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Constraining the evolution of Neogene ocean carbonate chemistry using the boron isotope pH proxy

S.M. Sosdian [a,*], R. Greenop [b,c], M.P. Hain [b,d], G.L. Foster [b], P.N. Pearson [a], C.H. Lear [a]

[a] Cardiff University, School of Earth & Ocean Sciences, Cardiff, CF10 3AT, UK
[b] Ocean and Earth Science, National Oceanography Centre Southampton, University of Southampton Waterfront Campus, Southampton, UK
[c] University of St. Andrews, School of Earth and Environmental Sciences, St. Andrews, UK
[d] Earth and Planetary Sciences, University of California, Santa Cruz, CA 95064, USA

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ABSTRACT

Over the course of the Neogene, the Earth underwent profound climatic shifts from the sustained warmth of the middle Miocene to the development of Plio-Pleistocene glacial–interglacial cycles. Major perturbations in the global carbon cycle have occurred alongside these shifts, however the lack of long-term carbonate system reconstructions currently limits our understanding of the link between changes in CO_2, carbon cycling, and climate over this time interval. Here we reconstruct continuous surface ocean pH, CO_2, and surface ocean aragonite saturation state using boron isotopes from the planktonic foraminifer *Trilobatus trilobus* and we perform a sensitivity analysis of the key variables in our calculations (e.g. $\delta^{11}B_{sw}$, $[Ca]_{sw}$, CCD). We show that the choice of $\delta^{11}B_{sw}$ influences both seawater pH and CO_2 while $[Ca]_{sw}$ reconstructed dissolved inorganic carbon exerts a significant influence only on CO_2. Over the last 22 Myr, the lowest pH levels occurred in the Middle Miocene Climate Optimum (MMCO; 17–14 Myr ago) reaching $\sim 7.6 \pm 0.1$ units in all our scenarios. The extended warmth of the MMCO corresponds to mean CO_2 and aragonite saturation state levels of 470–630 ppm and 2.7–3.5, respectively. Despite a general correspondence between our CO_2 record and climate, all CO_2 scenarios show a peak at ~9 Ma not matched by corresponding changes in climate reconstructions. This may suggest decoupling (i.e. significant CO_2 change without a discernible climate response) for a limited interval in the Late Miocene (11.6–8.5 Ma), although further refinement of our understanding of the temporal evolution of the boron isotopic composition of seawater is necessary to fully evaluate the nature of the relationship between CO_2 and climate. Nonetheless, from our long-term view it is clear that low-latitude open ocean marine ecosystems are unlikely to have experienced sustained surface pH and saturation levels below 7.7 and 1.7, respectively, during the past 14 million years (66% CI).

1. Introduction

Boron isotopes ($\delta^{11}B$) in marine carbonates have been exploited as a proxy for the marine carbonate system (i.e. pH, pCO_2) on multiple timescales within the Cenozoic (e.g. Sanyal et al., 1995; Palmer et al., 1998; Pearson and Palmer, 2000; Foster et al., 2012; Penman et al., 2013; Anagnostou et al., 2016; Gutjahr et al., 2017; Chalk et al., 2017). Plio-Pleistocene foraminiferal $\delta^{11}B$ derived reconstructions exhibit glacial–interglacial variability in pH and pCO_2, in good agreement with independent records (e.g. ice cores) (Seki et al., 2010; Bartoli et al., 2011; Hönisch et al., 2009; Henehan et al., 2013; Martínez-Botí et al., 2015a; Chalk et al., 2017). However, application of this proxy beyond the Plio-Pleistocene is not straightforward as calculation of pH and pCO_2 requires records of seawater chemistry (e.g. $\delta^{11}B_{sw}$, $[Ca]_{sw}$) and a second carbonate system parameter (e.g. total alkalinity (ALK), or dissolved inorganic carbon (DIC)) which currently have considerable uncertainties (Horita et al., 2002; Brennan et al., 2013; Pälike et al., 2012; Raitzsch and Hönisch, 2013; Greenop et al., 2017). Current reconstructions of the major ion composition of seawater, which impacts boron isotope reconstructions through influencing key dissociation constants and estimates of carbonate ($CO_3{}^{2-}$) concentration, rely on low-resolution fluid inclusion measurements (Horita et al., 2002; Brennan et al., 2013) and improved estimates await development of higher resolution records from a range of proxies. For the early Cenozoic, the likely upper and lower bounds of $\delta^{11}B_{sw}$ have been estimated using the $\delta^{11}B$-pH relationship, whilst estimates of the second carbonate system parameter

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[*] Corresponding author.
E-mail address: SosdianS@cardiff.ac.uk (S.M. Sosdian).

