Geochemical consequences of intense pulse-like degassing during the onset of the Central Atlantic Magmatic Province

Guillaume Paris a,b,c,e, Yannick Donnadieu a, Valérie Beaumont b, Frédéric Fluteau c,d, Yves Goddéris e

a) Laboratoires des Sciences du Climat de l’Environnement, CNRS-CEA Saclay, Orme des merisiers, Bât. 701, 91191 Gif-sur-Yvette cedex, France
b) Institut français du pétrole, 164 rue Béziès-Péret, 92 Rueil-Malmaison, France
c) Institut de Physique du Globe, UMR 7154, Sorbonne Paris Cité, 1 rue Jussieu, 75238 Paris cedex 05, France
d) UFR des Sciences de la Terre, de l’Environnement et des Planètes, Université Paris 7, Sorbonne Paris Cité, 35 rue Hélène Brion, 75205 Paris cedex 13, France
e) Géosciences Environnement Toulouse, CNRS-Université de Toulouse III, 14 Avenue E. Belin, 31400 Toulouse, France

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A B S T R A C T

The Triassic–Jurassic boundary (TJB) is marked by one of the five largest mass extinctions of the Phanerozoic and the eruption of a large igneous province: the Central Atlantic Magmatic Province (CAMP). The TJB is characterized by a carbonate production crisis, by negative excursions in the carbon isotopic ratio of buried organic matter, and by successive peaks in atmospheric CO2. Here we use the numerical model GEOCLIM to explore the possible connections between the CAMP emplacement and the observed carbon cycle perturbations. Different degassing scenarios linked to the CAMP eruption are explored. We show that the emission of realistic amounts of CO2 that follow a geologically constrained degassing scenario as short-term peaks (less than 10 ka) leads to successive decrease in carbonate production, as observed in the geological record. We also calculate the evolution of carbon isotope pools of light isotopic composition located at the transition zone [Cartigny, P. 2010, Earth and Planetary Science Letters, v. 296, p. 329–339] and not necessarily to biogenic methane release. Finally, the model predicts a succession of short-term CO2 rises, with an amplitude in close agreement with available proxy-based reconstructions.

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1. Introduction

The late Rhaetian is marked by one of the most important mass extinction of the Phanerozoic, in both the marine and terrestrial realms (Sepkoski, 1996; Hesselbo et al., 2007). The Triassic–Jurassic Boundary (TJB) crisis is coincident in time with the emplacement of the Central Atlantic Magmatic Province (CAMP), one of the largest Phanerozoic Large Igneous Provinces (LIP) in terms of area covered and volume of basalt emitted (Pálfy et al., 2001; McHone, 2002; Courtillot et al., 2003; Guex et al., 2004; Van de Schootbrugge et al., 2009; Blackburn et al., 2013; Dal Corso et al., 2014). The CAMP emplacement, similarly to other LIPs through the Mesozoic, affected the composition of the atmosphere through degassing of CO2 and sulfur gases (McHone, 2002; Schaller et al., 2011; Richoz et al., 2012; Callegaro et al., 2014) and is thought to be the trigger of the TJB environmental crisis, even though bolide impact has also been suggested (Olsen et al., 2002).

