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Unmixing of stable isotope signals using single specimen $\delta^{18}O$ analyses

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[1] The resolution at which foraminiferal stable isotopes are applied in paleo-environmental studies is ever increasing, resulting in continuous sampling of sediment cores. The resolution of such continuously sampled records depends on the rate of sedimentation of foraminiferal shells in its relation to the intensity of bioturbation. Bioturbation essentially mixes sediment layers of different age, altering the primary climate signal, thereby impacting the accuracy of both the timing and magnitude of reconstructed climate changes. A new approach to assess and correct the impact of bioturbation is investigated here, based on the $\delta^{18}O$ of individual specimens of planktonic foraminifera *Globorotalia inflata* from a series of boxcore samples in the Eastern North Atlantic. Average $\delta^{18}O$ values decrease southward from 1.62 to 1.07‰ with the exception of site T86-11 (1.35‰). The $\delta^{18}O$ distribution of each station can be fitted with a uni- to polymodal distribution. A nonunimodal distribution strongly suggests admixing of bioturbated individuals. Quantification of these distributions allows deconvolving the original and bioturbated signals and subsequently provides a correction for bioturbation.

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1. Introduction

[2] The oxygen isotope composition of foraminiferal test carbonate is a proven and established tool for reconstructing past changes in seawater temperature and ice volume [*Epstein et al.*, 1953; *Shackleton*, 1974; *Bemis et al.*, 1998]. The stable isotopic composition of foraminiferal test is increasingly applied in high-resolution studies. The study of sub-Milankovitch and sometimes even (sub-) centennial time scale variability has become increasingly important to understand climatic changes on time scales relevant to mankind [*Bradley*, 2000 and references therein]. This implies that cores are nowadays often studied at the highest possible resolution and thus sampled continuously. In such cases, the resolution of the records depends on sedimentation rate of the foraminiferal shells in relation to the intensity of bioturbation. Bioturbation is the process by which burrowing animals mix sediments from "older" and "younger" layers. This alters a primary climate signal in two ways. First, the recorded climate signal is lengthened by the upward/downward transport of sediment, which leads to an overestimation of the duration of the climate event. Second, in the case of short events, more intense bioturbation leads to dampening of the amplitude of the original climate signal, as both underlying and overlying sediments are mixed with the sediments deposited during the event, thereby altering the magnitude and duration of these short-lived events in paleo-environmental reconstructions over as much as 15 cm of sediment. The combined effects as a result of bioturbation have been widely hypothesized, modeled, recognized, and reported in numerous studies over the last 40 years [e.g., *Berger and Heath*, 1968; *Guinasso and Schink*, 1975; *Schink and Guinasso*, 1977; *Peng et al.*, 1979; *Hutson*, 1980; *Schiffelbein*, 1984; *Peng and Broecker*, 1984; *Bard et al.*, 1987; *Bard*, 2001; *Barker et al.*, 2007; *Löwemark et al.*, 2008; *Keigwin and Guilderson*, 2009]. Recognizing the impact of bioturbation is, thus, essential for assessing true timing and magnitude of the signals derived from stable oxygen analysis, since $\delta^{18}O$ signals are generally based on averaging analyses of multiple specimens, thereby including a bioturbated component. A number of studies indeed accurately modeled, applying a series of different modeling approaches, the impact of bioturbation on paleo-environmental reconstructions [*Berger and Heath*, 1968; *Peng and Broecker*, 1984; *Schiffelbein*, 1984; *Bard*, 2001; *Löwemark et al.*, 2008; *Keigwin and Guilderson*, 2009]. A direct proxy allowing a coupling between measured downcore $\delta^{18}O$ data and the quantification and subsequent correction of its bioturbated component is, however, still a highly sought after tool.

