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PAIRED ^{14}C AND $^{230}Th/U$ DATING OF SURFACE CORALS FROM THE MARQUESAS AND VANUATU (SUB-EQUATORIAL PACIFIC) IN THE 3000 TO 15,000 CAL YR INTERVAL

Martine Paterne[1,2] • Linda K Ayliffe[1,3] • Maurice Arnold[1,4] • Guy Cabioch[5] • Nadine Tisnérat-Laborde[1] • Christine Hatté[1] • Eric Douville[1] • Edouard Bard[6]

ABSTRACT. Paired radiocarbon and $^{230}Th/U$ dating was performed on 13 surface corals from submerged reefs in the Marquesas and from raised terraces in Vanuatu. The absolute ages of the corals analyzed ranged from 3000 to 15,000 cal yr. Estimates of the difference between the absolute and ^{14}C ages of these corals are in agreement with previous determinations up until 11,500 cal yr. The resulting mean sea surface reservoir age *R* is determined at 390 ± 60 yr for the Marquesas region (9°S), which is slightly higher than the *R* value at 280 ± 50 yr for the Tahiti Islands (18°S). Multiple ^{14}C analyses of 2 corals from the Marquesas present scattered ^{14}C ages at ~12,000 and ~15,100 cal yr. This could be attributed to rapid changes of the ^{14}C content of surface waters around the Marquesas Islands or to a subtle submarine diagenesis.

INTRODUCTION

Radiocarbon and/or $^{230}Th/U$ dating of surface corals have mainly been used to quantify the timing and amplitude of sea-level fluctuations, and also to estimate the deviation between the ^{14}C and calendar ($^{230}Th/U$) ages. Superimposed on the long-term ^{14}C variation over the past 40,000 cal BP (Stuiver et al. 1998; Edwards et al. 1993; Bard et al. 1990a, 1993, 1998; Voelker et al. 1993; Burr et al. 1998; Hughen et al. 1998, 2000; Kitagawa and van der Plicht 1998, 2000; Beck et al. 2000), short-term fluctuations have been recorded in both terrestrial and marine materials and are considered to be linked to changes of solar activity and of the global carbon cycle (Stuiver et al. 1998). In the marine environment, the modern oceanic circulation controls mixing of "old" waters from the deep ocean with surface ocean waters. This leads to latitudinal variations of the sea surface reservoir ages, *R* (Bard 1988). As the oceanic circulation has changed in the past, so have the *R* values at mid- to high latitudes (Bard et al. 1994; Sikes et al. 2000; Siani et al. 2001). Modern surface corals record seasonal to centennial ^{14}C changes of some 20–40‰, related to both the atmospheric ^{14}C and oceanic circulation changes (Druffel 1997; Burr et al. 1998; Guilderson and Schrag 1998). Substantial local intra-ocean variations in *R* were also recently suggested at similar latitudes for the Pacific Ocean (in Stuiver et al. 1998; Goslar et al. 2002).

We present here the results of coupled ^{14}C and $^{230}Th/U$ dating of surface corals, collected from raised terraces from Vanuatu (Cabioch and Ayliffe 2000) and from submerged reefs around the Marquesas Islands (Figure 1). The absolute ages obtained for these corals by $^{230}Th/U$ dating ranged from 3000 to ~15,000 cal yr. The difference between the absolute and ^{14}C ages of these corals are compared to those found in previous studies (Figure 2) (Stuiver et al. 1998; Bard et al. 1990a, 1993, 1998; Edwards et al. 1993; Burr et al. 1998; Hughen et al. 1998, 2000). *R* estimates from the Marquesas and Tahiti are directly compared in the time interval of 9000–11,000 cal yr.

[1]Laboratoire des Sciences du Climat et de l'Environnement, Domaine du CNRS, Avenue de la Terrasse, F-91198 Gif sur Yvette, France.
[2]Corresponding author. Email: Martine.Paterne@lsce.cnrs-gif.fr.
[3]Present address: Department of Geology and Geophysics, University of Utah, Salt Lake City, Utah 84112, USA.
[4]Unité Mixte de Service UMS 2572, CEA Saclay, F-91198 Gif sur Yvette, France.
[5]IRD (Institut de Recherche pour le Développement), B.P. A5, 98848 Nouméa cedex, New Caledonia.
[6]CEREGE, Université d'Aix-Marseille III, CNRS UMR-6635, Europôle de l'Arbois, BP80, 13545 Aix-en-Provence cdx4, France.

