Global warming and the end-Permian extinction event: proxy and modeling perspectives

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ABSTRACT

The mass extinction event that occurred at the close of the Permian Period (~252 million years ago) represents the most severe biodiversity loss in the ocean of the Phanerozoic. The links between the global carbon cycle, climate change and mass extinctions are complex and involve a whole range of often inter-related geochemical, biological, ecologic and climatic factors. It has become widely accepted that the end-Permian mass extinction was associated with a global warming event, because the age of the Siberian traps eruption, a potentially massive source of carbon dioxide, coincides within error with the extinction event. However, geologic data that are in support of this global warming event are relatively sparse. The chain of events and the causal relationship between the eruption of Siberian traps and mass extinction is not well established. Global warming, in particular, has only been reported from limited proxy data and climate models, for which the $p\text{CO}_2$ in the atmosphere just before and during the end-Permian extinction event is poorly known. This study critically assesses both the proxy climate data and the existing paleoclimate simulations with the goals of assessing our current understanding of the link between mass extinction and climate change and providing some guidance for future studies. Proxies indicate that prior to the end-Permian extinction event tropical sea surface temperatures ranged from ~22 to 25 °C, and possible $p\text{CO}_2$ values ranged from ~500 to ~4,000 ppm before the extinction event. During the peak extinction, tropical temperatures rose up to ~30 °C while $p\text{CO}_2$ perhaps increased up to ~8,000 ppm. Climate models use different pre-event $p\text{CO}_2$ values show similar amount of CO_2 doubling to replicate the observed carbon isotope excursions. We find that

26 the temperature anomaly during the end-Permian extinction is consistent with ~1.5 doublings of
27 atmospheric $p\text{CO}_2$, and that the implied climate sensitivity is 5-6 °C, within the upper range of
28 values produced by climate models.

29 **Key words:** end-Permian extinction event, climate model, geochemical proxies, temperature and
30 $p\text{CO}_2$

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1. Introduction

The earth system experienced a series of fundamental upheavals through the Permian-Triassic (P-T) transition (ca. 252 Ma), an interval marked by the largest mass extinction in the geologic record (Burgess et al., 2014). The configuration of the supercontinent Pangea, formed through collision of the southern supercontinent of Gondwana with the northern supercontinent of Laurasia during the late Paleozoic, has been proposed to be responsible for the icehouse to greenhouse transition during the Late Permian (Erwin, 1993). The extent of continental flooding (perhaps reflecting eustatic sea level) reached its minimum during the Late Permian as the supercontinent Pangea was established, leading to extreme continentality (Fig. 1 and reference therein). Reduced availability of fresh silicate rock for weathering due to a long orogenic gap might have caused increased atmospheric CO₂ concentrations and warmed up the Late Permian (Kidder and Worsley, 2004). The pole-equator temperature gradient was probably lower based on the observed high-paleolatitude floras adapted to warm climates (Rees et al., 2002; Taylor et al., 1992). Thick and widespread coals up to the Permian-Triassic boundary (Retallack et al., 1996; Veevers et al., 1994) disappeared for 10 million years, forming a global coal gap. Expansion of subtropical desert belts indicates arid conditions during the Late Permian (Fluteau et al., 2001).

Other lines of evidence, including extremes of the oceanic isotopic compositions of C, S, and Sr suggest that the global environment reached a critical state in the late Paleozoic for which perturbation, namely massive volcanism associated with the eruption of the Siberian Traps, could pitch it over a threshold into near uninhabitability (e.g. Erwin, 2006; Kiehl and Shields, 2005; Luo et al., 2010; Fig. 1). Some researchers have proposed that the end-Permian mass extinction event was a geologically instantaneous catastrophic event (e.g. Bowring et al., 1998; Rampino et al., 2000), but evidence for prolonged extreme environments following the event seems to argue against an instantaneous perturbation (e.g. Romano et al., 2012; Sun et al., 2012). Associated ocean acidification and deoxygenation, similar to that projected for the future, was the likely

consequence of volcanic CO₂ emissions and global warming (e.g. Clapham and Payne, 2011; Montenegro et al., 2011; Payne and Clapham, 2012). Following the end-Permian extinction event are widespread microbialite sequences in shallow water settings, reflecting global expansion of microbial ecosystem (Xie et al., 2007; Xie et al., 2010; Xie et al., 2005) and perhaps an anomalously low oceanic sulfate concentration in an anoxic ocean (Luo et al., 2010).

As we review below, over the past 20 years a number of climate proxy and modeling efforts have been put forward to investigate environmental change during the mass extinction event. Geologic data that are in support of this global warming event are relatively sparse (e.g. Kidder and Worsley, 2004; Joachimski et al., 2012; Sun et al., 2012), and estimates of the background CO₂ level are few and discordant (e.g. Ekart et al., 1999; Retallack, 2001; Royer, 2001; and Royer et al., 2004). In some ways the modeling has outpaced the proxy data collection (e.g. Kiehl and Shields 2005; Meyer et al., 2008, Cui et al., 2013), and there has been little effort to perform detailed model-data comparison, including geological, paleontological, sedimentological and geochemical data.

This review focuses on the status of modeling investigations into the Late Permian climate and its association with the end-Permian mass extinction event. We begin with a review of proxies used to identify high *p*CO₂ and warm climate in the Late Permian. We then compare the boundary conditions and results of various modeling studies. We explore the critical uncertainties in the current paleoclimatic models, focusing on uncertainties in *p*CO₂ and hydrological cycle. We also evaluate the climatic consequences of Siberian Traps volcanism from the release of sulfuric acid aerosol and greenhouse gases. We then provide analysis of the proposed hypotheses for the killing mechanisms of the mass extinction event. Finally, we suggest improved modeling approaches and model-data comparison to test the hypotheses invoked to explain the mass extinction event.

2. Climate change during the Permian-Triassic transition – Geochemical proxy perspective

Geological evidence in support of warming immediately prior to and during the Permian-Triassic boundary mainly comes from proxy studies including oxygen isotopes on well-studied stratigraphic sections and paleo- $p\text{CO}_2$ thermometers including paleosol carbonate nodules and plant stomatal indices. Indirect evidence of global warming comes from mathematic modeling based mainly on the carbon isotopes of carbonate rocks. We first review proxy studies on temperature and $p\text{CO}_2$ prior to and during the extinction event, and then consider the modeling studies..

2.1. Temperature proxies

2.1.1. Oxygen isotope paleothermometry

Temperature reconstruction is extremely important in studies of paleoclimatic change during critical geological transitions. The available proxies include $\delta^{18}\text{O}$ from bulk carbonates, or, preferentially, diagenetically unaltered brachiopod calcite, fossil conodont (mostly calcium phosphate), vertebrate bones and clumped isotopes on unaltered brachiopods. Oxygen isotope paleothermometry is based on the theory that partitioning of isotopes between two phases is a function of temperature. The observational data fit the theory quite well, and thus there has been widespread application of oxygen isotopes as a paleotemperature proxy. However, separating the contributions of temperature from variations in the water $\delta^{18}\text{O}$ caused by ice-sheet size, local salinity variations, and long-term evolution of seawater $\delta^{18}\text{O}$ requires additional constraints to uniquely interpret calcite $\delta^{18}\text{O}$ variations in terms of temperature. There are also diagenetic effects, namely recrystallization and secondary calcification of calcite shells, which complicate the use of oxygen isotopes as a paleotemperature proxy. Studies on individual shells of well-preserved brachiopods have been more successful than those using bulk carbonate. However, the isotope composition of primary shells also depends on biological “vital” effects and burial conditions, including lithology, temperature, pore water chemistry and burial depth.

Oxygen isotope paleothermometry has been applied to the Late Permian, but this has proven to be more problematic than applications to the Mesozoic or Cenozoic records due to the generally deeper burial depth and secondary effects from diagenesis. More than 20 years ago, Holser et al. (1989) reported rapid shifts in stable carbon and oxygen isotopes observed in a continuous drill core known as the Gartnerkofel-1 core on the north slope of Gartnerkofel near Nassfeld in the Carnic Alps of Austria. Key features of this event were a rapid onset (which subsequently estimated to be a few thousand years, see Rampino et al. 2000), a negative shift in the $\delta^{13}\text{C}$ of carbonate ($\sim -3\text{‰}$), a decline in $\delta^{18}\text{O}$ ($\sim -3\text{‰}$ to -4‰ excursion, interpreted as $\sim 5^\circ\text{C}$ warming), and anomalous concentration of iridium and other metals indicating anoxia. All these changes were synchronous with the known extinction event. However, the magnitude of sea surface temperature change and the key greenhouse gases concentration in the atmosphere associated with the P-T event are all subjects of current debate.

Oxygen isotopic signals preserved in conodont calcium phosphate have been used as proxy for paleotemperature because of their resistance to diagenetic alteration. Joachimski et al. (2012) measured oxygen isotopes on monogeneric conodonts from both Meishan and Shangsi sections in south China, including the taxa *Clarkina* and *Hindeodus*. The measured $\delta^{18}\text{O}$ values of conodonts at Meishan section, converted to paleotemperatures of P-T seawater, range from 23 to 27°C in beds 24 and 25, and reach a maximum of $\sim 35^\circ\text{C}$ in bed 28 (Fig. 2, Table 1). It is important to note that the high temperature (35°C) derived from these conodont data as well as the sharp temperature increase both postdate the P-T mass extinction event (bed 25) so cannot be the cause of it (Fig. 2). A question remains though, whether conodonts are reliable indicators of seawater temperature. Pucéat et al. (2010) challenged the idea that conodont is resistant to diagenetic alteration, and suggested that the assumption that conodonts incorporated oxygen isotopes into phosphate in equilibrium with their ambient seawater is not well substantiated (Brand et al., 2012).

Sun et al. (2012) built upon the methodology developed in Joachimski et al. (2012) and extended the $\delta^{18}\text{O}$ measurements of biogenic apatite to the entire Early Triassic. The minimum $\delta^{18}\text{O}$ value of conodonts during late Smithian indicates a maximum sea surface temperature as high as 40 °C. Variations in $\delta^{18}\text{O}$ of conodonts covary with $\delta^{13}\text{C}$, suggesting warming events recurred into the Early Triassic (Sun et al., 2012), which could be associated with carbon releases and significant buildup of CO_2 from Siberian Traps eruptions or the sources of methane (Payne and Kump, 2007).

Overall, temperature and CO_2 proxies and modeling all suggest CO_2 buildup and warming events occurred episodically into the Early Triassic. The relationships between Siberian Traps volcanism, CO_2 and warming are tentative, however, and need to be further refined with spatially and temporally extensive proxy data collection. $\delta^{18}\text{O}$ measurements of biogenic apatite provide important P-T temperature records, but because the data are sparse, the reconstructed temperature increase could be further refined with better spatially and temporally resolved proxy data collected from stratigraphically complete sections in higher latitude regions.