[3] Because of technical improvements allowing to accurately measure $\delta^{18}O$ of individual planktonic foraminifera, paleoceanographers no longer have to rely on $\delta^{18}O$ values based on multiple specimens, but can also use the distribution of $\delta^{18}O$ values from individual specimens around this average to reconstruct past environments [*Spero and Williams*, 1989; *Tang and Stott*, 1993; *Billups and Spero*, 1996; *Koutavas et al.*, 2006]. This distribution of single specimen $\delta^{18}O$ values can for instance be used as a tool to reconstruct the seasonal cycle in sea surface temperatures [*Tang and Stott*, 1993; *Koutavas et al.*, 2006; *Wit et al.*, 2010; *Ganssen et al.*, 2011]. This interpretation, however, requires that the impact of bioturbation can be quantified. Here, we investigate the impact of bioturbation by measuring single specimen $\delta^{18}O$ of planktonic foraminifera *Globorotalia inflata* from a series of boxcore samples in the Eastern North Atlantic.

2. Methods

[4] Samples from a north-south transect (57.9–35.6°N) in the North East Atlantic Ocean were recovered during two cruises of the R/V *Tyro* in the North Atlantic (Figure 1) [*Ganssen and Kroon*, 2000]. Surface sediments (0–3 cm) were taken from boxcores and stored with Rose Bengal stain to differentiate between living and fossil foraminiferal specimen. Sedimentation rates between 31 and 34°N were low (1 cm/ky or lower) [*Ganssen and Kroon*, 2000]; samples from below 34°N were therefore not used here. Surface sediment was subsequently sieved over a 63 μm sieve. Premeasurement sample treatment followed standard lab procedures for oxygen isotope measurements [*Wit et al.*, 2010]. Single specimens of planktonic species *G. inflata* from the 355 to 425 μm size range were measured for $\delta^{18}O$ on a Mat Finnigan 252 gas-source mass spectrometer with an automated Kiel type carbonate preparation line at the Vrije Universiteit Amsterdam. Results for $\delta^{18}O$ are reported relative to the Vienna Pee Dee Belemnite (V-PDB), using the NBS-19 standard, and have an internal reproducibility of 0.08‰. Sample averages are based on the unweighted average of the individual $\delta^{18}O$ measurements of each station.

[5] Single specimen $\delta^{18}O$ data were plotted as a histogram with a bin size of 0.2‰ (closely resembling 1°C per bin) in order to analyze the

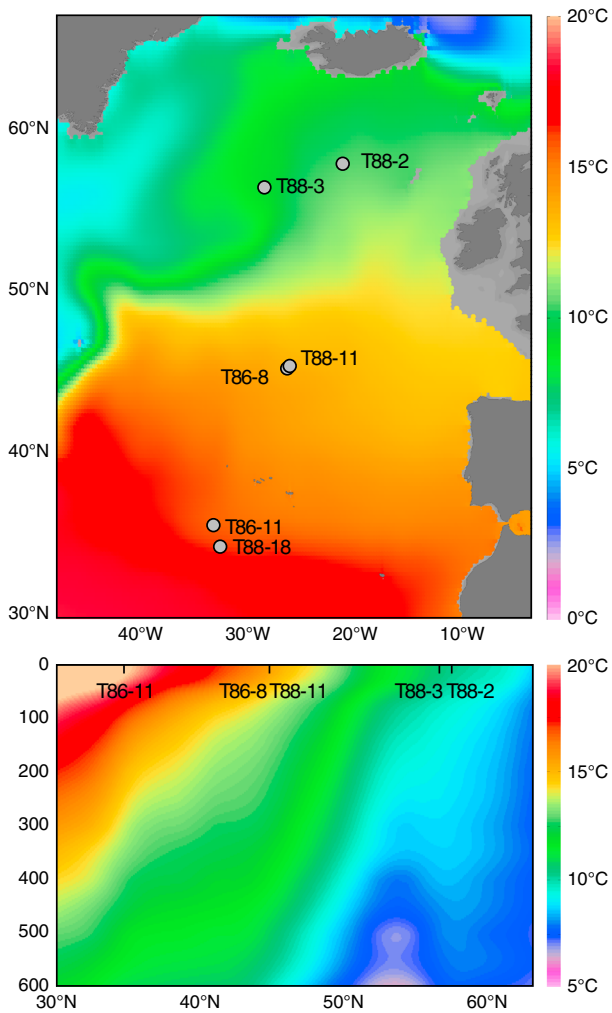

Figure 1. The upper panel: Annual average North Atlantic seawater temperatures at a depth of 200 meters from the WOA01, with the locations of the used core locations [*Conkright et al.*, 2002]. Lower panel: north-south transect of the temperature of the first 600 meters in the North Atlantic [*Conkright et al.*, 2002].