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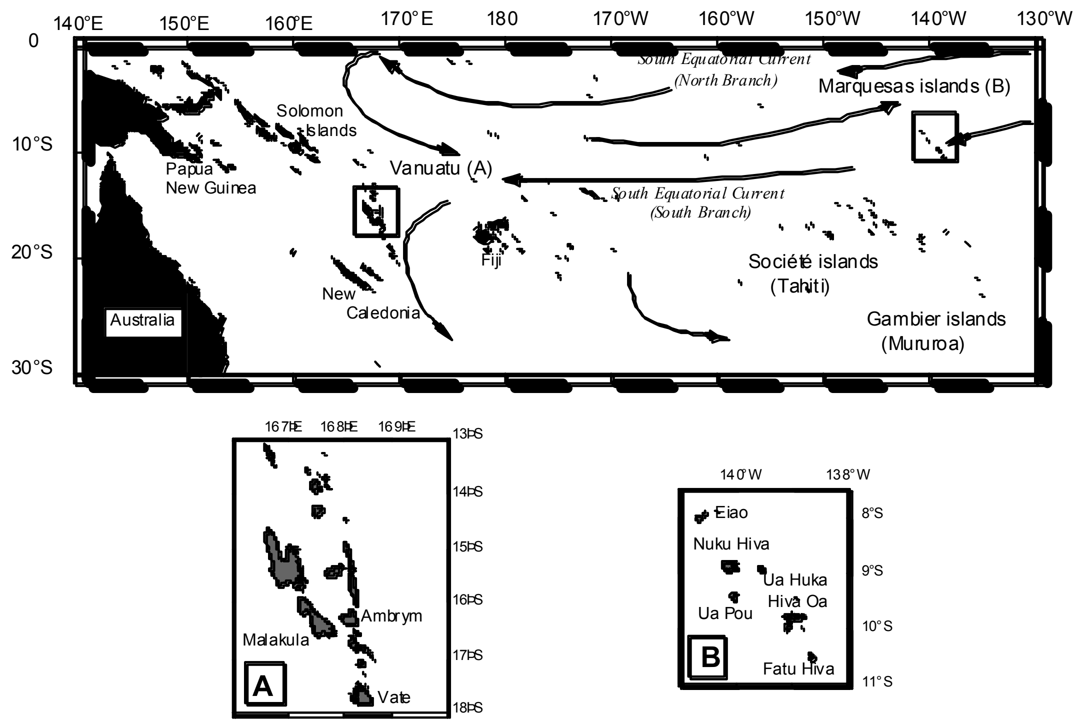

Figure 1 Sample locations; surface currents are also represented

MATERIAL AND METHODS

The surface corals (*Porites sp.*) were collected in the Marquesas Islands (6°S; 140°W) by dredging of submerged coral reefs in water depths greater than 86 m during the cruise conducted by the IRD in 1997 (Musorstom and Paleomarq), and in Vanuatu (20°S; 170°E) by direct sampling of emerged marine terraces raised by tectonic uplift (Figure 1). The corals from the Marquesas have been submerged in seawater since the time of their formation and have as a result most likely been preserved from major recrystallization/dissolution processes.

Coral specimens were cut into small slabs with cross-sectional areas between 4–6 cm^2 and thickness of ~0.1 to 0.2 cm. The shortest axis of these slabs were oriented parallel to the direction of growth. Growth bands were visible and continuous in the corals sampled. The slabs cut from each specimen probably represent some 1 to 15 yr in time, given the range of possible growth rates documented by Priess (1997) of ~2 to 40 mm per yr for the *Porites* species. Each coral slab was then subsampled for X-ray diffractometry (XRD), ^{14}C, and $^{230}Th/U$ analyses. Coral samples having a magnesian calcite or pure calcite content lower than 2% were selected for dating with 1 exception (Table 1).