2.1.2. Clumped isotopes

The analysis of clumped isotopes is a relatively new technique that emerged less than 10 years ago. It is based on the theory and experiments that the proportions of the “rare-rare” bonds in minerals, such as ^{18}O - ^{13}C in carbonate minerals, are dependent on temperature and independent of the oxygen isotopic composition of the fluid from which the mineral is precipitating (Eiler, 2007). The variable Δ_{47} is defined as the measurement of the excess of mass-47 isotopologues relative to the abundances expected for a random distribution of all isotopes among all possible isotopologues. Δ_{47} is calculated using the following formula:

$$\Delta_{47} = \left(\frac{R_{\text{measured}}^{47}}{R_{\text{stochastic}}^{47}} - 1 \right) \times 1000 \quad (1)$$

where $R_{measured}^{47}$ is the measured abundances of mass 47 CO_2 , and $R_{stochastic}^{47}$ can be expressed approximately by the following equation:

$$R_{stochastic}^{47} = \frac{2 \cdot [18] \cdot [16] \cdot [13] + [17]^2 \cdot [13] + 2 \cdot [18] \cdot [17] \cdot [12]}{[16]^2 \cdot [12]} \quad (2)$$

where [16], [17], and [18] are the concentrations of ^{16}O , ^{17}O , and ^{18}O in the pool of all oxygen atoms, and [12] and [13] are the concentrations of ^{12}C and ^{13}C in all carbon atoms contributing to a given population of CO_2 molecules (Eiler and Schauble, 2004). Δ_{47} can be converted to carbonate growth temperature based on the following equation (Ghosh et al., 2006):

$$\Delta_{47} = 0.0592 \times (10^6 \times T^{-2}) - 0.02 \quad (3)$$

The only published clumped isotope study related to the P-T extinction event is from Brand et al. (2012), in which they measured eight samples on the well-preserved biogenic low-Mg calcite (shell of brachiopod) from Sass de Putia and Val Brutta in the Southern Alps, northern Italy. The range of Δ_{47} varies from 0.589 to 0.641‰ up section, which is interpreted as a temperature rise from ~35 °C to 39 °C just prior to the extinction event (Fig. 2). One advantage of clumped isotopes over the traditional oxygen isotopes in carbonate is that this paleotemperature proxy is thermodynamically based and is independent of the $\delta^{18}O$ of seawater and dissolved inorganic carbon from which carbonate grew, and thus is suitable for interpreting the geologic record at times, such as the Late Permian, when sea water $\delta^{18}O$ is more difficult to constrain. However, because of the challenging techniques involved and persistent issues including discrepancies between previously published synthetic carbonate calibrations (Dennis et al., 2011; Eiler, 2011; Huntington et al., 2009), clumped isotopes have not been applied widely despite the unique advantages the technique provides.

2.2. Atmospheric pCO_2 proxies

Carbon dioxide (CO_2) is a greenhouse gas: it absorbs outgoing infrared radiation, warms the

atmosphere, and then re-emits infrared radiation back to Earth's surface. It has been demonstrated that atmospheric CO₂ is a primary driver for global climate change during the Phanerozoic (Kump, 2002; Royer et al., 2004). Reconstructing reliable paleo-*p*CO₂ levels during key biological and geological events is fundamental to understanding how the biosphere operates under different CO₂ levels relative to the pre-industrial level (~280 parts per million by volume, or ppmv).

The paleo-*p*CO₂ proxies for times prior to the Mesozoic include δ¹³C from pedogenic carbonates (Cerling, 1991, 1992; Mora et al. 1991, 1996; Ekart et al., 1999) and trace carbonate in goethite (Yapp and Poths, 1992, 1996), and plant stomatal index (Royer, 2001; Royer et al. 2004; Retallack, 2001). In the following section, we discuss these two paleo-*p*CO₂ approaches and their application to the Late Permian to Early Triassic *p*CO₂ reconstruction.

2.2.1. Plant stomatal density and index

The conductance of water vapor per unit area of leaf is regulated by the opening of plant stomata, and is sensitive to a number of environmental factors including atmospheric *p*CO₂. Two measures of plant conductance have been used as proxies of atmospheric *p*CO₂, including stomatal density and stomatal index (SI). Stomatal density is the numbers of stomata per unit area, a feature that is established during an early stage of leaf development (Woodward, 1987) (Eq. 4). Besides atmospheric *p*CO₂, stomatal density of modern plants has been shown to be sensitive to irradiance, water stress, and the position of the pore within a cell. In contrast, SI minimizes these effects by relating atmospheric *p*CO₂ to the proportion of pores relative to epidermal cells of fossil leaf cuticles (Royer, 2001) (Eq. 5).

$$\text{Stomatal density} = \text{number of pores per unit area} \quad (4)$$

$$\text{Stomatal index} = \frac{\text{stomatal density}}{\text{stomatal density} + \text{epidermal cell density}} \times 100 \quad (5)$$

Observations and experiments indicate that plant stomatal density and index decreases in response to increase in atmospheric $p\text{CO}_2$ (Woodward, 1987; Woodward and Bazzaz, 1988). Application of SI as a $p\text{CO}_2$ proxy, however, requires calibration to a SI – $p\text{CO}_2$ relationship under known atmospheric $p\text{CO}_2$. Under ideal conditions, the calibration would be based on the same species of plant as that found in the fossil record. However, the reconstruction of paleo- $p\text{CO}_2$ is by necessity based on calibration datasets from modern tree and herbaceous species that differ from their fossil counterparts. Moreover, its sensitivity diminishes as atmospheric $p\text{CO}_2$ increases, although an upper limit for effective use of the proxy has yet to be determined (Royer, 2001). Applying the SI paleo- $p\text{CO}_2$ proxy, Retallack (2001) reconstructed the paleo- $p\text{CO}_2$ level during the past 300 million years from fossil plant leaf cuticles. The SI paleo- $p\text{CO}_2$ proxy has also been applied to the Permian-Triassic interval recently by Retallack et al. (2011) and Retallack (2013). Using an empirical relationship derived from *Ginkgo* leaves grown in greenhouse experiment (Retallack, 2009; Wynn, 2003), $p\text{CO}_2$ was calculated using the following equation:

$$p\text{CO}_2 = 294.1 + \left[\frac{1}{(4.84 \times 10^{-10}) \times \text{SI}^{7.93}} \right] \quad (6)$$

This inverse relationship between SI and $p\text{CO}_2$ suggests plant leaves have fewer stomates when $p\text{CO}_2$ is higher (Botha and Smith, 2007; Krassilov and Karasev, 2009; Retallack, 2001; Retallack, 2009; Retallack, 2013; Retallack et al., 2011). We compiled SI $p\text{CO}_2$ – proxy data for the interval of 255 Ma to 245 Ma, representing estimates of how atmospheric $p\text{CO}_2$ evolved through the Permian-Triassic transition based on Retallack (2013) (Fig. 3). SI has been calculated using the fossil plants *Tatarina* and *Lepidopteris* (pteridosperm genera), showing values ranging from 4.9 to 11, which indicates $p\text{CO}_2$ condition varying from 300 to >7,000 ppm, with uncertainties as high as >2,000 ppm (Retallack, 2013; Retallack et al., 2011). The coarse sampling of fossil plants and uncertainties in age from terrestrial sections leads to significant uncertainty in atmospheric $p\text{CO}_2$ immediately prior to, during and after the end-Permian extinction event in these studies (Fig. 3),

although a significant increase in $p\text{CO}_2$ across the boundary is consistent with the global warming suggested by oxygen isotopes (Joachimski et al., 2012).

Because of the perplexing factors that affect ambient $p\text{CO}_2$ such as elevation and respiration/photosynthesis within the canopy, and different responses among species to changes in $p\text{CO}_2$, caution needs to be exercised in selecting the most appropriate fossil plant for establishing the proxy. There are significant disagreements between $p\text{CO}_2$ reconstructions during the same time period at the same location using different fossil plant species (Kürschner et al., 1996; Retallack, 2001). These discrepancies highlight the need to apply multiple proxies in various sites across the Permian-Triassic boundary to detect $p\text{CO}_2$ level prior to, during and after end-Permian extinction event to disentangle the cause and effect of the extinction event.

2.2.2. Carbon isotopes of carbonate nodules in paleosol

Cerling (1991) first proposed that the $\delta^{13}\text{C}$ of pedogenic carbonates could be used to estimate the $p\text{CO}_2$ at the time of pedogenic carbonate formation, based on the fact that the stable isotopic composition of soil CO_2 is strongly influenced by atmospheric CO_2 level. Pedogenic carbonates in paleosols are the most widely applied atmospheric $p\text{CO}_2$ proxy for pre-Cenozoic times because they are common in sedimentary records (Cotton and Sheldon, 2012) and the presumed error for $p\text{CO}_2$ estimate is relatively small (Royer et al., 2001). The atmospheric $p\text{CO}_2$ level over the last 400 Myr has been estimated following the method of Cerling (1991). One conclusion is that the inferred $p\text{CO}_2$ levels of the late Paleozoic are significantly higher than today (Mora et al., 1991). However, the $\delta^{13}\text{C}$ of pedogenic carbonate can be influenced by a number of factors, including the soil respiration rate, porosity, $\delta^{13}\text{C}$ of respired CO_2 , the temperature and depth of carbonate formation, and the type of vegetation providing organic matter to the sediment (Cerling, 1991). The equation based on a diffusion-reaction model used to calculate the atmospheric $p\text{CO}_2$ is as follows:

$$C_a = S(z) \frac{\delta^{13}C_s - 1.0044\delta^{13}C_\phi - 4.4}{\delta^{13}C_a - \delta^{13}C_s} \quad (7)$$

where $\delta^{13}C_s$, $\delta^{13}C_\phi$, and $\delta^{13}C_a$ is the isotopic composition of soil CO₂, soil respired CO₂, and the atmospheric CO₂ respectively (Ekart et al. 1999). The term S(z) is soil respired CO₂ (in units of ppmv), expressed as the difference between the actual soil CO₂ and the atmosphere CO₂ concentration, which is presumed to asymptote with depth when the calcite horizon is below depth 20-30cm (Cerling and Quade, 1993).

Like many other proxies, assumptions and limitations exist for the paleosol carbonate paleobarometer. Modern and recent soil studies show that the isotopic composition of soil carbonate is constant below ~20 cm, and thus it is essential to sample pedogenic carbonate below <20cm depth, which can be difficult to determine in paleosols that have undergone compaction and erosion. Carbon isotope analysis on 251 Ma pedogenic carbonate from the Quartermaster Formation (Ochoan; time equivalent to Changhsingian in stratigraphic age) from Texas, US indicates that the atmospheric pCO_2 level was about 1000 ppmv (the range of pCO_2 level varied from 600 to 1500 ppmv) (Ekart et al., 1999; Tabor et al., 2004) (Fig. 3). However, the pCO_2 level prior to the extinction is indiscernible from that during and after the event due to the low temporal resolution of paleosol sampling. There is also a discrepancy with pCO_2 estimate using plant stomatal indices (Royer et al., 2004); the pCO_2 reconstructed using carbon isotopes of pedogenic carbonate seems to be lower than that derived from plant stomatal indices. Uncertainties that might lead to this discrepancy include assumptions regarding S(z) in equation (8), a factor that is dependent on climate, especially mean annual precipitation (Cotton and Sheldon, 2012), or the $\delta^{13}C$ of soil respired CO₂. Given the error in these two estimates, the pCO_2 reconstruction around 255 Ma from these two approaches is indiscernible, both showing values similar to or higher than 500 ppm (Fig. 3).

3. Climate change during the Permian-Triassic transition – Modeling perspective

The Pangean continental configuration has been a target of climate model application since the early days of general circulation modeling of Earth's climate. As more geologic evidence became available and the model techniques advanced, increasingly sophisticated and computationally complicated models have been applied to the end-Permian extinction event. We categorize the paleoclimatic models into four types, including 1) Conceptual models and process modeling, including energy balance models (EBMs) and geochemical box models; 2) Atmosphere general circulation models (AGCM) typically with a highly simplified "slab ocean," and ocean GCMs (OGCMs) with a simple atmosphere; 3) Earth system models of intermediate complexity (EMICs); 4) Fully coupled atmosphere-ocean general circulation models (AOGCMs). These models vary in complexity and sophistication, and they represent the processes being parameterized based on the understanding of the climate system at the time the studies were being conducted. Most studies that we review included sensitivity analyses, in which key parameters were varied to test the response of the models to changes in these variables.

