# Marine anoxia and ocean acidification due to CO2 degassing from Siberian Traps volcanism during the end-Permian extinction

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The largest mass extinction event in the Phanerozoic, known as the end-Permian mass extinction (or EPME, ca. 252 Ma) is coincident with the main eruption phase of Siberian Traps volcanism (ca. 252 to 250 Ma). This volcanism is estimated to have a volume larger than $2 \times 10^6$ km$^3$, and can release both mantle carbon dioxide (CO2) through extrusions and thermogenic methane (CH4) and CO2 through intrusions into the atmosphere. The climatic consequences of these greenhouse gases are devastating to both marine and terrestrial lives and delay the recovery of ecosystems after the extinction. Quantitatively, the amount of CO2 released can be estimated using global carbon cycle model or plant and soil-based proxies with varying time resolution. The extent of increase in oceanic anoxic area can be estimated using uranium isotopes ($\delta^{238}$U) and a uranium mass balance model. Calcium isotope ($\delta^{44}$Ca) records across the end-Permian extinction event may be used to evaluate ocean acidification. We suggest that lethally hot temperature, excessive nutrient load in the ocean, and decreased strength of meridional
overturning circulation, along with ocean acidification in a poorly buffered ocean, potentially triggered by the Siberian Traps LIP, worked together to create the most severe bio crisis and delayed recovery in the Earth history.
Marine anoxia and ocean acidification due to CO₂ degassing from Siberian Traps volcanism during the end-Permian extinction

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Abstract

The largest mass extinction event in the Phanerozoic, known as the end-Permian mass extinction (or EPME, ca. 252 Ma) is coincident with the main eruption phase of Siberian Traps volcanism (ca. 252 to 250 Ma). This volcanism is estimated to have a volume larger than 2×10⁶ km³, and can release both mantle carbon dioxide (CO₂) through extrusions and thermogenic methane (CH₄) and CO₂ through intrusions into the atmosphere. The climatic consequences of these greenhouse gases is devastating to both marine and terrestrial lives and delay the recovery of ecosystems after the extinction. Quantitatively, the amount of CO₂ released can be estimated using global carbon cycle model or plant and soil-based proxies with varying time resolution. The extent of increase in oceanic anoxic area can be estimated using uranium isotopes (δ²³⁸U) and a uranium mass balance model. Calcium isotope (δ⁴⁴Ca) records across the end-Permian extinction event may be used to evaluate ocean acidification. We suggest that lethally hot temperature, excessive nutrient load in the ocean, and decreased strength of meridional overturning circulation, along with ocean acidification in a poorly buffered ocean, potentially triggered by the Siberian Traps LIP, worked together to create the most severe bio crisis and delayed recovery in the Earth history.

Key words: end-Permian, mass extinction, Siberian Traps large igneous province, Earth system model, uranium isotopes, calcium isotopes

Introduction

The end-Permian mass extinction event (or EPME, ca. 252 Ma) (Burgess et al., 2014) is the largest biodiversity loss in the Phanerozoic (Benton, 2018). The EPME is accompanied by a rapid temperature increase of 5 to 10 °C (Chen et al., 2016; Joachimski et al., 2012), and is considered as a “hyperthermal” event (Foster et al., 2018). The initial warming started at 251.939±0.031Ma, and has a duration less than 31 kyr (Shen et al., 2019). An abrupt CO₂ release during the rapid emplacement of the Siberian Traps large igneous province (LIP) is thought to be the trigger of the rapid warming (Ganino and Arndt, 2009; Ogden and Sleep, 2012; Svensen et al., 2009; Burgess et al., 2017). Because of the rapidity of the CO₂-induced warming, the EPME is considered as one of the best analogues for the 21st century global warming (Payne and Clapham, 2012). The exact amount and pace of such CO₂ release cannot be readily estimated due to the uncertainties in emission durations and the type of crustal material intruded by the magma (Black et al., 2012; McElwain et al., 2005; Svensen et al., 2009; Svensen et al., 2018). Volcanic degassing estimates...
of CO₂ release through contact metamorphism with carbon-rich sediments range from 10^{19} to 10^{20} g CO₂ during multiple brief pulses, each lasted less than 10 kyr (Black and Manga, 2017). Carbon isotope inverse modeling estimates the rate of CO₂ release during the EPME that matches the observed carbon isotope excursion (CIE) in marine carbonate, with a best-fit scenario consistent with the magmatic intrusion into organic-rich sediments in the Tunguska basin (Cui et al., 2015; Cui et al., 2013). Although there is no consensus on how much carbon was released associated with the Siberian Traps volcanism, it is clear that the rapid increase in CO₂ concentration is responsible for the abrupt warming across the extinction event and the prolonged warming into the Early Triassic (Sun et al., 2012).

