

1 **Refining the planktic foraminiferal I/Ca proxy: results from the Southeast**

2 **Atlantic Ocean**

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4 Wanyi Lu ¹, Alexander J. Dickson ², Ellen Thomas ^{3,4}, Rosalind E.M. Rickaby ⁵, Piers Chapman ⁶
5 and Zunli Lu ^{1*}

6
7 1 Department of Earth Sciences, Syracuse University, Syracuse, NY, USA

8 2 Department of Earth Sciences, Royal Holloway University of London, Egham, UK

9 3 Department of Geology and Geophysics, Yale University, New Haven, CT, USA

10 4 Department of Earth and Environmental Sciences, Wesleyan University, Middletown, CT, USA

11 5 Department of Earth Sciences, University of Oxford, Oxford, UK

12 6 Department of Oceanography, Texas A&M University, College Station, TX, USA

13

14 *Correspondence to: zunlilu@syr.edu

15

16 **Abstract**

17 Profound changes in upper ocean oxygenation have taken place in recent decades and are
18 expected to continue in the future, but the complexity of the processes driving these changes has
19 yet to be fully unraveled. Planktic foraminiferal I/Ca is a promising tool to reconstruct the extent
20 of past upper ocean oxygenation, but a thorough assessment is necessary to evaluate both its
21 potential and its limitations. We used foraminifers from Holocene core-tops (Southeast Atlantic
22 Ocean) to document planktic I/Ca across a range of oceanographic conditions. Subsurface O₂
23 concentrations may be the dominant control on planktic foraminiferal I/Ca and planktic I/Ca
24 decreases rapidly at low O₂ conditions (O₂ < ~70–100 μmol/kg). We thus document that low
25 planktic I/Ca can be used empirically to indicate hypoxia in the upper water column, but
26 questions remain as to the mechanistic understanding of the relation between seawater iodine
27 speciation change, its O₂ threshold and foraminiferal I/Ca. Planktic I/Ca records from core

28 GeoB1720-2 (Benguela Upwelling System, SE Atlantic) suggest that hypoxic waters were
29 present near the site persistently during the last 240 ka, without clear glacial-interglacial
30 variability.

31

32 **1. Introduction**

33 The carbonate I/Ca proxy as used on planktic foraminifera has great potential to reconstruct
34 upper ocean oxygenation changes, for which few proxies are available (Hoogakker et al., 2018;
35 Lu et al., 2018; Lu et al., 2016). Inorganic iodine in the oceans exists as two thermodynamically
36 stable species: iodate (IO_3^- , oxidized form) and iodide (I^- , reduced form), and the equilibration
37 between the two species is highly redox-sensitive. Iodate is completely reduced to iodide in
38 anoxic waters, and re-oxidized under well-oxygenated conditions (Rue et al., 1997). Only IO_3^- is
39 incorporated into the calcite structure (Lu et al., 2010) by substituting for the CO_3^{2-} ion (Feng
40 and Redfern, 2018; Podder et al., 2017). Higher foraminiferal I/Ca values thus generally record
41 higher IO_3^- concentrations in seawater, and therefore indicate better-oxygenated water conditions.
42 Planktic foraminiferal I/Ca has been shown to primarily record upper ocean oxygenation
43 (Hoogakker et al., 2018; Lu et al., 2016; Zhou et al., 2014). A threshold value ($\text{I/Ca} < \sim 2.5$
44 $\mu\text{mol/mol}$) was proposed to indicate low O_2 upper ocean waters, based on a limited number of
45 globally-distributed core-top foraminiferal samples (Lu et al., 2016). We collected more core-top
46 data to further elucidate the behavior of I/Ca across different oxygenation windows: anoxic ($\text{O}_2 =$
47 0), suboxic ($\text{O}_2 < 10 \mu\text{mol/kg}$), hypoxic ($\text{O}_2 < \sim 70\text{--}100 \mu\text{mol/kg}$), and oxic ($\text{O}_2 > 100 \mu\text{mol/kg}$).

48 Planktic I/Ca and bulk sediment nitrogen isotopes ($\delta^{15}\text{N}$) both have been used to indicate low

49 O₂ conditions in the upper water column. One of the motivations of this study is to compare and
50 differentiate the behavior of planktic I/Ca and bulk $\delta^{15}\text{N}$ across hypoxic and suboxic windows. In
51 suboxic waters (e.g., eastern tropical Pacific and Arabian Sea), water column denitrification
52 preferentially removes ¹⁴N, leaving the residual nitrate enriched in ¹⁵N, thus bulk $\delta^{15}\text{N}$ is
53 interpreted to reflect the relative degree of water column denitrification under suboxic conditions
54 (Altabet et al., 1999; Galbraith et al., 2013; Robinson et al., 2009). In areas of incomplete nitrate
55 consumption on surface waters (e.g., high nutrient regions), bulk $\delta^{15}\text{N}$ signals are generally
56 thought to reflect relative degrees of nitrate utilization by the phytoplankton community
57 (Galbraith and Jaccard, 2015; Galbraith et al., 2008; Pichevin et al., 2005b). Therefore, a study of
58 planktic foraminiferal I/Ca in low oxygen regions of the Atlantic where there is no water column
59 denitrification should provide new insights into these two oxygen proxies targeting a similar part
60 of the water column.

61 Ocean deoxygenation has been observed in large areas of the Southeast Atlantic Ocean in the
62 past five decades (Schmidtko et al., 2017). Previous studies reconstructed glacial-interglacial
63 histories of sea surface temperature (SST) (e.g., Farmer et al. (2005); Mollenhauer et al. (2003);
64 Pichevin et al. (2005a)) and primary productivity (e.g., Mollenhauer et al. (2002); Romero et al.
65 (2015)), but few studies focused on reconstructing water column oxygenation (e.g., McKay et al.
66 (2016)). Information on glacial-interglacial changes in oceanic oxygenation may help inform us
67 on the extent of and controls on potential future ocean deoxygenation.

