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Large igneous provinces and mass extinctions: An update

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ABSTRACT

The temporal link between mass extinctions and large igneous provinces is well known. Here, we examine this link by focusing on the potential climatic effects of large igneous province eruptions during several extinction crises that show the best correlation with mass volcanism: the Frasnian-Famennian (Late Devonian), Capitanian (Middle Permian), end-Permian, end-Triassic, and Toarcian (Early Jurassic) extinctions. It is clear that there is no direct correlation between total volume of lava and extinction magnitude because there is always sufficient recovery time between individual eruptions to negate any cumulative effect of successive flood basalt eruptions. Instead, the environmental and climatic damage must be attributed to single-pulse gas effusions. It is notable that the best-constrained examples of death-by-volcanism record the main extinction pulse at the onset of (often explosive) volcanism (e.g., the Capitanian, end-Permian, and end-Triassic examples), suggesting that the rapid injection of vast quantities of volcanic gas (CO_2 and SO_2) is the trigger for a truly major biotic catastrophe. Warming and marine anoxia feature in many extinction scenarios, indicating that the ability of a large igneous province to induce these proximal killers (from CO_2 emissions and thermogenic greenhouse gases) is the single most important factor governing its lethality. Intriguingly, many voluminous large igneous province eruptions, especially those of the Cretaceous oceanic plateaus, are not associated with significant extinction losses. This suggests that the link between the two phenomena may be controlled by a range of factors, including continental configuration, the latitude, volume, rate, and duration of eruption, its style and setting (continental vs. oceanic), the preexisting climate state, and the resilience of the extant biota to change.

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INTRODUCTION

The possibility that volcanism is capable of driving mass extinctions has long been posited (e.g., Kennett and Watkins, 1970; Vogt, 1972), and large igneous provinces—the most voluminous manifestation of volcanism on Earth—have been the most frequently preferred culprits. Improvements of radioisotopic dating in the past two decades have considerably strengthened this notion because four of the "Big 5" extinction events of the Phanerozoic, as well as every minor crisis since the Permian, are shown to coincide with large igneous province eruptions (Fig. 1; Courtillot, 1999; Wignall, 2001). Only the first of the "Big 5," the end-Ordovician crisis, remains uncorrelated to a large igneous province culprit, although one has been mooted for this interval (Courtillot and Olson, 2007; Lefebvre et al., 2010).

The volcanism-extinction link is now well documented (e.g., Rampino and Stothers, 1988; Wignall, 2001, 2007; Courtillot and Renne, 2003; Kravchinsky, 2012), but temporal coincidence does not prove a causal link, although the frequency of the association is sufficiently high to imply this. Perhaps the strongest criticism comes from the observation that many large igneous province eruptions, especially those of the oceanic plateaus of the Cretaceous, are not associated with significant extinction losses (Figs. 1 and 2). Were post-Jurassic biotas more resistant to the deleterious effects of massive volcanism, or was the lack of lethality a consequence of other factors?

The current challenge for earth scientists is to better understand the variable environmental effects of large igneous province eruptions and identify the causal mechanism(s) whereby they sometimes cause catastrophic extinctions. This paper reviews our knowledge of the potential climatic effects of volcanism for several crises that show the best correlation with mass volcanism: the Frasnian-Famennian Viluy Traps; the Capitanian Emeishan flood basalts; the end-Permian Siberian Traps; the end-Triassic Central Atlantic magmatic province; and the Toarcian Karoo and Ferrar Traps. The celebrated extinction at the end of the Cretaceous is associated with both the mighty Deccan Traps and the Chicxulub impact crater, making for a rather special and contentious case study. This event is treated in detail elsewhere in this volume and is not expanded on here.

At this stage, it is pertinent to define what is meant by both "large igneous province" and "mass extinction." The former term was introduced by Coffin and Eldholm (1991), but we follow the succinct revised definition of large igneous provinces of Bryan and Ernst (2008). The latter authors define large igneous provinces as magmatic provinces with $>0.1 \times 10^6$ km^2 extent, volumes $>0.1 \times 10^6$ km^3, and a maximum eruption duration of <50 m.y. They are characterized by igneous pulse(s) of short duration (~1–5 m.y.), during which a large proportion (>75%) of the total

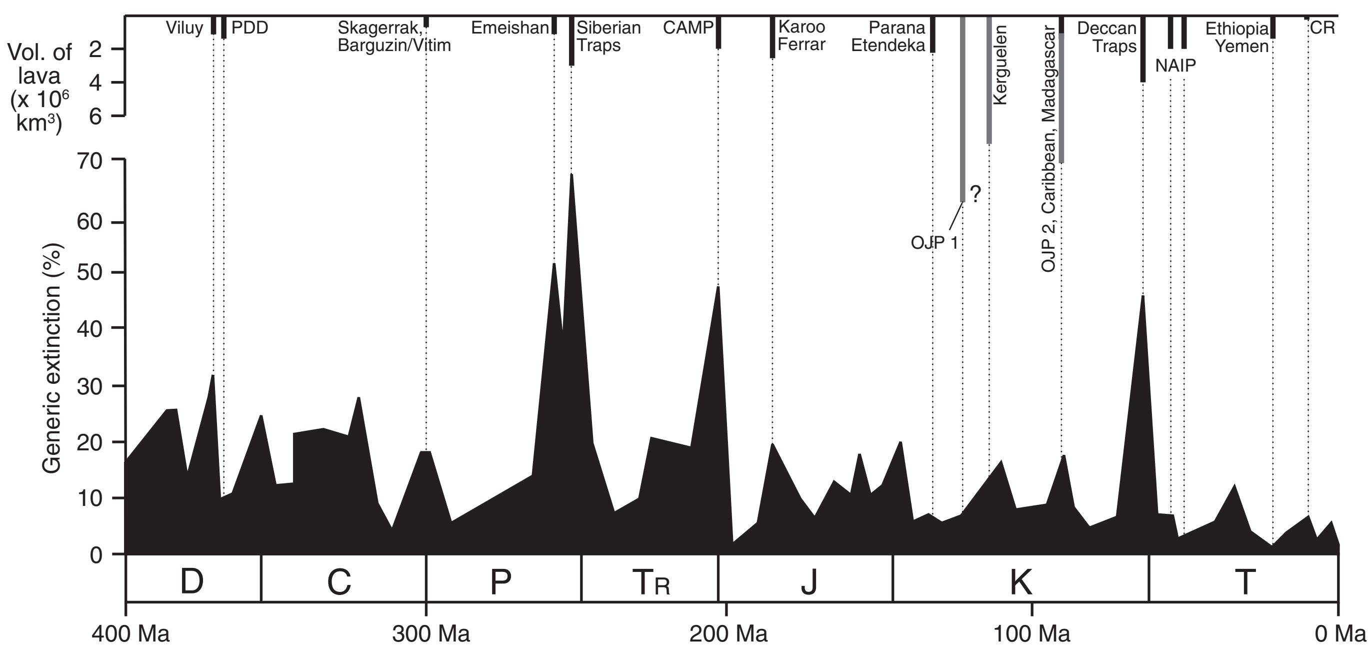

Figure 1. Generic extinction magnitude through the past 400 m.y. (based on Sepkoski, 1996, 2002) vs. the age and estimated original volume of large igneous provinces (volume estimates based on Courtillot and Renne, 2003; Kravchinsky, 2012). PDD—Pripyat-Dnieper-Donets rift; CAMP—Central Atlantic magmatic province; OJP 1/OJP 2—Ontong Java Plateau phases 1 and 2; NAIP—North Atlantic igneous province; CR—Columbia River Basalt Group. Continental flood basalt–volcanic rifted margin provinces (after Bryan and Ernst, 2008) are shown as black bars, while oceanic plateaus are shown as gray bars. Note the apparent correlation between mass extinction events (peaks in generic extinction) and large igneous province emplacement, but no major extinctions associated with the three volumetrically largest episodes of volcanism in the Cretaceous. This figure does not show the possible range of ages for the Viluy Traps (ca. 377–364 Ma). Figure is adapted from Bond et al. (2010a). D—Devonian; C—Carboniferous; P—Permian; Tr—Triassic; J—Jurassic; K—Cretaceous; T—Tertiary.

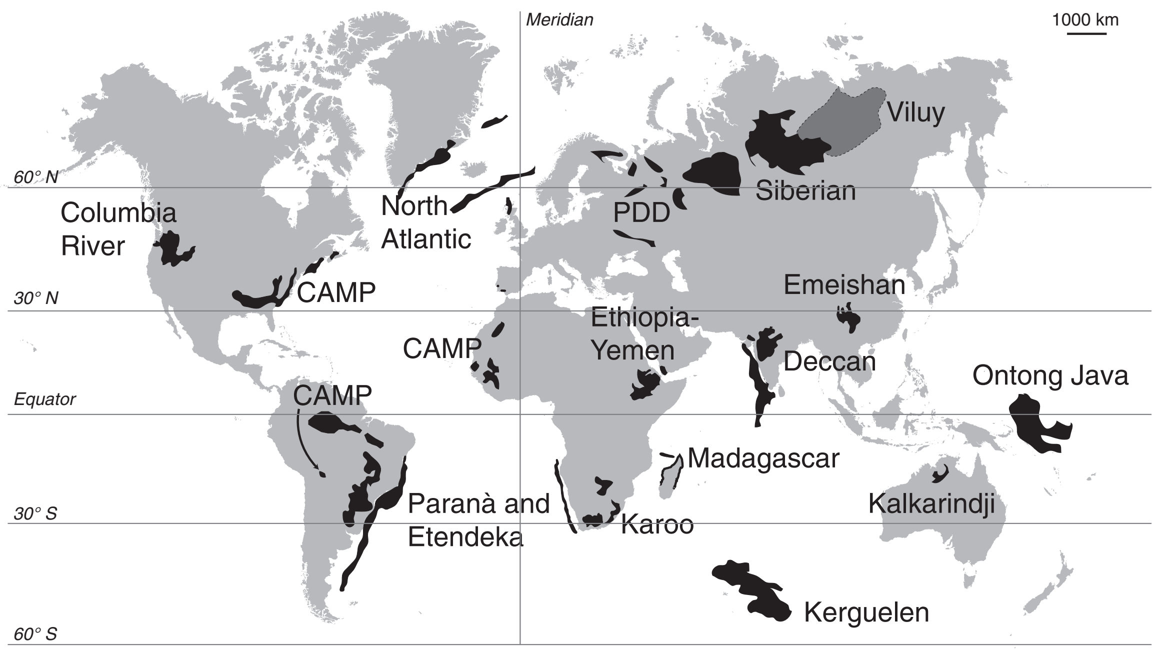

Figure 2. Map of major large igneous provinces mentioned in the text (adapted from Coffin and Eldholm, 1994; Bryan and Ernst, 2008; Marzoli et al., 2011). The Ferrar Traps, located in Antarctica, are not shown on this map. Postulated area of the Viluy Traps is very uncertain. The apparently vast distribution of the Siberian Traps reflects the suggested westward extension of volcanics beneath Jurassic and Cretaceous basin fill, based on Early Triassic basalts found in boreholes (Westphal et al., 1998; Reichow et al., 2005; Saunders et al., 2005).

igneous volume is emplaced (Bryan and Ernst, 2008). The majority of large igneous provinces fall into two subdivisions, continental flood basalt provinces and oceanic plateaus, with a few being a combination of continental flood basalts and volcanic rifted margins. A mass extinction records a globally widespread and rapid loss of species from numerous environments, and the "Big 5" extinctions of the Phanerozoic are those in which >50% of species disappeared from the fossil record (sensu Raup and Sepkoski, 1982; Sepkoski, 1996). The Capitanian event should probably also be included in a revised "Big 6." It has been proposed that the Frasnian-Famennian and end-Triassic "mass extinctions" be demoted to "mass depletions," since those events were likely a diversity decrease due to failure to originate, rather than elevated species loss (e.g., Bambach et al., 2004). Indeed, different treatments of taxonomic databases have rendered some interesting results (Table 1). Nevertheless, for now, the Frasnian-Famennian and end-Triassic events maintain their place at the top table of mass extinctions.

