Quantifying volcanism and organic carbon burial across Oceanic Anoxic Event 2

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ABSTRACT

Oceanic Anoxic Event 2 (ca. 94 Ma; OAE2) was one of the largest Mesozoic carbon cycle perturbations, but associated carbon emissions, primarily from the Caribbean large igneous province (LIP) and marine burial fluxes, are poorly constrained. Here, we use the carbon cycle box model LOSCAR-P to quantify the role of LIP volcanism and enhanced marine organic carbon (Corg) burial as constrained by the magnitude and shape of the positive stable carbon isotope (∆13C) excursion (CIE) in the exogenic carbon pool and atmospheric pCO2 reconstructions. In our best fit scenario, two pulses of volcanic carbon input—0.065 Pg C yr⁻¹ over 170 k.y. and 0.075 Pg C yr⁻¹ over 40 k.y., separated by an 80 k.y. interval with an input of 0.02 Pg C yr⁻¹—are required to simulate observed changes in ∆13C and pCO2. Reduced LIP activity and Corg burial lead to pronounced pCO2 reductions at the termination of both volcanic pulses, consistent with widespread evidence for cooling and a temporal negative trend in the global exogenic ∆13C record. Finally, we show that observed leads and lags between such features in the records and simulations are explained by differences in the response time of components of the carbon cycle to volcanic forcing.

INTRODUCTION

Oceanic Anoxic Event 2 (OAE2) was an ∼430–930-k.y.-long (Voigt et al., 2008; Gangl et al., 2019) interval of high atmospheric pCO2 and temperatures that is generally attributed to greenhouse gas emissions from large igneous provinces (LIP) magmatism, primarily the Caribbean–Colombian LIP (CLIP) (Turgeon and Creaser, 2008; Jenkyns, 2010). The greenhouse cycle promoted deep ocean deoxygenation and enhanced burial of organic carbon (Corg) (e.g., Kuypers et al., 2002). A positive carbon isotope (∆13C) excursion (CIE), consisting of a stepped increase of 3‰ (average; Owens et al., 2018) to a maximum “a,” a negative excursion (“trough”); termed the Plenus CIE; O’Connor et al., 2020), a second maximum “b,” a plateau, and a gradual return to pre-OAE2 values (Fig. 1), marks OAE2 in sedimentary records (e.g., Jenkyns, 2010). Records of pCO2 generally show an increase across the onset of OAE2, two phases of lower values associated with the carbon isotope maxima, and another increase within the Plenus CIE (e.g., Sinninghe Damsté et al., 2008; Barclay et al., 2010; Kuhnt et al., 2017). Presumably, both of these drops in pCO2 are associated with cooling phases, one of which is the stratigraphically complex Plenus Cold Event (see the Supplemental Material; O’Connor et al., 2020)

Trends and the timing of key features in ∆13C and pCO2 records across OAE2 are determined by LIP volcanism and enhanced Corg burial. LIP emission rates are estimated between 0.03 and 4.7 Pg C yr⁻¹ and total emission masses between 14,000 and 46,000 Pg C (Table S1 in the Supplemental Material). Corg burial records (e.g., Kolonic et al., 2005) suggest burial of a total of at least 41,000 Pg C across OAE2 (Owens et al., 2018). The ~25% drop in pCO2 marking the CIE maximum “a” has been attributed to increased Corg burial (e.g., Barclay et al., 2010) and/or decreased LIP volcanism (e.g., Clarkson et al., 2018). The Plenus CIE may be the result of decreased Corg burial following the reduction in pCO2 and/or an increase in LIP volcanism. Yet, a comprehensive, mechanistically plausible scenario for volcanic input and excess Corg burial that explains all observations is still lacking.

In this study, we present the first scenario for LIP volcanism and Corg burial for OAE2 that reproduces the shape and magnitude of the CIE and the timing of its major features relative to pCO2 reconstructions (Fig. 1). We use the carbon cycle box model LOSCAR-P (Komar and Zeebe, 2017) to assess the impact of a range of volcanic emission scenarios on sedimentary ∆13C records, pCO2, and Corg burial.