frequency distribution of each station. Frequency distributions were tested for normality and subsequently fitted with a Gaussian distribution, using a standard curve fit in an Excel spreadsheet (Appendix A). The Gaussian curve was fitted to the data using the sum of squared error and the Excel solver function to minimize the error between the measured data and the modeled Gaussian distribution.

[6] Since bioturbation results in the mixing of sediments of different ages, $\delta^{18}O$ distributions affected by bioturbation should display a bi- or polymodal distribution in case of abrupt changes in environmental conditions. More gradual changes impact the distribution by displaying a wide plateau with an unrealistically large standard deviation.

3. Results

[7] Average $\delta^{18}O$ values decrease southward from 1.62 to 1.07‰ with the exception of site T86-11 (1.35‰) (Figure 3). A Shapiro-Wilk test was performed for each station, using the individual $\delta^{18}O$ measurements to verify whether distributions significantly deviate from normality (Tables 1 and 2). A Shapiro-Wilk test shows whether there is a significant difference between a theoretical perfect normal distribution and measured distribution [*Field*, 2009]. Identified outliers (outlier > average ± 3 standard deviations) were excluded from the Shapiro-Wilk analyses, as they have a major impact on the test [*Field*, 2009], but are not excluded from the dataset. For most of the stations, the $\delta^{18}O$ values are normally distributed according to the Shapiro-Wilk test. The probability statistic (*p*-value) for site T86-11, however, was significant, indicating that the $\delta^{18}O$ values for this site are not normally distributed.

Table 1. Core Location, Depth, Average $\delta^{18}O$ With Range (Max-Min), Standard Deviation, p-Value, and Degrees of Freedom (DF) From the Shapiro-Wilks test. A p-Value < 0.05 is Significant and Indicates That the Distribution Is Deviating From Normality

Sample	Location			$\delta^{18}O$ (V-PDB)			
	Latitude (N)	Longitude (W)	Depth (m)	Average	σ	DF	p-Value
T88/2	57.9	20.5	2911	1.64 (0.36–3.01)	0.39	25	0.82
T88/3	56.4	27.8	2819	1.62 (0.74–2.20)	0.27	36	0.41
T88/11	45.4	25.4	2741	1.14 (0.57–2.18)	0.27	34	0.66
T86/8	45.3	25.7	3232	1.07 (1.01–1.84)	0.32	36	0.26
T86/11	35.6	32.6	2220	1.35 (0.54–2.57)	0.59	40	0.00

Table 2. Single Specimen Oxygen Isotope Values per Station for *G. inflata*

$\delta^{18}O$ (V-PDB)	T88/2	T88/3	T88/11	T86/8	T86/11
1	1.49	1.79	0.99	1.26	1.13
2	1.83	1.41	1.07	0.90	2.44
3	1.64	1.46	1.18	0.94	0.91
4	1.23	0.74	1.08	1.05	1.98
5	1.25	1.58	1.27	1.20	2.57
6	1.58	1.59	1.64	1.02	1.19
7	1.84	1.57	1.56	1.09	0.88
8	1.70	1.78	1.11	0.87	1.29
9	2.06	1.53	1.15	1.11	0.93
10	1.51	1.05	0.97	1.09	0.68
11	1.48	1.42	0.92	0.94	1.10
12	1.59	2.20	0.68	1.24	0.91
13	1.66	1.69	1.13	0.87	2.20
14	1.78	1.50	1.58	1.21	1.17
15	1.59	1.67	1.20	1.20	2.20
16	1.49	1.40	1.43	1.26	0.87
17	1.32	1.52	1.03	1.04	1.02
18	1.51	1.72	1.22	1.14	2.07
19	1.71	1.80	1.09	1.08	0.76
20	1.01	1.40	1.41	2.16	2.41
21	1.66	1.91	0.66	0.57	1.33
22	1.63	1.41	1.43	0.95	0.54
23	1.29	1.80	1.01	0.81	1.90
24	3.10	1.79	1.15	0.65	1.87
25	1.44	1.74	1.23	1.19	1.09
26	2.17	1.39	0.84	1.02	1.98
27		1.30	1.10	1.08	0.76
28		1.56	1.38	2.18	0.80
29		1.69	1.02	0.86	1.50
30		1.61	0.36	0.77	1.22
31		1.80	1.23	0.78	1.58
32		1.78	1.24	0.93	1.76
33		1.91	0.96	0.60	1.89
34		1.81	1.49	1.32	0.81
35		1.80	1.22	1.11	0.67
36		2.06		1.24	2.22
37		1.79		0.86	0.73
38				0.95	0.85
39					0.80
40					1.07

