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GSA DATA REPOSITORY 2009198 Khelifi et al.

Supplemental Information

METHODS

Our MOW records from the northeast Atlantic were obtained from Deep Sea Drilling Project (DSDP) Site 548, at the continental margin southwest of Ireland (48°54´N, 12°09´W; 1250 m w.d.; Fig. 1). Today, this site is bathed by water masses near the base of MOW (Reid, 1979). Complementary records from the western Mediterranean Sea were reconstructed from Ocean Drilling Program (ODP) Site 978 in the Alboran Sea (36°13´N, 2°3´W; 1930 m w.d.; Fig. 1). To reach millennial-scale resolution, the cored sediment records were sampled with spacing of 10 cm at Site 548 and of 10–20 cm at Site 978 (20 cc each).

Bulk sediment samples were weighed, oven-dried at 40 °C, weighed again (to obtain dry bulk density), and were then washed through a 63 µm mesh-size sieve. The residue was dried at 40 °C and finally sieved into 5 size fractions. All foraminifera, to be analyzed for $\delta^{18}O$ and Mg/Ca, were picked from the >250-µm fraction (Table DR1 in the Data Repository). Foraminiferal samples were analyzed on a Finnigan MAT251 system, with a precision of ±0.07‰ for $\delta^{18}O$ and ±0.05‰ for $\delta^{13}C$, at the Leibniz Laboratory in Kiel.

For Mg/Ca analyses, foraminiferal samples (Table DR1 in the Data Repository) were cleaned according to the protocol of Martin and Lea (2002). Cleaning efficiency was monitored using Fe/Ca, Al/Ca, and Mn/Ca (Barker et al., 2003). Mg/Ca values were measured, on simultaneous inductively coupled plasma–optical emission spectrometer (ICP–OES), at the Institute of Geosciences, University of Kiel. Intensity ratio calibration followed the method of de Villiers et al. (2002). Analytical precision of Mg/Ca ratios was better than 0.1–0.2% (relative standard deviation), equivalent to ±0.02 °C. Standard deviation of repeated analyses, of the same sample, over different days, is 0.12 mmol/mol, resulting in a temperature uncertainty of ±0.6 °C.

Bottom water temperatures (BWT), at North Atlantic DSDP Site 548, were derived from the Mg/Ca ratio of *Cibicidoides mundulus*, using the global calibration curves of Elderfield et al. (2006) defined for common *Cibicidoides* spp. (Mg/Ca = 0.9 exp [0.11 x BWT]). At ODP Site 978, we consistently used a "glassy" morphotype of *C. mundulus*, which leads to Mg/Ca-based BWT ~5 °C higher than values of *Cibicidoides wuellerstorfi*, when measured on the same sample. We corrected the Mg/Ca-based BWT of *C. wuellerstorfi* for this offset, which is obviously due to a vital effect (Elderfield et al., 2006; Healey et al., 2008). In case we had not corrected the Mediterranean Mg/Ca record of *C. wuellerstorfi*, the resulting BWT and $\delta^{18}O_{water}$ values would drop to levels significantly lower than those found for Atlantic Site 548, which is clearly not realistic.

Where *C. mundulus* was not sufficiently abundant to perform both isotopic and Mg/Ca measurements, we employed the $\delta^{18}O$ signal of *C. wuellerstorfi* to generate a common $\delta^{18}O_{water}$ signal. This signal was obtained from benthic $\delta^{18}O$ values, which were normalized for Mg/Ca-based BWT, using the equation of Shackleton (1974), and taking the Mg/Ca values as face values of temperature variability (ignoring Yu and Elderfield, 2008; for details see Discussion section). The $\delta^{18}O_{water}$ signal was not converted to local $\Delta\delta^{18}O_{water}$ values, which reflect regional changes in bottom water salinities, because of the absence of a reliable global $\delta^{18}O$ ice volume record for the Pliocene. We assume that global $\delta^{18}O$ ice volume affects both study sites in the same manner, and therefore neglect its effect when comparing $\delta^{18}O_{water}$ signals. $\delta^{18}O_{water}$ signals (vs PDB) were transferred to SMOW by adding a standard correction of 0.20‰ (Bemis et al., 1998).