68 We report I/Ca data on eight planktic foraminiferal species (depth habitats from near-surface
69 to the thermocline) in 19 core-tops from the Southeast Atlantic Ocean (Southwest African margin,

70 Fig. 1). We aim to better constrain the signal of planktic foraminifera I/Ca in hypoxic as
71 compared to suboxic hydrographic regimes. In addition, we show a downcore I/Ca record of
72 GeoB1720-2 (28°59'S, 13°50'E, 1997 m) within the Benguela Upwelling System (BUS), and
73 compare it to a bulk sediment $\delta^{15}\text{N}$ record from the BUS (Pichevin et al., 2005b) to reconstruct
74 the upper water column conditions over the last two glacial cycles.

75

76 **2. Samples and Methods**

77 **2.1. Study site**

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

88 Shelf water along the west coast of southern Africa commonly contains low dissolved O_2
89 (e.g., < 2 ml/l, approximately < 90 $\mu\text{mol/kg}$), and the O_2 concentrations vary significantly
90 spatially (Fig. 1, 2). Upper ocean waters close to the southwest African coast are affected by both

91 the southward Poleward Undercurrent (PUC), down to 200 m depth along the shelf break, and by
92 the northward Benguela Current, further offshore, down to 1200 m depth. The Benguela Current
93 forms the eastern limb of the South Atlantic gyre, and contains water from the South Atlantic
94 Current with additional inputs of warm, salty Indian Ocean water from the Agulhas Current
95 (Stramma and England, 1999). The PUC originates from the Equatorial Undercurrent and the
96 Angola Gyre, and transports low oxygen waters southward along the shelf north of 27°S (Fig. 1).
97 The low O₂ conditions of the BUS in the coastal area between 30°S and 34°S are most likely due
98 to local decomposition of organic matter (Chapman and Shannon, 1985) (Fig. 1, 2).

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

104

105 **2.2. Samples materials**

106 A total of 19 core-top samples were obtained from the upper 5 cm of cores from the
107 Lamont-Doherty Core Repository (Table S1). The core-top sediments were wet-sieved to the >
108 63 µm fraction with MilliQ water, then oven-dried at 40°C. Specimens from eight planktic
109 foraminiferal species (*Globigerinoides ruber*, *Neogloboquadrina incompta*, *Globigerina*
110 *bulloides*, *Globorotalia truncatulinoides* (sinistral and dextral), *Globigerinoides sacculifer*,
111 *Globorotalia inflata*, *Neogloboquadrina dutertrei*, and *Globorotalia menardii*) were picked, and

112 25-80 individuals from the 150-300 μm size fraction were used for I/Ca analyses. Two species, *G.*
113 *truncatulinoides* (sinistral) and *N. incompta*, were picked from sieved sediments from core
114 GeoB1720-2. Around 25 specimens of *G. truncatulinoides* (sinistral) and ~80 specimens of *N.*
115 *incompta* from 150-300 μm size fraction were used for I/Ca analyses.

116

117 **2.3. Age model**

118 Radiocarbon dating of the planktic foraminifer *G. inflata* from selected samples shows a
119 Holocene age (Table S1). Radiocarbon was analyzed at the Keck Carbon Cycle AMS Facility at
120 University of California, Irvine. The age model of core GeoB1720-2 is based on nine AMS ^{14}C
121 dates between 0 and 200 cm depth for the planktic foraminifer *G. inflata* (Dickson et al., 2009),
122 and is extended down-core by tying the *N. incompta* $\delta^{18}\text{O}$ stratigraphy to the global benthic
123 foraminiferal $\delta^{18}\text{O}$ stack (Lisiecki and Raymo, 2005) between 200 and 900 cm depth (Fig. S1
124 and Table S2), assuming the GeoB1720-2 $\delta^{18}\text{O}$ record can be correlated to the global stack. The
125 *N. incompta* $\delta^{18}\text{O}$ data for core GeoB1720-2 are here first reported. They were measured on the
126 150 – 250 μm size fraction from homogenized sample sizes of ~20 individuals on a Thermo
127 MAT Delta V Advantage mass spectrometer coupled to a Kiel Device at the Department of Earth
128 Sciences, University of Cambridge, and the Department of Physical Sciences, The Open
129 University. Calibration to Vienna Pee Dee Belemnite was via NBS19 standards. Precision is
130 ± 0.1 ‰ (1 S.D.).

131

132 **2.4. Foraminiferal I/Ca analyses**

133 The foraminiferal I/Ca analytical methods follow Lu et al. (2016). The samples were gently

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

147

148 **2.5.Planktic foraminiferal habitat**

149 Calcification depths where the average geochemical signal is locked into the planktic
150 foraminiferal shell are usually estimated from comparison of δ¹⁸O of foraminifera with that of
151 equilibrium calcite, based on historical temperature and salinity data (Anand et al., 2003).
152 Calcification depths for several of the species used in this study have been calibrated to depth
153 habitats of ~100 m (summer) and ~80 m (winter) for *N. incompta*; and ~340 m (summer) and

154 ~300 m (winter) for *G. truncatulinoides* (dextral) in multi-core GeoB1720-3 (28°59'S, 13°50'E,
155 2004 m) (Dickson et al., 2010). This core is located within a few meters of GeoB1720-2, thus the
156 data are broadly applicable to our study region.

157

158 **2.6. Hydrographic data**

159 Oxygen data for core-top sites were obtained from high-resolution CTD profiles in the
160 World Ocean Database (WOD) 2013 (https://www.nodc.noaa.gov/OC5/WOD/pr_wod.html)
161 (Boyer et al., 2013) (Fig. 2a). We divided the studied area into three geographic regions: a
162 tropical region at latitudes between 5°N and 15°S; a Southern BUS region at latitudes between
163 30°S and 35°S; and a Walvis Ridge region at latitudes between 23°S and 32°S (Fig. 2a). Many of
164 the core-top samples are in areas with great spatial variability in O₂ conditions, thus we
165 determined the minimum O₂ concentrations in the water column from the nearest location, and
166 within an 0.25°×0.25° area of the core-top samples in WOD2013. Minimum O₂ in the water
167 column is used because O₂ has to drop below a certain threshold to trigger iodate reduction,
168 recorded as low foraminiferal I/Ca (Lu et al., 2016). Minimum O₂ values generally occur in the
169 bottom waters over the shelf, but are found in mid-water off the shelf. Minimum O₂ maps were
170 produced using Ocean Data View's gridding tool, and the individual minimum O₂ values were
171 calculated using the statistics tool in that program (Schlitzer, 2018).