EFFECTS OF VOLCANISM ON CLIMATE

Is it realistic to suggest that large igneous province volcanism can affect global climate to the extent that extinction is inevitable, even in regions distant from the site of eruptions? Here,

TABLE 1.TAXONOMIC-SEVERITY RANKING OF THE 11 LARGEST PHANEROZOIC CRISES SINCE THE ORDOVICIAN*

Rank	Event	%[1]	Event	%[2]	Event	%[3]	Ecological severity ranking†
1	End-Permian	–58	End-Permian	–57	End-Permian	–83	End-Permian
2	End-Ordovician	–49	End-Ordovician	–43	End-Triassic	–73	End-Cretaceous
3	Capitanian	–47	Capitanian	–36	End-Ordovician	–52	End-Triassic
4	End-Triassic	–40	End-Cretaceous	–34	End-Devonian	–50	Frasnian-Famennian
5	End-Cretaceous	–39	End-Triassic	–33	End-Cret., Late Dev. (=)	–40	Capitanian
6	Frasnian-Famennian	–35	Frasnian-Famennian	–22	N.A.	N.A.	Serpukhovian
7	Givetian	–30	Serpukhovian	–13	Serpukhovian	–39	End-Devonian, End-Ordovician (=)
8	End-Devonian	–28	Givetian	–10	Givetian	–36	N.A.
9	Eifelian	–24	End-Devonian, Ludford. (=)	–7	Eifelian	–32	Givetian
10	Serpuk., Ludford. (=)	–23	N.A.	N.A.	Capitanian	–25	Eifelian, Ludfordian (=)
11	N.A.	N.A.	Eifelian	–6	Ludfordian	–9	N.A.

Abbreviations: N.A.—not applicable; Serpuk.—Serpukhovian; Ludford.—Ludfordian; Dev.—Devonian; Cret.—Cretaceous.
*Ranked by the percentage marine genera extinction magnitude in the analyses of [1]Sepkoski (1996), [2]Bambach et al. (2004), and [3]McGhee et al. (2013).
†Ecological severity ranking (McGhee et al., 2013) is a measure of the "ecological impact" of a crisis (see McGhee et al., 2004). The Ludfordian, Eifelian, Givetian, and Serpukhovian are relatively minor intra-Silurian, Devonian, and Carboniferous bioevents.

we review the major climate-changing products of volcanism and provide a brief overview of recent developments in modeling work that provide clues to the "missing link" between large igneous province eruptions and mass extinctions.

Products of Volcanism

Volcanic eruptions inject gases and ash into the troposphere and stratosphere, where their residence time, behavior, and dispersal vary greatly. Apart from water vapor (H_2O), carbon dioxide (CO_2) and sulfur dioxide (SO_2) are volumetrically the most important volcanic gases. Both are greenhouse gases, but their warming effects operate over very different time scales: Only CO_2 causes significant warming over geological time. While SO_2 causes localized short-term warming over periods of days to weeks, its major effect is that of cooling because it forms sunlight-blocking aerosols. Chlorine and fluorine are other important products of volcanism, contributing to ozone depletion and acid rain (e.g., Sigurdsson, 1990; Thordarson and Self, 1993, 2003).

Sulfur Dioxide

Basaltic lavas, such as those associated with large igneous provinces, are especially rich in sulfur dioxide (Palais and Sigurdsson, 1989; Sigurdsson, 1990), and its atmospheric conversion to aerosols is one of the key drivers of cooling during eruptions (e.g., Robock, 2000). This effect can last for 2–3 yr after an eruption, but rarely longer, because rain out occurs quite rapidly. For SO_2 to be effective in causing cooling, it must be injected into the stratosphere, where it is rapidly dispersed around the hemisphere (crossing the equator is a slower process). This has been observed for a number of modest (by large igneous province standards) volcanic eruptions over the past few centuries that have caused significant global cooling (Briffa et al., 1998; de Silva and Zielinski, 1998). A recent example is provided by the Mount Pinatubo eruption of 1991, which injected 20 megatons (Mt) of SO_2 more than 30 km into the stratosphere. The result was a global temperatures decrease approaching 0.5 °C for 3 yr (although this cooling was probably exacerbated by the contemporaneous Mount Hudson eruption in Chile).

One of the largest historical eruptions occurred in 1783–1784 from the Laki fissure in Iceland when an ~15 km^3 volume of basaltic magma was extruded, releasing ~122 Mt of SO_2, 15 Mt of HF, and 7 Mt of HCl (Thordarson and Self, 1993, 2003). Laki's eruption columns extended vertically up to 13 km, injecting sulfate aerosols into the upper troposphere and lower stratosphere, where they reacted with atmospheric moisture to produce ~200 Mt of H_2SO_4. This aerosol-rich fog hung over the Northern Hemisphere for 5 mo (Thordarson and Self, 2003), leading to short-term cooling (Williams-Jones and Rymer, 2000), and harmful acid rain in both Europe and North America. Additionally, HCl and HF emissions damaged terrestrial life in Iceland and mainland Europe, as a low-level fluorine-rich haze stunted plant growth and acidified soils (Frogner Kockum et al., 2006).

The temporal link between the Laki eruptions and cooling is apparently compelling; Iceland was 5 °C colder than normal (Wood, 1992), and the eastern United States recorded its coldest ever winter in 1783–1784, with average temperatures 4.8 °C below the 225 yr average (Scarth, 2001). However, the causal link between the two has been questioned by D'Arrigo et al. (2011), who argued that the 1783–1784 winter saw a combined negative phase of the North Atlantic Oscillation and an El Niño–Southern Oscillation warm event (a pattern repeated during the unusually harsh Northern Hemisphere winter of 2009–2010). Thus, Laki may not have been the sole contributor to cooling during 1783–1784. Another link between volcanism and cooling was seen during one of the largest episodes of volcanic stratospheric H_2SO_4 loading of the past 500 yr from Huaynaputina, in Peru, which erupted in 1600 coincident with the coldest global average temperatures of the time (de Silva and Zielinski, 1998).

With a volume of 15 km^3, Laki was tiny in comparison to the scale of eruptions encountered during large igneous province emplacement. However, it is unclear if the cooling effects of larger eruptions can be simply scaled up from the known effects of observed historical eruptions. Sulfate aerosol formation during large eruptions may be limited by the amount of water vapor in the atmosphere, with the result that not all of the injected SO_2 is converted into aerosols immediately (Pinto et al., 1989). Larger eruptions could in theory cause more prolonged cooling than small eruptions, but the cooling effect need not necessarily be any more intense because of the limiting role of water vapor availability.

The past few years have seen major advances in the use of global aerosol microphysics models, partially stemming from the geoengineering debate on injecting SO_2 into the stratosphere to mitigate global warming (e.g., English et al., 2012). These models have supported the assertion that there is an upper limit to the radiative forcing that can be obtained with sulfate aerosols due to the particle size distribution and growth effect (Heckendorn et al., 2009; Timmreck et al., 2009, 2010; Niemeier et al., 2011; Hommel and Graf, 2011; English et al., 2012). For a given sulfate load, the scattering of shortwave radiation is modulated by particle size, and as aerosol particle size increases, scattering of radiation decreases (Rasch et al., 2008; Timmreck et al., 2009).

There is a positive correlation between mass of sulfur released during historic volcanic eruptions and Northern Hemisphere temperature decline (Fig. 3; Devine et al., 1984; Sigurdsson, 1990), but it does not appear to be a linear one (Blake, 2003). Thus, eruptions between A.D. 1400 and 1994 with <2 km^3 magma volume generated insignificant cooling, while those with >4 km^3 volumes induced cooling of 0.35 °C on average (Blake, 2003). Indeed, by far the largest eruption of the late Quaternary, at Toba, Sumatra (73,000 yr ago), injected ~4400 Mt of sulfate aerosols into the stratosphere (Rampino and Self, 1992; Zielinski et al., 1996), but contemporaneous cooling is not clearly evident from the $\delta^{18}O$ record (Rampino and Self, 1992). Even the time of year that eruption occurs may affect the impact of aerosols. Frölicher et al. (2013) postulated that the El Niño–Southern Oscillation controls atmospheric response to volcanic gases, implying that past continental configuration and ocean circulation may have been a factor in the response of climate to large igneous province volcanism.

Schmidt et al. (2010, 2012a, 2012b) modeled the importance of aerosol-induced indirect radiative forcing of climate from Laki-style eruptions. While direct radiative forcing derives from the scattering of incoming solar radiation in the stratosphere, indirect forcing is caused by the effect of aerosols on the radiative properties of clouds in the troposphere, usually restricted to the region of volcanism. Schmidt et al.'s simulations showed that tropospheric volcanic aerosols are an important contributor to cloud condensation nuclei, and that the additional indirect climate forcing caused by increased cloud formation can be substantial (the cloud albedo effect). Intriguingly, Schmidt et al. (2012a) found that the global annual mean cloud albedo effect was about twice as strong under pre-industrial conditions (-1.06 W m^{-2}) as under present-day conditions (-0.56 Wm^{-2}), suggesting that there may be an upper limit to aerosol-induced indirect radiative forcing. Nevertheless, it is possible that indirect radiative forcing was an additional contributor to volcanic darkness and cooling in past episodes of large igneous province volcanism and/or extinction, albeit localized to the eruption site.

The preceding section concentrated on relatively small, recent injections of SO_2 into the atmosphere. Modeling work has emphasized the complexity of the behavior of SO_2 in the atmosphere, and we should take great care in extrapolating these models to large-scale large igneous province volcanism. While it is apparent that the relationship between the size of the gas flux and cooling or radiative forcing is not linear, it is possible that volcanism on a large igneous province scale would induce changes to Earth's climate that are far greater than anything associated with historical eruptions. Thus, Self et al. (2005) proposed that each huge eruption (10^2–10^3 km^3) associated with continental flood basalt volcanism could last for a decade or more and could inject ~1 Gt of SO_2 per year. Potentially, decadal-length fluxes of gas could cause longer-term cooling, especially if the recurrence interval between flows was brief (<100 yr).

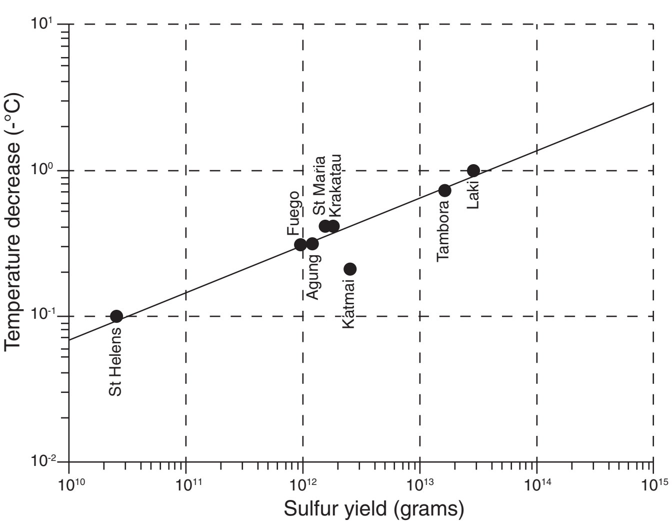

Figure 3. Correlation between volcanic sulfur yield to the atmosphere and the observed Northern Hemisphere temperature decrease for several historical eruptions. Sulfur yield is based on petrologic estimate (Devine et al., 1984; Palais and Sigurdsson, 1989). Figure is after Sigurdsson (1990).

Carbon Dioxide

Carbon dioxide is the other principal volcanogenic gas, alongside SO_2, and its greenhouse effects are another potential consequence of large igneous province eruptions, especially given its longer atmospheric residence time. However, the key debate is whether volcanic CO_2 degassing is sufficiently voluminous to have significant effects.

The estimated annual volcanic CO_2 flux of 130–440 Mt (Gerlach, 2011) is injected into an atmosphere of 3000 Gt of CO_2. This is two orders of magnitude smaller than the current anthropogenic CO_2 flux (Sabine et al., 2004). In comparison, Self et al. (2005) calculated that a single large igneous province eruption with a volume of 1000 km^3 (with a top-end estimate of 0.5 wt% CO_2 in the magma and 100% degassing) would inject around 13 Gt of CO_2 into the atmosphere, i.e., less than 1/200th the mass of the atmospheric reservoir. In isolation, a single eruption is unlikely to cause a climatically significant increase in atmospheric CO_2. However, the atmospheric lifetime of CO_2 is at least several hundred years, far longer than that of SO_2, and about a fifth of CO_2 remains in the atmosphere for several thousands of years (Archer, 2005). The cumulative effects of repeated, closely spaced flood basalt eruptions could potentially promote global warming. The total CO_2 release from a large igneous province such as the Siberian Traps has been estimated at 30,000 Gt CO_2, i.e., 10 times the mass in today's atmosphere (Courtillot and Renne, 2003), based on an original volume of ~3 × 10^6 km^3 for the Siberian Traps.

Underlying the discussions of large igneous province CO_2 release is the assumption that plumes of undepleted mantle are the source of large igneous province magma and their volatiles. However, recent modeling work and study of mantle inclusions in the Siberian Traps led Sobolev et al. (2011) to suggest that recycled ocean crust may form a substantial proportion (15%) of plumes. The consequences for volatile release are considerable because this material would yield substantial volumes during partial melting. Driven off ahead of the ascending magma, the initial volatile release is therefore calculated to release 170,000 Gt of CO_2 and about a tenth this amount of HCl (Sobolev et al., 2011). If this gas was released in a few, closely spaced blasts, the environmental effects would be devastating.

