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Glacial–interglacial changes in bottom-water oxygen content on the Portuguese margin

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1. Calibration equation $\Delta\delta^{13}C$ - O_2 relationship

Table 1 summarizes location details, oxygen concentration, carbon isotope gradients between bottom water/epifaunal benthic foraminifera and pore water/deep infaunal foraminifera (*Globobulimina* spp.) and source references.

Data from shallow (<1000 m) locations were excluded, as these could be set in strongly reducing environments where fermentation can produce $\delta^{13}C$ depleted methane and $\delta^{13}C$ enriched CO_2, which would cause isotopically heavy benthic foraminifera $\delta^{13}C$ /DIC (McCorkle and Emerson, 1988). Only benthic foraminiferal $\delta^{13}C$ data of recent (either living specimens determined by Rose Bengal staining, or those obtained from recent Holocene (dated younger than 5,000 years)) sediments were used. Dead benthic foraminifera $\delta^{13}C$ from undated core-tops were excluded because of potentially significant age uncertainties.

From the McCorkle and Emerson (1988) study, only sites where the depth of the anoxic boundary is well-constrained by a Mn^{2+} profile measured on the same pore water are included. Data from the other sites of McCorkle and Emerson (1988) are excluded from our calibration; anoxic depths of those sites were inferred from pore water measurements on nearby cores, which could have been mis-identified. This explains why the $\Delta\delta^{13}C$ versus $[O_2]$ plot of McCorkle and Emerson (1988) looks more scattered than our Figure 1.
Two of the BENBO sites (B and C) of the Papadimitriou et al. (2004) study reached the anoxic boundary. At site B, $[O_2]$ and $\delta^{13}C$ were measured on the same material. Because the anoxic depth at site C was inferred from Mn^{2+} release in pore water at and below the anoxic boundary at a nearby core from the previous year (Thomson et al., 2001), data from this site was not included in our calibration.

Mackensen and Licari (2004) measured $\delta^{13}C$ of epifaunal (*Fontbotia wuellerstorfi*= *Cibicidoides wuellerstorfi*) and deep infaunal (*G. pacifica*) benthic foraminifera at five core top locations in the South Atlantic west African margin. Although Rose Bengal stained, *F. wuellerstorfi* $\delta^{13}C$ (1.0‰) at GeoB3713 was ~0.4‰ higher compared with recent observations of seawater DIC $\delta^{13}C$ (Kroopnick, 1985) and also of other *F. wuellerstorfi* measurements nearby (Bickert and Mackensen, 2003). Instead, *F. wuellerstorfi* $\delta^{13}C$ at GeoB3713 were similar to LGM $\delta^{13}C$ values (Bickert and Mackensen, 2003), suggesting that they are not recent specimens. All $\delta^{13}C$ measurements on dead and live (Rose Bengal stained) specimens are within 0.2‰ of each other, apart from GeoB4915 where *G. pacifica* $\delta^{13}C$ of dead specimens are 0.4‰ more depleted compared with stained specimens. Because of these inconsistencies data from GeoB3713 and GeoB4915 were not included in the calibration.

Bottom-water $[O_2]$ data was mainly obtained using the World Ocean Data Base select and search engine. Oxygen concentrations were converted from ml/l to μmol/kg by multiplying by 44.658 ($[O_{2\mu mol}/l=[O_{2ml/l}]*44.658$) and dividing by seawater density (assumed constant at 1.029 kg/l).

Inclusion of correct density (calculated from salinity, temperature and pressure at the sites water depth) has only a minor impact on the conversion (±0.2 μmol/kg).

Table 1

Name	Ocean basin	Lat.	Long.	Water depth (m)	O_2 (μmol/kg)*	$\Delta\delta^{13}C$ (‰)	Origin	Reference
K-104-10-1	North Atlantic	41.5N	64W	3000	275±2	4.24±0.33 N=3	bottom and pore water	McCorkle and Emerson (1988)
K-104-10-3	North Atlantic	42N	65W	1575	270±1	3.62±0.19 N=3	bottom and pore water	McCorkle and Emerson (1988)
K-104-10-4	North Atlantic	42N	65W	1075	267±1	3.67±0.13 N=3	bottom and pore water	McCorkle and Emerson (1988)
Site B	North Atlantic	57.4N	15.7W	1104	233±7	2.25±0.07 N=2	bottom and pore water	Papadimitriou et al. (2004); assumed $\delta^{13}C$ 1‰ bottom water from nearby GLODAP data ~ 1000 m water depth. 0.2‰ uncertainty added
TT-163-10	Eastern Pacific	24.5N	114W	3480	127±5	1.36±0.03 N=3	bottom and pore water	McCorkle and Emerson (1988)
MANOP Site M BC-20	Eastern Pacific	9N	104W	3100	114±4	1.33±0	bottom and pore water	McCorkle and Emerson (1988)
Station A	North Atlantic	44.2N	2.3W	1012	188±1	2.03	bottom water and *G. affinis* (RB stained)	Fontanier et al. (2006)
Station H	North Atlantic	44.5N	2.6W	1993	256	3.26	bottom water and *G. affinis* (RB stained)	Fontanier et al. (2006)
K-104-10-1 (2)	North Atlantic	41.5N	64W	2975	272±4	3.91	bottom water and *G. affinis* (RB	McCorkle et al. 1990

