Ocean acidification during the early Toarcian extinction event: Evidence from boron isotopes in brachiopods

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ABSTRACT

The loss of carbonate production during the Toarcian Oceanic Anoxic Event (T-OAE, ca. 183 Ma) is hypothesized to have been at least partly triggered by ocean acidification linked to magmatism from the Karoo-Ferrar large igneous province (southern Africa and Antarctica). However, the dynamics of acidification have never been directly quantified across the T-OAE. Here, we present the first record of temporal evolution of seawater pH spanning the late Pliensbachian and early Toarcian from the Lusitanian Basin (Portugal) reconstructed on the basis of boron isotopic composition (δ11B) of brachiopod shells. δ11B declines by ~1‰ across the Pliensbachian-Toarcian boundary (Pl-To) and attains the lowest values (~12.5‰) just prior to and within the T-OAE, followed by fluctuations and a moderately increasing trend afterwards. The decline in δ11B coincides with decreasing bulk CaCO3 content, in parallel with the two-phase decline in carbonate production observed at global scales and with changes in pCO2 derived from stomatal indices. Seawater pH had declined significantly already prior to the T-OAE, probably due to the repeated emissions of volcanic CO2. During the earliest phase of the T-OAE, pH increased for a short period, likely due to intensified continental weathering and organic carbon burial, resulting in atmospheric CO2 drawdown. Subsequently, pH dropped again, reaching the minimum in the middle of the T-OAE. The early Toarcian marine extinction and carbonate collapse were thus driven, in part, by ocean acidification, similar to other Phanerozoic events caused by major CO2 emissions and warming.

INTRODUCTION

The Pliensbachian-Toarcian (Pl-To) boundary and the Toarcian Oceanic Anoxic Event (T-OAE, ca. 183 Ma) constituted a transient interval of global warming, development of widespread anoxia, enhanced organic carbon burial, and acceleration of the hydrological cycle, resulting in a mass extinction and a collapse of carbonate production (e.g., Jenkyns, 1988; Bailey et al., 2003; Cohen et al., 2004; Suan et al., 2010; Trecalli et al., 2012). These changes and the associated ecosystem crisis have been linked to the emplacement of the Karoo-Ferrar large igneous province (southern Africa and Antarctica) and consequent greenhouse gas release (Caruthers et al., 2013). During the T-OAE, volcanicogenic greenhouse gas emissions induced by thermal metamorphism of coal deposits in the Karoo basin most likely triggered carbon-cycle perturbations (McElwain et al., 2005; Percival et al., 2015), although other sources, such as dissociation of methane hydrates from marine sediments or terrestrial hydrates from marine sediments or terrestrial methane, have also been postulated (Hesselbo et al., 2000; Them et al., 2017).

The changes in the carbon cycle are globally expressed as a short negative shift in the carbon-isotope record at the Pl-To boundary (Littler et al., 2010), followed by a broad positive excursion that is interrupted by a major negative (~6‰) carbon isotope excursion (CIE) during the T-OAE (Hesselbo et al., 2007; Müller et al., 2017). Marine carbonate factories dominated by bivalves, corals, and algae disappeared after the onset of the negative CIE (Trecalli et al., 2012; Bram et al., 2019), and nannoplankton fluxes declined in epicontinental basins (Mattioli et al., 2009). The coincidence between the timing of the CIE, indicating a major increase in CO2 emissions, and the collapse in carbonate production indicate ocean acidification as one of the potential drivers of these changes (Trecalli et al., 2012). However, a direct quantification of pH is lacking. To fill this gap, we measured the boron isotope composition (δ11B) of brachiopod shells in conjunction with their δ13C and δ18O from the Peniche section (Global Boundary Stratotype Section and Point of the Toarcian Stage) in the Lusitanian Basin (Portugal; Comas-Rengifo et al., 2015; Duarte, 2007). This section combines exceptional stratigraphic resolution across the Pl-To boundary and the T-OAE with reliable preservation of geochemical signals in calcitic shells (Suan et al., 2008; Rocha et al., 2016). Here, we evaluate the timing and intensity of ocean acidification by reconstructing temporal evolution of seawater pH.