$^{230}Th/U$ Dating

The U/Th age determination follows the procedure by Cabioch and Ayliffe (2000). Exterior surfaces of corals samples were initially cleaned by physical abrasion with a dental drill bit. The coral samples were then further cleaned by ultrasound treatment and several rinses with quartz distilled (QD) water. U and Th fractions were extracted and purified from coral samples using standard ion exchange chemistry as described by Stirling et al. (1995). The purified U and Th separates were loaded onto zone-refined Re filaments between 2 layers of colloidal graphite. Isotopes of U and Th

Table 1 $^{230}Th/U$ and ^{14}C ages on surface corals from the Marquesas and Vanuatu. Columns referred to (1) the AMS ^{14}C laboratory code GifA, (2) the dredge code (and water depth in m) for Marquesas corals and the altitude in m relative to sea level for Vanuatu corals (Cabioch and Ayliffe 2000), and (3) coral code and the number of measured Fe-C targets. The ^{14}C ages are expressed in conventional ages and are not corrected for reservoir ages. ^{14}C ages for samples 17b marked by * and $ were used to calculate the weighted mean and error similarly noted. The underlined χ^2 values are larger than the $P_{0.95}$ values (3.841 n = 2; 5.991 for n = 3; 7.815 n = 4). The $\Delta^{14}C = (A_{sample}/A_{calendar\ age} - 1) \times 1000$ correspond to the marine values and the atmospheric $\Delta^{14}C$ values in parentheses are calculated using the reservoir age correction of 400 yr.

(1)	(2)	(3)	U conc (ppm)	2 σ	$\delta^{234}U_{initial}$	2 σ	[230/232]	2 σ	$^{230}Th/U$ cal yr	2 σ (yr)	^{14}C age (BP)	2 σ (yr)	^{14}C age* (BP)	2 σ (yr)	χ^2	$\Delta^{14}C$ (‰)	2 σ (‰)	R (yr)	2 σ (yr)	Aragonite %
Marquesas																				
100449	DW1281c	78a 1	3.895	0.002	146.4	2.6	2330	30	3230	30	3420	100				–35 (15)	13	390	110	99.2
100450	DR1261 (850 m)	68a 1	3.984	0.003	145.5	2.4	4770	40	3260	30	3480	100				–38 (11)	13	420	110	98.7
100451	DW1281d	79a 1	2.992	0.002	146.6	2.3	7720	40	9450	70	8750	180				56 (110)	25	360	190	98
100435	DW1281	09b 1	3.139	0.002	147.0	2.2	4920	20	10,230	70	9520	260	9500	110	0.430	57 (111)	17	410	260	100
100452	(450–455 m)	09b 1									9460	160						350	170	
100737		09b 1									9540	200						430	200	
100453	DW1281a	76a 2	3.205	0.002	145.9	2.4	8120	60	10,320	80	9530	140	9590	115	1.940	57 (111)	18	340	150	97.8
100738		76a 1									9700	200						510	210	
100454	DW1281b	77a 2	3.108	0.002	144.7	2.7	7400	30	10,940	80	9960	140	9950	115	0.060	88 (143)	19	370	150	96.3
100739		77a 1									9930	200						340	210	
100455	DW1281	75a 2	3.362	0.002	144.1	2.7	14,330	90	11,470	90	10,600	140	10,540	100	1.725	78 (134)	18	570	150	98
100740		75a 2									10,470	140						440	150	
100456	DR1183(2)	81a 1	3.533	0.002	141.8	2.4	370	2	11,990	90	11,220	220			10.377	55 (109)	31			100
100741	(86–120 m)	81a 2									10,800	140				111 (168)	23			