Despite the limitations in constraining the CO₂ quantity, several lines of geochemical evidence support the expected consequences of large release of CO₂. In addition to global temperature rise, catastrophic increase in continental chemical weathering rates (Sephton et al., 2005; Sun et al., 2018), excessive nutrient levels in the ocean (Shen et al., 2015), expansion of ocean anoxic area (Bond and Wignall, 2010; Zhang et al., 2018a,b), and ocean acidification (Cui et al., 2015; Payne et al., 2010) have all been observed related to the mass extinction. However, there is no agreement on whether ocean acidification or anoxia is the ultimate killing mechanism. Studies on marine extinction pattern suggest that organisms with poor buffered physiology such as rugose corals and brachiopods preferentially suffered higher extinction rate than other well-buffered groups (Clapham and Payne, 2011). Deep water anoxia has also long been proposed to be the cause of mass extinction (Wilde and Berry, 1982), and thought to provide a leading killing mechanism for the end-Permian (Wignall, 2007; Wignall and Twichett, 1996). These two competing mechanisms are not mutually exclusive, as suggested by recent studies on stable calcium (δ^{44}Ca) and uranium isotopes (δ^{238}U), serving as proxies for ocean acidification and deep sea anoxia respectively (Hinojosa et al., 2012; Payne et al., 2010; Zhang et al., 2018). With the development of Earth system model of intermediate complexity (EMIC) that tracks global carbon cycle (Hülse et al., 2018; Ridgwell and Hargreaves, 2007), it provides an opportunity to evaluate the two mechanisms in the context of rising CO₂ across the extinction event.

In this review, we begin with the recent applications of EMIC to the EPME, and introduce the rationales for applying δ^{44}Ca and δ^{238}U as proxies for ocean acidification and anoxia, and also suggest opportunities to use model-data comparison to further evaluate these two hypotheses.

**Link between the weak buffering and the mass extinction**

It has long been recognized that the end-Permian extinction in the ocean is linked to physiological stress due to elevated pCO₂ and temperature, leading to reduced saturation state (ocean acidification) and oxygen concentration (marine anoxia) (Clapham and Payne, 2011; Knoll et al., 2007). A multiple logistic regression study revealed that genera with poorly buffered physiology in their intercellular chemistry and shell calcification suffered severe extinction during the extinction event (Clapham and Payne, 2011). These poorly buffered organisms have either calcite or aragonite shell and skeletal mineralogy, and include brachiopods, bryozoans, corals, crinoids and sponges according to the classification by Kiessling and Simpson (2011) and Knoll et al. (1996). Among these organisms, corals and sponges are the major reef builders, which have high ratio of skeleton/biomass and have encountered the largest reef-building crisis (Kiessling, 2009), likely due to the rapid increase in atmospheric CO₂ and associated decline in surface ocean pH and carbonate ion concentration (Cui et al., 2015). However, direct evidence for pH change, such as
boron isotope proxy (δ¹¹B) remains controversial, because δ¹¹B did not show a pH decline until after the main phase of the mass extinction (Clarkson et al., 2015). Other indirect evidence, such as calcium isotopes from carbonate and calcium phosphate of conodont fossils and biomineralization pattern of brachiopods supports ocean acidification (Hinojosa et al., 2012; Payne et al., 2010; Garbelli et al; 2017; Silva-Tamayo et al., 2018).

To evaluate the extent of ocean acidification and its effect on marine organisms, it is important to know the rate of CO₂ increases, because the degree of seawater-pH and CaCO₃ saturation state changes depends largely on the rate at which atmospheric CO₂ increases (Hönisch et al., 2012). The total CO₂ release associated with Siberian Traps volcanism ranges from ~7,000 to 43,000 PgC within 20 to 400 Kyr (Clarkson et al., 2015; Cui et al., 2013; Shen et al., 2011; Sobolev et al., 2011; Svensen et al., 2009). The rate of CO₂ release varies from 0.7 to 66 Pg C yr⁻¹, depending on the δ¹³C value of the carbon source (Cui et al., 2015; Svensen et al., 2009). The numerical model solution for the carbon source is not unique and relies on comparing the simulated ocean temperature to proxy records. The global temperature increase across the extinction event is 5 to 10 °C based on oxygen isotopes of well-preserved conodonts and clumped isotopes (Brand et al., 2012; Chen et al., 2016; Joachimski et al., 2012; Shen et al., 2019), which exclude the possibility of volcanic CO₂ as a single source because the temperature increase would have been too high compared to the proxy records (Cui et al., 2015). Quantifying the CO₂ release at better temporal resolution during the end-Permian extinction event is not only critical to better understand the extinction mechanism of the EPME, but also offers important insight to the anthropogenic CO₂ emissions-induced future climate change (Clapham and Renne, 2019).

Moreover, the Late Permian ocean is less well buffered to the carbon cycle perturbation relative to today’s ocean due to the lack of pelagic carbonate producers (Ridgwell, 2005; Ridgwell et al., 2003; Ridgwell and Zeebe, 2005). The lower sea level (Haq and Schutter, 2008; Yin et al., 2014), resulted in reduced area for carbonate deposition (Fig. 1). Increased weathering rate due to elevated temperature at the Late Permian and the smaller available area for carbonate burial leads to extreme imbalance of the carbon cycle, which perhaps allowed for the buildup of the ocean dissolved inorganic carbon reservoir (Rothman et al., 2014). The poor buffering of the Late Permian ocean makes it extremely sensitive to the light carbon addition, in terms of ocean saturation state, as well as the ocean oxygen concentration. With a poorly buffered pre-existing condition, a rapid large pulse of carbon addition might have overwhelmed the silicate weathering feedback, which would have prolonged the Early Triassic warming (Kump, 2018).
Figure 1. Modern vs. end-Permian carbonate production diagram. A. modern steady state, where weathering input of Ca\(^{2+}\) and CO\(_3^{2-}\) equals the burial of CaCO\(_3\) in both shallow neritic setting ("coral reef") and the deep sea ("Cretan ocean"). B. end-Permian imbalance between the weathering input and the burial of CaCO\(_3\) with lower sea level and no pelagic carbonate production.

