

We would like to take this opportunity to thank the editor and all reviewers for their thoughtful and constructive comments, from which our manuscript has greatly benefited. For the most part the changes that were made in response to the reviewer's comments are outlined in the individual responses to reviewer's comments. All minor typos, rewording and changes to the figures have been made. Outlined below is a list of the major changes we have made to the manuscript and an instance where we found it was not possible to fulfill the request of the reviewer during revision of the manuscript.

Major issues addressed:

1) Presentation of other datasets

We have made considerable revisions to the introduction. Here, we now present the pre-existing $\delta^{11}\text{B}_{\text{sw}}$ records, focusing on the similarity between records. The discussion of these various records has been extended later in the manuscript in comparison to our new $\delta^{11}\text{B}_{\text{sw}}$. As with the introduction, we follow the referee's suggestion and the revised discussion section now clearly emphasises the similarity between the various records, building towards consensus. Only in the case of specific discrepancies between the records do we explore the differences in methodology between the $\delta^{11}\text{B}_{\text{sw}}$ reconstructions as a way to explain any of the differences.

2) More detailed discussion of uncertainties and modeling parameters.

The uncertainties used in the Monte Carlo simulation and the variables changed in the modeling studies have now been tabulated in order to improve the clarity in these sections of the manuscript. Included in the table of uncertainties is also a justification of the 2σ that we apply.

3) Simplifying the $\delta^{11}\text{B}_{\text{sw}}$ output and applying the most appropriate $\delta^{13}\text{C}/\text{pH}$ relationship

Reviewer 1 suggested that given the overlap in uncertainties between the different records we presented, it wasn't appropriate to recommend the use of one of our $\delta^{11}\text{B}_{\text{sw}}$ record over another. This valuable comment led us to re-think the presentation of our central argument with regard to the uncertainty of $\Delta\text{pH}/\Delta\delta^{13}\text{C}$ relationship and thereby, we think, both simplified and improved our study. We now present a single record that captures a broader range of different $\delta^{13}\text{C}/\text{pH}$ relationships than any of our

initial scenarios. In practical terms, this is done by applying a flat probability (ie. Equal rather than normally distributed) of ± 0.05 to the ΔpH estimate using the central $\Delta\text{pH}/\Delta\delta^{13}\text{C}$ slope of $0.175/\text{‰}$ diagnosed from our extensive sensitivity tests using both the CYCLOPS and GENIE models. This nominal uncertainty is equivalent to the broad range of $\Delta\text{pH}/\Delta\delta^{13}\text{C}$ slopes of $0.14/\text{‰}$ and $0.21/\text{‰}$ – covering the vast majority of our model simulations and removing the need to present separate “slope scenarios”. That is, because we have used a flat probability there is an equal likelihood of any value between about $0.14/\text{‰}$ and $0.21/\text{‰}$. To avoid confusion and given the evidence from our $\delta^{13}\text{C}$ data and modeling work we have also now discarded the hypothetical scenario where the pH gradient was assumed to have remained the same as modern. The second motivation for following this broad approach is that it is not possible to test the $\delta^{13}\text{C}/\text{pH}$ relationship at our specific sites as requested by reviewer 1, nor for the low latitudes. Currently pre-industrial surface water $\delta^{13}\text{C}$ data is only available for the North Atlantic $>20^\circ\text{N}$ (Olsen and Ninnemann, 2010). When a wider dataset of pre-industrial water column $\delta^{13}\text{C}$ is available in the future, it will be possible to refine our $\delta^{11}\text{B}_{\text{sw}}$ record. We now make this point explicitly.

4) Exploration of the smoothing parameter and the impact on the record

In order to test the dependence of the output record on the smoother we have undertaken a binning exercise where we have averaged our data over 8 Myr intervals. The calculated mean and two standard errors of the data in each interval show that the difference between the middle Miocene $\delta^{11}\text{B}_{\text{sw}}$ and modern is significant. The presence of the rise in $\delta^{11}\text{B}_{\text{sw}}$ across this interval in a number of other published records suggests that our record adds to the growing consensus on the evolution of $\delta^{11}\text{B}_{\text{sw}}$ in the Neogene.

1 A record of Neogene seawater $\delta^{11}\text{B}$ reconstructed from paired $\delta^{11}\text{B}$ 2 analyses on benthic and planktic foraminifera.

3 Greenop Rosanna^{1,2*}, Hain, Mathis P.¹, Sosdian, Sindia M.³, Oliver, Kevin I.C.¹,
 4 Goodwin, Philip¹, Chalk, Thomas B.^{1,4}, Lear, Caroline H.³, Wilson, Paul A.¹, Foster,
 5 Gavin L.¹

6
 7 *Corresponding author

8 ¹ *Ocean and Earth Science, National Oceanography Centre Southampton, University*
 9 *of Southampton, Waterfront Campus, European Way, Southampton SO14 3ZH, UK*

10 ² *School of Geography & Geosciences, Irvine Building, University of St Andrews,*
 11 *North Street, St Andrews, KY16 9AL, UK*

12 ³ *School of Earth & Ocean Sciences, Cardiff University, Cardiff, CF10 3AT, UK*

13 ⁴ *Department of Physical Oceanography, Woods Hole Oceanographic Institution,*
 14 *Woods Hole, Massachusetts, USA*

16 Abstract:

17 The boron isotope composition ($\delta^{11}\text{B}$) of foraminiferal calcite, which reflects
 18 seawater pH, is a well-established proxy for reconstructing past seawater carbonate
 19 chemistry and, in the case of planktic foraminifera, past atmospheric CO_2 . However,
 20 to translate $\delta^{11}\text{B}$ measurements determined in calcareous fossils into pH we need to
 21 know the boron isotope composition of the seawater in which they grew ($\delta^{11}\text{B}_{\text{sw}}$).
 22 While a number of $\delta^{11}\text{B}_{\text{sw}}$ reconstructions exist, more work is needed to build
 23 confidence in our knowledge of this important parameter. Here we present a new
 24 Neogene $\delta^{11}\text{B}_{\text{sw}}$ record based on the $\delta^{11}\text{B}$ difference between paired measurements of
 25 planktic and benthic foraminifera and an estimate of the coeval water column pH
 26 gradient derived from planktic/benthic $\delta^{13}\text{C}$ data. To underscore this approach we
 27 present extensive tests using the CYCLOPS and GENIE carbon cycle models to
 28 demonstrate that the planktic/benthic $\Delta\text{pH}/\Delta\delta^{13}\text{C}$ relationship is relatively insensitive
 29 to ocean and carbon cycle changes. In keeping with previously published records, our

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reconstruction suggests that $\delta^{11}\text{B}_{\text{sw}}$ was $\sim 37.5\text{‰}$ during the early and middle Miocene and rapidly increased from ~ 12 to 5 Ma to reach a plateau near the modern value of 39.61‰ . A similar pattern of change is evident in the seawater composition of the Mg, Li and Ca stable isotope systems. Concurrent shifts in the seawater isotopic composition of all four of these elements during the late Miocene are suggestive of a common forcing mechanism. Based on the observed direction of change we hypothesise that an increase in secondary mineral formation during continental weathering may have affected the isotopic composition of the riverine input to the ocean since $\sim 12\text{-}15\text{ Ma}$.

1. Introduction

Key to determining the relationship between CO_2 and climate in the geological past is the calculation of reliable estimates of absolute CO_2 through time. In recent years the boron isotope composition ($\delta^{11}\text{B}$) of foraminiferal calcite has become a high-profile tool for reconstructing CO_2 beyond the last 800 kyrs and throughout the Cenozoic Era (Foster, 2008; Hönisch et al., 2009; Pearson et al., 2009; Bartoli et al., 2009; Foster et al., 2012; Badger et al., 2013; Henehan et al., 2013; Greenop et al., 2014; Martínez-Botí et al., 2015a). Yet long-term change in the boron isotope composition of seawater ($\delta^{11}\text{B}_{\text{sw}}$) is currently poorly constrained and represents a major source of the uncertainty associated with $\delta^{11}\text{B}$ -determined CO_2 estimates (e.g. Pearson et al., 2009). In the modern ocean boron is a conservative element with a spatially invariant isotope ratio (39.61‰ ; Foster et al., 2010), but this value is subject to change through geological time. The residence time of boron in the ocean is estimated to lie between 11 and 17 Myrs (Lemarchand et al., 2000). Therefore we can expect the uncertainty associated with $\delta^{11}\text{B}_{\text{sw}}$ to be an important factor in CO_2 estimates beyond the late Pliocene ($\sim 4\text{-}5\text{ Ma}$, Palmer et al., 1998; Lemarchand et al., 2000; Pearson et al., 2009; Foster et al., 2012).

The ocean boron budget and its isotopic composition are controlled by a number of inputs and outputs (Fig. 1). However, because the magnitude of the boron fluxes between land, the ocean and the atmosphere in the modern are still poorly understood, the residence time and changes in both concentration ($[\text{B}]_{\text{sw}}$) and isotopic composition ($\delta^{11}\text{B}_{\text{sw}}$) through time remain uncertain. The main inputs of B into the

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ocean are silicate weathering delivered to the ocean by rivers (Lemarchand et al., 2000), hydrothermal vents (You et al., 1993) and fluid expelled from accretionary prisms (Smith et al., 1995). The major **loss terms** are oceanic crust alteration (Smith et al., 1995), adsorption onto sediments (Spivack and Edmond, 1987) and co-precipitation into carbonates (Hemming and Hanson, 1992). In case of all three **outputs**, the light ^{10}B isotope is preferentially removed **relative to ^{11}B** , such that the **seawater $^{11}\text{B}/^{10}\text{B}$ ratio ($\delta^{11}\text{B}_{\text{sw}}$, 39.61‰)** is significantly greater than that of the **cumulative inputs ($\delta^{11}\text{B}$ of $\sim 10.4\text{‰}$; Lemarchand et al., 2000)**. Our understanding of the modern boron fluxes outlined above, and illustrated in Fig. 1, implies a significant **imbalance between inputs and outputs and consequently the poorly constrained ocean-atmosphere boron fluxes may also be an important part of the ocean's modern boron mass balance** (Park and Schlesinger, 2002). In the context of this study, however, we follow Lemarchand et al., (2000) and assume atmospheric fluxes are unlikely to have varied significantly on geological timescales and therefore will not be discussed further in reference to the Neogene record.

Unlike many other isotopic systems (e.g. $\delta^7\text{Li}_{\text{sw}}$, $\delta^{26}\text{Mg}_{\text{sw}}$, $\delta^{44/40}\text{Ca}_{\text{sw}}$, $\delta^{87}\text{Sr}/^{86}\text{Sr}$) to date no archive has been discovered that simply records unaltered $\delta^{11}\text{B}_{\text{sw}}$. This is a result of the **pH-dependent boron** speciation in seawater upon which the $\delta^{11}\text{B}$ -pH proxy is based (Hemming & Hanson 1992) that imparts a pH dependency on the $\delta^{11}\text{B}$ of all marine precipitates so far examined. Empirical reconstructions of $\delta^{11}\text{B}_{\text{sw}}$ must therefore use “indirect” approaches. So far, four approaches have been applied to the problem (Fig. 2): (1) geochemical modeling (Lemarchand et al., 2000), (2) $\delta^{11}\text{B}$ analysis of halites (Paris et al., 2010), (3) measurements of benthic foraminiferal $\delta^{11}\text{B}$ coupled to various assumptions about past changes in ocean pH (Raitzsch and Hönisch, 2013), and (4) measurements of $\delta^{11}\text{B}$ in surface and thermocline dwelling foraminifera coupled with additional information on the pH gradient of the surface ocean (Palmer et al., 1998; Pearson and Palmer 1999, Pearson and Palmer 2000; Anagnostou et al., 2016). Geochemical modelling of the changes in the flux of boron into and out of the ocean through time has been used to suggest that $\delta^{11}\text{B}_{\text{sw}}$ increased from 37‰ at 60 Ma to 40‰ \pm 1‰ today, driven by a combination of processes including changing boron continental discharge (Lemarchand et al., 2000). In the case of approach 2, while modern natural halites reflect $\delta^{11}\text{B}_{\text{sw}}$ (39.7‰) with no apparent fractionation, measurement of $\delta^{11}\text{B}$ in ancient halites yield isotopic ratios

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that are significantly lower than all other approaches (Fig. 2; Paris et al., 2010), with implausible variability among samples of the same age (7‰ range), thereby casting doubt over the reliability of this approach (Raitzsch and Hönisch, 2013). In the case of approach 3, $\delta^{11}\text{B}_{\text{sw}}$ is calculated from globally distributed benthic $\delta^{11}\text{B}$ data with an imposed degree of deep-ocean pH change (Fig. 2; Raitzsch and Hönisch, 2013). This method hinges on two key assumptions: (a) a near linear surface water pH increase of 0.39 over the past 50 Myrs taken from the intermediate pH output from two modeling studies (Berner and Kothavala, 2001; Tyrrell and Zeebe, 2004; Ridgwell, 2005), and (b) a prescribed constant surface-to-deep ocean pH gradient of 0.3 (Tyrrell and Zeebe, 2004, and modern observations). The modeled surface pH and estimated fixed pH gradient is then used to estimate deep ocean pH, and then convert benthic foraminiferal $\delta^{11}\text{B}$ measurements to $\delta^{11}\text{B}_{\text{sw}}$. This approach yields broadly similar results to geochemical modeling (Fig. 2). The fourth approach exploits the non-linear relationship between $\delta^{11}\text{B}$ and pH alongside estimated pH gradients in the ocean to constrain $\delta^{11}\text{B}_{\text{sw}}$ (Palmer et al., 1998; Pearson and Palmer 1999, Pearson and Palmer 2000) and is the basis of the approach used in this study. The advantage of this method is that $\delta^{11}\text{B}_{\text{sw}}$ can be reconstructed empirically without relying on dependent pH constraints. The non-linear relationship between $\delta^{11}\text{B}$ and pH means that the pH difference between two $\delta^{11}\text{B}$ data points varies as a function of $\delta^{11}\text{B}_{\text{sw}}$ (Fig. 3). Consequently, if the size of the pH gradient can be estimated then there is only one $\delta^{11}\text{B}_{\text{sw}}$ value that is consistent with the foraminiferal $\delta^{11}\text{B}$ measurements and the specified pH gradient irrespective of the absolute pH (Fig. 3c). Previously this approach has been applied to pH variations in the surface ocean and used in studies of Cenozoic $p\text{CO}_2$ to account for changes in $\delta^{11}\text{B}_{\text{sw}}$ (determined using $\delta^{11}\text{B}$ in surface and thermocline-dwelling foraminifera) (Fig. 2) (Palmer et al., 1998; Pearson and Palmer 1999, Pearson and Palmer 2000; Anagnostou et al., 2016). This approach uses a constant pH gradient between the surface and some depth proximal to the oxygen minimum zone and the boron isotope values of a mixed layer dwelling species and thermocline dweller to calculate a value for $\delta^{11}\text{B}_{\text{sw}}$ (Pearson and Palmer, 1999). The resulting record suggests that $\delta^{11}\text{B}_{\text{sw}}$ varies between 37.7‰ and 39.4‰ through the Neogene (Fig. 2) (Pearson and Palmer, 2000).

The same method, but using planktic-benthic instead of surface planktic- thermocline planktic $\delta^{11}\text{B}$ gradients to calculate $\delta^{11}\text{B}_{\text{sw}}$, was recently applied to the middle

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348 Miocene where it yielded a $\delta^{11}\text{B}_{\text{sw}}$ of $37.6^{+0.4}_{-0.5}$ ‰ (Foster et al., 2012). A further
 349 modification to the method of Pearson and Palmer (1999) was also proposed in that
 350 study wherein $\delta^{13}\text{C}$ in foraminiferal calcite was used to estimate the surface-to-deep
 351 pH gradient (Foster et al., 2012). Here, we reconstruct $\delta^{11}\text{B}_{\text{sw}}$ for the last 23 Ma, the
 352 Neogene, based on this modified approach. We undertake extensive sensitivity tests
 353 using both the CYCLOPS carbon cycle box model and the GENIE Earth system
 354 model to define the plausible range in the relationship between surface/deep pH
 355 difference and $\delta^{13}\text{C}$ difference, which is an essential parameter for this approach.
 356 Finally, we employ a Monte Carlo approach for comprehensive propagation of
 357 uncertainty in all input parameters and we focus on reconstructing $\delta^{11}\text{B}_{\text{sw}}$ – the
 358 implications of our work for understanding the evolution of Neogene ocean pH and
 359 atmospheric $p\text{CO}_2$ will be documented elsewhere.

360 2. Methods

361 2.1 Site Locations and Age Models

362 Foraminifera from four sites are used to construct the planktic-benthic $\delta^{11}\text{B}$ pairs;
 363 Ocean Drilling Program, ODP, Site 758 and ODP Site 999 for the Pleistocene and
 364 Pliocene samples and ODP Site 926 and Site 761 for the Miocene (Fig. 4) (this study;
 365 Foster et al., 2012; Martinez-Boti et al., 2015a, Sossian et al., *in prep*). We also
 366 incorporate the middle Miocene planktic-benthic pair from Site 761 in Foster et al.
 367 (2012). To place all data from all sites on a single age model we use the nanno and
 368 planktic foraminifera stratigraphy from sites 999, 926 and 761 (Shipboard Scientific
 369 Party, 1997; Shipboard Scientific Party, 1995; Zeeden et al., 2013; Holbourn et al.,
 370 2004) updated to GTS2012 (Gradstein et al., 2012). At Site 758 the
 371 magnetostratigraphy (Shipboard Scientific Party, 1989) is used and updated to
 372 GTS2012 (Gradstein et al., 2012).

