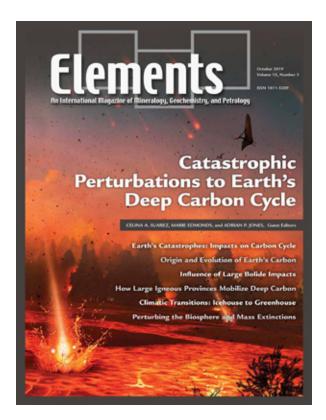




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Earth Catastrophes and their Impact on the Carbon Cycle

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arbon is one of the most important elements on Earth. It is the basis of life, it is stored and mobilized throughout the Earth from core to crust and it is the basis of the energy sources that are vital to human civilization. This issue will focus on the origins of carbon on Earth, the roles played by large-scale catastrophic carbon perturbations in mass extinctions, the movement and distribution of carbon in large igneous provinces, and the role carbon plays in icehouse-greenhouse climate transitions in deep time. Present-day carbon fluxes on Earth are changing rapidly, and it is of utmost importance that scientists understand Earth's carbon cycle to secure a sustainable future.

KEYWORDS: impacts, Earth's origin, extinction, climate change, volcanism, large igneous province

INTRODUCTION

Great strides have been made in quantifying the diverse world of carbon in Earth. Our understanding now encompasses the amount and forms of carbon storage in the Earth's core, mantle and crust; how carbon is mobilized via melting and outgassing from the Earth's interior; and the extent and diversity of carbon that is bound in the form of microbial life on the seafloor and in the crust. Much of this work has been carried out under the auspices of the Deep Carbon Observatory (DCO; a global network of over 1,000 scientists on a 10-year quest to better understand all aspects of Earth's carbon cycle). Important synthetic outputs of the DCO are steady-state models based on groundbreaking new data that can be used to evaluate the contemporary fluxes between carbon reservoirs in the deep Earth and their effects on everything from the evolution of life to the air we breathe.

Armed with this understanding, we can better evaluate perturbations to, or nonlinearities in, the Earth system through deep time. Catastrophic events have caused measurable, perhaps irreversible, changes to Earth's carbon cycle on land, in the air, and under the sea, as evidenced spectacularly by mass extinction events at significant stratigraphic boundaries associated with major carbon cycle perturbations (i.e., major influxes, or draw-downs, of carbon into, or out of, the surface reservoir). The

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search for catastrophic causes of perturbations in the carbon cycle ranges from the tipping points reached during slow accretion of tectonic plates into megacontinents, to shifts in atmospheric or ocean circulation, to instantaneous megaenergy events delivered by Earth's inevitable orbital space encounters with bolides, to large-scale volcanism. These major events are often associated with biological diversity crises and mass extinctions. Deciphering the complex and often faint signals of distant catastrophes requires a multidisciplinary effort and the

most innovative analytical technology.

This issue of *Elements* focuses on large-scale catastrophic perturbations to the modern day "steady state" carboncentric Earth, exploring the fundamental connections between deep processes and life at the Earth's surface. Our contributors apply and synthesize what we have learned over the past decade into our current understanding of carbon through deep time while addressing gaps in knowledge and areas of focus for future deep carbon research.

THE DEEP (GEOLOGIC) CARBON CYCLE

The Earth's carbon cycle is complex and operates on multiple spatial and temporal scales. Biologists, ecologists, and paleontologists tend to focus on the "terrestrial biosphere" portion of the carbon cycle which is encompassed by photosynthetic organisms (plants, algae, some bacteria) acquiring carbon from the atmosphere and ocean; the transfer of carbon to animals that eat those organisms; the death and burial of both organisms, their consumption by scavengers, bacteria, and fungi; and then the regrowth of organisms from the substrate (e.g., plant growth). This

