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Eastern North Atlantic deep-sea corals: tracing upper intermediate water $\Delta^{14}C$ during the Holocene

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Abstract

Paired $^{230}Th/U$ and ^{14}C dating were performed on deep-sea corals (*Lophelia pertusa* and *Madrepora oculata*) from the northeastern North Atlantic at ∼730 m bsl to investigate past changes of the thermohaline circulation. These were estimated using the $\Delta^{14}C$ value of the upper intermediate waters, based on the ^{14}C ages of the top and base of each coral, where possible, and the $^{230}Th/U$ dating. The reliability of these estimates was checked by dating two very young corals of the species *L. pertusa*. One of these corals, collected alive in 1999 AD, gave a $^{230}Th/U$ age of 1995 ± 4 AD after correction for non-radiogenic ^{230}Th. Another coral, the top of which dated to 1969 ± 6 AD, recorded the atmospheric $^{14}C/^{12}C$ increase due to the nuclear tests in the early 1960s. The calculated $\Delta^{14}C$ values from these two corals agree with those measured at GEOSECS Station 23 in 1972–1973 [Östlund et al., Earth Planet. Sci. Lett. 23 (1974) 69–86] and 1991–1992 [Nydal and Gisfelos, Radiocarbon 38 (1996) 389–406]. This, together with the 100% aragonite content and the $\delta^{234}U$ and $^{230}Th/^{232}Th$ values of all the dated corals, indicates that none of the corals behaved as open systems with respect to their U-series nuclides and that they closely represent the water mass properties in which they lived. The pre-anthropogenic $\Delta^{14}C$ value of the North Atlantic intermediate waters was estimated at −69 ± 4‰. The reservoir age varies from ∼400 years to ∼600 years, and this variation is due to atmospheric $^{14}C/^{12}C$ changes. A reservoir age of 610 ± 80 years, close to the pre-anthropogenic value, was determined from one coral dated at 10 430 ± 120 cal yr BP, when the global sea level was approximately at −35 m [Bard et al., Nature 382 (1996) 241–244]. This suggests a modern-like pattern of the oceanic circulation prevailed in the Northeast Atlantic Ocean at this time although the deglaciation was not completely achieved.

Keywords: deep-sea corals; Northeast Atlantic; $^{230}Th/U$ dating; radiocarbon dating; reservoir age

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1. Introduction

Estimating rates of past ocean ventilation is important for paleoceanographic and climate modelling studies, especially considering the increasing evidence of close relationships between climate fluctuations and global oceanic circulation changes. Abrupt climatic changes such as the Dansgaard–Oeschger cycles and the Heinrich events observed in Greenland ice cores [4,5] and in marine and continental sediments [6,7] are thought to result from changes of heat and moisture transport from low to high latitudes via the thermohaline circulation. Paleoventilation rates of the intermediate/deep water masses, expressed as the difference between the marine and terrestrial (atmospheric) ^{14}C ages, were first determined from ^{14}C measurements from paired benthic–planktonic foraminifera after correction of the surface ^{14}C ages for a constant reservoir age [8–10]. However, the $^{14}C/^{12}C$ content of surface waters in the northern North and Southern Atlantic Ocean [11–13], the southwestern Pacific Ocean [14] and the Mediterranean Sea [15] changed in the past. This was related to past fluctuations of the atmospheric $^{14}C/^{12}C$, to variations in the amount of mixing between the surface and underlying ^{14}C-depleted intermediate waters [11,16] and to changes in the ^{14}C age of the intermediate waters [15,17]. The latter depend on the transfer time from the source of intermediate water formation and of the ^{14}C age of this source. Tracing changes in the extent of past oceanic ventilation using marine ^{14}C ages, corrected for a constant sea surface reservoir age, is therefore inadequate. Recently combined mass spectrometric $^{230}Th/U$ and accelerator mass spectrometric ^{14}C dating on deep-sea corals [17–20] have enabled the investigation of deep ocean circulation changes within the framework of an absolute timescale. Atmospheric ^{14}C ages can be estimated from coral $^{230}Th/U$ ages using the radiocarbon calibration INTCAL 98 record [21] enabling the determination of paleoventilation ages from the coral ^{14}C measurements over well-constrained time intervals of the calibration record.

The northern North Atlantic Ocean, where North Atlantic Deep Water forms, is a key area for understanding past deep-water circulation changes [22], and their impact on heat transport over northwestern Europe. Extensive deep-sea coral reefs have been discovered along the Northeast Atlantic continental shelves from Ireland, Scotland and Norway [23–25]. Previous coupled radiocarbon and $^{230}Th/U$ dates have been successfully applied to several species of deep-water corals in the Atlantic, providing accurate determinations of past oceanic circulation changes [17,20].

In this paper, we present radiocarbon and $^{230}Th/U$ dating on deep-sea corals sampled at ~730 m bsl from the Rockall and Porcupine Banks, off the Irish shelf. The $^{14}C/^{12}C$ content of the seawater at the time of coral growth was estimated, together with the reservoir age of the upper intermediate water. They are compared to the modern values of the intermediate waters in the North Atlantic Ocean.

