Effects of the Pliensbachian–Toarcian Boundary Event on Carbonate Productivity of a Tethyan Platform and Slope

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Abstract We explore the effects of the Pliensbachian–Toarcian Boundary Event (P–ToBE) on tropical carbonate productivity in the interior to margin and slope of the Venetian Platform (Northern Italy). We document the P–ToBE for the first time in the shallow-water platform margin, and we bio- and chemostratigraphically tie it to transgressive/regressive cycles. Following the latest Pliensbachian sea-level drop and emergence, transgressive grainstones at the platform edge record the P–ToBE negative carbon isotope excursion (CIE) of 1–1.5‰, also found in marl/limestone couplets on the slope. Recovery of platform productivity was ephemeral, as the platform drowned right after the peak negative CIE and was covered by deep-sea thin-bedded micritic limestones. The end of the P–ToBE correlates with a regression and renewed recovery of carbonate productivity. The negative CIE of the subsequent Toarcian Oceanic Anoxic Event is recorded in open-sea cherty limestones both at the marginal and interior platform. These limestones document an even wider transgression and the renewed partial drowning of the platform in the Serpentinitus Zone. We investigate the causes of the carbon perturbation at the P–ToBE, using a simple carbon cycle model. The duration and magnitude of the CIE suggest a rapid release of methane in driving the CIE, perhaps related to the preceding sea-level drop and associated cryosphere perturbation, or to thermogenic alteration of coals near the Karoo-Ferrar Large Igneous Province (LIP). The extent of the warming and the magnitude of the P–ToBE CIE implies a contribution of volcanogenic carbon dioxide from the Karoo-Ferrar LIP.

1. Introduction

The Toarcian Oceanic Anoxic Event (T–OAE) (ca. 183 Ma) of the Early Jurassic is considered the oceanic expression of a global perturbation of the carbon cycle and has been extensively studied since its definition by Jenkyns and Clayton (1986). During the T–OAE, severe environmental and biological changes drove increased rates of extinction and the widespread deposition of organic carbon-rich shales in deep-marine and epicontinental settings (Jenkyns, 2010). The T–OAE is characterized by a negative carbon isotope excursion (CIE) in both organic matter (δ13Corg) and carbonates (δ13Ccarb) of 3–8‰ in the Early Toarcian (Serpentinus/Falciferum Zone), which is visible in stratigraphic sections all over the world (e.g., Al-Suwaidi et al., 2010; Hesselbo et al., 2007; Izumi et al., 2012; Jenkyns et al., 2002; Them II et al., 2017; Woodfine et al., 2008). The negative CIE of the T–OAE is generally attributed to an increased input of volcanic CO2 from the coeval LIP of the Karoo-Ferrar (Ikeda & Hori, 2014; Palfy & Smith, 2000; Xu, Mac Niocaill, et al., 2018) and/or the release of isotopically light methane from marine clathrates (Hesselbo et al., 2000), or metamorphism of Gondwana coals (McElwain et al., 2005; Svensen et al., 2007; Woodfine et al., 2008). Prior to the T–OAE—at the Pliensbachian–Toarcian boundary (Spinatum to Tenuicostatum Zones)—a similar, but less pronounced negative CIE (~1–2.5‰) has been documented in carbonates, kerogen, and fossil wood in different sections in Europe and Africa (Bodin et al., 2016; Fantasia et al., 2019; Hesselbo et al., 2007; Jenkyns & Clayton, 1997; Littler et al., 2010; Rodrigues et al., 2019). This perturbation, which has been referred to as the Pliensbachian–Toarcian Boundary Event (P–ToBE) is, like the T–OAE, associated with rapid and pronounced global warming, increased hydrological cycling and a second order marine extinction (e.g., Caruthers et al., 2013; Menini et al., 2019; Suan et al., 2010). The P–ToBE coincides with a crisis of Tethyan carbonate platforms including local incipient drowning, which was proceeded by a drop in eustatic sea level and the emersion of platforms, likely related to a background icehouse climate (Cobianchi & Picotti, 2001; Gómez et al., 2016; Hinnow & Park, 1999; Price, 1999; Ruebsam et al., 2019; Silva & Duarte, 2015; Suan et al., 2010).

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The perturbation of the carbon cycle at the P–ToBE and its effects on the carbonate factory have not been well studied and possible links to the T–OAE, which is in many ways similar, are yet poorly understood. One explanation for the small number of studies of the Late Pliensbachian and of the P–To transition is that stratigraphic successions spanning the uppermost Pliensbachian Spinatum Zone often have hiatuses or are very condensed (e.g., Léonide et al., 2012; Morard et al., 2003), which prevents a detailed, high-resolution analysis. The continuous sections presented in the literature mostly come from deep-water settings, preventing the understanding of the amplitude and effects of the sea-level fluctuations associated with the CIE. Here, we present new δ13Ccarbon and δ18Owater data from a well-dated and continuous carbonate slope section across the P–To boundary and δ13Ccarbon isotope data from the corresponding marginal and inner platform sections from the Southern Alps of Italy. The correlation of these three different paleoenvironments allows to follow the effects of the P–ToBE and the T–OAE from the carbonate platform to the open sea, defining a link between sea-level, the global carbon cycle, and carbonate productivity. Finally, we discuss, with the help of a numerical model, the main parameters likely controlling the P–ToBE carbon perturbation. The relative role of the duration and the provenance of the additional CO2 are tested and discussed, using the observed carbon isotope curve as the primary constraint for the model.

2. Geological Setting

The study area is located in the central Southern Alps of Northern Italy in the Mesozoic paleogeographic realm of the Lombardian Basin and the Venetian (or Trento) Platform (Figure 1). These domains were located in the western Tethys and were formed as a consequence of the rifting of Pangea from the Late Triassic onward (Bertotti et al., 1993, Figure 1). These Mesozoic units were telescoped southward in the Neogene into a fold and thrust belt (not shown in Figure 1), perpendicular to the main rift boundaries, thereby preserving the original Mesozoic paleogeography. During the Early Jurassic, the shallow water Venetian Platform was roughly 100 km-wide bordered by the Ballino-Garda fault, a west-dipping normal fault separating it from the deep-water Lombardian Basin. In the east, the Belluno Basin was a fault-bounded trough separating the Venetian Platform from the Friuli Platform where shallow water conditions persisted until the end of the Mesozoic (Masetti et al., 1998, Figure 1). The Early Jurassic succession of the Venetian Platform consists of carbonates formed in a Bahamian-type rimmed platform, the so-called Calcari Grigi (Hettangian–Pliensbachian). The Lombardian Basin, a realm of pelagic sedimentation, recorded the growth and demise of the adjacent Venetian Platform that was supplying it with periplatform deposits (Cobianchi & Picotti, 2001; Picotti & Cobianchi, 1996). Across the P–To boundary, a thin wedge of pelagic deposits from the Tofino Fm. of the Lombardian Basin transgressed over the western side of the Venetian Platform, which experienced a drop in the sedimentation rate. The subsequent regression allowed the progradation of oolitic and crinoidal sand bars in a ramp setting—the Oolite di San Vigilio (lower Toarcian—lower Aalenian)—and, to the north, the Encrinite del Peller (lower Toarcian–lower Bajocian, Cobianchi & Picotti, 2001). After the early Middle Jurassic shelf wedge progradation, the Venetian Platform drowned, and an open-sea plateau developed, with red condensed facies, significantly reducing the contribution of sediments to the Lombardian Basin, where radiolarian-rich deposits developed (Chiari et al., 2007).