172

173 **3. Results**

174 Low core-top I/Ca values (< ~2.5 μmol/mol), regardless of species, are observed in the

175 tropical and Southern BUS regions, which generally contain hypoxic waters at mid-depths or
176 bottom depths ($O_2 < \sim 70\text{-}100 \mu\text{mol/kg}$) (Fig. 3 and 4). High core-top I/Ca values ($> \sim 4$
177 $\mu\text{mol/mol}$), regardless of species, are found in the Walvis Ridge region, where waters generally
178 are well oxygenated ($O_2 > \sim 100 \mu\text{mol/kg}$).

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

188 Higher core-top I/Ca values are generally associated with higher O_2 conditions in the water
189 column as estimated from the nearest site in the WOD2013 database (Fig. 5), consistent with Lu
190 et al. (2016). At three sites in the Southern BUS region (V19-238, V19-228, and V14-70, see
191 Table S1 for details), however, high modern minimum O_2 concentrations ($150\text{--}220 \mu\text{mol/kg}$)
192 apparently are associated with low I/Ca ($< \sim 2 \mu\text{mol/mol}$), but the O_2 values around these
193 core-top sites are highly variable spatially (Fig. 2).

194 In the downcore record of GeoB1720-2, almost all *G. truncatulinoides* (sinistral) and *N.*
195 *incompta* I/Ca values are $< 2.5 \mu\text{mol/mol}$ during the last two glacial cycles (Fig. 6).

196

197 **4. Discussion**

198 **4.1. Subsurface O₂ conditions**

199 Measurements of the core-top samples in the Southeast Atlantic Ocean confirmed that low
200 planktic I/Ca values can reveal the presence of low-O₂ waters in the upper ocean (Fig. 5c), as
201 previously demonstrated (Lu et al., 2016). However, we also found high O₂ - low I/Ca values in
202 the Southern BUS region (Fig. 5c), which may be explained by different scenarios: (1) O₂ values
203 from the WOD2013 do not represent the actual conditions during foraminiferal growth, due to
204 short-term or spatial variability of O₂; (2) the foraminifera calcified in high O₂ - low IO₃⁻ water,
205 due to slow kinetics of I⁻ oxidation; (3) the planktic foraminifera lived at nearby locations with
206 lower O₂ and were transported to their current sites (Fig. 2); (4) unknown factors are limiting
207 IO₃⁻ uptake by foraminifera at these sites.

208 Examining the first of these possibilities, hypoxic waters are common in the shelf areas of
209 the BUS system and their extent and level of oxygen depletion vary spatially and on seasonal,
210 interannual, and decadal timescales (Jarre et al., 2015). Significant vertical and seasonal changes
211 in water column oxygen concentrations are more likely in the nearshore than in the offshore
212 regions (Lamont et al., 2015; Pitcher et al., 2014). However, episodic hypoxic conditions in the
213 water column have been reported offshore of the BUS (Pitcher et al., 2014), and may provide
214 low O₂ water at our core-top sites not captured in the WOD2013 dataset, which does not
215 comprise seasonal or annual O₂ measurements in the Southern BUS region. The O₂ data in
216 WOD2013 also span a considerable time period, representing an additional source of uncertainty.

217 Thus the uncertainty arising from modern measurements of O_2 and its short-term variability may
218 at least partially explain the high O_2 – low I/Ca cases in the Southern BUS region.

219 In addition, the high O_2 - low I/Ca cases in the Southern BUS region may be related to the
220 slow kinetics of iodide re-oxidation. Estimated I^- oxidation rates range from 4 to 670 nM per
221 year, whereas reduction of IO_3^- at an anoxic boundary is rapid (~50 nM per hour) (Chance et al.,
222 2014). Shelf waters in the Southern BUS (all water depths < 200 m) were reported to have highly
223 variable O_2 concentrations (10–400 $\mu\text{mol/kg}$) but low IO_3^- concentrations (< ~0.25 μM) (Fig. 5b)
224 (Chapman, 1983). Intense water column mixing in the shelf region of Southern BUS may bring
225 bottom waters with low IO_3^- signals from peripheral locations into the photic zone, where the
226 concentrations of nutrients and chlorophyll α are exceptionally high (Truesdale and Bailey, 2000).
227 During this transport, oxygen concentrations may have begun to rise due to photosynthesis or
228 mixing with O_2 -rich waters, but the IO_3^- concentration remained low due to the slow oxidation of
229 I^- (Chapman, 1983; Truesdale and Bailey, 2000).

230 Central to these different scenarios for the occurrence of high O_2 - low I/Ca in the Southern
231 BUS is the key concept that low foraminiferal I/Ca may reflect low O_2 conditions that vary on
232 small space- and time-scales. To visualize such a spatial uncertainty, we plot I/Ca against
233 minimum O_2 values within a $0.25^\circ \times 0.25^\circ$ area around each core-top location (Fig. 5). All
234 core-top samples with low I/Ca in the Southern BUS come from a region where hypoxia occurs
235 within 0.25° of the sample site (Fig. 5d). These results caution against the use of planktic I/Ca as
236 a proxy for *in-situ* O_2 conditions, especially in settings with strong hydrographic gradients and
237 mixing. However, we emphasize that these high O_2 - low I/Ca cases only occurred in the

238 Southern BUS region with high spatial and temporal variability of O₂, and not in the tropical and
239 Walvis Ridge regions.

240

241 **4.2. Planktic I/Ca as a hypoxia proxy**

242 Water column IO₃⁻ and O₂ profiles from the core-top sites would provide the ideal
243 constraints of the O₂ threshold driving the foraminiferal I/Ca signal. However, such modern
244 seawater data are only available for a relatively small area from the Southern BUS (Chapman,
245 1983). In that study, dissolved IO₃⁻ concentrations do not correlate with surface O₂ (depth < 50
246 m), but decrease rapidly when O₂ in subsurface waters (depth > 50 m) approaches ~70–100
247 μmol/kg (Fig. 5b). Similarly, our core-top I/Ca data exhibit abrupt decreases when minimum O₂
248 values drop to these levels, with the exception of the above described high O₂ – low I/Ca areas
249 (Fig. 5c). This O₂ threshold for rapid IO₃⁻ or I/Ca decrease is generally consistent with the
250 estimates based on globally-distributed core-top foraminifera (Lu et al., 2016).