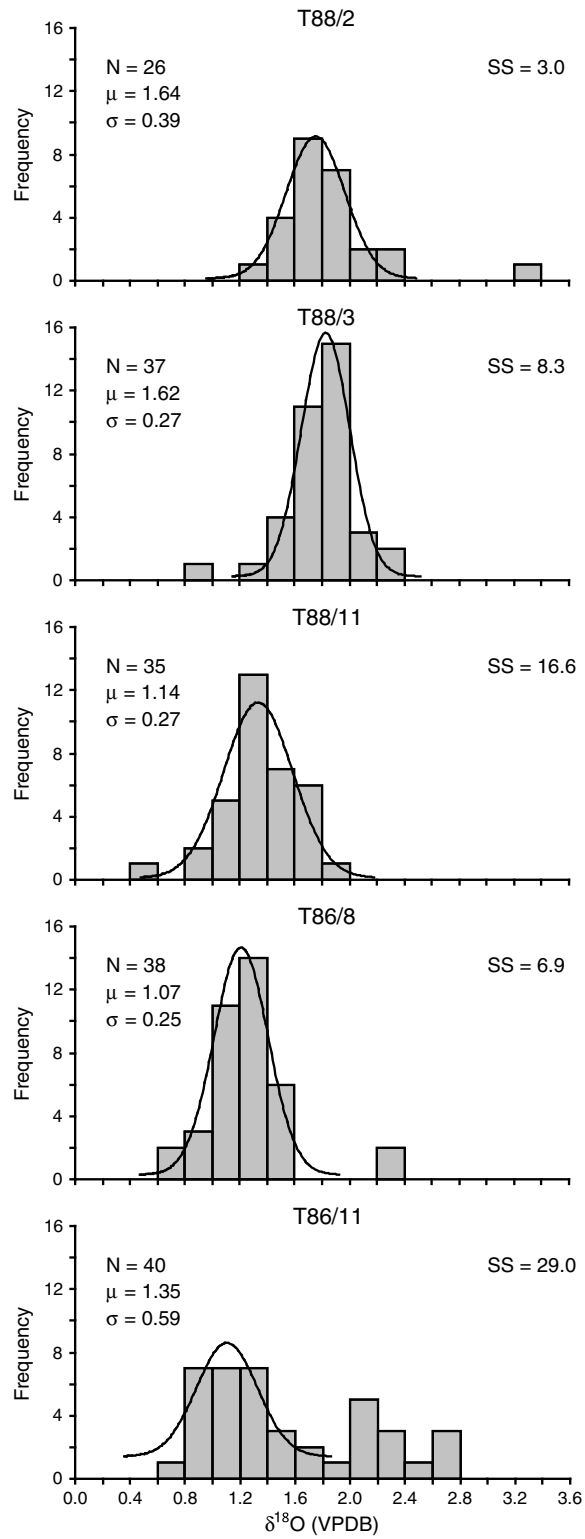

Figure 2. Frequency and modeled Gaussian distributions for measured $\delta^{18}O$ of *G. inflata*, with the number of measurements (N), the average $\delta^{18}O$ (μ) and standard deviation (σ). The sum of squares (SS) is used as a fit between the measured and modeled frequency distribution. Data includes outliers that were removed for the Shapiro-Wilk test.