Our estimates of bottom water salinities (not shown in this study) were derived from $\delta^{18}O_{water}$ records (0.5‰ equal to ~1 psu; e.g., Cacho et al., 2006), that were corrected for mid-Pliocene variations in the stacked benthic $\delta^{18}O$ record LR04 (Fig. 3), which may largely reflect changes in global ice volume (Lisiecki and Raymo, 2005). Bottom water densities were deduced from paired bottom water salinity and BWT values, following Fofonoff and Millard (1983). Because of large uncertainty ranges, we build our discussion on major and long-term trends in bottom water densities only.

Sea-surface temperatures (SST) in the western Mediterranean were reconstructed from a C_{37} alkenone unsaturation ($U^{k'}_{37}$) record using the analytical technique of Prahl and Wakeham (1987) and the transfer equation of Conte et al. (2006). Alkenones were analyzed, at a multi dimensional gas chromatograph system (MDGC), at the Institute of Geosciences, University of Kiel. Sample and standard replicates show a temperature uncertainty of 0.3 °C. SST data served to calculate $\delta^{18}O_{water}$ of sea-surface water using the equation of Bemis et al. (1998).

For Nd isotope measurements, bulk sediment samples were leached following the method of Gutjahr et al. (2007) to extract the seawater fraction of Nd. The Nd in the leach solutions were chemically treated and purified following Cohen et al. (1988). Nd isotope ratios are expressed as ε_{Nd} values, which correspond to the deviation of the measured $^{143}Nd/^{144}Nd$ ratio of a sample from that of the chondritic uniform reservoir CHUR (0.512638) multiplied by 10,000. The samples were measured on a Nu instruments multi collector–inductively coupled plasma mass spectrometer (MC–ICPMS) and on a Triton thermal ionisation mass spectrometer (TIMS) at IFM–GEOMAR Kiel. Repeated measurements of the JNdi-standard showed an error of external 2σ precision ±0.3 ε_{Nd} units. All Nd isotope ratios presented were normalized to the accepted value for the standard JNdi-1 of 0.512115 (Tanaka et al., 2000).

All data are available on www.pangaea.de at http://doi.pangaea.de/10.1594/PANGAEA.716847

AGE MODEL

The Site 548 age model (Fig. DR1A) integrates evidence from (1) shipboard biostratigraphy and (2) magnetostratigraphy of DSDP Leg 80 (Graciansky et al., 1985), showing the top and the base of the Gauss Chron at 131.6–132.8 and 164.2–165.7 mbsf, respectively. Orbital-scale stratigraphy was obtained by tuning the oscillations of planktic and benthic $\delta^{18}O$ records from Site 548 to the stacked benthic $\delta^{18}O$ record LR04 of Lisiecki and Raymo (2005). The resulting age model covers an interval from 3.68 to 2.56 Ma and results in sedimentation rates of 1.4–7.2 cm/1,000 years and sampling intervals of 700–3500 years. The sediment record of Site 548 suffered from three hiati, where parts of MIS G13 to G15, KM2 to KM3, and MG4 were lost. Minor sediment sections may have been lost at core breaks near MIS G20, M2, and Gi2. Here, sampling intervals may reach 7,900 to 32,000 years (Fig. DR1A).

The Site 978 age model (Fig. DR1B) likewise integrates evidence from biostratigraphy, magnetostratigraphy (ODP Leg 161, Shipboard Scientific Party, 1996), and from tuning the oscillations of the planktic $\delta^{18}O$ (!) record to the LR04 record (Lisiecki and Raymo, 2005). This age model covers an interval from 3.62 to 2.72 Ma, resulting in sedimentation rates of 5.1–12.7 cm/1,000 years and sampling intervals of 1000–1800 to 2500 years, occasionally of 4000–5000 years, at core breaks up to 12,500 years (Fig. DR1B).