CARBON CYCLE MODEL SET UP AND CONSTRAINTS

The LOSCAR-P model with the Paleocene–Eocene model configuration represents the ocean, including the Tethys Ocean, but not marginal and restricted environments (Zeebe, 2012; Komar and Zeebe, 2017). It enables us to study bulk carbonate ∆13C and atmospheric pCO2 as a function of volcanism, weathering, and marine Corg burial. The redox-dependency of Corg and phosphorus burial enhances phosphorus recycling relative to Corg upon ocean deoxygenation (Komar and Zeebe, 2017). We used the setup of Komar and Zeebe (2017) but with increased initial calcium (25 mmol kg⁻¹) and magnesium (35 mmol kg⁻¹) concentrations (Zeebe and Tyrrell, 2019) and a mid-Cretaceous ∆13C value (~−28‰; Kump and Arthur, 1999).

The onset of volcanism likely preceded the OAE2 onset by <60 k.y. (Jones et al., 2020). A 1–3‰ negative CIE precedes the positive CIE in some ∆13Corg records (Kuroda et al., 2007; Kalanat et al., 2018). The OAE2 CIE ranges in magnitude from 1‰ to 8‰ (average 5‰; Owens et al., 2018), and the Plenus CIE drop ranges from 0.5‰ to 4‰ (Forster et al., 2007; Voigt et al., 2007). Atmospheric pCO2 increased by ~20% over background values at the onset of OAE2 (~460 ± 100 ppm; Barclay et al., 2010).

1Supplemental Material. Supplemental information and methods, Figures S1–S4, and Tables S1 and S2. Please visit https://doi.org/10.1130/GEOL.S.18173069 to access the supplemental material, and contact editing@geosociety.org with any questions.

and decreased by ~25% before the Plenus CIE (e.g., Sinninghe Damsté et al., 2008; Barclay et al., 2010; Jarvis et al., 2011). We evaluated our emission scenarios with these constraints to simulate the key characteristics of the OAE2 carbon cycle.

We increased the model volcanic CO$_2$ flux ($\delta^{13}$C$_{volc}$: −5‰) to force our simulations. The impact of redox-dependent $C_{org}$ and P burial on $\delta^{13}$C was tested with a maximum excess input rate of 0.2 Pg C yr$^{-1}$ over 90 k.y., with and without redox-dependency. The effect of emission rate and duration was tested in four simulations of 90 k.y. and 540 k.y., with maximum emission rates of 0.2 Pg C yr$^{-1}$ and 0.04 Pg C yr$^{-1}$, and redox-dependent burial. All scenarios started with a linear rate increase over 20 k.y., which reproduced the ~60 k.y. lag, and ended with a 20 k.y. linear recovery to zero. Then we conducted sensitivity analyses for the rate, mass, duration, and shape of volcanism scenarios (Fig. S1) and derived a best-fit scenario. Information about further sensitivity analyses with thermogenic methane ($\delta^{13}$C$_{meth}$: −35‰) and reduced circulation are provided in the Supplemental Material. Due to the various processes affecting $\delta^{13}$C signatures, the results of $\delta^{13}$C models are non-unique. We minimized the impact on our results by constraining them with atmospheric $p$CO$_2$ and $C_{org}$ burial rates in addition to $\delta^{13}$C variations.

RESULTS

All scenarios forced by volcanism result in a small negative CIE (Fig. 2), followed by a larger positive CIE that is mainly caused by enhanced, redox-dependent $C_{org}$ burial (Figs. 2A, 2B, and 2D). In all cases (Fig. 2E), the peak in $\delta^{13}$C is preceded by a peak in $p$CO$_2$. Following the return to background volcanic activity, $\delta^{13}$C and $p$CO$_2$ recover to their background values on time scales of 400 k.y. and 100 k.y., respectively.