373 2.2 Boron Isotope Analysis and pH Calculation

374 The boron isotope measurements (expressed in delta notation as $\delta^{11}\text{B}$ – permil
 375 variation) were made relative to the boric acid standard SRM 951; (Catanzaro et al.,
 376 1970). Boron was first separated from the Ca matrix prior to analysis using the boron

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specific resin Amberlite IRA 743 following Foster et al. (2013). The boron isotopic composition was then determined using a sample-standard bracketing routine on a ThermoFisher Scientific Neptune multicollector inductively coupled plasma mass spectrometer (MC-ICPMS) at the University of Southampton (following Foster et al., 2013). The relationship between $\delta^{11}\text{B}$ of $\text{B}(\text{OH})_4^-$ and pH is very closely approximated by the following equation:

$$\text{pH} = \text{p}K_B^* - \log \left(- \frac{\delta^{11}\text{B}_{\text{SW}} - \delta^{11}\text{B}_{\text{CaCO}_3}}{\delta^{11}\text{B}_{\text{SW}} - \alpha_B \cdot \delta^{11}\text{B}_{\text{CaCO}_3} - 1000 \cdot (\alpha_B - 1)} \right) \quad (1)$$

Where $\text{p}K_B^*$ is the equilibrium constant, dependent on salinity, temperature, pressure and seawater major ion composition (i.e., [Ca] and [Mg]), α_B is the fractionation factor between the two boron species and $\delta^{11}\text{B}_{\text{sw}}$ is the boron isotope composition of seawater. Here we use the fractionation factor of 1.0272, calculated from spectrophotometric measurements (Klochko et al., 2006). No temperature correction was applied as a number of recent studies suggest that it is not significant over our investigated temperature range (Rae et al. 2011; Henehan et al., 2013; Martínez-Botí et al. (2015b); Kaczmarek et al. 2016). Although the $\delta^{11}\text{B}$ of foraminifera correlates well with pH and hence $[\text{CO}_2]_{\text{aq}}$, the $\delta^{11}\text{B}_{\text{calcite}}$ is often not exactly equal to $\delta^{11}\text{B}_{\text{borate}}$ (Sanyal et al., 2001; Foster, 2008; Henehan et al., 2013). The planktic species used to construct the benthic-planktic pairs changes through time, as a single species is not available for the entire Neogene (this study; Foster et al., 2012; Martínez-Botí et al., 2015a, Sosdian et al., in prep). Here *Globigerinoides ruber* is used for 0 to 3 Ma, *Trilobatus sacculifer* (formally *Globigerinoides sacculifer* and including *Trilobatus trilobus*; Hembleden et al., 1987; Spezzaferri et al., 2015) for 0 to 20 Ma and *Globigerina praebulloides* for 22 to 23 Ma. The calibration for *G. ruber* (300-355 μm) is derived from culturing data supported by core top data (Henehan et al., 2013). The *T. sacculifer* calibration (300-355 μm) is from Sosdian et al., (in prep) where the *T. sacculifer* calibration of Sanyal et al., (2001) is used with a modified intercept so that it passes through the core top value for *T. sacculifer* (300–355 μm) from ODP Hole 999A (Seki et al., 2010). Unlike the asymbiotic modern *G. bulloides*, *G. praebulloides* appears to be symbiotic at least in the latest Oligocene (Pearson and Wade, 2009). Therefore, we apply the *T. sacculifer* (300-355 μm) calibration to this

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species. For *T. sacculifer* (500-600µm) between 0 and 1 Ma, we use the calibration from Martínez-Botí et al. (2015b) where the calibration of Sanyal et al. (2001) measured using NTIMS is corrected for the offset between MC-ICPMS and NTIMS using a comparison of core-top *T. sacculifer* measured by the two different methods from adjacent sites (Foster, 2008; Sanyal et al., 1995). In order to constrain deep-water pH, analysis was conducted on benthic foraminifera *Cibicidoides wuellerstorfi* or *Cibicidoides mundulus* depending on which species were most abundant in each sample. The $\delta^{11}\text{B}$ of both *Cibicidoides* species shows no offset from the theoretical $\delta^{11}\text{B}$ of the borate ion and therefore no calibration is needed to adjust for species-specific offsets (Rae et al., 2011).

As mentioned above, in addition to $\delta^{11}\text{B}_{\text{calcite}}$, temperature, salinity, water depth (pressure) and seawater major ion composition are also needed to calculate pH from $\delta^{11}\text{B}$. We use the MyAMI specific ion interaction model (Hain et al., 2015) to calculate the appropriate equilibrium constants based on existing [Ca] and [Mg] reconstructions (Horita et al., 2002; Brennan et al., 2013). Sea surface temperature (SST) is calculated from tandem Mg/Ca analyses on an aliquot of the $\delta^{11}\text{B}$ sample (with a conservative 2σ uncertainty of 2°C). Adjustments were made for changes in Mg/Ca_{sw} using the records of Horita et al. (2002) and Brennan et al. (2013), and correcting for changes in dependence on Mg/Ca_{sw} following Evans and Muller (2012) using $H = 0.41$ calculated from *T. sacculifer* (where H describes the power relationship between test Mg/Ca incorporation and Mg/Ca_{sw}; Delaney et al., 1985; Hasiuk and Lohmann, 2010; Evans and Muller, 2012) using the equations:

$$\text{Mg/Ca}_{\text{sw.c}} = (\text{Mg/Ca}_{\text{sw.a}} / \text{Mg/Ca}_{\text{sw.m}})^{0.41} \quad (2)$$

Where Mg/Ca_{sw.c} is the correction factor applied to the temperature equation for changing Mg/Ca_{sw}, Mg/Ca_{sw.a} is the estimated Mg/Ca_{sw} for the age of the sample and Mg/Ca_{sw.m} is modern Mg/Ca_{sw}. Temperature is then calculated using the generic planktic foraminifera calibration of Anand et al. (2003) and including a correction factor for Mg/Ca_{sw}.

$$\text{Temperature} = \ln(\text{Mg/Ca}_{\text{test}} / (0.38 * \text{Mg/Ca}_{\text{sw.c}})) / 0.09 \quad (3)$$

Mg/Ca analysis was conducted on a small aliquot of the sample dissolved for isotope analysis at the University of Southampton using a ThermoFisher Scientific Element 2

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483 XR. Al/Ca was also measured to assess the competency of the sample cleaning.
 484 Because of complications with the Mg/Ca-temperature proxy in *Cibicidoides* species
 485 (Elderfield et al., 2006), bottom water temperatures (BWTs) are estimated here by
 486 taking the global secular temperature change from the Mg/Ca temperature
 487 compilation of Cramer et al. (2011), using the calibration of Lear et al. (2010) and
 488 applying this change to the modern bottom water temperature at each site taken from
 489 the nearest GLODAP site (with a conservative 2σ uncertainty of 2°C). Salinity is held
 490 constant at modern values determined from the nearest GLODAP site (2σ uncertainty
 491 of 2 ‰ uncertainty) for the entire record. Note that temperature and salinity have
 492 little influence on the calculated pH and the uncertainty in $\delta^{11}\text{B}_{\text{sw}}$ is dominated by the
 493 uncertainty in the $\delta^{11}\text{B}$ measurement and the estimate of the pH gradient.

494 The majority of the $\delta^{13}\text{C}$ data were measured at Cardiff University on a
 495 ThermoFinnigan MAT 252 coupled with a Kiel III carbonate device for automated
 496 sample preparation. Additional samples were measured on a gas source mass
 497 spectrometer Europa GEO 20-20, University of Southampton, equipped with
 498 automated carbonate preparation device and on a Finnigan MAT 253 gas isotope
 499 ratio mass spectrometer connected to a Kiel IV automated carbonate preparation
 500 device at the Zentrum für Marine Tropenökologie (ZMT), Bremen. The Pliocene
 501 benthic $\delta^{13}\text{C}$ from Site 999 were taken from the nearest sample in Haug and
 502 Tiedemann, (1998). In almost all cases $\delta^{13}\text{C}$ was analysed on the same foraminiferal
 503 species as $\delta^{11}\text{B}$ and Mg/Ca (38/44 samples). Where this was not possible another
 504 surface dweller/benthic foraminifera was used from the same depth habitat. *C.*
 505 *wuellerstorfi* or *C. mundulus* were measured in all cases for benthic $\delta^{13}\text{C}$. Stable
 506 isotope results are reported relative to the Vienna Pee Dee belemnite (VPDB)
 507 standard. We use a carbon isotope vital effect for *G. ruber* (+0.94 ‰; Spero et al.,
 508 2003), *T. sacculifer*/*G. praebuloides* (+0.46 ‰; Spero et al., 2003; Al-Rousan et al.,
 509 2004;), *C. mundulus* (+0.47 ‰; McCorkle et al., 1997) and *C. wuellerstorfi* (+0.1 ‰;
 510 McCorkle et al., 1997) to calculate the $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC).

511 2.3 Carbon isotopes as a proxy for vertical ocean pH gradient

512 The use of $\delta^{13}\text{C}$ in foraminiferal calcite to estimate the surface to deep pH gradient
 513 requires knowledge of the slope of the pH- $\delta^{13}\text{C}$ relationship in the past. In this section

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520 | we briefly outline the main factors that contribute to the pH- $\delta^{13}\text{C}$ relationship in order
521 | to underpin our analysis of extensive carbon cycle model simulations.

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522 | The production, sinking and sequestration into the ocean interior of low- $\delta^{13}\text{C}$ organic
523 | carbon via the soft-tissue component of the biological pump (e.g., Hain et al., 2014a)
524 | leads to a broad correlation between $\delta^{13}\text{C}$, $[\text{CO}_3^{2-}]$ and macronutrients in the ocean.
525 | The remineralization of this organic matter decreases $\delta^{13}\text{C}$ and titrates $[\text{CO}_3^{2-}]$ so as to
526 | reduce pH, while nutrient concentrations are increased. In waters that have
527 | experienced more soft tissue remineralization both pH and $\delta^{13}\text{C}$ will be lower (Fig.
528 | 5a,b), which is the dominant cause for the positive slope between $\delta^{13}\text{C}$ and pH in the
529 | modern ocean (e.g., Foster et al., 2012; Fig. 5c).

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530 | Another significant factor affecting the spatial distribution of both $\delta^{13}\text{C}$ and pH is
531 | seawater temperature, which affects both the equilibrium solubility of DIC and the
532 | equilibrium isotopic composition of DIC. Warmer ocean waters have decreased
533 | equilibrium solubility of DIC and so increased local $[\text{CO}_3^{2-}]$ and pH (Goodwin and
534 | Lauderdale, 2013), while warmer waters have relatively low equilibrium $\delta^{13}\text{C}$ values
535 | (Lynch-Stieglitz et al, 1995). This means that a spatial gradient in temperature acts to
536 | drive $\delta^{13}\text{C}$ and pH in opposite directions: warmer waters tend to have higher pH but
537 | lower $\delta^{13}\text{C}$. These opposing temperature effects act to reduce the pH difference
538 | between two points with greatly different temperature to below the value expected
539 | based on $\delta^{13}\text{C}$ alone. That is, when using $\delta^{13}\text{C}$ differences to estimate the pH gradient
540 | between the warm low latitude surface and cold deep waters the appropriate pH- $\delta^{13}\text{C}$
541 | relationship will be less than expected when only considering the effect of the
542 | biological pump. For this reason, in our modeling analysis we focus on the warm-
543 | surface to cold-bottom $\Delta\text{pH}/\Delta\delta^{13}\text{C}$ rather than the slope of the overall pH- $\delta^{13}\text{C}$
544 | relationship, with the latter expected to be greater than the former.

545 | In the modern ocean, and for the preceding tens of millions of years, the two
546 | dynamics described above are likely dominant in setting spatial variation in $\delta^{13}\text{C}$ and
547 | pH (and $[\text{CO}_3^{2-}]$). However, other processes will have a minor effect on either pH or
548 | $\delta^{13}\text{C}$. For instance, the dissolution of CaCO_3 shells increases $[\text{CO}_3^{2-}]$ and pH
549 | (Broecker and Peng, 1982), but does not significantly affect $\delta^{13}\text{C}$ (Zeebe and Wolf-
550 | Gladrow, 2001). Moreover, the long timescale of air/sea isotopic equilibration of CO_2

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558 | combined with kinetic isotope fractionation during net carbon transfer is an important
 559 | factor in setting the distribution of $\delta^{13}\text{C}$ on a global ocean scale (Galbraith et al.,
 560 | 2015; Lynch-Stieglitz et al., 1995), while the effect of CO_2 disequilibrium on $[\text{CO}_3^{2-}]$
 561 | and pH is modest (Goodwin and Lauderdale, 2013).

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563 2.4 Modelling the pH to $\delta^{13}\text{C}$ relationship

564 | After correcting for the shift in $\delta^{13}\text{C}$ due to anthropogenic activity, or Suess effect
 565 | (Keeling 1979), modern ocean observations demonstrate a near linear relationship
 566 | between global ocean data of seawater *in situ* pH and $\delta^{13}\text{C}$ DIC with a slope of
 567 | 0.201 ± 0.005 (2 σ) (Foster et al., 2012; Fig 5c.) This empirically determined slope
 568 | might well have been different in past oceans with very different nutrient cycling,
 569 | carbon chemistry and circulation compared to today, and it does not appropriately
 570 | represent the temperature effect described above (i.e., warm-surface to cold-bottom
 571 | water $\Delta\text{pH}/\Delta\delta^{13}\text{C}$). Here we use an ensemble approach with two independent carbon
 572 | cycle models to investigate changes in the $\Delta\text{pH}/\Delta\delta^{13}\text{C}$ regression. Below we provide
 573 | pertinent information on the GENIE and CYCLOPS model experiments:

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574 | We use the Earth System model GENIE-1 (Edwards and Marsh, 2005; Ridgwell et al.
 575 | 2007) to assess the robustness of the pH-to- $\Delta\delta^{13}\text{C}$ relationship and its sensitivity to
 576 | physical and biogeochemical ocean forcing. The configuration used here is closely
 577 | related to that of Holden et al. (2013), in which the controls on oceanic $\delta^{13}\text{C}$
 578 | distribution were assessed, with an energy and moisture balance in the atmosphere,
 579 | simple representations of land vegetation and sea ice, and frictional geostrophic
 580 | ocean physics. In each of 16 vertical levels in the ocean, increasing in thickness with
 581 | depth, there are 36x36 grid cells (10° in longitude and nominally 5° in latitude, with
 582 | higher resolution at low latitudes). Modern ocean bathymetry and land topography is
 583 | applied in all simulations. The ocean biogeochemical scheme (Ridgwell et al. 2007)
 584 | is based on conversion of DIC to organic carbon associated with phosphate uptake
 585 | with fixed P:C:O stoichiometry. Organic carbon and nutrients are remineralized
 586 | according to a remineralization profile with a pre-defined *e*-folding depth scale. This
 587 | depth scale, as well as the rain ratio of inorganic to organic carbon in sinking
 588 | particulate matter, is among the parameters examined in the sensitivity study. In these

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600 simulations, there is no interaction with sediments. As a result of this, the steady state
 601 solutions reported here are reached within the 5000-year simulations, but are not
 602 consistent with being in secular steady state with regard to the balance of continental
 603 weathering and ocean CaCO₃ burial.

604 The sensitivity study consists of seven sets of experiments, each varying a single
 605 model parameter relative to the control simulation with preindustrial atmospheric
 606 pCO₂. This enables us to assess which processes, if any, are capable of altering the
 607 ocean's ΔpH-to-Δδ¹³C relationship, and the uncertainty in the predictive skill of this
 608 relationship due to spatial variability. These experiments are therefore exploratory in
 609 nature and intended to study plausible range rather than determine magnitude of past
 610 changes. The seven parameters varied are (1) the ocean alkalinity reservoir; (2) the
 611 ocean's carbon reservoir; (3) the parameter "S. Lim gas exchange" which blocks air-
 612 sea gas exchange south of the stated latitude, significant here because of the
 613 dependence of δ¹³C on surface disequilibrium (Galbraith et al., 2015); (4) inorganic
 614 to organic carbon rain ratio, controlling the relationship between DIC and alkalinity
 615 distributions; (5) "Antarctic shelf FWF", a freshwater flux adjustment (always
 616 switched off in control experiments with GENIE) facilitating the formation of brine
 617 rich waters, which produces a high-salinity poorly-ventilated deep ocean at high
 618 values; (6) "Atlantic-Pacific FWF", a freshwater flux adjustment equivalent to
 619 freshwater hosing, leading to a shut-down of the Atlantic meridional overturning
 620 circulation at low values; (7) remineralization depth-scale of sinking organic matter,
 621 which affects the vertical gradient both of pH and δ¹³C. A wide range of parameter
 622 values is chosen for each parameter in order to exceed any plausible changes within
 623 the Cenozoic.

624 For the second exploration of the controls on the slope of ΔpH-Δδ¹³C relationship we
 625 use the CYCLOPS biogeochemical 18-box model that includes a dynamical
 626 lysocline, a subantarctic zone surface box and a polar Antarctic zone box (Sigman et
 627 al., 1998; Hain et al., 2010, 2014b). The very large model ensemble with 13,500
 628 individual model scenarios is designed to capture the full plausible range of (a)
 629 glacial/interglacial carbon cycle states by sampling the full solution space of Hain et
 630 al. (2010), and (b) reconstructed secular changes in seawater [Ca] (calcium
 631 concentration), carbonate compensation depth (CCD), weathering and atmospheric

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CO₂ (Table 1). The following seven model parameters are systematically sampled to set the 13,500 model scenarios: (1) shallow versus deep Atlantic meridional overturning circulation represented by modern reference north Atlantic deep water (NADW) versus peak glacial North Atlantic intermediate water (GNAIW) circulation; (2) iron driven changes in nutrient drawdown in the subantarctic zone of the Southern Ocean; (3) changes in nutrient drawdown of the polar Antarctic; (4) changes in vertical exchange between the deep Southern Ocean and the polar Antarctic surface; (5) range in seawater [Ca] concentration from 1x to 1.5x modern as per reconstructions (Horita et al., 2002); (6) Pacific CCD is set to the range of 4.4-4.9 km via changes in the weathering flux, as per sedimentological evidence (Pälike et al., 2012); (7) atmospheric CO₂ is set from 200 ppm to 1000 ppm by changes in the ‘weatherability’ parameter of the silicate weathering mechanism. The ensemble spans predicted bulk ocean DIC between 1500 and 4500 $\mu\text{mol/kg}$, a wide range of ocean pH and CaCO₃ saturation states consistent with the open system weathering cycle, and widely different states of the ocean’s biological pump. All 13,500 model scenarios are run for two million years after every single ‘weatherability’ adjustment, part of the CCD inversion algorithm, guaranteeing the specified CCD depth and steady state with regard to the balance of continental weathering and ocean CaCO₃ burial for the final solution (unlike the GENIE simulations CaCO₃ burial was entirely neglected due to computational cost of the long model integrations it would require). The inverse algorithm typically takes at least ten steps to conversion, resulting in ~300 billion simulated years for this ensemble.

