Earth's Outgassing and Climatic Transitions: The Slow Burn Towards Environmental "Catastrophes"?

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On multimillion-year timescales, outgassing from the Earth's interior provides the principal source of CO_2 to the ocean–atmosphere system, which plays a fundamental role in shaping the Earth's baseline climate. Fluctuations in global outgassing have been linked to icehouse–greenhouse transitions, although uncertainties surround paleo-outgassing fluxes. Here, we discuss how volcanic outgassing and the carbon cycle have evolved in concert with changes in plate tectonics and biotic evolution. We describe hypotheses of driving mechanisms for the Paleozoic icehouse–greenhouse climates and explore how climatic transitions may have influenced past biotic crises and, in particular, how variable outgassing rates established the backdrop for carbon cycle perturbations to instigate prominent mass extinction events.

Keywords: carbon cycle, outgassing, weathering, climate, biodiversity, mass extinction

LONG-TERM CARBON CYCLE

Earth has transitioned between two major baseline climate states throughout its history: icehouse (or Ice Age) intervals that consist of generally cool climates with well-developed polar ice sheets, and warm greenhouse intervals devoid of ice caps. Transitions between icehouse and greenhouse intervals are largely influenced by the partial pressure of atmospheric carbon dioxide ($p$$CO_2$). The transfer of carbon between the solid Earth (endogenic system) and the ocean–atmosphere (exogenic system) on million-year timescales is governed by the long-term carbon cycle. The $p$$CO_2$ is a result of the balance between the rate of CO_2 inputs through magmatic/metamorphic degassing and the rates of carbon removal via silicate weathering and organic carbon burial (Berner 2004) (Fig. 1). Due to the small size of the surface carbon reservoir relative to the inputs from the solid Earth, a negative feedback between silicate weathering and temperature is required to stabilize atmospheric CO_2 and climate on timescales of longer than 10^5 years (Walker et al. 1981). Thus, steady-state $p$$CO_2$ levels are determined by the input and the relative strength of the silicate weathering feedback mechanisms (Berner 2004).

Solid Earth carbon degassing occurs at mid-ocean ridges, rifts, volcanic arcs in subduction zones, orogenic belts, and large igneous provinces (Fig. 1). The global volcanic flux of CO_2 probably varied significantly throughout geologic time. Changes in subduction zone length, in the volume of a mantle plume, and/or in the global oceanic crust production rate can result in at least a two-fold increase in volcanic CO_2 inputs (Lee et al. 2013). Variation in the CO_2 input would, therefore, play a fundamental role in changing long-term baseline climate states. These tectonic/magmatic processes also contribute to modifying the climate–silicate weathering feedback strength, which is influenced by the exhumed supply of weatherable minerals, dissolution kinetics, and hydrologic conditions (Hartmann et al. 2014; Maher and Chamberlain 2014; Jiang and Lee 2019). The long-term carbon cycle stabilizes planetary climate due to the temperature sensitivity of silicate weathering—at high temperatures weathering rates increase and rapidly draw CO_2 out of the atmosphere, so cooling the climate. Because surface temperature is, in part, controlled by $p$$CO_2$, the relation between CO_2 inputs and the weathering feedback can be represented as the curve in Figure 2. In general, we expect a positive correlation between the input or output with steady state $p$$CO_2$, with the slope of the curve representing the feedback strength. With linear

