SUPPLEMENTAL MATERIAL

Quantifying volcanism and organic carbon burial across Oceanic Anoxic Event 2

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The Plenus Cold Event and the Plenus CIE

The southward migration of boreal fauna (e.g. [Gale and Christensen, 1996](#); [van Helmond et al., 2016](#)) and multi-proxy records (e.g. [Gale and Christensen, 1996](#); [Forster et al., 2007](#); [Jarvis et al., 2011](#)) provide evidence for decreasing temperatures for one or multiple cooling stages within the first half of OAE2. This interval of cooling is generally referred to as the Plenus Cold Event ([Gale and Christensen, 1996](#)) and attributed to decreasing atmospheric CO₂ (e.g. [Sinninghe Damsté et al., 2010](#); [Jarvis et al., 2011](#)).

Since its original identification, the nature of the Plenus Cold Event has become more complex. On timescales of thousands of years, a lag between atmospheric *p*CO₂ and global temperature should be absent. Therefore, the multiple intervals of decreased *p*CO₂ identified in proxy records (see [O'Connor et al., 2020](#)) should have caused multiple phases of cooling. This is indeed observed in several temperature records ([Forster et al., 2007](#); [Sinninghe Damsté et al., 2010](#); [van Helmond et al., 2014](#); [2015](#); [Desmares et al., 2016](#); [Jenkyns et al., 2017](#); [Kuhnt et al., 2017](#)). But the presence of multiple cooling pulses and the timing of major cooling relative to key features of the $\delta^{13}\text{C}$ record (“a”, “b” and the trough that separates them, i.e. “Plenus CIE”) depend on local processes as well as global changes (see [O'Connor et al., 2020](#) for extended discussion). Because global correlations of the various recorded drops in temperature and species migrations at individual locations are currently complicated, [O'Connor et al. \(2020\)](#) introduced the Plenus CIE as a suitable stratigraphic marker for global correlations.

In this study, our best-fit scenario simulates two maxima in *p*CO₂, both followed by a decrease, and a $\delta^{13}\text{C}$ curve with a 200-k.y. trough separating “a” and “b”, in line with recent

orbital timescales (e.g. Jones *et al.*, 2020). Two intervals with lower atmospheric $p\text{CO}_2$, around “a” and “b”, are consistent with records of multiple phases of cooling. The second phase of lower atmospheric $p\text{CO}_2$ should match with the Plenian Cold Event (*sensu stricto*) at Eastbourne (see O’Connor *et al.*, 2020) that is marked by the incursion of boreal fauna. As a result of the (stratigraphic) uncertainties concerning the use of the term Plenian Cold Event, we avoid linking it to our simulation results.

Oceanic Anoxic Event 2 age model

Age models for OAE2 based on orbitally tuned sediment records provide a range of durations from 430 k.y. (Voigt *et al.*, 2008) to 955 k.y. (Gangl *et al.*, 2019). The duration of key sections of the positive carbon isotope excursion (CIE) thus varies depending on the applied age model. In the main text we provide minimum and maximum values for the duration of the lag between the onset of volcanism and the CIE, the total CIE, the onset to “a” and the Plenian CIE from “a” to “b” (Figure 1), taking into account the range in age estimates.

The onset of Large Igneous Province (LIP) activity is set at 0 k.y.. The minimum value for the time between the onset of volcanism and the positive CIE is 23 k.y. (Turgeon and Creaser, 2008), and the maximum is 60 k.y. (Jones *et al.*, 2020). The duration of the onset of OAE2, up to point “a” is between ~30 k.y. (Gangl *et al.*, 2019) and 110 k.y. (Li *et al.*, 2017). Jones *et al.* (2020) give a duration of 50 k.y. and Kuhnt *et al.* (2017) estimate it to be between 80 and 100 k.y.. This places $\delta^{13}\text{C}$ maximum “a” between 63 k.y. and 170 k.y. after LIP onset. Li *et al.* (2017) calculate a minimum duration of 55 k.y. for the Plenian CIE, similar to Kuhnt *et al.* (2017), which is considerably shorter than the 200 k.y. of Jones *et al.* (2020) and maximum 225 k.y. of Gangl *et al.* (2019). Taking all these values into account, the $\delta^{13}\text{C}$ maximum “b” occurs between 118 k.y. and 395 k.y. after LIP onset. With a duration of 490 k.y. to 590 k.y. (Li *et al.*, 2017; Gangl *et al.*, 2019) for the $\delta^{13}\text{C}$ plateau and recovery, the end of the OAE2 CIE at the end of the recovery phase falls between 608 k.y. (minimum) and 985 k.y. (maximum) after LIP onset.