2. Samples and methods

2.1. Samples and hydrographical setting

The deep-sea corals were sampled in three box cores collected off the western continental margin of Ireland in the northern North Atlantic [26,27] (Fig. 1, Table 1), where numerous carbonate mounds were identified [24]. Around the Rockall Trough, a series of carbonate mounds up to 250 m high were discovered in water depths of 500 m to about 1000 m on the slopes of the Porcupine Bank and along the Rockall Bank. Box cores ENAM 9915 and ENAM 9910 were taken from 725 m bsl on the Southwest Rockall Bank (55°32′N, 15°40′W), and ENAM 9828 from 745 m bsl on the Porcupine Bank (53°48′N, 13°54′W). Samples of *Lophelia pertusa* were collected from down-core ENAM 9915 and from the surface of core ENAM 9910. Sample LOP.1 located at the surface of core ENAM 9915 included living coral polyps at the time of collection in 1999. Two samples of *Madrepora oculata* were taken from the surface of the two box cores ENAM 9910 and ENAM 9928. All coral samples selected were well-preserved and free of visible manganese and iron oxide/hydroxides coatings. Corals polyps

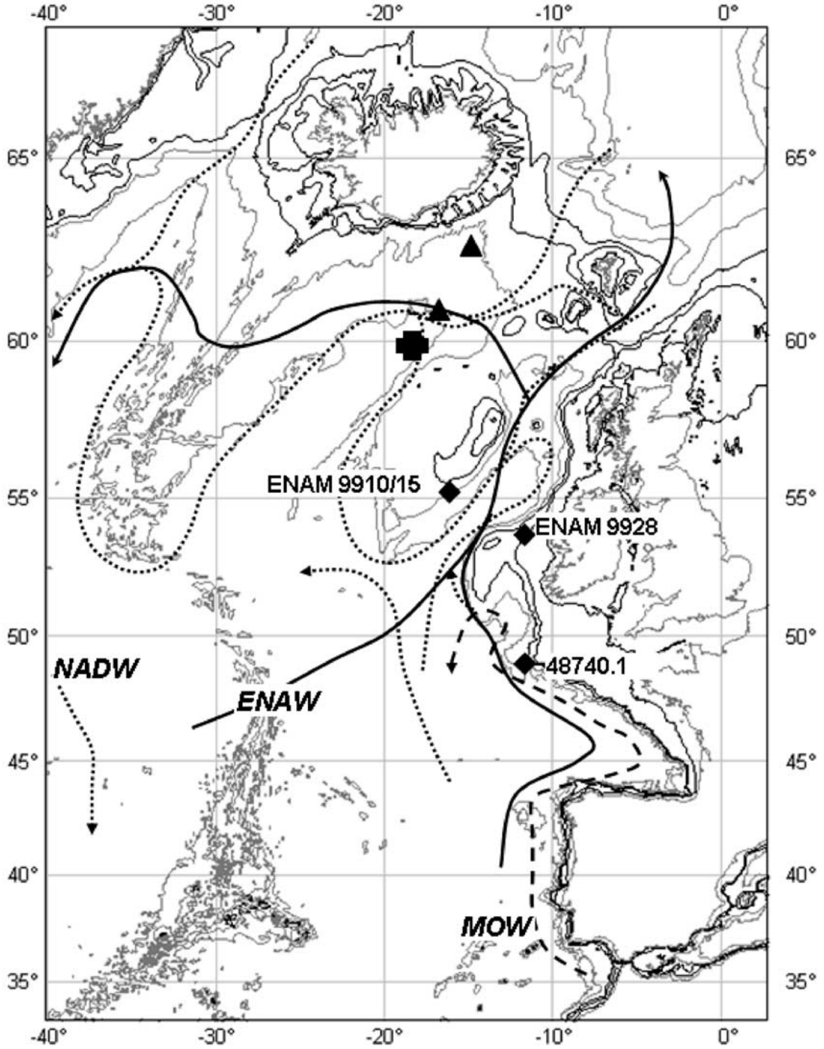

Fig. 1. Location of the box cores, GEOSECS station 23 (black cross: 60.41°N and 18.62°W), AMS.Arizona MO16 and JH9 (black triangles: *MO16* 62°35′N and 15°31′W; *JH9* 61°31′N and 16°20′W) and topography (thick black line = 750 m bsl). Surface as well as deep water currents in the eastern North Atlantic are redrawn from Dickson and Brown [22] and New and Smythe-Wright [30]. Deep-sea corals are shown as black squares. Coral 48740.1 was sampled on the southern slope of the Porcupine Bank [19].

were cut along their growth axis to obtain aliquots for mass spectrometric ^{230}Th/U and AMS ^{14}C dating.

The water depths of the deep-sea corals correspond to the transition between the North Atlantic near-surface and upper intermediate waters. Today, the well-mixed North Atlantic surface and sub-surface waters in the Rockall Trough (0 to 500–700 m) result from the mixing of a freshwater component of a northwestern origin with the saline eastern water of a southern origin ([28,29]) (see also [30] for a review). Below the near-surface layer between 1000 and 1200 m, a high salinity core is thought to originate either from the Mediterranean Outflow Water and/or from subsidence of saline sub-surface waters north of the Rockall Trough (Fig. 2). The deeper water masses are formed by the Labrador Sea

Table 1
U concentrations, isotopic ratios and ages for *Lophelia pertusa* (LOP) and *Madrepora oculata* (MAD) deep-sea corals