251 We suggest that low planktic I/Ca can empirically indicate hypoxia in the upper water
252 column, but it is not clear why planktic I/Ca responds to water column hypoxia, which warrants
253 further discussion. We approach this question from two directions: the relationship between IO₃⁻
254 and O₂ in hypoxic waters, and the relation between IO₃⁻ reduction and denitrification.

255 Currently, water column data are insufficient to unambiguously demonstrate whether there is
256 a uniform O₂ threshold for global seawater IO₃⁻ reduction, and if there is such a threshold, at
257 what concentration of O₂. IO₃⁻ concentrations rapidly decrease when waters become near
258 suboxic ([O₂] < 10 μmol/kg) in the Pacific (Huang et al., 2005; Rue et al., 1997) and Indian

259 oceans OMZs (Farrenkopf and Luther, 2002) (Fig. 5a). However, the Benguela data seem to
260 indicate that IO_3^- reduction may occur at hypoxic conditions with somewhat higher oxygen
261 levels ($[\text{O}_2] < 70\text{-}100 \mu\text{mol/kg}$) (Fig. 5b), as also found over the shelf in the northern Gulf of
262 Mexico (Chapman and Truesdale, 2011). Maybe, the O_2 threshold for seawater IO_3^- reduction
263 varies across different ocean basins, or there are other processes that control the balance between
264 IO_3^- and Γ in seawater (e.g., the uptake rate of IO_3^- versus Γ by plankton, iodide oxidation rates
265 vary in different oceans). Further work on seawater IO_3^- and O_2 are required to discern these O_2
266 thresholds.

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

280 reductase enzymes responsible for IO_3^- reduction and their O_2 sensitivities coupled with water
281 column IO_3^- and O_2 concentrations.

282 Another possibility to explain a hypoxic threshold for rapid I/Ca decrease may involve
283 anaerobic metabolism of microbes (including IO_3^- reduction) in microenvironments of sinking
284 organic aggregates in oxic-hypoxic water. Denitrification is often described as occurring in
285 suboxic or anoxic waters only (Ulloa et al., 2012), but denitrification and even sulfate-reduction
286 by microbes have been reported at $\text{O}_2 > 20 \mu\text{mol/kg}$ (Ganesh et al., 2014; Wolgast et al., 1998).
287 Possibly, particle microenvironments in hypoxic waters may have sufficiently low O_2
288 concentrations to support anaerobic metabolism, including denitrification and sulfate reduction
289 (Bianchi et al., 2018) and potentially iodate reduction. These low IO_3^- signals formed in
290 microenvironments could be subsequently released into ambient hypoxic seawater where the
291 planktic foraminifera calcify. Such a scenario could be an explanation for IO_3^- reduction in
292 hypoxic water, and I/Ca may be sensitive to water column denitrification in microenvironments.

293 In summary, we suggest that planktic I/Ca remains an empirical proxy – low I/Ca values can
294 reliably indicate the presence of hypoxia in the water column, in contrast to bulk sediment $\delta^{15}\text{N}$
295 as a proxy for denitrification in suboxic water. In future studies, foraminiferal I/Ca, paired O_2 and
296 iodate data from low O_2 regions may improve the mechanistic understanding of the proxy and
297 also the marine biogeochemistry of iodine. Iodate will not be used as oxidant until O_2 is
298 significantly depleted, but iodate reduction may not necessarily occur in the habitat of calcifying
299 organisms. The foraminiferal I/Ca signature for low O_2 reflects iodate reduction somewhere very
300 close to the foraminiferal habitat. If the *in-situ* iodate level indeed is low, it can be caused by

301 diffusion/advection and slow oxidation of iodide. On the other hand, culture experiments show
302 that two modern planktic species (*O. universa*, symbiotic species, and *G. bulloides*,
303 non-symbiotic species) can survive, add chambers, feed, and undergo gametogenesis in low-O₂
304 conditions (~22 μmol/L) (Kuroyanagi et al., 2013). Some species (*N. dutertrei* and *G. bulloides*)
305 can even survive episodic or temporary exposure to H₂S (< 24 hr) (Kuroyanagi et al., 2019). We
306 cannot rule out the possibility that planktic foraminifera may survive in hypoxic waters and
307 directly record a low I/Ca signal. Such foraminifera culture experiments may also be helpful for
308 testing vital effects in different species.

309

310 **4.3. Planktic I/Ca downcore record in the BUS**

311 We use the I/Ca values in *N. incompta* and *G. truncatulinooides* (sinistral) from core
312 GeoB1720-2 from the Southeast Atlantic to reconstruct the upper water oxygenation history over
313 the last 240 ka, and compare these results with δ¹⁵N data from nearby site MD96-2087 (25.60°S,
314 13.38°E, 1029 m) (Pichevin et al., 2005b). The downcore I/Ca values are consistently low, < 2.5
315 μmol/mol, over the last two glacial cycles (Fig. 6), indicating the persistent presence of hypoxic
316 waters near the study site (e.g., within 0.25°×0.25° area). It is possible that low IO₃⁻ water was
317 advected to this site from nearby locations. Nutrient levels, indicated by bulk sediment δ¹⁵N
318 records from MD96-2087 (Fig. 6), likewise do not show a clear glacial-interglacial pattern
319 (Pichevin et al., 2005b). The narrow amplitude of this δ¹⁵N record was interpreted to reflect that
320 nitrate was never severely depleted over the shelf (Pichevin et al., 2005b). Thus the upwelling
321 dynamics in the near-shore region of BUS may have persistently fueled relatively high levels of

322 surface nutrient and subsurface hypoxia through glacial-interglacial oscillations, which remained
323 a dominant oceanographic feature in this area. On the other hand, downcore records for excess
324 Ba (Ba_{xs}) and the $\delta^{13}C$ difference between *G. ruber* (a summer calcifier) and *N. incompta*
325 (calcifying below the mixed layer) ($\Delta\delta^{13}C$) suggest changes in organic carbon export and upper
326 ocean nutrient partitioning over the latter part of the last glacial cycle (Fig. 7). Given the very
327 low I/Ca values, it is likely that subtle alternations of enhanced organic matter export and upper
328 ocean mixing (high Ba_{xs} , low $\Delta\delta^{13}C$) and lower organic matter export with more stratified
329 surface waters (lower Ba_{xs} , higher $\Delta\delta^{13}C$) could maintain persistently oxygen-depleted
330 subsurface waters during the past ~50 ka (Fig. 7). It is possible that such variations in export
331 production were relatively small, thus insufficient to drive nutrient utilization ($\delta^{15}N$) and hypoxia
332 patterns (I/Ca).