The maximum value of the positive CIE and $p$CO$_2$ rise varies with the duration and rate of volcanic input (Figs. 2C–2E). From the 90 k.y. scenario to the 540 k.y. scenario, the $p$CO$_2$ peak shifts from the end of the negative CIE interval to the increasing $\delta^{13}$C section of the positive CIE. In the 90 k.y. scenarios, the recovery of $p$CO$_2$ and $\delta^{13}$C to background values begins immediately after their maximum. For the 540 k.y. scenarios, the final recovery is preceded by a $\delta^{13}$C decrease and a second peak. In these simulations, the minimum in $p$CO$_2$ coincides with the first $\delta^{13}$C maximum and occurs within the interval of enhanced volcanic activity, while volcanism decreases within the $\delta^{13}$C trough. This is not the case for the 90 k.y. scenarios.

TWO VOLCANIC PULSES

In our simulations, a negative $\delta^{13}$C excursion precedes the positive CIE, which is not a common feature (e.g., Tsikos et al., 2004), but it is present in several OAE2 $\delta^{13}$C$_{org}$ records (e.g., Kuroda et al., 2007). This negative $\delta^{13}$C excursion may have been enhanced or masked by site-specific processes. The simulations show that it could be forced by volcanic CO$_2$ emissions alone.

Two $\delta^{13}$C maxima, a negative CIE between them, and a decrease in $p$CO$_2$ near the first maximum are reproduced only by the longer (540 k.y.) forcing scenarios and are most distinct in the high emission scenario (0.2 Pg C yr$^{-1}$). Yet, the large positive CIE (~7.9‰), high maximum $p$CO$_2$ (~400 ppmv), and large drop in $p$CO$_2$ (45%) for this scenario far exceed OAE2 variability estimates, while there is no clear increase in $p$CO$_2$ within the negative CIE (Fig. 1). A variable emissions scenario is therefore required to
reproduce the key features of the $\delta^{13}\text{C}_{\text{bulk}}$ and $p\text{CO}_2$ records.

In our best-fit scenario, LIP volcanism consists of two pulses, 0.065 Pg C yr$^{-1}$ over 170 k.y. and 0.075 Pg C yr$^{-1}$ over 40 k.y., separated by an 80 k.y. interval of 0.02 Pg C yr$^{-1}$ (Fig. 3A; see the Supplemental Material). The duration of the first pulse and the decrease from the first maximum both last 20 k.y. The increase, as well as the termination, of the second pulse last 80 k.y. The total duration of LIP activity is 490 k.y. with a total emission mass of $\sim 24,000$ Pg C (Table S1). Multiple volcanic pulses are supported by osmium isotope records (Sullivan et al., 2020). Additionally, Clarkson et al. (2018) reproduce their uranium isotope records using a two-pulse $\text{CO}_2$ model emission scenario. Our two-pulse scenario reproduces the main characteristics of our target scenario (“a”, Plenus CIE, “b”) and the relative timing between $\delta^{13}\text{C}$ and $p\text{CO}_2$ (Figs. 1 and 3). The initial $\delta^{13}\text{C}$ increase to “a” (2.96‰) is equal to the global average of 3‰ (Owens et al., 2018), and our simulated Plenus CIE (0.52‰) has a magnitude similar to the drop in $\delta^{13}\text{C}_{\text{carb}}$ at Eastbourne (Tsikos et al., 2004) and in $\delta^{13}\text{C}_{\text{org}}$ at Ocean Drilling Program site 1276 (Sinninghe Damsté et al., 2010). Also, the simulated 35% (660 ppmv) drop in atmospheric $p\text{CO}_2$ agrees with proxy reconstructions (Sinninghe Damsté et al., 2008; Barclay et al., 2010; Jarvis et al., 2011).