**cGENIE configuration for the end-Permian**

Carbon cycle Grid-ENabled Integrated Earth system model (cGENIE) is a type of EMIC model, which has an efficient climate model (Edwards and Marsh, 2005), and allows for multi-million year simulation of the carbon cycle within the ocean and sedimentary systems (Colbourn et al., 2015; Hülse et al., 2017; Ridgwell and Hargreaves, 2007). The model treats the ocean biogeochemistry as an open system, which allows for inputs from continental weathering and outputs through the burial of marine sediments on the seafloor (Colbourn, 2011; Ridgwell, 2007). Because the deep ocean seafloor is subducted and there is effectively no pelagic carbonate producers prior to 150 Ma (Knoll and Follows, 2016; Ridgwell, 2005), the sediment model of the Late Permian needs to be configured to simulate the preservation of calcite and aragonite in shallow-marine sediments, known as “reef” in cGENIE (Ridgwell et al., 2003) (Fig. 1). The extent to which calcite or aragonite is preserved is a function of water chemistry and the rain ratio of CaCO\(_3\) and particulate organic carbon (CaCO\(_3/\)POC) (Archer, 1991). The ocean carbonate chemistry of the end-Permian is poorly known, but the carbonate saturation state \(\Omega_{\text{calcite}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]/K_{sp}\) is generally thought to be slightly lower than today with respect to calcite, with a value of around 5 (Ridgwell, 2005). These neritic production of carbonate is set as a function of local saturation state for the Late Permian:

\[
f_{\text{CaCO}_3} = A \times \lambda \times (\Omega_{\text{calcite}} - 1)^n
\]

where \(A\) is the neritic area estimated to be \(27 \times 10^6\) m\(^2\) (Menard and Smith, 1966), \(\lambda\) is a scaling factor for neritic production of carbonate set to be 0.4, and \(n\) is a ‘process’ power with a value of
1.7 (Ridgwell, 2005). At steady state, the burial rate has to equal to the flux of weathering delivery of [Ca$^{2+}$], [CO$_3^{2-}$], and [HCO$_3^{-}$]. The primary producers of the surface ocean fix CO$_2$ through photosynthesis and the maximum rate of respiration and decomposition occur at the e-folding depth (m). Cui et al. (2013) simulated CO$_2$ emission using a carbon isotope inversion approach using an EMIC. Before any perturbations were imposed, the cGENIE model was run to steady state to balance the weathering flux of dissolved inorganic carbon (DIC) and alkalinity (ALK) and the sedimentary burial of CaCO$_3$ (Cui et al., 2013). The DIC flux at steady state has been set to be 17 Tmol yr$^{-1}$ from carbonate rocks and 11 Tmol yr$^{-1}$ from silicate rocks (Colbourn, 2011; Cui et al., 2013). The ALK flux is set at 56 Tmol yr$^{-1}$, consistent with the end-Permian sea-level and the weathering regime (Gibbs et al., 1999). The volcanic outgassing flux is set to equal the silicate weathering flux at 11 Tmol yr$^{-1}$. [Ca$^{2+}$] concentration is commonly estimated from fluid inclusion, and is set to be 13 mmol kg$^{-1}$. The atmospheric CO$_2$ level of the end-Permian is perhaps the most uncertain parameter of the model. Values ranging from 300 (Li et al., 2018) to 7000 ppm (Ekart et al., 1999; Retallack, 2013) have been reported for the Late Permian, but significant uncertainties are associated with these estimates (Cui and Kump, 2015). The EMIC model used 10× preindustrial atmospheric level (10× PAL; ca. 2800 ppm), a slightly lower CO$_2$ level compared to that chosen by Kiehl and Shields (2005) (ca. 3500 ppm), but similar to Hotinski et al. (2001) to compensate the weak solar luminosity and to guarantee an ice-free condition (Black et al., 2018; Cui et al., 2015; Cui et al., 2013). This CO$_2$ level has not been tested for uncertainty with a reliable proxy that is suitable for this time period, but is much needed to understand the pre-existing background climate condition of the Late Permian.

The modeled spatial distributions of ocean anoxia and ocean acidification are shown in Fig. 2. These results are from the best-fit scenario, where the exogenic carbon source is assumed to be organic matter/coal burning ($\delta^{13}$C = -25‰) through contact metamorphism during the sill intrusion of the Siberian Traps volcanism. Before any perturbation is applied to the ocean-atmosphere system, the model was run to steady-state to allow a balance between the weathering and the burial flux of calcium carbonate. At steady state, the vigorous ocean circulation leads to a well-oxygenated ocean, with a global average oxygen concentration of 156 μmol kg$^{-1}$ and calcite saturation state of 5. After 30,000 Gt C was added to the system, $p$CO$_2$ level doubled two times from 2,800 to ~11,000 ppm, and global temperature rises by more than 6 degrees, consistent with a climate sensitivity of 3 °C per doubling of CO$_2$ (Knutti and Hegerl, 2008). Both oxygen concentration and carbonate saturation state decreased dramatically after the carbon is added (Fig. 2). The global average oxygen concentration decreases to 110 μmol kg$^{-1}$, while the deep ocean oxygen concentration down to 50 μmol kg$^{-1}$, reaching the lethal threshold for many marine species (Vaquer-Sunyer and Duarte, 2008), including fishes, mollusks, crustacea, bivalve and gastropoda. Ocean calcite saturation state ($\Omega_{\text{calcite}}$) decreases by 50% globally, while large areas in high-latitude surface regions suffer under saturation which allows calcite dissolution to occur (Fig. 2D). Global draw down of dissolved oxygen and decreased calcite saturation state in the ocean can both lead to the deteriorated environmental condition to marine organisms, forcing them to find refugees or become extinct.
Figure 2. cGenie model results of the best-fit scenario (exogenic carbon source with $\delta^{13}C$ of -25‰). A. steady-state ocean oxygen concentration at time 0 before any forcing is applied; B. Ocean oxygen at 70 kyr of model simulation time when carbon emission rate and mass reaches its maximum; C. Steady-state carbonate saturation state; and D. Carbonate saturation state at 70 kyr.