From a geochemical point of view, the surficial Earth system appears to have been strongly disturbed at the TJB boundary. First, reconstructions of atmospheric CO2 levels across the TJB based on paleosol data from North America suggest the existence of 4, and possibly 5, ample peaks (Schaller et al., 2011, 2012). Those peaks might be the consequence of paroxysmal degassing episodes during the onset of the CAMP. Second, a major decrease in carbonate production is recorded at the TJB, together with a perturbation of the biological pump in the Te- thys water column and possibly connected with ocean acidification (Kürschner et al., 2007; van de Schootbrugge et al., 2007, 2008; Clémente et al., 2010a, 2010b; Paris et al., 2010; Greene et al., 2012). Third, two negative carbon isotope excursions (CIE) in sedimentary organic carbon (δ13Corg) are recorded worldwide during the late Rhaetian and during the early Hettangian successively (Pálfy et al., 2001; Ward et al., 2001; Hesselbo et al., 2002; Guex et al., 2004; Galli et al., 2005; Kürschner et al., 2007; Ruhl et al., 2009; Whiteside et al., 2010; Bartolini et al., 2011; Meyer et al., 2013). The late Rhaetian CIE is also observed in carbonate carbon isotopic composition (δ13Cmin) (Galli et al., 2005; Pálfy et al., 2007; Clémente et al., 2010b; Paris et al., 2010). However, in the section of St Audrie’s bay (UK), the Hettangian excursion is...
recorded as a shift towards more negative \( \delta^{13}C_{\text{org}} \) values and not as an actual excursion (Ruhl et al., 2010).

General circulation models and carbon cycle models are a powerful tool to reconstruct carbon cycle perturbation in the past. Huynh and Poulsen (2005) used a coupled ocean–atmosphere climate model to explore the consequence of an atmospheric CO2 increase on the late Rhaetian climate. They concluded that the Earth system would have been deeply perturbed by an increase in atmospheric CO2, with warm and dry summers affecting terrestrial ecosystems (Huynh and Poulsen, 2005). The consequences of a CO2 degassing on the oceanic carbon chemistry have also been explored using the global carbon cycle model GEOCARB (Beerling and Berner, 2002; Berner and Beerling, 2007). These authors suggested that the late Rhaetian negative \( \delta^{13}C \) excursion is due to clathrate dissociation and that the late Rhaetian carbonate production crisis was driven by the undersaturation of seawater with respect to calcite, as a result of the acidification promoted by the massive emissions of CO2 and SO2 from the CAMP (Beerling and Berner, 2002).

Here, we use the coupled climate–carbon cycle model GEOCLIM to explore the consequences of a geologically constrained scenario of CO2 emissions from the CAMP (Fig. 1). Indeed, degassing of CO2 from LIPs is usually modeled as a Gaussian distribution over the duration of the eruption. This assumption has been proven to be wrong, since the CAMP emplacement occurred as a succession of intense and short-lived pulses (Knight et al., 2004; Schaller et al., 2011). Concentrating the total release of CO2 by the CAMP within a few peaks will impact the Earth system differently than assuming a continuous release. Release of CO2 peak on timescales shorter than, or close to, the mixing time of the ocean–atmosphere system (~2–3 ka) forces the system out of steady state. The consequences of such short-lived CO2 peaks on the late Triassic carbon cycle have never been explored before; which is the goal of this paper in the specific paleoenvironmental context of the TJB. We show in this work that a peak scenario allows the model to reproduce two of the global geochemical features of the TJB (evolution of the atmospheric CO2 concentration and carbonate crisis), while the carbon isotope record requires a reconsideration of the mantle source carbon isotopic composition.

### 2. Model description

#### 2.1. General description

GEOCLIM (Donnadieu et al., 2006a) couples the FOAM general circulation model (GCM) (Donnadieu et al., 2006b) to a model of the main biogeochemical cycles called COMBINE (Goddéris and Joachimski, 2004). The GCM is used to generate an offline grid of continental air temperature \( T_{\text{air}} \) and runoff \( R \) with a spatial resolution of 7.5°long × 4.5°lat. The atmospheric CO2 concentrations used in the FOAM simulations range from 200 ppm up to 4200 ppm, with incremental steps every 200 ppm. At each time step, GEOCLIM calculates the atmospheric CO2 concentration and the corresponding spatially distributed \( T_{\text{air}} \) and \( R \) above the continents through a linear interpolation procedure from the offline catalogue. For the purpose of the present study, we use a Rhaetian paleogeography (Donnadieu et al., 2006a).

