to space (Hu and Thomas, 2022). We then expanded this work to place self-consistent constraints on the ancient atmospheric abundances of N₂, CO₂ and Ar that are similarly consistent with Mars's evolution to its present-day state (Thomas, Hu, and Lo, 2023). Finally, we studied the photochemical and climatic implications of these potential atmospheres when including crustal reactions that release H₂ (Adams...Thomas et al., 2025). Taken together, these studies show that a CO₂-N₂-H₂ atmosphere on ancient Mars can provide the necessary warming to support surface liquid water and that it is consistent with observational constraints on Mars's geochemical evolution.

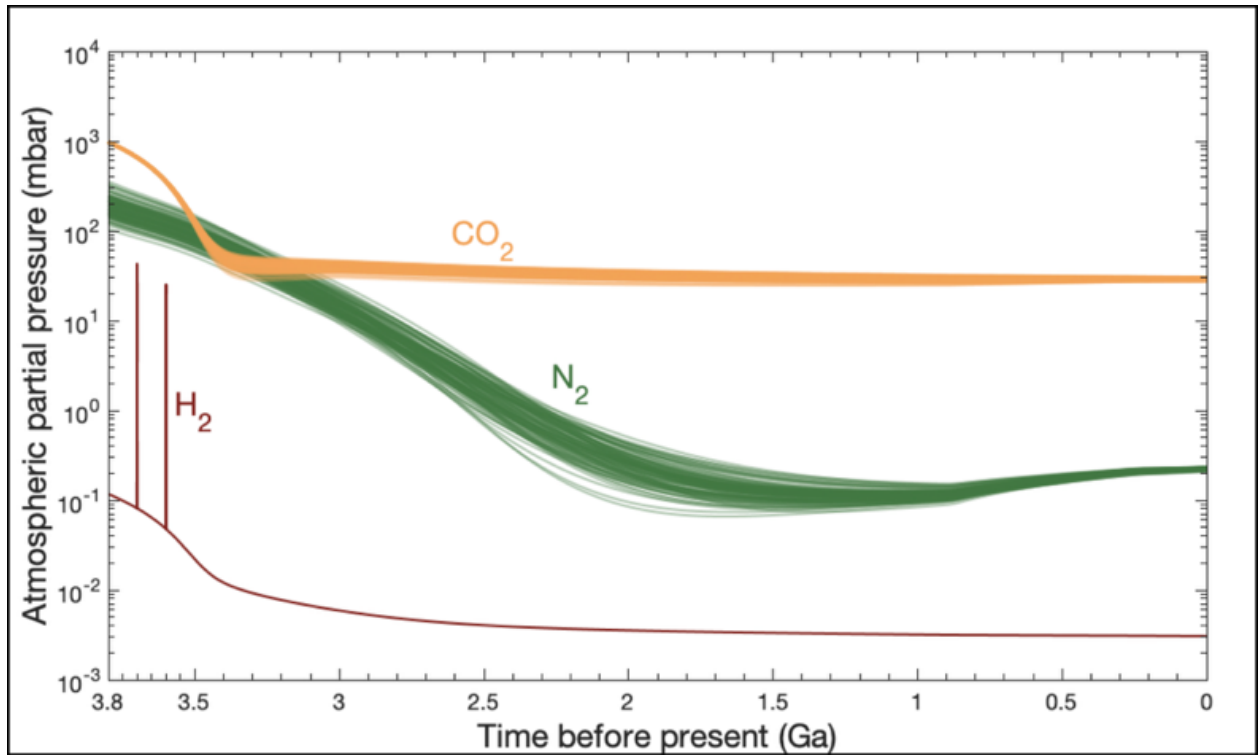


Figure A1: The proposed evolution of volatiles in Mars's atmosphere. The CO_2 - N_2 - H_2 atmosphere is an emerging explanation for how ancient Mars's surface was warm enough to support liquid water.