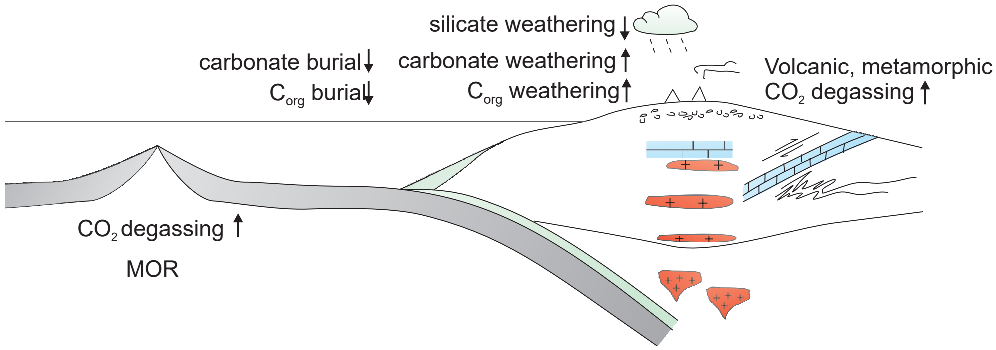

Figure 1 Schematic of tectonic controls on the long-term carbon cycle. Oceanic crust is in light grey; sediments on the oceanic crust and that form the accretionary prism are in light green; limestones (unmetamorphosed and metamorphosed) in blue; granite bodies in red. Abbreviations: C_{org} = organic carbon; MOR = mid-ocean ridge.

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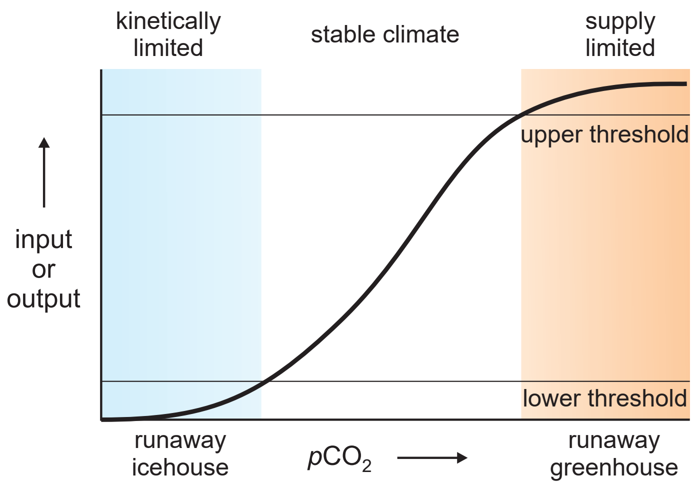

Figure 2 Schematic illustration of climate states having varying weathering feedback and outgassing conditions. Low outgassing rates combined with kinetically limited weathering regimes allows Earth to reach a state where extensive icehouse (or snowball) conditions can be achieved. Conversely, elevated outgassing combined with supply-limited weathering (i.e., a negligible silicate weathering feedback) can push Earth into a runaway greenhouse. Adapted from Lee et al. (2019).

weathering feedback, the system remains regulated and runaway processes cannot happen. However, global or regional weathering processes can be either “rate-limited”, wherein an excess of weatherable minerals are available and the weathering rate is limited by kinetic rate, or “supply-limited”, which occurs when all weatherable substrates are exhausted and the weathering rate is limited by the supply of fresh materials. As such, the negative feedback mechanism may not scale linearly with exogenic CO_2 content. For example, in a low pCO_2 scenario, temperature could drop below some threshold where weathering kinetics become negligible because surface temperatures are, in part, controlled by pCO_2. As a result, the system reaches a threshold of atmospheric pCO_2 such that weathering rates are insensitive to CO_2, and further decreases in carbon input combined with ice albedo effects could result in runaway icehouse conditions. Similarly, silicate weathering may become supply-limited even with high temperature and high pCO_2, where the system reaches a threshold above which increased CO_2 does not result in increased weathering. This can result in runaway greenhouse conditions (Fig. 2).

Therefore, “thresholds” in the silicate weathering feedback exist, above or below which weathering rates become insensitive to pCO_2, leading to failure of silicate weathering feedback in climate regulation (Foley 2015; Kump 2018). Crossing these thresholds would move the planet to a new steady state with different feedback parameters. For example, in a low pCO_2 scenario, temperature could drop below the water freezing point where weathering kinetics become sluggish, or even cease completely. If the system maintains low CO_2 input, the planet would remain ice-covered and be dominated by runaway ice-albedo feedback. In a globally supply-limited scenario, the system reaches a threshold above which increased CO_2 does not result in increased weathering, thus rapid emission of large quantity of CO_2 may exhaust the capacity of the long-term climate regulator associated with silicate weathering, resulting in runaway greenhouse conditions (Foley 2015; Kump 2018) (Fig. 2).