Calcium isotopes in marine carbonates and phosphates
The marine Ca cycle interacts with the C cycle through chemical weathering and carbonate precipitation, therefore, Ca isotope ($\delta^{44/40}Ca$) records could provide constraint on environmental changes across the EPME. Isotopically depleted Ca ions are delivered by continental weathering, groundwater, and hydrothermal fluxes into the oceans where they are removed via calcium carbonate precipitation (Christina and DePaolo, 2000; Fantle, 2010; Fantle and Tipper, 2014; Milliman, 1993). Accordingly, the imbalance of input and burial fluxes of Ca impart the changes of $\delta^{44/40}Ca$ in the ocean and in sediments. During the precipitation of calcium carbonate, the light stable isotope of calcium, $^{40}Ca$, is preferentially incorporated into the mineral phase, leaving seawater enriched in $^{44}Ca$ (AlKhatib and Eisenhauer, 2017b; Böhm et al., 2006; Gussone et al., 2003). The $\delta^{44/40}Ca$ ratios of bulk marine carbonates, therefore, has been suggested as a proxy to reconstruct environmental changes and chemical evolution of seawater over tens of thousands to hundreds of millions of years (Blättler et al., 2011; Du Vivier et al., 2015; Farkaš et al., 2007; Griffith et al., 2015; Payne et al., 2010). Recent studies have documented negative shifts (up to ~0.6‰) in $\delta^{44/40}Ca$ records of bulk carbonate and conodont across the EMPE in several globally
distributed sections (Fig. 3) (Hinojosa et al., 2012; Payne et al., 2010; Silva-Tamayo et al., 2018). Previous research suggests that this proxy can respond to several factors in a variety of ways and invite non-unique interpretations.

Recent advances in our understanding of the Siberian Traps volcanism suggests that the CO$_2$ emission induced by the eruption of this LIP can lead to severe perturbations of the carbon cycle, which led to changes in carbonate chemistry and the mass extinction (Burgess et al., 2017; Payne and Clapham, 2012; Wignall, 2001). Conceptually, reduction in carbonate deposition allows Ca ion to accumulate in seawater, while carbonate dissolution releases isotopically depleted Ca into seawater, both conditions could result in negative $\delta^{44/40}$Ca excursions (e.g. Payne et al., 2010). However, recent modeling suggests that ocean acidification can only explain a small $\delta^{44/40}$Ca excursion in seawater (Komar and Zeebe, 2015; Silva-Tamayo et al., 2018), suggesting other factors, such as increase in Ca isotope fractionation and extensive calcium input, should also have attributed to the 0.6‰ negative excursions.

The increase in Ca isotope fractionation may stem from kinetic fractionation effect associated with increased carbonate precipitation rate (AlKhatib and Eisenhauer, 2017a; Tang et al., 2008) or the different Ca fractionation between aragonite and calcite (Blättler et al., 2012; Gussone et al., 2005; Gussone et al., 2003; Pruss et al., 2018). However, large increase in $\rho$CO$_2$ from volcanic outgassing is unfavorable to carbonate burial as indicated by negative $\delta^{13}$C excursions in both carbonate and organic matter (Corsetti et al., 2005; Korte and Kozur, 2010; Shen et al., 2013; Shen et al., 2011). Although microbial carbonate precipitation and inorganic carbonate accumulation in the form of oolites and carbonate cements increased in the Lower Triassic (Lehrmann et al., 2003; Reinhardt, 1988; Schubert and Bottjer, 1995), they overlie the negative $\delta^{44/40}$Ca excursions in most of places and may indicate the alkalinity overshoot effect as the aftermath of large CO$_2$ emission (Cui et al., 2013; Cui et al., 2011; Kump et al., 2009; Penman et al., 2016). The precipitation of aragonite exhibits a larger magnitude of Ca fractionation (up to $\sim$0.6‰), lowering $\delta^{44/40}$Ca value in aragonite compared to calcite. This fractionation offset is sufficient to produce local negative $\delta^{44/40}$Ca shift if the initial polymorphs changed from calcite to aragonite across the EMPE (Lau et al., 2017). A universal mechanism leading to this mineralogy shift, therefore, is needed because negative $\delta^{44/40}$Ca excursions occurred globally across the EMPE.