The components of the biogeochemical cycles are calculated using a box model where the ocean is longitudinally divided into three parts, two polar oceans and one low- to mid-latitude ocean (Fig. 2). The polar oceans are located between −90° and −60° latitude for the southern hemisphere and +60° and +90° latitude for the northern hemisphere. Each polar ocean includes a photic zone and a deep ocean reservoir. The low- to mid-latitude ocean is divided vertically into three parts: the photic zone, the thermocline and the deep ocean.

![Fig. 1. Synchronicity between the late Rhaetian-early Hettangian sedimentary organic carbon isotopic composition negative excursion in UK, biological events around the TJB and CAMP volcanic events from North America and Morocco.](image-url)
reservoir. Two boxes representing epicontinental seas are also included, with a photic zone and a deep epicontinental reservoir. A twelfth box represents the atmosphere. A full description of GEOCLIM and its components can be found elsewhere (Goddéris and Joachimski, 2004; Donnadieu et al., 2006a, 2006b; Simon et al., 2007). Key equations are summarized in Table 2.

2.2. Short description of the model key fluxes

The model describes the biogeochemical cycles of carbon, phosphorus, alkalinity and oxygen. We set the CO2 degassing background value to the modern one; i.e. 6.8 × 10^{12} molC/a (prior to the CAMP eruption), because oceanic crust production occurred at a constant rate for the last 180 Ma (Rowley, 2002), we assume the same rate for the late Triassic as well. The modern atmospheric CO2 consumption rate through silicate weathering is 13.6 × 10^{12} molC/a (Gaillardet et al., 1999), half of the amount delivered is ultimately stored in carbonate sediments at the geological timescale. The calibration constants k_{silw} and k_{basw} for weathering of granite-type silicates and basalts respectively (Table 2) are calibrated for the present day using a FOAM climatic simulation by (Dessert et al., 2003). The calibration constant for phosphate weathering k_{pw} is set so that the modern flux F_{pw} equals 45 × 10^{9} mol/a, within the estimated range for the present day (Buendia et al., 2010). Primary productivity in surface oceanic reservoirs is proportional to the flux of phosphate entering the reservoir from either oceanic mixing or, for the epicontinental seas, continental weathering. The organic carbon produced in the photic zone aggregates from either oceanic mixing or, for the epicontinental seas, continental weathering. The organic carbon produced in the photic zone aggregates from either oceanic mixing or, for the epicontinental seas, continental weathering. We do not set any constraint to the total carbonate deposition flux. It dynamically evolves to balance between the alkalinity flux removed through carbonate deposition and the alkalinity flux delivered by continental weathering. The shelf platform area where neritic carbonates accumulate is assumed to be 18 times larger in the late Triassic/early Jurassic than the modern one (Walker et al., 2002). The global carbonate factory is calibrated so that present-day deep-sea carbonate accumulation equals 8.7 × 10^{12} molC/a (Catubig et al., 1998), the rest being buried as neritic carbonates (11.7 × 10^{12} molC/a). Both fluxes are a function of the calculated saturation state of the surface seawater with respect to carbonate minerals (Ω, Table 2) (Donnadieu et al., 2006a). If seawater gets undersaturated with respect to aragonite in any surface oceanic reservoir, the local carbonate production stops. For the purpose of the present TJB numerical simulations, we assume that the production of pelagic carbonate is restricted to surface epicontinental seas (Ridgwell, 2005).