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Table 1 ^{230}Th/U and ^{14}C ages on surface corals from the Marquesas and Vanuatu. Columns referred to (1) the AMS ^{14}C laboratory code GifA, (2) the dredge code (and water depth in m) for Marquesas corals and the altitude in m relatively to sea level for Vanuatu corals (Cabioch and Ayliffe 2000), and (3) coral code and the number of measured Fe-C targets. The ^{14}C ages are expressed in conventional ages and are not corrected for reservoir ages. ^{14}C ages for samples 17b marked by * and $ were used to calculate the weighted mean and error similarly noted. The underlined χ^2 values are larger than the $P_{0.95}$ values (3.841 n = 2; 5.991 for n = 3; 7.815 n = 4). The $\Delta^{14}C = (A_{sample}/A_{calendar\ age} - 1) \times 1000$ correspond to the marine values and the atmospheric Δ^{14}C values in parentheses are calculated using the reservoir age correction of 400 yr. *(Continued)*

(1)	(2)	(3)	U conc (ppm)	2 σ	$\delta^{234}U_{initial}$	2 σ	[230/232]	2 σ	^{230}Th/U cal yr	2 σ (yr)	^{14}C age (BP)	2 σ (yr)	^{14}C age* (BP)	2 σ (yr)	χ^2	Δ^{14}C (‰)	2 σ (‰)	R (yr)	2 σ (yr)	Aragonite %
Marquesas																				
100437	DR1183	17b 2	3.429	0.001	143.7	2.1	2570	20	15,050	120	12,830*	180			<u>29.166</u>					100
100457		17b 2									13,410$	200								
100742		17b 1									13,560$	260	12,920*	150	3.364	236 (298)	25			
100743		17b 1									13,120*	260	13,470$	160	0.836	155 (214)	24			
100458	DR1183(1)	80a 1	3.653	0.003	143.7	2.6	2980	20	15,100	120	13,360	240			<u>13.086</u>	178 (238)	36			98.8
100744		80a 1									12,720	260				276 (341)	42			
Vanuatu																				
100434	13	15a 1	2.360	0.001	149.8	2.2	1750	10	6400	60	6000	160				28 (93)	22	385	165	100
100471	6	74a 2	2.938	0.002	143.5	2.8	18,730	90	8390	70	8060	140	8020	91	0.5765	17 (81)	15	415	95	100
100771		74a 2									7990	120								
100472	15	73a 2	2.945	0.002	147.7	2.4	920	10	8500	60	8010	120				32 (97)	17	270	130	100

