Earth's oceanic oxygen history from Phanerozoic to Pleistocene glacial cycles: insights from the carbonate iodine-to-calcium proxy

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Abstract

Oxygen in the oceans is an important part of the significant and complex evolution of Earth’s climate, with great significance for the evolution of life in the oceans. My PhD research has been primarily driven by three major questions: (1) How can we reliably reconstruct oxygen levels in ancient oceans? (2) How did oceanic oxygen levels evolve throughout Earth’s history? (3) How did oceanic oxygen levels affect habitability of the Earth? Most studies of the Earth’s oxygen history have focused on the atmosphere and deep oceans, but in contrast, I focused on the upper ocean (the top tens to a few hundred meters in the water column) where we see the oxygen minimum zones in the present oceans. This is a critical zone where animals have diversified most dramatically in Phanerozoic (542 million years ago (Ma) to present day) and where geologists have the best fossil record for biology/environment comparison. I used a novel proxy, the iodine-to-calcium ratio (I/Ca) in carbonate rocks and planktic microfossils, which can track oxygen changes over a range of values where most modern marine animals are sensitive, i.e., at higher oxygen levels rather than euxinia (containing H₂S) or anoxia (no O₂). Four major projects in my dissertation are:

1) **Phanerozoic upper ocean oxygenation history and its coevolution with life.**

When and how oceanic oxygen had evolved to modern-like levels has remained elusive in Earth’s oxygen history, because few redox proxies can track secular variations in dissolved oxygen concentrations around threshold values for metazoan survival in the upper ocean. To address this question, we measured I/Ca in an extensive Phanerozoic collection of shallow marine carbonates and simulated marine iodine cycle in an Earth system model. We found that (1) I/Ca spiked during the Devonian, supporting a major rise in atmospheric O₂ at ~400
Ma. (2) a step change in the oxygenation of the upper ocean to relatively sustainable near-modern conditions at ~200 Ma, likely driven by a shift in organic matter remineralization to greater depths, which may be due to increasing size and biomineralization of eukaryotic plankton.

2) **Planktic foraminiferal I/Ca proxy in the Southeast Atlantic Ocean.**

Planktic foraminiferal I/Ca is a promising tool to reconstruct the extent of past upper ocean oxygenation, but a thorough assessment is necessary to evaluate both its potential and its limitations. We used foraminifers from Holocene core-tops (Southeast Atlantic Ocean) to document planktic I/Ca across a range of oceanographic conditions. We found that low planktic I/Ca can be used empirically to indicate hypoxia (O$_2$ < 70–100 μmol/kg) in the upper water column. At a site located in the Benguela Upwelling System, down-core I/Ca records suggested that only small changes occurred in upper ocean oxygenation during the past 240 ka, probably related to strong upwelling dynamics in this region.

3) **Bottom water oxygen changes in the glacial oceans and their driving mechanisms.**

Reliable, quantitative paleo-O$_2$ data is needed to test whether climate models can replicate past climate conditions in order to improve the forecast of future oceanic oxygenation changes under possible global warming. To address this question, we developed I/Ca in the benthic foraminiferal *Cibicidoides* spp. as a novel semi-quantitative bottom water oxygen proxy. We then applied this proxy to five ocean drilling cores to reconstruct the bottom water oxygen levels in the glacial-interglacial oceans. Using a multi-proxy approach, we found that low-O$_2$ water (< 50 μmol/kg) may have been more extensive in the glacial Atlantic and Pacific Oceans compared to modern/Holocene, and the driving mechanisms for
glacial deoxygenation may vary by ocean basin.

4) **Direct comparison of benthic foraminiferal surface porosity and I/Ca proxies.**

Benthic foraminiferal surface porosity (the mean percentage of surface area covered by pores; higher porosity: lower oxygenation) and I/Ca (higher I/Ca: higher oxygenation) are both promising paleoceanographic proxies that need testing in down-core studies. Here we report the first down-core comparison (~45 kyr) of these proxies in a core from a cold seep site on the southern Brazilian margin (26°40′S, 46°26′W, 475 m water depth). The two proxies are overall consistent, with porosity values generally low (< 10%) and I/Ca ranges between ~4 and ~6 μmol/mol throughout the core, suggesting that bottom water oxygen concentrations at the site remained above 50 μmol/kg during the last 45 kyr. Potential seafloor methane release during the last glacial period (40-20 ka), as indicated by anomalously negative δ¹³C values in foraminifera, apparently had limited impact on bottom water oxygenation, and interactions between competing processes potentially affecting bottom water oxygenation (i.e., water column stratification and productivity) may have limited the magnitude of changes in bottom water oxygen levels at the core site.
Earth’s oceanic oxygen history from Phanerozoic to Pleistocene glacial cycles: insights from the carbonate iodine-to-calcium proxy

by

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Chapter 1

Late inception of a resiliently oxygenated upper ocean

Chapter 1 has been published as:

Abstract

Rising oceanic and atmospheric oxygen levels through time have been crucial to enhanced habitability of surface Earth environments. Few redox proxies can track secular variations in dissolved oxygen concentrations ([O₂]) around threshold levels for metazoan survival in the upper ocean. We present an extensive compilation of iodine to calcium ratios (I/Ca) in marine carbonates. Our record supports a major rise in atmospheric pO₂ at ~400 million years ago (Ma), and reveals a step-change in the oxygenation of the upper ocean to relatively sustainable near-modern conditions at ~200 Ma. An Earth system model demonstrates that a shift in organic matter remineralization to greater depths, which may have been due to increasing size and biomineralization of eukaryotic plankton, likely drove the I/Ca signals at ~200 Ma.

Main Text

The evolution and survival of marine animals depends on oxygen availability, particularly in upper ocean waters – ranging from the sea surface to the thermocline – during early Earth history (1). The [O₂] in the upper ocean commonly decreases from the well-mixed surface ocean (top few tens of meters) into deeper subsurface waters (a few hundred meters). This [O₂] gradient is controlled by three key factors: (i) the partial pressure of oxygen in the atmosphere (pO₂), (ii) the intensity of upper ocean mixing and (iii) oxidation of organic matter in the water column which consumes oxygen (2). Atmospheric pO₂ changes through time have been estimated via geochemical proxy data and box models (3). Oceanic paleo-redox proxies typically track the areal extent of euxinic waters (containing H₂S) and the presence/absence of anoxia (positive/zero [O₂]) (4, 5). Since most modern marine animals
are sensitive to \([O_2]\) changes between \(~10 \text{ and } 100\) mol/kg (2), development of long-term proxy reconstructions for \([O_2]\) in this critical range (oxic–hypoxic) would help elucidate when and how oceanic oxygenation evolved to accommodate the modern ecological landscape.

Carbonate I/Ca is one of the novel proxies developed for the oxic–hypoxic window with the potential to reconstruct secular trends in upper-ocean oxygenation (6, 7). The long residence time of iodine (~300 kyr) leads to generally uniform total iodine concentrations in the modern ocean, but speciation changes of iodine between iodate (IO\(_3^-\)) and iodide (I\(^-\)) are controlled locally (8, 9). IO\(_3^-\) is completely reduced to I\(^-\) in waters at low \([O_2]\) (8, 9) and re-oxidized under well-oxygenated conditions. Since IO\(_3^-\) is the only chemical form of iodine incorporated into the carbonate structure (7) by replacing the CO\(_3^{2-}\) ion (10), carbonate I/Ca records of local seawater [IO\(_3^-\)] through time can indicate changes in \([O_2]\). Carbonate I/Ca has been shown to be a reliable tracer responding primarily to \([O_2]\) variations in marine environments over a wide range of geological periods (6, 11-16).

We measured I/Ca in an extensive Phanerozoic collection of shallow marine carbonates likely forming within the top 200 m of the water column and compiled them with published data (Table S1 and Fig. 1A). Maximum I/Ca values for individual localities were generally low in the Proterozoic, except for periods which have been associated with potential atmospheric \(pO_2\) rises [e.g., the Great Oxidation Event (12) and some Neoproterozoic carbon isotope excursions (11, 15), when maximum values temporarily increased to Cenozoic levels (3–4 mol/mol) (Fig. 1A). Paleozoic maximum values are comparable to those of the Proterozoic, despite a relatively short spike during the Devonian, at approximately 400 Ma,
when the 75\textsuperscript{th} percentile values reached Cenozoic levels. Break point analyses indicate a step-change at Triassic to early Jurassic (~200 Ma, Fig. S1), after which maximum values remain above 4 mol/mol and 75\textsuperscript{th} percentile values are mostly higher than 3 mol/mol (6, 13). The Devonian I/Ca excursion and the step-change at ~ 200 Ma are two key observations in this data compilation.

The stark contrast between predominantly low Paleozoic values and high Meso-Cenozoic values (excluding the Triassic, i.e., <200 Ma) cannot be explained by sampling biases. The sample size for the Paleozoic (n = 894) is comparable to that for the Proterozoic (n = 1078) and the Meso-Cenozoic (n = 926). The sampling density (number of samples per unit time) is similar in the Paleozoic and Meso-Cenozoic, although lower in the Proterozoic (Fig. 1B). For Paleozoic samples, we targeted carbonate- and fossil-rich (shallow) continental-shelf locations, i.e., relatively well-oxygenated settings, which are prone to record high I/Ca values. By contrast, many Mesozoic data were generated from sections recording well-established global oceanic anoxic events (OAEs), which, if anything, would bias that dataset toward low values. Cenozoic I/Ca values were measured in sediment coarse fraction, which may better preserve primary I/Ca signatures than bulk-rock samples. Existing early Cenozoic (14) and Cretaceous I/Ca data (13) are generally comparable across different lithologies, although comparisons between the Cenozoic and other periods are more tenuous. The current data set has relatively denser sample coverage for intervals coinciding with Earth-system perturbations (e.g., major carbon-isotope excursions and mass extinctions) than for extended intervals with limited environmental changes, but this should not influence main features of the data compilation.
I/Ca values can potentially be reduced during subaerial exposure, marine burial and dolomitization, but no post-depositional alterations are known to increase I/Ca (I1). A variety of diagenesis indicators were considered in previous studies of samples that we used here (7, 15-17). In all of those case studies, the number of potentially altered samples was limited and did not influence the central trend of the majority of the data through time, as represented by the 25th and 75th percentile values (Fig. 1A). High I/Ca values throughout the record (Fig. 1A) are not consistently tied to a specific inferred primary carbonate mineralogy (e.g., calcite vs aragonite seas, Fig. S2A). The distinct behaviors of I/Ca before and after ~200 Ma (Fig. 1A) cannot be explained by secular changes in seawater [Ca$^{2+}$] (Fig. S2B). No evidence suggests that differences in Paleozoic and Mesozoic I/Ca distributions were due to uniformly greater alteration of the Paleozoic samples (Fig. S3). Lower relative standard deviations (RSD) of neighboring samples in each section (i.e., smoother I/Ca profiles; Fig. S4) may reflect better preservation of the Paleozoic than the Proterozoic samples (Fig. S4).

We interpret I/Ca in marine carbonates primarily as a qualitative indicator for the depth of the oxycline (Fig. 2), i.e., that part of water column where the [O$_2$] decreases relatively abruptly. Carbonate rocks formed in the upper ocean record surface or near-surface seawater [IO$_3^-$], which is strongly affected by the presence/absence of a proximal oxygen minimum zone (OMZ) or a shallow oxycline. Due to the relatively slow oxidation kinetics of I (I8), surface waters may retain a low iodate signal despite high *in situ* [O$_2$] levels. For instance, core-top (modern) planktonic foraminiferal shells exhibit low I/Ca values (~0.5 mol/mol) in waters above a shallow OMZ in the equatorial Pacific, but record higher values (>3 mol/mol) at other well-oxygenated locations (6).
The large I/Ca excursion during the Devonian (Fig. 3) most likely reflects deepening of the oxycline and development of better oxygenated conditions in the upper ocean, consistent with published proxy data and modeling results (4, 5, 19, 20). Although different box models yield somewhat divergent interpretations of atmospheric $pO_2$ variation through the Phanerozoic (21-24), a Devonian rise in $pO_2$ levels is plausible, based on the COPSE model and charcoal proxy reconstructions (Fig. 3A), and was most likely due to increased abundance of vascular land plants (19, 20). Previous work interpreted $^{98}$Mo, iron-speciation and biological data (Fig. 3C) to reflect oceanic redox changes, supporting the idea of atmospheric $pO_2$ rise during the Devonian (4, 5). The combination of these independent proxies indicates that the Devonian atmospheric $pO_2$ rise impacted the whole atmosphere-ocean system, across the entire redox spectrum (Fig. 3).

I/Ca values returned to Proterozoic-like levels following the transient Devonian excursion, but there is no evidence for a $pO_2$ decrease to pre-Devonian levels between the Carboniferous and the Triassic. Instead, the post-Devonian atmosphere was probably relatively O$_2$-rich (Fig. 3A). High atmospheric $pO_2$ likely altered terrestrial weathering feedbacks and enhanced nutrient delivery to the ocean (25, 26), leading to intensified O$_2$ consumption in the upper ocean, a generally shallow oxycline, and low I/Ca values between ~400 and 200 Ma (Fig. 3B). Under such conditions, carbonates formed in surface-oceans rapidly equilibrated with the high-$pO_2$ atmosphere would record low in situ [IO$_3^-$] due to the slow oxidation of I during mixing between surface and subsurface waters (Fig. 2B). If the oxycline were indeed shallow, marine animals on continental shelves at that time (~ 200-400 Ma) would have been living in a thin layer of well-oxygenated surface water directly
underlain by an OMZ (Fig. 2B). Our dataset (Fig. 1A) implies that well-oxygenated upper-ocean conditions became persistent and resilient only by the Triassic-Jurassic (~200 Ma), much later than previously inferred (27). The prerequisites for achieving such well-oxygenated upper-ocean conditions are a combination of high atmospheric $pO_2$ and a generally deep oxycline (Fig. 2C). The position of the oxycline is strongly controlled by the depth of organic-matter remineralization, which is dependent on the efficiency of organic-matter export from the photic zone, and has been proposed as a governing parameter for OMZs during the Phanerozoic (28).

We hypothesize that changes in remineralization of organic matter strongly influenced the upper-ocean I/Ca signature (Fig. 2), and we tested this hypothesis by simulating the marine iodine cycle in the ‘cGENIE’ Earth system model (see Methods, Fig. S5) (29). We aimed to identify possible causes for low I/Ca during the Paleozoic through ensembles of model runs using a range of values for atmospheric $pO_2$, the depth of organic-matter remineralization in the water column, and the mean concentrations of iodine and phosphate in seawater. For each Paleozoic model run, surface-water [IO$_3^-$] values along continental margins were extracted to calculate a relative frequency distribution (Fig. S6). The modeled IO$_3^-$ distributions were compared with observed Paleozoic I/Ca distributions (Fig. 1C) to obtain the residual sum of squares (RSS) (see Materials and Methods, Fig. 4A and Fig. S7).

We found that the lowest RSS values (<0.05), representing the best data-model fits, were achieved at shallow remineralization depths [i.e., <0.5 present oceanic level (POL)]. In the same set of cGENIE runs (Fig. 4B), lower RSS values correlated with lower average $[O_2]$ in the subsurface layer (80-176 m), which is consistent with a shallower oxycline. Even as
Paleozoic oceans experienced transitions between greenhouse and icehouse climate conditions, $p$CO$_2$ levels appear to have had minimal influence on IO$_3^-$ distributions (Fig. S8). Global-scale changes in ocean circulation and continent configuration also do not significantly influence the oxycline depths independently of $p$O$_2$ and subsurface oxygen consumption (Fig. S9). The RSS contours differed only slightly when the Paleozoic I/Ca distribution was compared with modeled [IO$_3^-$] distributions in the top four layers in the upper ocean (from 0 to 410 m, Fig. S10). Thus, a lack of precise constraints on the paleo-depths of carbonate formation is unlikely to have affected the main conclusions of our data–model comparison. Additional model runs also suggest that oceanic nutrient levels and total iodine concentrations are unlikely to dominate the secular trends in proxy data (Fig. S11-12). Our data-model comparison (Fig. 4A) should not be viewed as a precise estimate of the atmospheric $p$O$_2$ for any single time slice, since the data were compiled over the entire Paleozoic under varying $p$O$_2$ levels. Thus, the lower RSS values at $p$O$_2$ below 1 PAL suggest that some portions of the Paleozoic may have had $p$O$_2$ levels lower than today (5, 23).

Based on our data compilation and model analyses, we attribute the transition at ~200 Ma from Proterozoic-like low I/Ca values in the Paleozoic (except for the mid-Devonian) to modern-like high values in the Meso-Cenozoic, to a profound increase in the average remineralization depth of organic matter in the water column. The timing of this transition is consistent with the proliferation of eukaryotic phyto- and zooplankton after the Permian-Triassic extinction (Fig. 3A)(30, 31), which eventually shaped the ecological landscape of the modern ocean (32). The larger size of primary producers (33), grazing/repackaging of organic matter into fecal pellets (34), and/or the advent of mineralized
plankton (32) may have led to faster sinking of organic matter, which reduced O₂ utilization in the upper water column and caused a pervasive deepening of the oxycline (28).