We begin by summarizing the earlier Pangaean climate studies, which focused on the effect of large continents on monsoons. We then summarize the climate modeling studies chronologically, each driven by a specific hypothesis related to the end-Permian mass extinction event. The hypotheses being explored to explain the extinction event are constantly being refined (if not refuted) with the appearance of new geological evidence as new outcrops, cores or techniques become available. We do not attempt to review all the paleoclimatic studies during the Permian-Triassic transition, but rather provide an overview of how our quantitative understanding of the Permian-Triassic climate system has progressed over the last two decades.

Key questions of interest in this review include: 1) How did the global mean temperature and the

equator-pole temperature gradient respond to this proposed greenhouse gas-driven climate event?
2) How sensitive are the climate modeling studies to uncertainties of greenhouse gas concentrations, paleogeography, paleobathymetry and topography? 3) How sensitive was the Late Permian climate to changes in orbital configuration? 4) What was the distribution of vegetation, and how important was this feedback to Permian climate?

3.1. Conceptual models and EBMs

Early climate modeling study of the Late Permian was focused on the effect of the Pangea supercontinent, a landmass distribution fundamentally different than today, using conceptual models (Parrish, 1993), energy balance models (EBMs) (Crowley et al., 1989; Crowley et al., 1987) and atmospheric general circulation models (Kutzbach, 1994; Kutzbach and Gallimore, 1989; Kutzbach et al., 1990; Kutzbach and Ziegler, 1993).

Conceptual or modern-analog modeling studies have been conducted by Nairn and Smithwick (1976), Parrish (1982) and Parrish et al. (1986). One common result from these modern-analog models is that strong seasonality exists during the Late Permian due to the amalgamation of Pangea. A strong monsoonal circulation is also the expected consequence of the large land mass.

EBMs estimate the changes in the climate system using the energy budget of the Earth; they determine global temperature based on a balance between the net absorbed solar radiation and the net emitted terrestrial radiation (Budyko, 1969; Sellers, 1969). They do not include ocean circulation, topography, vegetation and other important variables (Crowley and North, 1991) which limit their application in realistic paleoclimatic studies. However, due to their simplicity and fast computational speed, and the general lack of spatially resolved observations to justify more sophisticated models, EBMs were applied to the Late Permian to investigate the temperatures of Pangea (Crowley et al., 1989). Key forcing factors that were investigated in

these models include paleogeography (idealized Pangea and Pangea A and B) (Table 1), topography, atmospheric $p\text{CO}_2$, solar luminosity, and distributions of extended lakes or seas within the supercontinent. One common finding from these models was extreme seasonal temperature contrast with a hot summer ($>40\text{--}50\text{ }^\circ\text{C}$) and a cold winter ($< -15\text{ }^\circ\text{C}$) within the large continent during the Late Permian and a strong monsoon circulation characterized by high precipitation along the Tethys coast and arid continent interior. These simulations were broadly consistent with the distribution of climate indicators. However, they failed to simulate high latitude warmth that was indicated by well-preserved forests from the Upper Permian of Antarctica (Taylor et al., 1992; Taylor et al., 2000).

3.2 Geochemical box models used to investigate hypotheses associated with the end-Permian extinction event

It has been widely accepted that there was a negative carbon isotope excursion (CIE) in the global ocean-atmosphere system, as recorded in both marine carbonate/organic matter and terrestrial organic material. The CIE recorded in marine carbonate shows a long-term, slowly decreasing trend, followed by a sharp drop (about 4‰ on average; see Korte and Kozur, 2010 for review) immediately at the extinction horizon (e.g. Zhang et al. 2005) and a slight increase after the main extinction, whereas the terrestrial CIE is complicated by the organic C source variation. Absolute age determinations suggest the duration of the CIE (contemporaneous with the main extinction event) was less than 165 kyr (Bowring et al., 1998). Newly published U-Pb zircon ages indicate the sharp decline of $\delta^{13}\text{C}$ occurred within about 20 kyr (Burgess et al., 2014; Shen et al., 2011b). One commonly proposed interpretation of the rapid, large magnitude CIE is the release of a large amount of ^{13}C -depleted carbon, either in the form of oxidized coal or organic matter (CO_2 with $\delta^{13}\text{C}$ of about -25‰), biogenic methane clathrate and permafrost on the seafloor (with $\delta^{13}\text{C}$ of about $< -60\text{‰}$), or thermogenic methane (with $\delta^{13}\text{C}$ of about -40‰) associated with dike and sill intrusion of coal during the Siberian Traps emplacement. To test the ^{13}C -depleted carbon source,

geochemical box models have been widely applied. Box models involve solving a series of ordinary differential equations associated with the carbon cycle (e.g., Slingerland and Kump, 2011) reflecting the time-dependent mass balance equations for some combination of total carbon, alkalinity, phosphorus, oxygen and carbon isotopes.

Berner (2002) utilized a version of the “GEOCARB” carbon cycle model based on Beerling and Berner (2002) to evaluate several hypotheses associated with global carbon cycle perturbations invoked to explain the mass mortality during the P-T transition. He concluded that the Knoll et al. (2007) hypercapnia hypothesis would imply a lack of CaCO_3 sedimentation, up to a few hundred meters depth on the seafloor, which contradicts observation. He also evaluated the methane hypothesis using the simplified carbon cycle model, where he specified a rapid release (20,000 years) of ^{13}C -depleted methane to the ocean/atmosphere assuming oxidation of CH_4 to CO_2 was instantaneous. The total amount of methane required to replicate the magnitude of CIE at the P/Tr boundary was about 4,200 Gt C (1 Gt C = $1 \text{ Pg C} = 10^{15} \text{ g C}$) which, after oxidation of CO_2 , resulted in only a few hundred ppmv increase in atmospheric $p\text{CO}_2$, deemed insufficient to cause global warming or mass extinction. Nonetheless, Berner (2002) acknowledged the important role methane hydrate may have played in driving down $\delta^{13}\text{C}$ and increasing UV-B radiation from loss of ozone by reaction with excessive methane. Berner (2002) also tested the sudden mass mortality on land hypothesis for the carbon isotope perturbation. The supporting evidence for terrestrial extinction at the P/Tr boundary is a “fungal spike” (Steiner et al., 2003; Visscher et al., 2004; Visscher et al., 2011) suggesting woody plants decomposition, catastrophic soil erosion (Nabbefeld et al., 2010; Sephton et al., 2005; Wang and Visscher, 2007; Xie et al., 2007), loss of terrestrial animals, plants and insects (Dennis et al., 2011; Eiler, 2007) and the disruption of fluvial depositional systems (Newell et al., 2010; Ward et al., 2000). He also suggested that the mass mortality of marine plankton could cause the biological pump to falter, preventing the fecal pellets from settling down to the deep water – the so called “Strangelove Ocean” (Rampino and

Caldeira, 2005). However, the mass mortality itself was not sufficient to cause the magnitude of CIE in sedimentary records, and the amount of CO₂ increase could not explain the mass extinction. The fourth hypothesis Berner evaluated was a drop in the total global organic matter burial rate resulting from a shift in the locus of deposition from terrestrial-plus-marine environments to marine environment alone. By assuming a drop in burial rate and the consequent imbalance between organic burial and organic weathering, the model calculation suggested a slow but prolonged *p*CO₂ increase and a negative CIE, although the rate of change calculated was slower than indicated by the geochronology. Finally, Berner combined the above-mentioned hypotheses (including carbon cycle reorganization, sudden mass mortality of land plants and marine biota, Siberian volcanism and rapid methane release from clathrates) and the calculated results were in good agreement with the observations at the P-T boundary. As a result, a combination of these processes seemed to account for, at least partly, the observed geochemical patterns and the mass extinction. Berner (2002) concluded that the shift in organic carbon deposition from terrestrial to marine environments was the key long term effect of the extinction event, which caused a global organic matter burial rate decrease, driving down atmospheric *p*O₂ and increasing atmospheric *p*CO₂ through the Triassic. It is important to note that the isotope data used in Berner (2002) were found to be affected by diagenesis (Xie et al., 2007), reducing the need to infer a strong decrease in organic matter burial.

Another carbon cycle modeling study coupled a geochemical box model to a 1-D energy balance climate model to show that the CIE could be reproduced with a massive release of ¹³C-depleted CO₂ from mantle degassing associated with the Siberian traps, and a rapid collapse in biological productivity (Grard et al., 2005). They also proposed that phosphorus, as a driver for primary production in their model, played a critical role on the recovery of biological productivity and CIE. Their model adopted a pre-perturbed global average surface ocean temperature of ~21.7 °C, and *p*CO₂ level of 3080 ppmv before the Siberian Traps volcanism and the end-Permian

extinction event (Fig. 4), which is broadly consistent with the temperature proxies and at the high end of the error bars of the $p\text{CO}_2$ proxy data discussed above. They also used a 2% reduced solar luminosity relative to today and the Late Permian paleogeography (Budyko, 1969; Parrish, 1985). The model was forced with both a main eruption phase, which lasted for 600 kyr, and a marine ecosystem collapse with a duration of 100 kyr. The carbon input from volcanic outgassing of CO_2 and mass extinction led to an atmospheric $p\text{CO}_2$ as high as >6000 ppm, resulting in a reduced pole-to-equator temperature gradient and a warmer and wetter pole. Their model seems to reasonably reproduce the extent of the CIE, but failed to match the pattern and rapidity of the CIE across the P-T boundary. A source of uncertainty in their estimated $p\text{CO}_2$ level and temperature arises from the volume of Siberian Trap volcanism, with estimates ranging from 2×10^6 to 4×10^6 km^3 of lava erupted. Their model also generated a large and prolonged positive excursion after the short-lived negative CIE, which was not shown in the P-T isotopic records (Korte and Kozur, 2010), from a simulation with reduced organic burial and the resulting phosphate buildup.

Rampino and Caldeira (2005) used a similar box model to study whether severe reduction of marine productivity could drive the observed CIE across the P-T boundary. They adopted a Late Permian land-ocean area ratio of 90% of the present value as in Berner (1994), which itself required a Late Permian atmospheric $p\text{CO}_2$ level of about $3 \times \text{PAL}^1$ (~850 ppm) to balance the C cycle (Fig. 4). This Late Permian $p\text{CO}_2$ level is lower than the estimate from most other geochemical models (Grard et al., 2005; Payne and Kump, 2007) (Table 2) or proxy studies (Retallack, 2001) but is in general agreement with long-term $p\text{CO}_2$ reconstruction based on geochemical models (Berner, 1991; Berner, 1994; Berner, 2006b; Fig. 3). They also pointed out that the Late Permian was similar to a “Neritan” ocean proposed originally by Zeebe and Westbroek (2003), one that lacked pelagic carbonate production. In their model simulation,

¹The preindustrial atmospheric partial pressure ($p\text{CO}_2$)_{ref} is 280 ppmv unless otherwise noted in this review.

biological productivity was shut down abruptly and allowed to recover to its pre-perturbed value logarithmically over a one million year time scale. They also allowed a 15% organic carbon burial reduction to account for the long-term negative shift in carbonate $\delta^{13}\text{C}$. Their simulated results suggested that both the increase in atmospheric $p\text{CO}_2$ (up to 1700 ppmv increase) and the negative CIE at P-T boundary was the consequence of mass mortality (Fig. 4). Their model also reasonably explained the observed algal/microbial calcification in response to increases in alkalinity. However, Rampino and Caldeira (2005) didn't consider the effect of Siberian Trap volcanism, which has subsequently been shown to be coeval with the biological crisis across the P-T boundary (see below).