Box 1 FORMS OF TERRESTRIAL CARBON

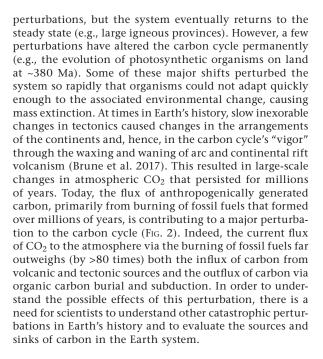
Carbon exists in a diverse range of solid, fluid and gaseous forms in, and on, the Earth. Some of these phases involve combinations of carbon with oxygen (e.g., carbonate minerals, carbonatite magmas, carbon dioxide), elemental carbon (e.g., graphite, diamond, and amorphous carbon), combinations of carbon with iron (e.g., carbides and carbon-bearing iron melts), combinations of carbon with hydrogen (e.g., kerogen, coal, petroleum, methane and its clathrates), and combinations of carbon with other elements (e.g., silicon, sulfur, nitrogen). Experiments, observations and theory suggest that perhaps >90% of Earth's carbon resides in the iron alloy core of the Earth, whilst the rest is distributed between the mantle, crust (including sediments), biosphere, and ocean and atmosphere. The oceans and atmosphere combined likely hold <<1% of the total amount of Earth's carbon, yet this carbon has enormous implications for our climate and for the habitability of our planet's surface.



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is a short-term carbon cycle ("surface carbon" in Fig. 1) and operates on a timescale of carbon turnover from tens to thousands of years. The long-term, or geologic, carbon cycle encompasses the emission of CO₂ from volcanic sources (e.g., spreading ridges and volcanoes at subduction zones); carbon drawdown via silicate weathering and the formation of carbonates, or carbon drawdown via the photosynthesis of carbon by phytoplankton and plants; its burial as either organic carbon or inorganic carbonate; its subduction into the mantle; its eventual return to the atmosphere via volcanic and metamorphic outgassing sources. The two cycles are linked via the emissions of carbon to the atmosphere from volcanic and metamorphic sources and via biological weathering of silicates and burial of that organic matter. This large-scale system is kept in balance as long as the influx of carbon into the system (namely carbon from volcanic and metamorphic sources) is approximately equal to the carbon taken out of the system via weathering, burial, and subduction (assuming that the Earth does not receive or lose carbon). When the flux of carbon emissions from deep carbon is significantly altered, for example, it can result in a "perturbation" to both cycles. FIGURE 2 illustrates current estimates of the fluxes of carbon into and out of the surface reservoir by the long-term (geologic) carbon cycle. Fluxes of carbon from the surface carbon reservoir are shown for the burial of organic carbon and for the subduction of carbon (which includes carbonate in the oceanic crust and mantle and carbonate in sediments) into the mantle. The fluxes in and out of the surface reservoir are large compared to the size of the atmosphere-ocean system, which leads to relatively rapid turnover (residence) times for carbon in the atmosphere–ocean system (~ 2.5×10^5 years) (Berner 1999).

By analyzing the carbon and carbon isotopic composition (see side bar Fundamentals of Carbon Isotope Geochemistry) of the geological record over time, we can identify major shifts, or perturbations, to Earth's longterm carbon cycle. Some short-term, rapid events produce



PERTURBATIONS TO EARTH'S DEEP CARBON

The goal of this issue of *Elements* is to discuss how perturbations to the steady-state carbon cycle of Earth occur, and the consequences for the evolution of life and the planet itself. The concepts of uniformitarianism are well established in the Earth sciences: the idea that the present is the key to the past is fundamental to explaining long timescale geological processes such as orogeny, erosion, continental drift, and sedimentation. There is, however, widespread understanding, borne out of early theories on catastrophism but now based on well-constrained data and