							stained)	
K-104-10-2 (1)	North Atlantic	42N	64.7W	2225	270±3	3.10±0.07 N=10	bottom water and *G. affinis* (RB stained)	McCorkle et al. 1990
K-104-10-3 (1)	North Atlantic	42N	65W	1575	270±1	2.88±0.20 N=3	bottom water and *G. affinis* (RB stained)	McCorkle et al. 1990
K-104-10-3 (2)	North Atlantic	42N	65W	1575	270±1	2.96±0.07 N=5	bottom water and *G. affinis* (RB stained)	McCorkle et al. 1990
K-104-10-4 (1)	North Atlantic	42N	65W	1075	267±1	2.47	bottom water and *G. affinis* (RB stained)	McCorkle et al. 1990
CH14 1(1) and (2)	North Atlantic	38.233N	71.5W	3000	269±4	3.56	bottom water and *G. affinis* (RB stained)	McCorkle et al. 1990
Gyre 2-3	North Atlantic	38.6N	72.9W	2020	263±1	2.76±0.11 N=2	bottom water and *G. affinis* (RB stained)	McCorkle et al. 1990
86/2:7-4:22	North Atlantic	38.22N	71.5W	3000	270±2	3.39±0.02 N=4	bottom water and *G. affinis* (RB stained)	McCorkle et al. 1990
86-G-14	North Atlantic	14.67N	17.83W	1332	185±2	1.99	bottom water and *G. affinis* (RB stained)	McCorkle et al. 1990
CH90-BC5	North Atlantic	35.65N	74.84W	1477	264±5	2.28	bottom water and *G. affinis* (RB stained)	McCorkle et al. 1997
AUSCAN MC05	South Indian	36.73S	136.55E	2476	179±2	1.98±0.29 N=8	bottom water and *G. pacifica* (RB stained)	Basak et al. (2009)

AUSCAN MC04	South Indian	36.81S	136.82E	1634	167±3	1.6	bottom water and *G. pacifica* (RB stained)	Basak et al. (2009)
JD88TC37	North Pacific	53.617N	163.21W	1988	62±3	0.82±0.16 N=4	bottom water and *G. pacifica* (RB stained)	Basak et al. (2009)
SCB-BC-3	North Pacific	32.5N	118W	1800	56±0	0.84±0.30 N=4	bottom water and *G. affinis* (live)	McCorkle et al. 1990
PSII-BC227	North Pacific	35.47N	122.35W	3807	137±6	1.44±0.12 N=6	bottom water and *G. pacifica* (live)	McCorkle et al. 1997
RAPID 11 7B	North Atlantic	62.30N	17.15W	2126	275±3	3.14±0.13 N=3	*C. wuellerstorfi* and *G. pacifica*	This work **
Station I	North Atlantic	44.8N	2.5W	2800	246±4	2.66±0.04 N=5	bottom water and *G. affinis* (RB stained)	Fontanier et al. (2008)
GeoB3706	South Atlantic	22.7S	12.6E	1313	186±2	1.79	*C. wuellerstorfi* and *G. pacifica* (RB stained)	Mackensen and Licari, 2004
GeoB3708	South Atlantic	21.1S	11.8E	1283	179±15	1.75	*C. wuellerstorfi* and *G. pacifica* (RB stained)	Mackensen and Licari, 2004
GeoB3725	South Atlantic	23.3S	12.4E	1980	221±2	1.90	*C. wuellerstorfi* and *G. pacifica* (RB stained)	Mackensen and Licari, 2004
GeoB3004	Arabian Sea	14.6S	52.9E	1803	85	0.96±0.14 N=3	*C. wuellerstorfi* and *G. affinis*	Schmiedl and Mackensen, 2006
ODP 1242	Equatorial Pacific	7.86N	83.6W	1364	65±0	1.09±0.08 N=3	*C. wuellerstorfi and G.* spp	This work