A complete carbon isotopic budget is solved at each time step. It includes the isotope partition during carbonate speciation, and the preferential incorporation of the light isotope in organic carbon during photosynthesis. The carbon isotopic fractionation between organic matter (OM) and aqueous CO2 is defined as εP (Eq. (1)). This εP is directly influenced by the concentrations of dissolved CO2 ([CO2]aq) and phosphate in seawater (Pagani et al., 1999), which are both calculated at each time step for each oceanic photic reservoir:

\[
25 - \varepsilon_P = \frac{(159.5[PO_4]) + 38.39}{[CO_2]_{aq}}. \tag{1}
\]

3. CAMP degassing: constraints and scenarios

3.1. Description of the CAMP

The CAMP consists of floods, sills and dykes with outcrops in Africa, South and North America and Meridional Europe (Marzoli et al., 1999; Prévoit and McWilliams, 1989). The CAMP has been investigated mostly in three locations: High Atlas (Morocco), Newark basin (USA) and Fundy basin (Canada). Each basin contains successive basalt layers and sills that have been correlated as possible single emission units (Fig. 1). The total surface of the CAMP is estimated at 2–6 × 10^6 km^2 with a mean thickness of 150–300 m (Marzoli et al., 1999). The duration

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Table 1: Estimates of the CO2 volume emitted by the CAMP.

<table>
<thead>
<tr>
<th>Basalt volume (km^3)</th>
<th>CO2 content wt.%</th>
<th>% Degassed CO2</th>
<th>GeCO2</th>
<th>GeC</th>
</tr>
</thead>
<tbody>
<tr>
<td>McHone (2002) low hypothesis</td>
<td>2.385 × 10^6</td>
<td>0.117</td>
<td>70%</td>
<td>5200</td>
</tr>
<tr>
<td>Olien (1996) high hypothesis</td>
<td>8 × 10^6</td>
<td>0.6</td>
<td>100%</td>
<td>128,000</td>
</tr>
</tbody>
</table>

1 Estimate by Beerling and Berner (2002).
of the CAMP paroxysmal activity phase was estimated at 580 ± 100 ka (Olsen et al., 1996; Nomade et al., 2007). A strong temporal coincidence exists between the late Triassic mass extinction, the first CIE and the CAMP emplacement (Marzoli et al., 1999; Schaltegger et al., 2008; Cirilli et al., 2009; Schoene et al., 2010; Whiteside et al., 2010; Schaller et al., 2012). Such a scenario is strongly in agreement with the total estimated duration of the CAMP eruption (Marzoli et al., 1999; Schaltegger et al., 2008; Dessert et al., 2001) and lasted less than the deposition of a single lava unit, we allow for possible diachronicity within the enormous area covered by the CAMP. Nonetheless, we use available ages as a geochronological constraint for our scenario.

As stated, individual peaks could have been emitted in much less than 10 ka (Knight et al., 2004). To test the influence of the duration of one given peak, we run two versions of scenario B (B-10 ka and B-1 ka). In B-10 ka, we assume 10 ka peaks, as described above, and in B-1 ka, we assume 1 ka peaks. In both versions of scenario B-1 ka, however, peak 3 lasts for 60 ka. The other peaks emit the same amount of CO2 in both B-1 ka and B-10 ka, but ten times as fast in B-1 ka as in B-10 ka (Table 3).

**3.2. Degassing pattern**

The degassing produced during the onset of a LIP is usually modeled as a Gaussian distribution or a step function spanning the trap emplacement duration (Dessert et al., 2001; Beerling and Berner, 2002; Grard et al., 2005). To test the role played by the CAMP in the TJB events, two distinct degassing scenarios have been considered (Fig. 3). The first scenario (A) is represented by a single Gaussian degassing over 500 ka, in close agreement with the total estimated duration of the CAMP. The second scenario (B) follows the timeline established by Blackburn et al. (2013), as described in the following and in Table 3.