Emission mass sensitivity test

Carbon isotope model results are non-unique and different combinations of parameters can lead to the same results. Here, we first test the impact of different volcanic emission rates ($\delta^{13}\text{C}$ of -5‰) and durations on the initial positive isotope excursion. We force LOSCAR with a gradual 20 k.y. increase to maximum emissions, followed by a 50 k.y., 100 k.y., 200 k.y., 300 k.y. or 500 k.y. plateau at maximum values and ending with a gradual 20 k.y. termination interval (Supplemental Figure S1). The maximum tested rates are $0.005 \text{ Pg C yr}^{-1}$, $0.05 \text{ Pg C yr}^{-1}$, 0.1 Pg C yr^{-1} and $0.15 \text{ Pg C yr}^{-1}$. As expected, the average value of the OAE2 positive excursion of 3‰ (Owens *et al.*, 2018) is generated by different combinations of volcanism rates and durations. At shorter durations, higher emission rates are required, and the opposite is true for longer durations. The total emission mass corresponding to a 3‰ excursion increases from ~10,500 Pg C at 50 k.y. to ~26,000 Pg C at 500 k.y..

A. Simulation Setup

B. Maximum positive CIE

Supplemental Figure S1. Stable carbon isotope response to varying volcanic emissions. Simulations were run with a 20 k.y. onset, 50 to 500 k.y. emission plateau and 20 k.y. termination (A). Positive excursions associated with different emission rates and durations are presented in (B), with the emission mass corresponding to a 3‰ positive excursion at 50 k.y., 100 k.y., 200 k.y., 300 k.y., 400 k.y. and 500 k.y.. Circles indicate total emission values in Pg C for a positive excursion of 3‰ at a given combination emission setup.

Two-pulse sensitivity tests

To derive an emission scenario with two pulses of LIP activity that accurately reproduces the characteristics of the $\delta^{13}\text{C}$ and $p\text{CO}_2$ records for OAE2 we performed a large number of sensitivity simulations. We tested different durations and rates for the different parts of a two-pulse scenario, with and without a trough separating the two pulses. The term “stepped” is used to refer to scenarios with two pulses unequal in their rate of emission but without a trough. We present key examples here (**Supp. Fig. S2**), while the best-fit scenario, and one “stepped” scenario are presented in the main text (**Fig. 3**). The positive CIE of OAE2 is less than 3‰ in scenarios (A) – (E). Scenarios (B) – (H) fail to reconstruct the Plenus CIE. The second maximum in $\delta^{13}\text{C}$ is much higher than the first in scenarios (A) – (C) and (E), whereas it is not present in (H). A second peak in $p\text{CO}_2$, following a clear decrease, is not present in scenarios (F) and (H). This peak is much higher than the first $p\text{CO}_2$ maximum in scenario (B), which does not reproduce the decrease after the first peak. The relative decrease in $p\text{CO}_2$ is too large in scenario (A) and too small in scenarios (D) and (E).

Supplemental Figure S2. LIP volcanism, bulk $\delta^{13}\text{C}$ and atmospheric $p\text{CO}_2$ for key sensitivity simulations. Vertical lines indicate the steady state value in each panel. Red circles indicate the section of the $\delta^{13}\text{C}$ or $p\text{CO}_2$ curve that does not match the target curve for OAE2 (Fig. 1) for each LIP volcanism scenario from (A) to (H). For further details, see text.

The response of $\delta^{13}\text{C}$ and other carbon cycle components to volcanic emissions also depends on the amount of C_{org} that is buried during the perturbation. Additionally, the Paleocene-Eocene

paleogeography of LOSCAR does not capture the location of anoxia and C_{org} burial, which during OAE2 were largely focused in the proto-North Atlantic and in shallow seas and continental shelves (e.g. [Jenkyne, 2010](#); [Takashima et al., 2006](#)). We test the sensitivity of our main LIP volcanism scenario to the amount of C_{org} burial and the location of burial by doubling the fraction of C_{org} that is buried (f_{OCB} ; see [Komar and Zeebe, 2017](#)) and by reducing total deep water formation (17 instead of 25 Sv; [Zeebe, 2012](#)) and the amount of deep water formation in the Atlantic (2 instead of 10 Sv; [Zeebe, 2012](#)) (Supp. Fig. 3B), while keep it unchanged in the Pacific and Indian Oceans (7.5 Sv each). This last change promotes anoxia specifically in the Atlantic Ocean, an approximation of the low oxygen conditions in the proto-North Atlantic (e.g. [van Helmond et al., 2014](#)). The results of these simulations are similar to the standard run, but a slowdown in circulation in particular results in a $\sim 0.5\%$ increase in the initial positive excursion.