(1)	(2)	(3)	(4)	XRD (% A)	^{238}U (μg g^{-1})	^{232}Th (pg g^{-1})	$\delta^{234}U_0$ (‰)	[$^{230}Th/^{232}Th$]	$^{230}Th/U$ age[a] (yr)	$^{230}Th/U$ age[b] (cal yr BP)	Labcode: GifA	pMC	^{14}C age (yr BP)
9915	0	LOP.1[c]	top	> 99	3.4	162	146.7 ± 4.0	13.3 ± 0.2	20.5 ± 1.0	−45 ± 6	100102	103.20 ± 1.30	
		LOP.1	base								100101	103.30 ± 0.60	
	30	LOP.2	top	> 99	3.1	224	146.0 ± 3.4	23.1 ± 0.3	54.0 ± 1.2	−19 ± 12	100104	100.32 ± 0.80	
		LOP.2	base								100103		520 ± 100
	50	LOP.3	top								100106		1 200 ± 100
		LOP.3	base	> 99	3.8	454	146.2 ± 3.0	202.3 ± 1.0	785 ± 11	696 ± 22	100105		1 240 ± 90
9910	0	LOP.10	top								100099		1 140 ± 200
		MAD.10	top	> 99	4.2	491	145.3 ± 3.3	179.0 ± 1.0	681 ± 12	593 ± 22	100100		1 000 ± 100
9828	0	MAD.28	top	> 99	3.9	331	146.7 ± 3.5	3657 ± 20	10 510 ± 120	10 430 ± 140	100098		9 870 ± 140
		MAD.28	base								100097		9 860 ± 140

(1) Core name ENAM#. (2) Depth in core in cm. (3) Sample identification. (4) Sub-sampling of coral polyp. $\delta^{234}U = ([\{^{234}U/^{238}U_{measured}\}/\{^{234}U/^{238}U_{equilibrium}\} - 1] \times 1000)$ with $^{234}U/^{238}U_{equilibrium} = 54.89 \pm 0.1 \times 10^{-6}$ [32] and is given here as initial $\delta^{234}U_0$ using ISOPLOT [58]. $\Delta\delta^{234}U$ values reflect the 2σ uncertainties of counting statistics. [$^{230}Th/^{232}Th$] values represent activity ratios calculated from measured isotopic ratios. Δ[$^{230}Th/^{232}Th$] is given as 2σ uncertainties of counting statistics. Half-lives were taken from Cheng et al. [32]. Corrected ages are referenced to 1950 AD. Note: 2σ errors are given for $^{230}Th/U$ ages and ^{14}C ages. $^{14}C/C$ analyses have been carried out at the Gif-sur-Yvette AMS facility and are given as conventional ^{14}C ages [46].

[a] $^{230}Th/U$ ages are calculated from measured activity ratios of [$^{230}Th/^{238}U$] and [$^{234}U/^{238}U$] using ISOPLOT [58].

[b] $^{230}Th/U$ ages are corrected for contamination with excess ^{230}Th from seawater by assuming a marine [$^{230}Th/^{232}Th$] of 10 ± 4 based on measurements of nearby seawater [39,40].

[c] Living coral specimen.

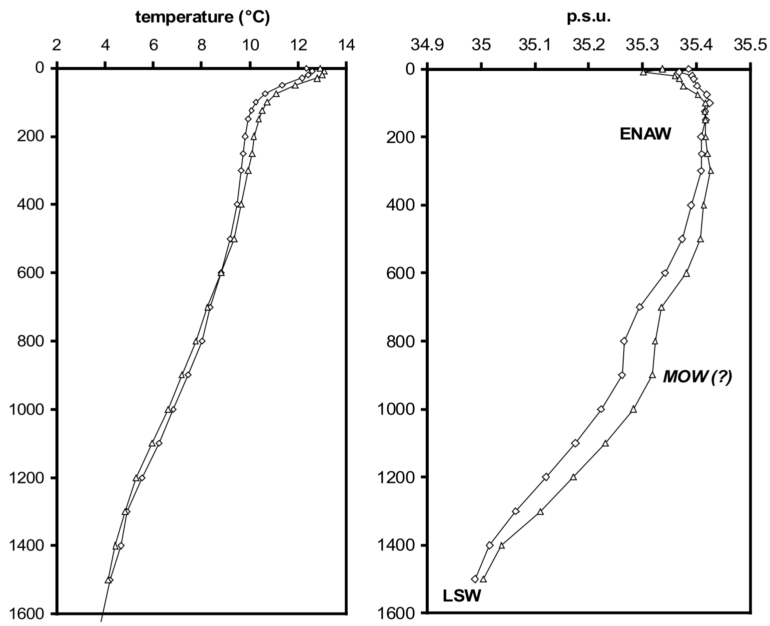

Fig. 2. Annual average temperature and salinity near Rockall Bank (squares) and Porcupine Bank (triangles) taken from Levitus94 oceanographic atlas [59,60].

Water at about 1600 to 1900 m and the Northeast Deep Atlantic Water (NEADW) originating in the Norwegian Sea at depths of 2300 to 2500 m. Below NEADW, the water masses are formed by the Antarctic Bottom Water.