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

340

341 **5. Conclusions**

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

355

356

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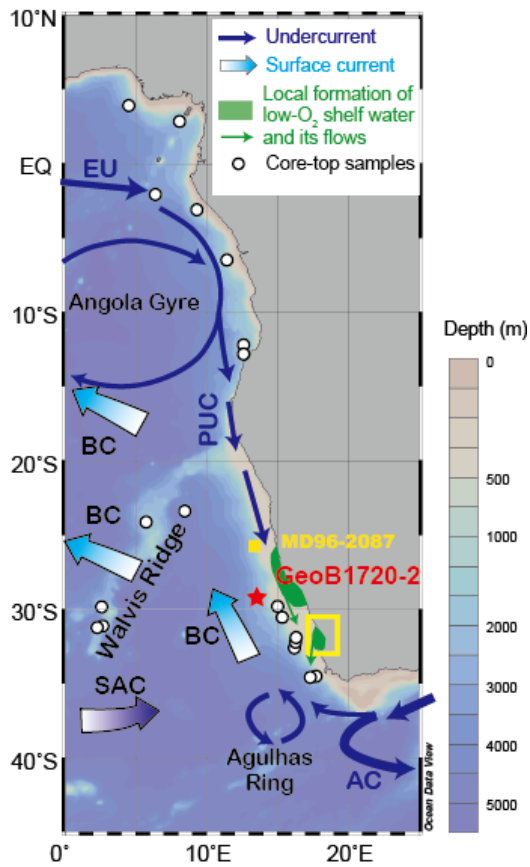
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367 **Figures**

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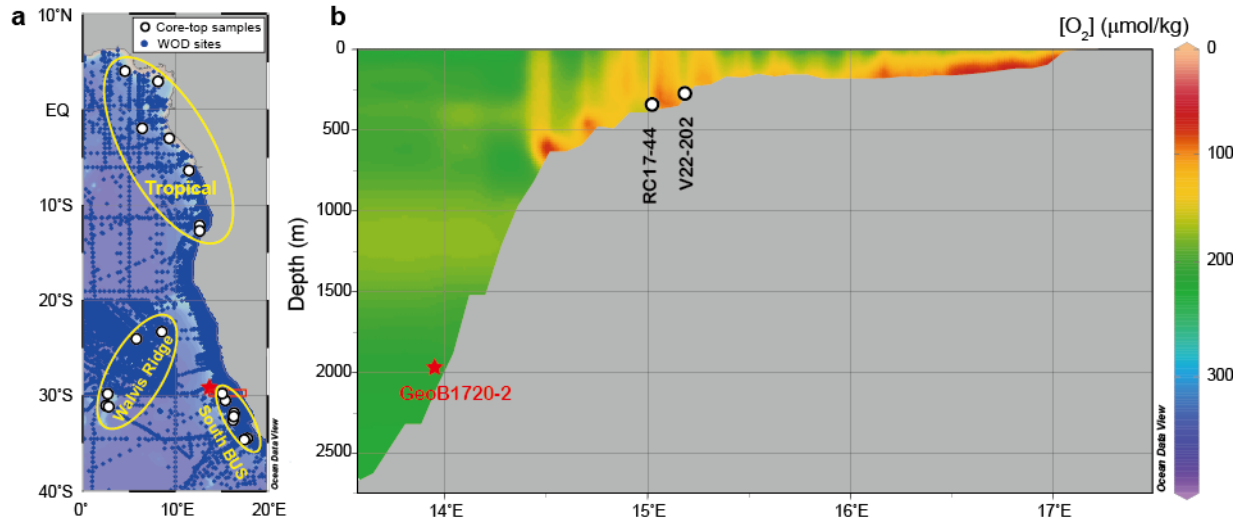
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370 **Fig. 1.** Locations of core-top samples and site GeoB1720-2. The yellow box marks the sampling
371 area of dissolved iodate and O₂ concentrations in seawater in the Southern BUS region in Fig. 5b
372 (Chapman, 1983). The yellow square marks site MD96-2087 in Fig. 6, for comparison with I/Ca
373 records. The upper ocean circulation in the Southeast Atlantic Ocean is modified after Chapman
374 and Shannon (1985) and Stramma and England (1999). EU: Equatorial Undercurrent; PUC:
375 Poleward Undercurrent; BC: Benguela Current; SAC: South Atlantic Current; AC: Agulhas
376 Current.