In contrast, Payne and Kump (2007) demonstrated, again using a simple box model, that Siberian Traps volcanism could have been responsible for the large carbon isotope fluctuations observed in the latest Permian and Early Triassic, but that other factors, including oxidation of crustal carbon, also likely played a role. The box model they used was similar to that of Grard et al. (2005), but also explicitly balanced carbonate alkalinity, atmospheric oxygen and phosphate. Carbonate alkalinity was delivered to the ocean from carbonate and silicate weathering and removed from the ocean through carbonate burial. Their model utilized a somewhat smaller equilibrium atmospheric $p\text{CO}_2$ level (1500 ppmv) following Berner and Kothavala (2001), compared to that of Grard et al. (2005) (~3000 ppm) (Fig. 4). They tested the model using three eruption scenarios, namely release of 3×10^{18} mol of volcanogenic CO_2 (with $\delta^{13}\text{C} = -5\text{‰}$) over timescales of 100 kyr, 300 kyr and 600 kyr respectively. Any single source, from methane clathrate, oxidized organic carbon or volcanic carbon source alone failed to account for the series of observed CIEs. Several pulses of CO_2 release from volcanic eruption or organic carbon oxidation were required in their model to account for the Early Triassic large fluctuations of $\delta^{13}\text{C}$ records.

3.3. Atmospheric General Circulation Models (AGCMs)

Unlike EBMs or geochemical box modeling, general circulation models (GCMs) are spatially resolved and include calculations of the important state variables at each grid cell using partial differential equations solving the equations of motion of the atmosphere (AGCMs) and oceans (OGCMs). The first climate models that were applied to the Permian climate problem were uncoupled GCMs of two sorts. One was a model with a 3D atmosphere and a simple 2D “surface slab” ocean without ocean circulation (e.g. Kutzbach and Gallimore, 1989; Gibbs et al., 2002), in which the temperature of the ocean was either prescribed or allowed to adjust through energy exchanges with the atmosphere. The other was a model with a 3D ocean and no atmosphere (e.g. Hotinski et al., 2001; Zhang et al., 2001), in which the ocean model was forced with prescribed winds, surface temperature and salinity.

The first general circulation model used to simulate the idealized Pangean climate was a low-resolution, global GCM coupled to a 50 m deep mixed-layer ocean using idealized land-ocean distribution and no topography (Kutzbach and Gallimore, 1989). The authors conducted four suites of sensitivity experiments, in which two different mean elevations (0 m vs. 1000 m), two different snowcovers, two atmospheric $p\text{CO}_2$ levels (1×PAL vs. 5×PAL) and two solar luminosities (modern vs. 1% decreased) were used. The simulations performed confirmed the conceptual models of the Pangean climate, suggesting strong monsoonal circulation, equatorial and continental interior aridity and extreme seasonal temperature variations. Their model results highlighted the importance of geologic boundary conditions, including geography, topography and atmospheric greenhouse gas composition (key boundary conditions are summarized in Table 1).

In order to improve on the previous study of Kutzbach and Gallimore (1989), Kutzbach and Ziegler (1993) simulated the Late Permian climate using the community climate model version 1 (CCM1) of the National Center for Atmospheric Research (NCAR). This model also included a

50 m thick mixed layer ocean with a prescribed poleward transport of heat by the oceans. The advantages of this model in comparison to Kutzbach and Gallimore (1989) were that the horizontal and vertical resolution was higher (12 levels atmosphere), and there were improvements in parameterizations of radiation, clouds, snow cover, and vertical diffusion. The boundary conditions being prescribed in their model included 1) land-ocean distribution and topography from the maps of Ziegler (1990), showing a relatively coarse resolution, a maximum elevation of 2300 m, and an average of 480 m (4.4° latitude $\times$ 7.5° longitude model grid); 2) a prescribed land surface albedo, ranging from 0.13 to 0.24 using the vegetation biome maps for the Kazanian (Ziegler, 1990); 3) a prescribed poleward zonal average ocean heat flux; 4) 1% reduced solar irradiance (1356 W m^{-2} vs. modern value at 1370 W m^{-2}), modern axial tilt (23.5°) and a circular orbital; and 5) atmospheric $p\text{CO}_2$ prescribed at $5\times\text{PAL}$ (Table 1). Kutzbach and Gallimore (1989) tested the effect of the inclusion of extensive inland seas and lakes, and the results indicated that these lakes make a considerable difference in local temperature because of the differences in low-level heating of the atmosphere and the damping of local seasonal temperature range. Modeled climate and biome distribution agreed well with the observed Late Permian distribution. However, there were some important limitations of this type of AGCMs, including the coarse modeling resolution, the oversimplification of treatment of the ocean and the lack of an interactive vegetation model that might bias the regional climate. Another key uncertainty was topography, which had been demonstrated to be a critical parameter as shown by the importance of the uplift of Tibetan plateau on global climate and Asian monsoon (Kutzbach et al., 1989; Kutzbach et al., 1993; Ramstein et al., 1997).

To understand the patterns of Early Triassic ocean circulation, temperature and salinity, a dynamical ocean model with eight vertical levels driven by prescribed surface forcings from Kutzbach and Gallimore (1989) was run by Kutzbach et al. (1990). Their idealized Pangaeian ocean model had a horizontal resolution of 5° latitude $\times$ 5° longitude and 4 km ocean depth. Four

experiments were conducted to investigate the ocean temperature distribution and circulation response to variations in the depth and salinity of the Tethys Ocean. The model results indicated a much warmer high-latitude surface and deep-water temperature in comparison to the present, subtropical anticyclonic (~30° latitude) and subpolar cyclonic (~60°) latitude gyres in the Pathalassic ocean, eastward and poleward flowing equatorial currents and a relatively cool and fresh polar water and warmer and saline Tethys. Unfortunately, there was little, if any geological data that could be directly compared with the model results. With the exception of deep sea sediments of Permian-Triassic age in Japanese and North American subduction-accretion complexes (Isozaki et al., 1990), no deep-sea sediments of Late Permian age remain. Several other limitations to OGCM used by Kutzbach et al. (1990) include its coarse resolution, the idealized Pangaeon geography and ocean bathymetry, its short integration time, prescribed surface forcing from previous OGCM simulations, and the possibility that dynamic coupling between ocean and atmosphere might lead to quite different circulations for the Pangean ocean.

The Wordian (ca. 265 Ma) climate was simulated by Gibbs et al. (2002) using the AGCM GENESIS2 (Global Environmental and Ecological Simulation Interactive Systems version 2; Thompson and Pollard, 1997), and the results compared with the geographic distribution of climate sensitive sediments, including coals, evaporites, eolian sands, carbonate, organic-rich shales, dropstones, tillites and phosphorites. GENESIS2 consisted of an 18 level atmosphere with a land-surface model and a simple 50 m slab ocean, and had a horizontal resolution of 3.75° latitude × 3.75° longitude. Like other A/OGCMs, boundary conditions needed to be specified for GENESIS2 (Table 1), including 1) the Ziegler (1997) land-sea distribution paleogeography and topography map; 2) a 2.1% decrease in solar luminosity (1336 Wm⁻² vs. 1365 Wm⁻² used in GENESIS2); 3) a uniformly distributed vegetation consisting of mixed tree, savanna and grassland; 4) atmospheric *p*CO₂ values of 4× and 8× present levels (345 ppmv was the assigned “present level”); 5) a modern axial tilt (23.5°) and a circular orbital, similar to that in Kutzbach

and Gallimore (1989), although two extreme values for the Pleistocene from Berger (1978) were adopted to investigate the possibility of ice-sheet reappearance, including a warm summer orbit (eccentricity = 0.06 and obliquity = 24.5°) and a cold summer orbit (eccentricity = 0.06 and obliquity = 22.0°). Similar to the findings in previous modeling studies, their model simulated extreme seasonality and aridity in the continental interior during the Wordian. The northward movement of land from Sakmarian (ca. 280 Ma) to Wordian might have led to a cool high latitude winter, stronger winter westerlies and a southward shift of the storm-track precipitation. The model simulations were in generally good agreement with the climate sensitive sediments, except that the simulated extremely cold high-latitude temperatures were inconsistent with the observations, a situation that was attributed to either an incorrect interpretation of the paleoclimate data or limitations of the model.

As a key boundary condition, the configuration of Pangaea has been strongly debated for decades (Irving, 1977; Livermore et al., 1986; Torcq et al., 1997; Van der Voo and French, 1974). Two paleogeographic configurations were proffered: Pangea A and Pangea B, and the differences between them were mainly in the different relative position of Gondwana and Laurussia. Fluteau et al. (2001) conducted a number of climate modeling experiments to help resolve this debate, using a 3D LMD 5.3 (Laboratoire de Météorologie Dynamique version 5.3) AGCM based on that presented in Harzallah and Sadourny (1995), coupled to a soil vegetation model. This model had a mid-latitude horizontal resolution of 400 × 400 km and 11 vertical levels including 8 in troposphere and 3 in stratosphere. The boundary conditions included a prescribed 3×PAL atmospheric $p\text{CO}_2$ (~900 ppm), a similar-to-present pole (0 °C) to equator (25 °C) temperature gradient, and present values of orbital parameters and solar constant (1365 W m^{-2}) (Table 1). The paleogeographic configuration including Pangea A and Pangea B, the land-sea distribution and the paleoelevations of mountain belts were tested in a number of sensitivity analyses. Their

results indicated that the Pangaea B configuration seems to be more consistent with the Late Permian climatic status.

3.4. Ocean General Circulation Models (OGCMs) and the oceanic anoxia hypothesis

Ocean general circulation models coupled to a simple atmosphere with biogeochemistry components have been used to test the following two hypotheses invoked to explain the end-Permian extinction event: 1) anoxic water propagated into shelf regions and epicontinental seas and caused the extinction (Wignall and Twitchett, 1996); and 2) catastrophic release of deep ocean CO₂ upon invigorated ocean circulation and upwelling resulted in CO₂ toxicity (hypercapnia) and led to the extinction (Knoll et al., 1996). Both hypotheses presume a causal relationship between ocean stagnation and the development of large chemical gradients, a relationship that was intuitive but when subject to quantitative evaluation using numerical models, proved largely incorrect.

The ocean anoxia hypothesis was first proposed about 20 years ago by Wignall and Hallam (1992), who found syngenetic pyrite associated with the maximum flooding surface at the P-T boundary in sediments from a couple locations. This finding led to the proposition that anoxia might have caused the end-Permian mass extinction event. Wignall and Twitchett (1996) later extended the evidence of anoxia to a more global extent and into shallow water. Supporting evidence of global deep ocean anoxia came from a number of studies from the obducted accretionary complexes in Japan, which were interpreted to represent pelagic sediments deposited in an anoxic, deep Panthalassic ocean (Isozaki, 1997; Isozaki et al., 1990; Kajiwarara et al., 1994). This proposal of a prolonged “superanoxic” event that significantly preceded the Permian-Triassic boundary and continued into the Early Triassic prompted a number of studies, both modeling and data gathering, aimed at evaluating the extent and duration of anoxia and the mechanisms that might have generated and sustained it.