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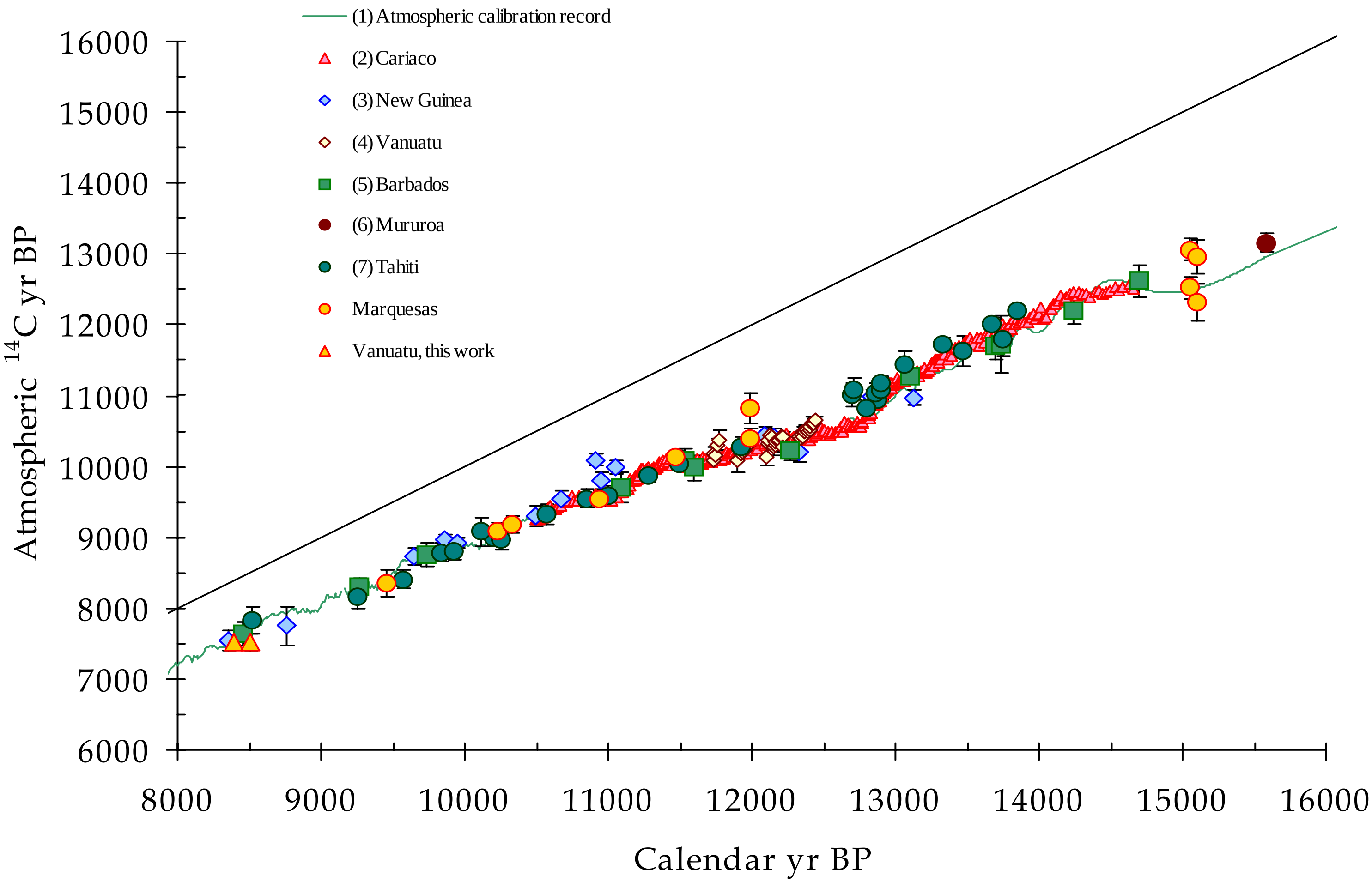

Figure 2 Atmospheric ^{14}C ages (error bars at 2 σ) as a function of calendar ages (error bars not represented). Calendar ages refer to $^{230}Th/U$ dating. (1) Stuiver et al 1998; (2) Hughen et al. 2000; (3) Edwards et al. 1993; (4) Burr et al. 1998; (5, 6, 7) Bard et al. 1993, 1998. The ^{14}C ages of the Marquesas and Vanuatu corals were corrected for a reservoir age of 400 yr.

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were measured with a Finnigan MAT 262 solid-source mass spectrometer using a peak jumping routine with a secondary electron multiplier. Repeated analyses of the uraninite standard HU-1 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). Decay constants used in the age calculations were $\lambda^{230}Th = 9.1954 \times 10^{-6} \pm 7.19 \times 10^{-8}$ yr^{-1} and $\lambda^{234}U = .8349 \times 10^{-6} \pm 5.7 \times 10^{-9}$ yr^{-1}. The reported $^{234}U/^{238}U$ and $^{230}Th/^{232}Th$ activity ratios of all the dated corals were corrected for machine biases by normalization to the corresponding ratios determined for HU-1.

^{14}C Dating

Secondary crystallization in skeleton pores of corals or surface contaminants are usually eliminated by strong acid or stepwise leaching procedures (Bard et al. 1990b; Burr et al. 1992; Yokoyama et al. 2000). Such procedures are time consuming due to the partial dissolution of the sample in several aliquots and then accordingly to the increase of the number of ^{14}C measurements to check cleaning efficacy (Burr et al. 1992; Yokoyama et al. 2000). In this study, coral samples (~20 mg in size) were first pre-cleaned by sand blasting until the elimination of micrite forms around skeleton pores (Figure 3), which can be carefully controlled under a microscope. Under this procedure, coral samples lose between 20–60% of their initial weight. Next, the abraded coral sample is rinsed and ultrasonically cleaned and then crushed in an agate mortar. About 10 mg of the fine powder is then immediately introduced into 1 side of a reaction vessel with 2 side arms. The coral powder is then leached in a 2-cm^3 solution of HNO_3 (0.01N) for 15 min and then rinsed to neutral pH. The second arm of the reactor is then filled with 1 cm^3 of H_3PO_4 and the vessel containing the wet powder is immediately attached to the vacuum line and evacuated as suggested by Schleicher et al. 1998. After hydrolysis of the coral powder by reaction with the H_3PO_4 *in vacuuo*, the evolved CO_2 is trapped into an ampoule. The CO_2 is then reduced into graphite according to the procedure of Arnold et al. (1989).