ICEHOUSE–GREENHOUSE CONDITIONS IN DEEP TIME

Since the Cryogenian Period (716–635 Ma), Earth has shifted between numerous icehouse–greenhouse states (Fig. 3). The Cryogenian was one of the most extensive icehouses, being characterized by two Snowball Earth events when ice sheets reached paleo-shorelines in equatorial regions. The first of these Snowball Earth events, known as the Sturtian glaciation, occurred ~716 Ma, and the second was the Marinoan glaciation that terminated ~635 Ma. Subsequent relatively short-lived, yet expansive, glaciations included the Ediacaran Gaskiers glaciation (~580 Ma) and the Hirnantian glaciation at the end of the Ordovician Period (~440 Ma). The Late Paleozoic icehouse extended from the Carboniferous to the late Permian, and our current Cenozoic icehouse climate was initiated

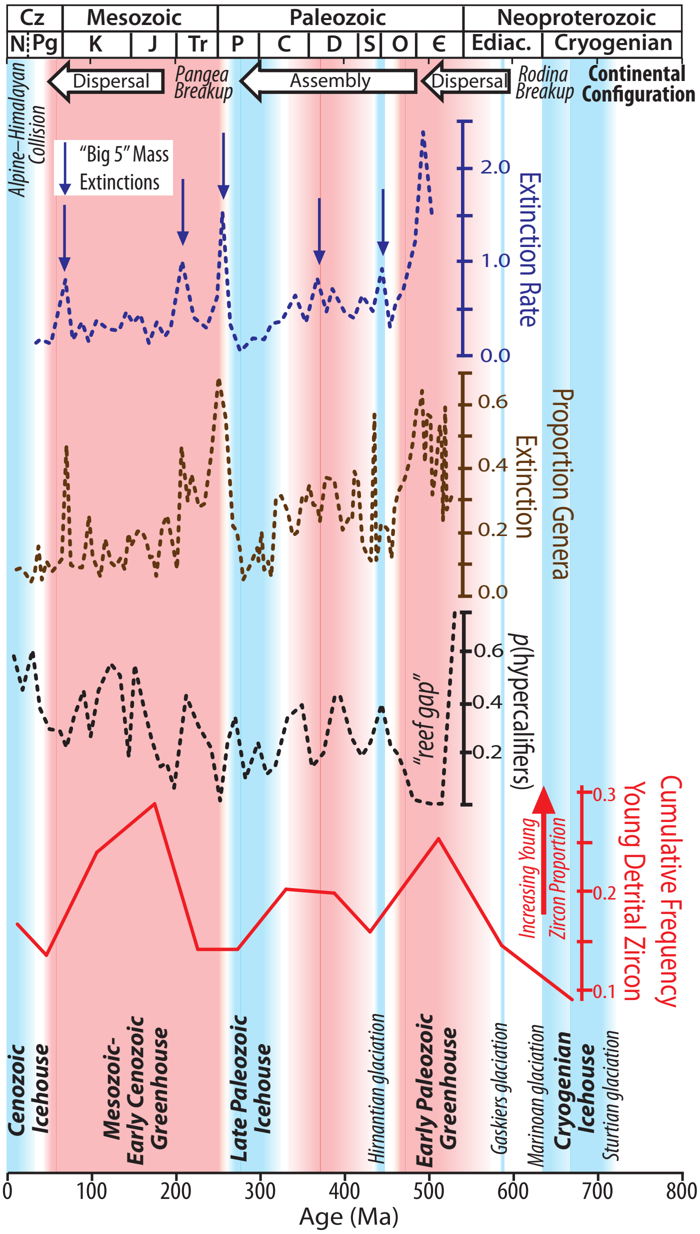

Figure 3 Composite of climate states over last ~720 million years, including the proportion of young detrital zircons, the proportion of benthic hypercalcifiers, the proportion of genera extinctions, the extinction rates, and the various continental configurations. Red = greenhouse conditions; blue = icehouse conditions. Ediac. = Ediacaran. Modified after McKenzie et al. (2014, 2016), Alroy (2008), and Bambach et al. (2004).