The rise of oxygen levels over geological time has been linked to increases in animal body size (24, 35). A comprehensive compilation of Phanerozoic marine animal body-size data (36) shows that maximum bio-volume probably co-varied with I/Ca to some extent (Fig. 3B), indicating that O₂ availability in the global upper ocean may have been an important factor in Phanerozoic metazoan evolution. New forms of organisms (e.g., mineralized plankton, larger animals) fundamentally influenced oceanic environments, which in turn affected the evolving biosphere, representing a prime example of the co-evolution of life and planet.
**Figure 1. Carbonate I/Ca through time.** A. Candlestick plot showing ranges of I/Ca values for Proterozoic (red) (11, 15), Paleozoic (blue) and Meso-Cenozoic (purple). Boxes mark the 25th and 75th percentiles of values at each locality, and the whiskers show the maximum and minimum. Note that the Proterozoic values from dolostones are I/(Mg+Ca). B. Number of samples measured at each section. C. Relative frequency distributions of I/Ca.
Figure 2. Schematic illustrations for the evolution of oxygenation conditions. These simplified cartoons are not intended to capture all temporal and spatial variations.
Figure 3. Phanerozoic I/Ca compared with atmospheric $pO_2$, oceanic oxygenation and animal evolution trends. A. Modeled atmospheric $pO_2$ curves (5, 21, 23, 24) in comparison with the charcoal proxy record (20). Dashed lines (5) mark a broadly defined ocean-atmospheric $O_2$ level, not just atmospheric $pO_2$. B. I/Ca records through Phanerozoic.
Blue boxes for bulk carbonate rock, gray boxes for bulk coarse fraction of Ocean Drilling Project samples (>63 μm). C. Marine animal body size record (36). Thickness of green bars indicates relative generic diversity modified from literature (31, 32). The red vs blue bars mark greenhouse vs icehouse climate conditions, respectively.
Figure 4. Residual sum of squares (RSS) and subsurface $[O_2]$ at different $pO_2$ levels and remineralization depths. A. Shallow remineralization depths (POL for present oceanic level) produce the best model fit (the smallest RSS < 0.05) to Paleozoic I/Ca distribution, at 1× CO$_2$ condition. White dots represent 45 cGENIE simulations defining the contours. B. Averaged $[O_2]$ in the shallowest subsurface layer in each cGENIE run as an indicator of oxycline depth correlating with the RSS.
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**Competing interests:** The authors declare that they have no competing interests. **Data and materials availability:** all I/Ca data are available in the supplementary materials and online from [https://www.pangaea.de/](https://www.pangaea.de/).

**Supplementary materials**

Materials and Methods

Figures S1 to S12

Captions for Tables S1 and S2

References (37-51)

Tables S1 and S2
Supplementary Materials and Methods

I/Ca analyses

Bulk carbonate samples were crushed and homogenized to fine powder. Cenozoic sediment samples were wet sieved at 63 µm to obtain coarse-fraction samples (mostly foraminiferal tests), then crushed to powder. About 4 mg of powder from each sample were weighed and thoroughly rinsed with de-ionized water. 3% nitric acid was added for carbonate dissolution, and 0.1% tertiary amine solution was added to stabilize iodine. Iodine and calcium concentrations were then measured on a quadrupole inductively coupled plasma-mass spectrometer (ICP-MS) at Syracuse University. Iodine calibration standards were prepared daily from KIO₃ powder. The sensitivity of iodine was tuned to ~80 kcps for a 1 ppb standard. The precision for $^{127}$I is normally better than 1%. The reference material JCp-1 was measured repeatedly to maintain long-term accuracy. The detection limit of I/Ca is approximately 0.1 µmol/mol.

Earth system modeling

We employ the ‘cGENIE’ Earth system model comprising a 3-D dynamic ocean circulation model with simplified energy-moisture balance atmosphere, and biogeochemical cycling of elements and isotopes in the ocean (29). This model has been extensively evaluated against modern observations of nutrients, oxygen, and carbon (29, 37, 38). We introduced new tracers for dissolved IO₃⁻ and I⁻, iodine associated with particulate organic matter, and a set of transformations between them. We simulated four steps in iodine cycling in the water column that are most relevant to I/Ca. (1) Iodate is taken up by export production from surface water with a fixed iodine to organic carbon (I:C) ‘Redfield’-like ratio (39). (2)
In the reverse process – the remineralization of organic matter back to dissolved constituents – we release iodine back into solution in the form of iodide. (3) In subsurface waters, when \([O_2]\) falls below a specified threshold, \(\text{IO}_3^-\) is reduced to \(\Gamma\). (4) Finally, we parameterize the oxidation of iodide to iodate according to a prescribed lifetime. Some of these processes are associated with significant uncertainties, e.g. the lifetime of iodide in oxic seawater (18).

In a series of 10-kyr-long model runs to steady state, the iodine cycle was then calibrated to the modern sea-surface iodate distribution to determine the \([O_2]\) threshold for complete \(\text{IO}_3^-\) reduction and \(\Gamma\) oxidation kinetics (iodide lifetime) (Fig. S5). For this data-model comparison, we calculated the residual sum of square (RSS) as follows:

\[
\text{RSS} = \sum_{i=1}^{n} (F_i - \hat{F}_i)^2
\]

where \(F_i\) is the relative frequency of \(i^{th}\) bin of measured data, and \(\hat{F}_i\) is the corresponding relative frequency of \(i^{th}\) bin of cGENIE results. Modern sea-surface iodate data (18) are distributed in 21 bins beginning at 0 and ending at 1.05 with bin size of 0.05. These parameter settings were then applied to model Paleozoic scenarios, for which we adopted a published end-Permian configuration (28) to represent average Paleozoic conditions. For data-model comparisons in our paleo experiments, I/Ca data are distributed in 24 bins beginning at 0 and ending at 12 with bin size of 0.5. Model results for the Paleozoic only use surface-water \([\text{IO}_3^-]\) along continental margins (Fig. S6). For testing the paleo-environmental parameters, we allowed each ensemble to have 45 runs and two varying parameters. Preliminary experiments show that \(pO_2\), remineralization depth, and \([\text{PO}_4]\) are the most important parameters for \([\text{IO}_3^-]\) distribution patterns and, hence, for I/Ca ratios. Iodine
inventory changes in the model do not produce $[\text{IO}_3^-]$ distributions resembling the Paleozoic I/Ca distribution and were therefore not tested in an ensemble.
Fig. S1. Break point analyses (40). We used a maximum likelihood approach, via the R package ‘segmented’ version 1.4 to estimate the breakpoint time of I/Ca shift. Our analysis used an initial linear model of the I/Ca as a function of approximate sample age (Ma), to generate the best-fit number of breakpoints and fit separate regression lines to each segment. We performed a bootstrap of 1,000 replicates to estimate uncertainty in model parameters and age at which the breakpoint(s) occur. The result shows that the I/Ca shift began at 235 Ma. We further did a series of sensitivity tests by performing the same analysis while removing the data from a few different sections in each sensitivity test. The break point age could vary between 190 and 250 Ma, which suggest that we do not have sufficient data coverage to narrow down this age. Therefore, we refer to a generic number “~200 Ma” in the main text.
Fig. S2. A. I/Ca values in aragonite–calcite seas. No consistent association between high I/Ca values and carbonate mineralogy is observed (41). Proterozoic high I/Ca values were found more often in intervals characterized by aragonite seas, whereas the Phanerozoic high I/Ca values appear more frequently in intervals characterized by calcite seas. This pattern is the opposite of that predicted if diagenetic recrystallization of aragonite to calcite in reducing pore fluids were the main control on I/Ca through time. B. Secular changes in seawater [Ca$^{2+}$] can influence carbonate I/Ca trends, in addition to oxygenation conditions. Iodate substitution in calcite (10) probably involves a double substitution, e.g. $\text{IO}_3^- + \text{Na}^+ \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}$. Therefore, corrections to I/Ca should be based on $[\text{Ca}^{2+}] \times [\text{CO}_3^{2-}]$, instead of based on $[\text{Ca}^{2+}]$. Blue dots show the uncorrected 75th percentile values through the Phanerozoic, as in Figure
3B. Black diamonds show I/Ca corrected to modern seawater [Ca$^{2+}]$×[CO$_3^{2-}$] using Phanerozoic seawater [Ca$^{2+}$] estimates derived from Ca-isotope data (42) and [CO$_3^{2-}$] estimates from modeling (43). The gray band brackets the maximum and minimum of corrected 75th percentile values based on four different paleo-seawater [Ca$^{2+}$] reconstructions (42, 44-46). Such corrections may improve the qualitative secular trend of I/Ca, but do not necessarily produce more reliable absolute values of I/Ca, because iodate substitution kinetics and partition coefficients may change in a non-linear fashion relative to [Ca$^{2+}]$×[CO$_3^{2-}$]. Thus, this correction procedure can only qualitatively test first order impacts of seawater chemistry on the Phanerozoic I/Ca record.
**Fig. S3.** $R^2$ of the correlation between $\delta^{13}C_{\text{carb}}$ and $\delta^{18}O_{\text{carb}}$ for each study section plotted against its range of I/Ca values. Higher $R^2$ indicate a greater possibility of diagenetic alteration. All known diagenetic alteration processes would decrease I/Ca ratios or have no effects. No evidence here indicates that the low I/Ca values of Paleozoic samples are due to significantly poorer preservation relative to Mesozoic samples.
**Fig. S4.A.** Histograms for relative standard deviation (RSD) of I/Ca values in every three neighboring samples of each section. Low RSD values are much more frequently observed in the Paleozoic samples than in Proterozoic samples. **B.** Paleozoic profiles are often smoother than Proterozoic profiles, as shown in some examples for the low RSD values indicating better preservation in Paleozoic samples. Note that these selected profiles are used to demonstrate the source of low RSD values in Paleozoic samples, but not all Paleozoic profiles are smoother than all Proterozoic profiles. The lower RSDs of Mesozoic-Cenozoic samples compared to Paleozoic samples are likely due to higher absolute I/Ca values for Mesozoic-Cenozoic samples.
Fig. S5. A. Residual sum of squares (RSS) between cGENIE results and modern sea-surface iodate distributions to determine the $[O_2]$ threshold for complete IO$_3^-$ reduction to I$^-$ and iodide lifetime. Simulations employed a modern configuration. The black circle represents the selection of iodide lifetime of 40 years and $[O_2]$ threshold of 30 µmol/kg. These parameter values are used for all of the following model runs. Note that a lifetime of 50 years produced the lowest RSS, but the maximum lifetime in the literature is 40 years (18).
Consequently, this value is adopted for Paleozoic model runs. **B.** Relative frequency distribution of modern sea-surface iodate (µM) ($I\delta$) vs cGENIE results (40 years iodide lifetime and 30 µmol/kg [O$_2$] threshold). **C.** Surface-water iodate map simulated with these settings.
**Fig. S6.** A. Modeled surface-ocean $[\text{IO}_3^-]$ map with the lowest RSS (0.01), which is the best fit to Paleozoic I/Ca data. The simulation employed an end-Permian geographic configuration, and $0.5 \times \text{O}_2$, $8 \times \text{CO}_2$, $0.1 \times$ remineralization depth, $1\times [\text{PO}_4]$, $1\times$ Total iodine, iodide lifetime of 40 years and 30 μmol/kg $[\text{O}_2]$ threshold. B. All Paleozoic surface-ocean $[\text{IO}_3^-]$ data generated within the purple shaded fields were treated as continental-margin locations. They were extracted to compute frequency distributions and RSS values.
Fig. S7. Examples of modeled continental surface-ocean iodate histograms to illustrate low, medium, and high RSS values. All simulations employed an end-Permian geographic configuration, modern-level [PO₄] and total iodine, an iodide lifetime of 40 years, and a 30 µmol/kg [O₂] threshold. eL1 denotes remineralization depth.
**Fig. S8.** Shallow remineralization depths produce the best model fit to Paleozoic I/Ca distributions regardless of atmospheric $pCO_2$ levels (Fig. 4).
**Fig. S9.** Model-based analysis of the influence of changing continental configuration and climate on the oxycline. Panels A-E are the continental configurations and bathymetry for the 5 experiments. F-J show the zonal mean distribution of dissolved oxygen in the ocean, overlain for illustration with the global overturning stream-function (solid contours representing positive, clockwise overturning circulation, and dashed contours anticlockwise circulation). Panels K and L summarize the global mean distribution of dissolved oxygen, as absolute values (K) and anomalies (L) relative to mean modern surface dissolved oxygen concentrations in the model.

We used a suit of previously published continental and climate configurations for modern and the past (29, 37), the late Paleocene/early Eocene (55 Ma) (47), the end Cretaceous (67 Ma) (48), the mid Cretaceous (97 Ma) (49), and the late Permian (251 Ma) (28). These configurations encompass continental configurations ranging from the Pangea supercontinent (late Permian) to highly dispersed (modern), atmospheric CO$_2$ varying from 278 ppm (modern) through 2,800 ppm (late Permian), and sea level stand from low (modern and late Permian) to high (mid Cretaceous). We hence are testing a reasonably full range of potential states of ocean circulation. In order to remove effects of changing atmospheric oxygen and organic matter remineralization (the two key controls we explore in the paper in order to explain the I/Ca data), we keep atmospheric O$_2$ fixed in the model at modern concentrations, and the remineralization depth of organic matter fixed and according to the modern calibration in cGENIE (37). In addition, we employ a surface ocean PO$_4$-restoring scheme in which organic matter export is diagnosed according to a relaxing of surface ocean PO$_4$ concentrations towards zero. We do this in order to achieve an approximately constant
global export of organic matter across all the experiments (and indeed find that the range is relatively restricted – ranging from 8.8 PgC yr\(^{-1}\) (0 Ma) to 10.0 PgC yr\(^{-1}\) (251 Ma)). Hence, across all the modern configurations the total ocean oxygen consumption will be approximately equal and the only fact that can significantly influence the shape of the oxycline is ocean circulation and mixing. We run all experiments for 10 kyr to steady state. It can be seen that the slope of dissolved oxygen against depth – the steepness of the oxycline, is approximately invariant across all configurations (panels K, L). The only minor differences are in the apparent depth of the base of the oxycline, with the configuration from 251 Ma showing a very slightly deeper (no more than a few 100 m) point at which the rate of decline of dissolved oxygen with depth starts to flatten out. From this we conclude that on a global scale, the only factors that would substantially affect the slope and/or depth of the oxycline through time will be the organic carbon remineralization depth (28) and atmospheric oxygen.
**Fig. S10.** [IO$_3^-$] distributions in the top four layers of ocean waters in cGENIE compared with Paleozoic I/Ca distributions, showing similar RSS patterns.
Fig. S11. A. High phosphate concentrations in seawater required to produce low RSS would result in widespread anoxia in deep oceans. Two red dots in RSS contours mark the $pO_2$ and $[PO_4]$ settings corresponding to the two deep-ocean $[O_2]$ maps below. B. Shallow remineralization depth produces good data–model fit and well-oxygenated deep oceans. In addition to remineralization depths, $[IO_3^-]$ distributions can be affected by the ocean $PO_4$ inventory, which influences productivity and oxygen consumption in subsurface waters. Increasing $[PO_4]$ in seawater up to 2.5 POL reduces RSS values, but triggers anoxia in the deep ocean, which is inconsistent with generally stable $^{98}$Mo values since 400 Ma (50). By contrast, model runs with shallow remineralization depths can produce a similar range of RSS values while maintaining oxygenated deep-ocean conditions. Furthermore, there is no independent proxy evidence for a step-wise decrease in seawater $[PO_4]$ at ~200 Ma to account for the observed I/Ca increase.
Fig. S12. Surface-ocean iodate IO$_3^-$ distributions with decreasing ocean iodine inventory. These frequency distributions do not reproduce the lognormal type of distribution as observed in Paleozoic I/Ca data. Modern fluxes of iodine input and output from seawaters may be orders of magnitude lower than that of iodine recycling in the water column (7). IO$_3^-$ (instead of I$^-$) sorption on organic matter at the sediment-water interface is a major sink of iodine, which appears to be stabilized by a negative feedback between the amount of organic matter as a substrate on the seafloor and bottom-water oxygenation preventing IO$_3^-$ reduction (51). No evidence supports either global organic matter burial rate or bottom water [O$_2$] level mimicking the I/Ca record. Therefore, secular changes in total iodine concentration are also unlikely to dominate the trends observed in our I/Ca record.
References


Chapter 2

Refining the planktic foraminiferal I/Ca proxy: results from the Southeast Atlantic Ocean

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Abstract

Profound changes in upper ocean oxygenation have taken place in recent decades and are expected to continue in the future, but the complexity of the processes driving these changes has yet to be fully unraveled. Planktic foraminiferal I/Ca is a promising tool to reconstruct the extent of past upper ocean oxygenation, but a thorough assessment is necessary to evaluate both its potential and its limitations. We used foraminifers from Holocene core-tops (Southeast Atlantic Ocean) to document planktic I/Ca across a range of oceanographic conditions. We conclude that subsurface O$_2$ concentrations may be the dominant control on planktic foraminiferal I/Ca from core-tops, because planktic I/Ca decreases rapidly at low O$_2$ conditions (O$_2$ < ~70–100 µmol/kg). We thus document that low planktic I/Ca can be used empirically to indicate hypoxia in the upper water column, but questions remain as to the mechanistic understanding of the relation between seawater iodine speciation change, its O$_2$ threshold and foraminiferal I/Ca. Planktic I/Ca records from core GeoB1720-2 (Benguela Upwelling System, SE Atlantic) suggest that hypoxic waters were present near the site persistently during the last 240 ka, without clear glacial-interglacial variability.