Another potentially important effect of CO_2 release is increased acidity of the oceans. Huybers and Langmuir (2009) modeled the effect of increased atmospheric CO_2 on carbonate saturation and showed that a rapid injection of ~3000 Gt of CO_2 into the ocean, accompanied by a 4 °C ocean warming and 100 ppm increase in atmospheric CO_2 concentration, would cause the carbonate saturation horizon to shoal by ~1 km (Fig. 4). If correct, Huybers and Langmuir's (2009) modeling implies that the largest subaerial large igneous province eruptions were able to generate significant ocean acidification, as has been proposed for the end-Permian mass extinction (Payne et al., 2007). However, these effects would only be severe in cooler, higher-latitude oceans and in deeper waters.

Other Gases and Ash

Water vapor (H_2O) is volumetrically the largest volcanic gas, and its immediate effect is to act as a positive radiative forcing agent in the stratosphere that may in part counteract the cooling effects of sulfate aerosols. Joshi and Shine (2003) applied a general circulation model to the Pinatubo eruption scenario and calculated a global average radiative forcing due to H_2O of +0.1 W m^{-2}. Radiative forcing due to Pinatubo's volcanic aerosols peaked at −3.5 W m^{-2} (Myhre et al., 2001), and so it seems probable that the effect of water vapor is to partly counteract the effect of aerosols.

Hydrogen chloride and hydrogen fluoride (HCl and HF), volcanic ash in the form of silicate particulate matter, and methane (CH_4) are other important products of volcanism. Some of these have been documented as causing environmental harm during recent eruptions, leading to their effects being invoked in mass extinction scenarios (without much acclaim). In particular, HCl causes damage downwind from volcanoes because HCl and H_2O condense readily on ash particles and fall as acidic rain. This mechanism affected crops and livestock in Iceland and mainland Europe during the 1783–1784 Laki eruptions, which released 7 Mt of HCl (Thordarson and Self, 1993, 2003). However, this rainfall also ensures the swift removal of volcanic HCl from the atmosphere, and it is unlikely that HCl could cause long-term damage on a global scale. HCl also destroys ozone as reactive chlorine atoms are released through interaction with sulfate aerosols, but due to the rapid scrubbing of HCl from the troposphere by rain, there is limited opportunity for stratospheric ozone destruction.

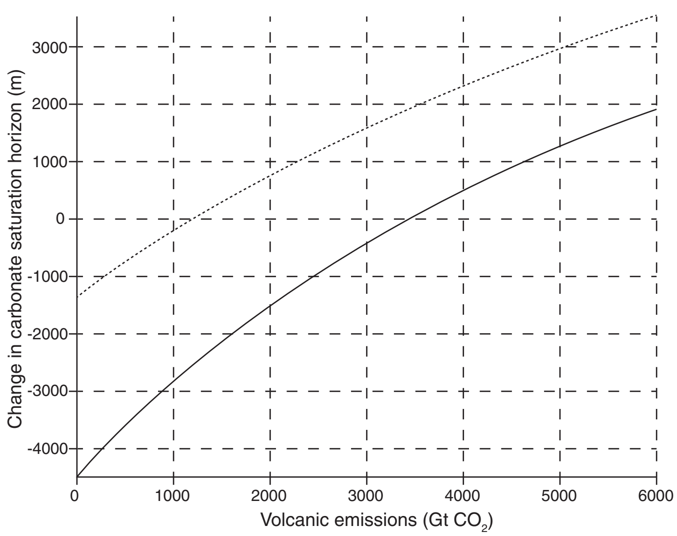

Figure 4. Modeled change in the carbonate saturation horizon between the last glacial and present interglacial for various volcanic inputs of CO_2 into the ocean-atmosphere system. One scenario considers only changes in CO_2 and temperature (dotted line), and the other also includes organic storage of carbon on the continents (solid line). Figure is after Huybers and Langmuir (2009). Negative values on the *y* axis will not affect the carbonate saturation horizon.

Hydrogen fluoride also promotes acid rain downwind of the eruption site, but its primary deleterious effect is that of poisoning. The gas combines with fine ash particles, poisoning animal and plant life wherever it falls in volume. The 15 Mt HF released during the Laki eruptions caused widespread crop failure as well as bone damage and excess mortality in livestock and humans. Like HCl, though, HF is rapidly removed from the atmosphere, and it is unlikely to be of great relevance in global mass extinction scenarios.

Early attempts to understand the climatic effects of volcanism by Humphreys (1940) assumed that volcanic ash was responsible for major cooling by backscattering incident solar radiation, an effect that we now know actually derives from sulfate aerosols. In fact, ash particles have only a very minor, localized effect on climate (lasting days), because they remain in the atmosphere for such a brief duration. Even the 1991 Pinatubo eruption, which saw a huge umbrella plume extending 35 km vertically, deposited almost all of its 5.2 km^3 ash over the South China Sea in just a few days (Wiesner et al., 2004). Clearly, with such short atmospheric residence times, ash is not a great threat to global biodiversity. Ash layers are, however, extremely useful to paleontologists, stratigraphers, and geochronologists, because they can provide a datable record of volcanism (the "smoking gun") in stratigraphic sequences distant from the eruption site that contain the record of mass extinctions (e.g., Wignall et al., 2009b).

Thermogenic Greenhouse Gases

In recent years, an additional source of large igneous province–related gas flux has been identified. In order to explain the abrupt warming associated with the Paleocene-Eocene thermal maximum, Svensen et al. (2004) suggested that baking of organic-rich sediments by high-level intrusives could generate great volumes of greenhouse gases, perhaps thousands of gigatons of CH_4 (rapidly oxidized to CO_2 in the atmosphere). Such thermogenic gases will have the light isotopic signature of their source sedimentary organic matter and so can account for the negative $\delta^{13}C$ excursions often encountered during large igneous province eruption intervals. Tangible evidence for gas release comes in the form of thousands of hydrothermal vent complexes (small diatremes) developed above igneous intrusions of large igneous provinces (Svensen et al., 2004, 2007). If such structures were simultaneously active, then it is possible their gas effusion rates were considerable. Svensen's hypothesis has gained considerable favor as a cause of the rapid global warming often observed during extinction crises (Heydari et al., 2008; Retallack and Jahren, 2008; Ganino and Arndt, 2009).

What Makes a Large Igneous Province a Global Killer?

One of the great enigmas of the geological record is the great variability of the consequential effects of large igneous province eruptions (Wignall, 2001). Prior to the Cretaceous, most large igneous province eruptions can be convincingly linked with biotic crises, but the effects of younger provinces seem much more variable. Understanding the cause of this variability may lie in factors like continental configuration, latitude of eruption, scale and duration of eruptions, their style and setting (continental vs. oceanic), and the pre-eruption climate state.

Volume, Rate, and Style of Eruption

Large igneous provinces are mostly constructed of individual sheet flows, primarily of tholeiitic basalt, that range in volume from several hundred to several thousand cubic kilometers. Other volumetrically important extrusive components of continental flood basalt provinces are mafic volcaniclastic deposits (e.g., Ukstins Peate and Bryan, 2008) and typically late-stage silicic ignimbrites (Bryan, 2007). Estimating the original volume of large igneous provinces is notoriously difficult, but the best-known continental flood basalt provinces emplaced between 0.2×10^6 km^3 (Columbia River flood basalts) and $>3 \times 10^6$ km^3 of lava (e.g., Siberian and Deccan Traps). There is no direct correlation between total volume of lava and extinction magnitude (Wignall, 2001; Courtillot and Renne, 2003; Fig. 1). This conclusion is not surprising, given the observations that there is likely always sufficient recovery time between individual eruptions to negate any cumulative effect of successive flood basalt eruptions. Instead, the environmental and climatic damage must be attributed to single-pulse gas effusions. Radioisotopic dating has constrained the total duration of many continental flood basalt province eruptions to 1–2 m.y. (Courtillot and Renne, 2003; Bryan et al., 2010; Kravchinsky, 2012), but the magnitude and recurrence time of individual eruptions are poorly understood.

The relatively small Columbia River flood basalts represent the most recently emplaced large igneous province, and its eruptive history is amongst the best known. It consists of stacked, pahoehoe lava flow fields ranging from 1 to 2000 km^3 in volume (Tolan et al., 1989) that were the products of individual, potentially sustained, eruptions (Self et al., 1997). Each flow consists of multiple, sheet-like lobes that are 20–30 m thick (Bryan et al., 2010). Each flow field is thought to have originated from eruptions lasting perhaps years or decades and with eruption rates of 4000 m^3 s^{-1} (Self et al., 1996, 1997, 1998). The stratigraphy of the province is well constrained and has shown that, although basaltic eruptions range in age from 17 Ma to 6 Ma, >90% of the total volume was erupted between 16.6 Ma and 15.3 Ma (Tolan et al., 1989; Camp et al., 2003; Hooper et al., 2007). Peak magmatism occurred during the initial eruptions and lasted for a much shorter duration than 1.3 m.y., possibly just tens of thousands of years (Bryan et al., 2002; Bryan and Ernst, 2008). A similar eruptive history has been proposed for some of the larger continental flood basalt provinces such as the Central Atlantic magmatic province (Knight et al., 2004) and the Deccan Traps (Chenet et al., 2007), which were probably emplaced during a series of very short-lived (hundreds of years or less) eruptions. If peak magmatism occupies only a short time interval, then it follows that gas fluxes peaked during the onset of eruptions—an observation that has additional pertinence when examining the relationship between large igneous province timing and extinction (see following).

Role of Eruption Site

Tropical eruptions generate heating in the tropical stratosphere that creates anomalous temperature and density gradients between the equator and the poles, causing a strengthening of zonal winds and a stronger stratospheric polar vortex (Driscoll et al., 2012). This strengthened vortex is associated with positive North Atlantic Oscillation and Arctic Oscillation, which generate high pressure at midlatitudes and low pressure at the poles (Black, 2002; Kolstad and Charlton-Perez, 2011). This mechanism ensures that aerosols from tropical eruptions, such as Pinatubo, quickly spread over the entire globe. In contrast, aerosols derived from high-latitude eruptions remain in the hemisphere in which they were injected, unable to escape the polar vortex (Oman et al., 2005). Although this modeling is based on historical-scale eruptions with a modern continental configuration, it suggests that eruption site is a key factor in the ability of aerosols to affect global climate and that only tropical large igneous province eruption could cause global mass extinctions through the cooling/darkness effect of sulfate aerosols. The troposphere is thinner at higher latitudes, and polar volcanic eruptions are more likely to inject aerosols into the stratosphere.

Of the five extinction-associated large igneous provinces discussed in this paper, the Emeishan Traps (paleolatitude of 10°S–10°N) and Central Atlantic magmatic province (paleolatitude of ~20°S–20°N) straddled the equator. The Karoo and Ferrar Traps (45°S) erupted in southern midlatitudes, while the Viluy Traps (~50°N–60°N) and Siberian Traps (>60°N) were emplaced in northern Boreal latitudes. So, clearly, eruption site alone is not crucial for a large igneous province–extinction link.

FRASNIAN-FAMENNIAN (LATE DEVONIAN) MASS EXTINCTION

Extinction Record

The Frasnian-Famennian mass extinction (at the stage boundary, dated to 372.2 Ma according to Gradstein et al., 2012) has long been considered one of the “Big 5” extinction events (Table 1). Many marine groups suffered marked extinctions, and spectacularly large Devonian reef ecosystems never fully recovered (Kiessling et al., 2000; Copper, 2002). The close temporal association between the Frasnian marine extinctions and the development of two discrete, geographically widespread anoxic

"Kellwasser events" supports an anoxia-extinction causal link in offshore level-bottom communities (Buggisch, 1972; House, 1985; Buggisch, 1991; Bond et al., 2004). The same cause has recently been implicated in the demise of shallow-water reefs (Bond et al., 2013). Both anoxic events correspond to pulses of sea-level rise that together form transgressive-regressive (T-R) cycle IId of the Late Devonian eustatic curve (Johnson et al., 1985; Bond and Wignall, 2008). A significant warming, derived from oxygen isotope data from conodont apatite (Joachimski et al., 2009), saw low-latitude sea-surface temperatures rise from 23 °C in the Middle Devonian to 30–32 °C by the end-Frasnian. This apparently simple climatic history is complicated by two Kellwasser-related cooling phases (Joachimski and Buggisch, 2002; Balter et al., 2008), perhaps induced by atmospheric CO_2 drawdown during black shale deposition, and it has been suggested that the biotic crisis has its origins in a "destabilised greenhouse" (Racki, 1998, p. 192). Could eustatic sea-level rise, climate changes including ~9 °C global warming, and widespread marine anoxia have their origins in contemporaneous large igneous province volcanism?