612

613 In order to investigate whether warming the poles would induce ocean stagnation and if
614 circulation changes would result in anoxia and high CO₂ in the Late Permian deep ocean,
615 Hotinski et al. (2001) conducted numerical experiments using a 3-D OGCM , the Geophysical
616 Fluid Dynamic Laboratory's Modular Ocean Model (MOM version 2), connected to a
617 biogeochemical model of phosphate and oxygen cycling. The model had 4°×4° horizontal
618 resolution, 16 vertical level and fixed values of horizontal and vertical mixing coefficients.
619 Hotinski et al. (2001) ran the model with two climatic forcings, including a high-gradient case
620 which used sea surface temperatures derived from 8×PAL GENESIS simulation for the Late
621 Permian (Gibbs et al., 2002), and a low-gradient, zonally averaged case using the reduced-
622 temperature gradient field from the Paleocene-Eocene Thermal Maximum (a period with extreme
623 polar warmth) simulation by Bice et al. (2000). The high pole-to-equator gradient (-2 – 33 °C)
624 case corresponded to a relatively cool polar ocean (< 0 to 5 °C), and the low pole-to-equator
625 gradient (12 – 28 °C) experiment showed a warmer polar ocean (12 °C), which was similar to that
626 during the Paleocene-Eocene and more consistent with geological observations (Yemane, 1993;
627 Ziegler, 1990). A vigorous ocean circulation and an oxic ocean was observed in their high-
628 gradient experiment, whereas a substantially decreased pole to equator surface density gradient
629 was found in the low-gradient experiment. This suggested that warming the poles slows ocean
630 overturning (although the circulation does not stagnate), and oxygen values are significantly
631 reduced. However, the low-gradient model result did not support lethal build up of H₂S and CO₂
632 in the deep ocean without invoking a large increase in oceanic nutrient level.

633

634 At the same time, two circulation scenarios were being tested by Zhang et al. (2001), who used
635 the MIT 3-D ocean circulation model and a box model of P and O cycles to investigate the issue
636 of anoxia in deep ocean. The two experiments included a vigorous “thermal mode” driven by
637 cooling in southern polar latitudes (sinking in high latitudes, “weak” meridional temperature

gradients) and a weaker “haline mode” driven by an enhanced hydrological cycle (in other words: evaporation from the subtropics) and/or weakened diapycnal mixing in the ocean. The boundary conditions used in these two scenarios were otherwise similar: surface temperatures were prescribed, and the mean salinity of the ocean was assumed to be 34.6 (Table 1). The “thermal” mode had weaker surface wind stress and weaker temperature in comparison to their “haline” mode. Zhang et al. (2001) did not get any significant reduction in deep ocean oxygen in the thermal mode, whereas deep-sea anoxia was observed in the haline mode with enhanced hydrological cycle, which is an expected consequence of the projected global warming (IPCC 2007) .

Differences between the Hotinski et al. (2001) and the Zhang et al. (2001) studies prompted a discussion about their somewhat different definitions of “weak” and “reduced” meridional temperature gradients (Hotinski et al., 2002; Zhang et al., 2003), in which Hotinski et al. (2002) argued that the “weak” T gradient in Zhang et al. (2001) was similar to the “high” T gradient case in Hotinski et al. (2001). The “weaker” meridional temperature gradient in Zhang et al. (2001) was based on an atmospheric GCM of Kutzbach and Gallimore (1989), where the high-latitude average surface temperature was less than 0 °C at 70° South. The “reduced” pole-equator temperature gradients in Hotinski et al. (2001) were based on a Paleocene-Eocene Thermal Maximum modeling study (Bice et al., 2000) indicating a high latitude temperature about 12 °C. These different definitions of “low” and “weak” gradient led to different rates of meridional overturning (zonally integrated mass transport in the north-south plane) and thus differing rates of ventilation of the deep ocean with oxygen. It is important to note that in contrast to Zhang et al. (2001), negative oxygen levels were allowed in the Hotinski et al. (2001) model under the assumption that they represent organic matter decomposition using alternative oxidants (nitrate or sulfate) when oxygen is depleted; Hotinski et al. (2002) argued that the resetting of negative oxygen values to zero in the Zhang et al. (2001) model led to an artificial oxygenation of the deep

ocean.

Kump et al. (2005) used a simple two-box ocean model coupled to an 1-D atmospheric photochemical model to explore the consequence of chemocline upward excursion, a process that is triggered by the destabilization of the chemocline (the transition from oxygenated surface waters to anoxic and sulfidic deepwaters) by sulfide accumulation in the deep sea under severe conditions of eutrophication. Their 1-D atmospheric photochemical modeling suggested that large fluxes of H_2S ($\geq 2000 \times$ present levels) to the atmosphere might have led to lethal levels of H_2S in the atmosphere, the destruction of the ozone layer, and increased atmospheric methane levels, providing a killing mechanism for the end-Permian extinction event in both marine and terrestrial realms. A key finding in Kump et al. (2005) was that in regions with elevated upwelling rate, chemocline upward excursion could be reached when H_2S was high ($\sim 1 \text{ mmol kg}^{-1}$) even under modern atmospheric $p\text{O}_2$ level. Lower levels of H_2S were required for chemocline upward excursion under lower levels of $p\text{O}_2$, such as the proposed low $p\text{O}_2$ atmosphere in the Late Permian (Berner, 2006a).

Subsequent work showed that the high H_2S flux envisioned by Kump et al. (2005) was likely insufficient to cause toxic H_2S levels in the troposphere and ozone destruction in the stratosphere (Beerling et al., 2007), unless a significant CH_4 flux accompanied the high H_2S flux (Lamarque et al., 2007).

3.5. Earth system models of intermediate complexity (EMICs) and fully coupled atmosphere-ocean general circulation models (AOGCMs)

EMICs are particularly useful for investigating long term, large-scale climate changes driven by

forcings with durations of millennia or longer (IPCC 2007), timescales for which high-resolution coupled ocean-atmosphere model simulations become computationally prohibitive. The EMICs used to investigate the late Permian climate systems include GENIE (Meyer et al., 2008), LSG/EBM (large-scale geostrophic ocean general circulation model and coupled atmospheric energy balance model; Winguth and Maier-Reimer 2005), PLASIM (PlanetSimulator Model; Roscher et al., 2011) and the UVic ESCM (University of Victoria Earth System Climate Model; Montenegro et al., 2011). The first two EMICs were used to investigate oceanic chemistry changes, such as oxygen or H₂S responses to increased nutrient contents and *p*CO₂ levels. The later two EMICs included a biome module; Montenegro et al. (2011) emphasized the sensitivity of ocean circulation and oxygen levels to uncertainties in paleogeography and paleobathymetry, and Roscher et al. (2011) focused on estimating climate sensitivity during global warming versus global cooling.

3.5.1 EMICs

Winguth and Maier-Reimer (2005) (hereafter W&M) used the Hamburg large-scale geostrophic ocean GCM coupled to an atmospheric energy balance model (LSG/EBM) to investigate the sensitivity of ocean's thermohaline circulation to a massive methane release and ensuing global warming. In order to study the response of export production and oxygen distribution to ocean circulation changes, W&M also incorporated a simplified marine carbon cycle component known as the Hamburg model of ocean carbon cycle (HAMOCC3). The W&M study was largely a continuation of Winguth et al. (2002) with the addition of a carbon cycle model and additional sensitivity analyses by varying boundary conditions. The boundary conditions of the W&M model were similar to that in Winguth et al. (2002), examining the effects of changes in topography in the polar regions on ocean circulation during the middle Permian. W&M first explored the model sensitivity of ocean circulation in response to changes in thermal and haline boundary conditions by adding a southern hemisphere freshwater source of 2 Sv (Sverdrups, 10⁶

715 $\text{m}^3 \text{s}^{-1}$) and doubled the $p\text{CO}_2$ from 4×PAL to 8×PAL. In their baseline 4×PAL experiment, the
716 deep sea was well oxygenated and lowest oxygen concentration was seen above regions with high
717 export production, which was found in eastern Panthalassic Ocean and east of S. China due to the
718 upwelling of nutrient-rich bottom water. A prominent oxygen minimum zone (OMZ) was
719 observed around ~1,000 m in the eastern equatorial Panthalassa ($[\text{O}_2]$ as low as $20 \mu\text{mol kg}^{-1}$).
720 Simply doubling the $p\text{CO}_2$ from 4×PAL to 8×PAL did not change the results significantly due to
721 the similar poleward heat transport and circulation strength in the deep sea. By inducing
722 freshwater input in the southern hemisphere and doubling the $p\text{CO}_2$, the oxygen-depleted area
723 expanded horizontally in response to a reduced circulation in the tropical region. This supported
724 the idea that a “more sluggish circulation may lead to extended anoxic conditions in the deep-sea”,
725 although the $[\text{O}_2]$ simulated in W&M was much higher than that in the low-gradient scenario of
726 Hotinski et al. (2001) and the haline mode of Zhang et al. (2001). Doubling the atmospheric $p\text{CO}_2$
727 and introducing freshwater input did change the oxygen distributions in the deep ocean, but these
728 changes were insufficient to generate widespread anoxia. W&M also did sensitivity analyses by
729 reducing the export production and adding methane-derived carbon to the atmosphere. They
730 reduced the export production by 10% and found that the oxygen content increased in response to
731 a reduction of organic matter remineralization. Two methane release scenarios were proposed
732 with the amount of carbon released of 7500 Gt C and 4200 Gt C to investigate the ocean
733 circulation changes in response to massive carbon release. They also allowed an atmospheric
734 $p\text{CO}_2$ increase to 18×PAL in response to an instant 7500 Gt C release (methane converted
735 instantaneously to CO_2). Increased atmospheric $p\text{CO}_2$ induced an increase in deep-sea
736 temperature, but did not result in a sluggish thermohaline circulation or widespread deep-sea
737 anoxia. Finally W&M compared their modeling results from three simulations, including the
738 4×PAL baseline experiment, the 8×PAL with southern hemisphere freshwater input experiment,
739 and the 4×PAL along with massive methane release (18×PAL) experiment to climate-sensitive
740 sediments and the reconstructed water mass from Ziegler et al. (1998). The water mass in Ziegler

et al. (1998) was classified in eight categories, including glacial, cold temperate, wet temperate, temperate, upwelling, dry subtropical, tropical, and wet tropical (also see Winguth et al. 2002). All the experiments seemed broadly consistent with the observed geological data, while the 8×PAL simulation generated tropical climate zones that were more consistent with the reconstructed water masses between 30°N and 30°S.

Montenegro et al. (2011) evaluated oceanic anoxia and ocean acidification as the killing mechanisms for the end-Permian mass extinction, using the UVic ESCM (University of Victoria Earth System Climate Model), which consisted of an energy-moisture balance mode, the MOM ocean model, a terrestrial carbon cycle, model and an ocean carbon cycle component. The model had a horizontal resolution of $1.8^{\circ} \times 3.6^{\circ}$ and 15 vertical levels in the ocean. The boundary conditions, including paleogeography, topography and winds were adopted from Kiehl and Shields (2005) (see below). Present-day solar insolation, orbital parameters, atmospheric albedo and zonally averaged atmosphere diffusion were used in the model. Nine experiments were conducted to investigate the effect of changing atmospheric $p\text{CO}_2$ (300, 3000 and 4500 ppmv), paleogeography and bathymetry (Table 1). Sensitivity analyses were performed to understand the impact on ocean circulation of the opening and closing of the seaway between Angara and Euroamerica. Three different ocean bathymetry configurations were evaluated, including a flat bottom with fixed depth at 4 km, arbitrarily distributed meridional ridges, and the best guess of realistic ridge distribution. The modeled temperature and precipitation patterns and biome distributions were in general agreement with the observed sedimentary records and paleontological data (Montenegro et al., 2011 and reference therein). The ocean saturation state dropped dramatically (undersaturated with respect to calcite) in response to an increase in $p\text{CO}_2$, but the widespread anoxia was not observed in the model when ocean bottom topography and paleogeography were changed.