4. Discussion and Conclusions

[8] North Atlantic surface water temperatures show a clear north-south gradient with temperatures increasing towards the South (Figures 2 and 3) [*Conkright et al.*, 2002]. *G. inflata* is a nonspinose planktonic foraminifera living around 100–400 m water depth, typically found in thermocline waters [*Fairbanks et al.*, 1982; *Hemleben et al.*, 1989; *Ganssen and Kroon*, 2000]. Average oxygen isotope values measured on planktonic foraminifer *G. inflata* along this north-south transect should, therefore, reflect this latitudinal temperature gradient. Measured average $\delta^{18}O$ values along this transect for *G. inflata*

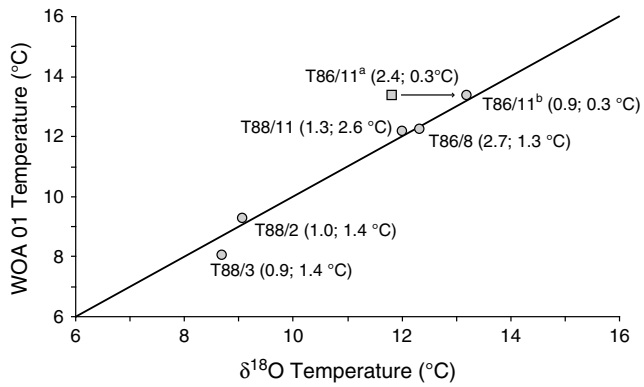

Figure 3. Average $\delta^{18}O$ derived temperature for *G. inflata* and the annual average seawater temperature between 100 and 400 meters water depth from the WOA01 [*Conkright et al.*, 2002]. T86/11^a (square) is the $\delta^{18}O$ derived temperature as measured, while T86/11^b is the temperature derived after correcting for bioturbation. (1.4; 0.9°C) indicate the seasonal range of the WOA01 and the standard deviation as measured in degrees Celsius for each station.

were converted to temperatures using the $\delta^{18}O$ temperature equation of *O'Neil et al.* [1969] as refitted by *Shackleton* [1974] (equation (1)).

$$T = 16.9 - 4.38\left(\delta^{18}O_c - \delta^{18}O_w\right) + 0.1\left(\delta^{18}O_c - \delta^{18}O_w\right)^2 \quad (1)$$

[9] Values for $\delta^{18}O_w$ were calculated using WOA01 salinity values and their relation to $\delta^{18}O_w$ for the North Atlantic [equation (2) from *Ganssen and Kroon*, 2000; *Conkright et al.*, 2002]

$$\delta^{18}O_w = 0.55S - 19.45 \quad (2)$$

[10] Values for $\delta^{18}O_w$ were converted from V-SMOW to V-PDB, using the 0.27‰ correction after *Hut* [1987]. Temperatures based on the average oxygen isotope values, with the exception of site T86/11, correlate well with annual mean temperatures between 100 and 400 m water depth from the World Ocean Atlas 2001 [*Conkright et al.*, 2002] (Figure 4). The standard deviations of the measured temperatures correlate well with the seasonal range in WOA01 temperatures, again with the exception of site T86/11. The average $\delta^{18}O$ of T86/11 is 1.35‰ (11.8°C), which is too cold compared to present-day temperatures (Figure 4). The Shapiro-Wilk test on the single specimen $\delta^{18}O$ distribution failed, and the frequency distribution for site T86/11 is thus deviating from normality (Table 1). The larger standard deviation, furthermore, indicates that multiple populations of foraminifera are present within the measured average. An end member model was used to dissect the distribution into multiple Gaussian distributions, all with their own average and standard deviation (Figure 4) (Appendix A). The average