The CAMP eruption occurred through several major volcanic phases across the Pangea (North and South America, Europe and Africa) separated by periods of quiescence that allow deposition of sediments. Most of the lava flows observed in the Newark basin have been deposited within a precession cycle (Schaller et al., 2012) and lasted less than 20 ka, maybe even as short as 400 years (Knight et al., 2004). Here, we assume the existence of four main peaks in scenario B (Table 3, Figs. 1 and 3) following geochronological and stratigraphic data for lava flows from the Newark basin (Schaller et al., 2012; Blackburn et al., 2013). Peak 1 (lower unit of the CAMP basalts) consists of different layers that cannot be unambiguously distinguished by ages but are stratigraphically resolved (lower and lower + intermediate compositions vs. intermediate composition, see Blackburn et al., 2013). Thus, we split peak 1 into two identical sub-peaks, peak 1a and peak 1b, separated by ~15 ka (Fig. 4 in Blackburn et al., 2013). Peaks 2 and 4 are modeled as a single peak of ~10 ka duration each. Peak 3 is less resolved than peaks 1 and 2 and is estimated to have lasted for possibly as long as ~60 ka (Schaller et al., 2012). Such a scenario is strongly influenced by detailed description or eruptive events in North America and Morocco. However, by allowing our peaks to last 10 ka, which is possibly much longer than the deposition of a single lava unit, we allow for possible diachronicity within the enormous area covered by the CAMP. Nonetheless, we use available ages as a geochronological constraint for our scenario.

**Fig. 3.** Modeled CO2 emissions. (a) The first peak (1) corresponds to the lowest volume of Table 1 (1440 GtC) and (2) corresponds to the highest volume possible (34,290 GtC). An intermediate volume 21,220 GtC (scenario A) emitted fits the CO2 emission calculated by Beerling and Berner (2002) and is the total flux used for scenarios A and B (Fig. 3b and c). Scenario B is based on Blackburn et al. (2013) ages, with durations for peaks 1, 2 and 4 of ~10 ka, scenario B-10 ka (b) and ~1 ka, scenario B-1 ka (c).
3.3. Volume of degassed CO2

The volume of CO2 likely released during CAMP emplacement is bracketed by a “low” and a “high” hypothesis (Table 1, Fig. 3). The first one (“low hypothesis”) corresponds to a total volume of 1400 GtC (McHone, 2002). The second one (“high hypothesis”) corresponds to the amount of CO2 that would be degassed by the highest possible estimated basalt volume of the CAMP, including outcrops, seaway dipping reflectors from eastern USA and also a volume of intrusive CAMP rocks (Beiling and Berner, 2002). The CO2 release is calculated using a CO2 content of 0.6 wt.% in the magma and a 100% degassing. Total CO2 emissions then reach an extreme 34,900 GtC. In the present study, we assume an emitted CO2 amount similar to the one used by Berner and Beiling (2007), 21,200 GtC, or 77,700 GtCO2, which is about four times the amount of CO2 suggested by Schaller et al. (2012) for one single peak (15,400 GtCO2). In scenario A, the total amount (77,700 GtCO2) is emitted in one single 500 ka Gaussian peak, while in our scenarios B, this total amount of CO2 is evenly distributed between the four peaks (and then split evenly the first peak – i.e. 25% of the total CO2 – between sub-peaks 1a and 1b).

4. Results

In this section, we discuss the impact of the CAMP degassing scenarios on the carbonate factory, the carbon isotopic budget, and the atmospheric CO2 evolution.

4.1. The CAMP and the carbonate factory

The results of the model are described in terms of carbon partition between the different reservoirs. In case A (Gaussian degassing), CO2 emissions from the CAMP are mostly buffered by continental weathering, transferring atmospheric carbon to the ocean, limiting the atmospheric CO2 increase. Average seawater Ω (weighted average value over all the oceanic reservoirs) decreases in the ocean from 2.15 to 1.65 and average pH by 0.25 unit. In epicontinental seas however, pH decreases by 0.16 units while alkalinity and DIC (dissolved inorganic carbon) increase strongly (resp. from 2.6 to 4 mmol·kg⁻¹ and from 2.65 to 3.85 mmol·kg⁻¹). Different responses are observed depending on the model ocean reservoir. Atmospheric CO2 increases and subsequent warming enhances continental weathering, which delivers alkalinity to the epicontinental seas and counteracts the ongoing ocean acidification due to the atmospheric CO2 increase. This modeled increase of the saturation state promotes the reef carbonate production, which increases from 22 × 10¹² to 31 × 10¹² molC·a⁻¹ (Fig. 4). Because of higher input of phosphate to the ocean, primary productivity is promoted. As a result, organic matter sedimentation increases from 3.5 × 10¹² to 4.7 × 10¹² molC·a⁻¹ and pelagic carbonate production from 3.4 × 10¹² to 4.4 × 10¹² molC·a⁻¹.