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METHODS

The δ¹¹B composition of marine biogenic carbonates is presently regarded as the most reliable pH proxy (Gutjahr et al., 2017). Articulate brachiopods secrete low-Mg calcitic shells nearly in isotopic equilibrium with seawater (Brand et al., 2013) and exhibit a pH-dependent δ¹¹B relationship (Lécuyer et al., 2002; Penman et al., 2013; Jurikova et al., 2019). We present major- and trace-element concentration, δ¹¹B, δ¹³C, and δ¹⁸O, as well as δ¹⁸Sr/δ¹³C composition of brachiopod shells collected from the upper Pliensbachian and lower Toarcian at the Peniche section, covering 51.5 m of the section (Fig. 1) and spanning ~3.8 m.y. (see the Supplemental Material). Sample preparation and elemental, as well as δ¹¹B and δ¹⁸Sr/δ¹³C analyses were performed according to the methods of Jurikova et al. (2019) and Krabbenhöft et al. (2009) on pre-cleaned dissolved powders, with major- and trace-element content (Ca, Mg, Al, Sr, Mn, B) determined on a quadrupole inductively coupled plasma–mass spectrometer (ICP-MS) (Agilent 7500x), δ¹¹B on a multicollector ICP-MS (Thermo Scientific Neptune Plus), and δ¹⁸Sr/δ¹³C via thermal ionization mass spectrometry (TIMS) (ThermoFisher TRITON). δ¹³C and δ¹⁸O were measured using a MAT253 isotope ratio mass spectrometer coupled with a Kiel IV (ThermoFisher Scientific) carbonate device (see the Supplemental Material and Table S1 therein).

To quantify pH from δ¹¹B values, we first tied our initial δ¹¹B-derived seawater pH from late Pliensbachian brachiopods to pre-event conditions (pH = 7.7) based on a Phanerozoic pH model for a Neotropical ocean (Ridgwell, 2005) because carbonate production was predominantly neritic during the Early Jurassic. The pH in this model has a mean value of 7.7 and ranges between 7.4 and 7.9 for the latest Pliensbachian (ca. 184 Ma). With this range of pre-event seawater pH, we computed δ¹¹B_preevent and seawater pH with two different δ¹¹B-pH calibrations: (1) scenario 1, where biological influence on boron incorporation into brachiopod shells is considered (Lécuyer et al., 2002), resulting in a mean δ¹¹B_preevent of 36.6‰ (range = 34.9‰–37.5‰); and (2) scenario 2, where boron incorporation follows inorganic fractionation (δ¹¹B_preevent = δ¹¹B_seawater-based on Klokho et al. [2006]), resulting in a mean δ¹¹B_preevent of 38.9‰ (range = 37‰–40‰) (Fig. 2; Fig. S2). Because brachiopods exert vital control over the incorporation of boron into their shells to some degree, we refer to scenario 1 below, while scenario 2 is discussed in the Supplemental Material. Using our δ¹¹B-pH values and δ¹³C-based temperatures estimated on the basis of our brachiopod shells and the formerly published pCO₂ estimates from stomatal indices (McElwain et al., 2005; Steinthorsdottir and Vajda, 2015), we first calculated seawater alkalinity at ammonite subzone-scale
stratigraphic resolution using the R package seacarb (https://cran.r-project.org/web/packages/seacarb/seacarb.pdf; Gattuso 2019) (Fig. S4). Second, we recomputed the atmospheric pCO₂ record on the basis of alkalinity (with constant values for each subzone), δ³¹B pH, and δ¹³O-based temperature values at bed-scale resolution. Third, we also computed calcite and aragonite saturation states (Ω) of seawater using the pH estimates and the stratigraphically refined pCO₂ estimates. δ³¹B data are derived from multiple species because no single species spans the entire Peniche section. Although δ³¹B values may be affected by species-specific fractionation (Penman et al., 2013), the major shift in δ³¹B from ~13.75‰ to ~12.5‰ within the Polymorphum Zone is recorded by the rhyenodell Nannirhynchia pygmaea, and inter-specific differences within weakly bioturbated beds are <0.5‰ (Fig. S4).