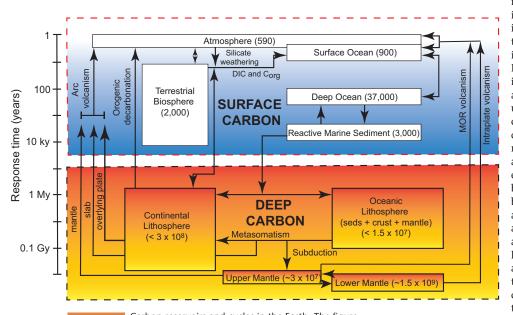


FIGURE 1 Carbon reservoirs and cycles in the Earth. The figure shows short- and long-term cycles; "surface" and "deep" carbon reservoirs and fluxes, and the relative sizes and residence times (y axis) of respective carbon. Numbers in brackets refer to the total mass of carbon in a given reservoir, in Pg C (1Pg C = 10^{15} g carbon). All reservoirs are pre-industrial. Abbreviations: Corg = organic carbon; DIC = dissolved inorganic carbon; MOR = mid ocean ridge; seds = sedimentary rocks. ADAPTED FROM LEE ET AL. (2019 AND REFERENCES THEREIN).

models, that high-energy, highimpact events have occurred at intervals through Earth history that have had lasting and important consequence on the Earth's biosphere and geochemical evolution. We present five articles in this issue aimed at understanding the origins of carbon in Earth via chondritic delivery, cometary bombardment and its timing (Mikhail and Furi 2019 this issue), the effects and implications of bolide impacts on the carbon budget of the Earth (Kamber and Petrus 2019 this issue), the abrupt inputs of carbon associated with the emplacement of large igneous provinces (Black and Gibson 2019 this issue), the tipping points in carbon cycling associated with slow tectonic processes and supercontinent assembly and breakup

(McKenzie and Jiang 2019 this issue), and the impacts of carbon cycle perturbations on the biosphere, and mass extinctions (Schobben et al. 2019 this issue).

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Origin and Distribution of Carbon in the Earth

Mikhail and Furi (2019 this issue) provide an introduction to the origin and distribution of carbon in the Earth. Arguably the greatest perturbation of them all was the violent birth of our solar system at ~4.55 Ga. Our planet was born out of a cloud of gas and dust, perhaps relatively poor in carbon. So, where did our planetary budget of carbon come from? How was it distributed in the Earth and how long did it take for the present-day distribution of carbon to be established? Cosmochemical constraints tell us that the inner planets of our solar system first grew "dry", then came volatile-rich objects (comets and chondritic meteorites) which later contributed much of the volatile inventory of the planet (Marty 2012). Detailed studies of the volatile inventory of the bulk Earth, divided into the different reservoirs, have shown that much of the noble gases reside in the atmosphere and a large fraction of the H, C and N are sequestered into the silicate Earth. This distribution of volatiles is largely due to planetary processing (melting, degassing, differentiation) and the existence of refractory phases in the mantle. The total volatile content of Earth is consistent with the addition of $\sim 2 (\pm 1)\%$ carbonaceous chondrite material during the main accretionary phase of Earth-forming events, rather than during the late veneer which happened after the main phase of differentiation and which is required to explain the abundance of platinum group elements (Marty 2012).

Carbon and Bolide Impacts

A bolide (asteroid or comet) is defined as a meteor brighter than Venus in the night sky, i.e., a fireball. Bolide impacts have been an essential part of the development of the solar system. The frequency and scale of bolide impacts are recorded in impact structures observed on the surfaces of planets and moons in our solar system. While the vast majority of these impacts are small in scale, with a negligible impact, a few are much larger and have had planetary consequences. As discussed by Kamber and Petrus (2019 this issue), impact events have shaped our solar system and the history of our planet. They are implicated in the delivery of volatiles such as carbon and water to the Earth, are variably responsible for both the origin and extinction of life on Earth (DePalma et al. 2019), and have even influenced deeper tectonic and melting processes (Reimold and Jourdan 2012).

There were periods in Earth's history when asteroid impacts occurred with great frequency. In fact, around 90% of all bolides associated with Earth may have impacted during the first billion years of our planet's history. The Late Heavy Bombardment (4.1–3.8 Ga) was such a period: this is when the inner rocky planets and moons were subjected to a prolonged period of high-energy impacts. The Earth's record of these has been largely erased by the renewal of the surface by plate tectonics. On other planets and moons, however, the impact structures are a testament to this violent period, which may have been linked to the migration of the large planets Jupiter and Saturn from the inner solar system to the positions they occupy today (Gomes et al. 2005). Intriguingly, life on Earth has been traced back to approximately the end of the Late Heavy Bombardment. This synchronicity raises the possibility that the building blocks of life were delivered by some of these ancient bolides (Sagan 1961). Impact structures have given rise to immense craters and may have initiated geothermal circulation and hydrothermal systems that were linked to the chemosynthesis of high-order organic molecules (Nisbet and Sleep 2001). Were large impact structures the cradle of life?