Meyer et al. (2008) used GENIE-1 (Grid Enabled Integrated Earth system model, version 1) to examine the distribution of euxinia in the Latest Permian ocean. GENIE is an EMIC, with 36×36 equal area horizontal grids and 8 or 16 vertical levels, a frictional-geostrophic ocean model and a coarse-resolution 2-D energy moisture balance atmospheric model (Edwards and Marsh, 2005). The key tracers incorporated in the Meyer et al. (2008) version of GENIE included phosphate (PO_4), dissolved inorganic carbon (DIC), alkalinity (ALK), sulfate (SO_4^{2-}), and hydrogen sulfide (H_2S). In Meyer et al. (2008), the atmosphere model in GENIE-1 was forced by the wind stress fields equilibrated at 12×PAL (pre-industrial atmospheric level) $p\text{CO}_2$ from the fully coupled modeling study of Kiehl and Shields (2005), and the same paleogeography and paleobathymetry as in Kiehl and Shields (2005) (Table 1). The atmospheric O_2 was set at the modern value (~0.2095 atm), similar to most other Permian model studies. It has been proposed that the atmospheric oxygen levels during the Late Permian were on its minimum in the Phanerozoic (Berner, 2005) (possibly as low as 15%), so the estimates of oceanic anoxia extent in the modeling study of Meyer et al. (2008) are possibly a minimum. Meyer et al. (2008) conducted two series of simulations to investigate the oceanic H_2S buildup in response to increased phosphate supply (from 1× to 10× modern phosphate content) and the metabolic effect of sulfur phototrophs on the surface ocean chemistry. Consistent with most other studies, at modern phosphate levels the high global average surface temperature does not result in widespread anoxia. However a strong oxygen minimum zone (OMZ) was observed in the Paleo-Tethys Ocean, while the Panthalassic Ocean remains well oxygenated ($[\text{O}_2] > \sim 150 \mu\text{mol kg}^{-1}$). Meyer et al. (2008) found that as PO_4^{3-} concentration increased, the extent of anoxia and ultimately euxinia increased. Upwelling region in Paleo-Tethys formed a “nutrient trap” that enhanced sulfide accumulation. However, including sulfur phototrophy in their experiment significantly reduced the extent of euxinia (as much as 25% decrease in surface $[\text{H}_2\text{S}]$). They proposed that the presence of H_2S in the surface ocean due to increased phosphate concentration (>3× modern levels) could lead to the extreme euxinia that caused the mass extinction in the end-Permian given the fact that H_2S is fatal

to most marine eukaryotes. The spatial distribution of surface-water euxinia in the Meyer et al. (2008) model was in broad agreement with geological evidence, including the known occurrences of the green-sulfur phototroph biomarker isorenieratane (Grice et al., 2005) and framboidal pyrite size distribution (Bond and Wignall, 2010; Wilkin et al., 1996).

While H₂S provides a potent killing mechanism for the end-Permian mass extinction event, the degree of euxinia due to phosphate buildup is uncertain due to the uncertainty about phosphate inventory. Winguth and Winguth (2012) proposed that only a small amount of phosphate increase likely occurred prior to the end-Permian extinction, invoking the arguments of Algeo and Twitchett (2010) that weathering intensity (interpreted as increased riverine phosphate delivery) did not increase until the Early Triassic. Moreover, the evidence for global deepwater anoxia, a feature of the Meyer et al. (2008) simulations above 3× modern [PO₄], has been challenged recently by studies in central Japan (e.g. Algeo et al. 2010), indicating an expansion of the oxygen minimum zone in Panthalassa but no deep basinal anoxia. Other studies in S. China also indicate that the anoxia occurred time-equivalent or slightly prior to the end-Permian extinction event (Brennecke et al., 2011), and did not last millions of years as suggested by Isozaki (1997).

Instead of investigating the extent of euxinia in the ocean, Cui et al. (2013) focused on the paleoclimatic consequences of the addition of three distinctive CO₂ sources, including the release of methane hydrate and thermogenic methane, and the oxidation of organic matter. The GENIE model simulations were forced by δ¹³C of atmospheric CO₂ based on the Meishan record. The rate and total amount of carbon being released was calculated and compared with modern fossil fuel burning. Their favored scenario, the oxidation of fossil organic matter, shows a maximum rate of C release six times smaller than the modern fossil fuel burning rate, the total amount of C much larger and the duration of emission more protracted than those estimated for the current fossil fuel reservoir. The climatic consequence is that global temperature rises up to 6 °C globally,

similar to that estimated by Joachimski et al. (2012) and Sun et al. (2012). The atmospheric $p\text{CO}_2$ almost triples at the peak of the event from 2800 ppm to about 8000 ppm (Fig. 4), while the peak value falls in the range of previous modeling results (e.g. Berner, 2002; Grard et al., 2005; Rampino and Caldeira, 2005) (also see Table 2).

3.5.2 AOGCMs

The fully coupled AOGCM that had been applied in the latest Permian is CCSM3 (Community Climate System Model, Version 3.0; Kiehl and Shields, 2005; Winguth and Winguth 2012) , which includes a 3-D ocean coupled to a 3-D atmosphere, and land and sea-ice using realistic geography and topography (Table 1). Kiehl and Shields (2005) used ideal water-mass age, which is an indicator of ocean mixing efficiency, to infer deep ocean oxygenation because the model did not include oxygen as an explicit tracer. The larger ideal age indicated less efficient ocean mixing, hence less oxygen. The model simulation suggested low oxygen levels at depth in the tropical Panthalassic Ocean, which led the authors to conclude that the simulation was in support of the observed geological data (Isozaki, 1997; Wang et al., 1994). The warm, less-dense water at high latitudes retarded deep-water formation and in turn reduced the efficiency of surface oxygen transport to the deep ocean, presumably resulting in widespread anoxia. The simulated extreme daily temperatures in the dry subtropical regions were consistent with some studies suggesting warming as a killing mechanism for terrestrial life during the P-T transition. Their ocean model indicated warmth over the high-latitude Panthalassic Ocean (zonal mean sea surface temperature up to 8 °C) and at depth (up to 5 °C at 3 km), indicating a weak pole-equator temperature gradient in the ocean. Additionally, their simulated ocean circulation pattern suggested a weak overturning circulation (about 10 Sv) in the latest Permian ocean, and an extremely stratified Tethys sea.

In order to further test the hypothesis of widespread anoxia due to elevated $p\text{CO}_2$ and nutrient supply, Winguth and Winguth (2012) continued the CCSM study of Kiehl and Shields (2005) by

adding a carbon cycle model to their existing 2700 year simulation. The carbon cycle model they used tracks seven variables that are transported in the ocean, including phosphate (PO_4), total dissolved inorganic iron (Fe), dissolved organic phosphorus and iron, dissolved inorganic carbon (DIC), total alkalinity, and dissolved oxygen (O_2). They use boundary and initial conditions from Kiehl and Shields (2005) to initiate and integrate the model for an additional 2,500 years, allowing the tracer distributions to reach equilibrium. They conducted 3 series of simulations to investigate the anoxia distribution due to elevated nutrient or dust input to the ocean and intensification of biological pump.

Similar to previous studies (Kiehl and Shields 2005; Meyer et al. 2008), at $1\times$ modern phosphate level, the Panthalassic and Tethys Ocean were well ventilated. However, the pole to equator sea surface temperature gradient was 5°C higher than the “weak” gradient scenario studied by Hotinski et al. (2001), which showed a widespread anoxia in the deep sea. The greater export productivity induced by nutrient-rich coastal upwelling caused an expansion and intensification of the OMZ in their model. Similar to Meyer et al. (2008), Winguth and Winguth (2012) found that as phosphate content increased from $1\times$ to $10\times$ modern levels, higher productivity induced higher O_2 demand at depth and both vertical and horizontal expansion of OMZ in their model. Their model included Fe limitation on primary productivity, but their experiment with $1\times$ modern phosphate level in combination with a high Fe dust supply ($10\times$ modern Fe supply, so no Fe limitation) didn’t change the O_2 distribution significantly relative to the one without elevated Fe levels, indicating that export production wasn’t severely limited by Fe in their $1\times \text{PO}_4$ experiment. However, with a more deeply penetrative biological pump in the $10\times$ modern phosphate experiments, widespread anoxic conditions were observed throughout the central deep Panthalassa (3,800 m depth), all deep Tethys Oceans, and eastern Boreal Ocean. Unfortunately, Winguth and Winguth (2012) didn’t perform the experiment that would have been most like the $10\times \text{PO}_4$ case of Meyer et al. (2008), i.e., $10\times$ Fe and $10\times \text{PO}_4$. Winguth and Winguth (2012)

concluded that the end-Permian ocean was better represented by the experiments with modern or a small increase in phosphate level, with the elevated nutrient delivery that caused anoxic conditions confined to the Early Triassic due to strong weathering in response to terrestrial ecosystem destruction. Because of this, they suggested anoxia was not widespread enough to have caused the end-Permian mass extinction event.

4. Climatic impact from the Siberian Traps

Investigation of the link between Siberian Traps volcanism and the end-Permian mass extinction event has been a topic of debate for the last 20 years (e.g. Campbell et al., 1992; Basu et al., 1995; Renne et al., 1995; Bowring et al. 1998; Mundil et al., 2004; Saunders and Reichow, 2009). The Siberian Traps large igneous province (LIP) (ca. 252 Ma) contains perhaps the largest eruption of continental basaltic magma known on Earth (Reichow et al., 2009; Reichow et al., 2002), with its volume being estimated between 2 to $5 \times 10^6 \text{ km}^3$ (Renne and Basu, 1991). The Siberian LIPs intruded into and erupted onto the thick sedimentary sequences of the Tunguska basin, including Cambrian evaporites with 1 to 2 km of anhydrites, halite and dolostone, and Ordovician to Permian marls, limestones, sandstones and coal, which contained abundant carbon (C), sulfur (S), fluorine (F) and chlorine (Cl). Geochronological evidence suggested that Siberian Trap eruptions and mass extinction were synchronous (Reichow et al., 2009).

Less attention has been paid in numerical modeling studies to the potential short-term climatic consequences from the eruption of the Siberian Traps, including a decadal scale cooling induced by sulfate aerosol particles produced from the SO_2 emissions and a long-term warming due to the large amount of volcanic CO_2 emissions (Renne et al., 1995). The amount of released volcanic sulfur, halogens, and magmatic waters has been difficult to measure and is highly dependent on the compositions of magma. Measurement of sulfur emission on melt inclusions from the Siberian Traps indicates that the total S degassing was approximately ~6300 to 7800 Gt S (Black

et al., 2012). Modern basalt volcanic eruption observations, such as the 1783-1784 Iceland Laki volcanic eruption that have caused temperature decrease of about 1 °C in the northern hemisphere overall, combined with the effect of acid rain formed through reactions between atmospheric water and sulfur-rich gases, killing livestock and crops (Thordarson and Self, 2003). The estimated emitted SO₂ from this relatively small-scale flood lava eruption is ~120 megatons (Mt) (1 Mt = 10⁶ t), about four orders of magnitude smaller than that estimated from the Siberian Traps, and an order of magnitude smaller than the proposed S release during the Deccan Traps event (Sigurdsson et al., 1992). Both theoretical and observational data confirm the cooling effect from sulfuric acid aerosols: such aerosols reduce the direct sun light reaching Earth surface, backscatter short-wave radiation, altering the energy balance between incoming solar radiation and the outgoing infrared radiation for periods up to several years (Self, 2005; Sigurdsson et al., 1992).