1. Introduction

The carbonate I/Ca proxy as used on planktic foraminifera has great potential to reconstruct upper ocean oxygenation changes, for which few proxies are available (Hoogakker et al., 2018; Lu et al., 2018; Lu et al., 2016). Inorganic iodine in the oceans exists as two thermodynamically stable species: iodate (IO$_3^-$, oxidized form) and iodide (I$^-$, reduced form), and the equilibration between the two species is highly redox-sensitive. Iodate is
completely reduced to iodide in anoxic waters, and re-oxidized under well-oxygenated conditions (Rue et al., 1997). Only IO$_3^-$ is incorporated into the calcite structure (Lu et al., 2010) by substituting for the CO$_3^{2-}$ ion (Feng and Redfern, 2018; Podder et al., 2017). Higher foraminiferal I/Ca values thus generally record higher IO$_3^-$ concentrations in seawater, and therefore indicate better-oxygenated water conditions. Planktic foraminiferal I/Ca has been shown to primarily record upper ocean oxygenation (Hoogakker et al., 2018; Lu et al., 2016; Zhou et al., 2014). A threshold value (I/Ca < ~2.5 µmol/mol) was proposed to indicate low O$_2$ upper ocean waters, based on a limited number of globally-distributed core-top foraminiferal samples (Lu et al., 2016). We collected more core-top data to further elucidate the behavior of I/Ca across different oxygenation windows: anoxic (O$_2$ = 0), suboxic (O$_2$ < 10 µmol/kg), hypoxic (O$_2$ < ~70–100 µmol/kg), and oxic (O$_2$ > 100 µmol/kg).

Planktic I/Ca and bulk sediment nitrogen isotopes (δ$^{15}$N) both have been used to indicate low O$_2$ conditions in the upper water column. One of the motivations of this study is to compare and differentiate the behavior of planktic I/Ca and bulk δ$^{15}$N across hypoxic and suboxic windows. In suboxic waters (e.g., eastern tropical Pacific and Arabian Sea), water column denitrification preferentially removes $^{14}$N, leaving the residual nitrate enriched in $^{15}$N, thus bulk δ$^{15}$N is interpreted to reflect the relative degree of water column denitrification under suboxic conditions (Altabet et al., 1999; Galbraith et al., 2013; Robinson et al., 2009). In areas of incomplete nitrate consumption on surface waters (e.g., high nutrient regions), bulk δ$^{15}$N signals are generally thought to reflect relative degrees of nitrate utilization by the phytoplankton community (Galbraith and Jaccard, 2015; Galbraith et al., 2008; Pichevin et al., 2005b). Therefore, a study of planktic foraminiferal I/Ca in low oxygen regions of the
Atlantic where there is no water column denitrification should provide new insights into these two oxygen proxies targeting a similar part of the water column.

Ocean deoxygenation has been observed in large areas of the Southeast Atlantic Ocean in the past five decades (Schmidtko et al., 2017). Previous studies reconstructed glacial-interglacial histories of sea surface temperature (SST) (e.g., Farmer et al. (2005); Mollenhauer et al. (2003); Pichevin et al. (2005a)) and primary productivity (e.g., Mollenhauer et al. (2002); Romero et al. (2015)), but few studies focused on reconstructing water column oxygenation (e.g., McKay et al. (2016)). Information on glacial-interglacial changes in oceanic oxygenation may help inform us on the extent of and controls on potential future ocean deoxygenation.

We report I/Ca data on eight planktic foraminiferal species (depth habitats from near-surface to the thermocline) in 19 core-tops from the Southeast Atlantic Ocean (Southwest African margin, Fig. 1). We aim to better constrain the signal of planktic foraminifera I/Ca in hypoxic as compared to suboxic hydrographic regimes. In addition, we show a downcore I/Ca record of GeoB1720-2 (28°59’S, 13°50’E, 1997 m) within the Benguela Upwelling System (BUS), and compare it to a bulk sediment δ¹⁵N record from the BUS (Pichevin et al., 2005b) to reconstruct the upper water column conditions over the last two glacial cycles.

2. Samples and Methods

2.1. Study site

The Southeast Atlantic Ocean is a region with severe low oxygen conditions linked to upwelling of nutrient rich waters and the resulting high productivity, particularly in the BUS
The BUS is bounded to the North by the Angola-Benguela frontal zone (between 14 and 17°S), to the South by the Agulhas retroflection (around 37°S) (Shannon and Nelson, 1996), and is one of the most highly productive regions in the world oceans. Wind-driven upwelling of nutrient-rich waters along the west coast of southern Africa is important for marine biodiversity and food production (Chapman and Shannon, 1985; Jarre et al., 2015). Mutually inconsistent observations have been made indicating the occurrence of (Hutchings et al., 2009) or lack of (Pitcher et al., 2014) long-term oxygen decline in the coastal waters in the BUS since the 1960s.

Shelf water along the west coast of southern Africa commonly contains low dissolved O$_2$ (e.g., < 2 ml/l, approximately < 90 µmol/kg), and the O$_2$ concentrations vary significantly spatially (Fig. 1, 2). Upper ocean waters close to the southwest African coast are affected by both the southward Poleward Undercurrent (PUC), down to 200 m depth along the shelf break, and by the northward Benguela Current, further offshore, down to 1200 m depth. The Benguela Current forms the eastern limb of the South Atlantic gyre, and contains water from the South Atlantic Current with additional inputs of warm, salty Indian Ocean water from the Agulhas Current (Stramma and England, 1999). The PUC originates from the Equatorial Undercurrent and the Angola Gyre, and transports low oxygen waters southward along the shelf north of 27°S (Fig. 1). The low O$_2$ conditions of the BUS in the coastal area between 30°S and 34°S are most likely due to local decomposition of organic matter (Chapman and Shannon, 1985) (Fig. 1, 2).

Site GeoB1720-2 is located on the Southwest African slope within the northward path of the Benguela Current (Fig. 1, 2). The upper ocean hydrography over this site is affected by
the upwelling of South Atlantic Central Water close to the African coast, Agulhas leakage of tropical Indian Ocean waters, and subantarctic waters from large-scale eddy mixing at the subtropical front (~42°S) (Dickson et al., 2010; Stramma and England, 1999).

2.2. Samples materials

A total of 19 core-top samples were obtained from the upper 5 cm of cores from the Lamont-Doherty Core Repository (Table S1). The core-top sediments were wet-sieved to the >63 µm fraction with MilliQ water, then oven-dried at 40°C. Specimens from eight planktic foraminiferal species (Globigerinoides ruber, Neogloboquadrina incompta, Globigerina bulloides, Globorotalia truncatulinoides (sinistral and dextral), Globigerinoides sacculifer, Globorotalia inflata, Neogloboquadrina dutertrei, and Globorotalia menardii) were picked, and 25-80 individuals from the 150-300 µm size fraction were used for I/Ca analyses. Two species, G. truncatulinoides (sinistral) and N. incompta, were picked from sieved sediments from core GeoB1720-2. Around 25 specimens of G. truncatulinoides (sinistral) and ~80 specimens of N. incompta from 150-300 µm size fraction were used for I/Ca analyses.

2.3. Age model

Radiocarbon dating of the planktic foraminifer G. inflata from selected samples shows a Holocene age (Table S1). Radiocarbon was analyzed at the Keck Carbon Cycle AMS Facility at University of California, Irvine. The age model of core GeoB1720-2 is based on nine AMS 14C dates between 0 and 200 cm depth for the planktic foraminifer G. inflata (Dickson et al., 2009), and is extended down-core by tying the N. incompta δ18O stratigraphy to the global benthic foraminiferal δ18O stack (Lisiecki and Raymo, 2005) between 200 and 900 cm depth
(Fig. S1 and Table S2), assuming the GeoB1720-2 δ¹⁸O record can be correlated to the global stack. The *N. incompta* δ¹⁸O data for core GeoB1720-2 are here first reported. They were measured on the 150 – 250 μm size fraction from homogenized sample sizes of ~20 individuals on a Thermo MAT Delta V Advantage mass spectrometer coupled to a Kiel Device at the Department of Earth Sciences, University of Cambridge, and the Department of Physical Sciences, The Open University. Calibration to Vienna Pee Dee Belemnite was via NBS19 standards. Precision is ±0.1 ‰ (1 S.D.).

2.4. *Foraminiferal I/Ca analyses*

The foraminiferal I/Ca analytical methods follow Lu et al. (2016). The samples were gently crushed with cleaned glass slides to open all chambers of the tests. Samples were cleaned by ultrasonication in MilliQ water to remove clays, a 10-minute boiling-water bath in NaOH-buffered 1% H₂O₂ solutions to remove organic matter, and 3 additional rinses with MilliQ water. The cleaned samples were dissolved in 3% HNO₃, and diluted to solutions with ~50 ppm Ca for analyses. A 0.1% tertiary amine solution was added to stabilize iodine in solution. The measurements were performed immediately, to minimize potential iodine loss due to iodine speciation change and volatilization. The I/Ca analyses were performed on a quadrupole ICP-MS (Bruker M90) at Syracuse University. The sensitivity of I-127 is tuned to 100–120 kcps for a 1 ppb standard. The reference standard JCp-1 (I/Ca value of 4.27 μmol/mol) was analyzed repeatedly to monitor long-term accuracy (Lu et al., 2010). The detection limit of I/Ca is on the order of 0.1 μmol/mol. Replicates of selected *G. truncatulinoides* (sinistral) from core GeoB1720-2 yielded a reproducibility ranging from ±3%
(0.03 µmol/mol; 1σ) to ±10% (0.15 µmol/mol; 1σ) for I/Ca (Table S3).

2.5 Planktic foraminiferal habitat

Calcification depths where the average geochemical signal is locked into the planktic foraminiferal shell are usually estimated from comparison of $\delta^{18}O$ of foraminifera with that of equilibrium calcite, based on historical temperature and salinity data (Anand et al., 2003). Calcification depths for several of the species used in this study have been calibrated to depth habitats of ~100 m (summer) and ~80 m (winter) for N. incompta; and ~340 m (summer) and ~300 m (winter) for G. truncatulinoides (dextral) in multi-core GeoB1720-3 (28°59’S, 13°50’E, 2004 m) (Dickson et al., 2010). This core is located within a few meters of GeoB1720-2, thus the data are broadly applicable to our study region.

2.6 Hydrographic data

Oxygen data for core-top sites were obtained from high-resolution CTD profiles in the World Ocean Database (WOD) 2013 (https://www.nodc.noaa.gov/OC5/WOD/pr_wod.html) (Boyer et al., 2013) (Fig. 2a). We divided the studied area into three geographic regions: a tropical region at latitudes between 5°N and 15°S; a Southern BUS region at latitudes between 30°S and 35°S; and a Walvis Ridge region at latitudes between 23°S and 32°S (Fig. 2a). Many of the core-top samples are in areas with great spatial variability in O$_2$ conditions, thus we determined the minimum O$_2$ concentrations in the water column from the nearest location, and within an 0.25°×0.25° area of the core-top samples in WOD2013. Minimum O$_2$ in the water column is used because O$_2$ has to drop below a certain threshold to trigger iodate
reduction, recorded as low foraminiferal I/Ca (Lu et al., 2016). Minimum O$_2$ values generally occur in the bottom waters over the shelf, but are found in mid-water off the shelf. Minimum O$_2$ maps were produced using Ocean Data View’s gridding tool, and the individual minimum O$_2$ values were calculated using the statistics tool in that program (Schlitzer, 2018).

3. Results

Low core-top I/Ca values (< ~2.5 µmol/mol), regardless of species, are observed in the tropical and Southern BUS regions, which generally contain hypoxic waters at mid-depths or bottom depths (O$_2$ < ~70-100 µmol/kg) (Fig. 3 and 4). High core-top I/Ca values (> ~4 µmol/mol), regardless of species, are found in the Walvis Ridge region, where waters generally are well oxygenated (O$_2$ > ~100 µmol/kg).

We do not observe any consistent or systematic differences in I/Ca between symbiont-bearing species (G. ruber and G. sacculifer) and symbiont-barren species (G. menardii, N. dutertrei, N. incompta, G. bulldoides, G. inflata, G. truncatulinoides) within the same core-top sample (Fig. S2). At Southern BUS (low oxygen region), symbiont-barren species record slightly wider ranges of I/Ca and the average I/Ca of symbiont-barren species are lower than the average values of symbiont-bearing species in two out of three core-top samples. In the high oxygen Walvis Ridge region, I/Ca values in three out of four samples show similar ranges and variabilities in symbiotic vs. non-symbiotic species, except for one sample with notably smaller variability in symbiotic species.

Higher core-top I/Ca values are generally associated with higher O$_2$ conditions in the water column as estimated from the nearest site in the WOD2013 database (Fig. 5), consistent
with Lu et al. (2016). At three sites in the Southern BUS region (V19-238, V19-228, and V14-70, see Table S1 for details), however, high modern minimum O$_2$ concentrations (150–220 µmol/kg) apparently are associated with low I/Ca (< ~2 µmol/mol), but the O$_2$ values around these core-top sites are highly variable spatially (Fig. 2).

In the downcore record of GeoB1720-2, almost all G. truncatulinoides (sinistral) and N. incompta I/Ca values are < 2.5 µmol/mol during the last two glacial cycles (Fig. 6).

4. Discussion
4.1. Subsurface O$_2$ conditions

Measurements of the core-top samples in the Southeast Atlantic Ocean confirmed that low planktic I/Ca values can reveal the presence of low-O$_2$ waters in the upper ocean (Fig. 5c), as previously demonstrated (Lu et al., 2016). However, we also found high O$_2$ - low I/Ca values in the Southern BUS region (Fig. 5c), which may be explained by different scenarios: (1) O$_2$ values from the WOD2013 do not represent the actual conditions during foraminiferal growth, due to short-term or spatial variability of O$_2$; (2) the foraminifera calcified in high O$_2$ - low IO$_3^-$ water, due to slow kinetics of I$^-$ oxidation; (3) the planktic foraminifera lived at nearby locations with lower O$_2$ and were transported to their current sites (Fig. 2); (4) unknown factors are limiting IO$_3^-$ uptake by foraminifera at these sites.

Examining the first of these possibilities, hypoxic waters are common in the shelf areas of the BUS system and their extent and level of oxygen depletion vary spatially and on seasonal, interannual, and decadal timescales (Jarre et al., 2015). Significant vertical and seasonal changes in water column oxygen concentrations are more likely in the nearshore than in the offshore regions (Lamont et al., 2015; Pitcher et al., 2014). However, episodic
hypoxic conditions in the water column have been reported offshore of the BUS (Pitcher et al., 2014), and may provide low O₂ water at our core-top sites not captured in the WOD2013 dataset, which does not comprise seasonal or annual O₂ measurements in the Southern BUS region. The O₂ data in WOD2013 also span a considerable time period, representing an additional source of uncertainty. Thus the uncertainty arising from modern measurements of O₂ and its short-term variability may at least partially explain the high O₂ – low I/Ca cases in the Southern BUS region.

In addition, the high O₂ - low I/Ca cases in the Southern BUS region may be related to the slow kinetics of iodide re-oxidation. Estimated I⁻ oxidation rates range from 4 to 670 nM per year, whereas reduction of IO₃⁻ at an anoxic boundary is rapid (~50 nM per hour) (Chance et al., 2014). Shelf waters in the Southern BUS (all water depths < 200 m) were reported to have highly variable O₂ concentrations (10–400 µmol/kg) but low IO₃⁻ concentrations (< ~0.25 µM) (Fig. 5b) (Chapman, 1983). Intense water column mixing in the shelf region of Southern BUS may bring bottom waters with low IO₃⁻ signals from peripheral locations into the photic zone, where the concentrations of nutrients and chlorophyll α are exceptionally high (Truesdale and Bailey, 2000). During this transport, oxygen concentrations may have begun to rise due to photosynthesis or mixing with O₂-rich waters, but the IO₃⁻ concentration remained low due to the slow oxidation of I⁻ (Chapman, 1983; Truesdale and Bailey, 2000).