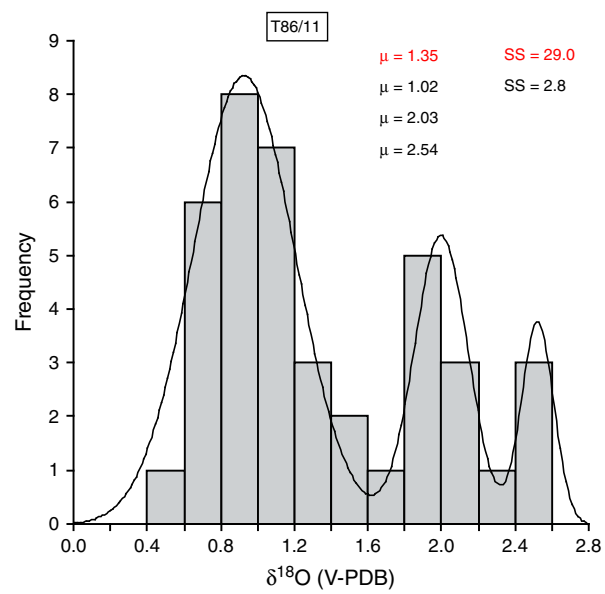

Figure 4. Frequency distribution and modeled Gaussian curve for site T86/11. The upper panel is the original modeled distribution. The lower panel displays the modeled Gaussian curves after recognizing multiple distributions present and entails the correction for bioturbation. The sum of squares (SS) is used to express the difference between the model and the measured frequency distribution.

of 1.35‰ consists of three different Gaussian distributions having an average of 1.02, 2.03, and 2.54‰, respectively. The relative contribution of each population to the measured average $\delta^{18}O$ is 68 (27 foraminifera), 23 (9), and 9 (4)%, respectively. The population with an average $\delta^{18}O$ of 1.02‰ seems to reflect the present-day situation since this value correlates well with what is expected based on temperature and salinity (Figure 5) [World Ocean Atlas 01, *Conkright et al.*, 2002]. The two populations with higher oxygen isotopic values (2.03 and 2.54‰) reflect lower temperatures, derived either from cold ring gyres spinning of the Polar Front [*Mittelstaedt*, 1987] or from cold periods in the past mixed in by bioturbation. The average oxygen isotope values correspond to temperatures between 6.8–8.6°C (2.03‰, $\delta^{18}O_w$ −0.4–0.07‰) and 4.9–6.7°C (2.54‰, $\delta^{18}O_w$ −0.4–0.07‰), which occur in the North Atlantic above 57°N below 400 m water depth or well above 60°N (Figures 1 and 2). T86/11 has been dated at a radiocarbon age of 32 y [*Ganssen and Kroon*, 2000], indicating that the cold populations are recent and thereby potentially derived from these cold ring gyres. However, this radiocarbon date is derived from pteropods, which might be of a more recent age than the foraminifera from the upper 3 cm [*Melkert et al.*, 1989]. A foraminiferal-based radiocarbon date from a nearby core (T88/18, Figure 1) in the same transect suggested an age of 6.7 Ky (UtC-1230: 6680 ± 140 BP), hinting at a much older source for the cold populations present in core T86/11 [*Ganssen and Kroon*, 2000]. Furthermore, the observed eddy braking of the Polar Front mainly traveled east-northeast, meaning that the low-temperature population cannot be derived from these cold rings, since the needed temperatures only occur above 57°N.