In case B with 10 ka peaks, the successions of peaks 1a, 1b and 2 generate short term peaks of ~2250 ppm CO2 (Fig. 3c) concomitant to an acidification of 0.15 pH units of the world ocean (and in epicontinental seas) and to a decrease of the saturation state (Fig. 4). Each volcanic pulse leads to a drop in reef carbonate production (decrease of 15 to 30% depending on the peak, Fig. 5), yet stacked on a long-term increase from 22 × 10¹² to 28 × 10¹² molC·a⁻¹ due to the progressive increase in alkalinity released by enhanced weathering. The changes are more pronounced in the case of scenario B-1 ka, but the consequences are qualitatively the same. Primary production is promoted by these peaks of CO2. The calcareous pelagic production is calculated as proportional to the global primary production (although modulated by the saturation state of the waters with respect to carbonate minerals). Therefore, the pelagic carbonate production is marked by short term increases of 0.5 × 10¹² to 4.2 × 10¹² molC·a⁻¹ superimposed on a long term increasing trend of 3.4 × 10¹² to 4.7 × 10¹² molC·a⁻¹.

Unlike the scenario assuming a continuous long-term degassing during the CAMP onset, a scenario accounting for short-term peak emissions of CO2 may produce a temporary decrease of the reef carbonate production. This result is the consequence of the interplay between various timescales. When CO2 is emitted continuously, with a characteristic timescale close to or longer than the residence time of carbon in the ocean–atmosphere system (about 200 ka), continental weathering controls the time evolution of the system. Weathering is fast enough to consume carbon as it is released by the CAMP. At the same time, alkalinity is transferred from the continental crust to the ocean at a rate close to the degassing rate. As a consequence, carbonate production increases in the epicontinental seas. When it is assumed that the CAMP releases short CO2 bursts, the time scale is largely below the carbon residence time in the ocean–atmosphere system, but quite close to the mixing time of the ocean–atmosphere (a few ka). Dissolution of CO2 in the ocean acidifies seawater faster than alkalinity is delivered by continental weathering. Consequently, reef carbonate production decreases. By contrast, the pelagic production is driven by weathering-delivered phosphorus. Indeed, the residence time of phosphorus in the ocean is much shorter than carbon (60 ka versus 200 ka). Therefore, pelagic productivity and associated carbonate production slightly increase during short term bursts.

Overall, the model suggests that undersaturation of the surface ocean with respect to carbonate is not reached during the degassing peaks, similarly to suggestions from previous studies (Greene et al., 2012). The predicted decrease in the saturation state of the seawater (Fig. 4a) forces reef carbonate production to decrease by up to 30%. As such it contributes to the carbonate crisis observed at the TJB, but may not be the unique cause. On a biological point of view, such a succession of fast changes in the saturation state might potentially drive some species to extinction. Furthermore, the succession of pulses could affect successively different species, potentially explaining the dispersion of extinctions as it is observed in available sections (Hesselbo et al., 2007).