Supplemental Figure S3. Stable carbon isotope response to different environmental controls and emission sources. The two-pulse scenario (solid line) (see main text) was used for all scenarios forced by LIP volcanism ($\delta^{13}C_{volc}$: -5%) and 20 k.y. onset, 390 k.y. plateau and 80 k.y. termination scenario was used for the thermogenic methane ($\delta^{13}C_{CH_4}$: -35%) scenarios (dashed lines) (A). The solid black line represents the central OAE2 scenario presented in the main text, in all panels. The colors for the methane scenarios are consistent in all panels: light red for a total emission of $\sim 3,500$ Pg CH₄, red for a total emission of $\sim 22,000$ Pg CH₄ and dark red for a total emission of $\sim 44,000$ Pg CH₄. The response of $\delta^{13}C$ to LIP volcanism was tested together with an increased C_{org} burial fraction (f_{OCB} ; [Komar and Zeebe, 2017](#)) (dark red), slowed circulation (red) and a combination of the two (light red) (B). The response of $\delta^{13}C$ to methane emissions without LIP volcanism (C) was also tested with a doubled f_{OCB} (D) and a doubled f_{OCB} with slowed circulation (E).

Mixed sources sensitivity test

Large Igneous Province magmatism is not only associated with CO₂ emissions, but can also result in the production of thermogenic methane (CH₄) (e.g. [Svensen *et al.*, 2004](#); [Jones *et al.*, 2019](#)). While volcanic CO₂ typically has a $\delta^{13}\text{C}$ value of -5‰, thermogenic CH₄ has an isotopic signature between -20‰ and -50‰ ([Whiticar, 1999](#)). As a result, the response of the components of the global carbon cycle to a certain mass of light carbon, depends on the source. While there is no clear evidence for the contribution of thermogenic CH₄ during OAE2, we tested a variety of scenarios to simulate the effect it would have on the carbon cycle components. Scenarios forced solely with thermogenic CH₄ ($\delta^{13}\text{C}_{\text{CH}_4}$: -35‰) produce large negative excursions, followed by a stepped return to approximately background $\delta^{13}\text{C}$ values (**Supp. Fig. S3c**). An increase in C_{org} burial or a reduction in Atlantic circulation only changes the magnitude of the excursions (**Supp. Fig. S3d, e**). Simulations that combine volcanic CO₂ and thermogenic CH₄ emissions result in complex $\delta^{13}\text{C}$ and $p\text{CO}_2$ responses (**Supp. Fig. S4**), depending on the magnitude and relative timing of the emissions. Our main, two-pulse scenario, combined with CH₄ emissions during the lower CO₂ rate interval results in three distinct peaks in $\delta^{13}\text{C}$, a large decrease in $p\text{CO}_2$ and a minor recovery. The two-pulse scenario combined with a pulse of CH₄ during the return to background volcanism levels results in a similar outcome to the main run (**Fig. 3**), but with a larger magnitude for the negative CIE and a larger recovery for $p\text{CO}_2$. The constant CO₂ emission and early CH₄ pulse simulation reconstructs only a minor first $\delta^{13}\text{C}$ peak and small negative CIE, followed by a very large increase to a second $\delta^{13}\text{C}$ peak. The $p\text{CO}_2$ response is characterized by a minor decrease and rapid recovery. For the constant CO₂ and late CH₄ pulse scenario, the results again resemble our main results, but with a much smaller second $\delta^{13}\text{C}$ peak. Based on these simulations, we suggest that thermogenic CH₄ could have played a role, most likely in the shape of pulses at a later stage of OAE2.