Central to these different scenarios for the occurrence of high O₂ - low I/Ca in the Southern BUS is the key concept that low foraminiferal I/Ca may reflect low O₂ conditions that vary on small space- and time-scales. To visualize such a spatial uncertainty, we plot I/Ca
against minimum \( \text{O}_2 \) values within a \( 0.25^\circ \times 0.25^\circ \) area around each core-top location (Fig. 5). All core-top samples with low I/Ca in the Southern BUS come from a region where hypoxia occurs within \( 0.25^\circ \) of the sample site (Fig. 5d). These results caution against the use of planktic I/Ca as a proxy for \textit{in-situ} \( \text{O}_2 \) conditions in settings with strong hydrographic gradients and mixing. However, we emphasize that these high \( \text{O}_2 \) - low I/Ca cases only occurred in the Southern BUS region with high spatial and temporal variability of \( \text{O}_2 \), and not in the tropical and Walvis Ridge regions.

4.2. Planktic I/Ca as a hypoxia proxy

Water column \( \text{IO}_3^– \) and \( \text{O}_2 \) profiles from the core-top sites would provide the ideal constraints of the \( \text{O}_2 \) threshold driving the foraminiferal I/Ca signal. However, such modern seawater data are only available for a relatively small area from the Southern BUS (Chapman, 1983). In that study, dissolved \( \text{IO}_3^– \) concentrations do not correlate with surface \( \text{O}_2 \) (depth < 50 m), but decrease rapidly when \( \text{O}_2 \) in subsurface waters (depth > 50 m) approaches \( \sim 70–100 \mu \text{mol/kg} \) (Fig. 5b). Similarly, our core-top I/Ca data exhibit abrupt decreases when minimum \( \text{O}_2 \) values drop to these levels, with the exception of the above described high \( \text{O}_2 \) – low I/Ca areas (Fig. 5c). This \( \text{O}_2 \) threshold for rapid \( \text{IO}_3^– \) or I/Ca decrease is generally consistent with the estimates based on globally-distributed core-top foraminifera (Lu et al., 2016).

We suggest that low planktic I/Ca can empirically indicate hypoxia in the upper water column, but it is not clear why planktic I/Ca responds to water column hypoxia, which warrants further discussion. We approach this question from two directions: the relationship
between IO$_3^-$ and O$_2$ in hypoxic waters, and the relation between IO$_3^-$ reduction and denitrification.

Currently, water column data are insufficient to unambiguously demonstrate whether there is a uniform O$_2$ threshold for global seawater IO$_3^-$ reduction, and if there is such a threshold, at what concentration of O$_2$. IO$_3^-$ concentrations rapidly decrease when waters become near suboxic ([O$_2$] < 10 µmol/kg) in the Pacific (Huang et al., 2005; Rue et al., 1997) and Indian oceans OMZs (Farrenkopf and Luther, 2002) (Fig. 5a). However, the Benguela data seem to indicate that IO$_3^-$ reduction may occur at hypoxic conditions with somewhat higher oxygen levels ([O$_2$] < 70-100 µmol/kg) (Fig. 5b), as also found over the shelf in the northern Gulf of Mexico (Chapman and Truesdale, 2011). Maybe, the O$_2$ threshold for seawater IO$_3^-$ reduction varies across different ocean basins, or there are other processes that control the balance between IO$_3^-$ and I in seawater (e.g., the uptake rate of IO$_3^-$ versus I by plankton, iodide oxidation rates vary in different oceans). Further work on in-situ seawater IO$_3^-$ and O$_2$ are required to discern these O$_2$ thresholds.

Since I/Ca and bulk $\delta^{15}$N can indicate low-O$_2$ conditions in the upper water column and iodate reduction can be carried out by nitrate reductase, we explore some potential connections between IO$_3^-$ reduction and denitrification. Laboratory cultures have suggested that various types of algae and bacteria are able to reduce iodate to iodide in seawater (Chance et al., 2007; Farrenkopf et al., 1997; Waite and Truesdale, 2003), but the exact mechanisms remain unclear. Nitrate reductase enzymes have been speculated to be responsible for IO$_3^-$ reduction (Tsunogai and Sase, 1969; Wong and Hung, 2001), but no clear distinction has been made between assimilatory vs. dissimilatory nitrate reductases and their
roles in seawater iodine speciation. Assimilatory nitrate reductases are generally associated with nitrate uptake in the euphotic zone (high $O_2$ water) (Wada and Hattori, 1990). Dissimilatory nitrate reductases are considered to function in suboxic conditions, although denitrifying bacteria isolated from marine sediment show nitrate reducing activity at $O_2$ concentrations up to $\sim 124$ µmol/kg (Bonin et al., 1989). It may be worth further investigation into the prevalence and distribution of specific nitrate reductase enzymes responsible for $IO_3^-$ reduction and their $O_2$ sensitivities coupled with water column $IO_3^-$ and $O_2$ concentrations.

Another possibility to explain a hypoxic threshold for rapid I/Ca decrease may involve anaerobic metabolism of microbes (including $IO_3^-$ reduction) in microenvironments of sinking organic aggregates in oxic-hypoxic water. Denitrification is often described as occurring in suboxic or anoxic waters only (Ulloa et al., 2012), but denitrification and even sulfate-reduction by microbes have been reported at $O_2 > 20$ mol/kg (Ganesh et al., 2014; Wolgast et al., 1998). Possibly, particle microenvironments in hypoxic waters may have sufficiently low $O_2$ concentrations to support anaerobic metabolism, including denitrification and sulfate reduction (Bianchi et al., 2018) and potentially iodate reduction. These low $IO_3^-$ signals formed in microenvironments could be subsequently released into ambient hypoxic seawater where the planktic foraminifera calcify. Such a scenario could be an explanation for $IO_3^-$ reduction in hypoxic water, and I/Ca may be sensitive to water column denitrification in microenvironments.

In summary, we suggest that planktic I/Ca remains an empirical proxy – low I/Ca values can reliably indicate the presence of hypoxia in the water column, in contrast to bulk sediment $\delta^{15}N$ as a proxy for denitrification in suboxic water. In future studies, foraminiferal
I/Ca, paired to in-situ O$_2$ and iodate data from low O$_2$ regions may improve the mechanistic understanding of the proxy and also the marine biogeochemistry of iodine. Iodate will not be used as oxidant until O$_2$ is significantly depleted, but iodate reduction may not necessarily occur in the habitat of calcifying organisms. The foraminiferal I/Ca signature for low O$_2$ reflects iodate reduction somewhere very close to the foraminiferal habitat. If the in-situ iodate level indeed is low, it can be caused by diffusion/advection and slow oxidation of iodide. On the other hand, culture experiments show that two modern planktic species (O. universa, symbiotic species, and G. bulloidies, non-symbiotic species) can survive, add chambers, feed, and undergo gametogenesis in low-O$_2$ conditions (~22 µmol/L) (Kuroyanagi et al., 2013). Some species (N. dutertrei and G. bulloides) can even survive episodic or temporary exposure to H$_2$S (< 24 hr) (Kuroyanagi et al., 2019). We cannot rule out the possibility that planktic foraminifera may survive in hypoxic waters and directly record a low I/Ca signal. Such foraminifera culture experiments may also be helpful for testing vital effects in different species.

4.3. Planktic I/Ca downcore record in the BUS

We use the I/Ca values in N. incompta and G. truncatulinoides (sinistral) from core GeoB1720-2 from the Southeast Atlantic to reconstruct the upper water oxygenation history over the last 240 ka, and compare these results with δ$^{15}$N data from nearby site MD96-2087 (25.60°S, 13.38°E, 1029 m) (Pichevin et al., 2005b). The downcore I/Ca values are consistently low, < 2.5 µmol/mol, over the last two glacial cycles (Fig. 6), indicating the persistent presence of hypoxic waters near the study site (e.g., within 0.25°×0.25° area). It is
possible that low IO$_2^-$ water was advected to this site from nearby locations. Nutrient levels, indicated by bulk sediment $\delta^{15}N$ records from MD96-2087 (Fig. 6), likewise do not show a clear glacial-interglacial pattern (Pichevin et al., 2005b). The narrow amplitude of this $\delta^{15}N$ record was interpreted to reflect that nitrate was never severely depleted over the shelf (Pichevin et al., 2005b). Thus the upwelling dynamics in the near-shore region of BUS may have persistently fueled relatively high levels of surface nutrient and subsurface hypoxia through glacial-interglacial oscillations, which remained a dominant oceanographic feature in this area. On the other hand, downcore records for excess Ba ($Ba_{es}$) and the $\delta^{13}C$ difference between $G$. ruber (a summer calcifier) and $N$. incompta (calcifying below the mixed layer) ($\Delta \delta^{13}C$) suggest changes in organic carbon export and upper ocean nutrient partitioning over the latter part of the last glacial cycle (Fig. 7). Given the very low I/Ca values, it is likely that subtle alternations of enhanced organic matter export and upper ocean mixing (high $Ba_{es}$, low $\Delta \delta^{13}C$) and lower organic matter export with more stratified surface waters (lower $Ba_{es}$, higher $\Delta \delta^{13}C$) could maintain persistently oxygen-depleted subsurface waters during the past ~50 ka (Fig. 7). It is possible that such variations in export production were relatively small, thus insufficient to drive nutrient utilization ($\delta^{15}N$) and hypoxia patterns (I/Ca).

Upwelling strength may well have an impact on upper ocean oxygenation conditions in the region (Fig. 6). The alkenone-based SSTs at MD96-2087 (Fig. 6) did not exactly follow glacial-interglacial cycles, but were strongly influenced by upwelling activity and wind-strength, as recorded by dust grain size distributions (Pichevin et al., 2005a). Weak upwelling periods at MD96-2087 coincided temporally with relatively weaker hypoxia as indicated by higher I/Ca of $G$. truncatulinoides in GeoB1720-2 (Fig. 6). Comparing I/Ca
records of hypoxic extent with independent proxies for upwelling strengths may be an intriguing future research direction.

5. Conclusions

New core-top I/Ca data in planktic foraminifera from the Southeast Atlantic Ocean are consistent with previous studies, generally showing low I/Ca corresponding to low oxygen in the upper ocean. This study thus further establishes planktic I/Ca as an empirical proxy for hypoxic conditions \((O_2 < \sim 70-100 \text{ mol/kg})\) in the Southeast Atlantic. Data from the Southern Benguela region show a more complex pattern, and indicate limitations on the use of planktic I/Ca as an \textit{in-situ} \(O_2\) proxy for the foraminiferal habitat. In areas with intense mixing/upwelling, seawater signals may be affected by short-term \(O_2\) variability and/or potential transport of hypoxia signals at nearby locations due to the slow kinetics of iodide re-oxidation. Future work may help better understand the relationship between \textit{in-situ} iodate, \(O_2\) and foraminiferal I/Ca. The down-core planktic I/Ca record at site GeoB1720-2 suggests that there were no significant glacial-interglacial variations in upper water hypoxic extent within the BUS during the last 240 ka, consistent with bulk \(\delta^{15}N\) signals at a nearby site. In this region, relatively small temporal variations in I/Ca shows a potential connection with upwelling intensity.

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Fig. 1. Locations of core-top samples and site GeoB1720-2. The yellow box marks the sampling area of dissolved iodate and O$_2$ concentrations in seawater in the Southern BUS region in Fig. 5b (Chapman, 1983). The yellow square marks site MD96-2087 in Fig. 6, for comparison with I/Ca records. The upper ocean circulation in the Southeast Atlantic Ocean is modified after Chapman and Shannon (1985) and Stramma and England (1999). EU: Equatorial Undercurrent; PUC: Poleward Undercurrent; BC: Benguela Current; SAC: South Atlantic Current; AC: Agulhas Current.
Fig. 2. a). Seawater CTD \([\text{O}_2]\) profile locations in the study area, World Ocean Database (WOD) 2013 (Boyer et al., 2013). We divided our dataset into three regions, as outlined by the yellow ellipses. b). Cross-section (red box with latitudes between 28°45’ S and 29°15’ S) shows site GeoB1720-2 on the continental slope, and the location of two cores in the coastal area of the BUS, showing significant spatial variation of \(\text{O}_2\) concentrations.
Fig. 3. Core-top planktic I/Ca spatial distribution maps. Background maps show the minimum $O_2$ concentrations in the water column. Numbers next to the symbols show the planktic I/Ca values.
**Fig. 4.** Planktic I/Ca in core-top samples. The locations of the three regions are shown in Fig. 2a.
Fig. 5. a) Dissolved IO$_3^-$ vs. O$_2$ in the Pacific and Indian Oceans (Farrenkopf and Luther, 2002; Huang et al., 2005; Rue et al., 1997). b) Dissolved IO$_3^-$ vs. O$_2$ in shelf waters in Southern BUS (Chapman, 1983). Depths of all water samples were < 200 m, locations are shown in the yellow box in Fig. 1. c-d) Core-top planktic I/Ca vs. minimum O$_2$ concentrations in the water column derived from the nearest location and within 0.25°×0.25° area in WOD2013. Closed symbols indicate new data in this study, and open ones denote published data (Lu et al., 2016).
Fig. 6. Planktic I/Ca record at site GeoB1720-2 (this study), and alkenone-based SST, mean dust grain size (Pichevin et al., 2005a), and bulk δ¹⁵N at site MD96-2087 (Pichevin et al., 2005b). Dark blue shadings indicate glacial periods, and light blue shadings indicate potential weak upwelling periods.
Fig. 7. Planktic I/Ca, the $\delta^{13}$C difference between *G. ruber* and *N. incompta*, and excess Ba mass accumulation rates (MAR) records at core GeoB1720-2 during the last 50 ka.
Supplementary Information

Table S1. Core-top planktic I/Ca data.

Table S2. Age model tie points at core GeoB1720-2.

Table S3. GeoB1720-2 downcore planktic I/Ca data.

Fig. S1. Age model for core GeoB1720-2.

Fig. S2. I/Ca differences between symbiont-bearing (upper panel) and symbiont-barren species (lower panel) species within the same core-top sample. Core-top samples with only symbiont-barren species are not shown.
Fig. S1

![Graph showing δ¹⁸O and LR05 δ¹⁸O stack over time](image)

Core depth (m)

$^{14}$C-ages

*N. incompta*

δ¹⁸O (%)

Age (ka)

LR05 δ¹⁸O stack (%)
Fig. S2

[Graph showing sample names (V18-230, V19-229, V16-49, V18-250, V19-254, V22-154, V27-214) plotted on a graph with I/Ca (μmol/mol) on the x-axis and sample names on the y-axis. Legend includes symbols for Symbiont-bearing (G. ruber (white), G. ruber (pink), G. squamifer) and Symbiont-barren (N. incompta, G. bulloides, G. inflata, G. trunc. (sin), G. trunc. (dax), G. menardii, N. dufresnei).]
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Chapter 3

I/Ca in epifaunal benthic foraminifera: a semi-quantitative proxy for bottom water oxygen used in a multi-proxy compilation for glacial ocean deoxygenation

Chapter 3 has been published as:

Abstract

The decline in dissolved oxygen in global oceans (ocean deoxygenation) is a potential consequence of global warming which may have important impacts on ocean biogeochemistry and marine ecosystems. Current climate models do not agree on the trajectory of future deoxygenation on different timescales, in part due to uncertainties in the complex, linked effects of changes in ocean circulation, productivity and organic matter respiration. More (semi-)quantitative reconstructions of oceanic oxygen levels over the Pleistocene glacial cycles may provide a critical test of our mechanistic understanding of the response of oceanic oxygenation to climate change. Even the most promising proxies for bottom water oxygen (BWO) have limitations, which calls for new proxy development and a multi-proxy compilation to evaluate glacial ocean oxygenation. We use Holocene benthic foraminifera to explore I/Ca in *Cibicidoides* spp. as a BWO proxy. We propose that low I/Ca (e.g., < 3 µmol/mol) in conjunction with benthic foraminiferal carbon isotope gradients and/or the surface pore area percentages in foraminiferal tests (e.g., >15%) may provide semi-quantitative estimates of low BWO in past oceans (e.g., < ~50 µmol/kg). We present I/Ca records in five cores and a global compilation of multiproxy data, indicating that bottom waters were generally less-oxygenated during glacial periods, with low O_2_ waters (< ~50 µmol/kg) occupying some parts of the Atlantic and Pacific Oceans. Water mass ventilation and circulation may have been important in deoxygenation of the glacial deep Pacific and South Atlantic, whereas enhanced remineralization of organic matter may have had a greater impact on reducing the oxygen content of the interior Atlantic Ocean.
1. Introduction

Observations and climate models show increased ocean deoxygenation as a response to global warming, due to decreased oxygen solubility in warmer waters combined with decreased ventilation of the deep ocean due to increased thermal stratification (Breitburg et al., 2018; Keeling et al., 2009; Schmidtko et al., 2017), and a decrease in the lateral advection of oxygenated waters (Gruber et al., 2001). However, current climate models tend to under-estimate spatial oxygen variability and temporal trends (Oschlies et al., 2017; Stramma et al., 2012), partially due to an inability to precisely tease apart contributions to deoxygenation from three main controls: (i) temperature related oxygen solubility; (ii) ventilation of water masses and other physical processes; (iii) biogeochemical processes (e.g., biological production and respiration) (Oschlies et al., 2018). Models tend to agree on (i), but disagree on (ii) and (iii), which leads to different projections of expanding vs. shrinking oxygen minimum zones (OMZ) over the long-term future (Resplandy, 2018).