The $\delta^{44/40}$Ca records of hydroxyapatite, which is independent from fractionation variations in different carbonate polymorphs, suggest that the Ca cycle perturbation has shifted seawater $\delta^{44/40}$Ca signatures to lower values across the EMPE. The most straightforward explanation for the negative $\delta^{44/40}$Ca excursions across EPME is increased carbonate weathering (and dissolution), which induced extensive delivery of light Ca over short period of time. Since the end-Permian features perhaps the lowest sea level in the Phanerozoic (Haq et al., 1987; Haq and Schutter, 2008; Yin et al., 2014), large-scale regression could have exposed massive amount of shelf carbonates. Geochemical evidence suggests that the CO$_2$ emission-induced climate change enhances carbonate weathering delivering excessive amount of Ca into the ocean system (Song et al., 2015). Shelf carbonates predominately comprise aragonite (Stoll and Schrag, 1998), which has relatively low $\delta^{44/40}$Ca values (Gussone et al., 2005). This effect combined with the transient carbonate burial stress created by acidification represents a state of disequilibrium between weathering and carbonate sedimentation in the poorly buffered Permian ocean, causing isotopically-depleted Ca to accumulate in seawater shifting the seawater $\delta^{44/40}$Ca signatures. With increased calcium and
alkalinity, the carbonate system will eventually overcome the acidification with extensive carbonate deposition (Caldeira and Wickett, 2003; Opdyke and Wilkinson, 1993). The $\delta^{44/40}$Ca records across EMPE provide valuable information for quantifying the amount and rate of volcanic CO$_2$ emission via carbonate weathering or depositional flux.

In addition, diagenetic issues merit attention when dealing with calcium isotopic measurements within bulk carbonate records. Recent studies raised concern that early diagenesis before lithification could alter the $\delta^{44/40}$Ca records while maintaining unaltered patterns for other diagenesis proxies, such as Mn/Sr (Ahm et al., 2018; Higgins et al., 2018). Recrystallized calcite or transformed calcite formed under early diagenesis are usually associated with a slower precipitation rate and smaller fractionation, resulting in higher $\delta^{44/40}$Ca values than normal carbonate (Fantle and DePaolo, 2007; Fantle and Higgins, 2014; Jacobson and Holmden, 2008). Therefore, detailed petrological analysis and measurements of paired proxies (e.g. $\delta^{13}$C, $\delta^{18}$O, trace metals, rare earth elements) needs to be carefully conducted to distinguish the diagenetic patterns (Banner and Hanson, 1990; Bathurst, 1972; Brand and Veizer, 1980, 1981; Swart, 2015).

Despite the multifaceted interpretations, negative calcium isotope excursion at the extinction horizon (Fig. 3) are consistent with the ocean acidification scenario. The onset of the $\delta^{44/40}$Ca negative excursion from four sites in S. China (Meishan and Dajiang sections), Italy (Tesero, GK-1 core) and Turkey (Taskent section) coincides with the onset of $\delta^{13}$C$_{\text{carb}}$ excursion, suggesting the driver that leads to $\delta^{13}$C$_{\text{carb}}$ decrease must have drawn down the $\delta^{44/40}$Ca as well (Hinojosa et al., 2012; Silva-Tamayo et al., 2018). Although distributed widely, these sites are all located around the Paleo-Tethys ocean, with limited connection to the open Panthalassic ocean. Therefore, future data from the Panthalassic ocean are needed to evaluate the global calcium cycle perturbation.
Figure 3. Combined δ¹³C (black circles) and δ⁴⁴/⁴⁰Ca (red circles) records from representative Permian-Triassic boundary sections. Meishan section - δ¹³C data of bulk sediment from Shen et al. (2012) and δ⁴⁴/⁴⁰Ca of hydroxyapatite records from Hinojosa et al. (2012); Dajiang section - δ¹³C and δ⁴⁴/⁴⁰Ca records of bulk carbonates from Payne et al. (2010); Tesero and Taskent sections - δ¹³C and δ⁴⁴/⁴⁰Ca records of bulk carbonates from Silva-Tamayo et al. (2018).

Uranium isotopes in marine carbonates across the end-Permian mass extinction

Widespread changes in marine redox condition across the EMPE have been inferred for decades, based on a variety of existing proxies (e.g., Isozaki, 1997; Grice et al., 2005; Cao et al., 2009). The EPME may have encountered the most significant change in marine redox condition, in terms of the extent and duration, in the last 500 Ma. While there is broad consensus that enhanced marine anoxia developed during the EPME crisis, the details of timing, duration, and extent are less clear. Existing models vary from an early onset versus development at the end-Permian mass extinction, from expansion of the oxygen-minimum zones to whole-ocean anoxia (e.g., Algeo et al., 2010; Brennecka et al., 2011; Grice et al., 2005; Isozaki, 1997; Kato et al., 2002; Wignall and Twitchett, 1996). These different models arise due to the application of local or indirect paleo-redox proxies to infer global marine redox perturbations. For example, pyrite framboids, biomarker, Fe mineralogy, Fe speciation, redox sensitive trace mental concentrations and ratios, and Ce anomalies are all powerful proxies of ocean anoxia, however, these are inherent local redox indicators and cannot be used to evaluate global mean marine redox changes. Clearly, redox chemistry changes in the global ocean is central to examine the causal relationship between marine anoxia and the EPME.