3. Materials and Methods

3.1. Sampled Sections

The measured sections were logged in detail and sampled at intervals of 10–20 cm across the expected locations of the P–ToBE and the T–OAE and at intervals of 1–2 m toward the end of the profiles. We combined field observations with a microfacies analysis of 27 thin sections. The Brasa section is a typical slope succession with pelagic sediments, locally slumped, channelized and rich in breccias. The stratigraphy was first described by Picotti and Cobianchi (1996) and is temporally calibrated using nanofossil biostratigraphy (>125 nanoplankton samples over 38 m of stratigraphy) by Cobianchi and Picotti (2001) that used the biozonal scheme of Mattioli and Erba (1999), recently revised by Ferreira et al. (2019). The section outcrops in a roadcut at the SS38 (Via Benaco) in the Brasa gorge, located around 700 m west of the western shore of Lake Garda (Figure 1). The newly investigated platform successions Prà Castron, Cima Benon, and Baita Nana are in the Brenta Dolomites that represent the marginal and thickest part of the Venetian Platform. The Cima Benon and Prà Castron sections are representative of the platform margin, since they are located around 2 km east of the abrupt break in slope of the Ballino-Garda fault, opening toward the Lombardian Basin (Figure 1). The Cima Benon section was measured a few tens of meters to the east of the peak, while the Prà Castron section is located at the pass of Prà Castron,
around 350 m distant. The Prà Castron section was only sampled for thin sections and nannofossils, given the presence of frequent marly interbeds. The Baita Nana site is the easternmost section and is situated within the platform interior around 1 km from the pinching out of the Toarcian deposits against a faulted scarp (Figure 1b).

The distance between this section and Cima Benon is around 4 km; the Brasa section is 56 km to the south. In its paleogeographic setting, however, the distance to the Brasa section would have been less—approximately 5 to 10 km—given the left lateral Alpine component of the Neogene reactivation of the Ballino-Garda line.

3.2. Nannofossil Analysis

In addition to the nannofossil study performed by Cobianchi and Picotti (2001) in the slope successions, we studied 13 new samples from marly interbeds in the platform successions of Prà Castron, Cima Benon, and Baita Nana for nannofossil biostratigraphy. Samples were prepared according to the standard smearing technique.

Figure 1. (a) Study sites (orange circles) indicated on a paleogeographic map of the central Southern Alps in the Early Jurassic (modified after Cobianchi & Picotti, 2001). (b) Paleogeographic (Early Jurassic) position of the three measured sections Brasa, Cima Benon and Prà Castron and Baita Nana (modified after Picotti et al., 1998). Note that the Brasa section is projected from 50 km south.
Paleoceanography and Paleoclimatology

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Bown, 1998) in order to retain the original composition and preventing selection of assemblages, already heavily impacted by diagenesis. Semiquantitative analyses of nannofossil assemblages were performed using a polarized light microscope under a magnification of 1250x, counting all the specimens recorded in 300 fields of view.

3.3. Carbonate Isotope (δ¹³C_<sub>carb</sub> and δ¹⁸O_<sub>carb</sub>) Analysis

We measured the δ¹³C_<sub>carb</sub> and δ¹⁸O_<sub>carb</sub> on 340 bulk rocks from the Brasa, Cima Benon, and Baita Nana sections using a ThermoFinnigan Gas Bench II coupled to a Delta V Plus mass spectrometer at ETH Zurich, on 90–140 µg of sample powder according to Breitenbach and Bernasconi (2011). Carbon and oxygen isotope compositions are reported in the conventional δ notation relative to VPDB (Vienna Pee Dee Belemnite) with a reproducibility better than 0.1‰ for both δ¹³C_<sub>carb</sub> and δ¹⁸O_<sub>carb</sub> (Breitenbach & Bernasconi, 2011).

3.4. Organic Carbon Isotope (δ¹³C_<sub>org</sub>) Analysis

δ¹³C_<sub>org</sub> on 134 samples from the Brasa section was determined with a ThermoFisher Flash-EA coupled to a Delta V Plus mass spectrometer at ETH Zurich. Prior to the measurement, the samples were decarbonated with 3N HCl. Ten milligrams of the acidified sample powder, 150–600 µg of the standard Peptone (43.4% C, 14.9% N, δ¹³C_<sub>org</sub> = −15.64‰), 200–400 µg of the standard Atropine (70.56% C, 4.84% N, δ¹³C_<sub>org</sub> = −21.4‰), and 110–475 µg of the standard Nicotinamide (59% C, 22.9% N, δ¹³C_<sub>org</sub> = −31.2‰) were weighted in tin capsules and combusted to CO₂, which was then introduced to the mass spectrometer. The isotope ratios are reported in the conventional δ notation relative to VPDB. Reproducibility of isotope measurements was better than ±0.2‰.

3.5. Numerical Modeling

We use a numerical model of the ocean-atmosphere carbon cycle to test how much carbon (C) from different sources is required to generate the characteristic negative CIE of the P–ToBE. The model code is written in R, and its equations and parameters are similar to those utilized by Caves Rugenstein et al. (2019), Kump and Arthur (1999), and Shields and Mills (2017). The forward model solves for the reservoirs and fluxes of carbon and alkalinity to and from the ocean-atmosphere given a perturbation to the initially steady-state carbon cycle. We consider two endmember sources: C released from volcanic outgassing with an isotopic signature of −5‰ and C from biogenic methane release with an isotopic signature of −60‰ (Dickens et al., 1997). In the discussion, we also consider the impact of different sources of C with different δ¹³C values. The model assumes that the carbon-cycle perturbation is of global extent. Model structure, equations, and initial parameters are given in the supplement.

4. Results

4.1. Stratigraphy of the Brasa Slope Section

The sampled section is 35 m thick, including an outcrop gap of 3 m (Figure 2). The base consists of light brownish-yellow, medium-bedded lime cherty mudstones with thin greenish marl interlayers yielding nannofossils from the Upper Pliensbachian (top NJT 4b to NJT 5a Zones, Mattioli & Erba, 1999). These peloidal limestones are rich in sponge spicules and locally contain cherty nodules and bands, minor crinoids, bivalves, and echi- noid fragments. The occurrence of Fontanelliceras sp. (Cobianchi & Picotti, 2001), found in a pinkish nodular lime mudstone bed (Figure 2) indicates a latest Pliensbachian age within the Hawskerense Subzone (Meister et al., 2017). This condensed layer is covered by a 3 m thick pebbly mudstone, which is floored and topped by two medium-bedded greyish marlstone interlayers (Figure 2). Within the matrix of the pebbly mudstone, we observed Pentacrinites and a few bivalves, as well as tiny (1–3 mm), black to red-brown, shiny flattened prisms, surrounded by pyrite framboids, most likely coalified plant debris. The overlying uppermost Pliensbachian to Middle Toarcian succession consists of thin-bedded couplets of lime mudstones and marls, interspersed with rare medium bedded slumps, pebbly mudstones, and lime packstones (Figure 2). The frequency of marly interbeds increases toward the P–To boundary and in the Lower-Middle Toarcian and the rock color changes from brownish-gray to darker gray. At 18.75 m, the top of the nannofossil NJT 5b Subzone (Tenuicostatum Zone, Mattioli & Erba, 1999), patches of phosphatized and silicified concentric ooids, possibly derived from the last unit of the Calcari Grigi (Massone Oolite, Upper Pliensbachian), can be observed within the spiculitic matrix (Figure 3a).
A few of the ooids, less phosphatized, display a radial structure, a character typical of the Toarcian San Vigilio ooids. Furthermore, benthic foraminifera as well as mollusk fragments and *Pentacrinites* occur, likely reworked from the platform margin. After an outcrop cover of ca. 3 m, the marl-limestone couplets in the Middle Toarcian (NJT 7 Zone, Mattioli & Erba, 1999) become darker toward the top. The lime wacke-packstones contain up to 30% sponge spicules, mostly rhaxes of *Selenaster* (Cobianchi & Picotti, 2001), as well as phosphatic and glauconitic grains, a few concentric and radial ooids, with phosphatic coating and *Pentacrinites*. Upwards, in the Middle Toarcian, the frequency of the lime packstones increases, with abundant thin shelled bivalves, crinoids, and echinoid fragments. The Toarcian succession ends abruptly against an erosional surface (Figure 2), likely formed by a channel scoured in the slope and filled with lower Bajocian grainstones (NJT 10 Zone, Mattioli & Erba, 1999), almost exclusively consisting of crinoids and *Bositra* shells reworked from the drowning Venetian Platform (Cobianchi & Picotti, 2001).