Geological records commonly link ocean deoxygenation to greenhouse climates (e.g., Jenkyns (2010); Penn et al. (2018)), but deoxygenation also occurred during cold periods in deep time (e.g., at the Late Ordovician – Early Silurian (Bartlett et al., 2018) and across the Frasnian – Famennian boundary (Song et al., 2017)). Thus, temperature alone does not dictate ocean deoxygenation, indicating that we need a better understanding of the interplay between physical and biogeochemical processes during climate change.

Deoxygenation was common during Pleistocene glacials (e.g., Bradtmiller et al. (2010); de la Fuente et al. (2017); Gottschalk et al. (2016a); (2018); Hoogakker et al. (2015); Jaccard et al. (2016); Jacobel et al. (2020); Loveley et al. (2017); Umling and Thunell (2018)), and
there is much evidence that global deep oceans (> 2 km) were less-oxygenated during the Last Glacial Maximum (LGM, 18-22 ka) than in the early Holocene (Jaccard and Galbraith, 2012). However, this evidence is generally qualitative (Jaccard and Galbraith, 2012), and quantitative \( O_2 \) estimates for the glacial oceans are needed to further assess and differentiate drivers for deoxygenation.

Qualitative bottom water oxygen (BWO) proxies traditionally used on glacial-interglacial time scales include sedimentary structures (e.g., lamination due to lack of bioturbation), benthic foraminiferal assemblages and species abundances, and trace metal concentrations (Jaccard and Galbraith, 2012). The authigenic uranium content of sediments (\( aU, i.e., \) accumulation of reduced \( U(IV) \) in excess of \( U \) in detrital sediments) (Bradtmiller et al., 2010; Durand et al., 2018; Jaccard et al., 2016; Jacobel et al., 2017; Loveley et al., 2017) is controlled by BWO and the rain of organic material from surface ocean (which consumes \( O_2 \) as it is respired) (Bradtmiller et al., 2010). If sediments become more reducing (higher \( aU \) values) with similar or lower export production (no increased \( O_2 \) consumption), it can be reliably inferred that higher \( aU \) is due to a decrease in BWO. But a lack of high \( aU \) values does not preclude deoxygenation: subsequent reoxygenation at the sampling site could obliterate sedimentary \( aU \) enrichments that had previously developed (Bradtmiller et al., 2010; Costa et al., 2018; Jacobel et al., 2020). The benthic foraminiferal oxygen index based on species assemblage and morphology data, also used to qualitatively trace BWO (Kaiho, 1994), is poorly supported by calibration with living foraminifera (Jorissen et al., 2007), and the impact of factors other than the BWO level (e.g., organic matter flux) cannot be easily separated from the overall signal.
Four recently developed proxies have promise to provide semi-quantitative constraints on BWO: (1) the pore area in benthic foraminiferal tests (Rathburn et al., 2018), (2) benthic foraminiferal carbon isotope gradients (Hoogakker et al., 2015), (3) preservation of organic compounds (Anderson et al., 2019), (4) and the benthic I/Ca proxy (Glock et al., 2014). We highlight these newly developed BWO proxies because they have been validated/calibrated to various degrees in modern sediments/foraminifera. Furthermore, they show some potential to reconstruct specific BWO values instead of being limited to qualitative reconstruction of higher/lower BWO or increased/decreased extent of suboxic water mass.

The pore area percentage in tests of the epifaunal (on or above the seafloor surface living) benthic foraminifer *Cibicidoides wuellerstorfi* is correlated with BWO in the modern ocean (Rathburn et al., 2018), but this proxy has not yet been tested in down-core studies. Several studies have related pore size of different species of benthic foraminifera to ambient conditions, but most have focused on taxa that live within sediments (infaunal) (e.g., Kuhnt et al. (2014)), and may be influenced by pore water conditions and nitrate respiration (Rathburn et al., 2018).

The benthic foraminiferal carbon isotope gradient ($\delta^{13}C$) between epifaunal (*C. wuellerstorfi*) and deep infaunal benthic foraminifera species (*Globobulimina* spp.) was quantitatively calibrated to BWO values (20 – 235 µmol/kg) in a global deep ocean dataset (Hoogakker et al., 2018; Hoogakker et al., 2015; McCorkle and Emerson, 1988). The application of this proxy is limited by the restricted occurrence of these species, with *Globobulimina* spp. requiring relatively high export productivity (Jorissen et al., 2007). In addition, $\delta^{13}C_{C. wuellerstorfi}$ may be influenced by seasonal variability in export productivity of
labile organic matter to the seafloor, i.e., the phytodetrital flux (‘Mackensen effect’) (Mackensen et al., 1993); and $\delta^{13}C_{\text{Globobulimina}}$ may be affected by isotopically light carbon released by anaerobic processes including denitrification and sulfate reduction, especially in high sediment accumulation environments, thus altering the relationship between $\delta^{13}C$ and BWO (McCorkle and Emerson, 1988; Jacobel et al., 2020).

Another recently proposed, empirical proxy is the use of the preservation of specific organic compounds (as observed in Arabian Sea sediments) to estimate BWO concentrations in the central Equatorial Pacific (Anderson et al., 2019): an order-of-magnitude greater accumulation of lipid biomarkers (e.g., C$_{37}$ alkenones) combined with evidence for lower export production was argued to indicate a BWO content of 20 – 50 µmol/kg, although uncertainty remains about the mechanism of organic matter preservation (Hedges and Keil, 1995) and the validity of applying this empirical relationship based on Arabian Sea data to other regions (Anderson et al., 2019).

The carbonate I/Ca proxy has been applied across different time scales, and can be used to resolve subtle changes in oceanic oxygenation (Lu et al., 2018; Lu et al., 2016). Iodate ([IO$_3^-$], oxidized form) and iodide ([I$^-$], reduced form) are the thermodynamically stable forms of iodine in seawater (Wong and Brewer, 1977); [IO$_3^-$] is completely reduced to [I$^-$] in anoxic environments (Rue et al., 1997). [IO$_3^-$] is the only iodine species incorporated into carbonate (Lu et al., 2010) by replacing [CO$_3^{2-}$] (Feng and Redfern, 2018; Podder et al., 2017), thus lower foraminiferal I/Ca generally records more O$_2$-depleted conditions (Lu et al., 2016).

Modern BWO concentrations at low ranges (2 – 34 µmol/kg) correlate with I/Ca in
infaunal and epifaunal living foraminifera (Glock et al., 2014). To date, only one calcitic epifaunal species, *Planulina limbata*, has been analyzed for its I/Ca in modern settings (Glock et al., 2014), documenting impingement of an OMZ on the seafloor. *Cibicidoides* spp. are more commonly used in paleoceanographic investigations, and thus I/Ca in cosmopolitan *Cibicidoides* species may have great potential as a BWO proxy for comparison with proxy data for other paleoenvironmental parameters. *Cibicidoides wuellerstorfi* and *C. lobatulus* are typically attached to objects projecting 0 – 2 cm above the sediment-water interface (Lutze and Thiel, 1989; Rathburn and Corliss, 1994; Schweizer et al., 2009). Other *Cibicidoides* spp. (e.g., *C. mundulus*, *C. pachyderma*) may live in the top 2 cm of the sediment, and can adapt from an epifaunal (bottom water exposure) to a shallow infaunal (pore water exposure) habitat (Wollenburg et al., 2018). *Cibicidoides* spp. are generally not abundant in low O$_2$ waters (Jorissen et al., 2007), but *C. wuellerstorfi* has been observed living in settings with O$_2$ < 50 µmol/kg (Rathburn et al., 2018; Venturelli et al., 2018).

Here we report a global *Cibicidoides* spp. I/Ca data set obtained from living (i.e., Rose Bengal stained and live-picked) and unstained (i.e., living and dead) benthic foraminifera tests in core-top sediments of Holocene-modern age. The intention is to characterize benthic I/Ca relative to modern BWO values. We combine I/Ca with $\delta^{13}$C and surface pore area values to explore how these proxies may be combined to provide more reliable (semi-)quantitative BWO estimates. We then estimate bottom water oxygenation changes in glacial oceans from five down-core I/Ca records, and integrate these with an updated global compilation of independent oxygenation proxies ($\delta^{13}$C, aU, and C$_{37}$ alkenones) to explore a broader pattern of glacial BWO conditions. We do not strictly focus on the LGM in the I/Ca
records because the temporal resolution of some records is relatively low, but focus instead on more broadly defined glacial periods, i.e., Marine Isotope Stages (MIS) 2–4 and 6.

2. Materials and Methods

2.1. Materials

For sampling locations of live-collected and unstained core-top foraminifera and core sites, see Fig. 1 and Table S1. Foraminifera were either collected alive onboard ship (living attached on the hard surfaces such as rocks, worm tubes or artificial substrates, and manually removed), or stained with Rose Bengal and determined to have been alive at the time of collection using conservative assessments (Rathburn et al., 2018). The living foraminifera were imaged using Scanning Electron Microscopy to determine the areal percentage of pores in their tests (Rathburn et al., 2018), then cleaned and dissolved to analyze the I/Ca of their tests.

Unstained foraminifera from core-top sediments contain both living and dead foraminifera. Gravity or piston cores may lose some seafloor surface sediments, and core-tops from such cores are likely to contain a higher percentage of dead foraminifera (Rathburn and Miao, 1995). Multicorer surface sediments are more likely to include the living population along with dead foraminifera. The living population represents conditions at the time of collection, whereas the dead assemblage (and living plus dead) may contain a different suite of species, including these living at the location in the recent and more distant past, depending on bioturbation and taphonomic processes (Loubere and Gary, 1990). Radiocarbon and $\delta^{18}$O values of selected core-top samples in this study reveal Holocene ages (Table S1).
2.2. Age models

We show five down-core I/Ca records: ODP Site 1242 (7.86°N, 83.61°W, 1400 m); ODP Site 849 (0.18°N, 110.50°W, 3800 m); TC493 (71.15°S, 119.92°W, 2096 m); GeoB1720-2 (28.98°S, 13.83°E, 1997 m), and GeoB9532-9535 (8.90°N, 14.90°W, 319-667 m) (Table S2). Age models for ODP Site 1242 and ODP Site 849 are after Hoogakker et al. (2018), core TC493 is after Lu et al. (2016), core GeoB1720-2 is after Dickson et al. (2009); Lu et al. (2019), and GeoB9532-9535 is after Huang et al. (2012).

2.3. Foraminiferal I/Ca analyses

Benthic foraminiferal I/Ca was measured following the method for planktic foraminiferal I/Ca (Lu et al., 2016). For each sample, 3 – 15 specimens from > 250 μm size fraction were used depending on foraminifera availability. The foraminifera were gently crushed between two clean glass plates to open the chambers, then cleaned following the Mg/Ca protocol (Barker et al., 2003). Crushed foraminiferal shells were ultra-sonicated in water to remove clays. NaOH-buffered H$_2$O$_2$ was then added, and the sample was kept in boiling water for 10 – 20 mins to remove organic matter. Reductive cleaning was not applied, as the effects of Mn oxide coatings on I/Ca signal are minimal (Zhou et al., 2014). After thorough rinsing, samples were dissolved in 3% HNO$_3$, then mixed with a matrix containing internal standard and buffered by tertiary amine. Iodine and calcium concentrations were measured by quadrupole ICP-MS (Bruker M90) at Syracuse University. Calibration standards were freshly made for each batch of samples. The 1 ppb iodine signal was tuned to > 80 kcps. The reference material JCp-1 was measured repeatedly to maintain long-term accuracy (Lu et al.,
2010). The standard deviation for each measurement was usually lower than 1%. Replicates of selected *C. wuellerstorfi* from core GeoB1720-2 show reproducibility ranging from ±2% (0.07 µmol/mol; 1σ) to ±9% (0.23 µmol/mol; 1σ) for I/Ca (Table S2).

2.4. O$_2$ data

The O$_2$ data for sample sites of living foraminifera are *in-situ* bottom water O$_2$ data after Rathburn et al. (2018). They were determined measuring high-resolution oxygen profiles from the overlying water into the sediment in multi-corer tubes taken at the collection site, using amperometric oxygen microelectrodes, or an oxygen sensor mounted on a CTD or submersible. For unstained core-top samples, *in-situ* O$_2$ data are not available, and we used O$_2$ data from the Electronic Atlas of the World Ocean Circulation Experiment (http://www.ewoce.org/). For core-top samples located in coastal areas in the Southeast Atlantic, we used O$_2$ data from the nearest site from the World Ocean Database 2013 (https://www.nodc.noaa.gov/OC5/WOD13/) (Boyer et al., 2013) because of the greater spatial variability in O$_2$ conditions in this region.

3. Results

I/Ca in shells of living and unstained foraminifera from core-top sediments decreases with lower BWO, except for the middle O$_2$ range (50 − 200 µmol/kg) (Fig. 2). Furthermore, benthic I/Ca does not appear to decrease gradually across the entire oxygenation spectrum from oxic (BWO > 70 µmol/kg), hypoxic (BWO < 70 µmol/kg), suboxic (BWO < 10 µmol/kg) to anoxic (no O$_2$) conditions. Instead, benthic I/Ca decreases rapidly below a BWO threshold (e.g., < ~50 µmol/kg). In general, low benthic I/Ca are consistent with low BWO,
but depending on the thresholds (definition of “low”), low BWO may not exclusively produce low benthic I/Ca. Lower I/Ca values in the tests of *C. wuellerstorfi* correlate significantly with greater surface pore percentages, a proxy for oxygenation (Rathburn et al., 2018), as measured on the same set of specimens (*R*² = 0.83, *p* < 0.01) (Fig. 2B-C).

In our five cores from the Eastern Equatorial Pacific (EEP), South Atlantic and Southern Oceans (Fig. 3 and 4, Table S2), low I/Ca values are generally found in glacial samples than in modern/late Holocene samples. At ODP Site 1242 (EEP) and core sites GeoB1720-2 and GeoB9532-9535 (Atlantic), the I/Ca values were close to or less than 3 µmol/mol during parts of the last glacial period. ODP Site 849 (EEP) shows I/Ca between 2.9 and 4.9 µmol/mol throughout the last 150 ka, without pronounced trends. Core TC493 from the Southern Ocean does not have enough *Cibicidoides* spp. specimens in MIS 2 sediments for I/Ca analyses. Where specimens could be found, the corresponding I/Ca values were relatively higher than in the other studied cores. *C. wuellerstorfi* I/Ca was ~6 µmol/mol during glacial MIS 6, increasing to ~12 µmol/mol during interglacial MIS 5e, and *C. lobatulus* I/Ca was ~10 µmol/mol during MIS 6, increasing to ~18 µmol/mol during MIS 5e.

4. Discussion: proxy development

4.1. Epifaunal I/Ca as a semi-quantitative O₂ proxy

The results from living and unstained foraminifera from core-top sediments confirm that low benthic I/Ca values indicate low BWO (Fig. 2). Epifaunal I/Ca does not linearly correlate with BWO, thus I/Ca cannot be calibrated as a quantitative proxy. However, low I/Ca values in epifaunal benthic foraminifera may be used to determine BWO above/below a threshold.
value as a semi-quantitative proxy. Such a semi-quantitative proxy can be valuable for tuning ocean models at locations, where fully quantitative proxies are not applicable (e.g., where *Globobulimina* spp. are absent).

We apply the statistical method “receiver operating characteristic” (ROC) (Zou et al., 2007) to determine the O$_2$ threshold for several cut-off values in I/Ca (see Fig. S1 for an example of the statistical results). The statistical results show that lower I/Ca cut-off values generally lead to lower O$_2$ threshold values (Fig. 2B). A parameter called the area under curve (AUC) describes how well the optimal O$_2$ threshold separates the two groups of high vs. low I/Ca in these ROC tests. The O$_2$ threshold values producing a high AUC (>0.95) and good separations are shown by thick dashed lines (Fig. 2B). Similar ROC tests were performed on the surface pore area data (Fig. 2C). These statistically optimal O$_2$ thresholds are influenced by the choice of cut-off value and available calibration dataset. For example, using only the living specimen dataset (a smaller calibration dataset), the ROC analyses show a slightly different optimal O$_2$ threshold for the same I/Ca cut-off value. Adding more I/Ca and surface pore area data in the O$_2$ < 50 μmol/kg window will very likely change the statistically-determined O$_2$ threshold value.