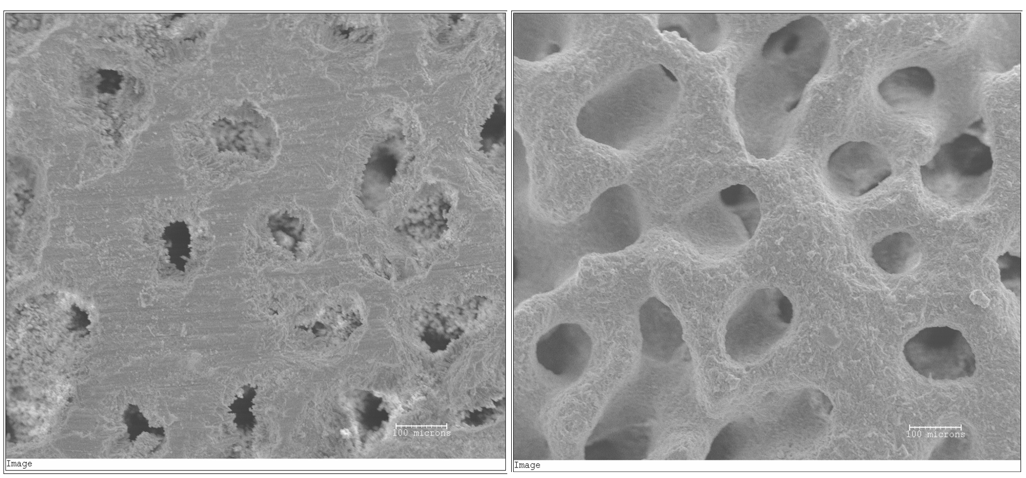

Figure 3 Scanning electron microprobe photographs of coral DR 1183 (17b) before (left) and after (right) cleaning. The sample on the right corresponds to an adjacent piece of coral treated for ^{14}C dating.

Two sub-samples were randomly picked from different parts of each coral slab and prepared independently. Given the range of growth rates observed for *Porites sp.* corals (Priest 1997), it is quite likely that the 2 sub-samples taken from each coral specimen grew during different seasons or years. Two targets of Fe-C powder were made from each graphite preparation in order to increase the pre-

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cision of the ^{14}C ages by accelerator mass spectrometry (AMS) at the Gif-sur-Yvette Tandétron facility (Arnold et al. 1987).

RESULTS AND DISCUSSION

Evaluation of Cleaning Procedure of Corals

The efficacy of our cleaning procedure was initially assessed through ^{14}C analyses of old corals (Table 2). In addition, we also proceeded to new ^{14}C dating of corals from Tahiti and Mururoa, previously dated by Bard et al. (1993, 1996, 1998) (Table 3).

Blank values were assessed from 3 corals from Mururoa (Bard et al. 1993), Vanuatu (Cabioch and Ayliffe 2000), and the Marquesas, determined by $^{230}Th/U$ dating to be beyond the limit of the ^{14}C dating method (Table 2). Although the mean and standard deviation obtained for the corals from the Marquesas and Vanuatu (0.21 ± 0.05 pMC: apparent age: 49,350 ± 1900 BP) are slightly higher than those obtained for 1 coral (Irene 30) from Mururoa (0.16 ± 0.02 pMC; apparent age: 51,800 ± 1050 BP), they are nevertheless statistically indistinguishable from one another. The mean and standard deviation for the old ^{14}C-depleted corals using this cleaning procedure are 0.20 ± 0.05 pMC (apparent age 50,100 ± 2070 BP) and are similar to slightly lower than those previously measured (Bard et al. 1990b; Burr et al. 1992; Yokoyama et al. 2000). The AIEA-C1 marble, currently used to assess the full procedural blank of the AMS ^{14}C dating method of our laboratory, has a value of 0.08 ± 0.02 pMC (n = 7; apparent age 57,280 ± 2000 BP). As for the old ^{14}C-depleted foraminifera reported by Schleicher et al. (1998) and Nadeau et al. (2001), the mean blank value of the old corals is larger than that of the geological C1 marble, which is thus inappropriate for ^{14}C age calculation of young biological materials.