Appendix B: Curriculum Vitae

Trent B. Thomas

EDUCATION

Ph.D. in Earth and Space Sciences, Astrobiology2026
University of Washington, Seattle (UW) – *Dual-title Ph.D. & Data Science Certificate*

B.S. in Astrophysics2020
University of California, Los Angeles (UCLA) – *Phi Beta Kappa*

PROFESSIONAL EXPERIENCE

National Science Foundation Graduate Research Fellow 2020-2026
University of Washington, Seattle

Visiting Researcher2024
Massachusetts Institute of Technology (MIT)

Research Intern 2018-2023
NASA Jet Propulsion Laboratory (JPL)

PEER-REVIEWED PUBLICATIONS

Forthcoming:

1. **Thomas, T. B.**, et al., (In prep.). Interior constraints from the volcanically-supported, SO₂-dominated atmosphere on the exoplanet L 98-59 b.
2. **Thomas, T. B.**, Stucky de Quay, G., & Mitchell, W.H. (In prep.). Automatic Image Segmentation of Alluvial Fans and Deltas on Mars with Deep Learning. [See the associated [GitHub repository](#)]

Published:

3. **Thomas, T. B.**, Macdonald, F.A., & Catling, D.C., 2026, *Geology*. [Seafloor Weathering Can Explain the Disparate Durations of Snowball Glaciations.](#)
4. **Thomas, T. B.**, Meadows, V.S., Krissansen-Totton, J., Gialluca, M., Wogan, N., & Catling, D.C., 2025, *The Planetary Science Journal*. [Statistical Geochemical Constraints on Present-Day Water Outgassing as a Source of Secondary Atmospheres on the TRAPPIST-1 Exoplanets.](#)
5. Adams, D., Scheucher, M., Hu, R., Ehlmann, B., **Thomas, T. B.**, Wordsworth, R., Scheller, E., Lillis, R., Smith, K., Rauer, H. & Yung, Y., 2025, *Nature Geoscience*. [Episodic Warm Climates on Mars Primed by Crustal Hydration.](#)

6. **Thomas, T.B.**, & Catling, D.C., 2024, *Nature Communications*. [Three-stage Formation of Cap Carbonates after Marinoan Snowball Glaciation Consistent with Depositional Timescales and Geochemistry.](#)
7. **Thomas, T. B.**, Hu, R., & Lo, D.Y., 2023, *The Planetary Science Journal*. [Constraints on the Size and Composition of the Ancient Martian Atmosphere from Coupled CO₂–N₂–Ar Isotopic Evolution Models.](#)
8. Hu R., & **Thomas, T.B.**, 2022, *Nature Geoscience*. [A Nitrogen-Rich Atmosphere on Ancient Mars Consistent with Isotopic Evolution Models.](#)

INVITED TALKS

Colloquium – Santa Fe Institute.....	2026
Department Seminar – University of Victoria, Earth and Ocean Sciences.....	2025
Astrophysics Colloquium – LMU Munich, Center for Geoastronomy	2025
Department Seminar – University of Southampton, National Oceanography Center	2025
Department Seminar – Dartmouth College, Earth Sciences	2025
Virtual Planetary Laboratory Seminar – NASA/UW.....	2023
High Performance Computing Seminar – NASA JPL	2022

FELLOWSHIPS AND AWARDS

David A. Johnston Award for Research Excellence – UW ESS	2025
Best Paleoclimate and Sedimentology Talk – UW ESS Research Gala	2025
Finalist, Student Poster Competition – Astrobiology Science Conference.....	2024
Winglee Endowed Graduate Support Fund and Space Physics Fellowship – UW ESS.....	2023
Best Astrobiology Talk – UW ESS Research Gala	2023
National Science Foundation Graduate Research Fellowship (NSF GRFP)	2020
Dean’s Prize for Excellence in Undergraduate Research – UCLA	2020
Early Career Collaboration Award – NASA Astrobiology.....	2019
Rudnick-Abelmann Scholarship – UCLA Physics & Astronomy	2019
<i>3 additional travel grants from NASA, AAS, & LPI</i>	

TEACHING AND MENTORSHIP

Classes taught:

Generative Design: Creating Art with Code (PI) – Coyote Central	Summer 2024, 2025
<i>I created and instructed a 20-hour course for K-12 students with no prior coding experience. See their final projects here: 2024, 2025.</i>	
Introduction to Geology and Societal Impacts (TA) – UW ESS.....	Fall 2024
Earth’s Origin and Transformation over 4.6 Billion Years (PI/TA) – UW ESS.....	Winter 2023

I developed ten 80-minute lectures, syllabus, and course material. I guest lectured “The history of life on Earth” and performed TA duties.