SUPPLEMENTAL REFERENCES

Barker, S., Greaves, M., and Elderfield, H., 2003, A study of cleaning procedures used for foraminiferal Mg/Ca paleothermometry: Geochemistry, Geophysics, Geosystems, v. 4, p. 8407, doi: 10.1029/2003GC000559.

Bemis, B.E., Spero, H.J., Bijma, J., and Lea, D.W., 1998, Reevaluation of the oxygen isotopic composition of planktonic foraminifera: experimental results and revised paleotemperature equations: Paleoceanography, v. 13, p. 150–160.

Cohen, A.S., O'Nions, R.K., Siegenthaler, R., and Griffin, W.L., 1988, Chronology of the pressure-temperature history recorded by a granulite terrain: Contributions to Mineralogy and Petrology, v. 98, p. 303–311.

Conte, M.H., Sicre, M.-A., Rühlemann, C., Weber, J.C., Schulte, S., Schulz-Bull, D., and Blanz, T., 2006, Global temperature calibration of the alkenone unsaturation index ($U^{k'}_{37}$) in surface waters and comparison with surface sediments: Geochemistry, Geophysics, Geosystems, v. 7, p. Q02005, doi:10.1029/2005GC001054.

de Villiers, S., Greaves, M., and Elderfield, H., 2002, An intensity ratio calibration method for the accurate determination of Mg/Ca and Sr/Ca of marine carbonates by ICP-AES: Geochemistry, Geophysics, Geosystems, v. 3, p. 1001, doi:10.129/2001GC000169.

Elderfield, H., Yu, J., Anand, P., Kiefer, T., and Nyland, B., 2006, Calibrations for benthic foraminiferal Mg/Ca paleothermometry and the carbonate ion hypothesis: Earth and Planetary Science Letters, v. 250, p. 633–649, doi: 10.1016/j.epsl.2006.07.041.

Fofonoff, P., and Millard Jr, R.C., 1983, Algorithms for computation of fundamental properties of seawater: Unesco Technical Papers in Marine Sciences, v. 44, 53 p.

Graciansky, P.C. de, Poag, C.W., and 29 others (Editors), 1985, Initial Reports DSDP, 80, U.S. Government Printing Office, Washington, DC, doi: 10.2973/dsdp.proc.80.117.1985.

Gutjahr, M., Frank, M., Stirling, C.H., Klemm, V., van de Flierdt, T., Halliday, A.N., 2007, Reliable extraction of a deepwater trace metal isotope signal from Fe-Mn oxyhydroxide coatings of marine sediments: Chemical Geology, v. 242, p. 351–370.

Healey, S.L., Thunell, R.C., and Corliss, B.H., 2008, The Mg/Ca-temperature relationship of benthic foraminiferal calcite: New core-top calibrations in the <4 °C temperature range: Earth and Planetary Science Letters, v. 272, p. 523–530. doi:10.1016/j.epsl.2008.05.023.

Loubere, P., 1987, Changes in mid-depth North Atlantic and Mediterranean circulation during the Late Pliocene – Isotopic and sedimentological evidence: Marine Geology, v. 77, p. 15–38, doi: 10.1016/0025-3227(87)90081-8.

Martin, P.A., and Lea, D.W., 2002, A simple evaluation of cleaning procedures on fossil benthic foraminiferal Mg/Ca: Geochemistry, Geophysics, Geosystems, v. 3, p. 8401, doi: 10.1029/2001GC000280.

Ostermann, D.R., and Curry, W.B., 2000, Calibration of stable isotopic data: An enriched δ^{18}O standard used for source gas mixing detection and correction: Paleoceanography, v. 15, p. 353–360.

Prahl, F.G., and Wakeham, S.G., 1987, Calibration of unsaturation patterns in long-chain ketone compositions for paleotemperature assessment: Nature, v. 330, p. 367–369.

Shackleton, N.J., 1974, Attainment of isotopic equilibrium between ocean water and the benthonic foraminifera genus *Uvigerina*: isotopic changes in the ocean during the last glacial: Colloques Internationaux du Centre National du Recherche Scientifique, v. 219, p. 203–210.