Corals from Tahiti and Mururoa, previously dated between 11,000 and 17,000 cal yr (Bard et al. 1990, 1993, 1998), were subjected to our new cleaning procedure and also to that previously introduced by Bard et al. (1990b), which involved a strong HCl leach (Table 3). The χ^2 tests for the ^{14}C ages obtained using the previous and new cleaning procedures suggest no significant differences (at the 95% confidence level) between any of them. Therefore, it appears that our new cleaning treatment is as efficient as the previous one for removing surface contaminants from such corals.

Comparison of the Marine Reservoir *R* Ages from the Tahiti and Marquesas Corals in the Time Interval 9000–11,000 cal yr

The ^{14}C and absolute ages of the coral sub-samples are reported in Table 1. By subtraction of the ^{14}C ages of the corals from Vanuatu and Marquesas from the corresponding atmospheric ^{14}C ages documented in the INTCAL98 tree-ring record, we estimate a reservoir age of ~400 yr for the surface of the central Pacific Ocean prior to 9000 cal yr (Table 1). Using a similar approach between 9000 to 11,000 cal yr, we determine a weighted mean R value of 390 ± 60 yr (weighted 2 σ error; n = 8) for the Marquesas corals, which is close to the mean global ocean value (Stuiver et al. 1998) (Figure 4). For the same time period, a slightly lower R of 280 ± 50 yr (weighted mean and 2 σ error; n = 8) is determined from the Tahiti corals. This small difference, as previously observed (Stuiver et al. 1998; Bard et al. 1998; Goslar et al. 2000), may be attributed to the location of these islands with respect to the Pacific surface water currents. While the Tahiti Islands are located in the well-ventilated South Pacific gyre, the Marquesas Islands are situated within the South Equatorial westward drift (Figure 1). The likely more extensive vertical mixing of surface waters with underlying ^{14}C-depleted waters due to the Eastern Tradewinds in this region may account for the slightly older Marquesas R value.

Table 2 Fraction of modern carbon determined from 3 old ^{14}C-depleted surface corals: Irène 30 (Favidae) from Mururoa (Bard et al. 1993); Marquesas (CP1262: Porites); Vanuatu (undetermined) (Cabioch and Ayliffe 2000). Sample GifA100489 underwent a strong HCl (0.5N) leach. The blank values for these old corals do not show any obvious relationship with species, location, and time of preparation.