during the later Paleogene (~33 Ma). Prominent greenhouse intervals spanned the Ediacaran through the early Paleozoic, the middle Paleozoic, and the Mesozoic to early Cenozoic. Interestingly, the Precambrian record is sparse with regard to icehouse intervals. Aside from a few putative glaciogenic deposits in Archean sedimentary sequences, the ~2.3 Ga Huronian glaciations represent the only well-documented icehouses prior to the Cryogenian, i.e., there is an ~1.6 billion year interval without any known evidence of icehouse climates. Understanding what processes drive deviations from one steady-state climate to a new one remains a topic of high interest, with ongoing debates focused on whether climatic transitions are controlled by changes in the CO_2 inputs or changes in the efficiency of the weathering sink.

Weathering-driven models for climate change seek out mechanisms that can enhance global weathering efficiency and CO_2 consumption. Weathering rates are dependent on temperature, precipitation, and exposed reactive surface area of the material being weathered. A leading hypothesis postulates that the concentration of continents in low-latitudes (i.e., the tropics) causes intense weathering due to high precipitation and hot and humid climates, which causes cooling and favors icehouse conditions (Marshall et al. 1988). This hypothesis has led to an increased focus on concentrations of mafic crustal rocks in low-latitudes because mafic minerals weather more rapidly, and at lower temperatures, than felsic minerals, thereby enhancing the "weatherability" of the crust. Increasing crustal mafic rocks in the tropics can be accomplished through the eruption of large igneous provinces (LIPs) or by accretion of island-arc terranes in low-latitudes. Cooling during the Cryogenian and Cenozoic has been attributed to low-latitude LIP emplacement (e.g., Goddéris et al. 2003; Kent and Muttoni 2013), whereas tropical arc-terrane accretion might be responsible for discrete cooling events during the Cretaceous and Cenozoic (Jagoutz et al. 2016) and for the end-Ordovician Hirnantian icehouse (Swanson-Hysell and Macdonald 2017). Mafic LIPs emplaced on stable cratons may have a large initial reactive surface area, but, without extensive uplift and physical erosion, that surface could be rapidly leached, leaving the greater volume of the unexposed rock blocked from the weathering zone—a process termed "soil-shielding" (e.g., Hartmann et al. 2014). This makes the arc-terrane collisions a more appealing mechanism by which to change weatherability and to drive cooling, because accretionary processes induce uplift, erosion, and exhumation of the bedrock, vastly increasing its reactive surface area and weathering potential. The interaction between mineral supply and reaction kinetics makes orogenic systems preferential sites for enhanced weathering. At present, tectonically active regions are thought to account for substantial CO_2 consumption (Hartmann et al. 2014). Still, the role of tectonics on weathering can be quite complicated and numerous factors need to be considered when assessing deep-time climatic influences.

Take the Himalayas as an example. The Himalayan foreland (the Indo-Gangetic plains) yields weathering fluxes comparable to basaltic provinces (West et al. 2002). While the Himalaya lie outside of the tropics, its extensive east–west strike and mountain heights interferes with the atmospheric circulation, which ultimately drives the South Asian Monsoon (Boos and Kuang 2009). The combination of the hot and humid monsoon with the continuous supply of fresh weatherable silicate minerals into the foreland basin via uplift and erosion of the orogenic belt is why the Himalayan system yields such high weathering fluxes. From a paleo-perspective, the Himalaya would not meet the assumed criteria for a prominent low-latitude weathering system, yet the Himalaya modifies the climate system such that it can play a major role in global weathering.