Late Devonian Volcanics

The Viluy Traps, which cover most of the northeast margin of the Siberian Platform, have been known for four decades (Masaitis et al., 1975; Gaiduk, 1988), but only relatively recently has their age become well constrained (Kravchinsky et al., 2002; Kiselev et al., 2006, 2007; Kuzmin et al., 2010; Kravchinsky, 2012). The lavas partially fill the Viluy rift, a graben 800 km long by 450 km wide (Kiselev et al., 2006), that is the western branch of a Devonian triple-junction rift (Kuzmin et al., 2010). Volcanism began in the Frasnian and continued into the Mississippian, emplacing a volcanic pile up to 7 km thick (Kuzmin et al., 2010). Most of the lava has been eroded or lies buried beneath the younger Siberian Traps to the west, making volume estimates difficult, but values of ~1 × 10^6 km^3 have been suggested (Courtillot et al., 2010; Kuzmin et al., 2010). Until recently, radioisotopic dates from the volcanics were rather sparse and gave a broad range of ages suggesting that magmatism lasted from 380 to 340 Ma (K-Ar ages in Shpount and Oleinikov, 1987; Ar-Ar ages in Kiselev et al., 2006). Courtillot et al. (2010) constrained the major pulse of Viluy volcanism between 370 and 360 Ma (K/Ar and Ar-Ar ages), concluding that the $^{40}Ar/^{39}Ar$ plateau ages of 370.0 ± 0.7 Ma (conventional calibration) or 373.4 ± 0.7 Ma (recalculated per Renne et al., 2010, 2011) are the most reliable ages for Viluy Traps volcanism. In accord with paleomagmatic data, the entire large igneous province could have been emplaced around 370 Ma, very close to the Frasnian-Famennian boundary (Kravchinsky et al., 2002). The latest time scale (Gradstein et al., 2012) places this stage boundary at 372.2 Ma (based on a cubic spine fit on 17 selected radioisotopic dates from the Devonian and lowermost Carboniferous), actually much closer to Courtillot et al.'s (2010) age determination for Viluy volcanism than previously thought. (In 2010, the Frasnian-Famennian boundary was placed at 376 Ma.) The most recently obtained K-Ar and Ar-Ar dates indicate multiphase emplacement of the Viluy Traps between 376.7 ± 1.7 Ma and 364.4 ± 1.7 Ma (Ricci et al., 2013), clearly strengthening its temporal link with the Frasnian-Famennian extinction (and also implying a causal link with the lesser crisis at the Devonian-Carboniferous boundary).

Other large traps are well known from the Late Devonian. The 2000 km Pripyat-Dnieper-Donets rift system, in the southwest of the Russian Platform, is estimated to have hosted a minimum of 1.5 × 10^6 km^3 of magma, making the Pripyat-Dnieper-Donets large igneous province potentially even larger than the Viluy Traps (Kravchinsky, 2012). Conversely, Courtillot and Renne (2003) dismissed the Pripyat-Dnieper-Donets system as both volumetrically minor, with <10,000 km^3 magma, and too young (367–364 Ma; Famennian Stage, based on forward modeling rather than radioisotopic dating; Kusznir et al., 1996; Wilson and Lyashkevich, 1996) to be implicated in the Frasnian-Famennian extinction. Extensive, but volumetrically relatively minor, alkaline magmatism on the Kola Peninsula in Russia has been dated to 380–375 Ma (Wu et al., 2013), i.e., slightly older than the Frasnian-Famennian boundary.

The Late Devonian was clearly a time of voluminous trap magmatism on the Russian and Siberian Platforms that could feasibly have injected enough CO_2 into the atmosphere to generate the estimated late Frasnian +9 °C sea-surface temperature shift (Joachimski et al., 2009), which in turn may have led to the development of widespread marine anoxia and mass extinction (Racki, 1998; Bond et al., 2004; Bond and Wignall, 2008). Ongoing improvements in radioisotopic dating of the Viluy Traps and Pripyat-Dnieper-Donets, as well as the marine extinction level and key developments in terrestrial ecosystems, are continuously improving the temporal link between Late Devonian volcanism and extinction(s).

CAPITANIAN (MIDDLE PERMIAN) MASS EXTINCTION

Extinction Record

The volumetrically relatively small Emeishan flood basalts and Capitanian (Capitanian Stage of the Guadalupian Series) mass extinction provide the clearest temporal link between these two phenomena, because the record of both coexists in the same sections in southwest China. It was in that region that a Capitanian mass extinction was first discovered in the record of fusulinacean foraminifera (Jin et al., 1994; Stanley and Yang, 1994), and it was subsequently ranked the third most severe biodiversity crisis of the Phanerozoic (Sepkoski, 1996; Bambach et al., 2004). These early studies were based on literature reviews that used a coarse temporal resolution of the available data with age ranges only resolved at the stage level. Consequently, the extinction was attributed to the end of the Guadalupian. Recent studies of fossil range truncations of diverse shallow-marine taxa in conodont-dated sections have shown that extinction occurred earlier (in the *Jinogondolella altudaensis*–*J. prexuanhanensis* conodont zones) in South China, making this a mid-Capitanian crisis (Fig. 5; Shen and Shi, 2009; Wignall et al., 2009a, 2009b; Bond et al., 2010a, 2010b).

The southwest China sections are probably unique, globally, in that they preserve not only the record of a mass extinction, but also of the smoking gun in the form of the Emeishan large igneous province. Thus, the provinces of Guizhou, Yunnan, and Sichuan preserve the remnants of an extensive Middle Permian carbonate platform composed of the 700-m-thick Maokou Formation (Yang et al., 1999, 2004; Wang and Sugiyama, 2000; Lai et al., 2008; Wignall et al., 2009a, 2009b; Bond et al., 2010a, 2010b). In western Guizhou and Yunnan, volcanics of the Emeishan large igneous province interdigitate with and overlie the Maokou Formation, enabling the fossil record both before and during the eruptions to be examined. This reveals that the mass extinction occurred at the onset of explosive Emeishan volcanism, and it coincides with the beginning of a major (–6‰) $\delta^{13}C_{carbonate}$ excursion (Fig. 5; Wignall et al., 2009a; Bond et al., 2010b). The Capitanian extinction record is best known from South China, but the event was clearly of global scale. Middle to Late Permian foraminiferal ranges and geographic distributions show provincialism throughout the Middle Permian, and all realms suffered severe losses (Bond and Wignall, 2009).

The plant fossil record in South China reveals a significant 24% species loss, suggesting that the Capitanian crisis also occurred on land. An intra-Capitanian extinction of 56% of plant species in the North China block sequences may also have coincided with these losses (Fig. 5; Bond et al., 2010a). Dating of these terrestrial sequences is notoriously difficult, but correlation using the paleomagnetic record (for examples, see Jin et al., 1998; Ali et al., 2002, 2005) provides two alternatives: Either turnover amongst plant species was contemporaneous with the marine extinction, or plant losses postdate the marine extinction and occurred during the waning phase of Emeishan volcanism. The Middle Permian also saw a major tetrapod crisis with the loss of the dominant dinocephalians (Lucas, 1998, 2009). Current understanding of the dinocephalian losses suggests that this event occurred during the preceding stage (the Wordian), but future improvements in both sampling and dating of this tetrapod crisis may reveal a synchronicity of plant, animal, and marine invertebrate extinctions.

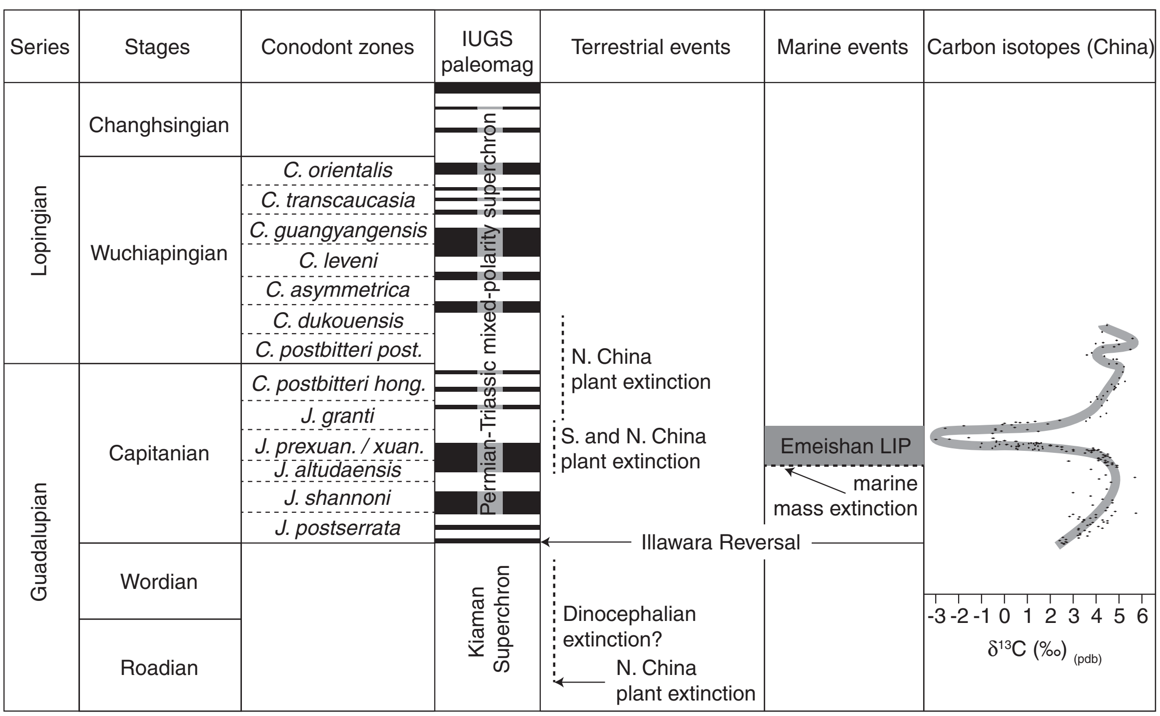

Figure 5. Summary of key Middle Permian events from China with carbon isotope curve (based on Wang et al., 2004; Wignall et al., 2009a; Bond et al., 2010b). Note the intra-Capitanian extinction level, contrasting assignments to an "end-Guadalupian" event in the literature. The International Union of Geological Sciences (IUGS) paleomagnetostratigraphic "bar code," in which periods of normal and reversed polarity are shown as black and white intervals, respectively, is currently the most reliable method of correlating between marine and terrestrial sequences. Placement of the Illawara reversal is after Isozaki (2009). LIP—large igneous province; pdb—Peedee belemnite. Abbreviations for conodont zones are as follows: *J.—Jinogondolella*; *C.—Clarkina; prexuan./xuan.—prexuanhanensis/xuanhanensis*; *hong.—hongshuensis*; *post.—postbitteri*. Figure is modified from Bond et al. (2010a).

Capitanian Volcanics

The Emeishan Basalt Formation is widely distributed in the provinces of Sichuan, Yunnan, and Guizhou in southwest China, and it represents one of the most recently identified large igneous provinces (Chung and Jahn, 1995, who ascribed a Permian-Triassic boundary age; Chung et al., 1998). In comparison to other large igneous provinces, the Emeishan traps are relatively small: Estimates of their areal extent range from 0.25–0.3 × 10^6 km^2 (Ali et al., 2005) to ~0.5 × 10^6 km^2 (Zhou et al., 2002). The thicknesses of the basalt piles range from several hundred meters in western Guizhou (Liu and Xu, 1994) to 5 km in its westernmost outcrops in northern Yunnan (Sun et al., 2010). Most estimates place the original volume at ~0.5 × 10^6 km^3 (Ali et al., 2005), but some have quoted a volume >1 × 10^6 km^3 (Courtillot and Renne, 2003). Extensive erosion and deformation ensure that estimations of their original volume are difficult.

The Emeishan Basalt was erupted onto the Maokou Formation platform carbonates, and there has been intensive debate as to the nature of this contact. He et al. (2003, 2004) favored an emplacement model that features mantle plume updoming prior to eruption, and thus they suggested a karstic surface with up to 200 m of relief developing prior to infill by lava flows. This observation and model have been challenged by several authors who contend that the initial eruptions occurred into a shallow sea (Ukstins Peate and Bryan, 2008; Ali et al., 2010; Sun et al., 2010). In some parts of the province, volcanism was preceded by a phase of partial platform carbonate collapse at the start of the *Jinogondolella altudaensis* zone (Sun et al., 2010). The age of onset of volcanism is thus tightly constrained to the mid-Capitanian *J. altudaensis*–*J. xuanhanensis* zonal interval. In contrast, radioisotopic age dating suffers from large errors. The compilation of Liu and Zhu (2009) shows the oldest and youngest U-Pb dates from Emeishan samples spanning 267–251 Ma, which was recently more tightly constrained to 260–257 Ma (Shellnutt et al., 2012), consistent with a Capitanian to Wuchiapingian age (see Gradstein et al., 2012).