** *C. wuellerstorfi* $\delta^{13}C$ data from nearby core RAPID 13 9B.

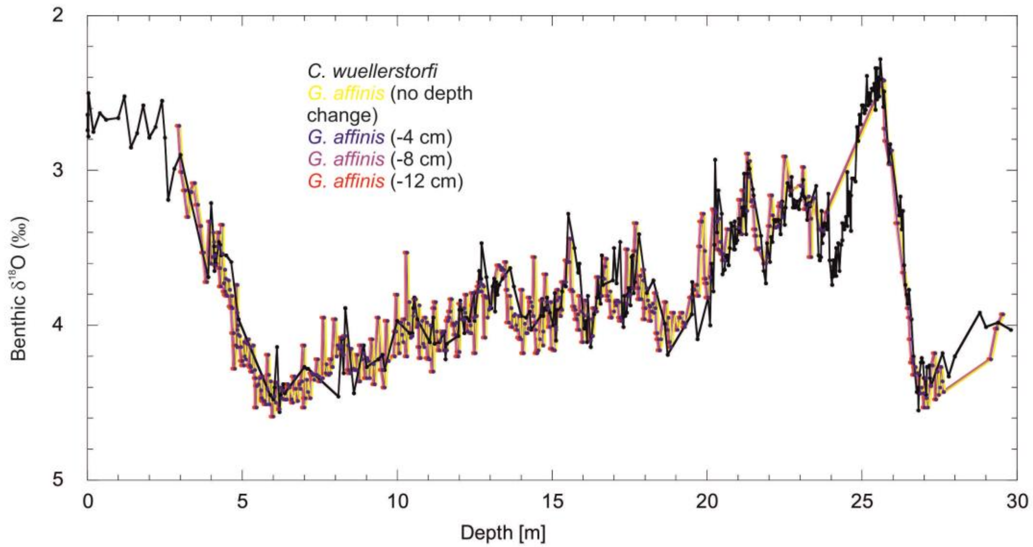
The total error ($\sigma t = sqrt(2x\sigma A^2+\sigma B^2+\sigma C^2+\sigma D^2+\sigma E^2)$) was calculated as follows:
A - represents errors relating to $\delta^{13}C$ measurements; currently they are 0.05‰ in most labs, but earlier values of 0.1‰ have been reported (e.g. McCorkle and Emerson, 1988). An error of 0.05‰ holds a 6 to 7 µmol/kg change in bottom water [O2], whereas one of 0.1‰ holds a 12 to 13 µmol/kg change. Here we used the average of the two (9 µmol/kg).
B - represents average $\delta^{13}C$ sample variability near the anoxic boundary and amounts to the average standard deviation of the samples (0.05‰, amounting to 7 µmol/kg). Where this involved Rose Bengal stained foraminifera, the average of all Globobulimids was taken, whereas at the pore water sites values nearest to the anoxic boundary depth were taken (generally 2 to 3 measurements).
C - relates to bottom-water [O_2] measurements; these used to be quite significant (up to 20 µmol/kg) in terms of error. Here we use nearby measurements extracted from the World Ocean Database select and search engine, with data exclusion using WOD quality control flags and assume a generous error of 5 µmol/kg.
D - bottom-water [O_2] variability taken as the average standard deviations of measurements nearby the core locations (where this was possible); these are given in the table 1 above for the individual sites (3 µmol/kg).
E - organic carbon $\delta^{13}C$ variability, where a 1‰ increase or decrease in this value would cause a ~0.04‰ change in the pore-water $\delta^{13}C$ gradient.

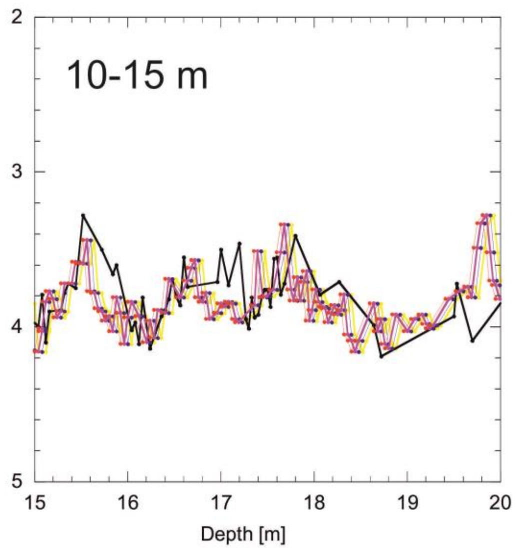
Together these uncertainties give a total error of ±17 µmol/kg in our bottom-water [O_2] reconstructions.