**Figure 2.** Stratigraphy and high-resolution δ¹³C_carb and δ¹³C_org data from bulk sediment rock samples of the Brasa section. The color of the rock samples is indicated in the color bars to the left of the stratigraphic column. The main nannofossil events are from Cobianchi and Picotti (2001).
4.2. Isotope Stratigraphy of the Brasa Slope Section

4.2.1. Carbonate Carbon Isotopes ($\delta^{13}C_{\text{carb}}$)

In the uppermost Pliensbachian, at the top of the NJT5a Subzone (Hawksenese Subzone), $\delta^{13}C_{\text{carb}}$ increases from values of 1.8–2‰ in the light brownish-yellow limestones to maximum values of 2.7‰ in the pebbly mudstone (Figure 2). This shift of 0.7‰ amplitude starts in the marly layer underneath the pebbly mudstone. This is...
followed by a negative CIE with an amplitude of ~1.4‰, spanning the uppermost part of the Pliensbachian to the Toarcian transition. The onset of this negative CIE occurs at the base of the thin bedded marl-limestone couplets. At the base of the NJT 5b Subzone (base of the Tenuicostatum Zone, Mattioli & Erba, 1999), the values return again to 1.6‰, which is slightly less than the initial δ¹³C$_\text{carb}$ of the upper Pliensbachian, prior to the perturbation. In the Middle Toarcian (NJT 7 Zone, Mattioli & Erba, 1999), δ¹³C$_\text{carb}$ does not show any perturbation. Rather, δ¹³C$_\text{carb}$ oscillates within the range of 1–1.5‰. The last sample taken at this section was heavily silicified and it may be that the δ¹³C$_\text{carb}$ measured from this sample derives from the weathered crust. This could explain the relatively low value of δ¹³C$_\text{carb}$ of 0.0‰ together with a notably negative δ¹⁸O$_\text{org}$ of ~4.0‰ (see Table S6, Fleischmann et al., 2021). As a whole, δ¹⁸O$_\text{org}$ in this section has a poor correlation with the δ¹³C$_\text{carb}$ (see Figure S4), which suggests that the δ¹³C$_\text{carb}$ has not been diagenetically altered (Dickson & Coleman, 1980). Furthermore, the microfacies study of the Brasa section confirms minimal early diagenetic alteration and documents the independence of δ¹³C$_\text{carb}$ trends from facies or lithological changes. It has been suggested by Swart and Eberli (2005) that variations in relative proportions of platform versus pelagic components in slope sediments could produce carbon isotope shifts that are unrelated to global changes in the carbon cycle. We consider this unlikely in our sections because the observed carbon isotope shifts are correlatable with the global reference curves. Further, the model of Swart and Eberli (2005) may not be applicable to our Early Jurassic sections, since pelagic components in Early Jurassic periplatform carbonates were found to be no more than 2% in volume (Cobianchi & Picotti, 2001). The δ¹³C$_\text{carb}$ curve across the P–To boundary and the Early Toarcian in this study is calibrated against nanofossil data and correlated with the ammonite biostratigraphy of the global reference Peniche section (Da Rocha et al., 2016; Hesselbo et al., 2007), as we will discuss later.

4.2.2. Organic Carbon Isotopes (δ¹³C$_\text{org}$)

δ¹³C$_\text{org}$ ranges from ~25‰ to ~30‰, with no correlation between the δ¹³C$_\text{carb}$ and the δ¹³C$_\text{org}$ values in the Brasa section. Trends and perturbations in the δ¹³C$_\text{org}$ record are difficult to observe, due to the noisy signal. Most of the δ¹³C$_\text{org}$ from the Upper Pliensbachian light brownish-yellow limestones sampled at the base of the section are between ~27‰ and ~25‰. Starting from the first pebbly mudstone sample at meter 9, a negative CIE with an amplitude of around 2‰ and minimum values of ~28.5‰ is visible. At the top of the Upper Pliensbachian, 1 m above the pebbly mudstone, values again increase and then oscillate between ~27‰ and ~26‰ at the base of the Lower Toarcian. Above the covered section, in the Middle Toarcian, we observe a trend toward higher values (from ~28‰ to ~25.5‰), which is superimposed on smaller variations.

4.3. Stratigraphy of the Prà Castron Platform Margin Section

Prà Castron (Figure 4) is a short section containing prominent marly interbeds and was measured at the edge of an around 20 m wide and 4 m deep large paleokarst depression. The paleokarst is carved in the uppermost Calcari Grigi and infilled with poorly bedded lime pack-grainstones, likely reworked by currents. We avoided the infilling and measured the transgressive deposits of the Tofino Fm. out of the paleokarst feature. We found around 4 m of medium-bedded and burrowed peloidal lime mudstones, with marly interbeds, bearing nanofossil assemblages characterized by the occurrence of *Carinolithus superbus* and frequent specimens of *Lotharingius frodoi* and *Mitro lithus jansae*, which are indicative of the lower part of the nanofossil NJT six Zone (Mattioli & Erba, 1999) of the Early Toarcian (late Tenuicostatum Zone). An erosional contact separates this unit from the overlying pebbly grainstone (Figure 3c) bearing micritized grains, intraclasts, fragmented crinoids, mollusks, echinoids, and bryozoans and large cubic pyrite crystals. Another unconformity separates the measured unit from an Upper Cretaceous succession.

4.4. Stratigraphy of the Cima Benon Platform Margin Section

The Cima Benon section (Figure 4) encompasses the top 3 m of the Calcari Grigi and 26 m of the transgressive Tofino Fm. The transition between the two units consists of an erosional unconformity demarcated by a reddish crust of carbonates that infiltrates the underlying karstic surface (Figure 3f), and can be physically correlated to the karstic base of Prà Castron (Figures 3d and 4). Above the unconformity, there is a 1.3 m thick sequence of poorly bedded peloidal intraclastic grainstones. The latter show more sparitic cement with respect to the Calcari Grigi and large intraclasts, increasing upward from 1 to 3–4 mm (Figure 3e). Furthermore, we observed silicified crinoids, large ostreids, a few ooids and sponge spicules in matrix and clasts. Pores are locally filled
with calcedony. The grainstone unit is followed by 4 m of thin and even-bedded pelagic lime mudstones, with an upward increase of marly interbeds. The peloidal matrix is interspersed with sponge spicules (monaxon and rhaxes) and minor thin-shelled bivalves. The overlying 2 m of medium-bedded lime grain-packstones show intraclasts of spiculitic mudstones, as well as micritized grains, partly silicified brachiopods, crinoids, and foraminifera (*Textularia*). The remaining stratigraphy includes thin-bedded lime mudstones, locally laminated and dark gray, with marly interbeds, as well as medium-bedded, locally burrowed, lime grain-packstones and cherty lime mudstones with chert nodules. Laminated gray mudstones locally show iron oxides and carbonates, replacing former wood, as suggested by *Teredolites* burrows. The sampling was performed until meter 26.60, under the 15 m high cliff of the eastern side of Cima Benon.