These statistically-determined O$_2$ threshold values must be viewed with caution in the context of a multi-proxy approach (see section 4.2): pore area percentages start to increase notably below 50 μmol/kg, and Δδ$^{13}$C has not yet been fully calibrated below 50 μmol/kg (Fig. 2C). Thus BWO of ~50 μmol/kg could be an important target for ocean biogeochemical models and carbon cycle models. Proposing a lower O$_2$ threshold value may lead to over-estimate the degree of deoxygenation in down-core studies. For now, we propose that
Cibicidoides spp. I/Ca < 3 µmol/mol in specimens with high pore density (i.e., > 15%) may be indicative of BWO < ~50 µmol/kg (Fig. 2). Future studies may more rigorously define the O₂ threshold for both I/Ca and pore density.

The attempt to infer BWO from benthic I/Ca values in the low O₂ range (< 50 µmol/kg) currently remains empirical, with several limitations. C. wuellerstorfi generally are not abundant at low BWO, making it challenging to tightly constrain the threshold O₂ value at which IO₃⁻ in seawater is reduced and its associated I/Ca in calcite drops (Fig. 2B). In the water column, the O₂ threshold values and kinetics are not completely resolved for either iodate reduction or iodide oxidation (Chance et al., 2014). Paired profiles of dissolved O₂ and [IO₃⁻] in the water column at OMZ sites in the EEP (Rue et al., 1997), Arabian Sea (Farrenkopf and Luther, 2002), Northwest Pacific (Huang et al., 2005) and Eastern Pacific off Peru (Cutter et al., 2018) demonstrate that rapid iodate reduction, with a lifetime of ~50 nM per hour (Chance et al., 2014), occurs at O₂ < 20 µmol/kg (Fig. 2A). Such studies are sparse, however, and there are no controlled laboratory experiments in seawater constraining the O₂ threshold of iodate reduction. Coupled seawater chemistry (iodine speciation and BWO) and living specimen I/Ca measurements at the same location may be required to precisely quantify the relationship between epifaunal I/Ca and BWO.

Our set of live-collected and core-top samples was selected to calibrate benthic I/Ca across a wide range of O₂ concentrations (2 – 270 µmol/kg), but other environmental parameters (such as temperature and water depths) are generally correlated with O₂ in these samples, making it difficult to deconvolve the relations between non-O₂ parameters and I/Ca. For example, we observe a weak correlation between bottom water temperature and benthic
I/Ca in living *C. wuellerstorfi* \( (R^2 = 0.14, p = 0.26) \), and a slightly positive correlation in unstained *C. wuellerstorfi* \( (R^2 = 0.16, p = 0.05) \). These correlations cannot be convincingly attributed to a potential temperature effect, because temperature is significantly correlated with BWO \( (R^2 = 0.55, p < 0.01) \). Further core-top studies are required to test non-O\(_2\) effects on I/Ca, under similar O\(_2\) conditions but under a broad range of temperature, salinity, water depths, etc.

### 4.2 Downcore proxy comparison

Next, we compare two I/Ca down-core records with quantitative BWO reconstructions from \( \Delta \delta^{13}C \) on the same core or a nearby core (Fig. 3). At ODP Site 1242 in the EEP, I/Ca values appear to be consistent between the two species (*C. wuellerstorfi* and *C. pachyderma*), with values < 3 \( \mu \)mol/mol (and thus < 50 \( \mu \)mol/kg BWO) throughout MIS 3 and MIS 2. The \( \Delta \delta^{13}C \) records suggest BWO were ~50 \( \mu \)mol/kg during parts of MIS 3 and throughout MIS 2 (Hoogakker et al., 2018).

In the Southeast Atlantic at Site GeoB1720-2, the *C. wuellerstorfi* I/Ca values show only a few values < 3 \( \mu \)mol/mol during late MIS 3 and the LGM. The \( \Delta \delta^{13}C \) reconstructions at nearby site GeoB3606-1 \( (25.47^\circ S, 13.08^\circ E, 1785 \text{ m}) \) suggest that BWO values were ~50 \( \mu \)mol/kg during late MIS 3 and the early and late phases of MIS 2 (McKay et al., 2016). Higher resolution and improved age models are necessary to better examine the temporal changes in this region.

The epifaunal I/Ca proxy thus is generally (but not perfectly) consistent with the \( \Delta \delta^{13}C \) proxy. The difference between I/Ca (GeoB1720-2) and \( \Delta \delta^{13}C \) (GeoB3606-1) in the South
Atlantic may be due to the relatively low temporal resolution of the records and different locations at which these two proxies were measured. At ODP Site 1242, values of I/Ca and Δδ\textsuperscript{13}C disagree between 10 ka and 15 ka, disregarding whether BWO was above or below 50 µmol/kg (Fig. 3). This discrepancy could be caused by several possibilities: There are still uncertainties in the behavior of Δδ\textsuperscript{13}C in the low BWO range (Fig. 2C) (Hoogakker et al., 2015). The best preserved \textit{C. wuellerstorfi} specimens were used for Δδ\textsuperscript{13}C measurements and the rest of the specimens was used for I/Ca, thus sample heterogeneity amongst foraminifera from the same depth interval in the sediment may also influence the comparison between these two proxies. Alternatively, iodide oxidation kinetics could be slow, with a lifetime ranging between ~4 nM per year and ~670 nM per year (Chance et al., 2014), implying that waters could have been re-oxygenated before the associated iodide was re-oxidized to iodate. We cannot rule out the possibility that the low I/Ca values between 10 – 15 ka result from slow recovery of O\textsubscript{2} at some “upstream” location, instead of recording \textit{in-situ} BWO at ODP Site 1242. The aU record at nearby site RC13-140 (2.87\textdegree N, 87.75\textdegree W, 2246 m) shows higher aU concentrations during the period from 10 – 15 ka than during the Holocene when opal flux was similar/slightly lower (Bradtmiller et al., 2010), suggesting the presence of low BWO water masses from 10 – 15 ka, similar to the I/Ca trend (Fig. 3).

During the Holocene, the Δδ\textsuperscript{13}C record at ODP Site 1242 shows that BWO first increased from ~80 µmol/kg at 10 ka to a maximum of ~140 µmol/kg at 8 ka, and then decreased to ~80 µmol/kg at modern day. In contrast, the I/Ca values steadily increased from ~3 µmol/mol at 10 ka to ~5 µmol/mol at present day, and aU concentrations steadily decreased from ~3 ppm at 10 ka to 0 ppm at present day. Both I/Ca and aU records can be interpreted
qualitatively to reflect lower BWO during the early Holocene compared to modern day; however we cannot infer any reliable BWO values from I/Ca and aU records because *C. wuellerstorfi* I/Ca values were > 3 µmol/mol and aU peaks were absent during the late Holocene. It is possible that BWO concentrations at the EEP were fluctuating throughout the Holocene as shown by the $\Delta \delta^{13}C$ record, but this variability cannot be inferred from I/Ca or aU records due to the limitations of these two proxies. Alternatively, the Holocene BWO reconstructions from $\Delta \delta^{13}C$ may be impacted by the incorporation of isotopically light carbon into *Globobulimina* spp. from anaerobic processes (Jacobel et al., 2020).

Epifaunal I/Ca thus can be a useful tool to place semi-quantitative constraints on paleo-BWO, combined with the $\delta^{13}C$, pore density, organic compound preservation, and aU data. The I/Ca proxy can be applied to regions, where epifaunal *Cibicidoides* spp. are present, but where there are no deep infaunal species for $\delta^{13}C$ calculation. Epifaunal I/Ca and pore density can provide confirmation of reconstructed $\delta^{13}C$ - BWO values. Given the complications and limitations of each proxy, we suggest that a multi-proxy approach is the best way forward, and low BWO conditions (< 50 µmol/kg) may be reliably detected, if more than one of the following are observed: low epifaunal I/Ca values (i.e., < ~3 µmol/mol); low $\delta^{13}C$ (i.e., < ~0.8 ‰); and high pore area percentages (i.e., > ~15 %) (Fig. 2).

5. Discussion: Global Compilations
5.1 Updating the global compilation of glacial BWO

We next combine our I/Ca records with a compilation of $\delta^{13}C$ data (9 sites) and $C_{37}$ alkenone data (7 sites) to show broad temporal and spatial patterns in (semi-)quantitative BWO (Fig. 5, Table S3). In addition, we update a global compilation of sediment aU records
(108 sites) (Table S3), from which we highlight sites with coupled higher aU and lower/similar productivity, indicative of lower BWO in the LGM than at present (Bradtmiller et al., 2010). Differences in aU values at sites exposed to the same water mass are likely caused by differences in diagenetic processes and/or sedimentation rates (Costa et al., 2018).

There are two key observations in this multi-proxy compilation (Fig. 5): (i) The four proxies are generally consistent in space and time, indicating that bottom waters experienced various degrees of glacial-time deoxygenation. (ii) The areal extent of low O$_2$ waters (< ~50 µmol/kg) was more extensive during the last glacial period than today, at water depths >1500 – 2000 m in the Atlantic and Pacific Oceans. ODP Site 849 (water depth 3800 m) in the EEP exhibits relatively small variability in I/Ca (~3 – 5 µmol/mol) throughout this low-resolution record. No aU peaks were found in down-core samples at ODP Site 849 (Pichat et al., 2004), but this does not exclude the possibility of deoxygenation because aU peaks can be removed by subsequent reoxygenation combined with intense bioturbation (Costa et al., 2018). The C$_{37}$ alkenone records at four intermediate to deep EEP sites (water depths 1.4 – 3.1 km) were interpreted to indicate BWO below 50 µmol/kg during the last glacial period (Anderson et al., 2019). Thus, low O$_2$ waters may have expanded to as deep as 3.1 km in the EEP as recognized by the (semi-)quantitative methods applied to date, but we do not yet have reliable semi-quantitative information about the degree of deoxygenation in the deepest EEP (> 3.1 km). Previous global compilations of qualitative BWO proxies have shown lower BWO during the LGM in the deepest parts (3 – 5 km) of the Atlantic, North Pacific, and Indian sector of the Southern Ocean from trace metal records (Jaccard and Galbraith, 2012), but more research is needed to quantitatively constrain glacial conditions in the deepest parts (≥ 4
km) of all oceans.

5.2 Drivers of deoxygenation in the glacial Atlantic vs. Pacific Oceans

The relative dominance of different drivers (ventilation, \(O_2\) utilization, the temperature-dependent \(O_2\) solubility effect) was unlikely to be identical across depths (shallow and deep circulation cells) and ocean basins (Pacific vs. Atlantic), in determining the spatial patterns in glacial-interglacial BWO changes (Fig. 5). Today, the deep ocean is less oxygenated in the Pacific than in the South Atlantic because of the significant aging of deep waters in the Pacific Ocean (Broecker and Peng, 1982). Ocean circulation reconstructions suggest stronger stratification and more sluggish deep circulation during the LGM in the Atlantic (Ferrari et al., 2014; Howe et al., 2016; Roberts et al., 2016), whereas arguments for (Basak et al., 2018; Du et al., 2018) and against (Hu and Piotrowski, 2018) reduced ventilation in the glacial deep Pacific have been made.

During the glacial, export production generally may have increased in the South Atlantic (Kohfeld et al., 2005). In the Sub-Antarctic Atlantic, north of the Antarctic Polar Front (APF), increased dust flux during glacial times was associated with iron fertilization and a strengthened biological pump (Martínez-García et al., 2014). On the other hand, export production decreased in the glacial equatorial and North Pacific (Costa et al., 2018; Costa et al., 2016; Kohfeld and Chase, 2011) (Fig. 5). In the equatorial Pacific, dust deposition was greater during glacial periods, but whether it was large enough to provide substantial iron fertilization remains controversial (Costa et al., 2016; Loveley et al., 2017; Murray et al., 2012; Winckler et al., 2016). In the Sub-Antarctic East Pacific and just south of the APF, both
dust deposition and export production increased during glacial relative to interglacials (Lamy et al., 2014).

This set of proxy records (Fig. 5C) covers the broadly defined glacial period, when the drivers for changes in the Earth system established for the LGM should largely apply. For glacial oceans, these records (Fig. 5C) obviously do not yet resolve the extent of low BWO (< 50 µmol/kg) globally, but they do show potential to generate a hypothesis for comparison with models of the glacial ocean circulation and associated biogeochemical parameters. For example, low BWO appeared more frequently in the intermediate-deep parts of the Pacific (1.4 – 3 km) than in the upper-intermediate depths in the Atlantic (< 2 km). The glacial deoxygenation in the deep circulation cells in both the South Atlantic and Pacific Oceans (Fig. 5) likely was driven by ventilation changes or air-sea disequilibrium (Eggleston and Galbraith, 2018; Ferrari et al., 2014; Khatiwala et al., 2019; Rae et al., 2018; Stephens and Keeling, 2000). Global temperature change might have influenced whole-ocean oxygenation more through reduced ventilation, than through changes in O₂ solubility due to cooling. In the glacial Pacific Ocean, lower productivity and deoxygenation at intermediate-deep water depths (1.4 – 3 km) suggests that ventilation changes may have had a major impact on BWO. In contrast, the enhanced biological pump in the Atlantic and possibly shallower deoxygenation (< 2 km) suggest that productivity might have played an important additional role in driving glacial deoxygenation (Fig. 5C). Ventilation and productivity thus might have differently affected deoxygenation in the two ocean basins. More (semi-)quantitative records are required to confirm this spatial pattern for modeling work to explore mechanistic explanations, such as changes in the westerlies, dust supply, changes in the remineralization
depth/efficiency, the nature of ecosystem communities, circulation rate/water mass extent, and density structure of the ocean.

### 5.3 Implications for glacial ocean carbon storage

Glacial bottom water deoxygenation is commonly associated with increased storage of respired carbon in the deep ocean (e.g., Anderson et al. (2019); Bradtmiller et al. (2010); Cartapanis et al. (2016); Hoogakker et al. (2018); Hoogakker et al. (2015); Jacobel et al. (2020)). \( \text{CO}_2 \) is removed from the surface ocean by photosynthesis, and oceanic \( \text{O}_2 \) is consumed through the respiration of fixed organic carbon, with a \( \text{CO}_2:\text{O}_2 \) stoichiometry of 0.7 below 400 m (Anderson and Sarmiento, 1994), although air-sea disequilibrium could alter the relationship between dissolved oceanic \( \text{O}_2 \) and carbon storage (Ito and Follows, 2013; Khatiwala et al., 2019). The respired carbon storage or respiratory \( \text{CO}_2 \) concentrations in the glacial-time ocean were estimated on a regional scale by calculating the oxygen utilization (the difference between measured BWO and the saturated dissolved \( \text{O}_2 \) concentrations of the water mass at each salinity and potential temperature) and using approximate Redfield ratios for \( \text{C}_{\text{org}}/\text{O}_2 \) of 117/170 (e.g., Hoogakker et al., 2015, 2018; Anderson et al., 2019). In future work, more (semi-)quantitative glacial BWO data with higher spatial coverage, especially in the same water mass, will help improve such calculations on carbon storage globally and in each ocean basin.

Global analyses of modern seawater show that \( ^{\delta^{13}}\text{C} \) of dissolved inorganic carbon is significantly correlated with deep water \( \text{O}_2 \) (Hoogakker et al., 2016). Down-core records show similar positive relations between averaged \( ^{\delta^{13}}\text{C}_{\text{Cibicoides}} \) and I/Ca values or
δ^{13}C-derived O_2 estimates, supporting that bottom waters were overall less-oxygenated and carbon storage was higher during the LGM (Fig. 6). Our semi-quantitative BWO values thus agree with other observations that the glacial ocean was less well-ventilated and stored more respired carbon than the modern ocean, despite lower global temperatures. Climate-driven changes in ocean ventilation and biological productivity thus can outweigh the effect of temperature-dependent O_2 solubility in determining past ocean deoxygenation and may have played different roles in the glacial Atlantic vs. Pacific Oceans.

6. Conclusions

We document the potential of epifaunal I/Ca as a promising semi-quantitative BWO proxy, and demonstrate that epifaunal I/Ca combined with independent other proxies (e.g., Δδ^{13}C and pore area percentages) can provide more reliable reconstructions of BWO in the world ocean than the use of a single proxy. The global compilation of I/Ca, δ^{13}C and C_{37} alkenone records indicates that waters with O_2 < 50 µmol/kg were more extensive in the Atlantic and Pacific Oceans during glacial periods than present day, and that the driving mechanisms of glacial-time deoxygenation may have differed between ocean basins. Our results support a glacial ocean with generally less-oxygenated bottom waters at water depths >1500-2000 m and increased carbon storage.