Elsewhere, the Panjal Volcanics of northwest India include basaltic lavas and lesser volumes of rhyodacitic tuffs emplaced between supposedly Lower and Middle Permian marginal marine strata and Late Permian pelagic strata (Nakazawa et al., 1975), and thus they might be considered contemporaneous with the Capitanian extinction level. Recently, however, Shellnutt et al. (2011) reported a zircon U-Pb laser-ablation inductively coupled plasma–mass spectrometry (ICP-MS) date from rhyolite in the lower-middle part of the volcanic sequence that yielded a mean $^{206}U/^{238}Pb$ age of 289 ± 3 Ma. This suggests that the Panjal Traps are considerably older than previously interpreted and are therefore unrelated to either the Capitanian or end-Permian extinctions.

The clear temporal link between Capitanian marine extinctions and shallow-water, explosive Emeishan volcanism implies that these eruptions triggered the crisis. The extinction appears to have been particularly selective toward shallow-water photosynthetic taxa (e.g., calcareous algae) or those that likely harbored photosymbionts (e.g., fusulinacean foraminifera, alatoconchiid bivalves), suggesting a role for volcanically induced darkness in the extinction scenario. Many of the extinction victims had poor physiological buffering (e.g., calcareous sponges and corals), implying a possibility of acidification-driven extinction (McGhee et al., 2013) and by implication significant fluxes of CO_2 to the atmosphere. However, Ganino and Arndt's (2009) suggestion that the Emeishan province released thermogenic CO_2 into the atmosphere does not explain the observed negative isotope excursion, because the basalts intruded into platform carbonates would have supplied isotopically heavy carbon.

In the best-dated Chinese sections, the main carbon isotope excursion is found to slightly postdate the extinction, which occurs at the end of an interval of exceptionally heavy $\delta^{13}C$ values that has been called the "Kamura event" (Isozaki, 2007a, 2007b), a supposedly long-lasting major global cooling episode. The small mismatch between the extinction level and the main carbon isotope excursion perhaps accords with an extinction scenario involving abrupt cooling and death-by-photosynthetic shutdown at the onset of volcanism, although there is little direct evidence for cooling. It is perhaps significant that Emeishan volcanism occurred at the equator, and thus had the potential to inject SO_2 into the stratosphere in both the Northern and Southern Hemispheres, causing short-term cooling prior to longer-term warming from volcanic CO_2 emissions.

END-PERMIAN MASS EXTINCTION

Extinction Record

The end-Permian mass extinction needs little introduction. With >90% marine species loss (e.g., Erwin, 1994) and widespread devastation on land (e.g., Retallack, 1995; Smith and Ward, 2001), it was the greatest crisis in Earth's history. With its temporal connection to the Siberian Traps (e.g., Renne et al., 1995), the end-Permian event has become the quintessential example of volcanically induced mass extinction. Almost all animals and plants in almost all environmental settings were affected.

The marine crisis has generally been attributed to a single pulse of extinction of relatively short duration (<20,000 yr) that affected marine and terrestrial ecosystems simultaneously in the latest Permian. Shen et al. (2011) dated the marine extinctions to just before 252.28 Ma with precise U-Pb dating of sections in South China. In biostratigraphic terms, this level is within the Late Permian *Neogondolella yini* zone (top of bed 24e at the Meishan global stratotype section), a level that was thought to account for >90% species loss (Jin et al., 2000). However, recently, more extensive collecting in numerous marine sections throughout South China has revealed that this first extinction pulse was followed by a 200 k.y. period of recovery and modest diversification before a second extinction phase in the *Isarcicella staeschi* conodont zone of the earliest Triassic (Song et al., 2012).

The severity of the end-Permian extinction on land has been questioned by Gastaldo et al. (2009) and Xiong and Wang (2011), the latter suggesting that land plant microfossil genera actually increased across the Permian-Triassic boundary, before suffering a major extinction in the early Early Triassic (possibly contemporaneous with the second pulse of marine extinctions identified by Song et al., 2012). Nevertheless, the majority of evidence suggests that terrestrial and marine communities were devastated at around the same time in the Permian-Triassic boundary interval (e.g., Shen et al., 2011; Song et al., 2012). The Karoo Basin and Greenland sections record a catastrophic event for terrestrial vegetation and vertebrates in high southern and northern latitudes (Twitchett et al., 2001; Ward et al., 2005). Thus, the extinction mechanism must include kill factors that simultaneously affect marine and terrestrial environments globally. A major negative carbon isotope shift, in the region of 5‰–8‰, accompanies the marine extinction (Holser et al., 1991; Holser and Magaritz, 1995; Wignall et al., 1998), pointing to rapid and large-scale destabilization of the carbon cycle.

Contemporaneous environmental changes at the time of the extinctions include the widespread development of anoxic conditions in a broad range of water depths (Wignall et al., 2010; Bond and Wignall, 2010), a rapid increase of sea-surface temperatures (Joachimski et al., 2012; Sun et al., 2012), and the widespread development of microbial carbonate deposition in equatorial waters (Pruss et al., 2006). The demise of terrestrial plant communities saw the cessation of coal deposition (Retallack et al., 1996) and a change in fluvial environments to braided-river–dominated settings (Ward et al., 2000).

Siberian Traps

The Siberian Traps outcrops cover 1.5×10^6 km^3 of the Tunguska Basin of northwest Siberia (Fig. 6). Magmas were erupted through the Tunguska sedimentary sequence, consisting of thick deposits of Cambrian evaporites (Meyerhoff, 1980) that include a volume of ~585,000 km^3 of rock salt (Zharkov, 1984). Flood basalts account for a relatively modest 3.4×10^5 km^3 of the outcrop area. Their original extent was undoubtedly greater because a major western extension of the volcanics occurs beneath the Jurassic and Cretaceous layers of the West Siberian Basin (Figs. 1 and 6; Westphal et al., 1998; Reichow et al., 2005; Saunders et al., 2005). Estimating the original volume of the Siberian Traps and West Siberian rift system is problematic, but upper-end figures of 3–4 × 10^6 km^3 (Courtillot et al., 1999; Fedorenko et al., 2000; Kuzmin et al., 2010) indicate that it is one of the largest known continental flood basalt provinces.

Age of Trap Volcanism and Extinction

The eruption of the Siberian Traps was first put forward as the trigger mechanism for end-Permian extinction over two decades ago (e.g., Renne and Basu, 1991; Campbell et al., 1992), and the temporal connection has greatly strengthened subsequently (Renne et al., 1995; Bowring et al., 1998; Kamo et al., 2003; Mundil et al., 2004; Shen et al., 2011). The age of an ash layer, Bed 25, 16 cm below the conodont-defined boundary at the Meishan stratotype in South China, has been variously dated to 251.2 ± 3.4 Ma (sensitive high-resolution ion microprobe [SHRIMP] U-Pb date from Claoué-Long et al., 1991), 249.91 ± 1.52 Ma (^{40}Ar-^{39}Ar date from Renne et al., 1995), 250.04 ± 1.13 Ma (^{40}Ar-^{39}Ar date of the same level at Shangsi from Renne et al., 1995), 251.4 ± 0.3 Ma (zircon U-Pb date from Bowring et al., 1998), 252.4 ± 1.8 Ma (SHRIMP U-Pb date from Metcalfe, 1999), and 253 Ma (zircon U-Pb date from Mundil et al., 2001). Most recently, Shen et al. (2011) dated the Bed 25 ash as 252.28 ± 0.08 Ma (U-Pb date) and an ash band from 12 cm above the boundary as 252.10 ± 0.06 Ma, and by interpolation placed the boundary itself to 252.17 ± 0.06 Ma.

Volcanism in western Siberia began with the formation of the predominantly basaltic Tuffaceous Series (Sadovnikov and Orlova, 1993, 1998). These underlie the flood basalts in most of the province, and they dominate the entire succession in the south of the region. Zircons are rare in this series, making the dating of

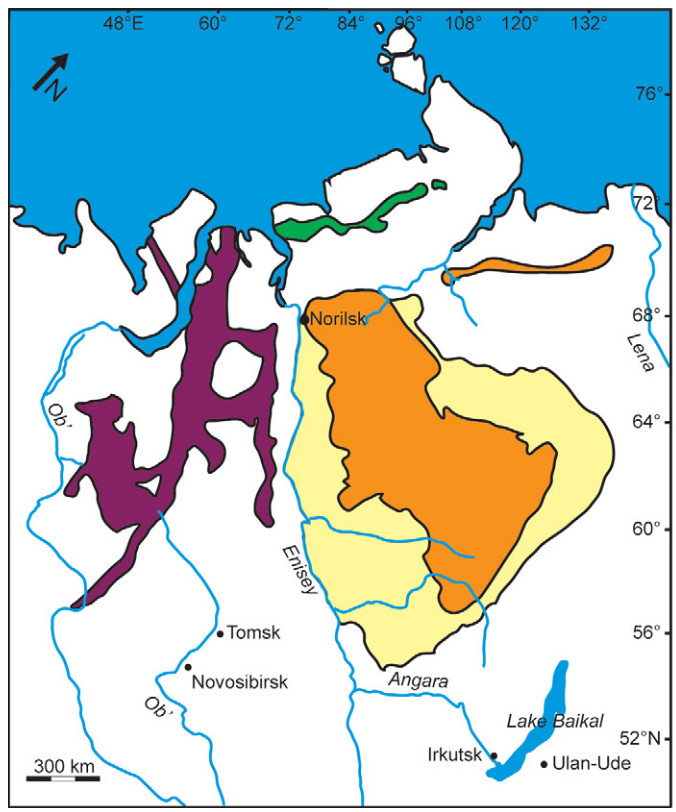

Figure 6. Map of Late Permian and Early Triassic magmatism of the Siberian Platform and West Siberian plain. Orange—extrusive volcanic rock exposure; yellow—intrusive volcanic rock exposure; purple—West Siberian Rift basalts, tuffs, and tuffites, where borehole samples have revealed basalts of the same age and chemistry as the main Siberian Traps basalts; green—Early Triassic Taimyr Traps; blue—water courses (names in italics). Major towns and cities are shown in regular text. Figure is modified from Kuzmin et al. (2010).

the onset of volcanism difficult, although the presence of conchostracans within intertuff sediments allows biostratigraphic correlation (Kozur, 1998; Kozur and Weems, 2011). Thus, Kozur and Weems (2011) suggested a middle Changhsingian to latest Permian age for the Tuffaceous Series, with the overlying flood basalt eruptions ensuing just below the Permian-Triassic boundary. Recent radioisotopic dates from within the flood basalt stratigraphy support synchronicity with the boundary in South China. Kamo et al. (1996) obtained a U-Pb age of 251.2 ± 0.3 Ma from the lower third of the lava pile in the Noril'sk area. Reichow et al. (2009) obtained an ^{40}Ar-^{39}Ar date of 250.3 ± 1.1 Ma for the final stages of extrusive volcanism at Noril'sk. Although the two techniques are not directly comparable, Renne et al.'s (2010, 2011) Ar-Ar recalibration would render Reichow et al.'s (2009) dates ~1% older and therefore close to, but slightly older than, Kamo et al.'s (1996) U-Pb dates. It seems likely that the entire Noril'sk lava pile erupted rather rapidly (also indicated by Venkatesan et al.'s [1997] much younger, but closely spaced ages for the base and top of the Noril'sk succession).

The Noril'sk succession is only a minor component of the Siberian Traps, and thus dates from this region may not agree with ages from other regions of the large igneous province. In the Maymecha-Kotuy region, the lava flows appear to be a chemically distinct suite of alkali-ultrabasics, which overlap in age within errors, but are most likely older than the Noril'sk succession according to a ^{40}Ar-^{39}Ar age of 253.0 ± 2.6 Ma (Basu et al., 1995). However, Kamo et al. (2003) obtained dates of 251.7 ± 0.4 Ma from the basal (Arydzhangsky) flow, and of 251.1 ± 0.3 Ma from the Delkansky flow, near the top of the pile. These ages suggest that the majority of volcanism may have been synchronous in Noril'sk and Maymecha-Kotuy, and the entire lava pile might have erupted in substantially less than a million years, but see also the recent compilation of Ivanov et al. (2013), who suggested a much more prolonged duration of magmatism. Again, further high-resolution dating is urgently required.

Style of Volcanism

The relatively high proportion of basaltic pyroclastics (>10% of the total volcanic pile in Noril'sk, and a significant contribution in Maymecha-Kotuy and Putorana to the south) and the relatively small volume of individual lava flows are unusual aspects of the Siberian Traps. Individual flows around Noril'sk are small compared to those of some other continental flood basalt provinces, rarely exceeding a few tens of meters thickness and a few tens of kilometers in extent (Sharma, 1997).