[11] Alternatively, the populations of 2.03 and 2.54‰ are bioturbated upward. The two most recent periods with appreciably lower temperatures in the North Atlantic compared to today are the Younger Dryas (YD) and the Last Glacial Maximum (LGM). Although temperatures during the Little Ice Age were probably somewhat lower than today, this would have an effect on stable oxygen isotopes of less than about 0.2‰ [*Keigwin*, 1996]. The oxygen isotope values of 2.03 and 2.54‰ are thus most probably originating from older sediments, the YD or LGM, respectively. This implies that specimen initially deposited during these two episodes have been bioturbated upward by at least 10–15 cm [Ganssen, unpublished data]. The relatively low sedimentation rates in this part of the Atlantic [1 cm/ky or lower, *Ganssen and Kroon*, 2000] and a nearby core (T88/18, Figure 1) having a surface radiocarbon date of 6.7 ky (UtC-1230: 6680 ± 140 BP) indicate that the contribution of pre-Holocene species, as recorded in core T86/11, is indeed potentially significant, although percentages up to 30% remain relatively high (Figure 4). Low sedimentation rates, however, result in a relatively shallow sediment depth of the YD and LGM (10–15 cm), around the maximum penetration depth of bioturbation in well-oxygenated sediments [*Thomson et al.*, 2000; *Löwemark et al.*, 2008 and references therein]. Furthermore, low sedimentation rates in nearby cores in the North-East Atlantic have been linked to a winnowing effect of ocean currents [*Thomson et al.*, 2000]. Fluctuations in the strength of this winnowing might have caused erosion events at core T86/11, as recorded during the Mid-Holocene in deeper cores at the Feni Drift [*Thomson et al.*, 2000], thereby enabling a large percentage of glacial foraminifera in the surface sediments. Comparing the values of these two deconvolved signals with a *G. inflata* based $\delta^{18}O$ record for the last 20 ka at a nearby location (33°42'N, 57°35'W) [*McManus et al.*, 2004] indeed shows that the $\delta^{18}O$ value of 2.03 is typical for the YD (12.5–14.2 ka), while 2.54 corresponds to the LGM (17.5–19.8 ka) [*McManus et al.*, 2004].

[12] Our data based on the measurement of single specimens of planktonic foraminifera show that frequency distributions can be fitted with a uni- to polymodal distribution. A nonunimodal distribution strongly suggests admixing of specimen from a different source, such as through bioturbation. The admixture of separate populations not coming from bioturbation, such as cold rings, can however also be recognized. Quantification of these distributions allows deconvolving the original and bioturbated signals. In the core studied here, one third of the $\delta^{18}O$ values measured were actually bioturbated upward from older sedimentary layers with a contrasting isotopic value. A similar contribution of younger specimen can be expected in the older layers. This shows that under low sedimentation rates, an appreciable part of the signal can be derived from bioturbated sediments, significantly impacting climate reconstructions depending on averaged $\delta^{18}O$ values of foraminifera.

Appendix A

Appendix A Simple Excel Spread Sheet Model for Generating Frequency Distributions and the Subsequent Modeled Gaussian Curve. SS = Sum of Squares

T88-11	$\delta^{18}O$ (V-PDB)
1	0.36
2	0.66
3	0.68
4	0.84
5	0.92
6	0.96
7	0.97
8	0.99
9	1.01
10	1.02
11	1.03
12	1.07
13	1.08
14	1.09
15	1.10
16	1.11
17	1.13
18	1.15
19	1.15
20	1.18
21	1.20
22	1.22
23	1.22
24	1.23
25	1.23
26	1.24
27	1.27
28	1.38
29	1.41
30	1.43
31	1.43
32	1.49
33	1.56
34	1.58
35	1.64

Amplitude	11.09
Width	0.59
Height	499.99
Transform	0.12
Peak Position	1.26

SS^2
16.64

Bin (V-PDB)	Frequency Measured	Modeled[1]	Fit
0.0	0	0.12	0.02
0.2	0	0.13	0.02
0.4	1	0.14	0.74
0.6	0	0.37	0.13
0.8	2	1.86	0.02
1.0	5	6.27	1.62
1.2	13	10.88	4.48
1.4	7	9.43	5.92
1.6	6	4.11	3.59
1.8	1	0.97	0.00
2.0	0	0.21	0.05
2.2	0	0.13	0.02
2.4	0	0.12	0.02
2.6	0	0.12	0.02
2.8	0	0.12	0.02

1: $Frequency = Transform + Height^{-0.5\left(\frac{Bin-Peak\cdot Position}{Width}\right)^2} \bullet Amplitude$

2: $SS = (Measured\ Frequency - Modeled\ Frequency)^2$

Acknowledgements

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