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have been determined using Earth System modelling (Anagnostou et al., 2016; Gutjahr et al., 2017). According to Anagnostou et al. (2016), the early Eocene CO_2 concentration was 1400 ± 470 ppm decreasing to 550 ± 190 ppm in the early Oligocene. The uncertainty window on these estimates reflects uncertainty in calcite saturation and $\delta^{11}B_{sw}$ estimates, $\delta^{11}B_c$ measurement error, and possible atmosphere–ocean disequilibrium. Despite these relatively large uncertainties, it is clear that early Cenozoic pCO_2 was much higher than in the Plio-Pleistocene and CO_2 change was an important driver of climate change in the early Cenozoic. However, application of the $\delta^{11}B$-pCO_2 proxy during the more recent Neogene (2.6 to 23 Myrs ago) transition to a bipolar icehouse world is complicated by the fact that most reconstructions indicate a relatively dramatic shift in $\delta^{11}B_{sw}$ in the late Miocene to Pliocene. While there is first-order agreement between different records for the late Miocene $\delta^{11}B_{sw}$ rise, the exact timing, magnitude and rate of change of this shift remains uncertain (Pearson and Palmer, 2000; Lemarchand et al., 2002; Raitzsch and Hönisch, 2013; Greenop et al., 2017), with implications for the structure of $\delta^{11}B$-based reconstructions of pH and pCO_2 during the period. Furthermore, the history of carbonate chemistry (i.e. DIC and alkalinity) in this interval is poorly understood and currently is limited to model estimates that use pCO_2 estimates from GEOCARB carbon cycle models and/or paleo-pCO_2 proxy estimates paired with estimates of the calcite compensation depth (CCD) (Tyrrell and Zeebe, 2004; Ridgwell, 2005).

During the Neogene period, the Earth underwent profound changes from the warmth of the Middle Miocene Climatic Optimum (∼14–17 Myrs ago; MMCO) to the expansion of the Antarctic ice sheet at 13.9 Ma (Lear et al., 2010). Dynamic changes in the carbon cycle have been proposed to be associated with these climatic shifts, involving changes in silicate weathering, volcanic emissions and the organic carbon subcycle (Derry and France-Lanord, 1996; France-Lanord and Derry, 1997; Raymo and Ruddiman, 1992; Raymo, 1994; Foster et al., 2012). The evolution of the carbonate system during this time interval therefore represents a critical gap in our understanding of climate–carbon cycle interactions. Previous CO_2 reconstructions derived from a disparate set of proxies (e.g. plant stomata, marine alkenones, paleosols, marine carbonate $\delta^{11}B$) have produced a wide range of estimates, yet with a general consensus that MMCO CO_2 levels were higher than preindustrial, and that CO_2 subsequently declined across the mid-Miocene climate transition (Kürschner et al., 2008; Foster et al., 2012; Zhang et al., 2013). Since CO_2 and pH are highly correlated variables in the ocean carbonate system, the discrepancies between existing CO_2 reconstructions (Pagani et al., 1999a, 1999b; Foster et al., 2012; Zhang et al., 2013) imply a lack in understanding of the ocean's history of pH change and the evolution of the carbon cycle and also, to some extent, an uncertainty in proxy systematics. Further, the degree of coupling between climate and CO_2 in the late Miocene is poorly constrained, limiting our ability to determine the importance of CO_2 variability in setting the evolution of Miocene climate (Pagani et al., 1999a, 1999b; LaRiviere et al., 2012). Thus, the lack of available records that constrain the ocean's carbonate chemistry is a critical impediment to establishing the relationship between the long-term Earth System evolution of carbon cycle and climate (Hönisch et al., 2012). Additionally, without detailed knowledge of long-term changes in seawater carbonate chemistry we are blind to its role in driving evolutionary adaptation and resilience of marine organisms to environmental change (Hönisch et al., 2012; Hain et al., 2015).