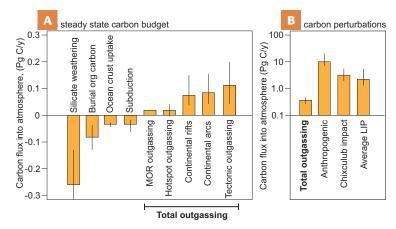


FIGURE 2 Histograms of carbon influx (positive values) and outflux (negative values) to the atmosphere and the oceans. Units are in Pg C/y. (**A**) Carbon fluxes based on steady state models. Abbreviations: MOR = mid ocean ridge; org carbon = organic carbon. (**B**) Carbon fluxes as a result of large-scale perturbations to the carbon cycle. Total outgassing refers to events listed in FIGURE 2A; anthropogenic is human contributions; Chicxulub (Mexico) refers to the end-Cretaceous asteroid impact and resultant mass extinction; average LIP refers to the input from large igneous provinces. DATA FROM KAWARAGI ET AL. (2009), LEE ET AL. (2019) AND BLACK AND GIBSON (2019 THIS ISSUE).

The Earth has also been subjected to more sparsely distributed (in time and space) impacts, but they have had enormous consequences for our habitable environment and for the storage and cycling of carbon and other volatiles in the deep and shallow reservoirs of Earth. The Cretaceous-Paleogene (K-Pg) event, which is widely correlated with the Chicxulub (Mexico) impactor, occurred 66 My ago in the region of the present-day Gulf of Mexico. It released ~108 Mt of energy on impact (Reimold and Jourdan 2012), a fraction of which was disseminated in providing energy for the dissociation of sedimentary carbonates into gaseous CO2 and other species (Kawaragi et al. 2009). Carbonate rocks are thermodynamically unstable at the high temperatures that are induced by shock heating and are devolatilized to form carbon-bearing gas species (including both CO₂ and CO). Laboratory experiments and thermodynamic modelling have suggested that CO may be the dominant gas produced during shock devolatilization, which would lead to enhanced O3 and CH4 due to photochemical reactions and so lead to a temperature rise of perhaps as much as 2-5°C (Kawaragi et al. 2009). This rise in temperature, even more so than the direct effects of a giant impact, may have led to the sudden collapse of biological systems and contributed to mass extinction. However, there is a large uncertainty associated with this scenario that arises from disagreements surrounding the impact scenario and the impact-driven devolatilization reactions of carbonates (limestones).

Other impacts may also have led to indirect perturbations of the carbon cycle. Impacts may have caused lithospheric decompression melting and associated magma degassing, causing widespread volcanism (Richards et al. 2015), although the links between melting and impacts remain controversial (Ivanov and Melosh 2003). The Sudbury Basin impact (Ontario, Canada), which occurred 1.85 Gy ago (Dietz 1964), is thought to have caused extensive crustal melting, and the igneous complex which developed is perhaps the world's largest deposit of nickel and copper.

Carbon and Large Igneous Provinces

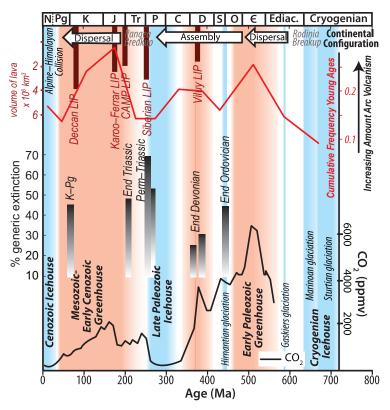
Large igneous provinces (LIPs) are voluminous outpourings of lava onto the surface of the Earth. They have been linked to severe environmental impacts and mass extinctions