Recent development in marine carbonate U isotope paleo-redox proxy provides a unique opportunity to quantitatively track the detailed timing, duration, and extent of global marine redox changes. The power of U isotope as a global marine redox proxy derives from the fact that U has a long residence time in the modern ocean (>10⁵ yr; e.g., Dunk et al., 2002) which is significantly longer than the time scale of ocean mixing (~10³ yr; e.g., Broecker and Peng, 1982). Because the oxic sinks and the anoxic/euxinic sinks are characterized by different U isotopic fractionation factors, the isotopic composition of the dissolved U in seawater is a sensitive indicator of the proportion of each removal mechanism, and hence to the redox conditions at the seafloor. During redox transformation, the reduction of dissolved U(VI) to U(IV), which is immobilized in anoxic sediments, results in a large and detectable change in δ²³⁸U, favoring heavy isotopes in the reduced U(IV) species (e.g., Andersen et al., 2014; Rolison et al., 2017). Thus, δ²³⁸U of U(VI) dissolved in seawater decreases as the global, areal extent of bottom water anoxia increases, providing a direct proxy of global ocean redox change (e.g., Brennecka et al., 2011; Lau et al, 2016; Clarkson et al., 2018; Zhang et al., 2018a,b,c,d; Zhang et al., 2019).

Measurements of modern biogenic carbonates (e.g., scleractinian corals, calcareous green and red algae, ooids, and mollusks) demonstrate that these primary carbonate precipitates closely record seawater δ²³⁸U (Romaniello et al., 2013; Chen et al., 2018). Measurements of both modern Bahamian shallow carbonate precipitates and drill cores suggest that carbonate sediments record δ²³⁸U of seawater with a positive offset range between +0.2‰ and +0.4‰ (averaging +0.27 ±
0.14‰; 1 SD) (Romaniello et al., 2013; Chen et al., 2018; Tissot et al., 2018). This offset likely arises due to authigenic enrichment of isotopically heavy U(IV) in carbonates and preferential incorporation of isotopically heavy U(IV) species into carbonates during early (syndepositional) diagenesis. Further diagenesis during deeper burial appears to have limited effects on this offset (Romaniello et al., 2013; Chen et al., 2018). Therefore, when properly screened for diagenesis, variations of $\delta^{238}$U in ancient marine carbonates can be used to reconstruct changes in global ocean redox conditions. This positive offset has been considered when performing U isotope mass balance model calculation below.

To date, a total of nine Permian-Triassic boundary carbonate sections have been studied for $\delta^{238}$U, the results have been summarized in Fig. 4. These studies include Dawen, Daxiakou, Dajiang, Guandao, and Zuodeng sections from South China, Taskent section from Turkey, Zal section from Iran, GK-1 drill core from Austria, and Kamura section from Japan (Brennecka et al., 2011; Lau et al., 2016; Elrick et al., 2017; Zhang et al., 2018a, b; Zhang et al., 2019). $\delta^{238}$U and $\delta^{13}$C from six sections are plotted versus age in Fig. 4. The $\delta^{238}$U data resolution from the Guandao and Zuodeng sections are extremely low (Lau et al., 2016) and the $\delta^{238}$U data from the Daxiakou section offsets the other sections by approximate 0.3‰ (Elrick et al., 2017); hence, these three sections are excluded in Fig. 4C and D. The six sections in Fig. 4A and B are aligned together based on $\delta^{13}$C profile and conodont biostratigraphy, and the absolute ages are from Burgess et al. (2014). The minimum $\delta^{238}$U value for the Zal section occurs slightly higher stratigraphically than the other sections, likely due to the poor constraints on conodont zonation at the Zal section, which resulted in poorly estimated sedimentation rate and unreliable absolute age for individual samples. In all other sections, $\delta^{238}$U shifts to lower values across the EPME, corresponding to the globally characterized negative shifts in $\delta^{13}$C$_{carb}$ (Fig. 4C). Samples from before the EPME (pre-EPME) have a mean $\delta^{238}$U value of $-0.16$‰ (Fig. 4). Samples deposited immediately after EPME (post-EPME) have a mean $\delta^{238}$U value of $-0.54$‰ (Fig. 4), significantly lower than pre-EPME carbonates by $-0.4$‰.

These prior $\delta^{238}$U studies have examined a series of established indicators of carbonate diagenetic (such as Mn and Sr contents, Mn/Sr ratio, Rb/Sr ratio, $\delta^{18}$O), indicators of local redox conditions (Mo, Fe, U concentrations, Mo/U ratios, Ce anomalies), indicators of detrital contaminations (Al contents, U/Al ratios, maximum fraction of total detrital U), and indicators of mineralogy/lithology changes (Mg/Ca molar ratio, Sr/Ca ratio). These studies show that there are no systematic correlations between $\delta^{238}$U values and these indicators, and that the negative shifts in $\delta^{238}$U across the EMPE represents a true global seawater signal. It is noteworthy that the six sections shown in Fig. 4 are from two major ocean basins (Tethys Ocean and Panthalassa Ocean) and have experienced completely different diagenetic histories but recorded congruent $\delta^{238}$U trends, which is the strongest evidence to argue against anything but a primary oceanographic signal.