2.2. ^{230}Th/U dating

The outermost surface of the corals was carefully ground off to avoid remains of organic tissue and surface contaminants. This mechanical cleaning was followed by a weak acid leach, ultrasound treatment, and several rinses with quartz distilled water and AR grade acetone. All samples were analyzed by X-ray diffraction (XRD) to check for purity of aragonite (Table 1). The samples were dissolved with double distilled HNO_3 in Teflon vials containing a triple spike of ^{229}Th, ^{233}U and ^{236}U. U and Th were extracted and purified from coral samples using standard ion exchange chemistry as described by Stirling et al. [31]. U and Th were then loaded onto single degassed Re filaments between a sandwich of graphite. U and Th isotope analyses were performed on a thermal ionization mass spectrometer (Finnigan MAT 262) using a peak jumping routine with a secondary electron multiplier. Repeated analyses of HU-1 reference material containing ^{238}U, ^{234}U, and ^{230}Th in radioactive equilibrium yielded an average [^{234}U/^{238}U] activity ratio of 1.0015 ± 0.0032 ($n = 9$) (= ^{234}U/^{238}U atomic ratio of $54.98 \pm 0.18 \times 10^{-6}$) and a [^{230}Th/^{238}U] activity ratio of 1.0004 ± 0.0044 ($n = 9$). These activity ratios were calculated from measured atomic ratios using the decay constants for ^{238}U, ^{234}U, and ^{230}Th of $\lambda_{238} = 1.5515 \times 10^{-10}$ yr^{-1}, $\lambda_{234} = 2.8263 \times 10^{-6}$ yr^{-1}, and $\lambda_{230} = 9.1577 \times 10^{-6}$ yr^{-1} [32], respectively. They are within external reproducibility of those reported by Cheng et al. [32] for HU-1. Full procedural blanks for U and Th determinations are 81 ± 67 pg (^{238}U, $n = 5$) and 74 ± 45 pg (^{232}Th, $n = 2$).

2.3. Radiocarbon dating

The surfaces of coral samples, ~20 mg in size, were mechanically cleaned by sand blasting resulting in about a 20–60% weight loss. Sub-samples of coral ~10 mg in size were rinsed in an ultrasonic bath and then crushed to a fine powder in

Table 2
Seawater $\Delta^{14}C$ values and reservoir age estimates for the deep-sea corals

Sample identification	Coral sampling	^{230}Th/U age (cal yr BP ± 1σ)	^{230}Th/U age (cal yr AD)	Intermediate $\Delta^{14}C$ (‰) (±1σ)	Atmospheric $\Delta^{14}C$ (‰) (±1σ)	R_{interm} age (years ± 1σ)
Post-bomb deep-sea corals:						
LOP.1	top	−44.9 ± 3.1	1995	27 ± 6	111 ± 5	
LOP.2	top	−19.4 ± 5.7	1969	0 ± 9	545 ± 5	
Holocene pre-bomb deep-sea corals						
48740		139 ± 9	1811	−70 ± 6	3 ± 5	620 ± 60
MAD.10	top	593 ± 9	1357	−51 ± 6	−4.6 ± 3	390 ± 60
LOP.3	base	696 ± 9	1254	−68 ± 5	−14.7 ± 0.9	450 ± 50
MAD.28	top	10 430 ± 70		35 ± 12	117 ± 4	610 ± 80

The $\Delta^{14}C_{sw}$ values at 1σ were calculated following the equation $\Delta^{14}C = (e^{(-\lambda_L t_{BP})})/e^{(-\lambda_t t_0)} - 1$ with $\lambda_L = 1.2449 \times 10^{-4}$ yr^{-1} the Libby decay constant, $o_t = 1.2097 \cdot 10^{\times 4}$ yr^{-1} the true decay constant, t_{BP} the ^{14}C-age, and t_0 the true age (^{230}Th/U age). $\Delta^{14}C_{atmos}$ at t_0 is obtained from the atmospheric radiocarbon calibration record [21]. The R_{interm} age at 1σ is derived from the $\Delta^{14}C_{sw}$ and $\Delta^{14}C_{atmos}$ values. The ^{230}Th/U dating and ^{14}C ages (620 ± 60 yr BP) of sample 48740 are published in [19]. The χ^2 value of 4.50, obtained from the $\Delta^{14}C_{sw}$ of the two pre-anthropogenic deep-sea corals MAD.10 and LOP.3, is larger than the $P_{0.95}$ value (3.841).

an agate mortar. The fine powder was then further cleaned by rinsing with a 0.01 N solution of HNO_3 and transferred into a vacuum reaction vessel. Transformation of the powdered samples into CO_2 and preparation of graphite targets follow previously described procedures [33]. AMS ^{14}C dating was performed at the Gif-sur-Yvette Tandetron. Blanks were obtained on a *Lophelia* coral dated > 100 000 years by the ^{230}Th/U method, and yielded a mean ^{14}C activity of 0.20 ± 0.05 pMC (apparent ^{14}C age ~50 000 yr). ^{14}C analyses were performed on the top and base of individual coral specimens, except for the two corals in core ENAM 9910 (Table 1).