If the volumes of Siberian flood basalts are unusually small, then, perhaps more significant, their volatile content may have been unusually high. Black et al. (2012) measured S, Cl, and F in melt inclusions from 10 Siberian Traps samples and discovered anomalously high concentrations. S peaked at 0.51 wt% in Maymechinsky lava flows, and Cl and F peaked at 0.78 wt% and 1.95 wt%, respectively, in an Ust-Ilimsk dolerite sill. Total magmatic degassing from the Siberian Traps alone (not including a likely substantial input from contact metamorphism of sedimentary rocks in the Tunguska Basin) is estimated as ~6300–7800 Gt sulfur, ~3400–8700 Gt chlorine, and ~7100–13,600 Gt fluorine (Black et al., 2012). Even these concentrations may be an underestimate of volatile release: Sobolev et al.'s (2011) estimates noted previously suggest even greater volumes.

Extinction Mechanisms

As one might expect for the greatest mass extinction, wide varieties of kill mechanisms have been put forward, including marine anoxia, volcanic winter, hypercapnia, ocean acidification, global warming, increased sediment flux to the oceans, ozone destruction, extreme atmospheric oxygen depletion, and poisoning by toxic trace metals (Fig. 7; see reviews of Benton and Twitchett, 2003; Racki and Wignall, 2005; Wignall, 2007). With the exception of some claims for bolide impact (Becker et al., 2001; Kaiho et al., 2001), all these mechanisms ultimately view the Siberian Traps as the origin of these environmental woes.

Of the competing theories, anoxia has become a popular kill mechanism in the marine scenario due to the abundance of evidence for oxygen depletion in boundary sections in regions as diverse as the Paleotethys (Wignall and Twitchett, 1996), marginal seas (Australia; Grice et al., 2005; Bond and Wignall, 2010), Panthalassa (Isozaki, 1994, 1997), the western United States (Wignall and Hallam, 1992; Woods and Bottjer, 2000), and the Boreal realm (Wignall et al., 1998; Dustira et al., 2013). The causal chain reaction has long related the warming of the oceans to the onset of anoxia (Wignall and Twitchett, 1996), although the role of increased nutrient supply is also important (Fig. 7). H_2S degassing from anoxic surface waters onto land has also been proposed as a terrestrial kill mechanism (Kump et al., 2005).

While oxygen restriction probably contributed to the first pulse of extinction, it was not the sole killer. The open-ocean record of radiolaria reveals that the main losses occurred before the onset of anoxia (Wignall and Newton, 2003; Wignall et al., 2010). The taxonomic selectivity of the first pulse of extinction, which preferentially affected warm, shallow-water habitats and particularly reef taxa, could accord with either a rapid phase of warming or an ocean acidification-driven crisis (e.g., Payne et al., 2007; Montenegro et al., 2011; Hinojosa et al., 2012; Heydari et al., 2013). The anoxia-extinction link is much clearer for the second pulse of extinction, in the Early Triassic, because it saw the replacement of benthos-dominated communities with nekton-dominated ones, the loss of all deep-water benthos, and the relative success of dysoxia-tolerant bivalves (Wignall and Hallam, 1992; Bond and Wignall, 2010; Song et al., 2012).

The Permian-Triassic boundary coincides with a well-known negative carbon isotope excursion of ~5‰–7‰ from bulk marine carbonates (e.g., Baud et al., 1989; Holser and Magaritz, 1995; and many subsequent studies) and marine organic material (e.g., Wignall et al., 1998; Riccardi et al., 2007; Grasby and Beauchamp, 2008). Although apparently abrupt in condensed sections, the isotopic shift is seen to be gradual (lasting

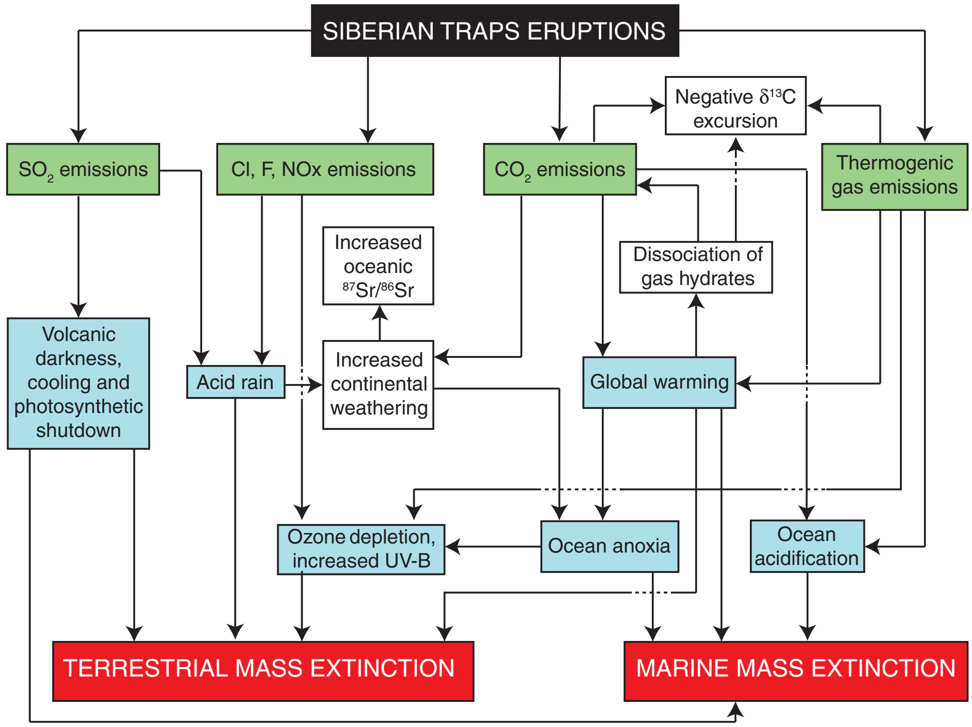

Figure 7. Flow chart summarizing proposed cause-and-effect relationships during the end-Permian extinction and Early Triassic protracted recovery period, modified from earlier versions by Wignall (2001, 2007) and Algeo et al. (2011). Green boxes—direct products of volcanism; blue boxes—kill mechanisms. The link between oceanic anoxia and ozone depletion was proposed by Kump et al. (2005) and derives from surface-water H_2S degassing. Thermogenic gas has been suggested to cause ozone depletion by injecting CH_3Cl from coal combustion (Beerling et al., 2007). UV-B—ultraviolet-B radiation.

0.5 m.y.) in more expanded sections (Korte et al., 2010). This suggests that short-lived events such as destabilization of methane hydrate reservoirs or catastrophic bolide impact are unlikely to have caused this shift. Instead, the onset and peak of the isotopic shift are seen to coincide with the start-up and peak effusion of the Siberian Traps (Korte et al., 2010). However, mantle-derived CO_2 has a $\delta^{13}C$ value of –5‰, which is only a little lighter than the ocean-atmosphere system of the latest Permian. Potentially, the carbon release from Siberian volcanism may have been substantially derived from recycled ocean crust incorporated into a mantle plume (Sobolev et al., 2011). Analyses of olivine grains separated from crushed lavas suggest that the $\delta^{13}C$ values of the C may have been substantially lighter (–12‰), and the volume of volatiles release substantially greater than that inferred by simply scaling up measurements from modern basaltic eruptions. If this is the case, then the $\delta^{13}C$ record could simply be read as a monitor of Siberian eruptions.

The ramifications of the Sobolev et al. (2011) proposal have yet to be incorporated into Earth system models for the end-Permian crisis. Instead, researchers frequently propose that the volcanic C flux was only a component of total C release. It may have acted as a stimulus: Modest global warming may have triggered destabilization of methane hydrates stored in permafrost soils and continental shelves (Racki and Wignall, 2005). Alternatively, Retallack and Jahren (2008) suggested that the $\delta^{13}C$ excursion could be attributed to injection of nearly 1 trillion tonnes of carbon in the form of thermogenic CO_2 release from coal beds beneath the Siberian Traps (Payne and Kump, 2007; Retallack and Jahren, 2008; Svensen et al., 2009). Support from such a major coal-burning episode comes from the discovery of coal fly ash (a product of combustion) in boundary beds of the Sverdrup Basin, Arctic Canada (Grasby et al., 2011). Ogden and Sleep (2012) tested the coal-volcanism scenario by modeling the effects of a massive mafic sill intruding, heating, and mixing with thick coal seams. The hot coal-basalt mixture is expected to extrude at numerous surface locations, combusting on contact with air, and injecting vast quantities of basaltic dust, CO_2, and methane into the atmosphere. All of the carbon in 1000 km^3 of coal would need to be liberated in order to generate the observed isotope excursion—a scenario not beyond the realms of possibility.

Volcanism and coal burning also contribute gases to the atmosphere, such as Cl, F, and CH_3Cl from coal combustion, that suppress ozone formation (Black et al., 2012). The mooted presence of abundant H_2S in the atmosphere (degassed from anoxic surface waters; Kump et al., 2005; Kaiho et al., 2006) would also destroy ozone by suppressing OH and H radicals involved in its formation. A further effect of H_2S may have been to prolong the residence time of methane in the atmosphere and thus indirectly reduce ozone generation rates (Lamarque et al., 2007). Ozone destruction and the consequent increase of ultraviolet-B radiation have become a popular terrestrial-extinction cause (e.g., Visscher et al., 2004; Kump et al., 2005; Sephton et al., 2005; Collinson et al., 2006; Beerling et al., 2007). This theory neatly ties Siberian Traps volcanism and thermogenic gas as the ultimate cause of extinctions on land and in the oceans, but modeling work has yet to produce the required level of ozone damage. Beerling et al.'s (2007) model of the input of large volumes of CH_3Cl from coal combustion at the eruption site indicated that the only significant damage to the ozone layer would occur at high latitudes, rather weakening the argument for ozone destruction as a cause of global mass extinction.

END-TRIASSIC MASS EXTINCTION

Extinction Record

In terms of severity of ecological disturbance, the end-Triassic crisis is behind only the end-Permian and end-Cretaceous events (Table 1; McGhee et al., 2013). The terminal Triassic Rhaetian Stage was notable for the extinction of reef communities that included the scleractinian corals' most severe crisis (Flügel, 2002; Flügel and Kiessling, 2002; Martindale et al., 2012). Bivalves and ammonoids were also prominent victims, although their record suggests a gradual decline in the latest Triassic before a major extinction a little below the ammonoid-defined Triassic-Jurassic boundary (Hallam, 2002).

The plant record also records a severe crisis, although it is unclear if it was precisely contemporaneous with the marine extinctions. Thus, a major floral turnover locally characterizes the (palynologically defined) Triassic-Jurassic boundary in the Newark Basin of the United States (Fowell and Olsen, 1993). Plant macrofossils from East Greenland reveal even greater species losses of 85% (McElwain et al., 1999, 2007), but, curiously, there are no associated losses in the palynological record (Raunsgaard Pedersen and Lund, 1980; Koppelhus, 1996). In parts of Europe, the end-Triassic sporomorph crisis is only marked by the loss of *Ovalipollis*, which was followed by diversification amongst microfloras (Hesselbo et al., 2004). The terrestrial record therefore suggests that globally, plants experienced disturbance and a major turnover, rather than catastrophic extinction losses.

The Triassic-Jurassic transition was marked by numerous paleoenvironmental changes. Stomatal density indices in fossil leaves suggest a fourfold increase in atmospheric CO_2 and global warming of 3–4 °C (McElwain et al., 1999) or possibly as much as 6 °C (Beerling and Berner, 2002; Huynh and Poulsen, 2005), presumably driven by volcanic CO_2 release in the same manner as the Siberian Traps–driven warming. A potential consequence of this enormous rise in atmospheric CO_2 is ocean acidification: a popular kill mechanism for the end-Triassic event that is consistent with the selective loss of shelly marine forms with little physiological buffering and especially of the corals (Hautmann, 2004; Hautmann et al., 2008a, 2008b; Greene et al., 2012; Martindale et al., 2012).

Destabilization of the carbon cycle is once again recorded by an initial sharp but brief negative ^{13}C shift, followed by recovery and then a more prolonged negative ^{13}C excursion, the onset of which marks the formal Triassic-Jurassic boundary. In total, there is an ~6‰ negative shift in the record of both organic and inorganic carbon (e.g., Pálfy et al., 2001; Hesselbo et al., 2002, 2004; Jenkyns et al., 2002; Korte et al., 2009; Ruhl et al., 2009, 2011). In the British Isles, the main excursion immediately postdates the main marine extinctions and occurs at a level of intensively deformed strata (often referred to as "seismite"). The seismite layer has been attributed to a single earthquake of exceptional intensity caused by a meteorite impact (Simms, 2003, 2007) or by seismic activity associated with the onset of Central Atlantic magmatic province volcanism (Hallam and Wignall, 2004; Wignall and Bond, 2008).

Central Atlantic Magmatic Province

The rifting of Pangea and breakup of the central Atlantic region were accompanied by extensive flood basalt volcanism that emplaced the Central Atlantic magmatic province across four continents (Fig. 2). The estimated original area is poorly constrained but may have approached 10×10^6 km^2, although most of the extrusives have been eroded away (McHone, 2003; Knight et al., 2004; Nomade et al., 2007; Greene et al., 2012). Estimates of the original volume range from ~2×10^6 km^3 (Holbrook and Kelemen, 1993; Marzoli et al., 1999) to ~4×10^6 km^3 (Olsen, 1999), making the Central Atlantic magmatic province one of the largest large igneous provinces of the Phanerozoic (Nomade et al., 2007).