### 4.5. Isotope Stratigraphy of the Cima Benon Platform Margin Section

Two major negative carbonate CIEs are found in this section. Starting from δ¹³C<sub>carb</sub> values of 1.2–1.6‰ measured in the Calcari Grigi underneath the unconformity, δ¹³C<sub>carb</sub> decreases sharply to 0.6‰ (amplitude of 1‰) within the grainstones above the unconformity (Figure 4). Toward the end of the grainstones, δ¹³C<sub>carb</sub> returns to around 1.5‰ and remains rather constant in the overlying thin-bedded mudstones of the Tofino Fm. The second negative CIE has an amplitude of 1.3‰ and begins at the transition from the dark-laminated micrite to the second grainstone bed at meter 6. Above, δ¹³C<sub>carb</sub> increases stepwise from a minimum value of 0.3‰ to around 2‰ toward the end of the sampled section. This is approximately 0.5‰ more than the initial pre–CIE values. Furthermore, in this section, a poor correlation of δ¹³C<sub>carb</sub> and δ¹⁸O<sub>carb</sub> (Figure S5) suggests no diageneric overprinting of the
4.6. Stratigraphy of the Baita Nana Inner Platform Section

In Baita Nana (Figure 5), we sampled and analyzed 71 m of the platform succession. A sharp drowning unconformity separates massive oolitic limestones of the Calcari Grigi (Oolite di Massone) from thin-bedded cherty limestones of the Tofino Fm. The top of the Oolite di Massone is rich in Pentacrinites and the concentric ooids are fringed by bladed early diagenetic cement. The overlying basal Tofino Fm. consists of peloidal lime wacke-mudstones with sponge spicules and pelagic bivalves. Between 1.45 and 2.48 m, the unit has thin/medium bedding (2–20 cm) with a few marl interbeds and is barren in nannofossils (Figure 3h). The unit continues with 4 m of thin/medium bedded wavy jointed limestone (Wollenkalk facies), containing peloids and some intraclasts, echinoid spines, bivalve shells, and crinoids. A 3 m down-cutting erosional surface, laterally passing in 10 m to a conformable contact, marks the boundary with the Encrinite del Peller. This unit consists of poorly bedded, coarse intraclastic crinoidal grainstones, with a coarsening upward trend. In thin sections, peloids, crinoids, benthic foraminifera (Textularia sp.), composite ooids, and intraclasts bearing sponge spicules are visible. The size of the intraclasts and peloids increases upsection. Crinoids, micritic ooids, benthic foraminifera (Lituloides), echinoids, and bivalve fragments occur at meter 13.30 (Figure 3g). The massive grainstone succession of the Encrinite del Peller is sharply interrupted by an interval of 6 m of mummocky cross bedded fine grainstones in medium beds (at meter 33.20), which contains very thin marly interlayers, barren of nannofossils. Another peculiarity of this massive carbonate outcrop is the reddish color of the carbonates and the occurrence of brachiopod levels toward the end of the sampled sequence.

4.7. Isotope Stratigraphy of the Baita Nana Inner Platform Section

Values of $\delta^{13}$C$_{\text{carb}}$ in the Baita Nana section range from 0.8 to 3.3‰ and are $\sim1.1$‰ heavier than the Brasa and Cima Benon sections. Oolitic grainstones from the Calcari Grigi show a rather constant $\delta^{13}$C value of 2–2.5‰. Starting from the drowning unconformity at the transition with the well-bedded Tofino limestones, a $\sim1.5$‰ negative CIE occurs (Figure 5). At around meter 10, in the Encrinite del Peller, $\delta^{13}$C$_{\text{carb}}$ values gradually increase and reach values that are 0.5‰ higher than the values measured in the Pliensbachian Calcari Grigi. In the upper part of the section, a small positive CIE with maximum values of 3.3‰ is visible, before the values return to around 2.3‰, which is about the same as the Calcari Grigi at the base of the Baita Nana section. In this section, as well as in Cima Benon, the correlation between $\delta^{16}$O$_{\text{carb}}$ and $\delta^{13}$C$_{\text{carb}}$ isotopes is poor (see supplementary plot Figure S6).

5. Discussion

Combined, our new stratigraphic and stable isotope results shed light on a critical and relatively understudied portion of the Jurassic—P–ToBE. The Late Pliensbachian is characterized by a cooling event with the lowest global temperatures of the Jurassic and most of the Mesozoic, low $p$CO$_2$ levels, and hypothesized polar ice cap formation (e.g., Gómez et al., 2016; Hinnov & Park, 1999; Price, 1999; Silva & Duarte, 2015; Suan et al., 2010). This cooling event is associated with a major short-lived regression (Haq, 2018), which led to the emersion of Tethyan carbonate platforms and a sharp reduction in carbonate productivity (Cobianchi & Picotti, 2001) as well as to a second order mass extinction at the P–To boundary (Caruthers et al., 2013; Dera et al., 2011). Though the Late Pliensbachian sea-level fall is often attributed to polar ice cap formation (e.g., Price, 1999),
other mechanisms, such as the arido-eustasy (Brikiatis, 2019) or limno/aquifer eustasy (e.g., Sames et al., 2020), have been hypothesized to additionally play a role in driving Early Jurassic sea-level. This eustatic sea-level fall was followed in the earliest Toarcian by warming and transgression (e.g., De Lena et al., 2019; Haq, 2018) and has been linked to the activity of the Karoo-Ferrar LIP (e.g., Ikeda & Hori, 2014; Korte & Hesselbo, 2011; Pálfy & Smith, 2000; Sell et al., 2014), culminating in the Early T–OAE. We use these well-established global environmental changes, combined with our new stratigraphic and stable isotope data to first correlate our sections from the slope to the platform interior. We then use these correlations to discuss the paleoenvironmental changes that occurred from the Late Pliensbachian to the Early Toarcian on the large Venetian carbonate platform. Lastly, we use our stable isotope data and paleoenvironmental data along with a numerical model of the carbon cycle to place constraints on the source and magnitude of the carbon pulse required to explain the negative CIE at the P–ToBE.

5.1. Platform to Slope Correlations and Perturbations of the Global Carbon Cycle

The stratigraphic correlation of biostratigraphically well-dated pelagic with poorly or non-dated shallow water successions represents a major challenge in sedimentary geology. When biostratigraphic constraints are absent, facies associations of the various tracts of the transgressive-regressive (T-R) cycles—such as “maximum flooding facies”—are used as tie points. However, a major pitfall in this case is that similar facies can develop at different times in different places during a T-R cycle. In the case of the latest Pliensbachian and Early Toarcian, this problem is compounded by the occurrence of two T-R cycles (Haq, 2018)—whose local effects are described in this paper—both close in time and also in space given the reduced sedimentation of the earliest Toarcian (Tenuicostatum Zone). In this respect, chemostratigraphy afforded by the \( \delta^{13}C_{\text{carb}} \) offers a powerful tool, as it permits us to create timelines across different (sub)environments. In order to define the effects of the carbon cycle perturbations on the sedimentary environment, we integrate litho- and chemostratigraphy to produce a general correlation (Figure 6) and tie this correlation to the Peniche section of Hesselbo et al. (2007) to integrate with the well-established ammonite biostratigraphy.

A negative CIE (both in \( \delta^{13}C_{\text{carb}} \) and \( \delta^{13}C_{\text{org}} \)) spanning the P–ToBE has been observed by some authors (Bodin et al., 2016; Hesselbo et al., 2007; Jenkyns & Clayton, 1997; Littler et al., 2010; Rodrigues et al., 2019; Trecalli et al., 2012), similar to what we observe in the \( \delta^{13}C_{\text{carb}} \) data of the Brasa section. The subsequent T–OAE, also a large negative CIE that occurs in the Early Toarcian (lowermost Serpentinus Zone), is, however, missing in the Brasa carbon isotope record, likely due to the covered outcrop. The subsequent positive \( \delta^{13}C_{\text{carb}} \) trend characterizes the upper part of the T–OAE in the shallow water sections of Cima Benon and Baita Nana and has also been observed elsewhere (e.g., Hesselbo et al., 2007; Pittet et al., 2014).