4.2. The CAMP and the carbon isotopic signals

The isotopic composition of organic and carbonate carbon produced in the photic zone of the epicontinental ocean are shown in Fig. 6 (“reference run”), the isotopic composition of emitted CO2 remains constant at δ¹³C₀₂ = −3.5‰, slightly above the canonical value of −5‰ to account for a possible contamination by sedimentary carbonates. In the model, organic carbon is affected by a modest negative CIE (< −3‰) while the carbonate isotopic composition does not change significantly. The model thus fails in reproducing either the ample CIE observed in organic carbon (up to −8‰ (Ruhl et al., 2009)) or the excursion in the δ¹³Ccrust record. An easy way to produce carbon isotope excursions
during major environmental crises is to add carbon with a very low isotopic signature to the atmosphere. This can be achieved by releasing biogenic methane in the atmosphere, similarly to the case of the Paleocene–Eocene thermal maximum (Dickens et al., 1995), which might be not the unique solution. We explore here the influence of changing the isotopic composition of the mantle carbon emitted by the CAMP.

The isotopic composition of carbon emitted by the CAMP used in the previous simulations is $-3.5^{\circ}$‰. Pools of lighter carbon exist in the mantle. $\delta^{13}C$ values between $-22^{\circ}$‰ and $-26^{\circ}$‰ have been measured in xenoliths from both hotspot and non-hotspot volcanoes and in xenoliths from kimberlites (Deines, 2002). The existence of such low values has been confirmed by the isotopic composition of the peridotic diamonds ($\delta^{13}C$ values ranging from $-26.4$ to $+0.2^{\circ}$‰) and eclogitic diamonds ($-38.5$ to $+2.7^{\circ}$‰; Cartigny, 2005). These values are supposed to reflect distinct mantellic carbon sources (Cartigny, 2005), with $^{13}C$-depleted carbon pools at the transition zone. We assume here that the CAMP could have been characterized by isotopically light carbon emissions. The origin of the CAMP tholeiitic series seems to be rooted in the 

![Diagram](image)

**Fig. 4.** Saturation state calculated in (a) the epicontinental sea photic zone (oceanic box 6) and (b) bottom waters (oceanic box 7), (c) the global ocean and (d) the open ocean photic zone (oceanic box 3). The CO$_2$ increase affects the continental weathering and the subsequent alkalinity delivering fluxes to the surface epicontinental waters, as shown in the onset. The concerned oceanic boxes are also indicated in the onset.

![Diagram](image)

**Fig. 5.** Flux of carbonate out of the ocean for scenarios A, B-10 ka and B-1 ka, for reef and pelagic productions.
knowledging that all or only part of the degassed CO2 could display composition of δ13C isotopic composition of inorganic carbon in paleosoils and comparison for organic carbon intensity of the modeled CIE is closer to the sedimentary geochemical signature. The ages of the Preakness basalt from Schaller et al. (2011) and Schaller et al. (2013) are consistent with the timing of the extinction event and the two solid lines indicate Peak 1a and 1b of our record from St Audrie’s bay, UK (Ruhl et al., 2010) and the compound-record specific record from the Newark and Hartford basins (Whiteside et al., 2010). The star indicates the first CIE/extension event, and the two solid lines indicate Peak 1a and 1b of our model. The comparison is achieved by aligning the first CIEs and the extinction event, assuming a constant sedimentation rate in St Audrie’s bay over 1 Ma and using the linear age model of the data is slightly modified, so that excursion, while the carbon isotopic composition of the carbonates follows a ~3‰ excursion. In the case of 1 ka peaks, the excursions are more pronounced, by 1‰. The results agree with the sedimentary records where organic carbon gets proportionally more enriched in 13C than carbonate carbon, which can be explained by the influence of pCO2 on the fractionation factor [Eq. (1)]. The important point here is that a pronounced negative CIE recorded in sediments can reflect a biogenic methane release into the ocean–atmosphere system, but such a release may not be required if carbon with lower δ13C values can be released by volcanism.