During full glacial conditions $\delta^{13}C_{org}$ was enriched by ~2‰ in the Northeast Atlantic (Rau et al., 1991) as a result of decreased [$CO_{2(aq)}$]. This would cause a decrease in $\Delta\delta^{13}C$ of ~0.08‰ unrelated to bottom-water [O_2] changes. Estimates of bottom-water [O_2] for the LGM and MIS 6 have therefore been corrected by +10 µmol/kg.

2. Changing depth habitats

While depth habitats of the two benthic foraminiferal species are epifaunal (*C. wuellerstorfi*) and deep infaunal (*G. affinis*), their oxygen isotope trends should be, and are, virtually synchronous due to mixing within the bioturbated mixed layer. Assumption of a deeper depth habitat for *G. affinis* that exceeds the typical bioturbated mixed layer depth (> 10 cm) causes significant erroneous delays in the timing of $\delta^{18}O$ changes of *G. affinis* compared with those of *C. wuellerstorfi* (see figure below).


C. wuellerstorfi
G. affinis (no depth change)
G. affinis (-4 cm)
G. affinis (-8 cm)
G. affinis (-12 cm)
Benthic δ18O (‰)
Depth [m]
2
3
4
5
0
5
10
15
20
25
30


10-15 m
Depth [m]
2
3
4
5
15
16
17
18
19
20

3. Calculation of increase in respired carbon concentrations in the Atlantic Ocean during the LGM and MIS 6.

Calculation of volumes of the North and South Atlantic basins below 2.8 km and respired carbon concentrations are shown in Tables 2 & 3. We assume that glacial bottom waters below 2.8 km from the North Atlantic basin were dominated by Southern sourced deep water. Furthermore, a fraction (here assumed 1/5) of the South Atlantic currently dominated by North Atlantic Deep Water was also dominated by Southern sourced deep waters. As mentioned in the main text, glacial [O_2] of Southern sourced deep waters must have decreased due to a decrease in ventilation; such a decrease was applied to 4/5 of the deep South Atlantic. These inferences are supported by nutrient and water mass proxies (Bickert and Mackensen, 2003; Curry and Oppo, 2005; Marchitto and Broecker, 2006; Gutjahr et al., 2008).

Table 2.

Basin	Volume km^3 (Eakins and Sharman, 2010)	Volume km^3 (Eakins and Sharman, 2010)	Volume below 2.8 km
Increase in respired carbon conc. due to change to Southern sourced bottom water mass (includes decrease in SO bottom water ventilation)			
North Atlantic	146×10^6	3.52	30×10^6
1/5 of South Atlantic	$0.2\times160\times10^6$	3.97	9×10^6
		Total volume	39×10^6
Increase in respired carbon conc. due to change in ventilation Southern sourced deep waters			
4/5 of South Atlantic	$0.8\times160\times10^6$	3.97	38×10^6
		Total volume	38×10^6

Apparent oxygen utilization concentrations were estimated by subtracting measured/reconstructed [O_2] from saturated [O_2] using LGM and MIS 6 deep water temperature and salinity of -1°C and 36, and recent temperature and salinity of 3°C and 35. Respired carbon concentrations were calculated using Redfield ratios (AOU*117/170) for µmol/kg, and then divided by 1.029 to give µmol/l. This was then multiplied by the volumes of the individual basins (in liters, so $\times10^{12}$) to get µmol C, divided by 10^6 and multiplied by 12 to get grams of carbon.

Table 3.1 Respired carbon increase associated with bottom water mass and ventilation change. LGM and MIS 6 [O_2] are corrected for a 2‰ increase in $\delta^{13}C$ by adding 10 µmol/kg as explained above.

Period	[O_2] (µmol/kg)	AOU (µmol/kg)	Respired C (µmol/kg)	Respired C (µmol/l)		
Recent/ pre-industrial at MD95-2042	245	80	55.1	53.5	Difference (µmol/l)	Respired carbon increase (Gt C)
LGM	200	156	107.4	104.4	50.9	23.8
MIS 6	180	176	121.1	117.7	64.2	30.0

Table 3.2 Respired carbon increase associated with decreased ventilation Southern sourced bottom waters. Again LGM and MIS 6 [O_2] are corrected for a 2‰ increase in $\delta^{13}C$ by adding 10 µmol/kg as explained above.

Period	[O_2] (µmol/kg)	AOU (µmol/kg)	Respired C (µmol/kg)	Respired C (µmol/l)	
Recent/ pre-industrial 40°S	205	130	89.1	86	Respired carbon increase (Gt C)
Diff with LGM		26	17.9	17.4	7.9
Diff with MIS 6		46	31.7	30.8	14.0

Added up, this gives an increase of 31.7 Gt of C and 44 Gt of C for the LGM and MIS 6, respectively.

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