3. Results

3.1. ^{230}Th/U analyses and ages

3.1.1. ^{230}Th/U analyses

The selected corals were all 100% aragonite. Furthermore no coral analyzed contained discernible traces of aragonite needles or micrite cement, suggesting that little or no post-depositional alteration or recrystallization processes had taken place (Table 1). The U concentrations ranged between 3.1 and 4.2μg g^{-1}, and were similar to those measured in modern and fossil surface and deep-sea corals [18,34–36]. The very small ^{232}Th concentrations in all the corals suggest a low content of detrital contaminant. The initial δ^{234}U values were very reproducible and gave an average of 146.2 ± 0.6‰ (1 S.D., $n = 5$). This value is close to the δ^{234}U measured for modern surface and deep-sea reef corals of 146.6 ± 1.4‰ (1 S.D., $n = 10$) [37] and at 145.3 ± 1.1‰ (1 S.D., $n = 20$) [34], respectively. The initial δ^{234}U values of the ENAM corals were also very similar to recent measurements of the δ^{234}U of present-day seawater of 149.6 ± 3.2‰ (1 S.D., $n = 23$) [37] and 146.6 ± 0.6‰ (1 S.D., $n = 14$) [38]. As a first approach, no detectable departure from closed-system U-series behavior was observed from all the analyses of the aragonite of the selected deep-sea corals (Table 1), and the ^{230}Th/U ages can be considered valid for all but the youngest corals.

The measured ^{232}Th concentrations and hence associated non-radiogenic ^{230}Th are very small at < 2 ng g^{-1} and < 20 fg g^{-1}, respectively. This non-radiogenic ^{230}Th component may affect the ^{230}Th/U age of samples younger than 1000 yr with radiogenic ^{230}Th concentrations of less than ~50 fg g^{-1}. In the northeastern North Atlantic, the measured ^{230}Th/^{232}Th activity ratios for intermediate waters at 500 and 1000 m are 6 and 14 [39,40], respectively. These values are close to the [^{230}Th/^{232}Th] determined for the modern coral LOP.1 of 13.3 ± 0.2, indicating this specimen had almost no ^{230}Th derived from in situ U decay.

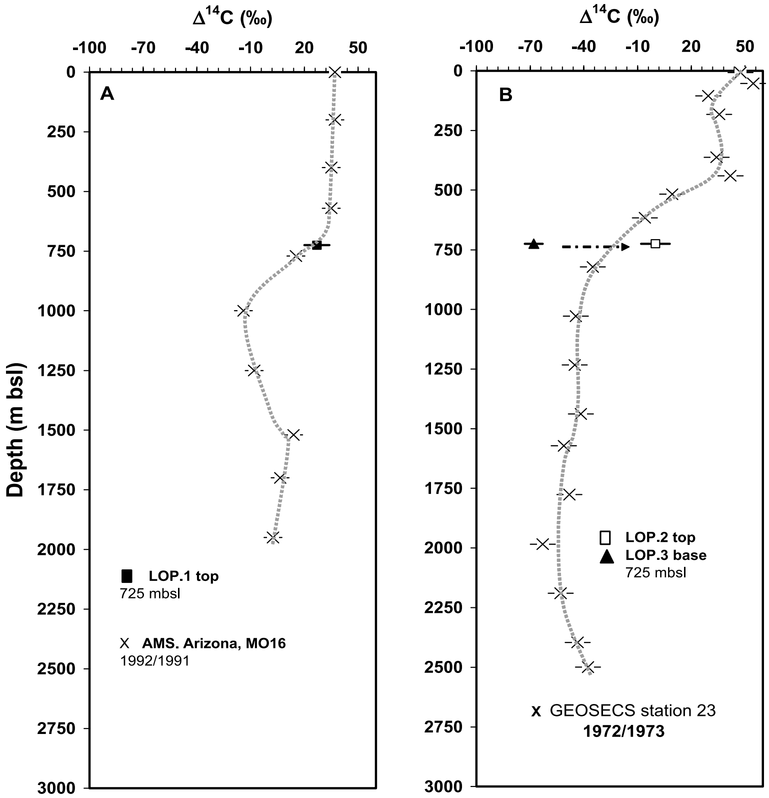

Fig. 3. Comparison of $\Delta^{14}C$ of modern deep-sea corals with seawater measurements in the Iceland basin. (a) A recently living coral is compared to seawater data obtained in 1992. (b) A coral that grew around 1969 is compared to GEOSECS seawater analyses obtained in 1972/73. Dotted lines represent the average depth distribution of $\Delta^{14}C$ from which $\Delta^{14}C$ at 725 m bsl was estimated.

Accordingly, we corrected the $^{230}Th/U$ ages of all the analyzed corals for this non-radiogenic ^{230}Th component in order to derive accurate ages. To do this we used the average of the measured $^{230}Th/^{232}Th$ activity ratios determined for North Atlantic intermediate waters of 10 ± 4 and took into account the uncertainty for the age calculation (Table 1). This resulted in about a 25 yr shift in the estimated ages of the young corals LOP.1, 2, 3 and MAD.10. The effect on the age estimate of the older coral MAD.28, however, is negligible (Table 1). This correction assumes that seawater is the only source of excess ^{230}Th to old corals. However, this age correction calculation would not be valid if excess ^{230}Th, without addition of ^{232}Th, is added to corals by α-recoil processes, as was recently shown for surface water corals by Thompson et al. [41] and Villemant and Feuillet [42]. The likely effect that such processes had on our age determinations was tested for the oldest dated coral MAD.28.