A direct comparison of the calculated carbon isotopic compositions with the δ13C records is not easy because of the lack of a robust timeline for the data. The first, or initial, δ13C negative excursion has been estimated to last less than 290 ka (Ward et al., 2001; Guex et al., 2004; Schoene et al., 2010) and even as short as 20–40 ka (Ruhl et al., 2010). It remains debated whether the emplacement of the CAMP is occurring right before or after the extinction event defined based on pollen stratigraphy (Marzoli et al., 2004; Deenen et al., 2011; Blackburn et al., 2013; Dal Corso et al., 2014). Blackburn et al. (2013) suggested that the very base of the High Atlas Lower Unit coincides with the extinction event itself, and therefore the first CIE. If this is the case, the volcanism could be the direct cause of the negative CIE observed in the late Rhaetian because the amplitude of the CIE (~6‰) agrees with the modeled excursion in the case of scenario B with a light isotopic composition of emitted carbon. However, the timing of the modeled CIE does not reflect the timing of the sedimentary record (Fig. 8). The discrepancy could be explained by an issue in the age model of either the CAMP lava flows or the various sedimentary records. Another explanation is that the δ13C sedimentary records have been affected by local or secondary processes, while the model output stands for the average δ13C of the organic matter buried in all epicontinental seas. Most of the studied sections are influenced by different environments, as reflected by the cyclicity of the records (Paris et al., 2010; Ruhl et al., 2010; Whiteside et al., 2010).

4.3. The CAMP and the atmospheric CO2

Fig. 7 shows the calculated pCO2 for scenarios B 1 ka and 10 ka. The results are shown as variations relative to the pre-volcanism background level. The age model of the data is slightly modified, so that...
the age of the lava flows used in the paleosoil studies (Schaller et al., 2011; Schaller et al., 2012) agree with the more recent ages established for the lava flows by Blackburn et al. (2013). We assign an age of 201.55 Ma to the Orange Mountain and Talcott basaits in the studies by Schaller et al. We average the ages of the Preackness Basaits and Rossville Intrusive, evaluated at 201.274 ± 0.032 Ma and 201.305 ± 0.034 Ma respectively (Blackburn et al., 2013) to evaluate the age of the Preackness/Holyoke basaits (peak 3) at 201.289 Ma. Finally, we use the age of the Butner Intrusive for the Hook Mountain/Hampden basaits (peak 4) despite differences in chemical compositions between the former and the latters (Callegaro et al., 2013; Merle et al., 2013). The calculated range of CO2 fluctuations is in close agreement with the paleosoil reconstructions. The only exception to this model-data agreement is the existence of a possible additional CO2 peak observed by Schaller et al. (2012) without known corresponding lava flows. Post-eruption lower atmospheric CO2 concentrations are attributed by Schaller et al. (2012) to the weathering of the fresh basaltic surfaces. This process is not considered in our modeling, as the post-CAMP evolution is not the focus of the present paper.

5. Discussion

Some disagreement exists between the model results and the geological observations. Calcareous organisms in epicontinental seas are affected by the TJB events and are supplanted by picoplankton or organic-walled organism (van de Schootbrugge et al., 2007; Clémence et al., 2010a, 2010b; Paris et al., 2010). Therefore, the increased pelagic carbonate production that follows the biological productivity enhancement is suspected to have contained SO2 and dusts, generating aerosols, seawater with other atmospheric changes, similarly to the simulations performed by previous works, such as sulfur cycle perturbations (Callegaro et al., 2014), togeth-er with walled organism (van de Schootbrugge et al., 2007; Clémence et al., 2010). The existence of such isotopic anomalies in the mantle could be considered range of isotopic composition (−20%) of the degassed mantle carbonate. Although such a low value may appear unrealistic, the existence of heterogeneities in the mantle displaying very low carbon isotope composition has been proposed recently by Deines (2002) and Cartigny (2010). The existence of such isotopic anomalies in the mantle could be considered in the future as an alternative to biogenic methane release systematically used to explain negative carbon isotopic excursions in the surficial environment. By assuming a −20% isotopic composition for the CO2 released by the CAMP, we reproduce the intensity of the first negative excursion in δ13Corg values.

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