Any cooling on the short term would ultimately have been followed by warming driven by volcanic CO₂ degassing. The total CO₂ released from volcanic degassing, and the extent to which metamorphic reactions driven by dike and sill penetration of organic-rich sedimentary layers released additional CO₂, are key uncertainties in constraining the global atmospheric CO₂ (and temperature) rise. There may also have been a catastrophic biogenic methane clathrate or permafrost methane release triggered by the initial warming from Siberian Traps through climate feedbacks, thus intensify the global warming effect (Krull and Retallack, 2000; Retallack and Jahren, 2008). It has been a challenge to estimate the total amount of CO₂ release due to a number of factors, including the uncertainty in the original volume of the Siberian Traps volcanism (Saunders and Reichow, 2009), contributions from various carbon sources (e.g. metamorphism of dolomite and organic carbon), and the uncertainty in gas generation potentials (Svensen et al., 2009). The CO₂ production potential from contact metamorphism of sediments during the Siberian Traps eruption in Tunguska Basin during pipe formation and the sill emplacement has been estimated (Svensen et al., 2009). Assuming the volume of Siberian Traps volcanism is 1×10⁶

km³ distributed across an area of 2.3×10⁶ km² (Reichow et al., 2002) with a degassing rate of ~0.2 Gt C yr⁻¹ (McCartney et al., 1990; Self et al., 2005), Svensen et al. (2009) estimated basin scale C production potential reaches as high as >30,000 Gt C (corresponding to >100,000 Gt CO₂) from a combination of some volcanic degassing but a significant amount of contact metamorphism of coal (See Table 3 for a summary of the Siberian Traps volcanism).

One can perform a simple mass balance calculation to derive the total amount of carbon release from various sources needed to replicate a -3‰ carbon isotope excursion in the ocean-atmosphere system. Allowing the duration of carbon release to vary from instantaneous (0 kyr), to 20 kyr and 100 kyr, one finds that more carbon is needed to produce the same amount of CIE as the duration of carbon release is prolonged (Fig. 5 and Table 4). There are also uncertainties in the initial total carbon inventory in the ocean-atmosphere system, which one can address by assuming a range of initial DIC conditions (in our case, 38,000 and 53,000 Gt C). One also finds that the calculated total amount of C needed to generate -6‰ CIE is a bit less than twice as large than the amount needed to create a -3‰ CIE (Table 4). Assuming that the ocean remains near saturation with respect to calcite, the equilibrium equation for the saturation state between calcite and atmospheric CO₂ (Broecker and Peng, 1982; Kump and Arthur, 1999) can be used to estimate the air-sea partition of added CO₂, assuming no change in the Ca concentration of seawater:

$$K = \frac{[\text{Ca}^{2+}] \times [\text{HCO}_3^-]^2}{p\text{CO}_2} \quad (8)$$

and the amount of CO₂ remaining in the atmosphere can be determined from the following equation:

$$\left(\frac{[\text{HCO}_3^-]_t}{[\text{HCO}_3^-]_0} \right) = \frac{[p\text{CO}_2]_t}{[p\text{CO}_2]_0} \quad (9)$$

Assuming the initial ocean DIC reservoir is 38,000 Gt C, and the initial atmospheric pCO₂ is

10×PAL, the total C being added is 30,000 Gt C, solving for equation (9) gives $[p\text{CO}_2]_t/[p\text{CO}_2]_0 \approx$
 3. equivalent to ~1.6 doublings of $p\text{CO}_2$. The calculation provided above is an extreme
 simplification of the complex climate system that involves a number of feedbacks and other
 climatic factors, but it does indicate that the magnitudes of CO_2 addition are in the range of what
 would be needed to drive the observed warming, within large uncertainties. This amount of $p\text{CO}_2$
 doubling from simple mass balance calculation is also consistent with the results from more
 sophisticated model (Table 2). If we adopt the suggested 8-9 °C warming for this time period
 from oxygen isotope paleothermometer, the temperature rise would be consistent with a climate
 sensitivity of 5-6 °C per doubling of $p\text{CO}_2$ (Table 2). The implied climate sensitivity should be
 used with caution because of the following reasons. Firstly, the available Permian-Triassic
 paleotemperature proxy data come from limited geographic coverage, thus do not provide an
 accurate representation of global mean surface warming. Secondly, the inferred $p\text{CO}_2$ increases
 throughout the extinction event are mostly based on C isotope inversion, lacking independent
 proxy-data at similar resolution.

5. Conclusions and Future challenges

5.1. Concluding points

1. In summary, from our review of the temperature and $p\text{CO}_2$ proxies that are applicable to the
 pre-Mesozoic sedimentary records, we conclude that Late Permian ocean temperature in the
 tropics could have been as high as 35 °C based on multiple temperature proxies study, and the
 temperature could have risen up to 5-9 °C across the P-T transition. We also find that the
 atmospheric $p\text{CO}_2$ prior to the end-Permian extinction event could have been as high as 4000
 ppm, and $p\text{CO}_2$ might have risen up to >8000 ppm during the event. We find that the temperature
 anomaly during the end-Permian extinction is consistent with ~1.5 doublings of atmospheric

$p\text{CO}_2$, and that the implied climate sensitivity is 5-6 °C, within the upper range of values produced by climate models.

2. From an analysis of the climate modeling studies conducted to date, we conclude that release of ^{13}C -depleted carbon associated with Siberian Traps volcanism is the most plausible explanation of the observed ~4‰ carbon isotope excursion in marine carbonates and the most likely trigger for the mass extinction. Warming was a likely consequence of this CO_2 and CH_4 release, and this, together with eutrophication induced by enhanced weathering input of phosphate from land, likely led to the spread of anoxia and euxinia into shelf waters, at least episodically, during and after the extinction event.

3. It appears that the huge uncertainties concerning boundary conditions, including paleogeography, paleobathymetry, vegetation, and other weaknesses including low model resolution do not significantly impact the fundamental conclusions from climate and ocean modeling concerning global warming during the event and the subsequent establishment of widespread anoxia. However, these conclusions are strongly dependent on estimates of greenhouse gas release and buildup in the atmosphere, as well as the response of the global P cycle to the resulting global warming event, both in magnitude of P delivery and accumulation in the ocean, and duration.

5.2. Future challenges

1. Improving age control will be essential in establishing the duration and relative timing of events, helping us to test the hypotheses of climate warming as a killing mechanism during the end-Permian mass extinction event.

2. More realistic boundary conditions for the ocean and atmosphere are needed to establish a more realistic end-Permian Earth system model that we can use for detailed model-data analysis.

3. Coupled ocean-atmosphere GCMs with biogeochemistry are clearly the best tool to facilitate model-data comparison, as demonstrated by the work of Winguth et al. (2002) and Winguth and Winguth (2012).

4. EMICs capable of performing complete, open system, time-continuous simulations of geological events such as the Permian-Triassic transition (ca. 1 million year time scale) are needed to fully understand the evolution of ocean and atmospheric chemistry and climate change.

Current models have various shortcomings (e.g., GENIE does not presently simulate organic carbon burial and oxidative weathering) that need to be overcome to achieve this objective.

5. Geochemical data collection should be geared more toward establishing regional patterns of ocean chemistry, especially redox conditions but also pH and nutrient availability, rather than with the goal of establishing some sort of average global curve. The geochemical and isotopic evolution of any location on the surface of the Earth is a result of local and global change, and deconvolving those two drivers is critical to a full understanding of the evolution of the biosphere during critical events in Earth history.

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Figure Captions

Figure 1. Long-term environmental variations from the Late Cambrian through the Pliocene. A) Resampled global continental flooding estimates of 5-million-year bin averages at the bin midpoints of 80 time intervals (modified from Hannisdal and Peters, 2011); B to E) Geochemical analyses from marine carbonates (modified from Hannisdal and Peters, 2011). $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ records are from low-latitude based on Prokoph et al. (2008). Solid black lines are averages for the time bins used in Hannisdal and Peters (2011), and the shadowed region brackets the data used in Prokoph et al. (2008); F) Total number of marine genera based on North American fossil occurrences (modified from Hannisdal and Peters, 2011); G) Atmospheric $p\text{CO}_2$ level based on $\delta^{13}\text{C}$ of pedogenic carbonate, plant stomatal density and index and GEOCARB III (modified from Royer et al., 2004).

Figure 2. A) Sea surface temperature (SST) reconstruction based on $\delta^{18}\text{O}$ of conodont *Clarkina* and *Hindeodus* from GSSP Meishan section S. China (modified from Joachimski et al. 2012); B) SST reconstruction based on clumped isotopes from Italy (modified from Brand et al. 2012), blue dots are data from Sass de Putia and red dots are data from Val Brutta.

Figure 3. Atmospheric $p\text{CO}_2$ reconstruction based on two proxies from 255 to 245 Ma. Red circle is $p\text{CO}_2$ value calculated based on $\delta^{13}\text{C}$ of pedogenic carbonate (modified from Ekart et al., 1999) and blue squares are $p\text{CO}_2$ reconstruction based on plant stomatal index (modified from Retallack, 2013). The error bars represent upper and lower limit of the estimated $p\text{CO}_2$ using both methods. Blue shadow indicates $p\text{CO}_2$ range estimated in GEOCARB III.

Figure 4. Atmospheric $p\text{CO}_2$ level across the P-T boundary based on modeling the carbon isotope Excursions. Data shown are modified from the “strangelove” scenario in Rampino and Calderia (2005), the volcanic scenario from Grard et al. (2005) and organic carbon scenario from Cui et al.

1042 (2013). P-T boundary age is based on Shen et al. (2011).

1043

1044 Figure 5. The calculated total amount of carbon required generating the carbon isotope excursion

1045 observed in marine carbonate records, assuming the source of ^{13}C -depleted carbon is volcanic

1046 CO_2 (-6‰ to -12‰), organic matter (-25‰), thermogenic methane (-40‰) and biogenic methane

1047 (-60‰) assuming an initial DIC reservoir of 38,000 Gt C.

1048

Table 1. Overview of the modeling boundary conditions and key results.

Model type	Paleogeography	Paleo-elevations (km)	Solar Luminosity (Wm^{-2})	$p\text{CO}_2$ (ppmv)	Resolution	Key findings	Reference
Low Res. Atm. GCM	Idealized Pangaeon	Mean elevation 0 and 1	1351	1× and 5× PAL	11.6×11.25°	Extreme continentality and large-scale winter and summer monsoon circulations	Kutzbach and Gallimore, 1989
CCM1 of NCAR	Kazanian/Wordian (Ziegler 1990)	0.48 on average	1351	5× PAL	4.4×7.5°	The existence of inland seas and lakes damps the extreme local seasonal range of temperature	Kutzbach and Ziegler 1993
GENESIS 2.0	Wordian map of Ziegler 1997	0-0.2 for lowlands; 0.2-1 for uplands; and >1 for mountains	1336	4× and 8× PAL	3.75×3.75°	The modeled wordian climate matches the data well broadly	Rees et al., 1999
GENESIS 1.02A	Pangaea A (Ziegler et al. 1997)	0.2 for lowlands, 1 for highlands, 2 for collisional mountain belts	1336	4× and 8× PAL	3.75×3.75°	Model simulates large seasonality and high aridity in continental interior	Gibbs et al., 2002
LMD5.3	Pangaea A and Pangaea B;	0.5 – 4.5	1365	900	400×400 km	Pangaea B seems to be the more probable Late Permian Pangaea Plate configuration	Fluteau et al., 2001
PLASIM (includes SECHIBA)	Pangaea A	<5	1340	800 – 10,000	300×300 km	Global cooling mechanisms have a higher climate perturbation potential	Roscher et al., 2011

Table 1 (continued). Overview of the modeling boundary conditions and key results.