The relationship between long-term climate transitions and low-latitude emplacement of mafic bodies in deep time is not clear (McKenzie et al. 2016; Mills et al. 2017). While some LIP and arc-terrane emplacement events may have been coincident with cooling events, many were not. Multiple LIPs have erupted in equatorial locations without any notable cooling effects, e.g., during the Cambrian and the Triassic. Similarly, extensive collisional belts existed around equatorial regions throughout the Cambrian, which remained a greenhouse interval (e.g., McKenzie et al. 2014; Cao et al. 2017; Mills et al. 2017). On the other hand, changes of the volcanic CO_2 flux into the surface system appear to be directly associated with major climatic transitions. Multiple studies focusing on paleogeographic volcanic arc distributions have shown that changes in arc length relate to icehouse–greenhouse transitions at various intervals in Earth history (e.g., Lee et al. 2013; Mills et al. 2017). Analysis of detrital zircons in global sedimentary deposits that span the past ~720 million years showed a direct relationship between zircon production—a proxy for regional continental arc magmatism—and all major climatic transitions throughout this interval (McKenzie et al. 2016) (Fig. 2). Continental arc systems are of particular interest because, via decarbonation reactions, they have the ability to liberate carbon from carbonates preserved in the upper plate (Lee et al. 2013; Mason et al. 2017).

While outgassing may generally determine baseline climate states, pCO_2 represents a balance between both sources and sinks. Quantifying outgassing rates is a difficult task in deep time due to the uncertainties in estimating modern CO_2 fluxes and the potential additive input from crustal carbon sources, which may be more complicated for LIPs. Furthermore, the development of continental arcs often involves compressional mountain building events that enhance weatherability, thereby dampening the outgassing contribution (Jiang and Lee 2017). As noted above, weathering rates are dependent on multiple variables that are difficult to estimate in Earth's history. Therefore, our understanding of ancient climatic transitions relies on our ability to interpret the rock record. For example, the lack of a consistent relationship between the sporadic occurrence of low-latitude mafic bodies and global cooling does not mean their occurrences did not influence climate change: their contributions may have depended on baseline conditions during their emplacement.

CLIMATE STEADY STATES, THRESHOLDS, AND "CATASTROPHES"

At some periods during Earth's history, long-term endogenic processes might have "pre-set" the climate baseline close to a threshold that could have been easily crossed from shorter-termed events, such as LIPs, bolide impacts, or seafloor methane release. The combination of long-term fluctuations in CO_2 emissions and short-term events could have played an important role in biologic evolution. Perturbations of Earth's carbon cycle can lead to mass extinctions if they exceed either a critical rate at long timescales or a critical size at short timescales (Rothman 2018). The influences of rapid CO_2 fluctuations from LIP events on mass extinctions are already discussed elsewhere in this issue of *Elements*; thus, we will speculate on the relative importance of changes in the baseline pCO_2 associated with variations in outgassing on carbon cycle perturbations and on Earth system "catastrophes".

Most major mass extinctions have occurred during greenhouse climates. This might be due to the fact that the Earth has spent more time in a greenhouse state (Fig. 3). However, a link between some extinctions and environmental conditions has been recognized that involves the carbon cycle. In particular, changes in carbonate saturation state have been postulated as key drivers of extinctions (Knoll and Fischer 2011). The early Paleozoic and the middle Permian through to the end-Triassic encapsulate the highest marine animal extinction rates (Bambach et al. 2004; Alroy et al. 2008) (Fig. 3). The Cambrian "dead interval" of the early Paleozoic is characterized by generally low biodiversity with multiple mass extinction events associated with ocean anoxia and carbon cycle perturbations, as well as an extensive "reef gap" when calcifying animals were of markedly low abundance (e.g., McKenzie et al. 2014 and refs therein) (Figs. 2 and 3). Three major mass extinction events occur around the transition from the Paleozoic to the Mesozoic: the mid-Permian "Guadalupian" (~260 Ma), the end-Permian (~251 Ma), and the end-Triassic (201 Ma) extinctions, all of which were coincident with LIP eruptions and carbon cycle perturbations. These extinctions are also noted for selection against calcifying animals (Clapham and Payne 2011; Knoll and Fischer 2011). Much like the Cambrian, the Mesozoic recorded numerous ocean anoxic events (OAEs) that are believed to have been the result of episodic CO_2 perturbations (Jenkyns et al. 2010). The end-Devonian mass extinction also exhibited selection