Based on stratigraphic observations and \( \delta^{13}C_{\text{carb}} \), we correlate the two platform sections and the corresponding slope (Figure 6). The negative CIE of the P–ToBE is recorded in the slope and platform margin sections, while the negative CIE of the subsequent T–OAE is only visible at the platform margin and inner platform section. The nanofossil NJT5a Subzone (Hawkskerense Subzone) at Brasa records the abrupt cessation of sediment supply to the slope and the subsequent platform margin gravitational instability, as testified by the condensed, pinkish nodular limestone followed by a pebbly mudstone. This interval is interpreted as an abrupt emersion of the platform (Cobianchi & Picotti, 2001) and can be correlated to the unconformity atop the Calcari Grigi at the platform margin (Cima Benon and Prà Castron). This unconformity is demarcated by a reddish carbonate crust with notably negative values of \( \delta^{13}O_{\text{carb}} \), with values of −5‰ to −8‰ (Figures 3f and S7, Table S6, Fleischmann et al., 2021), documenting the influence of meteoric waters. The negative CIE at Brasa and the first negative carbon isotope peak of Cima Benon correlate to the negative CIE at the P–ToBE (Hesselbo et al., 2007, see also Bodin et al., 2016; Littler et al., 2010). At Cima Benon, either the whole P–ToBE is preserved and very condensed, in comparison to the Brasa section (correlation 2 in Figure 6b), or only the last part of this CIE is documented in the transgressive succession of the platform margin (correlation 1 in Figure 6b). The positive CIE recorded in the slope sediments in the NJT5a (Hawkskerense Subzone) is missing in the platform sections that were subaerially exposed during the sea-level drop. We correlated the thin-bedded layers overlying the erosion-related unconformity at Cima Benon as the maximum flooding with the deepest water facies containing nanofossil assemblages of the upper part of the NJT 5b-base NJT6 Zones (Tenuicostatum Zone, Mattioli & Erba, 1999). The \( \delta^{13}C_{\text{carb}} \) data confirm this correlation and show values of around 1.5‰ in the lowest Toarcian of both slope (Brasa) and platform margin (Cima Benon) sections. In the inner platform section (Baita Nana), the
Figure 6. Stratigraphic correlations of different platform/slope sections across the Pliensbachian–Toarcian. (a) The solid red line is based on nannofossil observations and the red dashed line has been correlated based on lithostratigraphic observations. The gray dashed line indicates the baseline of the P–To boundary and is based on Figure 6. OAE is not recorded in the slope section. (b) Correlation of $\delta^{13}$C data of the three measured sections shown in (a) and the reference section at Peniche (Hesselbo et al., 2007). The P–ToBE is more condensed in the reference section of Peniche (ca. 2 m) than in the Brasa section (ca. 5.5 m). The P–ToBE is missing in the inner platform section, while the T–OAE is not recorded in the slope section.

Maximum flooding facies (i.e., thin/medium-bedded, fine-grained peloidal lime mudstones) occur between meter 1.45–2.48 (Figure 5). Based on lithostratigraphy only, this should correlate to the maximum flooding deposits above the unconformity at Cima Benon and Prà Castron. The $\delta^{13}$C data reveal, however, that this deep-water interval of Baita Nana bears the negative CIE of the T–OAE and matches the upper negative CIE preserved in the well-bedded cherty limestones at Cima Benon, and not the lower negative one at the Pliensbachian/Toarcian transition. This CIE of the T–OAE can also be correlated to the T–OAE observed in Portugal by Hesselbo.
et al. (2007), even though the amplitude of the platform margin and the inner platform CIE is slightly smaller than in Portugal. Absolute δ¹³C_carb values of this T–OAE interval in the inner platform section are in perfect accordance with the δ¹³C_carb of the T–OAE from two other sections (CDM and SDA) that are located a little further South on the Trento platform (see Woodfine et al., 2008). The end of the Lower Toarcian in the Baita Nana inner platform section is tentatively derived by comparison with the δ¹³C_carb record of the Mochras Borehole in Wales (UK; Jenkyns & Clayton, 1997), where the Lower Toarcian ends when the δ¹³C values return to similar, pre-perturbation values. According to this correlation, the entire time from the post-regression latest Pliensbachian (Hawskerense Subzone) to the Early Toarcian (earliest Serpentinus) is missing in the inner platform at Baita Nana due to emersion of the platform.

The record of two negative CIEs at the platform margin, but only one at the platform interior, has important implications for the regional stratigraphy of the Venetian Platform (Woodfine et al., 2008). Earlier work has attributed the top of the Calcari Grigi to the Early Toarcian, though this correlation is contingent on a conformable sequence between the top of the Calcari Grigi and the base of the Tofino Fm. We find, in contrast, a widespread unconformity, which we attribute to the emersion of the platform. Consequently, we can attribute the Calcari Grigi to the Pliensbachian and define an unconformity encompassing the entire early Early Toarcian (Tenuicostatum Zone) in the platform interior, eventually reached by the marine transgression in the Serpentinus Zone.

The positive and negative CIEs we document in the latest Pliensbachian and Early Toarcian correlate in time and amplitude with numerous sections available in literature (Bodin et al., 2016; Hesselbo et al., 2007; Jenkyns & Clayton, 1997; Littler et al., 2010; Trecalli et al., 2012). Therefore, we consider them to represent global perturbations of the carbon cycle and, next, we discuss the contemporaneous dynamics of carbonate productivity in the Venetian Platform in response to these global perturbations.

5.2. Carbonate Platform Evolution During the Late Pliensbachian and the Pliensbachian–Toarcian Transition

In the latest Pliensbachian (Hawskerense Subzone), we find evidence for a relevant sea-level drop, as already highlighted by Cobianchi and Picotti (2001) and Picotti and Cobianchi (1996). This prominent latest Pliensbachian sea-level drop correlates well with the Haq (2018) JPl8 sequence boundary at 184.3 Ma (see Figure 7a). This drop is evidenced in the slope sediments (Brasa) by both the condensed nodular limestone layer, which represents the sudden cessation of periplatform shedding, and by the subsequent pebbly mudstone, which likely records the wave-cutting steepening of the platform margins during the forced regression (Figure 7a). The pebbly mudstone contains material that has been eroded from the platform margins, such as the *Pentacrinites*, which is also observed in the uppermost oolitic limestones of the Calcari Grigi in the inner platform (Baita Nana). The occurrence of *Pentacrinites* indicates a humid climate, as this genus lives attached to floating wood (Simms et al., 1999). A shift from a cool and dry climate in the Late Pliensbachian to a relatively warmer and more humid climate in the Early Toarcian was also observed by Pieńkowski and Wąsowski (2009), who investigated the ratio of spores and bisaccate pollen grains of Lower Jurassic drillholes in Poland. Our results indicate that this change to a more humid climate and the associated increase of continental runoff had begun already in the latest Pliensbachian (Figure 7b). A Late Pliensbachian trend from semi-arid to humid climate culminating in the Spinatum Zone was recently documented as well to the north of the Iberian massif, in the Asturian basin, located at the same latitudinal belt as our study area (Deconinck et al., 2020). The enhanced input of terrestrial organic matter (see Figure S1b) to the slope may explain the consequent negative δ¹³C_carb values observed at the end of the Upper Pliensbachian. Increased terrigenous input to basins due to increased rainfall as climate became progressively more humid has also been proposed for the earlier negative CIE at the Sinemurian–Pliensbachian boundary (Franceschi et al., 2019).