Shipboard Scientific Party, 1996, Site 978, *in* Comas, M.C., Zahn, R., Klaus, A., and 25 others: Proceedings of the Ocean Drilling Program (ODP), Initial Reports, v. 161, College Station, TX (Ocean Drilling Program), p. 355–388. doi:10.2973/odp.proc.ir.161.108.1996.

Tanaka, T., Togashi, S., Kamioka, H., et al., 2000, JNdi-1: a neodymium isotopic reference in consistency with LaJolla neodymium: Chemical Geology, v. 168 (3-4), p. 279–281.

CAPTIONS FOR DR FIGURES

Figure DR1. Age control and sedimentation rates for Deep Sea Drilling Project (DSDP) Site 548 (A) and Ocean Drilling Program (ODP) Site 978 (B). Isotopic stages are labeled and tuned to benthic δ^{18}O stack LR04 (Lisiecki and Raymo, 2005). Age ranges of magnetic stratigraphy are plotted for comparison. For Site 548, no magnetic polarity reversals were defined between 158.58 and 149.32 mbsf (Graciansky et al., 1985) likewise for Site 978 between 400 and 370 mbsf (Shipboard Scientific Party, 1996). Vertical lines mark potential losses of sediment sections at core breaks.

Figure DR2. Epibenthic $\delta^{18}O$ and $\delta^{13}C$ records from Deep Sea Drilling Project (DSDP) Site 548 (A) and Ocean Drilling Program (ODP) Site 978 (B) measured on various species of *Cibicidoides spp.* (cf. Table DR1 in the Data Repository). Clear 23.7-kyr precessional cycles of $\delta^{13}C$ at ODP Site 978 additionally document the trustworthiness of the extreme $\delta^{18}O$ oscillations measured in parallel on the same foraminiferal specimens.

TABLE

Table DR1. Note: At Deep Sea Drilling Project (DSDP) Site 548, 41 out of 48 data of endobenthic *Uvigerina* spp., and 43 out of 416 data of epibenthic *Cibicidoides* spp. are from Loubere (1987). To adjust these $\delta^{18}O$ values to our dataset we corrected them by an empiric value of +0.31. This offset may be due, for example, to contamination of sample gas by reference gas during ionization for analyses generated before the 1990s (Ostermann and Curry, 2000). (†) A correction factor of +0.64 was applied to $\delta^{18}O$ values of *Cibicidoides* spp. to normalize them to $\delta^{18}O$ values of *Uvigerina*, which are in equilibrium with ambient seawater (Shackleton, 1974). Parallel measurements did not reveal any systematic offset between $\delta^{18}O$ of *C. wuellerstorfi* and *C. mundulus*. (*) Data from species with asterisks concern only the time interval after 3 Ma (Fig. DR1).