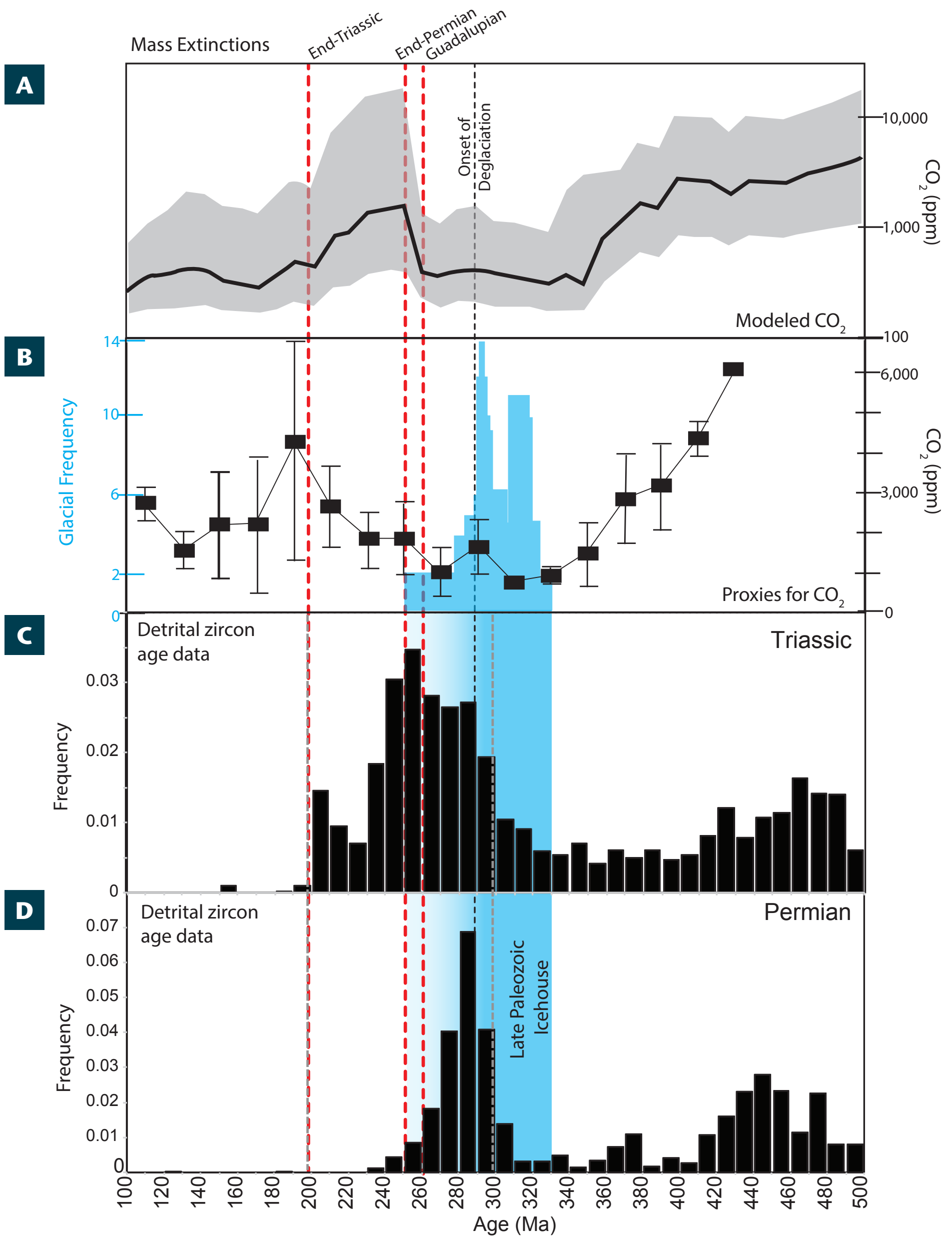

Figure 4 The Paleozoic–Mesozoic transition. (**A**) Modeled paleoconcentrations of CO_2. (**B**) Paleoconcentrations of CO_2 obtained from proxies. (**C**) Frequency of detrital "young" zircon ages from Triassic strata. (**D**) Frequency of detrital "young" zircon ages from Permian strata. Timing of mass extinctions are indicated by vertical red dashed lines. Glacial frequency is shown in blue with the onset of deglaciation from the Late Paleozoic icehouse beginning at ~290 Ma. The zircon data indicate there was a marked increase in outgassing from volcanic activity beginning at ~290 Ma that is coincident with the onset of deglaciation. The proxy and modeled CO_2 increase are decoupled by ~50 My from the onset of deglaciation. Late Paleozoic Icehouse duration from Montañez and Paulsen (2009); CO_2 proxy data from Zeebe (2012); modeled CO_2 curve from Royer et al. (2014) and zircon frequencies data from McKenzie et al. (2016).