2.5 Assessing uncertainty

$\delta^{11}\text{B}_{\text{sw}}$ uncertainty was calculated using a Monte Carlo approach where pH was calculated for deep and surface waters at each time slice using a random sampling (n=10000) of the various input parameters within their respective uncertainties as represented by normal distributions. These uncertainties (2σ uncertainty in parentheses) are: temperature ($\pm 2^\circ\text{C}$), salinity (± 2 units on the practical salinity scale) [Ca] (± 4.5 mmol/kg), [Mg], (± 4.5 mmol/kg), $\delta^{11}\text{B}_{\text{planktic}}$ ($\pm 0.15\text{-}0.42\text{‰}$) and $\delta^{11}\text{B}_{\text{benthic}}$ ($\pm 0.21\text{-}0.61\text{‰}$). For the estimate of the surface to sea floor pH gradient we use the central value of the ΔpH -to- $\Delta\delta^{13}\text{C}$ relationship diagnosed from our CYCLOPS and GENIE sensitivity experiments (i.e., 0.175‰ , see section 3.2 below)

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and then we assign a ± 0.05 uncertainty range with a uniform probability (rather than a normal distribution) to the resulting surface to sea floor ΔpH estimate (see also Table 2). Thus, the magnitude of this nominal uncertainty is equivalent to a 0.14‰ to 0.21‰ $\Delta\text{pH}/\Delta\delta^{13}\text{C}$ uncertainty range that spans the vast majority of our CYCLOPS and GENIE simulations, and the prediction error (RMSE) of fitting a linear relationship to the GENIE pH and $\delta^{13}\text{C}$ output (see section 3.2 below). The uncertainty in the $\delta^{11}\text{B}$ measurements is calculated from the long-term reproducibility of Japanese Geological Survey *Porites* coral standard (JCP; $\delta^{11}\text{B}=24.3\text{‰}$) at the University of Southampton using the equations:

$$2\sigma = 2.25 \exp^{-23.01[^{11}\text{B}]} + 0.28 \exp^{-0.64[^{11}\text{B}]} \quad (4)$$

$$2\sigma = 33450 \exp^{-168.2[^{11}\text{B}]} + 0.311 \exp^{-1.477[^{11}\text{B}]} \quad (5)$$

where $[^{11}\text{B}]$ is the intensity of ^{11}B signal in volts and equation (4) and equation (5) used with $10^{11} \Omega$ and $10^{12} \Omega$ resistors, respectively.

From the 10,000 Monte Carlo ensemble solutions of our 22 benthic-planktic pairs we construct 10,000 randomized records of $\delta^{11}\text{B}_{\text{sw}}$ as a function of time. Each of these randomized $\delta^{11}\text{B}_{\text{sw}}$ records are subjected to smoothing using the locally weighted scatterplot smoothing (LOWESS) algorithm with a smoothing parameter (span) of 0.7. The purpose of the smoothing is to put some controls on the rate at which the resulting individual Monte Carlo $\delta^{11}\text{B}_{\text{sw}}$ records are allowed to change, which in reality is limited by the seawater boron mass balance ($\sim 0.1 \text{‰}$ per million years; boron residence time is 11-17 million years; Lemarchand et al., 2000). Our choice of smoothing parameter allows for some of the individual Monte Carlo records to change as fast as $\sim 1 \text{‰}$ per million years, although in reality the average rate of change is much smaller than this (see section 3.3). Consequently this method removes a significant amount of uncorrelated stochastic noise (resulting from the uncertainty in our input parameters) while not smoothing away the underlying signal. As a result of anomalously low $\delta^{11}\text{B}$ differences ($< 1\text{‰}$) between benthic and planktic pairs, two pairs at 8.68 Ma and 19 Ma were discarded from the smoothing. It may be possible that preservation is not so good within these intervals in the core and the planktic foraminifera are affected by partial dissolution (Seki et al., 2010). The spread of the ensemble of smoothed $\delta^{11}\text{B}_{\text{sw}}$ curves represents the combination of the

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compounded, propagated uncertainties of the various inputs (i.e., Monte Carlo sampling) with the additional constraint of gradual $\delta^{11}\text{B}_{\text{sw}}$ change over geological time imposed by the inputs and outputs of boron to the ocean and the total boron inventory (i.e., the smoothing of individual Monte Carlo members). Various statistical properties (i.e., mean, median, standard deviation (σ), various quantiles) of this $\delta^{11}\text{B}_{\text{sw}}$ reconstruction were evaluated from the ensemble of smoothed $\delta^{11}\text{B}_{\text{sw}}$ records. Generally, for any given benthic-planktic pair the resulting $\delta^{11}\text{B}_{\text{sw}}$ estimates are not perfectly normally distributed and thus we use the median as the metric for the central tendency (i.e., placement of marker in Figure 10).

3. Results and Discussion

3.1 $\delta^{11}\text{B}$ benthic and planktic data

Surface and deep-ocean, $\delta^{11}\text{B}$, $\delta^{13}\text{C}$ and temperature broadly show a similar, but inverse, pattern to one another throughout the Neogene (Fig. 6). The $\delta^{11}\text{B}$ benthic record decreases from $\sim 15\text{‰}$ at 24 Ma to a minimum of 13.28‰ at 14 Ma before increasing to $\sim 17\text{‰}$ at present day (Fig. 6). This pattern and the range of values in benthic foraminiferal $\delta^{11}\text{B}$ is in keeping with previously published Neogene $\delta^{11}\text{B}$ benthic records measured using NTIMS (Raitzsch and Hönisch, 2013), suggesting that our deep-water $\delta^{11}\text{B}$ record is representative of large scale pH changes in the global ocean. While the surface $\delta^{11}\text{B}_{\text{planktic}}$ remained relatively constant between 24 and 11 Ma at $\sim 16\text{‰}$, there is a significant increase in $\delta^{11}\text{B}$ between the middle Miocene and present (values increase to $\sim 20\text{‰}$) (Fig. 6b). The reconstructed surface water temperatures show a long-term decrease through the Neogene from $\sim 28^\circ\text{C}$ to 24°C , aside from during the Miocene Climatic Optimum (MCO) where maximum Neogene temperatures are reached (Fig. 6c). Following Cramer et al. (2011) deep-water temperatures decrease from $\sim 12^\circ\text{C}$ to 4°C at the present day and similarly show maximum temperatures in the MCO. Surface and deep-water $\delta^{13}\text{C}_{\text{DIC}}$ both broadly decrease through the Neogene and appear to covary on shorter timescales (Fig. 6e, f).

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3.2 The relationship between $\delta^{13}\text{C}$ and pH gradients

As noted above, in the global modern ocean data, after accounting for the anthropogenic carbon, the empirical relationship between *in situ* pH and DIC $\delta^{13}\text{C}$ is well described by a linear function with a slope of 0.201 ± 0.005 (2σ) (Fig. 5; Foster et al., 2012). However, this slope is only defined by surface waters in the North Atlantic due to a current lack of modern data where the impact of the Suess effect has been corrected (Olsen and Ninneman, 2010). Consequently we are not currently able to determine the slope between the warm-surface and cold-deep ocean in the modern ocean at our sites. Instead, here we use the two modeling experiments to define this slope. In the control GENIE experiment (green star; Fig. 7), the central value for the slope of the pH/ $\delta^{13}\text{C}$ relationship is slightly greater than 0.2‰ for the full 3D data regression (not shown) and about 0.175‰ for the warm-surface-to-cold-deep ΔpH -to- $\Delta\delta^{13}\text{C}$ relationship (Fig. 7) – consistent with theory for the effect of temperature gradients (see section 2.3). For both ways of analysing the GENIE output the prediction uncertainty of the regressions, the root-mean-squared error (RMSE), is $\sim 0.05\text{‰}$ under most conditions (open red circles in Fig. 7), with the exception of where large changes in either DIC or ALK result in somewhat larger changes in the relationship between pH and $\delta^{13}\text{C}$ (see below). In our CYCLOPS model ensemble, the central value of the slopes of the full 3D pH/ $\delta^{13}\text{C}$ regressions and of the warm-surface-to-cold-deep $\Delta\text{pH}/\Delta\delta^{13}\text{C}$ is 0.2047‰ (1σ of 0.0196‰ ; Fig.8a) and 0.1797‰ (1σ of 0.0213‰ ; Fig.8b), respectively. If we restrict our analysis of the CYCLOPS ensemble to only the Atlantic-basin warm-surface-to-cold-deep $\Delta\text{pH}/\Delta\delta^{13}\text{C}$, where most of our samples come from, we find a relationship of only 0.1655‰ (1σ of 0.0192‰ ; Fig.8c). That is, overall, we find near-perfect agreement between modern empirical data and our GENIE and CYCLOPS experiments. Encouraged by this agreement we select the warm-surface-to-cold-deep $\Delta\text{pH}/\Delta\delta^{13}\text{C}$ central value of 0.175‰ to estimate the surface/sea floor pH difference from the planktic/benthic foraminifera $\delta^{13}\text{C}$ difference. To account for our ignorance as to the accurate value of $\Delta\text{pH}/\Delta\delta^{13}\text{C}$ in the modern ocean, it's changes over the course of the study interval and the inherent prediction error from using a linear ΔpH -to- $\Delta\delta^{13}\text{C}$ relationship we assign a nominal uniform uncertainty range of ± 0.05 around the central ΔpH estimate for the purpose of Monte Carlo uncertainty propagation. Our

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Deleted: and in all experiments in which ocean-physics parameters (Antarctic shelf FWF and Atlantic-Pacific FWF) are varied

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analysis also suggests that where surface-to-thermocline planktic/planktic gradients are employed, the plausible $\Delta p\text{H}/\Delta\delta^{13}\text{C}$ range should be significantly higher than applied here, in order to account for the relatively lower temperature difference. Based on the appropriate $\Delta p\text{H}/\Delta\delta^{13}\text{C}$ relationship we reconstruct a time varying surface to deep pH gradient, which ranges between 0.14 and 0.35 pH units over our study interval (Fig. 9) and apply a flat uncertainty of ± 0.05 . The reconstructed pH gradient remains broadly within the range of the modern values (0.19 to 0.3) although there is some evidence of multi-million year scale variability.

As a caveat to our usage of the $\Delta p\text{H}$ -to- $\Delta\delta^{13}\text{C}$ relationship we point to changes of that relationship that arise in our GENIE sensitivity experiments where carbon and alkalinity inventories are manipulated, which can yield values outside of what is plausible. We note that our CYCLOPS ensemble samples a very much wider range of carbon and alkalinity inventories with $\Delta p\text{H}/\Delta\delta^{13}\text{C}$ remaining inside that range. While CYCLOPS simulates the balance between weathering and CaCO_3 burial, which is known to neutralize sudden carbon or alkalinity perturbations on timescales much less than one million years, the configuration used for our GENIE simulations does not and is therefore subject to states of ocean carbon chemistry that can safely be ruled out for our study interval and likely for most of the Phanerozoic. The differing outputs from CYCLOPS and GENIE in the DIC and ALK experiments does highlight that $\Delta p\text{H}/\Delta\delta^{13}\text{C}$ actually depends on background seawater acid/base chemistry, in ways that are not yet fully understood. That said, the generally coherent nature of our results confirms we likely constrain the plausible range of $\Delta p\text{H}/\Delta\delta^{13}\text{C}$ for at least the Neogene, if not the entire Cenozoic, outside of extreme events such as the Palaeocene-Eocene Thermal Maximum.

3.3 $\delta^{11}\text{B}_{\text{sw}}$ record through the Neogene

Using input parameter uncertainties as described in section 2.5 yields individual Monte Carlo member $\delta^{11}\text{B}_{\text{sw}}$ estimates between 30 ‰ and 43.5 ‰ at the overall extreme points and typically ranging by ~ 10 ‰ (dashed in Fig. 10a) for each time point, suggesting that the uncertainties we assign to the various input parameters are generous enough not to predetermine the quantitative outcomes. However, for each

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Deleted: The slope of the $\text{pH}-\delta^{13}\text{C}$ relationship simulated by our CYCLOPS model ensemble across a range of perturbed states is 0.2047 ($1\sigma = 0.0196$) (Fig. 7a, 8), in perfect agreement with modern empirical data and our GENIE experiments. Varying the biogeochemical parameters (gas exchange, rain ratio and remineralizing depth scale) yields some change in the regressed slope of the $\text{pH}/\delta^{13}\text{C}$ relationship due to decoupled responses of pH and $\delta^{13}\text{C}$, but this gradient remains well within the 0.2 ± 0.05 range, and a RMSE of 0.05 in the spatial relationship remains robust (Fig. 6). We take this as evidence that the uncertainty in the $\text{pH}/\delta^{13}\text{C}$ relationship assumed in our carbon chemistry calculation is well represented by a central value of 0.2 with a 0.025 standard deviation. Experiments at very high DIC or low alkalinity, either of which yield high atmospheric $p\text{CO}_2$ and low mean ocean pH, yield gradients slightly outside the 0.2 ± 0.05 range, with an elevated RMSE. This is probably associated with the non-linearity of the pH scale, modifying the gradient for a very different pH. It is to be emphasised that such extreme decoupled changes in DIC and alkalinity are not plausible within the Cenozoic, and were only possible in these simulations because of the absence of interactive sediments. ... [13]

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Moved up [1]: The slope of the $\text{pH}-\delta^{13}\text{C}$ relationship simulated by our CYCLOPS model ensemble across a range of perturbed states is 0.2047 ($1\sigma = 0.0196$) (Fig. 7a, 8), in perfect agreement with modern empirical data and our GENIE experiments.

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Moved down [2]: The variability in the estimations of $\delta^{11}\text{B}_{\text{sw}}$ for each individual benthic/planktic foraminifera pair suggest that individual estimates of $\delta^{11}\text{B}_{\text{sw}}$ are sensitive to the different input parameters, particularly the assigned uncertainty in the pH gradient. However, by smoothing the record we effectively suppress error that is uncorrelated between individual benthic/planktic pairs ... [15]

planktic/benthic time point most individual Monte Carlo $\delta^{11}\text{B}_{\text{sw}}$ estimates fall into a much narrower central range ($\sim 1\text{‰}$ to 4‰ ; thick black line showing interquartile range in Fig. 10a). The $\delta^{11}\text{B}_{\text{sw}}$ for Plio-Pleistocene time-points cluster around $\sim 40\text{‰}$ while middle/late Miocene values cluster around $\sim 36.5\text{‰}$. The estimates at individual time points are completely independent from each other, such that the observed clustering is strong evidence for an underlying long-term signal in our data, albeit one that is obscured by the uncertainties involved in our individual $\delta^{11}\text{B}_{\text{sw}}$ estimates. The same long-term signal is also evident when pooling the individual Monte Carlo member $\delta^{11}\text{B}_{\text{sw}}$ estimates into 8 million year bins and evaluating the mean and spread (2σ) in each bin (Fig. 10b). This simple treatment highlights that there is a significant difference between our Plio-Pleistocene and middle Miocene data bins at the 95% confidence level and that $\delta^{11}\text{B}_{\text{sw}}$ appears to also have been significantly lower than modern during the early Miocene.

3.3.1 Data smoothing

The ~ 1 to 4‰ likely ranges for $\delta^{11}\text{B}_{\text{sw}}$ would seem to be rather disappointing given the goal to constrain $\delta^{11}\text{B}_{\text{sw}}$ for pH reconstructions. However, most of that uncertainty is stochastic, random error that is uncorrelated from time point to time point. Furthermore, we know from mass balance considerations that $\delta^{11}\text{B}_{\text{sw}}$ of seawater should not change by more than $\sim 0.1\text{‰}$ per million years (Lemarchand et al., 2000) and we use this as an additional constraint via the LOWESS smoothing we apply to each Monte Carlo time series. One consideration is that each and every individual Monte Carlo $\delta^{11}\text{B}_{\text{sw}}$ estimate is equally likely and the smoothing should therefore target randomly selected individual Monte Carlo $\delta^{11}\text{B}_{\text{sw}}$ estimates, as we do here, rather than smoothing over the likely ranges identified for each time point. In this way the smoothing becomes integral part of our Monte Carlo uncertainty propagation and the spread among the 10,000 individual smoothed $\delta^{11}\text{B}_{\text{sw}}$ curves carries the full representation of propagated input uncertainty conditional on the boron cycle mass balance constraint. A second consideration is that the smoothing should only remove noise, not underlying signal. As detailed above, for this reason the smoothing parameter we choose has enough freedom to allow the $\delta^{11}\text{B}_{\text{sw}}$ change to be dictated by the data, with only the most extreme shifts in $\delta^{11}\text{B}_{\text{sw}}$ removed. We also tested the robustness of the smoothing procedure itself (not shown) and found only marginal changes when changing algorithm (LOESS versus LOWESS, with and without

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robust option) or when reducing the amount of smoothing (i.e., increasing the allowed rate $\delta^{11}\text{B}_{\text{sw}}$ change). The robustness of our smoothing is further underscored by the good correspondence with the results of simple data binning (Fig.10b).

1003

1004 3.4 Comparison to other $\delta^{11}\text{B}_{\text{sw}}$ records

1005 The comparison of our new $\delta^{11}\text{B}_{\text{sw}}$ record to those previously published reveals that
 1006 despite the differences in methodology the general trends in the records show
 1007 excellent agreement. The most dominant common feature of all the existing estimates
 1008 of Neogene $\delta^{11}\text{B}_{\text{sw}}$ evolution is an increase through time from the middle Miocene to
 1009 the Plio-Pleistocene (Fig. 11). While the model-based $\delta^{11}\text{B}_{\text{sw}}$ record of Lemarchand et
 1010 al. (2000) is defined by a monotonous and very steady rise over the entire study
 1011 interval, all three measurement-based records, including our own, are characterized
 1012 by a single dominant phase of increase between roughly 12 and 5 Ma. Strikingly, the
 1013 Pearson and Palmer (2000) record falls almost entirely within our 95% likelihood
 1014 envelope, overall displaying very similar patterns of long-term change but with a
 1015 relatively muted amplitude and overall rate of change relative to our reconstruction.
 1016 Conversely, some of the second-order variations in the reconstruction by Raitzsch
 1017 and Hönisch (2013) are not well matched by our reconstruction, but the dominant
 1018 episode of rapid $\delta^{11}\text{B}_{\text{sw}}$ rise following the middle Miocene is in almost perfect
 1019 agreement. We are encouraged by these agreements resulting from approaches based
 1020 on very different underlying assumptions and techniques, which we take as indication
 1021 for an emerging consensus view of $\delta^{11}\text{B}_{\text{sw}}$ evolution over the last 25 Ma and as a
 1022 pathway towards reconstructing $\delta^{11}\text{B}_{\text{sw}}$ further back in time. Below we discuss in
 1023 more detail the remaining discrepancies between our new and previously existing
 1024 $\delta^{11}\text{B}_{\text{sw}}$ reconstructions.