The $^{40}Ar/^{39}Ar$ dates of Central Atlantic magmatic province basalts reveal that intrusive magmatism started around 202 Ma and was followed soon after by extrusive activity that peaked at 199 Ma (Nomade et al., 2007). Marzoli et al. (2011) recalibrated various Ar-Ar dates using the method described by Renne et al. (2010, 2011) and showed peak activity around 201 Ma, an age in accordance with recent U-Pb dates. Thus, Schoene et al.'s (2010) U-Pb dating places the earliest extrusive activity at 201.38 Ma, an age that provides the current definition of the Triassic-Jurassic boundary (Gradstein et al., 2012). Blackburn et al. (2013) applied U-Pb dating to Central Atlantic magmatic province lavas in several different regions, establishing ages of activity from ca. 201.5 Ma to 201.00 Ma. Early flows within Rhaetian-dated sediments in Morocco and Canada confirm that Central Atlantic magmatic province eruptions began in the latest Triassic (Marzoli et al., 2004; Cirilli et al., 2009; Deenen et al., 2010) and were therefore coincident with latest Triassic extinctions (Ruhl et al., 2010, 2011; Deenen et al., 2010), or at least within one precession cycle (20 k.y.; Deenen et al., 2010). In the United States, the oldest lavas postdate the palynological turnover (Fowell and Olsen, 1993) by a similar duration (Blackburn et al., 2013) and are of basal Jurassic Hettangian age. Thus, in the Newark Basin, the lowest lava flow is 30 m above the palynologically defined Triassic-Jurassic boundary. Some have suggested that pre-eruptive dike emplacement affected the global carbon cycle before the first lavas were extruded (e.g., Ruhl and Kürschner [2011], who discovered a small negative C excursion that slightly preceded the "initial" excursion of Hesselbo et al. [2002]). This is a convenient explanation for the slight diachroneity in the records of volcanism and extinction in the northeastern United States. In fact, the lava flows in the Newark and Hartford Basins probably do not record the full temporal extent of eruptions because the oldest flows in the Culpeper Basin of Virginia are of Rhaetian age (Kozur and Weems, 2011), just like their equivalents in Morocco and Canada.

The main phase of Central Atlantic magmatic province volcanism appears to have been of short duration. This has been estimated as ~1.6–2 m.y. (Marzoli et al., 1999, 2004; Nomade et al., 2007). An even shorter duration is estimated as 580 ± 100 k.y. for the Newark Basin (Olsen et al., 1997, 2003) and 840 ± 60 k.y. for the Hartford Basin (Schaller et al., 2012), although neither basin records the full eruption history. Knight et al. (2004) suggested that the entire volume of the Central Atlantic magmatic province lava pile in Morocco was erupted within 3–5 pulses, each potentially as brief as 450 yr. Such claims have major implications for the rate of volatile release. McHone (2003) calculated that total emissions of CO_2, S, F, and Cl ranged from 1110 to 5190 Gt (based on whole-rock analyses). Beerling and Berner (2002) calculated that as much as 17,500 Gt of carbon was released as CO_2, with methane hydrate degassing adding a further 12,000 Gt of carbon as CH_4 (based on magmatic CO_2 contents from modern Hawaiian basalts; Berner and Beerling, 2007), although thermogenic methane release has also been invoked (Ganino and Arndt, 2009; van de Schootbrugge et al., 2009). Such volumes can potentially explain the contemporaneous $\delta^{13}C$ excursions (Pálfy et al., 2001; Ruhl et al., 2011). However, the rate of gas effusion is a key factor when interpreting the isotopic excursions, and if the duration of peak eruptions was as brief as suggested by Knight et al. (2004), with intense eruption pulses lasting around 400 yr and most volcanism occurring in less than 20 k.y., then the Central Atlantic magmatic province represents a potent trigger for environmental disturbances that include global warming and ocean acidification.

EARLY JURASSIC (TOARCIAN) MASS EXTINCTION

The extinctions in the Toarcian Stage of the Early Jurassic are well understood thanks to the excellent northwest European record (e.g., Jenkyns, 1985, 1988; Hesselbo et al., 2000; McArthur et al., 2000; van de Schootbrugge et al., 2005; Wignall et al., 2005; Cohen et al., 2007; Sandoval et al., 2012). Estimates of 5% family-level global diversity loss indicate a relatively minor crisis, although significant losses were experienced by shallow-marine mollusks (Little and Benton, 1995). The extinction was originally thought to have been localized to northwest Europe (Hallam, 1986, 1996), but studies in South America (Aberhan and Fürsich, 1996), North America (Caruthers et al., 2011; Caruthers and Smith, 2012), Tibet (Wignall et al., 2006), and Japan (Hori, 1993; Wignall et al., 2010; Gröcke et al., 2011), as well as deeper-water facies of western Tethys (Vörö, 1993), have revealed the global nature of the crisis. Elevated extinction rates through five ammonite zones spanning the Pliensbachian-Toarcian boundary (Little and Benton, 1995) culminated with peak losses during an interval of widespread anoxia (the Toarcian oceanic anoxic event [OAE]) in the *Falciferum* zone (Little, 1996), suggesting a role for marine anoxia.

Pálfy et al. (2002) ascribed a U-Pb age of ca. 183 Ma to volcanic layers interbedded within strata of the contemporaneous North American ammonite zone—an age assignment that confirms a close temporal link between the Toarcian extinctions and the Karoo and Ferrar continental flood basalt province (Figs. 1 and 8). The Early Jurassic saw major basaltic volcanism that emplaced >2.5 × 10^6 km^3 of sills, dikes, and flows in southern Africa (Karoo Traps) and Antarctica (Ferrar Traps; Encarnación et al., 1996). Outcrops of the province cover an area of ~3.1 × 10^6 km^2 (Eldholm and Coffin, 2000; Courtillot and Renne, 2003). The province is well dated (Encarnación et al., 1996; Duncan et al., 1997; Jones et al., 2001; Le Gall et al., 2002; Jourdan et al., 2004, 2005, 2007a, 2007b; Riley et al., 2004, 2006), mainly from work in southern Africa. Jourdan et al. (2007b, 2008) provided a succinct summary of the main geochronologic findings: (1) The entire province was active for a duration of 10–12 m.y. (184–172 Ma), but the main volume of the basaltic sequence was emplaced over 3–4.5 m.y. around 180 Ma (Ar-Ar dating) and was therefore coincident with the main extinction pulse (Pálfy et al. [2002] used U-Pb dating to show that peak magmatism lasted only 2 m.y. and was clustered around 183 Ma; note that recalibration of Jourdan et al.'s [2007b, 2008] Ar-Ar dates as per Renne et al. [2010, 2011] renders them very close in age to those quoted by Pálfy et al. [2002]); (2) brief (1 m.y. or less), chemically distinct events such as the Okavango dike swarm (179.2 ± 0.4 Ma), the 800-m-thick southern Botswana lava pile (178.6 ± 0.5 Ma), and the 1.9-km-thick Lesotho lava pile (181.6 ± 0.7 Ma) have been identified; (3) a huge sill complex crops out in the main Karoo sedimentary basin, but it lacks precise dating; (4) basaltic magmatism was followed by late-stage silicic magmatism between 178 and 174 Ma; and (5) magmatic activity ended with the intrusion of the mid-ocean-ridge basalt (MORB)–like Rooi Rand dikes at 174–172 Ma.

The Toarcian marine losses in Europe coincided with global warming (Bailey et al., 2003; McElwain et al., 2005), black shale deposition, and carbon cycle perturbations. An ~2‰–3.5‰ negative $\delta^{13}C$ marine carbonate excursion was identified from the early *Falciferum* zone by Hesselbo et al. (2000), who also reported a –7‰ shift in the $\delta^{13}C$ record of marine organic matter and wood. The negative excursion is followed immediately by a positive $\delta^{13}C_{carb}$ shift of equal magnitude (Jenkyns, 1988), which is generally regarded to reflect the enhanced burial of organic matter in anoxic seas (Wignall et al., 2005). Superimposed on this negative-positive $\delta^{13}C$ isotope history, there are three 2‰–3‰ negative shifts. The lower two of these are purported to have lasted no more than 20 k.y. each (Fig. 8; Kemp et al., 2005).

The ultimate origin of the carbon isotope excursions may lie in volcanogenic CO_2 release from the Karoo and Ferrar Traps, but the magnitude of the excursion suggests that at least some component came from methane hydrate dissociation as a consequence of volcanically induced global warming (Hesselbo et al., 2000, 2007; Kemp et al., 2005). With the advent of the thermogenic gas hypothesis (Svensen et al., 2004), the addition of methane from magmatically heated coal and organic-rich shale beds

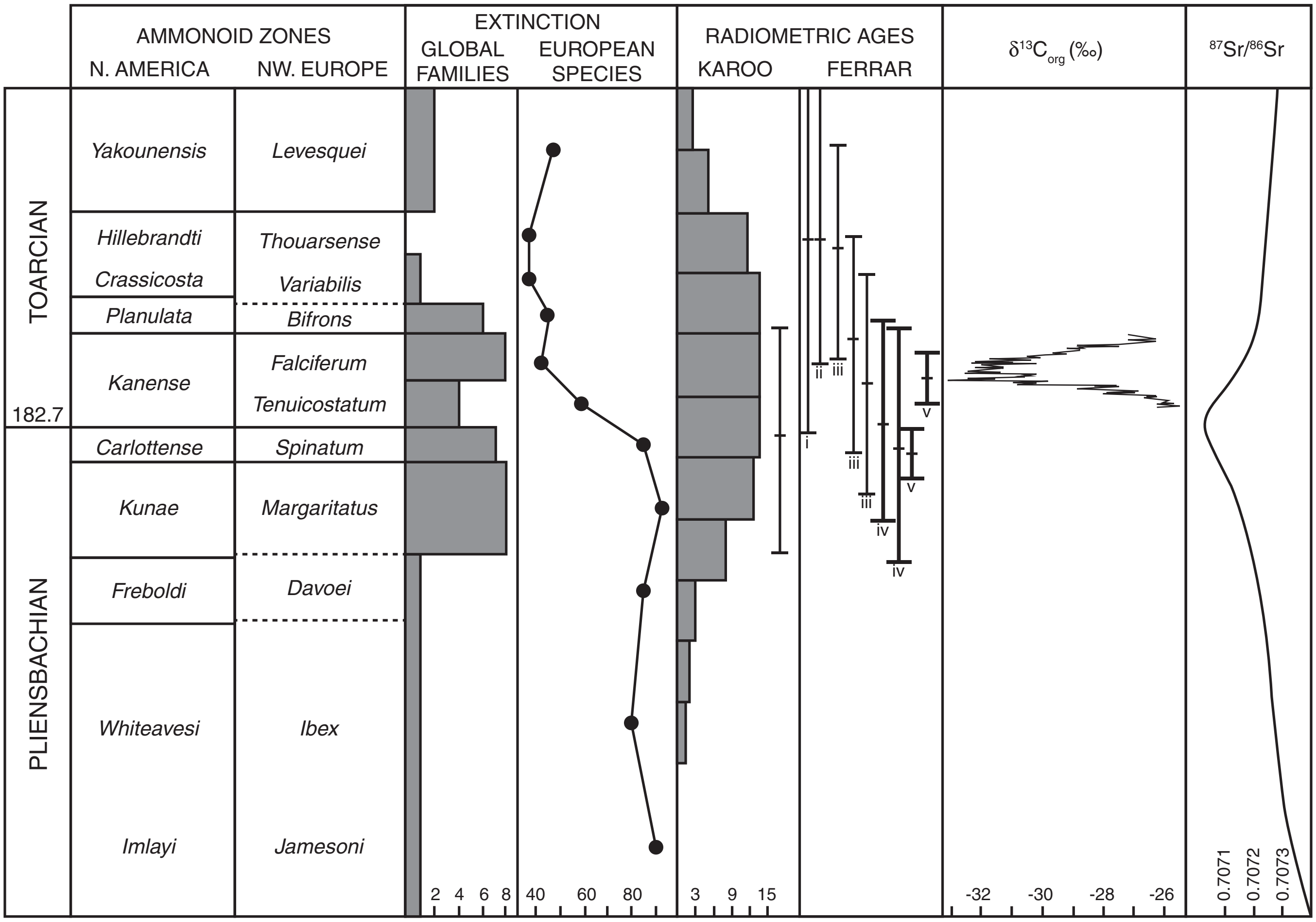

Figure 8. Pálfy et al.'s (2002) correlation of the Toarcian marine extinction, Karoo and Ferrar flood basalt volcanism, and carbon and strontium isotope stratigraphy within the ammonoid zonal framework. The histogram of number of global family extinctions by zone is based on Little and Benton (1995). The "European Species" column shows cumulative species diversity per zone, expressed in number of species of bivalves, ammonoids, rhynchonellid brachiopods, crinoids, foraminifera, and ostracods from Britain (Hallam, 1996). Radioisotopic ages from the Karoo Group were recalculated by Pálfy et al. (2002) from published sources. The histogram in this column represents the age spectrum of 28 $^{40}Ar/^{39}Ar$ dates from Duncan et al. (1997); the vertical bar is the error bar of the Karoo U-Pb age (Encarnación et al., 1996). Radioisotopic ages for the Ferrar Traps are based on $^{40}Ar/^{39}Ar$ (thin lines) and U-Pb (heavy lines) and were recalculated by Pálfy et al. (2002) from published sources. Ages and error bars for Ferrar dates are from left to right: (i) composite of 11 $^{40}Ar/^{39}Ar$ ages by Heimann et al. (1994); (ii) composite of two $^{40}Ar/^{39}Ar$ ages by Foland et al. (1993); (iii) three $^{40}Ar/^{39}Ar$ ages by Duncan et al. (1997); (iv) two U-Pb ages by Encarnación et al. (1996); and (v) two U-Pb ages by Minor and Mukasa (1997). The carbon isotope profile is from Kemp et al. (2005), rescaled for this figure. The seawater $^{87}Sr/^{86}Sr$ curve is simplified from Jones et al. (1994). Figure is modified from Pálfy et al. (2002). The Pliensbachian-Toarcian boundary is placed at 182.7 Ma in the *Geologic Time Scale 2012* (Gradstein et al., 2012).