At Brasa, the change in the slope sediments from the bright, well-bedded limestones to the pinkish condensed layer and the pebbly mudstone, is associated with a δ¹³C_carb positive shift of 0.7‰, which is primarily observed in the pebbly mudstone. However, the first increase in δ¹³C_carb is observed in the marl below the pebbly mudstone, while δ¹³C_carb decreases in the uppermost samples within the pebbly mudstone. Because this positive CIE spans two different lithologic units, we interpret the signal to reflect the original seawater δ¹³C value at the time of deposition rather than an artifact of reworking of older clastic carbonates. Since the uppermost Pliensbachian is condensed in nearly all other investigated sections around the world (e.g., Léonide et al., 2012; Morard et al., 2003; Storm et al., 2020), nor is it too expanded in Peniche (Hesselbo et al., 2007), it is difficult to assess
Figure 7. Time evolution of platform and slope across the Pliensbachian–Toarcian transition and the Early Toarcian. The δ13C record as well as transgression and regression cycles can be seen on the right. The left-hand panels show one representative moment out of the corresponding gray shaded intervals in the δ13C record. An estimate on the intensity of the Karoo-Ferrar volcanism over time is given with the red bar on the right and is based on U-Pb ages from different authors (e.g., Ikeda et al., 2018; Moulin et al., 2017) and the evolution of our inorganic carbon isotope curves over time. Paleotemperatures and pCO₂ values were taken from Gómez et al. (2016) and references therein and the movement of the shoreline is from Haq (2018).

if the positive CIE of the Brasa section is of global extent or if it only reflects a local phenomenon. Given the small amplitude of 0.7‰, this positive CIE might however also just represent a local increase in input of platform-derived carbonate with a higher δ13C (Swart & Eberli, 2005). It is worth noting that the other papers dealing with the Venetian platform observed a similar excursion (SDA section, Woodfine et al., 2008). This positive shift is recorded also in some Middle Atlas sections, particularly expanded in their Upper Pliensbachian intervals (Ait-Itto et al., 2017). Therefore, this positive excursion, immediately preceding the P–ToBE negative CIE was included in a recent paper summarizing the carbon isotopes excursions across the Pliensbachian to Toarcian (e.g., De Lena et al., 2019).
The positive CIE in the Spinatum Zone is preceded by other, global positive carbon isotope perturbations throughout the Pliensbachian (in the Ibex and Margaritatus Zones), as documented in Portugal (Silva et al., 2011), Northern Spain (Rosales et al., 2006), the UK (Korte & Hesselbo, 2011), Italy (Marino & Santantonio, 2010), and in Argentina (Valencio et al., 2005). A common interpretation of the origin of such positive CIEs is the rapid burial of large amounts of organic carbon with low δ13C to form black shales, termed Organic Matter Preservation Intervals (Late Pliensbachian OMPI; Silva et al., 2011). However, a recent review of the global oceans (Silva et al., 2021) did not document an important OMPI at the very end of the Late Pliensbachian. The positive CIE of the nannofossil NJT5a Subzone (Hawkskerense Subzone) is followed by a negative CIE of ~1.4‰ at Brasa, spanning the uppermost part of the Pliensbachian and the transition from the Pliensbachian to the Toarcian. This CIE is documented in the first marl-limestone couplets following the pebbly mudstone, and we assign this negative CIE to the P–ToBE (Bodin et al., 2016; Fantasia et al., 2019; Hesselbo et al., 2007; Littler et al., 2010).

Following the latest Pliensbachian emersion of the Venetian carbonate platform margin (Cima Benon, Figure 7b), the negative CIE of the P–ToBE is recorded in a 1.3 m-thick layer of poorly bedded peloidal grainstones immediately overlying the unconformity. The presence of crinoids, large Ostreid bivalves, a few ooids, and sponge spicules, documents the recovery of the carbonate platform productivity after the emersion (Figure 7b). Ocean waters at the time of deposition of the grainstone were probably eutrophic and energy conditions at the platform margin were most likely higher than before the emersion, which is indicated by the larger size of intraclasts. Since glauconite forms during early diagenesis under slightly reducing conditions (Harder, 1980), its presence during this interval suggests oxygen-poor water column conditions, possibly related to a high flux of organic particulates toward the seafloor. Following the P–ToBE, at the transition to the earliest Toarcian (Tenuicostatum Zone), carbonate productivity at the platform margin was unable to keep pace with the ongoing transgression, allowing the deposition of open-sea thin-bedded micritic limestones, which contain few bivalves and sponge spicules. The presence of siliceous sponges at the platform margin indicates the recovery of shallow water productivity and its transportation toward the seafloor. Following the P–ToBE, the transition to the earliest Toarcian (Tenuicostatum Zone), carbonate productivity at the platform margin was unable to keep pace with the ongoing transgression, allowing the deposition of open-sea thin-bedded micritic limestones, which contain few bivalves and sponge spicules. The presence of siliceous sponges at the platform margin is indicative of sustained, high organic particulate flux on the platform (Föllmi et al., 1994), which is unfavorable for platform growth (e.g., Hallock & Schlager, 1986; Hottinger, 1987). Eutrophication, combined with the ongoing transgression, dampened carbonate productivity. The top 75 cm of the interval, correlated isotopically to the Tenuicostatum Zone at Cima Benon (Figure 6), consists of a peloidal, intraclastic pack-grainstone, indicating the recovery of shallow water productivity and its transportation toward the platform margin at the onset of a depositional regression (Figure 7c). Using the average minimum duration of 810 kyr for the Tenuicostatum Zone that was obtained by Martinez et al. (2017), we estimate an average sedimentation rate of 0.55 cm/kyr for these micritic limestones and the pack-grainstone bed on top, which is slightly higher than the sedimentation rate during the same stratigraphic interval on the slope (0.44 cm/kyr). These values are an order of magnitude lower than the lowest rates of healthy (Photozoan, sensu James et al., 1997) carbonate platforms (Bosscher & Schlager, 1993) and document that the recovery of carbonate productivity during the earliest Toarcian (Tenuicostatum Zone) highstand was of short duration and weak, and the environmental conditions were not suitable for a Photozoan carbonate factory on the margins of the Venetian Platform.

The stratigraphic interval NJT5b-NJT6 p.p. corresponding to the Tenuicostatum Zone at the slope, based on isotopic data (Figure 6), is characterized by marl-limestone couplets and has rather constant δ13Ccarb values, similar to the platform margin. This interval is characterized by sparse occurrence of phosphatized ooids, which were formed in the tidal zone at the platform margins and were likely phosphatized on a seafloor experiencing a high flux of particulate organic matter (Kidder & Worsley, 2010), before being transported to the slope. The presence of radial ooids in the Tenuicostatum interval of the slope shows that the conditions for generating these radial ooids started earlier than previously believed for the onset of the San Vigilio Oolitic Lms (Cobianchi & Picotti, 2001). The amplitude of the top Pliensbachian and base of Toarcian T-R cycle documented at the Cima Benon platform margin was not enough to reach the Baita Nana inner platform (Figure 7c). This trend is also shown in the global sea-level curve of Haq (2018), which shows a minimum in the long-term curve in the earliest Toarcian. The 5 m of sediments recording this T-R cycle at the platform margin very likely filled the available accommodation space, documenting a similar minimum bathymetric difference between the margin and internal platform (Figure 7c).

Interestingly, the δ13Ccarb and δ13Corg values of the Brasa section (Figure 2) are decoupled in some parts of the section, notably in the Upper Pliensbachian, where the organic carbon isotopes show depleted values, while the carbonate carbon isotopes form a small positive CIE. This decoupling has been observed previously in slope
settings in other P–ToBE sections (Bodin et al., 2016) and in Neogene slope and platform settings by Oehler et al., (2012), who referred it to the highly variable organic composition of the platform organisms. In the Brasa section, this explanation seems likely and related to the T-R cycles, as we find limited covariation in the Upper Pliensbachian, during which there is either active periplatform shedding or reworking of periplatform material due to the platform emersion (NJTs, Hawskerense Subzone). A higher contribution of detrital organic carbon (possibly evidenced by the observed coalified plant debris in the pebbly mudstone), via transporting organic material to the slope during the sea level low-stand, could explain the more negative organic carbon values in this interval (compare with Jiang et al., 2012). At the very end of the Pliensbachian, and further upsection during the Lower Toarcian, the near absent periplatform influence at Brasa causes the pelagic-sourced δ13Corg and δ13Ccarb to covary. During the Middle Toarcian, the covariation tends to slightly decrease upsection. However, the environmental conditions that were re-established were not identical to the Upper Pliensbachian Photozoan platform (Cobianchi & Picotti, 2001), and, in this Heterozoan or non-skeletal carbonate factory, the variability of the organic sources was very likely greatly reduced, as evidenced by the decrease in biodiversity.