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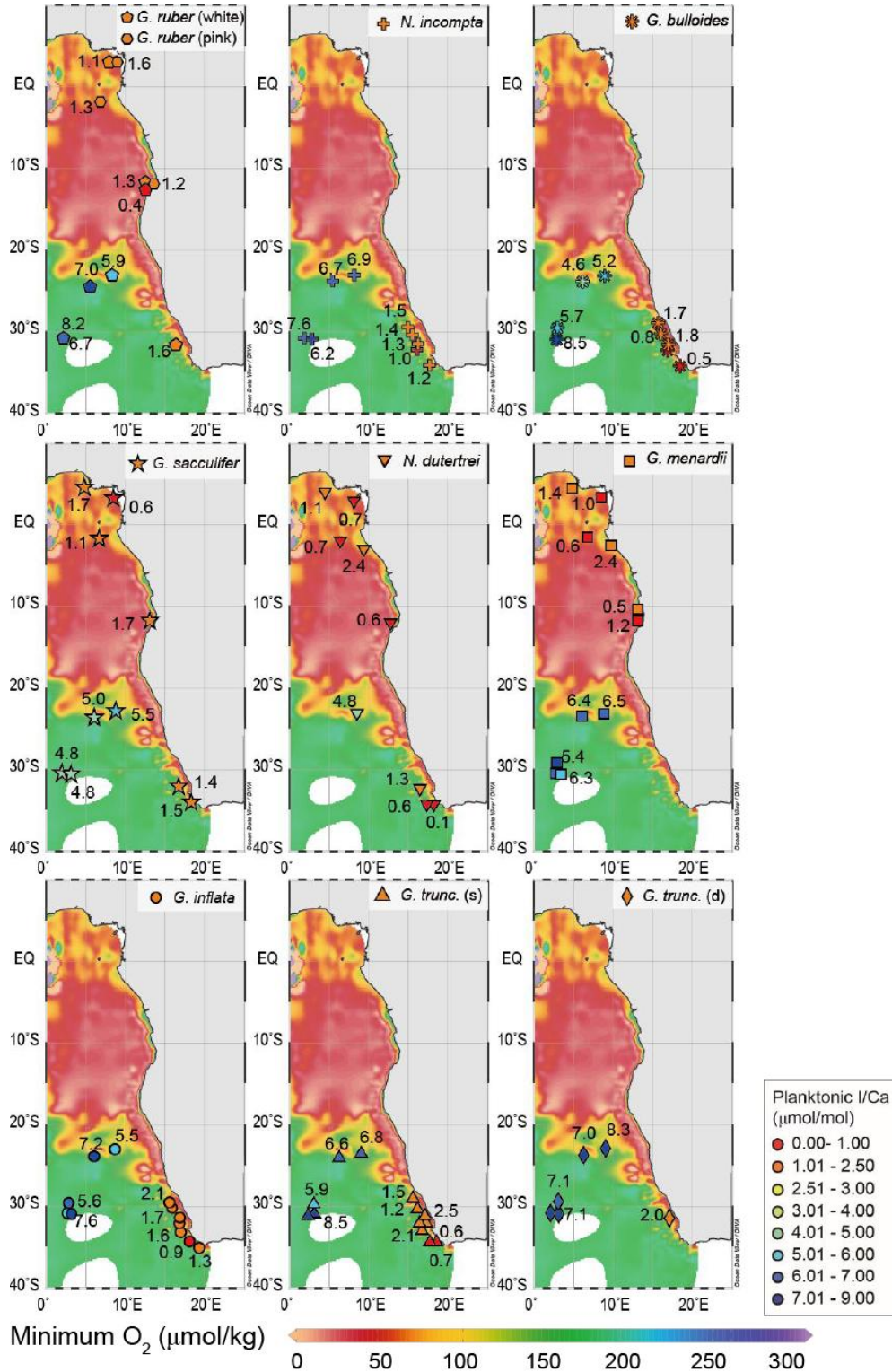
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381 **Fig. 2. a).** Seawater CTD [O₂] profile locations in the study area, World Ocean Database (WOD)
 382 2013 (Boyer et al., 2013). We divided our dataset into three regions, as outlined by the yellow
 383 ellipses. **b).** Cross-section (red box with latitudes between 28°45' S and 29°15' S) shows site
 384 GeoB1720-2 on the continental slope, and the location of two cores in the coastal area of the
 385 BUS, showing significant spatial variation of O₂ concentrations.

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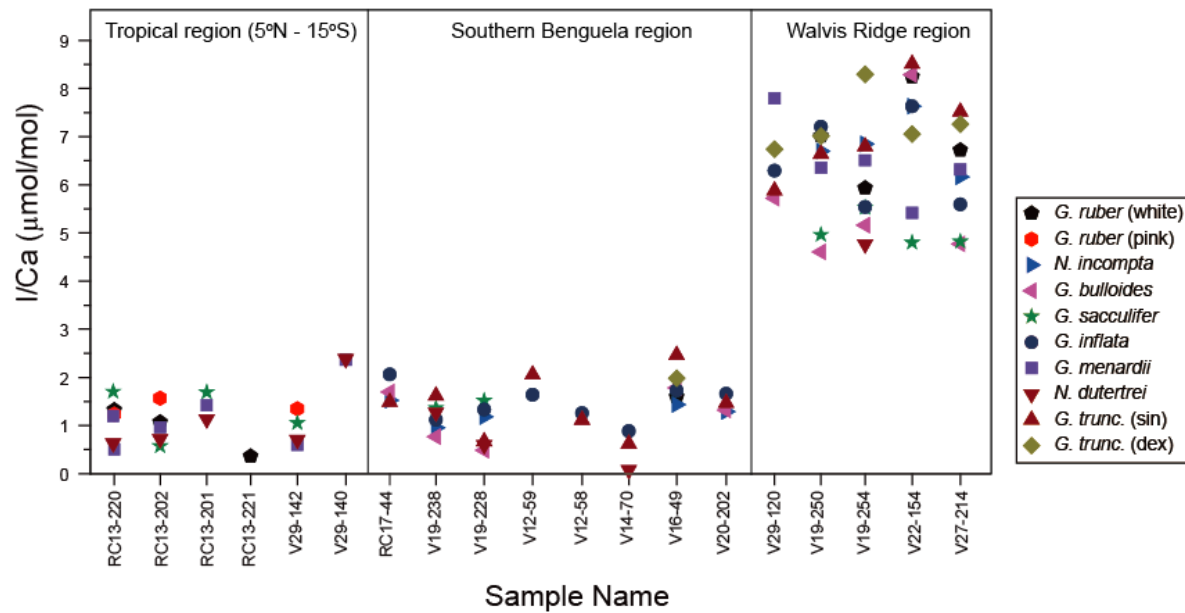
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Fig. 3. Core-top planktic I/Ca spatial distribution maps. Background maps show the minimum O₂ concentrations in the water column. Numbers next to the symbols show the planktic I/Ca values.