1025 The record by Pearson and Palmer (2000) is well correlated to our reconstruction, but
 1026 especially during the early Miocene there is a notable $\sim 0.5\text{‰}$ offset (Fig. 11). This
 1027 discrepancy could be due to a number of factors. Firstly, the applicability of this
 1028 $\delta^{11}\text{B}_{\text{sw}}$ record (derived from $\delta^{11}\text{B}$ data measured using NTIMS) to $\delta^{11}\text{B}$ records
 1029 generated using the MC-ICPMS is uncertain (Foster et al., 2013). In addition, this
 1030 $\delta^{11}\text{B}_{\text{sw}}$ record is determined using a fractionation factor of 1.0194 (Kakihana et al.,

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Deleted: Our new $\delta^{11}\text{B}_{\text{sw}}$ record is broadly similar to previously published estimates calculated using pH gradients in the surface ocean, in terms of both shape of the record and magnitude of the reconstructed changes, with the notable exception in the early and middle Miocene where $\delta^{11}\text{B}_{\text{sw}}$ in our record is 0.5‰ lower (Fig. 10) than the published estimates of Pearson and Palmer (2000). Unfortunately

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1046 1977), whereas recent experimental data have shown the value to be higher (1.0272 ±
 1047 0.0006, Klochko et al., 2006), although foraminiferal vital effects are likely to mute
 1048 this discrepancy. Thirdly, given our understanding of the $\delta^{11}\text{B}$ difference between
 1049 species/size fractions (Foster, 2008; Henehan et al., 2013), the mixed species and size
 1050 fractions used to make the $\delta^{11}\text{B}$ measurements in that study may have introduced
 1051 some additional uncertainty in the reconstructed $\delta^{11}\text{B}_{\text{sw}}$. Conversely, there is
 1052 substantial spread between our three time points during the earliest Miocene, which
 1053 combined with the edge effect of the smoothing gives rise to a widening uncertainty
 1054 envelope during the time of greatest disagreement with Pearson and Palmer (2000).
 1055 This could be taken as indication that our reconstruction, rather than that of Pearson
 1056 and Palmer, is biased during the early Miocene.

1058 The $\delta^{11}\text{B}_{\text{sw}}$ record calculated using benthic $\delta^{11}\text{B}$ and assumed deep ocean pH changes
 1059 (Raitzsch and Hönisch, 2013) is also rather similar to our $\delta^{11}\text{B}_{\text{sw}}$ reconstruction. The
 1060 discrepancy between the two records in the early Miocene could plausibly be
 1061 explained by bias in our record (see above) or may in part be as a result of the
 1062 treatment of surface water pH in the study of Raitzsch and Hönisch (2013) and their
 1063 assumption of constant surface-deep pH gradient (see Fig 9). The combined output
 1064 from two carbon cycle box models is used to make the assumption that surface ocean
 1065 pH near-linearly increased by 0.39 over the last 50 Myrs. The first source of surface
 1066 water pH estimates is from the study of Ridgwell et al. (2005), where CO_2 proxy data
 1067 including some derived using the boron isotope-pH proxy is used, leading to some
 1068 circularity in the methodology. The second source of surface water pH estimates is
 1069 from Tyrrell & Zeebe (2004) and based on GEOCARB where the circularity problem
 1070 does not apply. While this linear pH increase broadly matches the CO_2 decline from
 1071 proxy records between the middle Miocene and present, it is at odds with the CO_2
 1072 proxy data during the early Miocene that show CO_2 was lower than the middle
 1073 Miocene during this interval (Beerling and Royer, 2011). Consequently the proxy
 1074 CO_2 and surface water pH estimates are not well described by the linear change in pH
 1075 applied by Raitzsch and Hönisch (2013) across this interval, potentially contributing
 1076 to the discrepancy between our respective $\delta^{11}\text{B}_{\text{sw}}$ reconstructions..

1077 Our new $\delta^{11}\text{B}_{\text{sw}}$ record falls within the broad uncertainty envelope of boron mass

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Deleted: That said, the polynomial fit to the data applied by Raitzsch and Hönisch (2013) takes no account of the uncertainties of individual data points and produces an oscillating pattern that is inconsistent with our new reconstruction (Fig. 10). Furthermore, our

1092 | balance calculations of Lemarchand et al. (2000), but those modelled values do not
 1093 | show the same level of multi-million year variability of either Raitzsch and Hönisch
 1094 | (2013) or our new record, therefore suggesting that the model does not fully account
 1095 | for aspects of the changes in the ocean inputs and outputs of boron through time on
 1096 | timescales less than ~10 million years.

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1097 | In line with the conclusions of previous studies (e.g., Raitzsch and Hönisch, 2013),
 1098 | our data show that the $\delta^{11}\text{B}_{\text{sw}}$ signal in the fluid inclusions (Paris et al., 2010) is
 1099 | mostly likely a combination of the $\delta^{11}\text{B}_{\text{sw}}$ and some other factor such as a poorly
 1100 | constrained fractionation factor between the seawater and the halite. Brine-halite
 1101 | fractionation offsets of -20‰ to -30‰ and -5‰ are reported from laboratory and
 1102 | natural environments (Vengosh et al., 1992; Liu et al., 2000). These fractionations
 1103 | and riverine input during basin isolation will drive the evaporite-hosted boron to low-
 1104 | $\delta^{11}\text{B}$ isotope values such that the fluid inclusion record likely provides a lower limit
 1105 | for the $\delta^{11}\text{B}_{\text{sw}}$ through time (i.e. $\delta^{11}\text{B}_{\text{sw}}$ is heavier than the halite fluid inclusions of
 1106 | Paris et al. (2010)). In order for this halite record to be interpreted directly as $\delta^{11}\text{B}_{\text{sw}}$,
 1107 | a better understanding of the factor(s) controlling the fractionation during halite
 1108 | formation and any appropriate correction need to be better constrained.

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1110 3.5 Common controls on the seawater isotopic ratios of B, Mg, Ca and Li

1111 | Our new record of $\delta^{11}\text{B}_{\text{sw}}$ has some substantial similarities to secular change seen in
 1112 | other marine stable isotope records (Fig. 12). The lithium isotopic composition of
 1113 | seawater ($\delta^7\text{Li}_{\text{sw}}$; Misra and Froelich, 2012) and the calcium isotopic composition of
 1114 | seawater ($\delta^{44/40}\text{Ca}_{\text{sw}}$; Griffith et al., 2008) both increase through the Neogene, whereas
 1115 | the magnesium isotopic composition of seawater ($\delta^{26}\text{Mg}_{\text{sw}}$) decreases (Pogge von
 1116 | Strandmann et al., 2014) suggesting a similar control on the isotopic composition of
 1117 | all four elements across this time interval (Fig. 12). To further evaluate the
 1118 | correlation between these other marine isotope records and $\delta^{11}\text{B}_{\text{sw}}$, we interpolate and
 1119 | cross-plot $\delta^{11}\text{B}_{\text{sw}}$ and the $\delta^7\text{Li}_{\text{sw}}$, $\delta^{44/40}\text{Ca}_{\text{sw}}$ and $\delta^{26}\text{Mg}_{\text{sw}}$ records. This analysis suggests
 1120 | that the isotopic composition of $\delta^{11}\text{B}_{\text{sw}}$, $\delta^7\text{Li}_{\text{sw}}$, $\delta^{26}\text{Mg}_{\text{sw}}$ and $\delta^{44/40}\text{Ca}_{\text{sw}}$ are well
 1121 | correlated through the Neogene, although there is some scatter in these relationships

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1130 (Fig. 13). Although the Sr isotope record shows a similar increase during the
 1131 Neogene (Hodell et al., 1991), we focus our discussion on $\delta^{11}\text{B}_{\text{sw}}$, $\delta^7\text{Li}_{\text{sw}}$, $\delta^{26}\text{Mg}_{\text{sw}}$ and
 1132 $\delta^{44/40}\text{Ca}_{\text{sw}}$ given that the factors fractionating these stable isotopic systems are similar
 1133 (see below).

1134 To better constrain the controls on $\delta^{11}\text{B}_{\text{sw}}$, $\delta^7\text{Li}_{\text{sw}}$, $\delta^{26}\text{Mg}_{\text{sw}}$ and $\delta^{44/40}\text{Ca}_{\text{sw}}$ it is
 1135 instructive to compare the size and isotopic composition of the fluxes of boron,
 1136 lithium, calcium and magnesium to the ocean (Table 3). The major flux of boron into
 1137 the ocean is via riverine input (Lemarchand et al., 2000), although some studies
 1138 suggest that atmospheric input may also play an important role (Park and
 1139 Schlesinger, 2002). The loss terms are dominated by adsorption onto clays and the
 1140 alteration of oceanic crust (Spivack and Edmond, 1987; Smith et al., 1995).
 1141 Similarly, the primary inputs of lithium into the ocean come from hydrothermal
 1142 sources and riverine input and the main outputs are ocean crust alteration and
 1143 adsorption onto sediments (Misra and Froelich, 2012). The two dominant controls on
 1144 magnesium concentration and isotope ratio in the oceans is the riverine input, ocean
 1145 crust alteration and dolomitization (Table 3) (Tipper et al., 2006b). The main controls
 1146 on the amount of calcium in the modern ocean and its isotopic composition is the
 1147 balance between riverine and hydrothermal inputs and removal through CaCO_3
 1148 deposition and alteration of oceanic crust (Fantle and Tipper, 2014, Griffith et al.,
 1149 2008). Dolomitization has also been cited as playing a potential role in controlling
 1150 $\delta^{44/40}\text{Ca}_{\text{sw}}$, although the contribution of this process through time is poorly constrained
 1151 (Griffith et al., 2008).

1152 Analysis of the oceanic fluxes of all four ions suggests that riverine input may be an
 1153 important factor influencing the changing isotopic composition of B, Li, Ca and Mg
 1154 over the late Neogene (Table 3). In the case of all four elements, a combination of the
 1155 isotopic ratio of the source rock and isotopic fractionation during weathering
 1156 processes are typically invoked to explain the isotopic composition of a particular
 1157 river system. However, in most cases the isotopic composition of the source rock is
 1158 found to be of secondary importance (Rose et al., 2000; Kısakürek et al., 2005;
 1159 Tipper et al., 2006b; Millot et al., 2010). For instance, the $\delta^{11}\text{B}$ composition of rivers
 1160 is primarily dependent on isotopic fractionation during the reaction of water with
 1161 silicate rocks and to a lesser extent the isotopic composition of the source rock (i.e.

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the proportion of evaporites and silicate rocks; Rose et al., 2000). While some studies have suggested that the isotopic composition of rainfall within the catchment area may be an important factor controlling the $\delta^{11}\text{B}$ in rivers (Rose-Koga et al., 2006), other studies have shown atmospheric boron to be a secondary control on riverine boron isotope composition (Lemarchand and Gaillardet, 2006). The source rock also appears to have limited influence on the $\delta^7\text{Li}$ composition of rivers and riverine $\delta^7\text{Li}$ varies primarily with weathering intensity (Kısakürek et al., 2005; Millot et al., 2010). The riverine input of calcium to the oceans is controlled by the composition of the primary continental crust (dominated by carbonate weathering) and a recycled component, although the relative influence of these two processes is not well understood (Tipper et al., 2006a). In addition, vegetation may also play a significant role in the $\delta^{44/40}\text{Ca}$ of rivers (Fantle and Tipper, 2014). For Mg, the isotopic composition of the source rock is important for small rivers, however, lithology is of limited significance at a global scale in comparison to fractionation in the weathering environment (Tipper et al., 2006b). Given the lack of evidence of source rock as a dominant control on the isotopic composition of rivers, here we focus on some of the possible causes for changes in the isotopic composition and/or flux of riverine input over the Neogene.

In this regard, of the four elements discussed here, the Li isotopic system is the most extensively studied. Indeed, the change in $\delta^7\text{Li}_{\text{sw}}$ has already been attributed to an increase in the $\delta^7\text{Li}_{\text{sw}}$ composition of the riverine input (Hathorne and James, 2006; Misra and Froelich, 2012). The causes of the shift in $\delta^7\text{Li}$ riverine have been variably attributed to: (1) an increase in incongruent weathering of silicate rocks and secondary clay formation as a consequence of Himalayan uplift (Misra and Froelich, 2012), (2) a reduction in weathering intensity (Hathorne and James, 2006; Froelich and Misra, 2014), (3) an increase in silicate weathering rate (Liu et al., 2015) and 4) an increase in the formation of floodplains and the increased formation of secondary minerals (Pogge von Strandmann and Henderson, 2014). In all four cases the lighter isotope of Li is retained on land in clay and secondary minerals. A mechanism associated with either an increase in secondary mineral formation or the retention of these minerals on land is also consistent across Mg, Ca and B isotope systems. For instance, clay minerals are preferentially enriched in the light isotope of B (Spivack and Edmond, 1987; Deyhle and Kopf, 2004; Lemarchand and Gaillardet, 2006) and

Li (Pistiner and Henderson, 2003) and soil carbonates and clays are preferentially enriched in the light isotope of Ca (Tipper et al., 2006a; Hindshaw et al., 2013; Ockert et al., 2013). The formation of secondary silicate minerals, such as clays, is assumed to preferentially take up the heavy Mg isotope into the solid phase (Tipper et al., 2006a; Tipper et al., 2006b; Pogge von Strandmann et al., 2008; Wimpenny et al., 2014), adequately explaining the inverse relationship between $\delta^{11}\text{B}_{\text{sw}}$ and $\delta^{26}\text{Mg}_{\text{sw}}$. Consequently the increased formation or retention on land of secondary minerals would alter the isotopic composition of the riverine input to the ocean in the correct direction to explain the trends in all four isotope systems through the late Neogene (Fig. 13). The increased formation and retention of clays on land may have been related to the growth of the Himalayan orogeny and increased clay formation in the newly formed floodplains and foreland surrounding the mountains (Pogge von Strandmann and Henderson, 2014).

4 Conclusions

Here we present a new $\delta^{11}\text{B}_{\text{sw}}$ record for the Neogene based on paired planktic-benthic $\delta^{11}\text{B}$ measurements. Our new record suggests that $\delta^{11}\text{B}_{\text{sw}}$ (i) was $\sim 37.5\text{‰}$ at the Oligocene-Miocene boundary, (ii) remained low through the middle Miocene, (iii) rapidly increased to the modern value between 12 and 5 Ma, and (iv) plateaued at modern values over the Plio-Pleistocene. Despite some disagreements, the fact that our new record, and both of the published data based reconstructions capture the first-order late Miocene $\delta^{11}\text{B}_{\text{sw}}$ rise suggests that consensus is building for the $\delta^{11}\text{B}_{\text{sw}}$ evolution through the Neogene. This emerging view on $\delta^{11}\text{B}_{\text{sw}}$ change provides a vital constraint required to quantitatively reconstruct Neogene ocean pH, ocean carbon chemistry and atmospheric CO_2 using the $\delta^{11}\text{B}$ -pH proxy. When our new $\delta^{11}\text{B}_{\text{sw}}$ record is compared to changes in the seawater isotopic composition of Li, Ca and Mg the shape of the records across the Neogene is remarkably similar. In all four cases riverine input is cited as one of the key control of the isotopic composition of the elements in seawater. When we compare the isotopic fractionation of the elements associated with secondary mineral formation, the trends in the $\delta^{26}\text{Mg}_{\text{sw}}$, $\delta^{44/40}\text{Ca}_{\text{sw}}$, $\delta^{11}\text{B}_{\text{sw}}$ and $\delta^7\text{Li}_{\text{sw}}$ records are all consistent with an increase in secondary mineral formation through time. While a more quantitative treatment of these multiple stable

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isotope systems is required, the $\delta^{11}\text{B}_{\text{sw}}$ record presented here provides additional constraints on the processes responsible for the evolution of ocean chemistry through time.

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1627 Figure Captions:

1628 | Figure 1: The oceanic boron cycle. Fluxes are from Lemarchand et al. (2000) and
 1629 Park and Schlesinger (2002). Isotopic compositions are from Lemarchand et al.
 1630 | (2000), Foster et al., (2010) and references therein.

1631 | Figure 2: A compilation of published $\delta^{11}\text{B}_{\text{sw}}$ records. Seawater composition
 1632 reconstructed from foraminifera depth profiles (light blue squares and dark blue
 1633 cross) from Pearson and Palmer (2000) and Foster et al. (2012) respectively,

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numerical modelling (green line), with additional green lines shows $\pm 1\%$ confidence interval (Lemarchand et al., 2000), benthic $\delta^{11}\text{B}$ (purple diamonds and dark purple line is using the fractionation factor of Klochko et al., 2006, light purple line using an empirical calibration) from Raitzsch and Hönisch (2013), and halites (orange crosses) from Paris et al. (2010). The orange crosses in brackets were discarded from the original study.

Figure 3: Schematic diagram showing the change in pH gradient with a 3‰ change in $\delta^{11}\text{B}$ for $\delta^{11}\text{B}_{\text{sw}}$ of a) 39.6‰ and b) 37.5‰. Arrows highlight the different pH gradients. Note how a $\delta^{11}\text{B}$ difference of 3 ‰ is translated into different pH gradients depending on the $\delta^{11}\text{B}_{\text{sw}}$. Calculated using $B_T = 432.6\ \mu\text{mol/kg}$ (Lee et al., 2010) and $\alpha_B = 1.0272$ (Klochko et al., 2006). (c) The pH change for a $\delta^{11}\text{B}$ change of 3 ‰ at a range of different $\delta^{11}\text{B}_{\text{sw}}$.

Figure 4: Map of study sites and mean annual air-sea disequilibria with respect to $p\text{CO}_2$. The black dots indicate the location of the sites used in this study. ODP Sites 758, 999, 926 and 761 used in this study are highlighted with water depth. Data are from (Takahashi et al., 2009) plotted using ODV (Schlitzer, 2016).

Figure 5: Latitudinal cross-section through the Atlantic showing (a) pH variations; (b) the $\delta^{13}\text{C}$ composition. Data are plotted using Ocean Data View (Schlitzer 2016). pH data are from the CARINA dataset (CARINA group, 2009) and the $\delta^{13}\text{C}$ data are from the GLODAP data compilation (Key et al., 2004); (c) pH and $\delta^{13}\text{C}_{\text{DIC}}$ relationships in the modern ocean adapted from Foster et al., (2012). Because of anthropogenic acidification and the Suess effect only data from $>1500\text{ m}$ are plotted. Also included in the plot are the data from a transect in the North Atlantic (from 0 to 5000 m) where the effects of anthropogenic perturbation on both parameters have been corrected (Olsen and Ninneman, 2010).