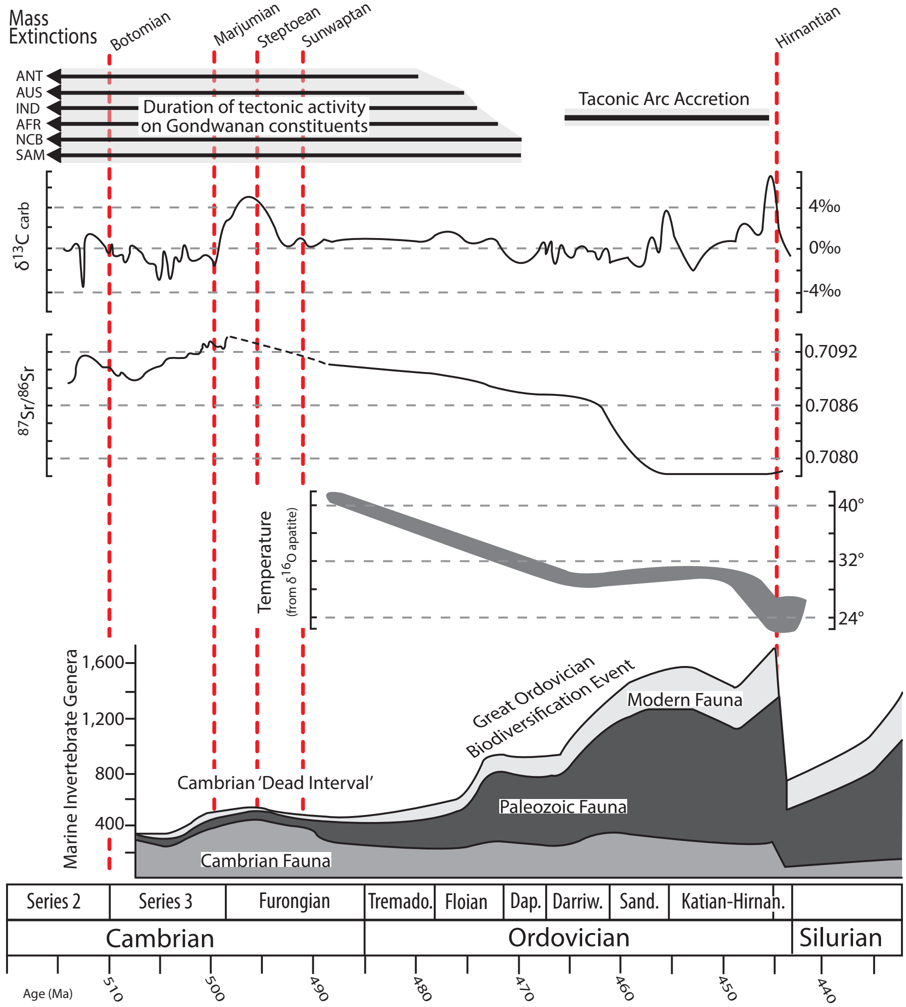

FIGURE 5 Early Paleozoic tectonics, climate, and biodiversity. Note that the reduction in Gondwanan tectonism coincides with a global cooling trend, consistent with the zircon record in FIGURE 3. Taconic arc exhumation had initiated by ~465 Ma. The timing of five mass extinction events (Botomian, Majumian, Steptoean, Sunwaptan, and Hirnantian) are indicated with vertical dashed red lines. Seawater $^{87}Sr/^{86}Sr$ relative highs indicate high radiogenic ^{87}Sr fluxes from chemical weathering of old continental crust. Carbonate $\delta^{13}C$ tracks carbon cycle variation and perturbations. Abbreviations on tectonic duration activity: ANT = Antarctica; AUS = Australia; IND = India; AFR = Africa; NCB = North China Block; SAM = South America. MODIFIED FROM MCKENZIE ET AL. (2014). TACONIC ARC-ACCRETION RANGE FROM SWANSON-HYSEL AND MACDONALD (2017).