(Schobben et al. 2019 this issue). The term "large igneous province" encompasses a wide range of tectonic settings: continental rift, mantle plume, and oceanic plateau. While each LIP is immensely variable in terms of eruptive environment, substrate (oceanic vs continental) and intensity, most (perhaps all) are marked in the geological record by large perturbations in carbon isotopes (Payne and Kump 2007). The negative excursions in carbon isotopes recorded in marine sediments have been interpreted as the result of an initial injection of light carbon (magmatic carbon has a carbon isotope composition of ~ -5%), followed by a protracted positive excursion when increased pCO_2 likely caused global warming, thereby enhancing marine anoxia and associated regeneration of phosphate and, thus, enhancing primary productivity (Kump 1991). The magnitude of the negative carbon isotope perturbations scales with the mass of carbon required, depending on the isotope signature of the carbon. Indeed, some LIP records, such as the end-Permian (synchronous with the Siberian Traps) and the end-Triassic (associated with the Central Atlantic Magmatic Province) are thought to require extremely large fluxes of CO₂, of the order of Pg/y, in order to explain them (Saunders 2005). Magmatic CO₂ may, therefore, be only part of the LIP carbon story: warming induced by magmatic CO₂ degassing might trigger the release of methane previously trapped as hydrates on the seafloor (Wignall et al. 2006). Magma could also have intersected organic carbonbearing sediments (e.g., coal) in the shallow crust, releasing methane and other organic species, which are isotopically much lighter than magmatic carbon (Svensen et al. 2009).

Critical to the interpretation of such perturbations in the carbon budget of the surface reservoir is a good understanding of how much carbon is brought to the surface by LIP magmas. Up to now, there has been no systematic review of the carbon budgets of LIP magmas: estimating the amount of carbon lost from mantle-derived melts, with very little evidence remaining in the rocks, is a supreme challenge. Black and Gibson (2019 this issue) bring together a range of methods for estimating the primary carbon contents of present-day ocean island basalts, which they use to improve our estimates of LIP-driven carbon emissions. There are many important questions surrounding the impact of LIPs on the surface reservoir carbon budget. How much carbon is released, and at what rate? Does the carbon come from the convecting mantle or from the subcontinental lithosphere? To what extent does large-scale mantle heterogeneity complicate the picture of degassing LIP magmas?

Tectonic Influences on the Long-Term Carbon Cycle

Plate tectonics exerts a primary control on the long-term carbon cycle (Raymo and Ruddiman 1992). Superimposed on the gradual movements of tectonic plates are shorter timescale perturbations in the deep carbon cycle prompted by thresholds and tipping points, or when feedbacks take effect (Fig. 3). So-called "icehouse" conditions governed the Cryogenian, late Ordovician, late Paleozoic and late Cenozoic. These icehouse conditions were interspersed with warm climates, so-called "greenhouse" periods, during the early Paleozoic and early Cenozoic. During the icehouse phases, the planet had ice sheets, of varying extent, and lower pCO_2 . The causes of these climate shifts, which occur over million-year timescales (Fig. 3), are thought to be due largely to tectonics. The effects of tectonics on climate may be "sink-driven" [controlled by the drawdown of CO₂ via silicate weathering during and after major orogenic events (Raymo and Ruddiman 1992)] or "source-driven" [the changes in balance between passive and active tectonic margins, which affects the outgassing



FICURE 3 Atmospheric *p*CO₂ over Earth history in relation to major environmental changes since the Neoproterozoic. These include five large igneous provinces (LIPs): the Viluy (Eastern Siberia), the Siberian, the Central Atlantic Magmatic Province (CAMP), the Karoo (Southern Africa) and Ferrar (Antarctica), and the Deccan (west central India). Also shown are the major tectonic events, five mass extinctions, and large changes in climate regimes. Abbreviations: Ediac. = Ediacaran. ADAPTED FROM MCKENZIE ET AL. (2016).

flux of magmatic and stored lithospheric carbon (McKenzie et al. 2016)]. There are periods during Earth's history when these climate changes were extreme. For example, the Earth was almost entirely glaciated during several periods in the Neoproterozoic, producing what has become known as a "Snowball Earth"—a state which persisted for many millions of years, possibly enabled by extreme positive feedbacks involving the enhanced albedo of surface ice sheets (Hoffman and Schrag 2000). The Earth may have escaped the clutches of ice and extreme cold when volcanism resurged above the ice to outgas enough CO_2 to cause global warming and, thus, melt the snowball.