The box model presented by Thompson et al. [41] described the redistribution of ^{234}U, ^{234}Th and ^{230}Th by pore fluids and within aragonite crystals due to α-recoil processes. This model is not readily applicable here, as excess ^{230}Th of deep-water corals has a significant seawater component which would result in a significant overestimation of the Th fractionation. The approach developed by Villemant and Feuillet [42] modelled the re-distribution of U-series nuclides based purely on a solution of the decay equations taking into account α-recoil processes and excess Th. This approach, therefore, does not overestimate the Th fractionation due to a seawater excess Th component. According to the model of Villemant

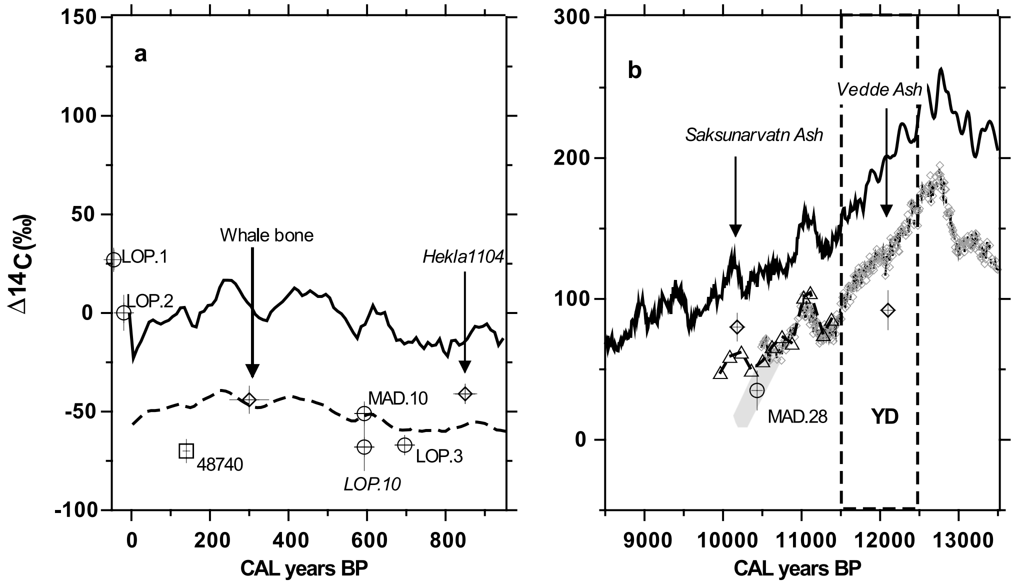

Fig. 4. (a,b) Comparison of deep-sea coral $\Delta^{14}C$ with the atmospheric and marine $\Delta^{14}C$ calibration INTCAL 98 [21], volcanic tephra layers Hekla1104 [13], Saksunarvatn Ash [55,56] and Vedde Ash [11], and the Cariaco Basin ^{14}C record [52,53]. Panel a also contains a ^{14}C measurement on a whale bone by Olsson [50]. The gray area underneath MAD.28 marks the potential change of $^{230}Th/U$ ages and thus $\Delta^{14}C_{sw}$ according to potential open system U-series behavior of old deep-water corals (see Section 3.1.1)

and Feuillet [42] such α-recoil effects may shift the $^{230}Th/U$ age estimate of coral MAD.28 by up to 400 years if seawater $\delta^{234}U$ values ranging from 146‰ (−200 yr) to 148‰ (+200 yr) are used in the calculations. Given that deep-water corals have a more robust skeleton compared to surface water species and the fact that they are not subject to the same continental weathering and recrystallization processes as surface water corals the estimated potential age shift of ±200 yr can probably be regarded as an upper limit. Further research is necessary to prove the applicability of these models for deep-sea corals to verify open system U-series behavior. Given that the influence of α-recoil processes on $^{230}Th/U$ age estimates of deep sea corals cannot be ruled out at this stage, we will take them into consideration for deep-sea coral MAD.28 in the following discussion.

3.1.2. $^{230}Th/U$ ages

The five selected deep-sea corals yield $^{230}Th/U$ ages ranging from modern to ~10 430 cal yr BP (Table 1). In core ENAM 9915, ages increase with core depth from 1995 AD to 696 ± 22 cal yr BP, indicating a very high, but irregular sedimentation rate.

The corals sampled at the surface of the box cores have very different ages. LOP.1, collected alive at the surface of core ENAM 9915, has an age of −45 ± 12 cal yr BP (2σ), agreeing well with the date of collection (1999 AD). In cores ENAM 9910 and ENAM 9828, the ages of corals at the surface of 593 ± 22 cal yr BP and 10 430 ± 140 cal yr BP, respectively, are substantially older. The absence of modern corals and sediments in these two box cores cannot be explained by a change in temperature, salinity, and nutrients of the upper intermediate waters, as living deep-sea corals were found in close proximity. This could be due to the seafloor substrate properties, as *Lophelia* colonies need a hard ‘rocky’ substrate to develop [43]. Alternatively the lack of modern corals, together with the observed irregular sedimentation rate, may also be the product of erosion due to strong currents, slope failure and/or gas hydrate-related uplift [25].