against calcifying animals (Knoll and Fischer 2011). The Cretaceous–Paleogene extinction—last of the "big 5"—corresponded with both the Deccan (India) LIP and a bolide impact at Chicxulub (Mexico), but lacks notable evidence for marked selectivity against calcifying animals. However, this extinction followed the Jurassic diversification of planktonic calcifying organisms that produced a new deep-ocean carbonate reservoir that could buffer against sustained acidification, thus changing carbon cycle dynamics (e.g., Zeebe 2012).

The collective similarities of environmental conditions and extinction dynamics during the early Paleozoic, mid Paleozoic, and late Permian–Triassic greenhouses imply that background CO_2 fluxes and greenhouse baseline conditions can increase the sensitivity of the surface environment to short-term sizeable CO_2 injections. Whereas the Cambrian corresponded to a protracted interval of widespread volcanism, the Permian–Triassic witnessed a dramatic rise in pCO_2 (Zeebe 2012; Royer et al. 2014) (FIGS. 2 and 4). The transition out of the late Paleozoic icehouse was associated with an increase in pCO_2 (Montañez and Poulsen 2008). Although detrital zircon data from Permian and Triassic strata may show low-abundances of "young" zircon dates with ages close to the depositional ages of the strata relative to the total populations (McKenzie et al. 2016) (FIG. 3), closer evaluation of the data shows that the relatively young grains present form a distinct young population that increase in abundance ~290 Ma, which is coincident with the onset of deglaciation (FIG. 4). These young <290 Ma zircons are seen on multiple geographic regions (North America, South America, China, Africa, Southeast Asia, Australia) and represent a rapid, nearly synchronous global increase in the volcanic CO_2 flux at this time (a magmatic "flare up") that may have caused warming (FIG. 4). This change in surface environment could have amplified the effects of the perturbations caused by LIPs during this time.

There is a final point for consideration. It has been shown that major cooling events, such as the Cryogenian "Snowball Earth" glaciations and the end-Ordovician Hirnantian glaciations, correspond with marked reductions in global magmatism (McKenzie et al. 2016; Mills et al. 2017). The Hirnantian glaciation follows an interval that had a progressive reduction in volcanism and global cooling and that was punctuated with a rapid drop in temperature coincident with the end-Ordovician Hirnantian extinction (FIG. 5). Ordovician cooling may have been driven by increased weathering due to low-latitude arc-terrane collisions of the Taconic orogenic system (Swanson-Hysell et al. 2017). Given a baseline climate state with reduced global outgassing and lower background pCO_2, the exhumation of a large mafic terrane in the tropics may have been sufficient to have changed global weathering kinetics and to have caused the drop in temperature needed to induce a rapid extinction-linked glaciation.

In summary, the Earth has experienced many carbon cycle perturbations, although their influences on the climate system and biosphere have been disparate. Whereas pCO_2 always represents a balance between carbon sources and sinks, changes in global outgassing appear responsible for driving multimillion-year swings in baseline climate state. Extended intervals of high volcanic outgassing may not sustain ocean acidification, but shifts in baseline conditions can influence the carbon cycle and make it more sensitive to perturbation. Effectively, greenhouse intervals may have been more amenable to mass extinctions. Conversely, reduced outgassing may allow temperatures to drop to the low levels that inhibit background weathering rates, where the tropical emplacement of large mafic terranes can change weathering kinetics to initiate short-lived "catastrophic" drops in temperature leading to Snowball Earth events or extinction-driving icehouses. Accordingly, the slow exchanges of carbon between the endogenic and exogenic systems profoundly influence Earth's climatic state and its biospheric stability.

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