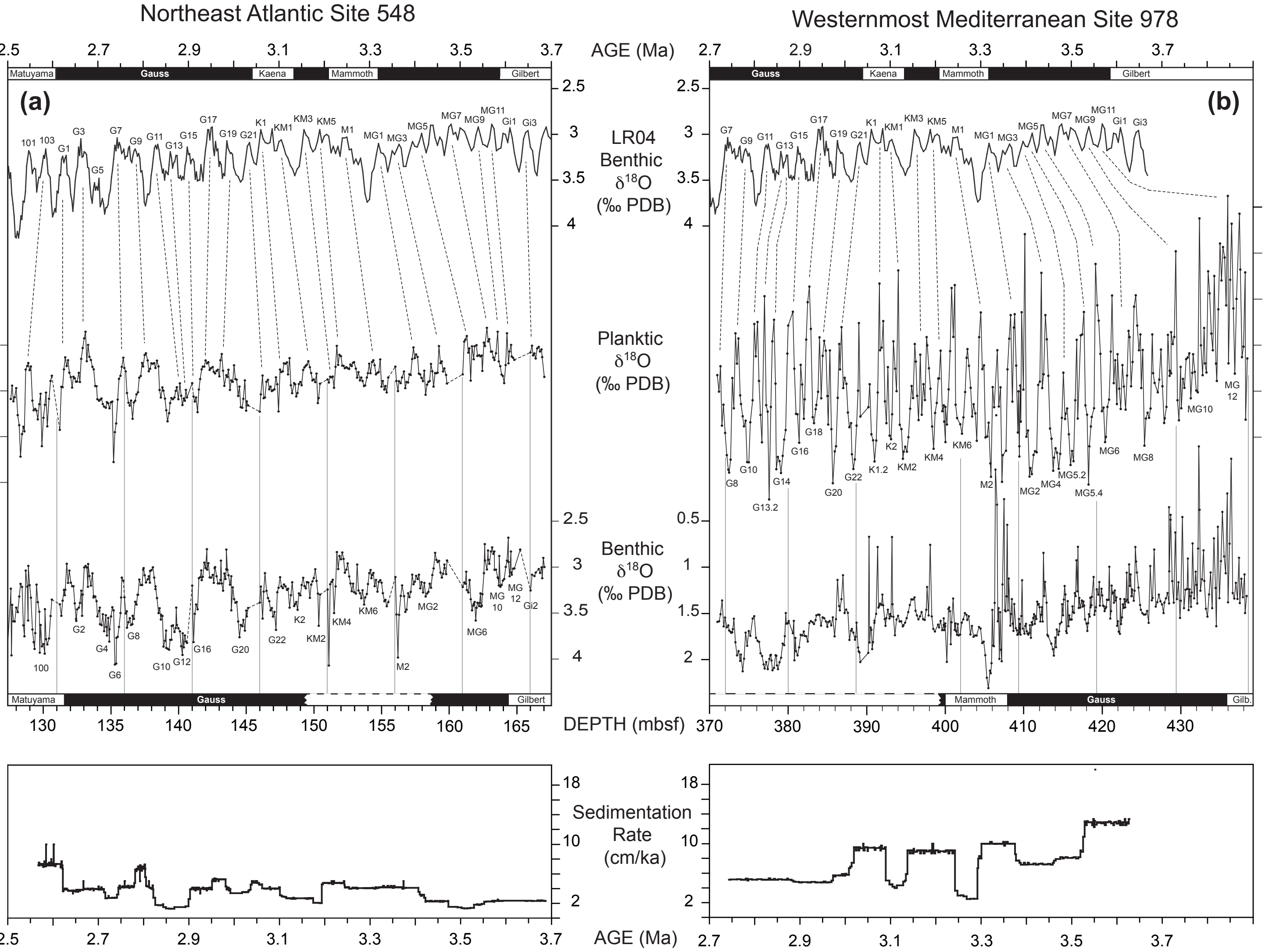
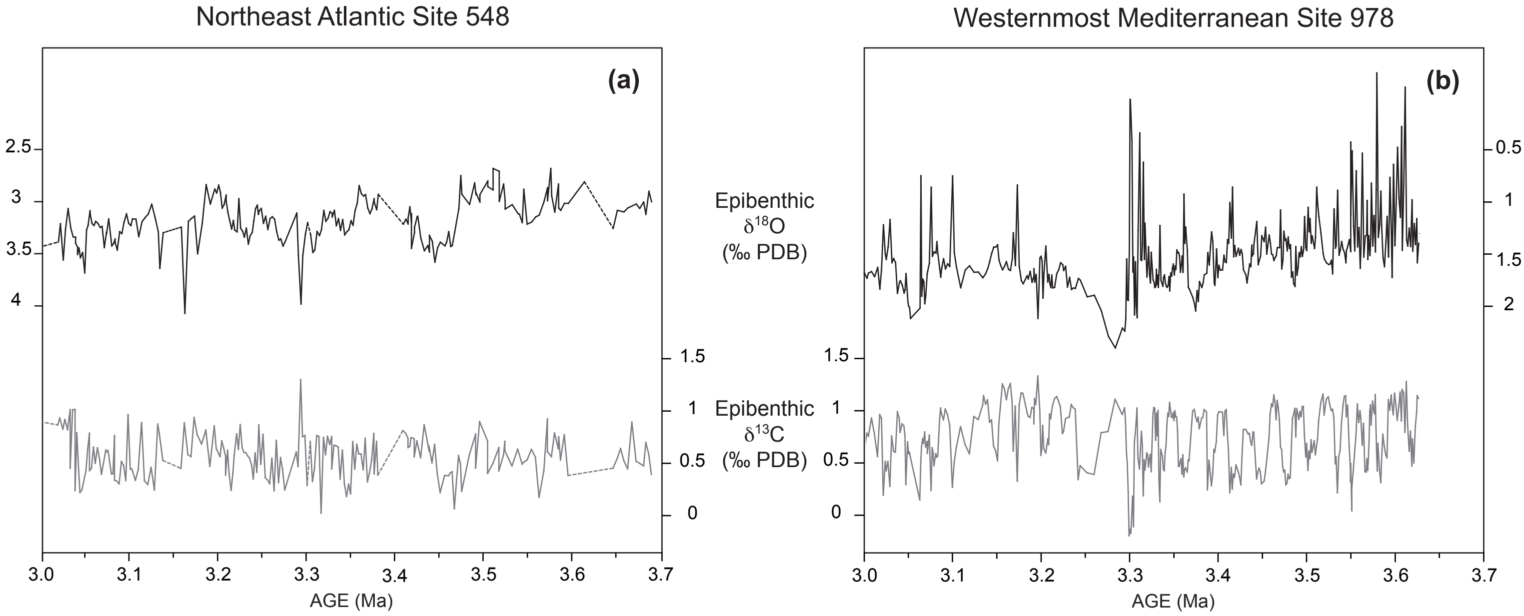