RESULTS AND DISCUSSION

The major and trace element composition (Sr/Ca ~0.4 – 2 mmol/mol, and Mn/Ca <0.46 mmol/mol; see the Supplemental Material and Fig. S1G) indicate very good preservation for the vast majority of our brachiopods. Brachiopod δ¹³C and δ¹⁸O records show trends similar to those previously reported from the PI-To boundary and T-OAE (Figs. 1 and 2; Bailey et al., 2003; Suan et al., 2008). The δ¹³C values define a short negative CIE of ~1.7‰ at the PI-To boundary, followed by a broad positive excursion up to ~4‰ in the Polymorphum Zone, which is interrupted by a ~4‰ negative CIE diagnostic for the T-OAE. The δ¹⁸O declines by ~1.8‰ within the Polymorphum Zone, followed by a negative trend up to ~2.5‰ in the Lesovisone Zone during the T-OAE, is also consistent with reports from elsewhere in Europe (Bailey et al., 2003; Suan et al., 2008) (Fig. 1). δ³¹B remains rather invariant within the Spinatum (Emancipatum) Zone (oscillating around 14‰), with major changes occurring at the PI-To boundary, where δ³¹B first increases to almost 16‰ and subsequently declines to a minimum of ~12.5‰ in the upper Polymorphum Zone, just prior to the onset of the T-OAE (Fig. 1). δ³¹B increases in the lower Lesovisone Zone (by ~0.8‰), but reaches the lowest value (12.47‰) in the middle of the T-OAE, followed by a slight increase. A considerable change in seawater pH following the PI-To boundary is evident from the δ³¹B record alone. The most positive δ³¹B values in the Spinatum Zone indicate higher pH, coinciding with the highest bulk CaCO₃ concentrations, the largest size of a dominant calcareous nannofossil (Schizosphaerella), and carbonate supersaturation (Fig. 2; Figs. S2 and S4). The overall δ³¹B drop in the Polymorphum Zone coincides with CaCO₃ decline (r = 0.36, p = 0.019) and with Schizosphaerella size change (r = 0.63, p = 0.02) (Fig. 2; Fig. S2; Suan et al., 2010). Furthermore, ω_{calcite} and ω_{aragonite} decline to very low values in the Polymorphum and early Lesovisone Zones (undersaturated or close to (ω<1), Fig. S4). The changes in δ³¹B closely follow the δ¹³O record (r = 0.75, p < 0.0001; based on three-point moving averages of the records). In contrast, the correlation between δ³¹B and δ¹³C is very weak (r = 0.27, p = 0.07).

The two ~3.5-m.y.-long δ³¹B-pH scenarios (1, brachiopod-specific δ³¹B incorporation [Lécuyer et al., 2002]; or 2, inorganic δ³¹B_{calcite} carbonate to δ³¹B_{marine-bird} relationship [Klochko et al.,
In 2006) of seawater pH evolution differ in the absolute pH range, albeit only slightly, as a consequence of the individual δ13C-δ18O calibration sensitivities. However, both display a sudden drop (~0.15) and an increase (~0.22) in pH in the late Pliensbachian (Margaritatus–Spinatum Zones) alongside a temperature rise and a negative CIE, implying that exogenic carbon-cycle perturbations probably started earlier in the Spinatum Zone (Fig. 2; Fig. S2). Seawater pH declined during the early Toarcian immediately after the Pi-To boundary and within an interval of ~600 k.y. during the Polymorphum Zone. The total negative shift in pH prior to the onset of the T-OAE is ~0.5. At the onset of the T-OAE (defined by the negative CIE), a sudden rise in pH by ~0.25 can be observed (Fig. 2; Fig. S2). Seawater pH reaches the minimum (~7.2) during the peak of the negative CIE and then slowly recovers, attaining pre-event values after the T-OAE. The overall decline in pH after the Pi-To boundary and prior to the T-OAE is marked by large fluctuations, which could suggest short episodic pulses (~10–200 k.y.) of volcanogenic CO2 into the ocean-atmosphere system.