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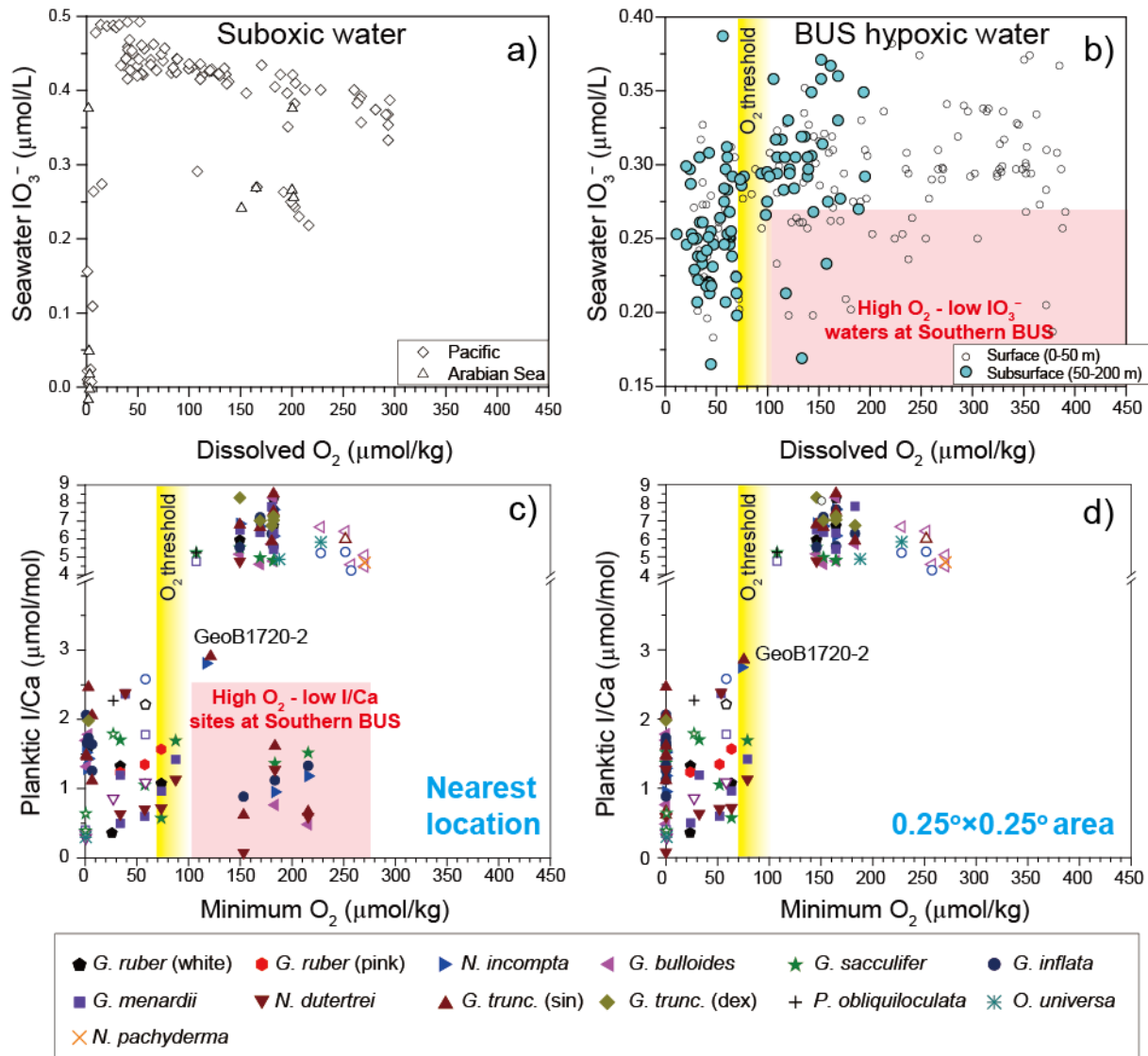
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395 **Fig. 4.** Planktic I/Ca in core-top samples. The locations of the three regions are shown in Fig. 2a.

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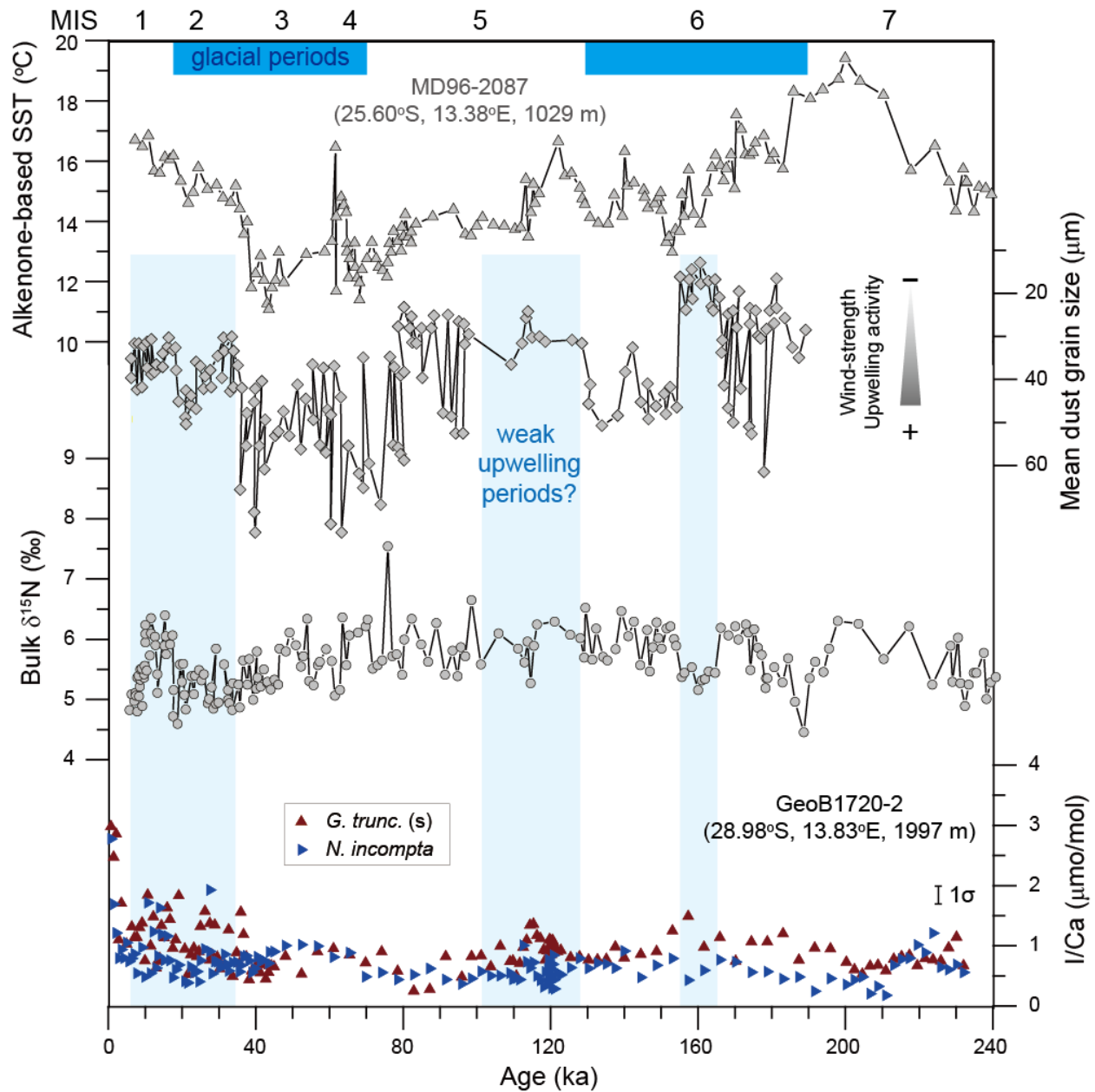
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 400 **Fig. 5. a).** Dissolved IO_3^- vs. O_2 in the Pacific and Indian Oceans (Farrenkopf and Luther, 2002;
 401 Huang et al., 2005; Rue et al., 1997). **b)** Dissolved IO_3^- vs. O_2 in shelf waters in Southern BUS
 402 (Chapman, 1983). Depths of all water samples were < 200 m, locations are shown in the yellow
 403 box in Fig. 1. **c-d).** Core-top planktic I/Ca vs. minimum O_2 concentrations in the water column
 404 derived from the nearest location and within $0.25^\circ \times 0.25^\circ$ area in WOD2013. Closed symbols
 405 indicate new data in this study, and open ones denote published data (Lu et al., 2016).