in the Karoo Basin has also been implicated in the isotope excursion (McElwain et al., 2005; Svensen et al., 2007). This model has been contested by Gröcke et al. (2009), who noted that the low vitrinite and liptinite contents of Karoo and other Gondwanan coals are at odds with an ability to release abundant methane. The Karoo and Ferrar Traps are marked by comparatively narrow contact aureoles surrounding intrusions, further limiting thermogenic gas release, some of which might have been captured as coalbed CH_4 or condensed as pyrolytic carbon (Gröcke et al., 2009). Instead, Wignall et al. (2006) noted that some of the rapid $\delta^{13}C$ excursions could be a local signature of recycling of isotopically light carbon from the lower water column. However, similarly large shifts have been reported in the $\delta^{13}C_{carb}$ record of the Paris Basin in France (Hermoso et al., 2009) and that of $\delta^{13}C_{org}$ from Haida Gwaii (Queen Charlotte Islands), Canada (Caruthers et al., 2011), suggesting that it is a global signal.

The association of the Karoo and Ferrar Traps with ocean anoxia and the Toarcian extinctions provides another clear case study of the large igneous province–extinction link. In this case, however, one of the largest continental flood basalts of the Phanerozoic is associated with only a minor ecological crisis, which returns us to the key theme of this review: Why do some large igneous provinces apparently trigger major extinctions, while other do not?

The Karoo magma erupted in contrasting styles: Initial brief and temporally distinct magmatic pulses emplaced a large proportion of the total volume of the province; these were followed by more persistent, but diffuse magmatism that lasted for several million years and also contributed a large component of total volume. Some of the thickest lava piles, such as that in Lesotho, were erupted in a brief interval (<0.8 m.y.; Jourdan et al., 2007b), but these individually contributed only a modest proportion of the total volcanogenic volatile flux. A relatively slow rate of volatile input to the atmosphere may have induced only gradual climate change, leaving enough time for the ecosystem to recover between each individual volcanic event (Jourdan et al., 2008). Modeling suggests that even adding thermogenic and/or methane hydrate emissions into the equation would have a limited impact on climate if individual pulses are spread over a protracted period (Beerling and Brentnall, 2007).

These subdued effects of Karoo-Ferrar volcanism are comparable to the Ontong Java and Kerguelen Plateaus eruptions. These two large oceanic plateaus emplaced unparalleled volumes of lava (the former has an estimated volume of 100 × 10^6 km^3; Gladczenko et al., 1997), and yet neither is associated with mass extinction. Potentially, most of the CO_2 released by these giant submarine eruptions would have been taken up by the oceanic sink, limiting the effects of global warming. However, at least some of the Ontong Java Plateau erupted close to sea level (Mahoney et al., 2001), and so it is difficult to envisage how at least some CO_2 could not have reached the atmosphere.

DISCUSSION AND CONCLUSIONS

Temporal Link

The temporal link between large igneous province eruptions and mass extinctions is well established and has been refined in recent years thanks to much effort and improvements in radioisotopic dating techniques. All but one of the "Big 5" extinctions are associated with large igneous provinces, the exception being the Late Ordovician crises. This suggests that the largest extinctions require a volcanic trigger, and yet the most voluminous examples from the Cretaceous are only associated with minor or no biotic crises. Of the 16 large igneous province episodes summarized in Table 2 (see also Fig. 1), only around half are temporally constrained to intervals of mass extinction—and that includes the tenuous deep time examples of the Volyn and Kalkarindji flood basalts. Previous assertions of links between the Paraná and Etendeka Traps and an end-Jurassic extinction, the North Atlantic igneous province and an end-Paleocene extinction, and the Columbia River Flood Basalts and an end–early Miocene extinction (Courtillot and Renne, 2003) do not stand up to scrutiny, because those events were not "mass extinctions."

Several of the post-Jurassic large igneous provinces triggered similar environmental responses to those associated with earlier large igneous province eruptions, chiefly global warming and marine anoxia (Table 2). The Deccan Traps apparently warmed global climates prior to the terminal Cretaceous bolide impact (see review of Keller et al., this volume). The massive Ontong Java phase 1 volcanism straddles the Barremian-Aptian OAE (Selli event). The Caribbean-Colombian and Madagascar Plateaus have been implicated in the Cenomanian-Turonian OAE (Bonarelli event) and minor extinction (although these probably predated volcanism). The North Atlantic igneous province is associated with extreme warming of the Paleocene-Eocene thermal maximum, but contemporaneous global extinction losses were minor. The most intriguing aspect of these large igneous provinces is their failure to trigger more severe biotic events, which raises several questions: Were post-Jurassic biotas more resilient to change? Have ecosystems adapted following repeated crises during the late Paleozoic and early Mesozoic or has Earth become more efficient at dealing with excess CO_2 fluxes and other volcanic phenomena? Or is the causal link between

TABLE 2. LARGE IGNEOUS PROVINCES AND ASSOCIATED EXTINCTION EVENTS AND ENVIRONMENTAL CHANGES

Large igneous province	Age (peak activity, Ma)	Coeval extinction	Global warming	C isotope excursion (‰)	Marine anoxia	Ocean acidification
Volyn CFB	580–545	Ediacaran? ca. 545–542 Ma				
Kalkarindji CFB	510–503	Early Cambrian? ca. 510 Ma	?	−4	✓	
Viluy Traps	380–340 (ca. 370)	Frasnian-Famennian? ca. 372 Ma	✓	+2 to +4	✓	
PDD Rift	367–364					
Emeishan Traps	260–257	Capitanian	?	−6		
Siberian Traps	253–250	End-Permian	✓	−5 to −7	✓	?
CAMP	202–199	End-Triassic	✓	−6 (carb and org)	?	?
Karoo and Ferrar Traps	184–172 (183–180)	Toarcian	✓	−7 then +7 (org)	✓	
Paraná and Etendeka Traps	134–132					
Ontong Java Plateau (phase 1)	122				✓	
Rajmahal Traps/Kerguelen Plateau	119–109					
Madagascar/Caribbean-Columbia/ Ontong Java Plateau (ph. 2)	90–87	End-Cenomanian? ca. 94 Ma	✓	+2	✓	
Deccan Traps	67–65	End-Cretaceous	✓	−2		
NAIP (ph. 1, ph. 2)	61, 56–54		✓ (PETM)	−3	✓	
Ethiopia and Yemen Traps	31–29					
Columbia River Flood Basalts	17–6 (16.6–15.3)					

Note: Carbon isotope excursions are based on the $\delta^{13}C$ record of marine carbonates, unless specified as "org". CFB—continental flood basalt province; PDD—Pripyat-Dnieper-Donets; CAMP—Central Atlantic magmatic province; NAIP—North Atlantic igneous province; PETM—Paleocene-Eocene thermal maximum. ✓—environmental changes with strong evidence; ?—environmental changes with tentative evidence.

volcanism and mass extinction broken, and their apparent temporal coincidence just that, a coincidence?

Key factors in large igneous province lethality may be the style, rate, and site of eruptions, and thus their ability to rapidly inject large fluxes of climate-changing volatiles into the stratosphere. The potential of thermogenic greenhouse emissions to add to the volatile budget has come to light in the past decade, and this represents a plausible explanation for the negative carbon isotope shifts that accompany several extinctions. The state of climate at the onset of volcanism, and the resilience of the extant biota may also be important. The key challenge for earth scientists now is to model, analyze, and understand *how* the products of volcanism can cause extinction, within an ever-improving age framework.

Triggers and Killers

This review has focused on five extinction events—including four consecutive crises in the 80 m.y. interval between the Middle Permian and Early Jurassic—that are clearly linked to large igneous province volcanism. The temporal relationship between the Frasnian-Famennian biodiversity crisis and the Viluy Traps has yet to be resolved but is becoming more convincing. In contrast, the Capitanian, end-Permian, end-Triassic, and Toarcian crises were all associated with a swathe of environmental changes consistent with the effects of volcanism. Of these five events, three (maybe four) are associated with marine anoxia, four (maybe five) are associated with warming, and four are associated with major negative carbon isotope excursions (Table 2). Ocean acidification has been invoked in two of these five extinctions, with the selectivity of extinctions touted as key evidence (e.g., Payne et al., 2007; Foster, 2008; Kiessling and Simpson, 2011), although a reliable proxy for past pH changes has yet to be devised.

Short-term global cooling and dimming are other obvious consequences of explosive volcanism, but the duration of such events, measured in years, is almost impossible to resolve in the geological record. The best evidence for cooling comes from extinction selectivity, and none of the crises documented here yields strong evidence for this kill mechanism, except perhaps the Capitanian crisis. Increasingly high-resolution extinction studies may yet reveal a role for volcanogenic cooling in the early stages of ecosystem perturbation.

Concluding Remarks

(1) The temporal link between large igneous provinces and mass extinction events has been recognized for nearly three decades. Recent advances in radioisotopic dating techniques have refined and confirmed the link for at least half of the major extinctions of the Phanerozoic. Almost all of Earth's most severe biotic crises, including four of the "Big 5" extinctions, are associated with large igneous provinces, implying that large-scale volcanism is a prerequisite for a really big extinction.

(2) Modeling, observations of recent eruptions, and detailed volcanological, geochemical, and paleontological studies have yielded clues to the causal mechanisms that link volcanism and extinctions. The relative importance of many factors in this extinction-volcanism nexus, including the continental configuration at the time of the eruption, the latitude and altitude of eruption, the volume, rate, and duration of eruption, its style, the preexisting climate state, and the resilience of the extant biota to change, have all to be evaluated and understood. However, the total volume of magma is clearly not an important factor, because some of the smallest large igneous provinces are associated with extinctions, whereas some of the largest are not.

(3) Of the five events examined here, four are clearly associated with global warming and other proximal killers such as marine anoxia. Three of these extinction and warming episodes are accompanied by large negative carbon isotope excursions, supporting a volcanogenic origin. In all three cases, the scale of the excursion is too big to be attributed to volcanic CO_2 and CH_4 alone (unless large igneous province CO_2 emissions were considerably lighter than mantle values). Methane hydrate release during warming episodes, and more recently thermogenic gas release, is commonly invoked.

(4) Volcanically induced warming is clearly a powerful driver of marine anoxia: All post-Paleozoic oceanic anoxic events coincide with intervals of large igneous province formation. These warming-anoxia events are associated with major extinctions (e.g., the end-Permian), minor extinction events (e.g., the Toarcian, and the Cenomanian-Turonian Bonarelli event), and very minor extinctions (e.g., the late Paleocene, the Aptian-Albian Selli event).

(5) Volcanic darkness and cooling have been invoked in several extinction scenarios, in particular the Capitanian, when shallow, warm-water, photosynthetic taxa suffered preferential losses. Both of these climatic effects are the anticipated result of the injection of large amounts of SO_2 into the stratosphere. Perhaps significantly, of all the large igneous provinces discussed in this paper, only the Emeishan Traps and Central Atlantic magmatic province were located at equatorial latitudes where they were potentially able to inject sulfate aerosols into both hemispheres and cause a global cooling event. Again, the site of eruption is seen to be important: Modeling and observations of recent events have shown that aerosols from mid- to high-latitude eruptions fail to cross the equator.

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