5.3. Paleoenvironmental Evolution During the T–OAE

During the Early Toarcian (Tenuicostatum Zone), seawater temperatures, based on the well-preserved belemnite record in the westernmost Tethys, increased by 2–6°C with respect to the Late Pliensbachian cold period (Gómez et al., 2016) and the atmospheric CO2 concentration is thought to have doubled from ~1000 to ~2000 ppm (Berner, 2006; Steinhorsdottir & Vajda, 2015). In the upper interval referable to the Tenuicostatum at Cima Benon, the well-bedded limestone succession is interrupted by a thicker grain-packstone bed, which most likely corresponds to the pebbly grainstone cut-and-fill in Prà Castron. This suggests a phase of progradation of the shore, in the highstand of the sea-level following the P–To transgression (Figure 7c). The reworked ooids found in the slope at Brasa suggest that this progradation, and associated highstand, was short-lived. The most intense warming occurred at the Tenuicostatum–Serpentinus boundary with an increase in temperature of ~8°C (Gómez et al., 2016 and references therein). This was caused by a severe perturbation to the global carbon cycle, with a negative CIE of up to ~3.5‰ in δ13Ccarb and up to ~8‰ in δ13Corg starting at the early Early Toarcian (latest Tenuicostatum, e.g., Bodin et al., 2016; Fantasia et al., 2018; Hesselbo et al., 2007; Pittet et al., 2014; Xu, Ruhl, et al., 2018). This perturbation comprises the T–OAE, and the negative CIE can be seen in the platform margin and inner platform successions (Figure 7d). At the platform margin (Cima Benon), the negative CIE of the T–OAE starts in the upper part of the poorly bedded peloidal intraclastic grain-packstone, deposited after the transgressive pelagic lime mudstones, and reaches higher δ13Corg values in the well-bedded cherty limestones at meter 6.30 (Figures 6 and 7). The latter interval can be correlated to the well-bedded lime mudstones of Baita Nana, indicating that the Serpentinitus Zone maximum transgression flooded the platform margin further inland than the maximum flooding within the Tenuicostatum Zone. The notion of two T-R cycles with increasing amplitude during the early Serpentinitus Zone (e.g., Haq, 2018; Ruebsam et al., 2019), is mostly based on interpretation of stable isotopes or other geochemical indicators. Our work is the first to document these two Early Toarcian T-R cycles with physical correlations, rather than purely with geochemical/isotopic records.

The cherty facies during and after the negative CIE of the T–OAE in Cima Benon points toward the abundance of siliceous sponges, which is in turn indicative of high particulate flux to the bottom (i.e., euphotic waters; Wiedenmayer, 1994) on the shallow water platform. High nutrient availability, which would hamper platform carbonate productivity, was most likely a side effect of the enhanced silicate weathering due to global warming during the T–OAE and the subsequent recovery. Woodfine et al. (2008) describe a similar concurrence of transgressive clay-rich cherty facies amid the negative CIE at the western margin of the Venetian/Trento platform. The Teredolites ichnofacies, observed at Cima Benon in the Lower Toarcian laminated cherty lime mudstones, are mostly documented in transgressive systems and the abundance and preservational state of Teredolites seem to be closely related to sea-level dynamics (Savrda, 1991). The crinoidal facies, starting at the negative CIE of the T–OAE at Baita Nana also indicate an open marine influence and a meso-eutrophic state of surface waters at this time (Cobianchi & Picotti, 2001).

5.4. Examining the Cause of the P–ToBE—A Numerical Modeling Approach

The most common causes proposed for the P–ToBE are similar to the ones suggested for the subsequent T–OAE and include: (a) massive dissociation of methane clathrates; (b) release of thermogenic methane by intrusion.
improbable, as they would increase the initial added C δ50 ka, 100 ka) assuming 20% of the excess C is sourced from methane (i.e., boundary. (b) Typical model output for different perturbation durations (10 ka, 50 ka, 100 ka) assuming 20% of the excess C is sourced from methane (i.e., added C δ13C of ~16‰) and the measured negative CIE of Brasa.

Figure 8. (a) Results of the numerical modeling shown in a diagram of C input (in mol C per year and in Gt C per year) versus isotopic signature (~5‰ = 100% volcanogenic C, ~60‰ = 100% C from methane) that are needed to generate a negative CIE of 1.4‰ (red lines; derived from our Brasa section) or 2.0‰ (blue lines; average value of δ13C_carb curves measured in Morocco, Portugal, Wales and Italy). Solid lines represent the results using a perturbation duration of 50 ka, whereas the dashed lines show results for a perturbation duration of 100 ka and are shown here for comparison. Carbon input values exceeding ~1 × 10^13 mol C/yr and 0.12 Gt C/yr (yellow bar) are improbable, as they would increase the initial pCO2 by more than a factor of 2, which—assuming an Earth system sensitivity of ~5°C/CO2 doubling—would correspond to a higher temperature change than was observed at the P–To boundary. (b) Typical model output for different perturbation durations (10 ka, 50 ka, 100 ka) assuming 20% of the excess C is sourced from methane (i.e., added C δ13C of ~16‰) and the measured negative CIE of Brasa.

We vary the δ13C of the additional carbon that is added to the ocean-atmosphere system and then determine the quantity of carbon needed to generate the negative CIE observed at Brasa for the prescribed δ13C. The δ13C of the added carbon can be interpreted in two ways: (a) the additional carbon could be from a single source that ranges in its δ13C from volcanogenic (~−5‰) to organic (~−22‰) to thermogenic (~−40‰) or biogenic (~−60‰) methane (Dickens et al., 1997; Frieling et al., 2016); or (b) the δ13C of the additional carbon can reflect mixing between two distinct, endmember sources (i.e., volcanogenic and biogenic methane), with the precise value representing the relative mixing of these two carbon sources. In the following, we treat the perturbation as representing the mixing of carbon between two distinct sources—volcanogenic and biogenic methane C—though we recognize that volcanic CO2 δ13C has likely not been constant through time (Mason et al., 2017). Since the amplitude of the P–To negative CIE is larger in other studied sections, we also simulate a negative CIE amplitude of 2.0‰, which is an average value of the P–ToBE CIE amplitudes measured by Bodin et al. (2016), Hesselbo et al. (2007), and Jenkyns and Clayton (1997) (Figure 8).

Estimates of the duration of the P–ToBE vary between authors: Martinez et al. (2017) suggests two possible durations of 170 ka and 270 ka for this event and Bouilla et al. (2019) estimated a duration of the P–ToBE of 120 ka from orbital tuning of P–To sections in Morocco. The duration of the event that caused the P–ToBE, however (i.e., the duration of excess C input to the exogenic carbon cycle), is unknown. Hence, we model the P–To negative CIE using three perturbation durations of 10,000 years, 50,000 years, and 100,000 years that encapsulate the likely range of possible event durations to evaluate their effect on the amount of carbon needed to generate the P–ToBE negative CIE. We do not consider perturbation durations of less than 10 ka as the model assumes a well-mixed ocean-atmosphere system, and events shorter than this timescale likely violate this assumption given the timescale of ocean overturning.