Our simulated OAE2, from onset to “b,” has an overall duration of $\sim 500$ k.y. Assuming that the plateau and recovery phases lasted several hundreds of thousands of years. (Gangl et al., 2019), our duration is in line with longer estimates (3700 k.y.; Jones et al., 2020). The onset of our CIE up to “a” is considerably longer (250 k.y.) than the longest estimate (110 k.y.; Li et al., 2017). This may be due to the lack of proto-North Atlantic restriction and/or the underrepresentation of shallow and restricted environments (e.g., epicontinental seas; see the Supplemental Material) where additional $\text{C}_{\text{org}}$ could be buried. For the same $\text{CO}_2$ emission scenario, more $\text{C}_{\text{org}}$ could potentially be buried in a simulation with Cenomanian–Turonian (C/T) paleogeography, which could result in a larger, and potentially more rapid, positive CIE. The duration of the Plenus CIE (200 k.y.) agrees with the estimate from the Western Interior Seaway (Jones et al., 2020) and further corroborates our two-pulse volcanism scenario.

**Figure 2. Response of $\delta^{13}\text{C}$ and $p\text{CO}_2$ to increased volcanism.** The effect of excess volcanic emissions (black solid line) on (A) 14,000 Pg C (90 k.y.); and (B) $\delta^{13}\text{C}$, with constant (black dashed line) and redox-dependent $\text{C}_{\text{org}}$ and phosphorus burial (red line). (C) The effect of additional volcanism scenarios, with maximum rates of 0.04 Pg C yr$^{-1}$ (dashed lines) and 0.2 Pg C yr$^{-1}$ (solid lines) over 90 k.y. (black) and 540 k.y. (red), on (D) $\delta^{13}\text{C}$ and (E) $p\text{CO}_2$, with redox-dependent burial. Vertical lines indicate the steady-state value in each panel.

**Figure 3. Key model output for Oceanic Anoxic Event 2 (OAE2) simulations.** (A) Large igneous province (LIP) volcanic forcing (Pg C yr$^{-1}$). (B) Bulk $\delta^{13}\text{C}$ (%). (C) atmospheric $p\text{CO}_2$ (ppmv). (D) $\text{C}_{\text{org}}$ burial rates (g C m$^{-2}$ yr$^{-1}$). Two forcing scenarios are used: two pulses separated by a reduction (solid red line) and a stepped increase (black dashed line). Horizontal dashed lines indicate the positions of the two $\delta^{13}\text{C}$ maxima “a” and “b.” Gray area represents OAE2. Purple bar shows the Plenus carbon isotope excursion.

**Figure 4.** Volcanism and its effect on organic carbon burial. Our best fit scenario requires a total emission of $\sim 24,000$ Pg C by LIP volcanism, or more
if thermogenic methane production is included (Supplemental Material). With a magmatic CO₂ content of 0.5 wt% (0.2–0.6 wt%; Jones et al., 2016), or an emission of 0.0035 Pg C km⁻² (Selt et al., 2005), our scenario requires a LIP volume of 6.8 × 10⁶ km³. The CLIP has an estimated volume of 4 × 10⁶ km³ (Kerr, 1998), though a total of 20 × 10⁶ km³ of basalts erupted around the C/T boundary and OAE2 during the emplacement of the CLIP, the Madagascar LIP, and part of the Ontong–Java Plateau (Bond and Wignall, 2014). The 500 k.y. duration of our scenario is short for LIP emplacement. Age constraints indicate that LIP magmatism generally spanned millions of years and often consisted of multiple phases (e.g., Bond and Wignall, 2014). A maximum of 4 × 10⁶ km³ of magma was erupted within ∼2 m.y. from the Late Permian Siberian Traps (Russia), causing a mass extinction (Reichow et al., 2009). Assuming the emplacement of 20 × 10⁶ km³ of ∼4 m.y. (Bond and Wignall, 2014), the average rate of eruption at the C/T boundary would be 2.5 times faster than at the Siberian Traps. Our best-fit, average emission rate is seven times larger than is estimated for the Siberian Traps, which seems high. The current resolution and precision of flood basalt dating does not allow us to directly evaluate our scenario, but osmium isotope records indicate that a 500 k.y. pulse of enhanced volcanism coincided with OAE2 (e.g., Du Vivier et al., 2015). Additionally, Joo et al. (2020) required the full mass of the CLIP emitted over 500 k.y. to simulate only the initial positive CIE of OAE2. The specifics of our emission scenarios may be further affected by pulse duration, basin morphology, and burial redox-sensitivity (see the Supplemental Material and Fig. S1); however, the general aspects of our best-fit scenario are plausible within the current constraints on Late Cretaceous LIP activity and the δ¹³C and pCO₂ records.