Here we use a new dataset of 40 planktic boron isotope measurements in conjunction with existing benthic data and new constraints on the evolution of seawater $\delta^{11}B$ (Lemarchand et al., 2002; Raitzsch and Hönisch, 2013; Greenop et al., 2017) to reconstruct surface pH and ocean carbon content for the past 22 million years. Combining our surface pH record with independent reconstructions of seawater calcium and magnesium concentrations, changes in the calcite compensation depth, deep-sea pH, and temperature, we calculate both atmospheric CO_2 and surface aragonite saturation state (Ω_{arag}). We also discuss the relative importance of the variable sources of uncertainty in these parameters on our reconstructions. With extensive uncertainty propagation using a Monte Carlo approach and sensitivity analysis we reconstruct long-term pH, aragonite saturation state and atmospheric CO_2 since the MMCO (0–17 Myrs ago). Our new record of ocean carbonate chemistry allows us to examine the role of CO_2 in the climate system over the course of the Neogene and contextualize future carbon emission pathways against this geological perspective.

2. Materials and methods

The boron isotope proxy relies on the principle that the ratio of the dominant boron species in seawater, borate ion and boric acid, varies as a function of pH (Dickson, 1990), which also controls the isotopic composition of the borate ion that is incorporated into a marine carbonate such as a planktic foraminiferal calcite (Vengosh et al., 1991; Hemming and Hanson, 1992; Foster and Rae, 2016). The foraminifer-derived pH record may then be used to estimate CO_2 levels and Ω_{arag} using assumptions about other carbonate system parameters. Early attempts at reconstructing pH and atmospheric CO_2 from fossil foraminifera over this interval (Spivack et al., 1993; Palmer et al., 1998; Pearson and Palmer, 2000) are qualitatively useful but have been superseded by a revised understanding of boron isotope systematics and analytical developments (see discussion in Seki et al., 2010; Foster et al., 2012; Anagnostou et al., 2016).

2.1. Sample locations and site details

In this study we analysed the $CaCO_3$ shells of a single planktic foraminifera species, *Trilobatus trilobus*. This species was formerly assigned to the genus *Globigerinoides* but is no longer considered part of that genus (Spezzaferri et al., 2015). The species is sometimes referred to as *T. sacculifer*, especially those individuals that bear a final sac-shaped final chamber, but the feature is ecophenotypic (André et al., 2013) and the name *trilobus* has priority. In this study we avoided individuals with sac-shaped chambers. Unusually for planktic foraminifera, *T. trilobus* displays no significant cryptic genetic diversity (André et al., 2013). It lives in the upper part of the water column in association with dinoflagellate photosymbionts, although it probably sinks towards the end of its life cycle at gametogenesis, somewhat complicating the shell chemistry (e.g. Birch et al., 2013). The species is widely used in boron isotope studies because it is one of the few to survive almost the entire Neogene and Quaternary periods (Spezzaferri et al., 2015) and a species-specific calibration for $\delta^{11}B$-pH exists (discussed further below; Sanyal et al., 2001; Seki et al., 2010; Foster et al., 2012; Greenop et al., 2014).

We analysed the $\delta^{11}B$ of 40 samples of this species from geographically diverse locations including Ocean Drilling Program (ODP) Site 926 ($n = 26$; western tropical North Atlantic), ODP Site 761 ($n = 3$; tropical Indian Ocean), ODP Site 872 ($n = 7$; tropical Pacific Ocean), and ODP Site 1000 ($n = 4$; Caribbean Sea). This dataset supplements previously published *T. trilobus* analyses from ODP site 668 (Hönisch et al., 2009), ODP Site 761 (Foster et al., 2012; Greenop et al., 2014), ODP Site 926 (Foster et al., 2012), ODP Site 999 (Bartoli et al., 2011; Seki et al., 2010; Caribbean Sea), ODP 1264 (Stap et al., 2016) and outcrops of the Blue Clay formation in Malta (Badger et al., 2013) and previously published *Globigeri-*