Figure 6: $\delta^{11}\text{B}_{\text{planktic}}$, temperature and $\delta^{13}\text{C}_{\text{DIC}}$ estimates for the surface and deep ocean through the last 23 million years. (a) $\delta^{11}\text{B}_{\text{planktic}}$ surface; (b) $\delta^{11}\text{B}_{\text{borate}}$ deep from benthic foraminifera (blue) from this study and (green) Raitzsch and Hönisch, (2013). The error bars show the analytical external reproducibility at 95% confidence; (c) Mg/Ca based temperature reconstructions of surface dwelling planktic foraminifera; (d) Deep water temperature estimates from Cramer et al. (2011); (e) $\delta^{13}\text{C}_{\text{DIC}}$ surface record; (f) $\delta^{13}\text{C}_{\text{DIC}}$ benthic record. Squares depict ODP Site 999, triangles are ODP

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1681 Site 758, diamonds are ODP Site 926, circles are ODP Site 761. Species are
 1682 highlighted by colour: Orange are *T. trilobus*, purple *G. ruber*, red *G. praebuloides*,
 1683 dark blue *Cibicidoides wuellerstorfi* and light blue *Cibicidoides mundulus*. The two
 1684 benthic-planktic pairs that were removed prior to smoothing are highlighted with
 1685 arrows.

1686 Figure 7: The output from GENIE sensitivity analysis showing the warm-surface-to-
 1687 cold-deep ΔpH -to- $\Delta\delta^{13}\text{C}$ relationship. A pre-industrial model setup was taken and
 1688 perturbations were made to alkalinity inventory, carbon inventory, Antarctic shelf
 1689 fresh water flux (Sv), Atlantic-Pacific freshwater flux, S. Lim gas exchange (blocks
 1690 air-sea gas exchange south of the stated latitude), remineralisation depth scale (m)
 1691 and rain ratio – as described in the methods section. Blue circles depict the ΔpH -to-
 1692 $\Delta\delta^{13}\text{C}$ relationship (where the colours reflect the CO_2 level of each experiment) and
 1693 red open circles show the root mean square of the regression (RMSE). The green
 1694 stars are the ΔpH -to- $\Delta\delta^{13}\text{C}$ relationship for the control experiment conducted at
 1695 292.67 ppm CO_2 . The green (open) points show the RMSE for this control run.
 1696 Inventories are dimensionless (1 is control). For the Atlantic-Pacific FWF 1 is
 1697 equivalent to 0.32 Sv. The alkalinity and carbon inventory experiments are very
 1698 extreme and inconsistent with geologic evidence.

1699 Figure 8: The output from sensitivity analysis of the relationship between pH gradient
 1700 and $\delta^{13}\text{C}$ gradient from the 13500 run CYCLOPS ensemble (see text for model
 1701 details). Panel (a) shows the mean gradient when the result from all 18 ocean boxes
 1702 are included in the regression. Panel (b) shows only the boxes from the low latitude
 1703 ocean from all basins and (c) shows the regression from only North Atlantic low
 1704 latitude boxes. Note the lower $\Delta\text{pH}/\Delta\delta^{13}\text{C}$ slope at the lower latitudes due to the
 1705 effect of temperature.

1706 Figure 9: The pH gradient between surface and deep through time calculated from the
 1707 $\delta^{13}\text{C}$ gradient and using a flat probability derived from the low latitude ensemble
 1708 regressions from the CYCLOPS model. The modern pH gradients at each site are
 1709 also plotted.

1710 Figure 10: The calculated $\delta^{11}\text{B}_{\text{sw}}$ from the benthic-planktic $\delta^{11}\text{B}$ pairs using a pH
 1711 gradient derived from $\delta^{13}\text{C}$. The uncertainty on each data point is determined using a
 1712 Monte Carlo approach including uncertainties in temperature, salinity, $\delta^{11}\text{B}$ and the

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Deleted: (green) (panel (b) Fig. 7) and low latitude North Atlantic only (red) (panel (c) Fig. 7) based

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1740 pH gradient (see text for details). Data are plotted as box and whisker diagrams
 1741 where the median and interquartile range as plotted in the box and whiskers show the
 1742 maximum and minimum output from the Monte Carlo simulations. The line of best
 1743 fit is the probability maximum of a LOWESS fit given the uncertainty in the
 1744 calculated $\delta^{11}\text{B}_{\text{sw}}$. The darker shaded area highlights the 68% confidence interval and
 1745 the lighter interval highlights the 95% confidence interval. The bottom panel shows
 1746 box plots of the mean and 2 standard error (s.e.) of 'binning' the individual $\delta^{11}\text{B}_{\text{sw}}$
 1747 measurements into 8 Myr intervals. The middle line is the mean and the box shows
 1748 the 2 s.e. of the data points in that bin. The smoothed record is also plotted for
 1749 comparison where the line of best fit is the probability maximum of a LOWESS fit
 1750 given the uncertainty in the calculated $\delta^{11}\text{B}_{\text{sw}}$. The darker shaded area highlights the
 1751 68% confidence interval and the lighter interval highlights the 95% confidence
 1752 interval. The black dot is the modern value of 39.61 ‰ (Foster et al., 2010).

1753 Figure 11: The $\delta^{11}\text{B}_{\text{sw}}$ curve calculated using the variable pH gradient derived from
 1754 $\delta^{13}\text{C}$. The median (red line), 68% (dark red band) and 95% (light red band)
 1755 confidence intervals are plotted. Plotted with a compilation of published $\delta^{11}\text{B}_{\text{sw}}$
 1756 records. Seawater composition reconstructed from foraminifera depth profiles (light
 1757 blue squares and dark blue cross) from Pearson and Palmer (2000) and Foster et al.
 1758 (2012) respectively, numerical modelling (green line), with additional green green
 1759 lines shows ± 1 ‰ confidence interval (Lemarchand et al., 2000) and benthic $\delta^{11}\text{B}$
 1760 (purple diamonds and dark purple line is using the fractionation factor of Klochko et
 1761 al., 2006, light purple line using an empirical calibration) from Raitzsch and Hönisch
 1762 (2013). All the published $\delta^{11}\text{B}_{\text{sw}}$ curves are adjusted so that at $t=0$, the isotopic
 1763 composition is equal to the modern (39.61 ‰).

1764 Figure 12: a) The $\delta^{11}\text{B}_{\text{sw}}$ curve from this study plotted with other trace element
 1765 isotopic records. On the $\delta^{11}\text{B}_{\text{sw}}$ panel, the darker shaded area highlights the 68%
 1766 confidence interval and the lighter interval highlights the 95% confidence interval),
 1767 $\delta^{26}\text{Mg}_{\text{sw}}$ record from Pogge von Strandmann et al. (2014) (error bars are ± 0.28 ‰
 1768 and include analytical uncertainty and scatter due to the spread in modern *O. universa*
 1769 and the offset between the two analysed species), $\delta^{44/40}\text{Ca}_{\text{sw}}$ record from Griffith et al.
 1770 (2008) (error bars show 2σ uncertainty) and $\delta^7\text{Li}_{\text{sw}}$ record from Misra and Froelich
 1771 (2012) (error bars show 2σ uncertainty). Blue dashed lines show middle Miocene
 1772 values, red dashed lines highlight the modern.

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1789 | Figure 13: Crossplots of the records of $\delta^{11}\text{B}_{\text{sw}}$ using the variable pH gradient derived
 1790 | from $\delta^{13}\text{C}$ (error bars show 2σ uncertainty) with $\delta^{44/40}\text{Ca}_{\text{sw}}$ from Griffith et al. (2008)
 1791 | (error bars show 2σ uncertainty), $\delta^7\text{Li}_{\text{sw}}$ from Misra and Froelich (2012) (error bars
 1792 | show 2σ uncertainty) and $\delta^{26}\text{Mg}_{\text{sw}}$ from Pogge von Strandmann et al. (2014) (error
 1793 | bars are $\pm 0.28\%$ and include analytical uncertainty and scatter due to the spread in
 1794 | modern *O. universa* and the offset between the two analysed species). The colour of
 1795 | the data points highlights the age of the data points where red = modern and blue =
 1796 | 23 Ma.

1797 | [Table 1: CYCLOPS model parameter values defining the ensemble of 13,500](#)
 1798 | [simulations.](#)

1799 | [Table 2: Uncertainty inputs into the Monte Carlo simulations to calculate \$\delta^{11}\text{B}\$. The](#)
 1800 | [sources of uncertainty are also added. All uncertainty estimates are \$2\sigma\$.](#)

1801 | Table 3: The average $\delta^{11}\text{B}$, $\delta^{26}\text{Mg}$, $\delta^{44/40}\text{Ca}$ and $\delta^7\text{Li}$ composition of major fluxes into
 1802 | and out of the ocean. Colour coding reflects the relative importance of each the
 1803 | processes (darker shading reflects greater importance). The colour coding for boron is
 1804 | based on Lemarchand et al. (2000) and references therein, lithium from Misra and
 1805 | Froelich (2012) and references therein, magnesium from Tipper et al. (2006b) and
 1806 | calcium from Fantle and Tipper (2014) and Griffin et al. (2008) and references
 1807 | therein. The isotopic ratio of each process is: (a) Lemarchand et al. (2000) and
 1808 | references therein; b) Misra and Froelich (2012) and references therein; (c) Burton
 1809 | and Vigier (2012); (d) Tipper et al. (2006b); e) Wombacher et al. (2011); f) includes
 1810 | dolomitisation; g) removal through hydrothermal activity; h) Griffith et al. (2008); i)
 1811 | Fantle and Tipper (2014) and references therein; j) dolomitisation may be an
 1812 | important component of the carbonate flux. Modern $\delta^{26}\text{Mg}_{\text{sw}}$ and $\delta^{11}\text{B}_{\text{sw}}$ from Foster
 1813 | et al. (2010), $\delta^7\text{Li}_{\text{sw}}$ from Tomascak (2004). The $\delta^{44/40}\text{Ca}$ presented here was
 1814 | measured relative to seawater and hence seawater has a $\delta^{44/40}\text{Ca}_{\text{sw}}$ of 0 permil by
 1815 | definition.

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such that seawater is isotopically heavier (39.61‰) than the inputs (which average at 10.4‰).

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such that seawater is isotopically heavier (39.61‰) than the inputs (which average at 10.4‰).

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such that seawater is isotopically heavier (39.61‰) than the inputs (which average at 10.4‰).

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Yet brine-halite fractionation offsets of -20‰ to -30‰ and -5‰ are reported from laboratory and natural environments respectively casting doubt over the validity of the assumption that no fractionation occurs during halite formation (Vengosh et al., 1992; Liu et al., 2000). These fractionations and riverine input during basin isolation will drive the evaporite-hosted boron to low- $\delta^{11}\text{B}$ isotope values such that the fluid inclusion record likely provides a lower limit for the $\delta^{11}\text{B}_{\text{sw}}$ through time (i.e. $\delta^{11}\text{B}_{\text{sw}}$ is heavier than the halite fluid inclusions of Paris et al. (2010)). Nevertheless, evaporites form from modified seawater in isolated basins making them unlikely archives of representative ocean $\delta^{11}\text{B}$.

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An alternative semi-empirical approach makes assumptions regarding the evolution of Cenozoic deep-ocean pH and a benthic $\delta^{11}\text{B}$ record to determine changes in $\delta^{11}\text{B}_{\text{sw}}$

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which can be converted to $\delta^{11}\text{B}_{\text{sw}}$ based on

While this approach yields a qualitative independent check on other approaches (e.g. halite inclusions, geochemical modeling), as a quantitative record of $\delta^{11}\text{B}_{\text{sw}}$ through time, it has a number of drawbacks. Firstly, some of the CO_2 data used in the modeling studies is derived using the boron isotope-pH proxy, leading to some circularity in the methodology. Secondly, given the structure in CO_2 proxy records, the assumption that surface ocean pH changed linearly through the Cenozoic is most likely an oversimplification (Beerling and Royer, 2011). Consequently, while this method may shed some light on the evolution of $\delta^{11}\text{B}_{\text{sw}}$ through time, it cannot be subsequently used to determine pH or atmospheric CO_2 from $\delta^{11}\text{B}$ of foraminiferal calcite because the $\delta^{11}\text{B}_{\text{sw}}$ record is itself based on assumptions of the secular evolution of pH and CO_2 .

One of the big challenges of reconstructing a

record empirically is determining $\delta^{11}\text{B}_{\text{sw}}$

One way to avoid using absolute pH reconstructions is to exploit the non-linear relationship between $\delta^{11}\text{B}$ and pH alongside estimated pH gradients in the ocean to constrain $\delta^{11}\text{B}_{\text{sw}}$.

Unfortunately, the applicability of this $\delta^{11}\text{B}_{\text{sw}}$ record (derived from $\delta^{11}\text{B}$ data measured using NTIMS) to $\delta^{11}\text{B}$ records generated using the MC-ICPMS is uncertain (Foster et al., 2013). In addition, this $\delta^{11}\text{B}_{\text{sw}}$ record is determined using a fractionation factor of 1.0194 (Kakihana et al., 1977), whereas recent experimental data have shown the value to be higher (1.0272 ± 0.0006 , Klochko et al., 2006). Thirdly, given our understanding of the $\delta^{11}\text{B}$ difference between species/size fractions (Foster, 2008; Henehan et al., 2013), the mixed species and size fractions used to make the $\delta^{11}\text{B}$ measurements in that study may have introduced some additional uncertainty in the reconstructed $\delta^{11}\text{B}_{\text{sw}}$. Consequently, while the estimates from Pearson and Palmer (2000) show that the rationale behind this

approach can yield useful $\delta^{11}\text{B}_{\text{sw}}$ estimates that may be qualitatively correct, the underlying measurements and some of the key assumptions have led to uncertainties in the record.

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The slope of the pH- $\delta^{13}\text{C}$ relationship simulated by our CYCLOPS model ensemble across a range of perturbed states is 0.2047 ($1\sigma = 0.0196$) (Fig. 7a, 8), in perfect agreement with modern empirical data and our GENIE experiments. Varying the biogeochemical parameters (gas exchange, rain ratio and remineralizing depth scale) yields some change in the regressed slope of the pH/ $\delta^{13}\text{C}$ relationship due to decoupled responses of pH and $\delta^{13}\text{C}$, but this gradient remains well within the 0.2 \pm 0.05 range, and a RMSE of 0.05 in the spatial relationship remains robust (Fig. 6). We take this as evidence that the uncertainty in the pH/ $\delta^{13}\text{C}$ relationship assumed in our carbon chemistry calculation is well represented by a central value of 0.2 with a 0.025 standard deviation. Experiments at very high DIC or low alkalinity, either of which yield high atmospheric $p\text{CO}_2$ and low mean ocean pH, yield gradients slightly outside the 0.2 \pm 0.05 range, with an elevated RMSE. This is probably associated with the non-linearity of the pH scale, modifying the gradient for a very different pH. It is to be emphasised that such extreme decoupled changes in DIC and alkalinity are not plausible within the Cenozoic, and were only possible in these simulations because of the absence of interactive sediments.

The slope of the pH- $\delta^{13}\text{C}$ relationship simulated by our CYCLOPS model ensemble across a range of perturbed states is 0.2047 ($1\sigma = 0.0196$) (Fig. 7a, 8), in perfect agreement with modern empirical data and our GENIE experiments. We take this agreement as evidence that the slope of the pH- $\delta^{13}\text{C}$ relationship is a feature of ocean biogeochemistry that is relatively conserved even if ocean carbon chemistry and circulation change drastically. For the purpose of calculating $\delta^{11}\text{B}_{\text{sw}}$ from our benthic/planktic foraminifera measurements we need to estimate the pH difference between the low latitude surface and deep ocean at the sample sites, most of which are in the subtropical North Atlantic. If we restrict our analysis of the CYCLOPS ensemble to only the low latitude surface boxes and the corresponding deep ocean boxes (i.e.,

Atlantic, Indian, South Pacific and North Pacific) the slope of the applicable pH- $\delta^{13}\text{C}$ relationship is 0.1797 ($1\sigma = 0.0213$) (Fig. 7b, 8), which is significantly less than the regression based on all 18 model boxes. Further, if only the Atlantic low latitude surface and deep ocean boxes are used to calculate the slope of the applicable pH- $\delta^{13}\text{C}$ relationship declines to 0.1655 ($1\sigma = 0.0192$) (Fig. 7c, 8). Thus, excluding the polar ocean and the ocean's mid-depth permanent thermocline from the analysis consistently yields a shallower slope of the pH- $\delta^{13}\text{C}$ relationship, with some evidence for water mass dependence also in the modern observations (Fig. 4). Here we calculate $\delta^{11}\text{B}_{\text{sw}}$ for all three estimates of the pH- $\delta^{13}\text{C}$ slope (global regression 0.201; low latitude surface and deep regression 0.1797; Atlantic low latitude surface to deep box gradients 0.1655) assuming a generous uncertainty of 0.05 (2σ) in all cases, and we provide all three $\delta^{11}\text{B}_{\text{sw}}$ scenarios as an online supplement. Overall, the slope between pH and $\delta^{13}\text{C}$ is dependent on the competition between spatial variations in remineralized soft tissue, increasing the slope between pH and $\delta^{13}\text{C}$, and seawater temperature, decreasing the slope between pH and $\delta^{13}\text{C}$. The largest concentrations of remineralized soft tissue occur in the thermocline, suggesting that a relatively steep pH- $\delta^{13}\text{C}$ slope is appropriate for estimating the pH gradient from the $\delta^{13}\text{C}$ difference. However, when comparing surface to deep waters, as is done in this study, the full range of the temperature effect is expressed and a relatively shallow pH- $\delta^{13}\text{C}$ slope is appropriate. This is particularly true given that our samples are from the low latitude surface and the cold deep ocean. Since most of our measurements are from the subtropical Atlantic it is perhaps most appropriate to use the slope regressed from the low latitude surface and deep boxes from this ocean basin (i.e., $\Delta\text{pH}/\Delta\delta^{13}\text{C} = 0.1655$; with $1\sigma = 0.025$) and we will focus on those calculations in the following discussion (Fig. 9).