Surface forcings	Experiments	Meridional overturning circulation (Sv.)	Maximum Poleward heat transport (PW)	Anoxia	Reference
The Pangea climate simulation from Kutzbach and Gallimore, 1989	I. Prescribed surface forcing				
	II. Same as I, but with increased salinity	N/A	From Kutzbach and Gallimore, 1989	N/A	Kutzbach and Guetter, 1990
	III and IV. Same as I but two different shapes for Tethys basin				
Scenario 1: prescribed zonal mean forcing from Rees et al. 1999; Scenario 2: T. from Paleocene-Eocene simulations in Bice et al. 2000	I. High T gradient;	>80 (S.H.), 15 (N.H.);			
	II. low T gradient	20 (S.H.), 15 (N.H.)	N/A	Large scale anoxia	Hotinski et al., 2001
	I. Thermal mode II. Haline mode	>80 (S.H.), 15 (N.H.); 20 (S.H.), 15 (N.H.)	1.8; 0.4	No large scale anoxia	Zhang et al., 2001
Scenario 1: Prescribed T. and fresh water flux from Kutzbach and Gallimore, 1989, e at 5× PAL and 1% reduction in solar luminosity Freshwater fluxes, momentum fluxes from Gibbs et al. (2002) and heat fluxes by EBM	I. 1×, 2×, 4× and 8×PAL II. Fresh water input from Southern polar III. CO ₂ increases to 18×PAL	~ 60	1.5 to 2.4	No large scale anoxia	Winguth et al., 2005
	10 × PAL	10	N/A	Large-scale anoxia/euxinia	Kiehl and Shields, 2005
CO ₂ : 3550 ppmv (10 × PAL); CH ₄ : 0.7 ppmv, N ₂ O: 0.275 ppmv Scenario 1: 1 × to 10 × [PO ₄] 12×PAL, pCO ₂ and wind stress fields from Kiehl and Shields 2005; 0.2095 atm O ₂ ; Scenario 2: Same as Scenario 1 except adding metabolic effect of sulfur phototrophs to the surface ocean	I. 1 × to 10 × [PO ₄] II. add metabolic effect of sulfur phototrophs to the surface ocean	20-25	N/A	At > 3×[PO ₄] nutrient level, surface H ₂ S builds up at strong upwelling region	Meyer et al., 2008

Table 1 (continued). Overview of the modeling boundary conditions and key results.

Model type	Paleogeography & Paleobathymetry	Salinity	Solar Luminosity (Wm^{-2})	Resolution	Run length (years)	$p\text{CO}_2$ (ppmv)	Reference
8-level dynamical ocean model	Idealized Pangaean ocean; Dmax = 4km, Dmin = 0.5km	34.6	1% reduced	$11^\circ \times 11^\circ$ horizontal	400 for exp. I, 250 for exp. II, III, and IV.	5 $\times$ PAL	al., 1990)(Kutzbach et al., 1990)(Kutzbach et al., 1990)(Kutzbach et
MOM linked to biogeochemical model with O and P cycle	Wordian Geography from Rees et al. 1999; 5.15 km depth flat ocean bottom	N/A	1336	$4^\circ \times 4^\circ$ horizontal, 16 vertical level	2700	2760	Hotinski et al., 2001
Biogeochemical model + 3-box model of O and Dioxide	From D. B. Rowley	34.6	N/A	$2.8^\circ \times 2.8^\circ$ horizontal, 15 vertical level	N/A	5 $\times$ PAL	Zhang et al., 2001
LSG/EBM+HA MOCC3	Wordian Geography from Rees et al. 1999?	35?	1336 (2.1% reduced/1365)	$3.5^\circ \times 3.5^\circ$ horizontal, 11 vertical level	2000	1 $\times$, 2 $\times$, 4 $\times$ and 8 $\times$ PAL	Winguth et al., 2005
CCSM3	From D. B. Rowley; flat bottom ocean bathymetry	35	1338	$3.75^\circ \times 3.75^\circ$ horizontal, 25 vertical level	2700	12.7 $\times$ PAL (3550)	Kiehl and Shields, 2005
GENIE-1	Same as Kiehl and Shields 2005	33.9	1339	36 $\times$ 36 equal area grid, 8 vertical level	10, 000	12 $\times$ PAL (3360)	Meyer et al., 2008

Table 1 (continued). Overview of the modeling boundary conditions and key results.

Surfae forcings	Experiments	Meridional overturning circulation (Sv.)	Maximum Poleward heat transport (PW)	Anoxia	Reference
Forced with present-day zonal mean atmospheric temperature and moisture, zonal means for ocean temperature and salinity and a vegetation free surface	I. $p\text{CO}_2 = 300$ ppm; II. $p\text{CO}_2 = 3000$ ppm; III. $p\text{CO}_2 = 4500$ ppm; IV. open and close ocean gateway between Angara and RuroAmerica; V. flat ocean bottom, arbitrary meridional ridge, and best guess estimate of realistic ridge distribution	15 to 30	N/A	No large-scale anoxia	Montenegro et al., 2011
CO_2 : 3550 ppmv ($10 \times \text{PAL}$); CH_4 : 0.7 ppmv, N_2O : 0.275 ppmv	I. $2 \times [\text{PO}_4]$ II. $4 \times [\text{PO}_4]$ III. $10 \times [\text{PO}_4]$	10	N/A	Large-scale anoxia/euxinia	Winguth and Winguth, 2003

Table 1 (continued). Overview of the modeling boundary conditions and key results.

Model type	Paleogeography &Paleobathymetry	Salinity	Solar Luminosity (Wm ⁻²)	Resolution	Run length (years)	pCO ₂ (ppmv)	Reference
UVic ESCM and a terrestrial carbon model	Same as K&S 2005	Present day	Present day	1.8° × 3.6° horizontal, 15 vertical level	8,000 to 12,000 years	300, 3000 and 4500	Mongenegro et al., 2011
CCSM3 linked to a carbon cycle model	From D. B. Rowley; flat bottom ocean bathymetry	35	1338	3.75° × 3.75° horizontal, 25 vertical level	2,500 additional years using K&S 2005 boundary conditions	12.7× PAL (3550)	Winguth and Winguth, 2012

Table 2. Comparison of sea surface temperature estimates based on proxy and $p\text{CO}_2$ based on modeling across the Permian-Triassic boundary. The inferred climate sensitivity is also shown.

Site	Reference	Proxy method	T (°C)	T (°C)	ΔT	
			pre-extinction	peak-extinction		
Meishan, South China	Joachimski et al., 2012	$\delta^{18}\text{O}_{\text{Hindeodus}}$	~25	~33	8	
	Joachimski et al., 2012	$\delta^{18}\text{O}_{\text{Clarkina}}$	23 to 27	29 to 30	5	
Shangsi, South China	Joachimski et al., 2012	$\delta^{18}\text{O}_{\text{Hindeodus}}$	-	32 to 35	-	
	Joachimski et al., 2012	$\delta^{18}\text{O}_{\text{Clarkina}}$	23 to 24	32	8 to 9	
Italy	Brand et al., 2012	Δ_{47}	30	38	8	
Amount of doubling $p\text{CO}_2$	Reference	Model method	$p\text{CO}_2$ (ppm)	$p\text{CO}_2$ (ppm)	$\Delta p\text{CO}_2$	Climate sensitivity given 8 °C warming
			pre-extinction	peak-extinction		
1.74	Berner et al., 2002	Box model	300	~1000	700	4.6
1.56	Rampino et al., 2005	Box model	850	2500	1650	5.1
1.61	Grard et al., 2005	Box model	3080	9380	6300	5.0
1.4	Payne et al., 2007	Box model	1500	up to 4000	2500	5.7
1.57	Cui et al., 2013	GENIE	2800	8300	5500	5.1

*amount of doubling is calculated from $\log_2(p\text{CO}_2/p\text{CO}_{2,0})$

1059 Table 3.
1060 Summary of Siberian Traps volcanism and its environmental consequences
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Parameter	Value	Reference
Area	$2.5 \text{ to } 5 \times 10^6 \text{ km}^2$	Reichow et al., 2009
Volume	$>2 \times 10^6 \text{ km}^3$ to $>4 \times 10^6 \text{ km}^3$, but only $4 \times 10^5 \text{ km}^3$ currently remain	Courtillot et al., 1999; Wignall, 2001
CO₂ release from Siberian Traps	$1.6 \times 10^{18} \text{ mol CO}_2$	Svensen et al., 2009
Age of initial Siberian Traps eruption	251.2±3.4 Ma (^{238}U - ^{206}Pb), 250±1.6 Ma ($^{40}\text{Ar}/^{39}\text{Ar}$), 252.0±0.4 Ma (^{238}U - ^{206}Pb), 253.3±2.6 Ma ($^{40}\text{Ar}/^{39}\text{Ar}$)	Basu et al. 1995; Renne et al., 1995; Kamo et al., 1996; Reichow et al., 2009; Svensen et al., 2009
Age of main phase Siberian Traps eruption	251.7 Ma (^{238}U - ^{206}Pb) from the lowermost lava unit	Kamo et al., 2003
Duration of eruptions	<2 million years	Reichow et al., 2009
Age of mass extinction	$252.28 \pm 0.08 \text{ Ma}$ (^{238}U - ^{206}Pb)	Shen et al., 2011
CO₂ consumption due to weathering of the Siberian Traps	$0.053 \times 10^{12} \text{ mol yr}^{-1}$	Grard et al., 2005
Volatiles release	Approximately 6300-7800 Gt S, 3400-8700 Gt Cl, and 7,100-13,600 Gt F	Black et al., 2012
Temperature rise	6 to 8 °C	Brand et al., 2012; Joachimski et al., 2012

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Table 4. Mass balance calculations for the total amount of carbon required generating the carbon isotope excursion (CIE) observed in marine carbonate.

Initial DIC (Gt C*)	Source of ¹³ C-depleted carbon	δ ¹³ C (‰)	Total amount (Gt C) if CIE = -3‰**	Total amount (Gt C) if CIE = -6‰
53,000	Mantle degassing CO₂	-6	35439	62018
	Pyroxene-derived melt**	-12	17719	31009
	Organic matter	-25	8505	14884
	Thermogenic methane	-40	5316	9302
	Biogenic methane	-60	3544	6202
38,000	Mantle degassing CO₂	-6	25333	44333
	Pyroxene-derived melt	-12	12667	22167
	Organic matter	-25	6080	10640
	Thermogenic methane	-40	3800	6650
	Biogenic methane	-60	2533	4433

*1 Gt C = 1 Pg C = 10¹⁵ g C

**C isotope mass balance calculation: (ΔM+M) * (δ¹³C+Δ¹³C) = M*δ¹³C + ΔM*δ¹³C_{source}

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Figure

Figure 2. A) Sea surface temperature (SST) reconstruction based on $\delta^{18}\text{O}$ of conodont *Clarkina* and *Hindeodus* from GSSP Meishan section S. China (modified from Joachimski et al. 2012); B) SST reconstruction based on clumped isotopes from Italy (modified from Brand et al. 2012), blue dots are data from Sass de Putia and red dots are data from Val Brutta.

Figure

Figure 3. Atmospheric pCO₂ reconstruction based on two proxies from 255 to 245 Ma. Red circle is pCO₂ value calculated based on $\delta^{13}\text{C}$ of pedogenic carbonate (modified from Ekart et al., 1999) and blue squares are pCO₂ reconstruction based on plant stomatal index (modified from Retallack, 2013). The error bars represent upper and lower limit of the estimated pCO₂ using both methods. Blue shadow indicates pCO₂ range estimated in GEOCARB III.

Figure 4. Atmospheric pCO_2 level across the P-T boundary based on modeling the carbon isotope Excursions. Data shown are modified from the “strangelove” scenario in Rampino and Calderia (2005), the volcanic scenario from Grard et al. (2005) and organic carbon scenario from Cui et al. (2013). P-T boundary age is based on Shen et al. (2011).

Figure

Figure 5. The calculated total amount of carbon required generating the carbon isotope excursion observed in marine carbonate records, assuming the source of ^{13}C -depleted carbon is volcanic CO_2 (-6‰ to -12‰), organic matter (-25‰), thermogenic methane (-40‰) and biogenic methane (-60‰) assuming an initial DIC reservoir of 38,000 Gt C.