Similar to many prior U isotope studies, we applied a dynamic ocean box model of $\delta^{238}$U evolution following Zhang et al. (2018d) to predict the fraction of seafloor overlain by anoxic waters across the EPME:

$$f_{\text{anox}} = \frac{J_{\text{anox}}(\delta^{238}U_{\text{anox}} - \delta^{238}U_{\text{seafloor}})}{N_{\text{seafloor}}} - \frac{d\delta^{238}U_{\text{seafloor}}}{dt} + k_{\text{anox}} \Delta_{\text{anox}} A_{\text{seafloor}} - k_{\text{oxic}} \Delta_{\text{oxic}} A_{\text{seafloor}}$$

(1)
where $N_{sw}$ is the oceanic uranium inventory, $\delta^{238}U_{sw}$ and $\delta^{238}U_{riv}$ are the U isotope compositions of seawater and the riverine source, respectively, $J_{riv}$ is the riverine U flux, $\Delta_{anox}$ (+0.6‰) is the average fractionation factor associated with anoxic/euxinic sediment deposition (e.g., Andersen et al., 2014), and $\Delta_{oxic}$ is the average fractionation factor associated with the remaining other sinks ($\sim$+0.005‰, calculated to maintain isotopic steady state in the modern ocean; e.g., Zhang et al., 2018d). The rate constants $k_{anox}$ and $k_{other}$ describes area-specific U burial rates in average anoxic/euxinic settings and all other settings, respectively and are derived from the modern marine uranium cycle (e.g., Dunk et al. 2002; Zhang et al., 2018d). The seafloor area overlain by anoxic bottom waters is $f_{anox}$, and $A_{seafloor}$ is the total seafloor area. Detailed references and choices of model parameters can be found in Table 6 in Zhang et al. (2018d).

Following Zhang et al. (2019), we used a Monte Carlo uncertainty propagation approach to evaluate the combined uncertainties introduced from early diagenetic offset (+0.24±0.16‰), analytical uncertainty (±0.08‰), the riverine inputs (−0.27±0.04‰), and the U isotope fractionation factor between seawater and anoxic sediments (0.6±0.1‰) to address uncertainties associated with the $\delta^{238}U$ data and isotopic mass balance model. The modeling result of the global ocean anoxia area fraction across the EPME is shown in Fig. 4D. Model result shows that before the EPME, the global ocean redox regime is similar to the modern ocean with a slightly larger seafloor areas overlain by anoxic waters. This situation changed markedly immediately prior to the EPME horizon, when $\delta^{238}U_{seawater}$ shifted towards lighter values. This rapid shift in $\delta^{238}U_{seawater}$ is interpreted as massive and rapid expansion of anoxic seafloor areas, where ~32% (±10%) seafloor was overlain by anoxic waters. The transition occurred within 10 kyr prior to the EPME horizon and lasted for 60 to 200 kyr. The anoxic peak closely overlaps with the main EPME horizon suggesting a causal link between the two. Interestingly, the Earth system model best-fit scenario predicts well-oxygenated ocean with a characteristic oxygen minimum zone at mid-depth prior to the extinction. As expected, the oxygen minimum zone expanded significantly during the peak extinction, when the CO$_2$ emission reaches its maximum rate. A large fraction of the seafloor (~30%) is covered by oxygen concentration lower than 60 μmol kg$^{-1}$ (Fig. 2), a critical threshold for lethal level of oxygen to many marine organisms (Vaquer-Sunyer and Duarte, 2008).

One of the interesting phenomena is that $\delta^{238}U$ show a short-lived positive excursion before a rapid dropping to very low values. We interpret this short positive event as an artifact associated with the rapid and extensive expansion of marine anoxia immediately prior to the EPME, which reduced the majority of dissolved U(VI) in seawater to less soluble U(IV) in a short period of time, leading to a massive accumulation of isotopically heavier U(IV) below water-sediment interface. These isotopically heavier U(IV) can incorporate into carbonate precipitates during syndepositional diagenesis. This process is well established in the modern Bahamian carbonate platform (Romaniello et al., 2013; Chen et al., 2018).
Figure 4: A and B. Compiled $\delta^{238}$U and $\delta^{13}$C data from six sections across the end-Permian mass extinction. Stratigraphic sections include Dajiang and Dawen located in south China along the eastern margin of the Tethys Sea (Brennecka et al., 2011; Lau et al., 2016; Zhang et al., 2018a); GK-1 core, Italy, Taskent, Turkey and Zal, Iran from the western margin of the Tethys (squares; Lau et al., 2016; Zhang et al., 2018b; Zhang et al., 2019); and Kamura, Japan, a seamount in Panthalassa (Zhang et al., 2018b; both diamonds). $\delta^{238}$U of carbonate across the EPME vs. geological time; C. Loess-fit to the integrated uranium isotopes from five sections in Dajiang, Dawen, Taskent, Zal, and GK-1 core; D. Uranium isotope mass-balance model and Monte-Carlo uncertainty propagation on the timing, duration, and extent of global ocean anoxia across the EPME.