Mentored undergraduates:

Veronica Fula (UW), Jasmine Singh (Purdue)

ADDITIONAL TRAINING

Mars Analog Workshop – UW Astrobiology	2023
Sagan Summer Workshop – NASA Exoplanet Science Institute.....	2023
Origin of Life Workshop – UW Astrobiology.....	2022
Storytelling Fellows Podcasting Workshop – UW Libraries	2022
Planetary Exploration Mission Design Workshop – UW Astrobiology.....	2022
VPLanet Developers Workshop – Virtual Planetary Laboratory	2021
ROCKE-3D GCM Tutorial – NASA GISS.....	2021
Quantitative Habitability Workshop – NASA NExSS	2020
Exoclines Simulation Platform Summer School – University of Bern.....	2019

SERVICE

Peer review: Nature Communications, Icarus, The Open Journal of Astrophysics

Early Career Committee – [NASA LIFE Research Coordination Network](#)..... 2025-Present
Responsibilities include organizing the virtual seminar series, workshops, and conference events.

Expert Screener – [CDRXIV](#), Preprints and Data for Carbon Dioxide Removal..... 2025-Present

Department Representative – UW CoEnv Student Advisory Council..... 2024-2025

Committee Member – UW ESS..... 2020-Present
Awards, computing, graduate-nominated speaker (x2), retreat, peer mentor, planetary science faculty hiring.

PUBLIC ENGAGEMENT

Community outreach:

Guest Speaker – Everett Rock and Gem Club	2025
Science Guest – Bandit Theater, Mad Science Improv	2025
Classroom Mentor (20 hours, 8 students) – Coyote Central Youth Arts Organization	2024
Contributor – NASA NExSS & NASA NFOld Science Communication	2022 – 2023
Speaker (Mars: Why the Hype?) – Astronomy on Tap, Seattle	2022
Volunteer Teacher (8 hours, 120 students) – Nelson Middle School, Seattle	2022
Page Creator (Prebiotic atmosphere) – Wikipedia	2022
Invited Speaker – Delran School System Family STEM Night.....	2022
Social Media Manager – UW Astrobiology	2021-2022
Creator & Moderator – UW Astrobiology Public Science Panel Series	2021

Volunteer Guide – UCLA Planetarium	2019-2020
Volunteer Scientist – UCLA Exploring Your Universe.....	2019

Media coverage:

<i>GSA</i> – Rudy Molinek: Understanding “Snowball Earth” Extreme Climates — When the World Is Covered in Ice	2026
<i>UW News</i> – Hannah Hickey: Explaining dramatic planetwide changes after world’s last ‘Snowball Earth’ event	2024
<i>NASA Astrobiology</i> – Aaron Gronstal: The Size and Shape of Mars’ Ancient Atmosphere	2023
<i>LPI Planetary News</i> – Isotopic Evidence that Ancient Mars’ Atmosphere was More Earth-Like	2022

CONFERENCE ACTIVITY

[O] = oral (12), [P] = poster (5), * = presentation award (3)