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Figures

Fig. 1. Core and sample locations (EEP: Eastern Equatorial Pacific).
Fig. 2. (A). Dissolved oxygen concentration ([O$_2$]$_{sw}$) versus dissolved iodate concentration in seawater ([IO$_3^-$]$_{sw}$) (Cutter et al., 2018; Farrenkopf and Luther, 2002; Huang et al., 2005; Rue et al., 1997). (B). I/Ca in shells of living and unstained benthic foraminifera from core-top sediments versus bottom water oxygen concentrations ([O$_2$]$_{bw}$). Error bars for y axis indicate the s.d. (1 s.d.) of duplicate measurements. (C). Surface pore areas in foraminiferal tests versus ambient [O$_2$]$_{bw}$ modified from Rathburn et al. (2018); $\Delta^{13}$C versus [O$_2$]$_{bw}$ modified from Hoogakker et al. (2015), and two open symbols are from Hoogakker et al. (2018). The orange shading in A, B and C marks [O$_2$] < ~50 µmol/kg. The dashed lines in B and C illustrate the I/Ca or pore area cut-off values and related optimal O$_2$ thresholds determined from the ROC method (for details see text). Thick dashed lines denote AUC > 0.95 (better ROC test results), and the thin dashed lines denote AUC < 0.95.
Fig. 3. Comparison of epifaunal I/Ca with O₂ reconstructions from Δδ¹³C in the EEP (Hoogakker et al., 2018) and Southeast Atlantic (McKay et al., 2016) over the last 45 ka and 75 ka, respectively. The aU record at site RC13-140 is from Bradtmiller et al. (2010). Yellow asterisks in the bottom panels denote the modern bottom water O₂ at the sites.
Fig. 4. Down-core records of benthic foraminiferal I/Ca plotted vs. time. Blue shaded areas indicate glacial periods and bold dashed orange lines indicate $[O_2] < \sim 50 \mu mol/kg$. 
Fig. 5. Global compilation of benthic I/Ca, Δδ^{13}C, C_{37} alkenones, and aU proxy records. (A)
Map view, (B) modern and (C) glacial transects through the Atlantic and Pacific Oceans. Red symbols highlight sites with glacial deoxygenation and glacial BWO < 50 µmol/kg, as estimated from I/Ca < 3 µmol/mol, or an order-of-magnitude higher of C_{37} alkenones, or calculated from Δδ^{13}C. “Uncertain” refers to sites without sufficient Holocene and/or glacial samples for I/Ca or Δδ^{13}C analyses and factors other than BWO hampering the interpretation of aU as BWO proxy, respectively. Note that the Δδ^{13}C calculated from C. kullenbergi at Sub-Antarctic Atlantic site MD07-3076Q (44.15°S, 14.23°W, 3.8 km) (Gottschalk et al., 2016a) has been re-calculated (Gottschalk et al., 2016b), because the calibration was only applicable for δ^{13}C_{C. wuellerstorfi}. The productivity changes at the LGM relative to the late Holocene are adapted from Costa et al. (2017); Kohfeld et al. (2005). The ocean circulation in panel B and C is adapted from Du et al. (2018); Sigman et al. (2010). NADW: North Atlantic Deep Water; AABW: Antarctic Bottom Water; AAIW: Antarctic Intermediate Water; GNAIW: Glacial North Atlantic Intermediate Water; PDW: Pacific Deep Water.
Fig. 6. A) Averaged *Cibicidoides* spp. $\delta^{13}C$ versus $[O_2]_{BW}$ and B) I/Ca at each site with down-core data between modern/Holocene and LGM (open symbols). The LGM $[O_2]$ values in panel A are derived from $\Delta \delta^{13}C$. Background scatter plot in panel A shows the modern global relationship between seawater $[O_2]$ and $\delta^{13}C$ of dissolved inorganic carbon based on seawater analyses (filled symbols) (Hoogakker et al., 2016). Red color band corresponds to $[O_2] < 50 \mu$mol/kg windows in Fig. 1B, and the y-axis are scaled to the proposed I/Ca - $O_2$ estimates discussed in the text. The arrows in panel B indicates the data trend towards decreased oxygenation and increased carbon storage in LGM. I/Ca values at site TC493 are not from the Holocene and the LGM but from MIS 5e and MIS 6.
Supplementary Materials

Table S1: Summary of the living and unstained foraminifera in the core-top sediments in Fig. 2B.

Table S2: Five down-core I/Ca records in Fig. 4.

Table S3: Compilations of Dδ\(^{13}\)C, C\(_{37}\) alkenones, and aU records in Fig. 5.

**Fig. S1.** Receiver Operating Characteristic (ROC) curve to identify the O\(_2\) threshold for the presence/absence of low I/Ca (< 3 µmol/mol). Two statistical measures of the ROC method are true-positive rate (i.e. the proportion of low I/Ca correctly identified as low I/Ca) and false-positive rate (i.e. the proportion of high I/Ca incorrectly identified as low I/Ca). A better performance of the binary classification test should have high true-positive rate and low
false-positive rate. The ROC results showed that to best classify the presence/absence of low I/Ca, the optimal O₂ threshold should be ~30 µmol/kg, with true-positive rate of 100% and relatively low false-positive rate of 13%. Using an O₂ threshold of ~55 µmol/kg can increase the false-positive rate to 32%, while the true-positive rate is still 100%. Statistical analyses were performed using IBM SPSS Statistics software (https://www.ibm.com/analytics/academic-statistics-software).
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Chapter 4

Comparison of benthic foraminiferal surface porosity and I/Ca proxies at a cold seep site on the southern Brazilian margin over the last 45 kyr

Chapter 4 is under review at *Paleoceanography and Paleoclimatology.*
Abstract

Benthic foraminiferal surface porosity (the mean percentage of surface area covered by pores; higher porosity: lower oxygenation) and I/Ca (higher I/Ca: higher oxygenation) are both promising paleoceanographic proxies that need testing in down-core studies. Here we report the first down-core comparison (~45 kyr) of these proxies in a core from a cold seep site on the southern Brazilian margin (26°40′S, 46°26′W, 475 m water depth). The two proxies are overall consistent, with porosity values generally low (< 10%) and I/Ca ranges between ~4 and ~6 µmol/mol throughout the core, suggesting that bottom water oxygen concentrations at the site remained above 50 µmol/kg during the last 45 kyr. Potential seafloor methane release during the last glacial period (40-20 ka), as indicated by anomalously negative δ¹³C values in foraminifera, apparently had limited impact on bottom water oxygenation, and interactions between competing processes potentially affecting bottom water oxygenation (i.e., water column stratification and productivity) may have limited the magnitude of changes in bottom water oxygen levels at the core site.

1. Introduction

Oxygen availability in the oceans, probably linked to Earth’s climate system, significantly influences marine life and biogeochemical cycling. Regions with reduced oceanic oxygen content have been increasing globally since 1960 (Schmidtko et al., 2017), with changes in oxygenation associated with a range of biological and ecological changes (Breitburg et al., 2018). Earth system models are being used to study the potential driving
mechanisms of changes in oceanic oxygenation across glacial-interglacial cycles (e.g., Buchanan et al. (2016); Galbraith and Jaccard (2015); Schmittner and Somes (2016); Yamamoto et al. (2019)), and to project future oceanic oxygenation changes under possible global warming scenarios (e.g., Bopp et al. (2013); Fu et al. (2018)). However, a large uncertainty remains in the results of current climate models, in part due to a lack of reliable, quantitative paleo-O$_2$ data against which to validate model results (Yamamoto et al., 2019).

Several (semi-)quantitative paleo-oxygenation proxies for glacial oceans have been proposed and calibrated to modern bottom water oxygen (BWO) values. These (semi-)quantitative proxies can be divided into two categories: (1) a biological proxy: the porosity or surface pore area percentages in benthic foraminiferal tests (Rathburn et al., 2018); (2) geochemical proxies: benthic foraminiferal carbon isotope gradients between epifaunal (living on or above the seafloor surface) (Cibicidoides wuellerstorfi) and deep infaunal (living within sediments) species (Globobulimina spp.) (Hoogakker et al., 2018; Hoogakker et al., 2015; McCorkle and Emerson, 1988); preserved organic compounds (Anderson et al., 2019); and the I/Ca in benthic foraminiferal tests (Glock et al., 2014; Lu et al., 2020). Each proxy has its own limitations and oxygen sensitivity window. The porosity, I/Ca, and organic compound preservation proxies are most sensitive in low O$_2$ windows (< 50 µmol/kg), and may have larger uncertainties in high O$_2$ windows. The $\Delta$δ$^{13}$C proxy is the only available proxy calibrated to a wider O$_2$ window (20 - 235 µmol/kg), but its application is limited due to the restricted occurrence of Globobulimina spp. (Jorissen et al., 2007), the potential influence of seasonal phytodetrital flux on $\delta^{13}$C$_{C.wuellerstorfi}$ (Mackensen et al., 1993), and the impact of anaerobic processes (including denitrification and sulfate reduction) on
$\delta^{13}C_{\text{Globobulimina}}$ (Jacobel et al., 2020; McCorkle and Emerson, 1988). A multi-proxy approach, with differing ranges of $O_2$-sensitivity, thus may provide more reliable paleo-$O_2$ estimates for the glacial oceans than a single proxy. Testing the consistency between new proxies in core-top and down-core samples is an important step during proxy development.

In this study, we apply the benthic foraminiferal surface porosity and the I/Ca proxy to foraminifera from a core in a seep site (GeoB6201-5) on the southern Brazilian margin. No glacial oxygenation record has yet been reported for the Southwest Atlantic Ocean (Galbraith and Skinner, 2020; Lu et al., 2020), and a down-core reconstruction using two independent oxygenation proxies may elucidate the BWO history in this area. At the location of core GeoB6201-5, seafloor methane release may have occurred during the last glacial period (40-20 ka), as inferred from anomalously negative $\delta^{13}C$ values in both planktic (down to $-6 \%$) and benthic foraminifera (down to $-4.6 \%$). These values are more negative than values in two cores in the same area, considered to reflect regional water mass conditions in glacial $\delta^{13}C$ values of $\sim 0.2 \%$ (Portilho-Ramos et al., 2018). Modern methane seepage has been linked to bottom water oxygen consumption (Boetius and Wenzhöfer, 2013), and we test the potential impact of methane release on BWO in paleoceanographic records.

In modern oceans, epifaunal foraminifera living in low-oxygen waters (e.g., < 50 $\mu$mol/kg) tend to have a higher percentage of their surface area occupied by pores (e.g., > 15%) (Rathburn et al., 2018), likely due to the increased demand for gas exchange (Glock et al., 2012; Rathburn et al., 2018). In contrast, foraminifera living in well-oxygenated waters (> 200-250 $\mu$mol/kg) are likely to have fewer pores on their surface (e.g., < 5%), and may acquire oxygen mainly through the aperture, the primary opening of the test (Rathburn et al.,
To date, the epifaunal porosity proxy has not yet been applied to down-core studies.

The I/Ca proxy has been calibrated on modern foraminifera and applied to several studies of glacial-interglacial intervals (Hoogakker et al., 2018; Lu et al., 2019; Lu et al., 2020; Lu et al., 2016). The thermodynamically stable iodine species in seawater are mainly iodate (IO$_3^-$, oxidized form) and iodide (I$, reduced form). Iodate is completely reduced to iodide under anoxic conditions, and re-oxidized in oxic waters (Rue et al., 1997). Only iodate can be incorporated into the calcite structure (Lu et al., 2010), by replacing the carbonate ion (Feng and Redfern, 2018; Podder et al., 2017), thus lower foraminiferal I/Ca values generally indicate less-oxygenated conditions. The combination of low epifaunal I/Ca values (<~3 µmol/mol) and independent oxygenation proxies has been proposed to be a more reliable approach to detect low-oxygen waters (<~50 µmol/kg) in glacial oceans than the use of a single proxy (Lu et al., 2020).

The motivation of this study is to further develop benthic foraminiferal surface porosity and benthic I/Ca as paleo-oxygenation proxies in down-core reconstructions, and in addition to use our record to investigate the potential impact of seafloor methane release on BWO conditions, as well as to explore the potential driving mechanisms of BWO history at the studied site.

2. Samples and Methods

2.1. Study site and age model

Core GeoB6201-5 (26°40′S, 46°26′W, 475 m water depth; 247 cm long) was taken at the center of a funnel-shaped depression (diameter 600 m, depth 70 m) on the upper slope of the
Santos Plateau, on the Brazilian margin, below the southward path of the Brazil Current (Schulz et al., 2001), and the location is bathed by well-oxygenated waters (BWO of ~225 µmol/kg) (Boyer et al., 2013; Schulz et al., 2001) (Fig. 1). Natural gas hydrates have been found in large pockmark fields (depressions of collapsed sediments) at water depths between 550 m and 1400 m on the southern Brazilian margin (Miller et al., 2015) (locations shown in Fig. 1). Gas venting occurred near the feather edges of the gas hydrate stability zone (510 m to 760 m), reflecting gas hydrate disassociation and methane release to the oceans (Ketzer et al., 2019). However, during the cruise (Schulz et al., 2001) no evidence of methane was measured during sampling, but H₂S was detected.

The age model for this core is after Portilho-Ramos et al. (2018), based on the combination of six AMS ¹⁴C ages on the planktic foraminifera Globigerinoides ruber, regional planktic foraminiferal biostratigraphy, and oxygen isotope stratigraphy. In order to avoid contamination from old carbon sources, sampling depths for AMS ¹⁴C were selected at levels without anomalously negative δ¹³C values (except for the basal age of 235 cm). The age model and associated uncertainty were calculated using a reservoir correction of 400 ± 100 years. The ¹⁴C-based age model was verified by comparing Cibicidoides spp. δ¹⁸O records at core GeoB6201-5 with those in well-dated core GeoB2107-3 (27°10’S, 46°27’W, 1,048 m water depth) (Hendry et al., 2012), and the regional, intermediate-depth South Atlantic benthic δ¹⁸O stack (Lisiecki and Stern, 2016). In addition, the ¹⁴C-based chronostratigraphy at core GeoB6201-5 was verified by comparing abundance changes of the planktic foraminiferal species Globorotalia menardii and Globorotalia inflata, indicative of glacial-interglacial biozones (Ericson and Wollin, 1968). The regional planktic foraminiferal
biostratigraphy and oxygen isotope stratigraphy support the $^{14}$C-based age model of GeoB6201-5.

2.2. Foraminiferal surface porosity analyses

Benthic foraminifer specimens of *C. wuellerstorfi* and *C. pseudoungerianus* were picked from the size fraction $\geq 150$ µm. The method to measure and calculate surface porosity of benthic foraminifera is after Petersen et al. (2016). For each sampling depth, at a resolution of 5 cm, three specimens of each species were analyzed, adding up to 275 individuals in 48 samples, and microphotographs were made in a Scanning Electron Microscope (SEM). The dorsal side of each specimen (the side exposed to bottom water) was imaged. We then determined the pore area percentages or porosity in the penultimate chambers of the foraminiferal test using the SEM images at 300× magnification using ImageJ, semi-automatic software to calculate the pore areas, based on a grayscale threshold applied to a specific frame. The frames were manually positioned using a macro developed by Petersen et al. (2016) (Supplementary material) that allowed us to place a frame of a fixed size on the SEM images. Some adjustments were made in the macro due to the image magnification (300×) used in this work, rather than the 500× used by Petersen et al. (2016). Five different frame sizes with different proportions (Petersen et al., 2016) were tested to select the frame that best represented the porosity of the chambers. A non-parametric analysis (Kolmogorov-Smirnov) using R-software was performed to verify the best frame and the representativeness of the data.

Previous studies linked pore density (number of pores per surface area) in different
species of infaunal foraminifera to ambient conditions, probably influenced by pore water conditions and nitrate respiration (e.g., (Kuhnt et al., 2013; Kuhnt et al., 2014)). Higher porosity can be due to higher pore density and/or greater pore size (Petersen et al., 2016), with porosity taking both variables into account. Porosity likely represents the individual foraminifer's oxygen accessibility better than pore density or pore diameter alone (Rathburn et al., 2018).

2.3. Foraminiferal I/Ca analyses

Foraminiferal I/Ca analyses were performed on the same specimens used to determine porosity after these measurements were completed, following Lu et al. (2020). Around 15 specimens of *C. pseudoungerianus* were used for each sampling depth. The samples were gently crushed using cleaned glass slides to open all chambers. Samples were then cleaned by ultrasonication in de-ionized water to remove clays, a 10-min boiling-water bath in NaOH-buffered 1% H$_2$O$_2$ solutions to remove organic matter, and three additional rinses with de-ionized water. The cleaned samples were dissolved in 3% HNO$_3$ and then diluted to solutions containing ~50 ppm Ca, internal standards (5 ppb In and Cs), and 0.5% tertiary amine (to stabilize iodine). The measurements were performed immediately on a quadrupole ICP-MS (Bruker M90) at Syracuse University. Calibration standards were freshly made for each batch of samples. The sensitivity of iodine is tuned to ~90 kcps for 1 ppb standard, and the standard deviation for three blanks in a row is <1 kcps. The precision for $^{127}$I is typically better than 1%. The reference standard JCp-1 was analyzed repeatedly to monitor long-term accuracy (Lu et al., 2018; Lu et al., 2010). The detection limit of I/Ca is on the order of 0.1
µmol/mol. Replicates of selected samples from glacial and interglacial intervals yielded a reproducibility ranging from ± 0% (0.002 µmol/mol, 1σ) to ± 9% (0.49 µmol/mol, 1σ) for I/Ca (Table S1).