**Ocean anoxia vs. ocean acidification**

The expected oceanographic consequence of the low pole-to-equator temperature gradient and the high global temperature is reduced strength of meridional overturning circulation (MOC) and increased intensity of ocean anoxia, both are supported by geological evidence (Bond and Wignall, 2010) and numerical models (Hotinski et al., 2001; Winguth and Winguth, 2012). Size distribution of pyrite frambooids suggests that anoxia extent is more intense in boreal high latitudes than equatorial regions, and does not support widespread euxinia (Bond and Wignall, 2010; Xiao et al., 2018). Organic biomarkers from well-preserved sections and/or drill cores are often used to infer paleo-redox conditions of the Late Permian ocean. Increased organic biomarkers in sections from the PaleoTethys (S. China and Bulla, Italy) and NeoTethys (Perth Basin Australia), which support depletion of oxygen (Chen et al., 2011; Grice et al., 2005; Cao et al., 2009, EPSL; Kaiho et al., 2016). Several redox-sensitive trace elements, such as uranium [U], vanadium [V], molybdenum [Mo] and chromium [Cr] suggest increased anoxic conditions during the extinction event (Algeo et al., 2010; Fio et al., 2010; Takahashi et al., 2014). Although
these proxies show evidence of global anoxia, none of them is a global proxy that can be used to estimate global seafloor anoxia area. As we summarized earlier, the uranium isotope proxy can be used to infer global extent of ocean anoxia, and a mass-balance uranium isotope box model along with a Monte Carlo uncertainty propagation has shown that during the peak mass extinction, the anoxia area has increased from 0 to 20-48% of the seafloor (Fig. 4). Such extreme depletion of the ocean oxygen concentration is consistent with all the proxy evidence, and provides a reasonable killing mechanism for the marine biota.

However, anoxia and euxinia alone may not be sufficient to account for the observed pattern of physiological selectivity (Knoll et al. 2007). Decreased CaCO$_3$ preservation in marine sediments, such as reduced wt.% of CaCO$_3$ and/or the occurrence of dissolution surface provides supporting evidence for ocean acidification (Payne et al., 2007). Such sedimentary feature has been observed widely in the deep ocean sites during the Paleocene-Eocene Thermal Maximum (Zachos et al., 2005). Paleontological evidence of selective extinction against heavily calcified marine organisms with little physiological buffering capacity (e.g. Knoll et al., 2007; Bush and Bambach, 2011; Payne and Clapham, 2011) and biomineralization pattern change on survived marine invertebrates across the extinction interval (Garbelli et al., 2017) has also been attributed to the CO$_2$-induced acidification and/or carbonate dissolution. Modeling studies have argued that CO$_2$ emissions from the Siberian Traps eruption caused the entire ocean to become undersaturated with respect to aragonite, with more limited areas becoming undersaturated with respect to calcite (Montenegro et al., 2011). The ocean acidification can account for the selectively extinction of heavily calcified marine with limited physiological buffering capacity (Knoll et al., 2007), biogeographic parameters (Clapham and Payne, 2011), and environmental preference (Chen et al., 2011).

Overall, the lethally hot ocean temperature, excessive nutrient delivered to the ocean through enhanced weathering or wind, and the stagnant ocean, along with increased ocean acidification in an already poorly buffered ocean, all potentially triggered by the Siberian Traps LIP, worked together to create the most severe bio crisis in the Earth history.

**Conclusions**

The voluminous nature of the Siberian Traps volcanisms coincides the severity of the end-Permian extinction event at 252 million years ago, suggesting a natural causal link between the two events. However, high-resolution geochronology has somewhat outpaced the understanding of the killing mechanism, whether it is ocean anoxia or acidification. Knowing either one as an ultimate killing mechanism requires reliable geochemical proxy for ocean anoxia and acidification on both spatial and temporal scales. Indeed, the development of these proxies are underway, but in need of further refinement. Establishing the causal link, however, is difficult. Negative excursions of boron isotopes from United Arab Emirates lag the main phase of extinction by 70 kyr, and cannot be the cause of the mass extinction. Similarly, oxygen isotopes of conodont the newly studied highly expanded Penglaitan section in S. China revealed the peak temperature did not occur until after the onset of most severe extinction horizon, suggesting warming perhaps is not a cause of the extinction. These puzzling pieces of information call for the need to examine the geological samples with more rigor. After reviewing the published uranium and calcium isotopes of the end-Permian sediments and EMIC model simulation, we suggest that lethally hot temperature, excessive nutrient load in the ocean, and decreased strength
of meridional overturning circulation, along with ocean acidification in a poorly buffered ocean, potentially triggered by the Siberian Traps LIP and volcanism near South China, worked together to create the largest mass extinction in the Earth history. This hypothesis would require future work on high-resolution lithium-strontium-uranium-boron measurement from expanded sections and combined with Earth system model of intermediate complexity to test.

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This draft is prepared for submission to AGU Book “Environmental Change and Large Igneous Province: The Deadly Kiss of LIPs”

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A Modern carbonate production and seafloor oxygen (well-buffered ocean)

weathering delivery of alkalinity ($\text{HCO}_3^-$ and $\text{CO}_3^{2-}$)

coral reef
neritic burial

carbonate mud
pelagic burial

lysocline

CCD

well oxygenated

B End-Permian ocean carbonate production and seafloor oxygen (poorly-buffered ocean)

increased weathering delivery of alkalinity ($\text{HCO}_3^-$ and $\text{CO}_3^{2-}$)

coral reef
neritic burial

lysocline

CCD

well oxygenated
A. Time 0, steady-state

B. Time 70 Kyr, peak extinction

C. Carbonate Saturation State

D. Carbonate Saturation State

**[O2] (µmol kg⁻¹)**

Depth (m)

Latitude

90°S 70°S 50°S 30°S 10°S 10°N 30°N 50°N 70°N 90°N

**dissolved oxygen (O2) (10⁻⁶ mol kg⁻¹)**

Data Min = 53, Max = 128

Data Min = 0, Max = 281

**Carbonate Saturation State (Ω)**

Data Min = 0, Max = 6

Data Min = 0, Max = 3

Time 0, steady-state

Time 70 Kyr, peak extinction