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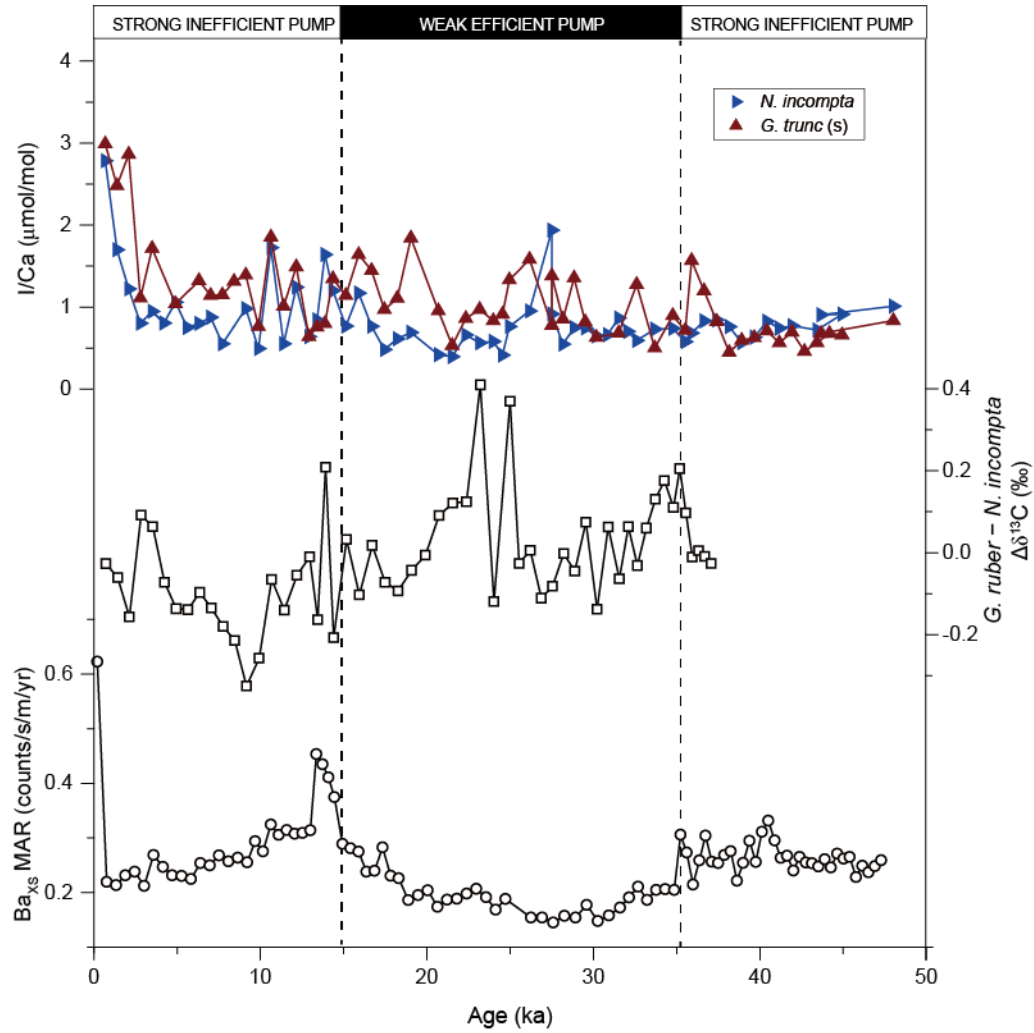


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410 **Fig. 6.** Planktic I/Ca record at site GeoB1720-2 (this study), and alkenone-based SST, mean dust grain size (Pichevin et al., 2005a), and bulk $\delta^{15}\text{N}$ at site MD96-2087 (Pichevin et al., 2005b).
 411
 412 Dark blue shadings indicate glacial periods, and light blue shadings indicate potential weak
 413 upwelling periods.

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417 **Fig. 7.** Planktic I/Ca, the $\delta^{13}\text{C}$ difference between *G. ruber* and *N. incompta*, and excess Ba mass
 418 accumulation rates (MAR) records at core GeoB1720-2 during the last 50 ka.

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