Environmental Disasters and Mass Extinctions

A major feature of catastrophic events is their association with mass extinctions (McKenzie and Jiang 2019 this issue). Mass extinctions occur when the rate of extinction exceeds the background extinction rate. Background extinction rates have been defined as 0.1–1.0 species extinctions per 10,000 species per 100 years (Ceballos et al. 2017): this is also related to the rate of evolution of new species (origination). Some mass extinctions (e.g., the end-Devonian) may be explained by a lack of origination rather than the extinction of many species. But why do species become extinct?

Four of the five largest mass extinctions are associated with large igneous provinces (LIPs). These LIPs are associated with major carbon cycle perturbations caused by large and rapid influxes of carbon into the system from both mantle and sedimentary sources (Svensen et al. 2009). The rate at which the carbon is input into the atmosphere, and its chemical nature (e.g., CO_2 versus CH_4) is likely to be

Box 2 FUNDAMENTALS OF CARBON ISOTOPE GEOCHEMISTRY

An isotope of an element has the defining number of protons for that element but a different number of neutrons; thus, different isotopes for a given element have different atomic masses. For example, all carbon atoms must have 6 protons, but different isotopes of carbon can have either 6, 7, or 8 neutrons, and so have atomic masses of 12, 13 and 14, respectively. These isotopes are denoted ¹²C, ¹³C, ¹⁴C. Of the three isotopes, ¹²C and ¹³C are stable. Carbon-12 is the most abundant in nature, having an abundance of 98.93% against only 1.07% for ¹³C. Carbon-14 is radiogenic and decays over short spans of geological time (half-life <6 ky) and so is not present in ancient rocks. It is difficult to measure precisely the absolute abundance of isotopes in natural substances, so the molar abundance ratios $({}^{13}C/{}^{12}C)$ are obtained instead, determined using isotope-ratio mass spectrometry. Stable carbon isotope values are, by convention, stated relative to VPDB (Vienna Peedee belemnite - a belemnite from the Peedee Formation of South Carolina, USA). This is achieved by measuring the certified reference (NBS 19), which has a known carbon isotope offset relative to VPDB. The carbon isotope values are expressed using the delta (δ) notation in "parts per thousand" (%), and derived from the following equation:

$$S^{13}C = \left(\frac{({}^{13}C/{}^{12}C)_{sample} - ({}^{13}C/{}^{12}C)_{reference}}{({}^{13}C/{}^{12}C)_{reference}}\right) \times 1000$$

Thus, a sample with a greater ¹³C relative to the standard is termed "enriched", and if found to be lesser, is "depleted". Kinetic and equilibrium effects are important determinants as to why a sample has a given isotopic composition. Isotope fractionation causes partitioning of the stable isotopes between phases, as observed in the different reservoirs of carbon in the Earth (see FIGURE below). Dissolved inorganic carbon in the ocean, for example, has heavier δ^{13} C than the organic carbon of plankton in the ocean because organic matter production during photosynthesis is an enzyme-mediated process, accompanied by a large carbon isotope fractionation that preferentially selects the light 12C isotope and shifts 13C by ~25‰ (on average) over the Phanerozoic. By contrast, carbon isotope partitioning during carbonate mineral precipitation from water causes only a small fractionation, and so limestone values closely approximate the dissolved inorganic carbon values of the contemporary ocean. The removal of inorganic and organic carbon from the ocean-atmosphere system is balanced on geological timescales (>10⁵ years) by carbon release from metamorphism and volcanic outgassing. The combined effect of these latter fluxes, and their isotopic compositions, dictate the size and isotope composition of the Earth's surface reservoirs. On geological timescales, the oceanic dissolved inorganic carbon pool and the atmospheric CO2 pool behave as one reservoir, because of the continuous exchange between them.