3.2. Radiocarbon dating

The two deep-sea corals LOP.1 and LOP.2 have ^{14}C activities greater than 100 pMC indicating that they grew after the nuclear tests in the early 1960s [44]. Such a young age for these corals is also indicated by their $^{230}Th/U$ ages (Table 1). Coral LOP.2 started to grow before bomb ^{14}C penetration into the North Atlantic upper intermediate waters as a ^{14}C age of 520 ± 100 years BP was obtained at the base of this 20 mm long coral, which is compatible with the high growth rate of 4.1–7 mm yr^{-1} for *L. pertusa* [45]. The two corals LOP.3 and MAD.28 have indistinguishable ^{14}C ages from the base to the top. The two coral species collected from the surface of core ENAM 9910 (*L. pertusa* and *M. oculata)* have similar ^{14}C ages at the 95% confidence interval.

4. Discussion

In the past, the marine ^{14}C ages varied as a function of changes of the atmospheric $^{14}C/^{12}C$, of CO_2 exchange between the atmosphere and ocean and of ^{14}C decay within the oceanic reservoir. To express these changes with respect to a standard reference [46], the seawater $\Delta^{14}C$ values ($\Delta^{14}C_{sw}$ in ‰) were calculated using the $^{230}Th/U$ ages (cal yr BP). From these, atmospheric $\Delta^{14}C$ values were derived from the INTCAL 98 calibration record [21], and then the intermediate water reservoir ages (R_{interm}) were determined as the difference between the marine and atmospheric ^{14}C ages at a similar absolute age (Table 2).

4.1. The post-1950 AD corals

The $\Delta^{14}C_{sw}$ values measured at the nearby GEOSECS Station 23 (1972) [1], revisited in 1991 and 1992 (MO16 and JH9) [2], permit a good chronological comparison with the determined $\Delta^{14}C_{sw}$ values calculated from the two dated post-bomb corals (Fig. 1, Table 2). The estimated $\Delta^{14}C_{sw}$ of +27 ± 6‰ for the living coral LOP.1 (1995 AD) compares well with the measured $\Delta^{14}C_{sw}$ of ∼+20‰ at ∼730 m in 1991–1992 [2]. For coral LOP.2 dated at ∼1969 AD, the estimated $\Delta^{14}C_{sw}$ of 0 ± 9‰ is not within error of the $\Delta^{14}C_{sw}$ measured in 1972 of about −20‰ [1]. The 1972–1973 GEOSECS value at 730 m is obtained from a linear fit between two $\Delta^{14}C_{sw}$ values at water depths characterized by a large change from ∼20‰ to ∼−45‰ (Fig. 3). This linear fit cannot be representative of the $\Delta^{14}C_{sw}$ profile in the water column, and this may account for the slight difference between the measured and estimated $\Delta^{14}C_{sw}$ values. A redeposition of dead deep-water corals from upper depths of the coral reefs (Fig. 3) remains a distinct possibility. As previously observed [19,47], we therefore considered the $\Delta^{14}C_{sw}$ values derived from deep-sea corals at the ENAM sites to be mainly representative of the $\Delta^{14}C_{sw}$ of dissolved inorganic carbon notwithstanding the potential influences of re-deposition of dead corals.

4.2. The pre-anthropogenic and Holocene deep-sea corals

Two $\Delta^{14}C_{sw}$ values of −68 ± 5‰ and −51 ± 6‰, which differ at the 95% confidence level, were determined for the deep-sea corals dated at 696 ± 22 cal yr BP (LOP.3) and 593 ± 22 cal yr BP (MAD.10), respectively (Table 2). Rapid fluctuations of surface and deep $\Delta^{14}C_{sw}$ values have occurred in the past due to atmospheric and oceanic circulation changes [11,15, 17,48,49]. The change in $\Delta^{14}C_{sw}$ of 17‰ observed between 696 and 593 cal yr BP could be related to the contemporaneous atmospheric $\Delta^{14}C$ increase of ∼15‰ (Fig. 4) [21]. However, the intermediate $\Delta^{14}C_{sw}$ of −51‰ at 593 cal yr BP is close to the pre-anthropogenic sea surface $\Delta^{14}C_{sw}$ value in the North Atlantic Ocean [16,49]. It is equivalent to that of −45 ± 8‰ estimated from the ^{14}C dating of one marine tephra from the Hekla volcano dated at 1104 AD (∼850 cal yr BP) [13] (Fig. 4). A similar value of −44 ± 7‰ was also determined from a North Atlantic whale bone dated at 1657 AD (∼300 cal yr BP) [50] (Fig. 4). The sea surface $\Delta^{14}C$ values would thus have a similar value at 850 cal yr BP and 290 cal yr BP while the atmospheric $\Delta^{14}C$ changed by 15‰. Therefore, a redeposition of MAD.10 from upper depths appears to be a more likely explanation. Additionally, one deep-sea coral dated at 139 ± 9 cal yr BP (1810 AD) and collected from a water depth of ∼1450 m south of the Porcupine Bank [19] also gave a $\Delta^{14}C_{sw}$ value of −70 ± 6‰, in agreement with that determined at 696 cal yr BP and with previous estimates [47]. Thus, the modern pre-anthropogenic intermediate $\Delta^{14}C_{sw}$ value in the North Atlantic Ocean would appear to be homogeneous at −69 ± 4‰ at water depths of 730 and 1450 m. Due to the rapid changes of the atmospheric $\Delta^{14}C$ (Fig. 4), related to fluctuations of solar activity [51], the modern pre-anthropogenic R_{interm} value may vary from 450 ± 50 yr to ∼620 ± 60 yr (Table 2).