We simulate two distinct maxima in Corg accumulation rates (Fig. 3D), which roughly double from ~0.2 to ~0.4 g C m⁻² yr⁻¹, similar to the average increase at Tarfaya (Kolonic et al., 2005). Our increase exceeds that of Clarkson et al. (2018) (1.3 times pre-OAE2), but their resulting CIE (1.5‰) is only half the global average value. Maximum Corg burial (~0.125 Pg C yr⁻¹) is lower than those modeled by Nederbragt et al. (2004) and Owens et al. (2018) (~0.185 Pg C yr⁻¹), but our rates, expressed per unit surface area, and the relative change in burial are in general agreement with their work. The amount of excess Corg burial required for the 3‰ CIE in LOSCAR is ~9100 Pg C, which is roughly equal to the value required in the simulation by Owens et al. (2018) for an equivalent CIE. Our total simulated Corg burial from the onset of OAE2 until “b” is ~51,400 Pg C (excess burial: ~20,500 Pg C), consistent with previous calculations (41,000–70,000 Pg C; Owens et al., 2018).

The relative impact of changes in volcanism and enhanced Corg burial on the carbon cycle during OAE2 are still heavily debated (O’Connor et al., 2020). In our LIP volcanism scenario, we showed that two pulses separated by a reduction are critical for reproducing the Plenus CIE, a large decrease in pCO₂ that is consistent with temperature records, as well as the second peaks in δ¹³C and pCO₂ without exceeding the average 3‰ CIE at Loscar (Figs. 2 and 3). The pCO₂ drop is forced by decreased volcanism and increased Corg burial and silicate weathering (21%). The CO₂ drawdown diminishes Corg burial, and the second pulse of LIP activity results in the negative Plenus CIE. A subsequent rise in burial, coupled with volcanism cessation, causes “b”. These features are not simulated by our stepped scenario (Fig. 3). Atmospheric CO₂ responds directly to changes in LIP activity, whereas the response in Corg burial is delayed, modulated by P input and regeneration with longer response time, and leads to a slower response of exogenic δ¹³C.

CONCLUSION

Our carbon cycle simulations show that two pulses of LIP volcanism, increased terrestrial weathering and P supply, and redox-dependent Corg and P burial are required to reproduce trends and patterns in global exogenic δ¹³C, atmospheric pCO₂, and Corg burial across OAE2. Our best-fit scenario reproduces the 3‰ CIE, δ¹³C maxima (“a” and “b”), and the Plenus CIE. The global pCO₂ decrease that occurred near “a” is caused by high Corg burial and a pause in LIP volcanism. Subsequent burial reduction and elevated LIP activity result in the Plenus CIE and an increase in pCO₂. The second pCO₂ and Corg burial maxima are only present in simulations with a second pulse of volcanism. Our scenario of variable volcanism and Corg burial quantitatively explains the key features of the OAE2 carbon cycle and climate dynamics and the relative timing between maximum δ¹³C, the Plenus CIE, and high pCO₂. We propose that future work should attempt to directly link osmium records to outgassing scenarios and incorporate carbon cycle perturbation studies that incorporate C/T paleogeography.

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