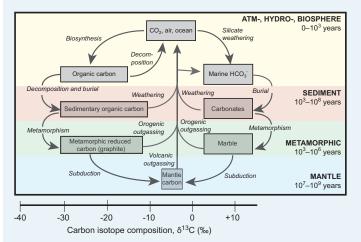


FIGURE The isotopic composition of the Earth's carbon reservoirs and the processes that modify them. ADAPTED FROM SUMMONS ET AL. (2011).

more important than the absolute amount. Although the sulfate aerosol that is formed from volcanic SO_2 , when injected into the stratosphere, has a cooling effect (Robock 2000), the residence time is only on the order of days to years; however, the effects may be prolonged due to frequent injections. Carbon, on the other hand, especially in the form of CO_2 , has the ability to warm the planet over

hundreds to thousands of years in the long-term carbon cycle because its residence time in the surface reservoir is longer, on the order of $10-10^4$ years. This warming can cause changes to the hydrologic cycle, thermal damage to plants, melting of ice-sheets, disruption to the thermohaline circulation of the ocean, anoxia, and ocean acidification. These components contribute to the habitable environment of communities or ecosystems. Therefore, it is not so much the carbon itself that causes extinction, but its effect on the environment and the life that inhabits it.

Critical to the study of mass extinctions in our planet's past is the reconstruction of past environments and climates. Most paleoclimate proxies are chemical in nature and measure the isotopic composition or elemental concentration of either minerals or fossils preserved in the rock record. Because we cannot travel back in time with a thermometer, we must rely on proxy measurements using materials that we can analyze chemically and for which that chemical composition is dependent on the climate parameter of interest (e.g., temperature, CO_2 , precipitation rate).

FRONTIERS

Deciphering the abrupt perturbations in the carbon cycle over our planet's history requires forensic studies of geological records combined with technological advances to allow precise dating and analysis of geochemical proxies. Accurate chronologic control of the geological record is needed for evaluation of the timing of species loss associated with LIPs and the extent and duration of carbon isotopic excursions that may be linked to environmental degradation and extinction. Although advances in techniques used to date volcanic material have allowed geologists to constrain ages of volcanic eruptions within ~10 ky resolution or less, our ability to obtain similar precision in the sedimentary record, to tie in with environmental proxies and fossils, is less well developed. Combinations of a variety of relative and absolute dating methods-astrochronology, biostratigraphy, magnetostratigraphy, chemostratigraphy, and geochronology, particularly in lake and ocean sedimentscan approach a precision of 10 ky, but it is difficult, timeconsuming and expensive. Most challenging is dating continental deposits of fluvial and overbank deposits where deposition is often episodic, with periods of nondeposition, pedogenesis, and periods of rapid deposition.

Models are a good way to link surface and deep reservoirs (Lenton et al. 2018). Of particular promise are plate tectonic reconstructions that allow quantification of elements of the deep carbon cycle, such as mid-ocean ridge carbon flux through time, the carbon in-gassing and outgassing through subduction zones, carbon fluxes produced from mantle plume-related magmatism, and the carbon produced from continental rifting (Brune et al. 2017). There is also great potential for modeling carbon sinks in the crust and lithosphere during orogenic events, as well as drawdown of CO₂ by silicate weathering and during ophiolite obduction. The new generation of surface reservoir carbon-climate models, such as COPSE (carbon-oxygen-phosphorous-sulfur evolution) (Lenton et al. 2018), allow forward modeling of C, S, P, O, and N cycling and can predict isotope records by testing hypotheses against data. A fruitful research direction would be to link carbon isotope box models to plate tectonic reconstructions. Such a link is necessary to understand the complexity of the long-term carbon cycle and the perturbations to the carbon cycle. Then one can understand their effects on the evolution of Earth's biologic and physicochemical system.

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