Considering the true age for the deep-sea coral MAD.28 to be 10 430 cal yr BP, this would result in estimates for $\Delta^{14}C_{sw}$ and R_{interm} values at 730 m of +35 ± 12‰ and 610 ± 80 years, respectively (Table 2). This R_{interm} value is close to that measured for year 1810 AD (Table 2). Assuming a constant sea surface $\Delta^{14}C_{sw}$ of ∼−45 ± 8‰ between 850 cal yr BP (1104 AD) and 696 cal yr BP (1254 AD), then the pre-anthropogenic $\Delta^{14}C_{sw}$ difference between the intermediate and surface waters would be ∼25 ± 10‰ (Table 2, Fig. 4). A similar value can be derived from the $\Delta^{14}C_{sw}$ value determined from the deep-sea coral 48470 [19] and the sea surface $\Delta^{14}C_{sw}$ of ∼−50‰ at ∼1810 AD [16,49]. Consequently, the sea surface $\Delta^{14}C_{sw}$ value in the Rockall and Porcupine region at ∼55°N would be estimated at 60 ± 16‰ at 10 430 cal yr BP, in close agreement with the $\Delta^{14}C_{sw}$ determination of about 55 ± 10‰ from the Cariaco record at an equivalent age [52,53]. According to this, no sea surface ^{14}C gradient existed from the low to high latitudes in the North Atlantic Ocean at ∼10 430 cal yr BP similar to the present-day hydrology.

Assuming then the actual age of MAD.28 to be closer to 10 630 cal yr BP, the upper limit after correction for redistribution of U-series nuclides by α-recoil processes (as discussed in Section 4.1), this will yield very similar estimates for the $\Delta^{14}C_{sw}$ value and the R_{interm} age of +60 ± 13‰ and 480 ± 70 years. In contrast to this however, the lower limit of the $^{230}Th/U$ age of MAD.28 corrected for α-recoil effects of 10 230 cal yr BP would substantially change the calculated values for the $\Delta^{14}C_{sw}$ and the R_{interm} age to 10 ± 13‰ and 770 ± 80 years. According to this using the pre-anthropogenic $\Delta^{14}C_{sw}$ difference between the surface and intermediate waters, the sea surface $\Delta^{14}C_{sw}$ would be ∼35 ± 16‰, which is slightly lower than the value determined at low latitudes [52,53]. This would indicate the establishment of a sea surface ^{14}C gradient from the mid to high latitudes of the North Atlantic Ocean due to changes of the oceanic circulation pattern as observed during the Younger Dryas event [11,15].

The validity of using the uncorrected $^{230}Th/U$ age for MAD.28 in these calculations of $\Delta^{14}C_{sw}$ value and the R_{interm} can be investigated using the dating of the Saksunarvatn tephra layer. This tephra was observed over large areas in northern European lake deposits [54,55], in North Atlantic deep-sea cores [56] and in the GRIP ice record at 10 180 ± 60 cal yr BP [57]. The absolute age of this tephra together with its marine and terrestrial ^{14}C ages of 9250 ± 70 years [56] and ∼9000 ± 100 years [54,55], respectively, enable the calculation of the sea surface $\Delta^{14}C_{sw}$ of 80 ± 12‰ and reservoir age of ∼300 years at high latitudes in the North Atlantic. These values are in agreement with those determined when using $^{230}Th/U$ ages of MAD.28 of 10 430 cal yr BP and 10 630 cal yr BP, but differ from those determined with a younger age at 10 230 cal yr BP. This implies therefore that no large systematic departure from a closed system behavior towards a younger $^{230}Th/U$ age has taken place in coral MAD.28.

5. Conclusion

Coupled $^{230}Th/U$ and ^{14}C measurements were applied to the deep-sea corals *L. pertusa* and *M. oculata* from the upper intermediate water in the northeast Atlantic Ocean. They provide new data points for pre-anthropogenic $\Delta^{14}C$ and R_{interm} values and the beginning of the Holocene and contribute to a better knowledge of past changes of the North Atlantic oceanic circulation.

The selected deep-sea corals at ∼730 m adequately recorded past changes of the $^{14}C/^{12}C$ content of the North Atlantic upper intermediate waters. None of these deep-sea corals exhibited open system behavior with respect to their U and Th isotopes as they all present initial $\delta^{234}U$ values close to that of modern seawater. Moreover, it was possible to apply a reliable correction for 'excess' non-radiogenic ^{230}Th based on the measured $^{230}Th/^{232}Th$ providing very accurate $^{230}Th/U$ dating for modern samples. After applying this correction the age of one living coral matched closely the date of collection. For another deep-sea coral, the top of which yielded a corrected $^{230}Th/U$ age of ~1969 AD, a clear record of atmospheric $^{14}C/^{12}C$ change due to ^{14}C injection during the atmospheric nuclear tests was observed. Finally, a coral dated at 10 430 cal yr BP provided evidence for the establishment of a modern-like hydrological pattern and ocean–atmosphere and surface to intermediate $^{14}CO_2$ exchanges in the North Atlantic despite the fact that the deglaciation is not completely achieved at this time.

These first accurate and reliable results on the Northeast Atlantic deep-sea coral mounds allow greater insights into the relationship between oceanic circulation changes and climatic fluctuations.

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