2.4. Benthic foraminiferal habitat

Epifaunal to shallow infaunal foraminifera are expected to record bottom water conditions, in contrast to deeper infaunal species, which reflect pore water conditions. *C. wuellerstofi* (an epifaunal species) thus records the bottom water conditions. *Cibicidoides pseudoungerianus*, also used in this study, is not taxonomically well-defined, and is morphologically close to *C. pachyderma* (Schweizer, 2006). The name is thought to be a synonym of *C. pachyderma* by some authors (e.g., Altenbach et al. (2003); Licari and Mackensen (2005)). It typically occurs on the deep and upper continental slope (< 2000 m), in areas with a broad range of organic carbon flux and primary productivity (Altenbach et al., 2003; Altenbach et al., 1999). It has been described as epifauna attached to hard substrates such as hydroids (Brasier, 1975; Dobson and Haynes, 1973), and as shallow infauna dwelling at between +1 and -1 cm of the sediment-water interface (Schweizer, 2006).

3. Results and Discussion

3.1. Comparing the porosity and I/Ca proxies

The porosity down-core values average 5.3% for *C. wuellerstofi* (n = 48, S.D. = 1.4%) and 8.4% for *C. pseudoungerianus* (n = 48, S.D. = 2.3%), and the I/Ca values average 4.9 µmol/mol for *C. pseudoungerianus* (n = 48, S.D. = 0.6 µmol/mol) (Fig. 2, Supplementary
Table S1). The porosity values in *C. wuellerstorfi* are generally lower than those in *C. pseudoungerianus* throughout the record, and both species show similar average values during the Holocene (0-10 ka), deglaciation (10-18 ka) and last glacial period (18-45 ka) (averages 5.4%, 6.0%, and 5.0% for *C. wuellerstorfi*, respectively; averages 8.8%, 9.7% and 7.7% for *C. pseudoungerianus*, respectively) (Fig. 3). The I/Ca values were slightly higher during the Holocene (average 5.6 µmol/mol), with similar values during the deglaciation and the last glacial period (averages 4.8 and 4.6 µmol/mol, respectively) (Fig. 3). The two-group Mann-Whitney test show that porosity values are significantly different in deglacial vs. glacial (*p* = 0.01 for *C. wuellerstorfi*, *p* = 0.02 for *C. pseudoungerianus*), but not significantly different in Holocene vs. deglacial (*p* = 0.58 for *C. wuellerstorfi*, *p* = 0.41 for *C. pseudoungerianus*); I/Ca values are significantly different in Holocene vs. deglacial (*p* < 0.01), but not significantly different in deglacial vs. glacial (*p* = 0.19). However, these variations are not large enough to reliably indicate changes in BWO, considering the existing modern calibration data. The core-top benthic foraminiferal porosity and I/Ca values at core GeoB6201-5 (ages < 5 ka) agree well with the values in the global core-top dataset of porosity and I/Ca values (Fig. 4) (Lu et al., 2020; Rathburn et al., 2018).

The presence of high-Mg calcite and elevated contents of Mg and S in the glacial samples in core GeoB6201-5 suggests overgrowths of post-depositional authigenic carbonate, possibly related to the anomalously negative δ¹³C values in some samples, although not all glacial samples contain high-Mg calcites (Portilho-Ramos et al., 2018). We examined the potential effects of authigenic carbonate overgrowths on our records by comparing the porosity and I/Ca data in glacial samples with high-Mg calcite vs. those without high-Mg
calcite (between 140 and 235 cm core depth) (Fig. 5, Supplementary Tables S2). We did not find consistent or systematic differences in porosity or I/Ca between samples with and without high-Mg calcite, suggesting that authigenic carbonate overgrowths probably did not significantly affect the porosity or I/Ca signals.

The core-top I/Ca values in *C. pseudoungerianus* from core GeoB6201-5 are similar to values in core-top *Cibicidoides* and living *C. wuellerstorfi* in a global core-top calibration, in which shallow infaunal species (e.g., *C. pachyderma* and *C. mundulus*) have I/Ca values similar to those in *C. wuellerstorfi* at the same locations. In a down-core record from the Eastern Equatorial Pacific, I/Ca values of *C. wuellerstorfi* and *C. pachyderma* over the last 45 kyr are similar (Lu et al., 2020). The porosity and I/Ca calibrations were developed on epifaunal *C. wuellerstorfi*, but shallow infaunal species may provide paleo-O$_2$ information. The porosity values in *C. pseudoungerianus* are generally higher than those in *C. wuellerstorfi*, probably because *C. pseudoungerianus* is partly influenced by pore water conditions or there are species-specific effects between these two species. The *C. pseudoungerianus* porosity data closely track the *C. wuellerstorfi* data, so we think that changes in *C. pseudoungerianus* are not completely due to its potential shallow infaunal habitat, and we think it more likely that both *Cibicidoides* species record BWO trends.

Most porosity and I/Ca proxy records (as represented by the 25th and 75th percentile values) in core GeoB6201-5 fall into the data range corresponding to modern BWO, i.e., between 50 and 250 µmol/kg, in the core-top data set (Fig. 4). A combination of low I/Ca (< 3 µmol/mol) and high porosity (> 15%) indicates low-O$_2$ waters (< 50 µmol/kg) (Lu et al., 2020). However, low porosity (< 10%) and high I/Ca (> 3 µmol/mol) are associated with a
wide range of values of O$_2$, i.e., between 50 and 250 µmol/kg in the core-top data set, and the causes of this variability remain unclear. The occurrence of this wide range of low porosity and high I/Ca values indicates a significant uncertainty in derived O$_2$ values. We suggest that the glacial BWO at the location of core GeoB6201-5 was most likely above the threshold of 50 µmol/kg. A more precise O$_2$ value cannot be inferred from porosity or I/Ca records at this stage, due to the limitations of both proxies at higher O$_2$ concentrations. Modeling studies suggested that O$_2$ values at ~500 m water depths at ~27°S in South Atlantic Ocean during the Last Glacial Maximum (LGM) were not significantly different from pre-industrial times (Schmittner and Somes, 2016; Yamamoto et al., 2019).

The development of the porosity and I/Ca proxies started only recently, thus there is only a limited amount of data from living C. wuellerstorfi, insufficient to clearly show how the two proxies relate to each other in a cross-plot of data measured on the same set of specimens (Fig. 6). We explore this relationship by including down-core data from core GeoB6201-5, which are not significantly different from the living C. wuellerstorfi, with values clustering in the middle range (2 - 10% for porosity; 4 - 7 µmol/mol for I/Ca). The living C. wuellerstorfi samples reflect a much wider O$_2$ range, from 2 to 277 µmol/L, than the downcore samples (Lu et al., 2020; Rathburn et al., 2018). Future studies of modern and down-core samples need to (1) obtain more high porosity - low I/Ca samples to better define the low O$_2$ endmember and (2) determine whether porosity shows a correlation with I/Ca at O$_2$ > 50 µmol/kg.

In summary, we suggest that the porosity proxy is generally consistent with benthic I/Ca values in this down-core record. Both porosity and I/Ca proxies are useful paleo-oxygenation
tools, which are most sensitive under relatively low O$_2$ conditions, but are as yet not so well constrained in higher O$_2$ conditions. Future work is required to improve our understanding of the relation between porosity and I/Ca, and test potential non-O$_2$ effects on porosity and I/Ca in both core-top and down-core samples.

3.2. No evidence for seafloor methane release on BWO

The anomalously negative $\delta^{13}$C values in glacial foraminifera at core GeoB6201-5 (Portilho-Ramos et al., 2018) and authigenic carbonate nodules with low $\delta^{13}$C values (down to -30 ‰) in glacial samples from nearby cores (Kowsmann and de Carvalho, 2002; Wirsig et al., 2012) (Fig. 1) have been interpreted as indicating that seeps on the southern Brazilian margin may have been active for thousands of years. Neither porosity nor I/Ca values show significant changes during the time period of potential seafloor methane release at core GeoB6201-5 (Fig. 2), suggesting no detectable impact of seafloor methane release on BWO. The potential methane release at the core site thus apparently was recorded by foraminiferal $\delta^{13}$C, but oxygenation proxies do not show a significant response. There are four possible explanations: (1) the low foraminiferal $\delta^{13}$C values at core GeoB6201-5 may have been influenced by factors other than methane release; (2) both porosity and I/Ca proxies have non-linear relationships with BWO, and BWO did not drop to $<$ 50 µmol/kg, so that the proxies did not respond (Fig. 3); (3) BWO may have been minimally affected by methane release; (4) methane release were short-lived events, the resolution of our samples may be too low to capture such events.

As to the first possibility, there have been arguments both for (e.g., Hill et al. (2004);
Mackensen et al. (2006); Rathburn et al. (2003)) and against (e.g., Stott et al. (2002); Torres et al. (2003)) a relation between low δ^{13}C in living benthic foraminifera and methane venting at the seafloor. Diagenetic overgrowths may have partly caused the low δ^{13}C, but were not responsible for all negative δ^{13}C signals from fossil foraminifera at core GeoB6201-5 (Portilho-Ramos et al., 2018). If diagenetic carbonates caused the low δ^{13}C, this process would have decreased I/Ca values (Hardisty et al., 2017), but we did not find indications of carbonate diagenesis in our down-core I/Ca record. Likewise, no carbonate overgrowths were evident in SEM images used in the pore analyses.

Regarding the second possibility, most bottom waters above modern seeps are well-oxygenated (250-350 µmol/kg) (Boetius and Wenzhöfer, 2013), including in our study area where natural gas hydrates are found (Miller et al., 2015) (see Fig. 1). Our BWO proxies are most sensitive to BWO below ~50 µmol/kg, thus we cannot rule out the possibility that a BWO decrease caused by methane release was not large enough to be discerned in our proxies. On the other hand, observations in the modern ocean are inconclusive regarding potential decrease in BWO during methane release (the third possibility mentioned above). Modern seeps can have similar or lower BWO than nearby non-seep environments (Boetius and Wenzhöfer, 2013; Levin et al., 2003; Rathburn et al., 2003). For example, at modern seepage areas in Monterey Bay, California, BWO ranges 1 to 80 µmol/L, compared to 80 µmol/L at a nearby non-seep site (Rathburn et al., 2003). A modern event of ‘rapid’ methane release, the 2010 Deepwater Horizon Oil spill in the Gulf of Mexico, had caused an oxygen anomaly in the seawater (average 5.6 ± 5.8 µmol/L) persisting for months (Kessler et al., 2011), and more reducing pore waters for two years (Hastings et al., 2016). A modeling study
also suggested that methane oxidation may cause ~5 µmol/L O$_2$ reduction in Southwest Atlantic Ocean (our study area) (Yamamoto et al., 2014). Methane oxidation theoretically must consume BWO, but the potential small O$_2$ changes may not have been detected by either porosity or the I/Ca proxy. Furthermore, mixing with bottom currents may have prevented the development of local oxygen depletion at the methane seeps (Boetius and Wenzhöfer, 2013), which we think most likely.

### 3.3. Potential mechanisms stabilizing BWO

In modern oceans, there are three main factors controlling the oceanic O$_2$ content: (1) the transfer of atmospheric oxygen to the surface ocean, linked to oxygen solubility; (2) ocean circulation (ventilation), which affects the transport of O$_2$-rich surface water into the deeper part of ocean; (3) O$_2$ consumption by the oxidation of organic matter (Keeling et al., 2010). Lower temperatures during the last glacial period would mean higher O$_2$ solubility, but changes in ocean circulation and biological respiration may have led to globally lower O$_2$ in the deep oceans (Anderson et al., 2019; Jaccard and Galbraith, 2012; Lu et al., 2020).

The water mass provenance in the mid-depth Southwest Atlantic (1000 – 3000 m) was likely similar during the LGM and early deglaciation, as inferred from neodymium isotope records (Howe et al., 2018; Howe et al., 2016; Pöppelmeier et al., 2020). However, little is known about the ocean circulation history in the upper part (< 1000 m) of the region. The upper water stratification history, as reconstructed from the δ$^{18}$O difference between the deep- and shallow-dwelling planktic foraminifera *Globorotalia truncatulinoides* and *Globigerinoides ruber* (Δδ$^{18}$O) in nearby core GeoB2107-3 (Fig. 7) (Pereira et al., 2018),
may be comparable to the ocean circulation history at the studied site. In addition, the marine productivity history in this core, as reconstructed from the relative abundance of the eutrophic planktic species *Globigerina bulloides* and *Globigerinita glutinata* (Pereira et al., 2018), may help explore the potential driving mechanisms of the BWO conditions at core GeoB6201-5.

At core GeoB6201-5, both porosity and I/Ca show similar values in the LGM and Heinrich Stadial 1 (HS1). During HS1, Atlantic meridional overturning circulation weakened, the Brazilian Current (BC) strengthened, and re-organization of atmospheric circulation may have led to increased river discharge and the flow of nutrient-rich coastal waters towards the study site, enhancing primary productivity (higher percentages of planktic assemblages). A strengthened BC may have enhanced the development of cyclonic vortices, reducing the stratification of upper waters (lower $\Delta^{18}O$), further promoting nutrient input to the euphotic zone (Pereira et al., 2018). The weaker upper ocean stratification (potentially better ventilated waters) and higher primary productivity (potentially more $O_2$ utilization) during HS1 may have counteracted to prevent strong BWO changes. The I/Ca values were slightly higher during the Holocene than during HS1, whereas there were no significant changes in the porosity. Stronger upper ocean stratification (higher $\Delta^{18}O$, potentially less ventilated waters) and lower primary productivity (lower percentages of planktic assemblages, potentially less $O_2$ utilization) during the Holocene may have been competing processes, resulting in a lack of significant BWO change. More oxygenation proxy records from more sites are required to define the spatial and bathymetrical $O_2$ pattern in the Southwest Atlantic Ocean during climate transitions.
4. Conclusions

The close correspondence between porosity and I/Ca proxies in a down-core record over the last 45 kyr builds confidence in using these proxies to reconstruct past changes in oceanic O₂. The BWO at the location of core GeoB6201-5 likely remained above ~50 µmol/kg over the last glacial period. The proxies did not show a change in bottom water oxygenation linked to potential seafloor methane release during the last glacial period, possibly because the resolution of the record is insufficient to capture the signals of rapid methane release, or the O₂ reduction due to aerobic methane oxidation was limited. The lack of change in oxygenation across the last deglaciation can be explained by competing effects of changes in stratification (thus ventilation) and productivity in the region.

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Figures

**Fig. 1.** Location of core GeoB6201-5 used in this study. **A)** Modern bottom water oxygen map in the Southwest Atlantic region. **B)** Depth profile (red box in A) showing well-oxygenated upper-intermediate waters on the southern Brazilian margin today. The white square shows the location of core GeoB2107-3 from which paleoceanographic records are compared. Yellow diamonds show the locations where natural gas hydrate was found in piston cores (Miller et al., 2015). Blue diamonds show the locations where authigenic carbonates with low δ¹³C were found in glacial samples at nearby cores (Kowsmann and de Carvalho, 2002; Wirsig et al., 2012). Figures are produced using the Ocean Data View software (Schlitzer, 2019).
Fig. 2. Benthic foraminiferal porosity and I/Ca records from core GeoB6201-5 (this study) along with benthic δ¹⁸O and δ¹³C records for the same core (Portilho-Ramos et al., 2018).
Fig. 3. Candlestick plot for porosity and I/Ca from core GeoB6201-5. The red box marks the 25th and 75th percentiles, the red horizontal line inside the box indicates the average, and the whiskers show the maximum and minimum values.
**Fig. 4.** Comparison of core-top foraminiferal porosity and I/Ca (ages < 5 ka) in core GeoB6201-5 (this study) with global calibration dataset (Lu et al., 2020; Rathburn et al., 2018). The box marks the 25th and 75th percentiles in the GeoB6201-5 down-core record, the horizontal line inside the box indicates the average, and the whiskers show the maximum and minimum values. Yellow shaded areas show the low-O₂ thresholds as proposed in Lu et al. (2020). Note that the porosity calibration dataset from Rathburn et al. (2018) represents average values of multiple specimens at each location.
Fig. 5. Comparison of porosity and I/Ca in glacial samples with and without high-Mg calcite. The identification of high-Mg calcite is based on bulk sediment mineralogy and Mg contents (Portilho-Ramos et al., 2018).
**Fig. 6.** Cross-plot of porosity and benthic I/Ca from living *C. wuellerstorfi* (Lu et al., 2020; Rathburn et al., 2018) and GeoB6201-5 *C. pseudoungerianus*. Note that porosity and I/Ca were measured on the same set of specimens. Yellow shaded areas show the low-O$_2$ thresholds in Fig. 4.
Fig. 7. Oxygenation proxy records from core GeoB6201-5 compared with paleoceanographic records from an adjacent core GeoB2107-3: $\Delta^{18}O_{G.truncatuloides−G.ruber}$ (black line is five-point running average) and planktic assemblages percentages (Pereira et al., 2018).
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