1. **Thomas, T.B.**, Macdonald, F.A., and Catling, D.C. (2025) “Seafloor weathering controls the duration of Neoproterozoic Snowball Earth glaciations”. American Geophysical Union Fall Meeting. New Orleans, Louisiana. [P]
2. **Thomas, T.B.**, Meadows, V.S., Krissansen-Totton, J., Gialluca, M., Wogan, N., and Catling, D.C. (2025) “Water outgassing as a source of secondary atmospheres on the TRAPPIST-1 exoplanets.” STScI Atmospheric Escape and Replenishment Workshop. Baltimore, Maryland. [O]
3. **Thomas, T.B.**, Macdonald, F.A., and Catling, D.C. (2025) “Seafloor weathering controls the duration of Neoproterozoic Snowball Earth glaciations”. Life and Planet Conference. London, England. [P]
4. **Thomas, T.B.**, Macdonald, F.A., and Catling, D.C. (2025) “Long duration of the ~56 Myr Sturtian Snowball Earth event suggests missing link in the geologic carbon cycle”. European Geoscience Union General Assembly. Vienna, Austria. [O]
5. ***Thomas, T. B.**, (2025) “Fundamental aspects of Snowball Earth revealed by a global carbon cycle model”. UW Earth and Space Science Research Gala. Seattle, Washington. [O]
6. ***Thomas, T. B.**, and Catling, D. C., (2024) “A New Model for the Formation of Cap Carbonates after Neoproterozoic Glaciations”. Astrobiology Science Conference. Providence, Rhode Island. [P]
7. **Thomas, T. B.**, et al., (2024) “Constraints on water outgassing rates on the TRAPPIST-1 planets from interior modeling”. Extreme Solar Systems V. Christchurch, New Zealand. [P]
8. **Thomas, T. B.**, and Catling, D. C., (2023) “Untangling Planetary Processes in the Neoproterozoic with Cap Carbonates and a Geologic Carbon Cycle Model”. Goldschmidt Conference. Lyon, France. [O]
9. ***Thomas, T. B.**, (2023) “The 4 Billion Year History of Mars’s Atmospheric Evolution Revealed by Isotopic Evolution Models”. UW Earth and Space Science Research Gala. Seattle, Washington. [O]

10. **Thomas, T. B.**, Hu, R., and Lo, D. Y., (2022) “Constraints on the Evolution and Ancient Composition of the Martian Atmosphere from Coupled CO₂-N₂-Ar Isotopic Evolution Models”. 54th Division for Planetary Science Conference. London, Ontario, Canada. [O]
11. **Thomas, T. B.**, and Catling, D. C., (2022) “A Self-Consistent Model for Generating Marinoan Cap Carbonates and Constraining Neoproterozoic Climate”. Astrobiology Science Conference. Atlanta, Georgia. [O]
12. **Thomas, T. B.**, (2022) “A Self-Consistent Model for Generating Marinoan Cap Carbonates and Constraining Neoproterozoic Climate”. UW Earth and Space Science Research Gala. Seattle, Washington. [O]
13. **Thomas, T. B.**, Hu, R., and Lo, D. Y., (2022) “Joint Models for the Evolutionary History of Carbon, Nitrogen, and Argon in the Martian Atmosphere”. 53rd Lunar and Planetary and Science Conference. The Woodlands, Texas. [O]
14. **Thomas, T. B.**, and Hu, R., (2020) “A Nitrogen-Rich Atmosphere on Ancient Mars Indicated by Isotopic Evolution”. American Geophysical Union Fall Meeting. Virtual. [O]
15. **Thomas, T. B.**, and Hu, R., (2020) “A Nitrogen-Rich Atmosphere on Ancient Mars Indicated by Isotopic Evolution. 52nd Division for Planetary Science Conference. Virtual. [O]
16. **Thomas, T. B.**, and Hu, R., (2020) “A Nitrogen-Rich Atmosphere on Ancient Mars Indicated by Isotopic Evolution”. UCLA Undergraduate Research Week. Virtual. [O]
17. **Thomas, T. B.**, and Hu, R., (2019) “Evolutionary History of the Isotopic Composition of Nitrogen in the Martian Atmosphere”. 9th International Conference on Mars. Pasadena, California. [P]

Session Organization

1. Primary Convener. “Global Environmental Changes and Increased Biological Complexity in the Neoproterozoic and Paleozoic”. American Geophysical Union Fall Meeting, New Orleans, Louisiana (2025)
2. Primary Convener. “Global Environmental Changes and Increased Biological Complexity in the Neoproterozoic and Paleozoic”. Astrobiology Science Conference, Providence, RI (2024)