At the onset of the T-OAE negative CIE, our data indicate a sudden increase in pH that was maintained for a duration of ~270 k.y. The timing coincides with osmium isotope evidence (Cohen et al., 2004) of enhanced continental weathering due to intense temperature rise, which could have led to enhanced sequestration of atmospheric CO2. Likewise, intensified organic carbon burial may have caused a short-term drawdown of CO2 (McElwain et al., 2005; Xu et al., 2017).

The subsequent pH drop suggests that maximum CO2 emission occurred at the peak of the negative CIE and/or that conditions maintaining carbon sequestration were no longer effective. pH evolution during the rebound phase of the negative CIE suggests slow reduction of CO2 emission rates. When averaged to the subzone-scale stratigraphic resolution, the decline in seawater pH covaries negatively with the stomata-based pCO2 (Pearson r = −0.9, p = 0.04, using first differences) that suggests an increase from ~850 ppm in the Spinatum Zone to ~1750 ppm throughout the T-OAE (McElwain et al. 2005; Steinhorsdottr and Vajda, 2015).

Our δ13C-based pH record, sustained by stomatal pCO2 estimates, supports a close temporal link between pH decline, early Toarcian carbon-cycle perturbations, the extinction event, and the calcification crisis. At Peniche, the late Pliensbachian–early Toarcian pH decline is associated with a long-term decline in CaCO3 content, supporting the hypothesis that the significant setback of carbonate production reflects the rise in pCO2 (Mattiolli et al., 2009). Although the envelope for Ω predicted from stomata-based pCO2, brachiopod-based pH, and δ18O-based temperature is broad owing to the uncertainties in seawater δ13C and δ18O-pH calibration, modeled δ18Ocarb and δ18Ocalc declined to the lowest levels during the late Polymorphum Zone and early Levisoni Zone (Fig. S4). Although a comparison of the δ18O signal to the high-resolution CaCO3 and Schizophaerella records is complicated by disparate temporal resolutions of the data sets and by a delayed decline in pelagic production (relative to the neritic production; Suan et al., 2008), bivariate relations mentioned above indicate that the minima in the δ18O-pH signal track low carbonate flux prior to and during the early phases of the T-OAE. The decrease in seawater pH during the Polymorphum Zone suggests that environmental conditions were already unfavorable prior to the T-OAE, and in spite of the short-term rebound in pH at the Polymorphum-Levisoni boundary, seawater likely remained undersaturated during the Levisoni Zone. Hence, in addition to warming and extensive anoxia, ocean acidification (i.e., suppressed pH and carbonate saturation state) was responsible for the biodiversity loss (Dera et al., 2010; García Joral et al., 2011; Caruthers et al., 2013) and the demise of lithiotid bivalve reefs and carbonate factories (Trecalli et al. 2012; Brame et al., 2019) during the Pl-To and T-OAE crises.

CONCLUSIONS

Our brachiopod δ18O-pH reconstruction from the latest Pliensbachian–early Toarcian interval provides evidence of seawater pH decline as a result of elevated CO2 emissions prior to the Pi-To boundary. Low-pH conditions may have developed already prior to the T-OAE. The early phase of the T-OAE was characterized by a short period of pH rebound most likely due to atmospheric CO2 drawdown as a result of enhanced continental weathering and organic carbon burial. Seawater pH attained the lowest values immediately prior to and during the T-OAE, followed by a protracted recovery toward pre-event conditions. Our findings are congruent with the hypothesis that ocean acidification contributed to the large-scale retreat of pelagic carbonate producers and to the extinction of neritic carbonate platform builders during the early Toarcian.

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REFERENCES CITED


Gutiérrez, M., Ridgwell, A., Sexton, P.F., Anagnostou, E., Pearson, P.N., Pålkeh, H., Norris, R.D.,


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