Our model demonstrates the exponential relationship between the amount of C needed to generate a specific negative CIE and the isotopic signature of the additional carbon. Assuming a negative CIE amplitude of 1.4‰, approximately 15,300–22,800 Gt C (over a 50 ka or 100 ka perturbation duration, respectively) must be released if the source of this carbon is 100% volcanogenic (i.e., ~−5‰), in contrast, 100% biogenic methane C input (i.e., ~−60‰) only requires ~1/17 of the latter (990–1,200 Gt C) to generate the same negative CIE. We note that a purely volcanic perturbation event lasting only 10 ka still requires a relatively high quantity of 13,220 Gt C and therefore a rate of carbon input to match the negative CIE that is nearly one order of magnitude higher (1.23 Gt C/yr) than for a perturbation duration of 50,000 and 100,000 (0.31 and 0.23 Gt C/yr, respectively). Given that this high quantity of carbon input over a relatively short time is physically unlikely, we do not discuss it further. To place these numbers in perspective, the annual C input from anthropogenic sources (fossil-fuel use and land-use change) today is ~12 Gt C (Le Quéré et al., 2018) and would, if continued over 50 ka, be ~39 times larger.
(600,000 Gt C), and if continued over 100 ka, be ~53 times larger (1,200,000 Gt C) than the total C input from a 100% volcanogenic source at the P-To. The model also reveals that for low δ^{13}C sources of C (i.e., toward the methane endmember), the required carbon input does not substantially change if the amplitude of the negative CIE is 2‰ or if the perturbation duration varies between 10 ka and 100 ka (Figure 8a).

To distinguish between these scenarios and differentiate the source of added C requires other independent evidence of the C input across the P-ToBE, and we use several lines of evidence to conclude that the P-ToBE must have been caused by CO_2 with an average value less than that of the volcanogenic endmember (~5‰). First, we use estimates of the temperature change across the P-ToBE from the δ^{18}O of well-preserved belemnites (Gómez et al., 2016 and references therein). Even when using the smaller CIE amplitude (1.4‰), a 100% volcanogenic C input results in a quadrupling of atmospheric pCO_2. According to data from Gómez et al. (2016), the maximum temperature change from the latest Pliensbachian to the Early Toarcian (Tenuicostatum Zone) is around 6°C, which corresponds to an approximate doubling of pCO_2, given current best estimates of Earth System Sensitivity (Knutti et al., 2017). An input of ~0.12 Gt C/yr causes a doubling of the initial pCO_2, and we therefore use this carbon release rate as the upper estimate of the amount of C input (yellow bar, Figure 8a), as a higher C input might cause a temperature change greater than that estimated by the δ^{18}O data. This in turn implies that the source of C cannot have been 100% volcanogenic, but that also C with a lower isotopic signature than ~5‰ must have been involved in generating the P-To negative CIE. Second, the relatively short duration of the entire P-ToBE (on the order of 190 ka, see e.g., Boulila et al. (2019) and Martinez et al. (2017)) suggests at least a partial non-volcanic source of C, as volcanogenic CO_2 from Karoo-Ferrar sources is thought not to be able to effuse rapidly enough to generate such a large C-cycle perturbation within these timescales (compare with Dickens et al., 1995; Hesselbo et al., 2000). Third, compared to the subsequent T-OAE, δ^{13}C values do not “overshoot” pre-CIE δ^{13}C values during the recovery phase; rather, during the P-ToBE, post-CIE δ^{13}C values are similar to or even lower than pre-CIE values. Further, the carbonate content of marine sediments following the P-ToBE decreases (Suan, Mattioli, et al., 2008; Suan, Pittet, et al., 2008), rather than increases as expected. A large volcanic source requires a greater C input, which will necessarily increase weathering fluxes and the subsequent supply of alkalinity to the ocean, resulting in an increase in the weight percent of CaCO_3 in sediments as this excess C is converted to alkalinity and ultimately buried on the seafloor (Penman et al., 2016). Further, the recovery from a volcanically driven C-cycle perturbation generates a larger, post-perturbation δ^{13}C overshoot due to the very large increase of carbonate burial necessary to remove this alkalinity from the ocean (Kump & Arthur, 1999). Combined, these observations point toward low-δ^{13}C carbon (possibly methane) as a substantial portion of the total C release.

However, the estimated temperature change of ~6°C across the P-To boundary (Gómez et al., 2016) suggests that at least some high δ^{13}C carbon (possibly volcanogenic) might have played a role in causing the P-ToBE, as the CO_2 produced by oxidation of methane alone might be too little to generate such an appreciable increase in temperature. In summary, we conclude that the maximum C release to cause the carbon cycle perturbation at the P-To boundary was on the order of around 0.12 Gt C/yr. The source of C was most likely a mixture of CO_2 from volcanic emissions and methane (biogenic, thermogenic or both), as has also been suggested for the T-OAE (Hesselbo et al., 2000).

5.5. Implications for the Causes of the P-ToBE

40Ar/39Ar dating of the sill complex of the Karoo LIP (Jourdan et al., 2008) and magnetostratigraphic correlations of the Toarcian succession of the Mochras Borehole in Wales with the basalt lava sequence of the Karoo-Ferrar LIP (Xu, Mac Niocaill, et al., 2018) suggest a link between the P-ToBE and the major volcanic activity of the Karoo-Ferrar LIP. The initial Karoo-Ferrar LIP volcanism may have been responsible for raising atmospheric CO_2, melting polar ice, and initiating the beginning of the Late Pliensbachian transgression. A warmer climate may have resulted in greater runoff and a more humid climate in the latest Pliensbachian, as evidenced by the appearance of Pentacrinites in the Upper Pliensbachian slope sediments. Further, this transgression and warming may have destabilized methane-rich deposits such as hydrates or permafrost causing a sudden, massive release of methane that ultimately resulted in the P-ToBE and associated negative CIE (Ruebsam et al., 2019; Silva & Duarte, 2015). Alternatively, interaction of Karoo-Ferrar LIP basalts—emplaced within organic-rich sediments—may have similarly triggered massive releases of thermogenic methane and/or oxidized organic matter (e.g., Jourdan et al., 2008; Svensen et al., 2007; Wignall, 2005), both of which would have been characterized by...
relatively low $\delta^{13}C$ (Clayton, 1998). In either case, Karoo-Ferrar LIP volcanism may have been the trigger that resulted in a series of feedbacks, causing a massive climatic perturbation and a major extinction.

6. Conclusion

We document a negative $\delta^{13}C_{\text{carb}}$ CIE of 1.5%e in the slope and 1%e in the platform margin of the Venetian Platform in Northern Italy, starting in the upper part of the Late Pliensbachian and spanning the Pliensbachian–Toarcian (P–To) boundary. This CIE, referred to as the P–ToBE, followed the emersion of the platform due to an abrupt and short-lived drop in sea-level, and it is associated to a transgression-regression cycle that caused the partial drowning of the Venetian Platform and a change from a rimmed platform to a distally steepened ramp (Cobianchi & Picotti, 2001). This is indicated by the presence of well-bedded pelagic lime mudstones that follow transgressive peloidal grainstones in the lowermost Toarcian (NJT5 Subzone, at the base of the Tenuicostatum Zone). We also report a depositional regression at the end of the Tenuicostatum Zone, evidenced by the presence of skeletal grainstones, overlying the micritic limestones at the platform margin, which has not been previously described in shallow-water environments. The subsequent transgression in the Serpentinitus was wider and reached the inner platform, yielding cherty micritic limestones across the platform during the T–OAE. Using our new $\delta^{13}C_{\text{carb}}$ record, we estimate the likely sources of carbon that resulted in the P–ToBE using a numerical model of the global carbon cycle. Numerical modeling results point toward low $\delta^{13}C$ carbon (possibly methane) as comprising a substantial portion of the total carbon release that caused the negative CIE at the P–To boundary. Methane release from biogenic sources on land or seas, after the pronounced glaciation in the latest Pliensbachian (mid-Spinatum Zone) or due to interaction of Karoo-Ferrar basalts with organic-rich sediments, appears likely. In either case, coeval volcanism in the Karoo-Ferrar LIP likely provided the trigger that resulted in a series of positive feedbacks that amplified the initial release of $CO_2$ into the atmosphere.

Data Availability Statement

All the datasets presented in this study, such as measured carbon and oxygen isotopes, field notes and photographs, as well as the numerical modeling code (including its description and the output calculations for Figure 8) that was used to model negative carbon isotope excursions are available in Fleischmann et al. (2021).

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