The individual $\delta^{11}\text{B}_{\text{sw}}$ estimates calculated using the modern pH gradient method vary from 34.9 ‰ to 42.2 ‰ (± 0.84 -4.77 ‰) across the Neogene with a predominance of higher values closer to the modern and lowest values in the middle Miocene (Fig. 9). After smoothing is applied to satisfy seawater B mass balance, the long-term $\delta^{11}\text{B}_{\text{sw}}$ is determined as 37.5 ‰ at 23 Ma, decreases to a minimum of 37.17 ‰ at ~ 13 Ma (± 0.34 -

1.81 ‰), and subsequently increases gradually towards modern values through the late Miocene, Pliocene and Pleistocene (Fig. 9). The variability in the estimations of $\delta^{11}\text{B}_{\text{sw}}$ for each individual benthic/planktic foraminifera pair suggest that individual estimates of $\delta^{11}\text{B}_{\text{sw}}$ are sensitive to the different input parameters, particularly the assigned uncertainty in the pH gradient. However, by smoothing the record we effectively suppress error that is uncorrelated between individual benthic/planktic pairs of similar age and thereby focus on the effect of changes in $\delta^{11}\text{B}_{\text{sw}}$ that are correlated over multi-million year timescales.

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The variability in the estimations of $\delta^{11}\text{B}_{\text{sw}}$ for each individual benthic/planktic foraminifera pair suggest that individual estimates of $\delta^{11}\text{B}_{\text{sw}}$ are sensitive to the different input parameters, particularly the assigned uncertainty in the pH gradient. However, by smoothing the record we effectively suppress error that is uncorrelated between individual benthic/planktic pairs of similar age and thereby focus on the effect of changes in $\delta^{11}\text{B}_{\text{sw}}$ that are correlated over multi-million year timescales.

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When using $\delta^{13}\text{C}$ gradients as predictors for the pH gradient the $\delta^{11}\text{B}_{\text{sw}}$ values calculated are broadly similar to the results with assumed constant pH gradient: $\delta^{11}\text{B}_{\text{sw}}$ varies from 34.1 ‰ to 42.3 ‰ (± 0.72 -4.0 ‰) across the Neogene with the predominance of higher values closer to the modern with the lowest values in the middle Miocene (Fig. 9). However, when the individual $\delta^{11}\text{B}_{\text{sw}}$ estimates are smoothed, while the $\delta^{11}\text{B}_{\text{sw}}$ calculated using this method is similar to the constant pH gradient scenario through the late and middle Miocene ($\sim 37.5 \text{ ‰} \pm 0.19$ -1.28 ‰), the subsequent increase occurs more rapidly and the $\delta^{11}\text{B}_{\text{sw}}$ record reaches modern values by ~ 5 Ma (Fig. 9). The variability in the estimations of $\delta^{11}\text{B}_{\text{sw}}$ for each individual benthic/planktic foraminifera pair suggest that individual estimates of $\delta^{11}\text{B}_{\text{sw}}$ are sensitive to the different input parameters, particularly the assigned uncertainty in the pH gradient. However, by smoothing the record we effectively suppress error that is uncorrelated between individual benthic/planktic pairs of similar age and thereby focus on the effect of changes in $\delta^{11}\text{B}_{\text{sw}}$ that are correlated over multi-million year timescales.

Given the variability we observe in the $\delta^{13}\text{C}$ derived pH gradient, and the consistency between the modelled pH gradient using GENIE and CYCLOPS, we conclude using the benthic-to-planktic pH difference calculated using the $\delta^{13}\text{C}$ gradient is indeed an improvement over the assumption that pH gradients remained constant through time. Therefore, we recommend the use of the $\delta^{13}\text{C}$ -corrected $\delta^{11}\text{B}_{\text{sw}}$ moving forward and in the following discussion we will limit our attention to this record.