Northeast Atlantic Site 548
Westernmost Mediterranean Site 978
AGE (Ma)
(a)
(b)
Matuyama
Gauss
Kaena
Mammoth
Gilbert
LR04
Benthic
δ18O
(‰ PDB)
Planktic
δ18O
(‰ PDB)
Benthic
δ18O
(‰ PDB)
DEPTH (mbsf)
Sedimentation
Rate
(cm/ka)
AGE (Ma)

Fig. DR1



Northeast Atlantic Site 548
Westernmost Mediterranean Site 978
(a)
(b)
Epibenthic
δ18O
(‰ PDB)
Epibenthic
δ13C
(‰ PDB)
2.5
3
3.5
4
1.5
1
0.5
0
0.5
1
1.5
2
1.5
1
0.5
0
3.0
3.1
3.2
3.3
3.4
3.5
3.6
3.7
AGE (Ma)

Fig. DR2

TABLE DR1. SPECIES USED IN THIS STUDY				
Record	*Core depth (m)*	*Species*	*# Tests*	*Size Fraction (µm)*
		Site 548		
$\delta^{18}O$ Planktic	127.60 – 167.03	*Neogloboquadrina atlantica (s)*	3 – 30	(250-400) µm
$\delta^{18}O$ Benthic †	128.70 – 166.51	*Cibicidoides wuellerstorfi*	1 – 10	> 250 µm
	127.60 – 167.03	*Cibicidoides mundulus*		
	143.89 – 165.25	*Cibicidoides robertsonianus*		
	124.99 – 143.90	*Uvigerina* spp. *	4 – 12	
Mg/Ca Benthic	132.91 – 142.10	*Cibicidoides wuellerstorfi* *	3 – 12	> 250 µm
	128.22 – 167.03	*Cibicidoides mundulus*		
	129.20 – 144.40	*Cibicidoides robertsonianus* *		
		Site 978		
$\delta^{18}O$ Planktic	371.00 – 398.10	*Globigerinoides ruber*	5 – 25	(250-400) µm
	420.30 – 438.38	*Globigerinoides ruber*		
	391.89 – 420.60	*Globigerina bulloides*	3 – 30	
	437.40 – 438.10	*Globigerinoides obliquus*	3 – 15	
$\delta^{18}O$ Benthic †	371.00 – 438.38	*Cibicidoides wuellerstorfi*	3 – 10	> 250 µm
Mg/Ca Benthic	371.98 – 438.38	*Cibicidoides wuellerstorfi*	5 – 15	> 250 µm
	371.79 – 435.30	*Cibicidoides mundulus*	4 – 12	