Early CH₄ pulse

Late CH₄ pulse

Supplemental Figure S4. Combined CH₄ ($\delta^{13}\text{C}_{\text{volc}}$: -35) (A, F) and CO₂ ($\delta^{13}\text{C}_{\text{meth}}$: -5) (B, G) emissions with $\delta^{13}\text{C}$ (C, H) and pCO₂ (D, I) response. The top panels correspond to CH₄ emissions from 210 k.y. to 290 k.y. and the bottom panels CH₄ emissions from 410 k.y. to 490 k.y.. Black lines correspond to the two-pulse, main CO₂ emission scenario (see main text) and red lines to a scenario with a 20 k.y. onset, 390 k.y. plateau at the maximum emission rate of 0.05 Pg C yr⁻¹.

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Supplemental Table S1. Overview of estimates of volcanic emissions for OAE 2, with rates in Pg yr⁻¹, masses in Pg and the duration of emissions in k.y., together with the estimated pulses and the method of calculation.

Reference	Rate (Pg/yr)	Mass (Pg)	Duration (k.y.)	Pulses	Calculation
Clarkson <i>et al.</i> , 2018	0.072 –	10.8 –	150	2	Model – Uranium
	0.18	27 x10 ³			
	0.048 –	7.2 –	150		
	0.126	18.9 x10 ³			
Joo <i>et al.</i> , 2020	0.028	14.16 x10 ³	500	1	LIP volume
Kuroda <i>et al.</i> , 2007	1.27 –	19 –	7 – 15	1	Model – δ ¹³ C
	4.67	32.7 x10 ³			

Supplemental Table S2. Large Igneous Province (LIP) volcanism forcing and key values and characteristics for $\delta^{13}\text{C}$ and $p\text{CO}_2$. The value for negative CIE is calculated from the starting value to the minimum value of the excursion. The value for the positive CIE is calculated from the minimum value of the negative to the maximum value of the positive excursion, if the positive CIE exceeds the background value. The Plenus CIE is calculated from the value at “a” to the minimum value. A recovery of $p\text{CO}_2$ to background values is not equal to a CO_2 decrease. A cross indicates that a certain characteristic is present in the records or simulation output. The scenarios presented in this table correspond to the simulations presented in **Figs. 2 – 4** in the main text.

LIP pulse		LIP recovery		CIE (%)			CO ₂ decrease (%) [ppmv]	Duration (k.y.)			Peak CO ₂ in OAE2 onset	CO ₂ decrease/ min. at “a”	CO ₂ increase /max. in Plenus CIE	“a” and “b” present
Number	Mass (x10 ⁵ Pg)	Mass (x10 ³ Pg)	Duration (k.y.)	Negative	Positive	Plenus		Lag first pCO ₂ – δ ¹³ C max.	OAE2 onset	Plenus CIE				
-	-	-	-	3 ^a	3 ^b	0.5-4 ^c	25 ^d	-	50 ^e	65-200 ^e	X ^f	X ^f	X ^f	
1	10	2	20	0.94	-	-	-	-	-	-	-	-	-	-
1	10	2	20	0.4	4.4	-	-	-	170.7	-	-	-	-	-
1	2	0.4	20	0.12	0.77	-	-	150	170.7	-	-	-	-	-
1	100	2	20	0.4	7.89	0.67	45 [1,700]	310	286.8	271	X	X	-	X
1	20	0.4	20	0.13	2.26	0.03	13 [200]	440	412	138	X	X	-	X
2 (no trough)	22.65	5.25	140	0.19	3.89	-	16 [300]	280	396.8	-	X	X	-	-
2 (trough)	20.3	3	80	0.19	2.96	0.52	35 [660]	145	260	222.2	X	X	X	X

LIP onset	Mass (x10 ³ Pg)	Duration (k.y.)
-	-	-
2	2	20
2	2	20
0.5	0.5	20
2	2	20
0.4	0.4	20
0.65	0.65	20
0.65	0.65	20

a: Kuroda *et al.*, 2007. b: Owens *et al.*, 2018. c: e.g. Forster *et al.*, 2007; Sinninghe Damsté *et al.*, 2010; Jarvis *et al.*, 2011. d: e.g. Barclay *et al.*, 2010. e: Kuhnt *et al.*, 2017; Jones *et al.*, 2020. f: e.g. O’Connor *et al.*, 2020.

Simulation
Target OAE2 (Fig. 1)
Base OAE2 w/o C-O ₂ -P (Fig. 2a, b)
Base OAE2 w/ C-O ₂ -P (Fig. 2a, b)
Short emissions (Fig. 2c-d)
Long emissions (Fig. 2c-d)
Stepped increase (Fig. 4)
Best fit (Fig. 4)