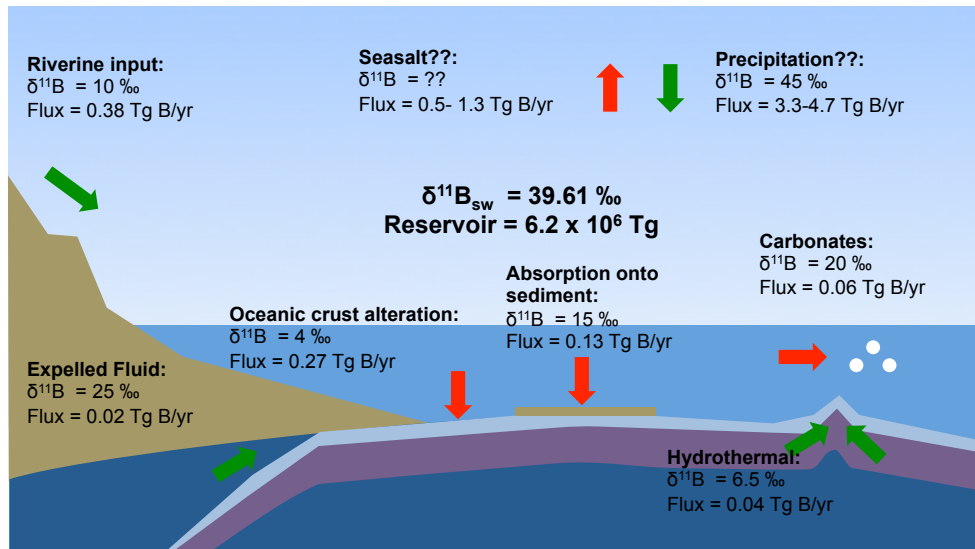


Figure 1

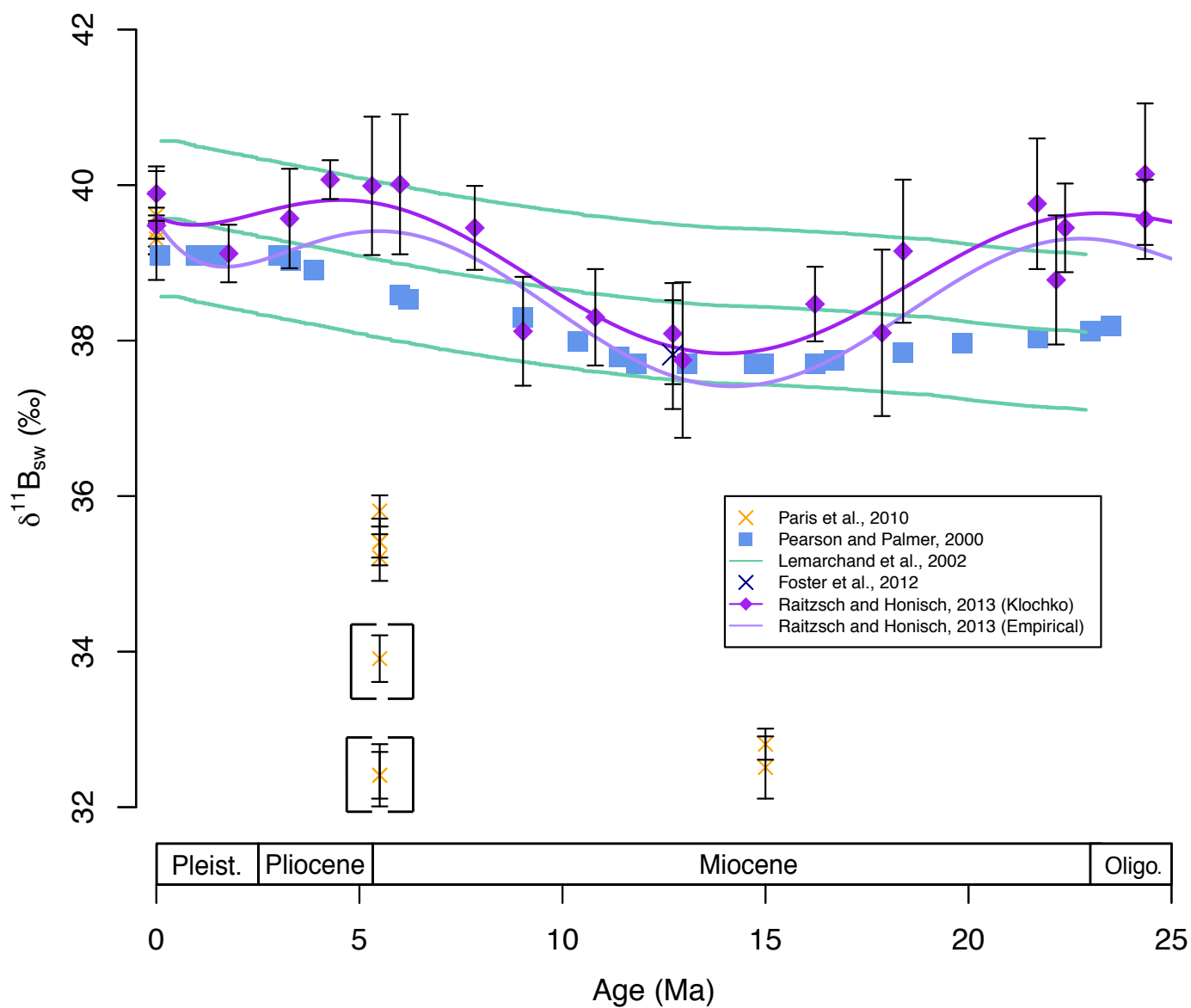


Figure 2

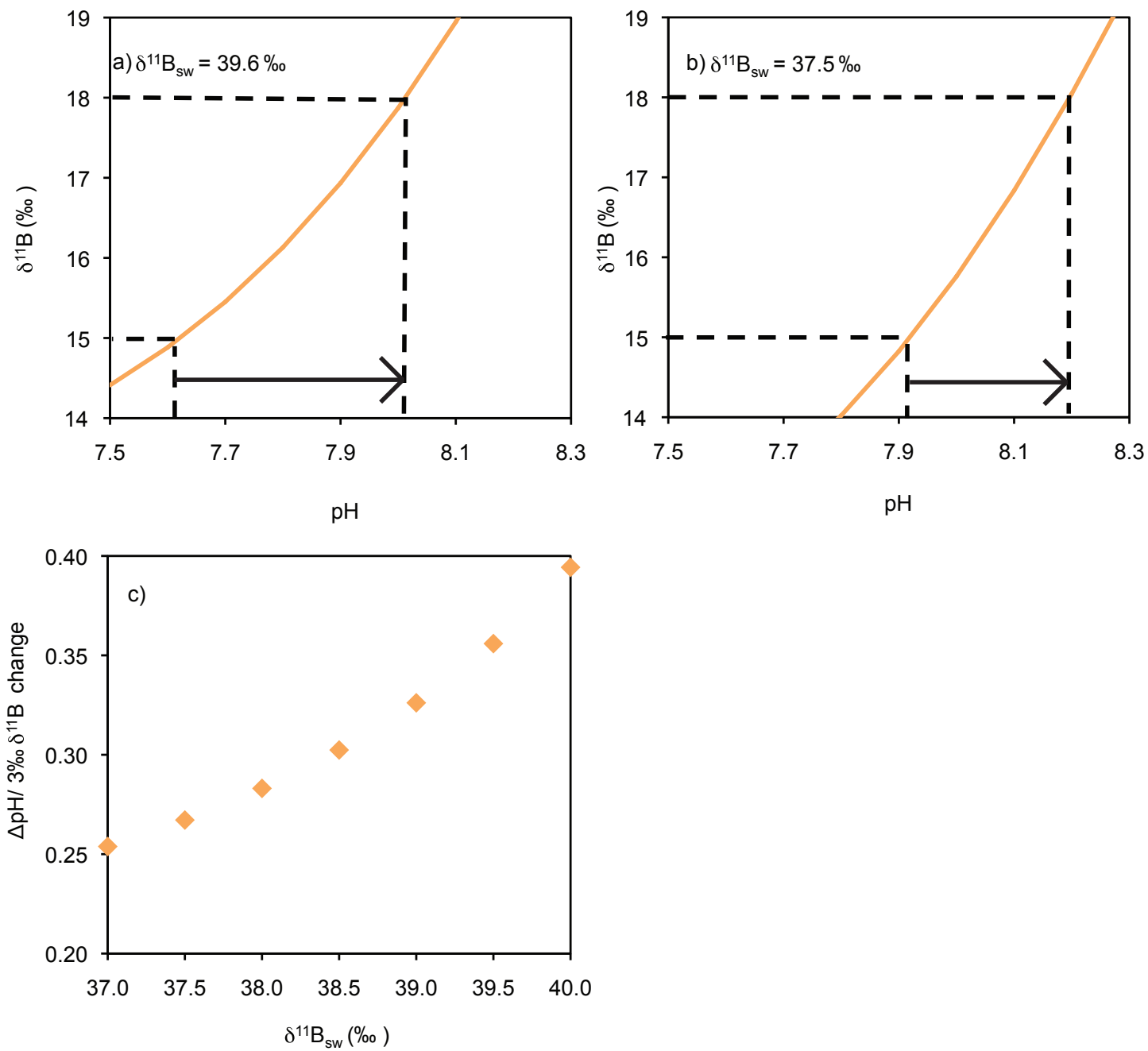


Figure 3

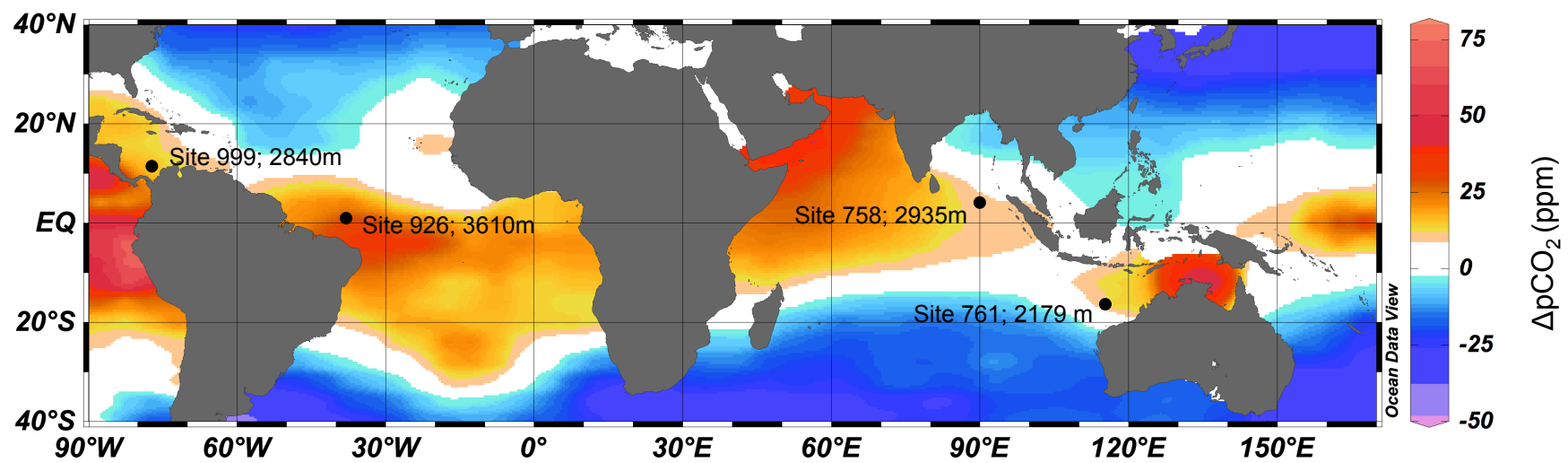


Figure 4

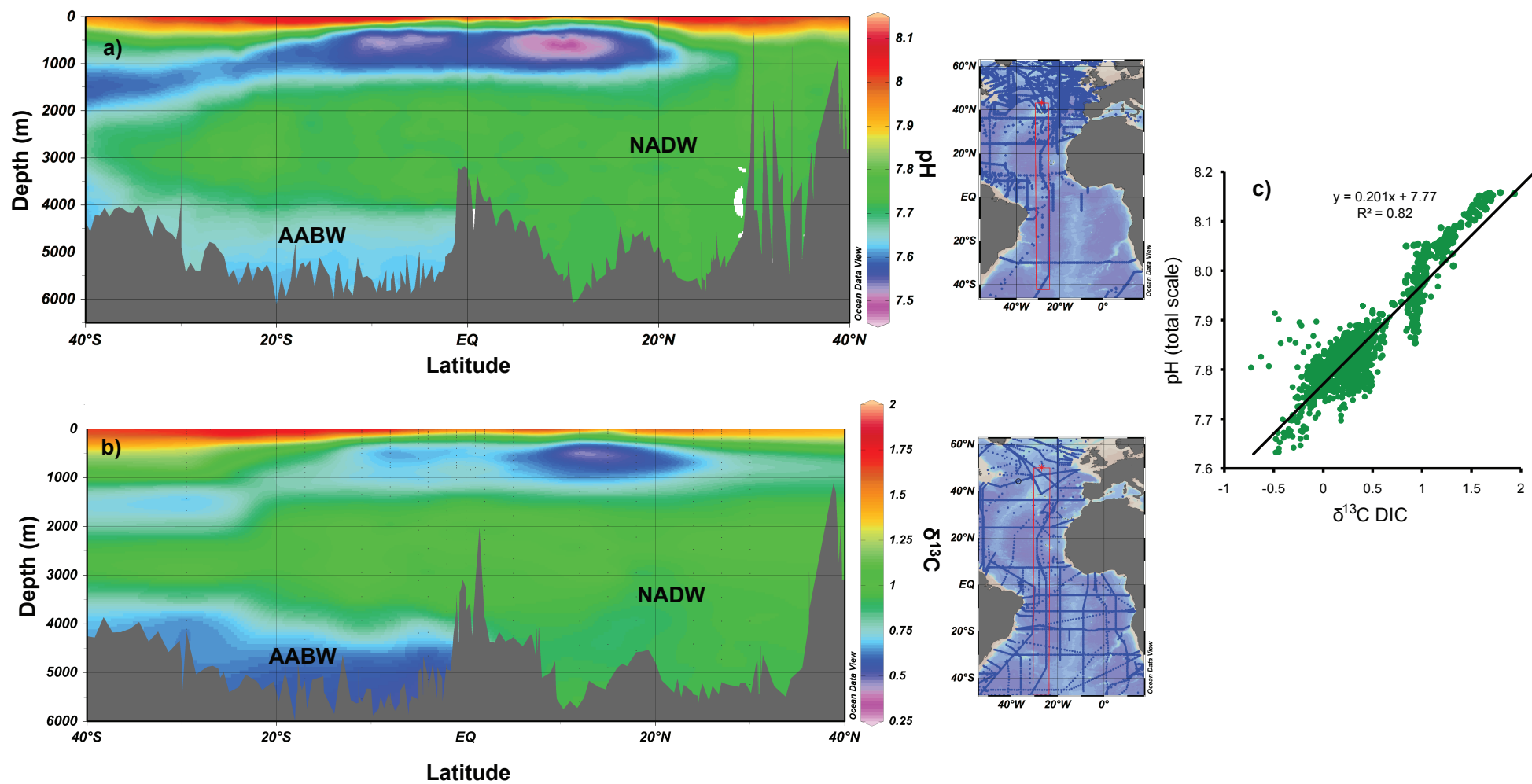
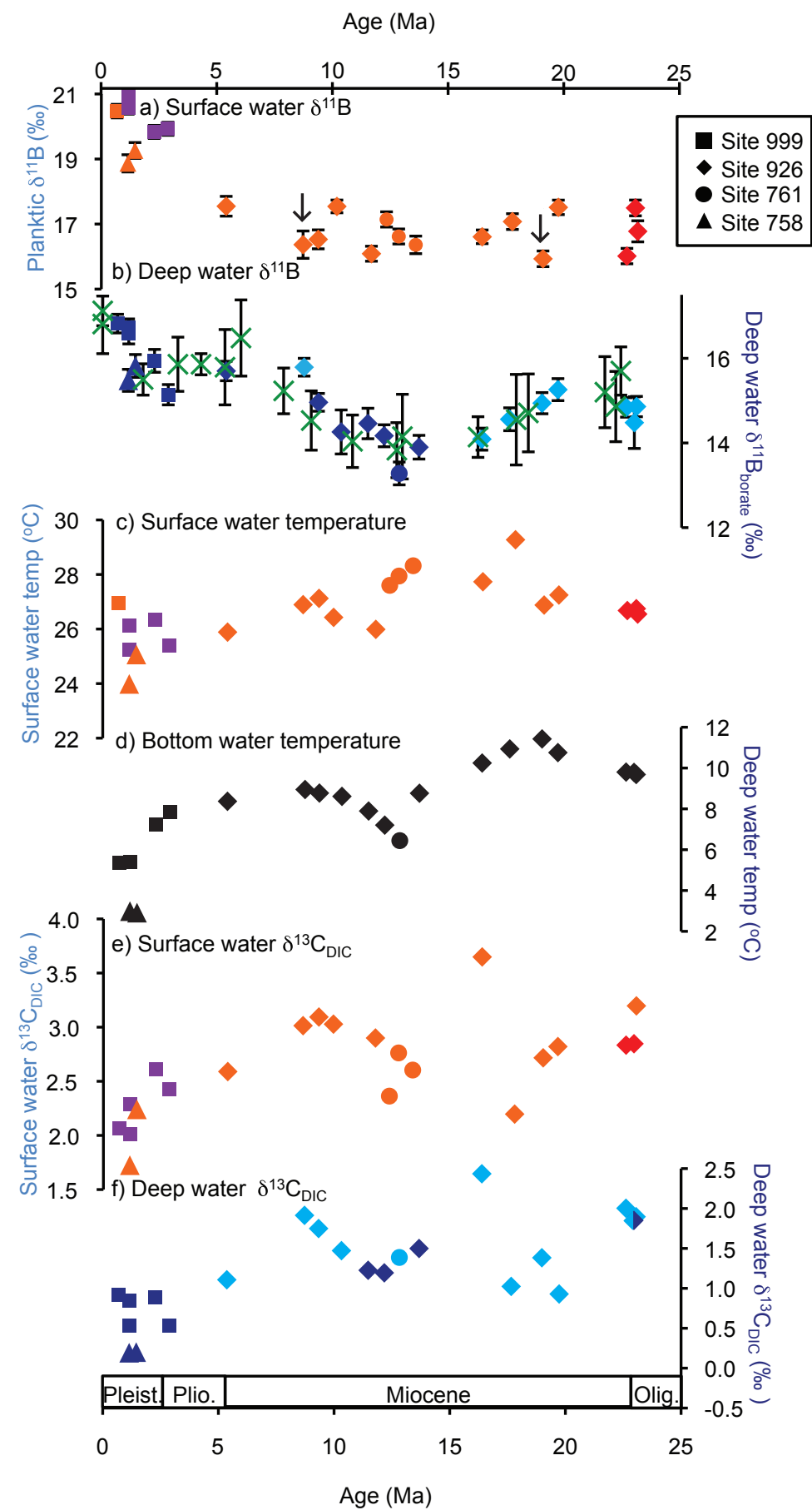


Figure 5

Figure 6



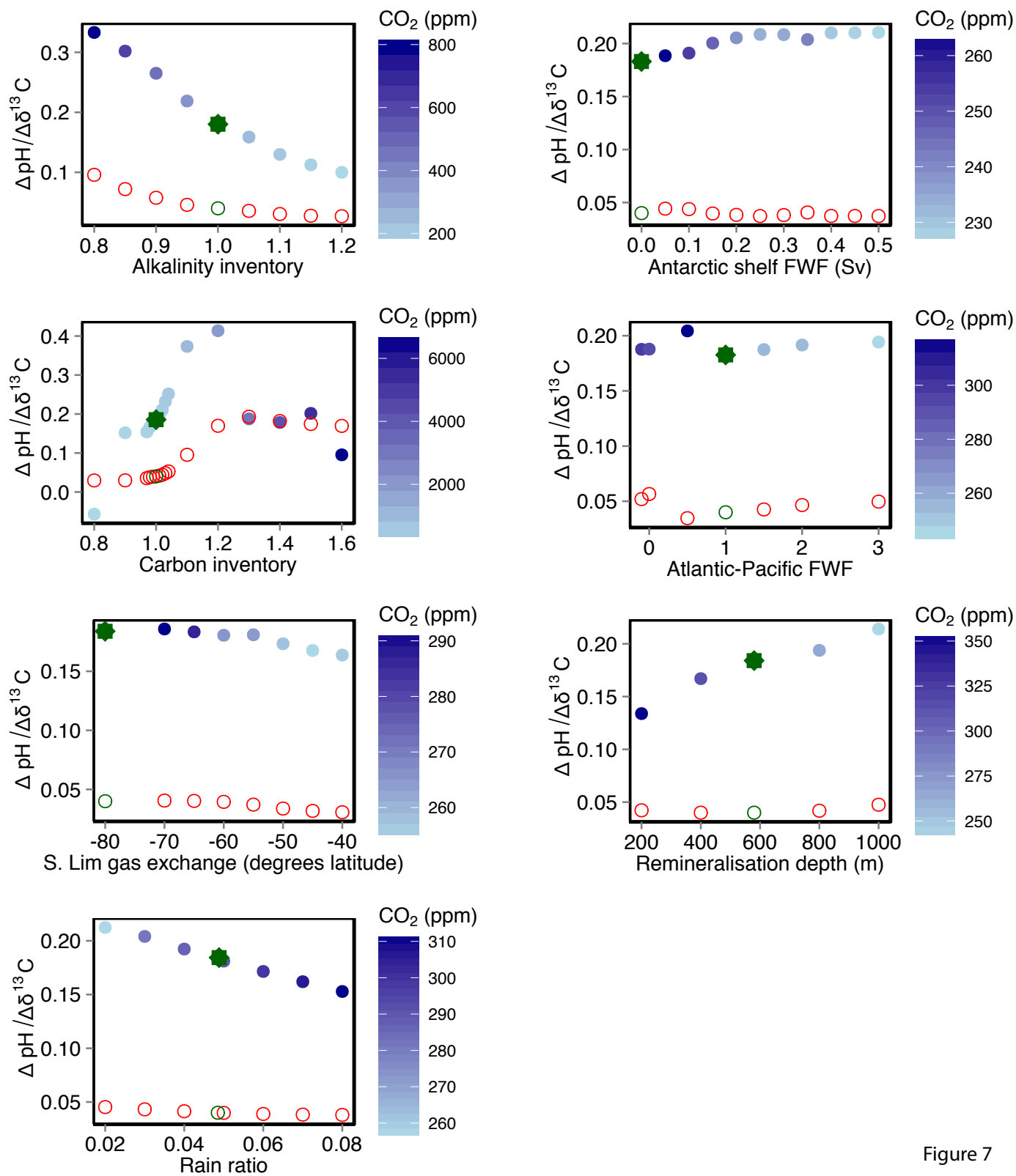


Figure 7

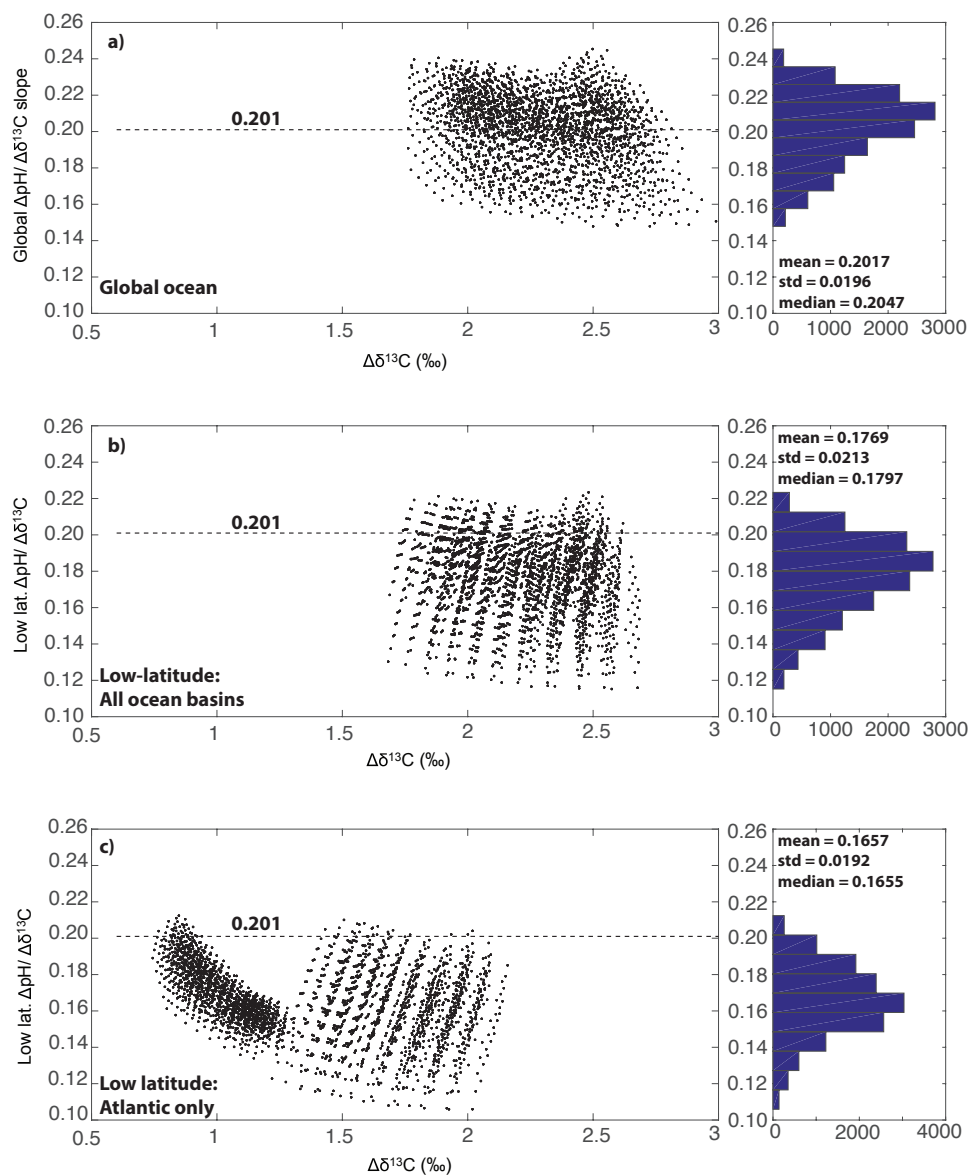


Figure 8

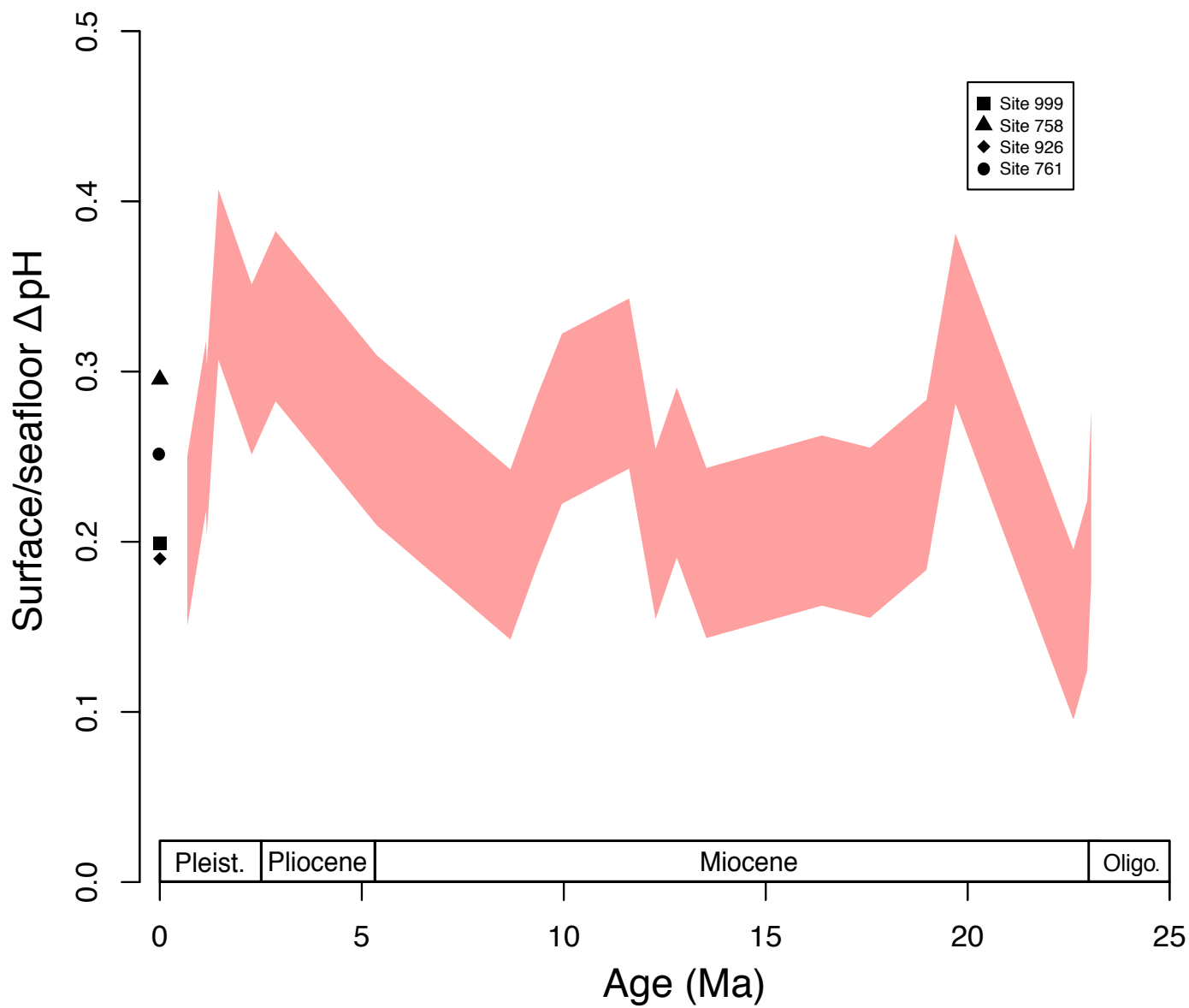


Figure 9

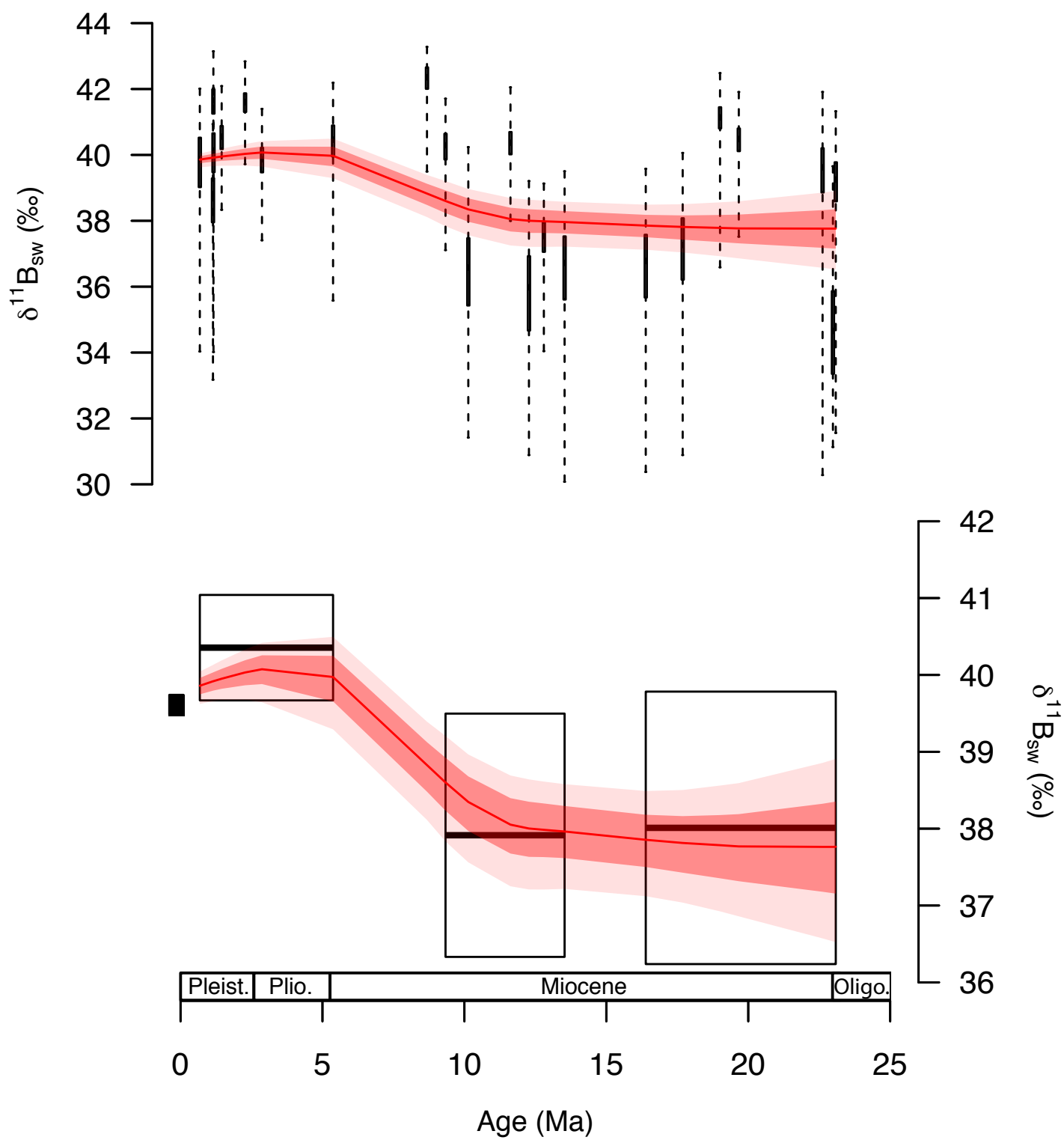


Figure 10

Figure 11

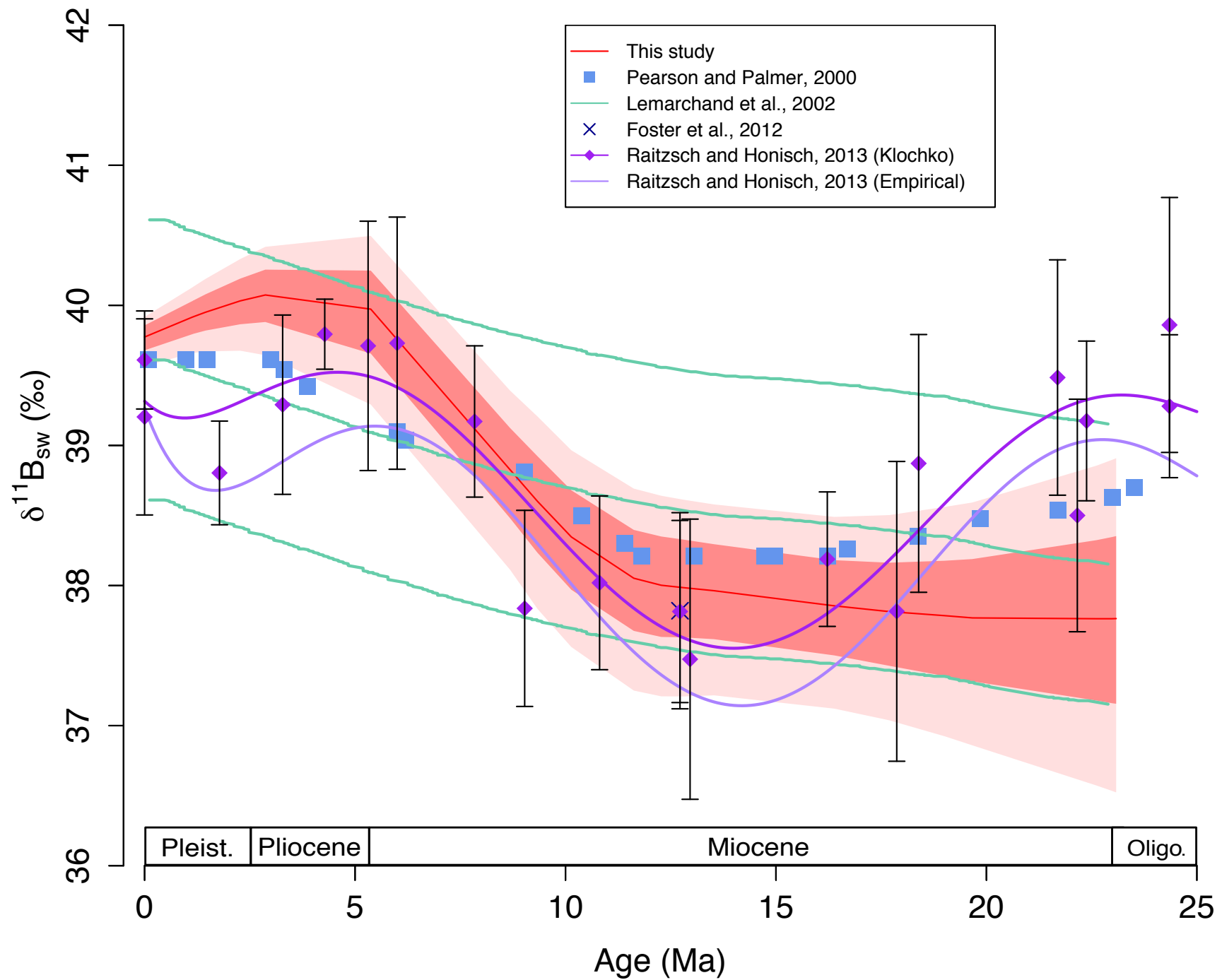
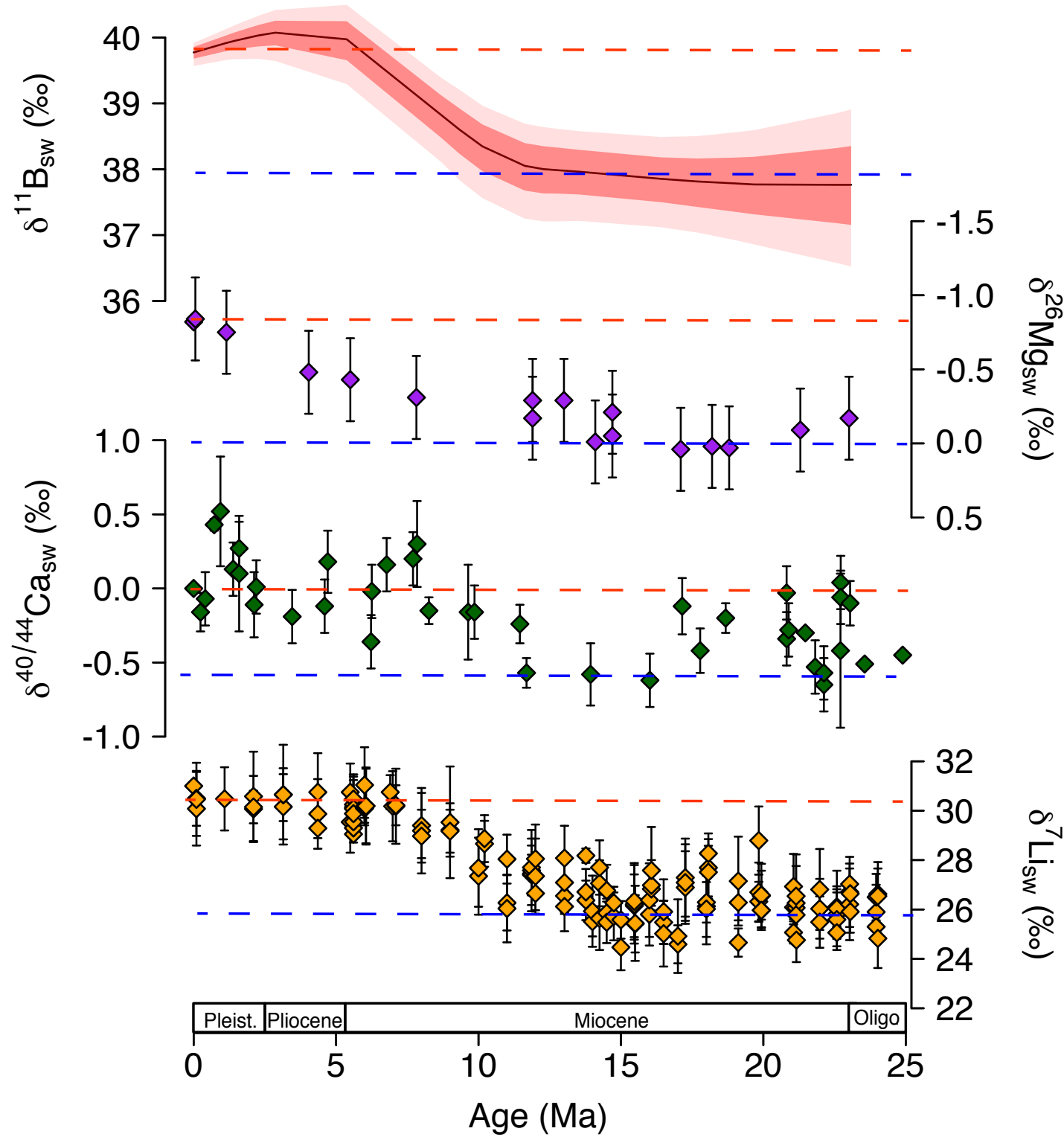


Figure 12



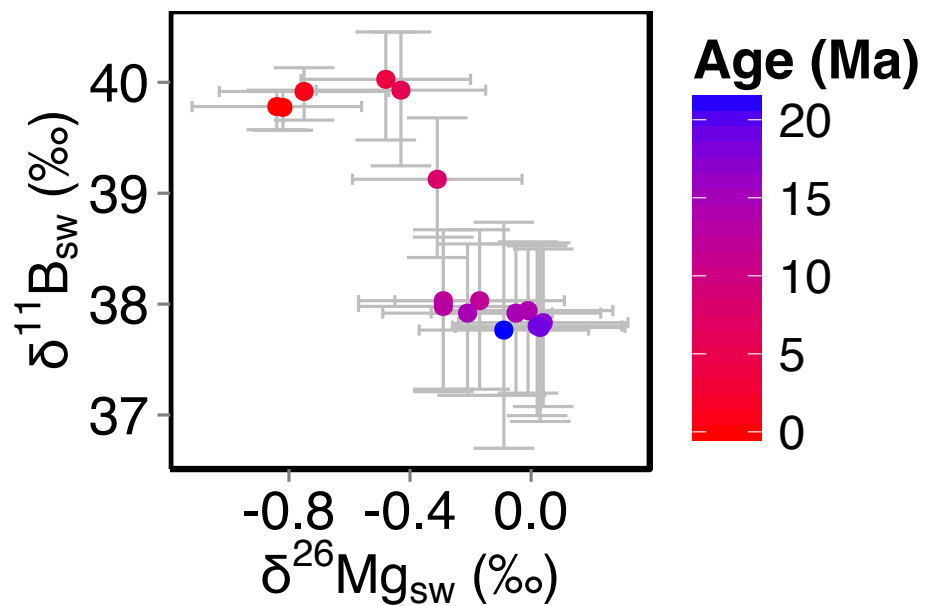
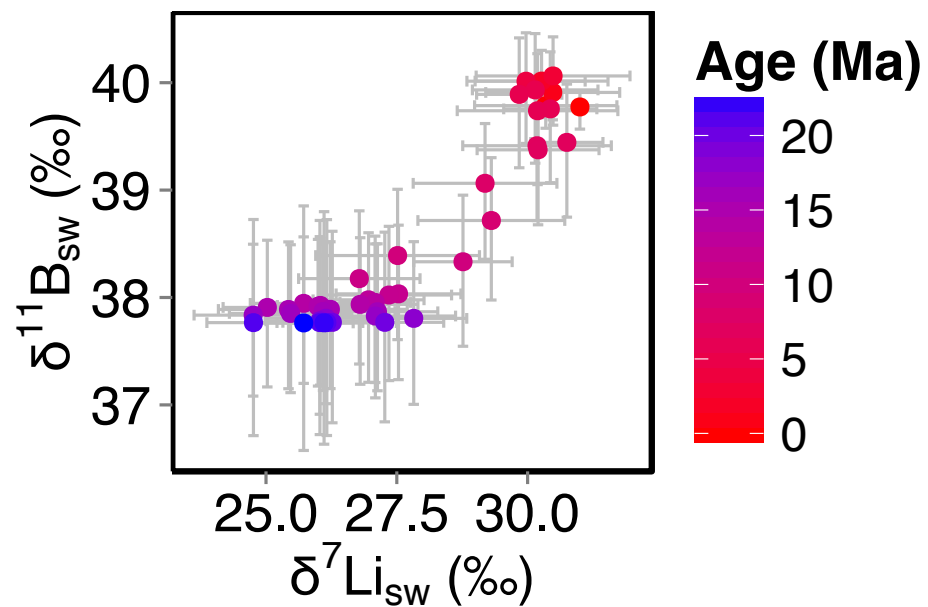
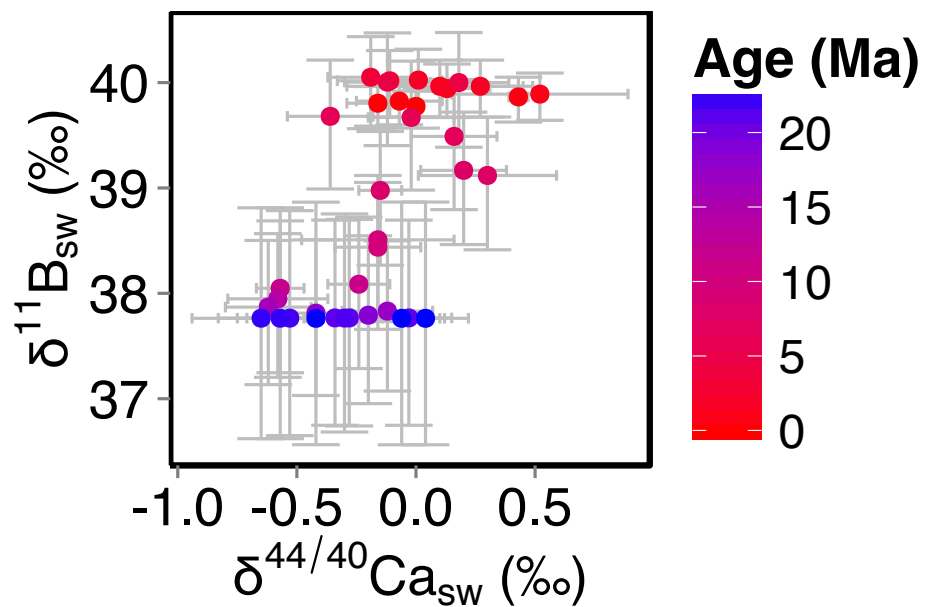


Figure 13

Table 1. CYCLOPS model parameter values defining the ensemble of 13,500 simulations*

Parameter	Description	Values assumed
PAZ surface phosphate**	unutilized polar nutrient	1μM, 1.25μM, 1.5μM, 1.75μM, 2μM
PAZ vertical exchange**	bottom water formation	2Sv, 7.75Sv, 13.5Sv, 19.25Sv, 25Sv
SAZ surface phosphate**	unutilized polar nutrient	0.7μM, 0.825μM, 0.95μM, 1.075μM, 1.2μM
AMOC circulation scheme*	deep vs. shallow overturning	NADW, GNAIW
representative timeslice***	Age ([Ca ²⁺]/CCD); calcium set outright; CCD set via riverine CaCO ₃ flux using inverse scheme	0Myr (10.6mM, 4.65km), 9Myr (12.89mM, 4.4km), 11Myr (13.33mM, 4.9km), 16Myr (14.28mM, 4.7km), 18Myr (14.57mM, 4.25km), 20Myr (14.86mM, 4.7km)
atm. CO ₂ ****	set via silicate weatherability	200ppm, 300ppm, 400ppm, 500ppm, 600ppm, 700ppm, 800ppm, 900ppm, 1000ppm

*= The six parameters assume 5, 5, 5, 2, 9 and 6 values, yielding 13,500 distinct parameter combinations

** = These parameters are intended to span the full range of ocean carbon cycling over late Pleistocene glacial-interglacial cycles, as describe in more detail in Hain et al. (2010)

*** = We selected representative timeslices based on local extrema in the CCD reconstruction of Pälike et al. (2012) and we combine these with appropriate reconstructed calcium concentrations based on Horita et al. (2002). These choices are intended to capture the range of long-term steady state conditions of the open system CaCO₃ cycle relevant to our study interval

**** = These atmospheric CO₂ levels are chosen to span a range wider than expected for the study interval. Following silicate-weathering-feedback paradigm, long-term CO₂ is fully determined by the balance of geologic CO₂ sources and silicate weathering, whereby faster acting processes of the open system CaCO₃ cycle compensate relative to that CO₂ level. All else equal, high CO₂ levels, low calcium concentrations and deep CCD correspond to high bulk ocean carbon concentrations (Hain et al., 2015) with many of the individual simulations of this ensemble exceeding 4000μM DIC.

Table 2

Input parameter	Uncertainty applied	Source of uncertainty estimate
Surface to sea floor ΔpH	Uniform +/- 0.05 pH units	Plausible range of $\Delta\text{pH}/\Delta\delta^{13}\text{C}$ in CYCLOPS and GENIE sensitivity tests; prediction error of linear $\Delta\text{pH}/\Delta\delta^{13}\text{C}$ regression in GENIE
$\delta^{11}\text{B}$ measurement	0.15-0.61‰	Long-term external reproducibility
Temperature	$\pm 2^\circ\text{C}$	Uncertainty in the Mg/Ca measurement and Mg/Ca-temperature calibration
Salinity	± 2 psu	In the absence of a salinity proxy this uncertainty is applied to cover variations through time.
Seawater [Mg]	± 4.5 mmol/kg	following Horita et al., (2002)
Seawater [Ca]	± 4.5 mmol/kg	following Horita et al., (2002)

Table 3

Sources	Isotopic Ratio			
Oceanic Inputs	$\delta^{11}\text{B}_{\text{sw}}$ 39.61 ‰	$\delta^7\text{Li}_{\text{sw}}$ 31 ‰	$\delta^{26}\text{Mg}_{\text{sw}}$ -0.83 ‰	$\delta^{44/40}\text{Ca}_{\text{sw}}$ 0 ‰
Input from hydrothermal	6.5 ^a	8.3 ^b	N/A	-0.96 ^h
Fluid from accretionary prisms	25 ^a	15 ^b	N/A	N/A
Riverine Inputs	10 ^a	23 ^b	-1.09 ^d	-1.28 ^h
Groundwater	N/A	N/A	-0.82 ^d	-1.02 ⁱ
Outputs				
Precipitation into carbonates	20 ^a	29 ^c	-3.5 ^{d,e,f}	-1.15 ^{h,j}
Ocean crust alteration	4 ^a	15 ^b	-0.83 ^{d,g}	-1.2 ^h
Absorption onto sediment	15 ^a	15 ^b	??	N/A