Lab code GifA	Dredge	Coral code	Date of preparation	C µg	pMC	1 σ (%)	Apparent age (BP)	1 σ (yr)	$^{230}Th/U$ cal yr	1 σ (yr)	Site
100443		Ir30	26/6	680	0.20	0.03	50,020	1100	259,000*	6000	Mururoa
100445			27/6	1350	0.17	0.03	51,400	1230			Mururoa
100489*			28/9	2000	0.15	0.02	52,470	1340			Mururoa
100499			2/10	2130	0.16	0.02	51,920	1230			Mururoa
100500			9/10	1790	0.15	0.02	52,470	1350			Mururoa
100768			24/11	1150	0.16	0.02	51,920	1230			Mururoa
100769			24/11	1240	0.14	0.02	53,070	1250			Mururoa
100469	CP1262(1)	83a	7/7	1420	0.22	0.03	49,220	1080	63,860	260	Marquesas
100469			7/7	1420	0.17	0.02	51,400	1190			Marquesas
100470	CP1262(2)	14a	10/7	1810	0.25	0.03	48,140	990	64,410	260	Marquesas
100470			10/7	1810	0.25	0.03	48,140	870			Marquesas
100756		83a	14/11	1540	0.27	0.04	47,500	1040			Marquesas
100757		14a	21/11	1700	0.23	0.03	48,840	990			Marquesas
100473	np11 (+59)	44a	3/7	1384	0.26	0.03	47,820	970	66,980	290	Vanuatu
100473			3/7	1384	0.29	0.03	46,910	870			Vanuatu
100764		44a	23/11	1450	0.22	0.03	49,220	970			Vanuatu
100764		44a	23/11	1450	0.20	0.03	50,020	1080			Vanuatu
100474	Mallicolo	13a	3/7	1494	0.10	0.02	55,180	1490	107,580	540	Vanuatu
100474	(204 m) d		3/7	1494	0.17	0.02	51,400	1130			Vanuatu
100765		13a	16/11	1930	0.20	0.03	50,020	1080			Vanuatu
100764		44a	23/11	1450	0.22	0.03	49,220	970			Vanuatu
100766	Espiegle(1)	45a	24/11	1860	0.17	0.02	51,400	1150	121,270	580	Vanuatu
			Mururoa		0.16	0.02	51,840	1040			
			Marquesas		0.23	0.04	48,780	1260			
			Vanuatu		0.20	0.06	49,810	2320			
			Total		**0.20**	**0.05**	**50,100**	**2070**			

Table 3 Comparison of the ^{14}C ages of corals, obtained from different pre-cleaning procedures; M = mechanical sand blasting. The ^{14}C ages are given in conventional yr BP uncorrected for the reservoir age. Samples noted by an asterisk were published in Bard et al. 1998. All samples have a carbon content higher than 500 µg, except sample GifA100494* (340 µg). The χ^2 values for $P_{0.95}$ are 3.841 for n = 2; 5.991 for n = 3; and 7.815 for n = 4.

Sample code	Lab code GifA	Nr of targets	$^{230}Th/U$ (cal yr)	2 σ (yr)	^{14}C age (BP)	2 σ (yr)	^{14}C age (weighted mean)	2 σ (yr)	χ^2 test	Comment
P7-8	95647*	2	11,280	30	10,100	140	10,160	90	1.293	HCl
P7-8	100480	2			10,200	160				HCl
P7-8	100490	2			10,210	180				M
P7-9	95648*	2	11,495	30	10,280	140	10,330	100	1.542	HCl
P7-9	100481	2			10,300	320				HCl
P7-9	100491	2			10,410	160				M
P7-11	95649*	2	12,875	40	11,130	140	11,230	90	5.215	HCl
P7-11	100482	2			11,240	160				HCl
P7-11	100492	2			11,390	180				M
P7-12	95650*	2	12,800	30	11,100	160	11,130	90	5.448	HCl
P7-12	100483	2			11,270	160				HCl
P7-12	100493	2			11,010	160				M
P8-1	95654*	1	12,905	30	11,510	220	11,480	90	2.942	HCl
P8-1	96092*	2			11,540	140				HCl
P8-1	100487	2			11,350	180				HCl
P8-1	100497	2			115,00	180				M
P8-2	95653*	2	13,335	30	11,970	160	12,030	80	4.209	HCl
P8-2	96091*	2			12,000	140				HCl
P8-2	100486	2			12,190	180				HCl
P8-2	100496	2			11,980	180				M
P8-3	95652*	2	13,665	35	12,250	160	12,260	90	3.113	HCl
P8-3	96090*	2			12,350	140				HCl
P8-3	100485	2			12,170	180				HCl
P8-3	100495	1			12,180	240				M
P8-4	95651*	2	13,850	35	12,570	160	12,490	90	6.202	HCl
P8-4	96087*	2			12,560	140				HCl
P8-4	100484	2			12,350	200				HCl
P8-4	100494	1			12,280*	280				M
Mu-8-30-315	95656*	2	17,170	40	14,860	180	14,790	120	1.274	HCl
Mu-8-30-315	100488	1			14,690	280				HCl
Mu-8-30-315	100498	1			14,750	200				M

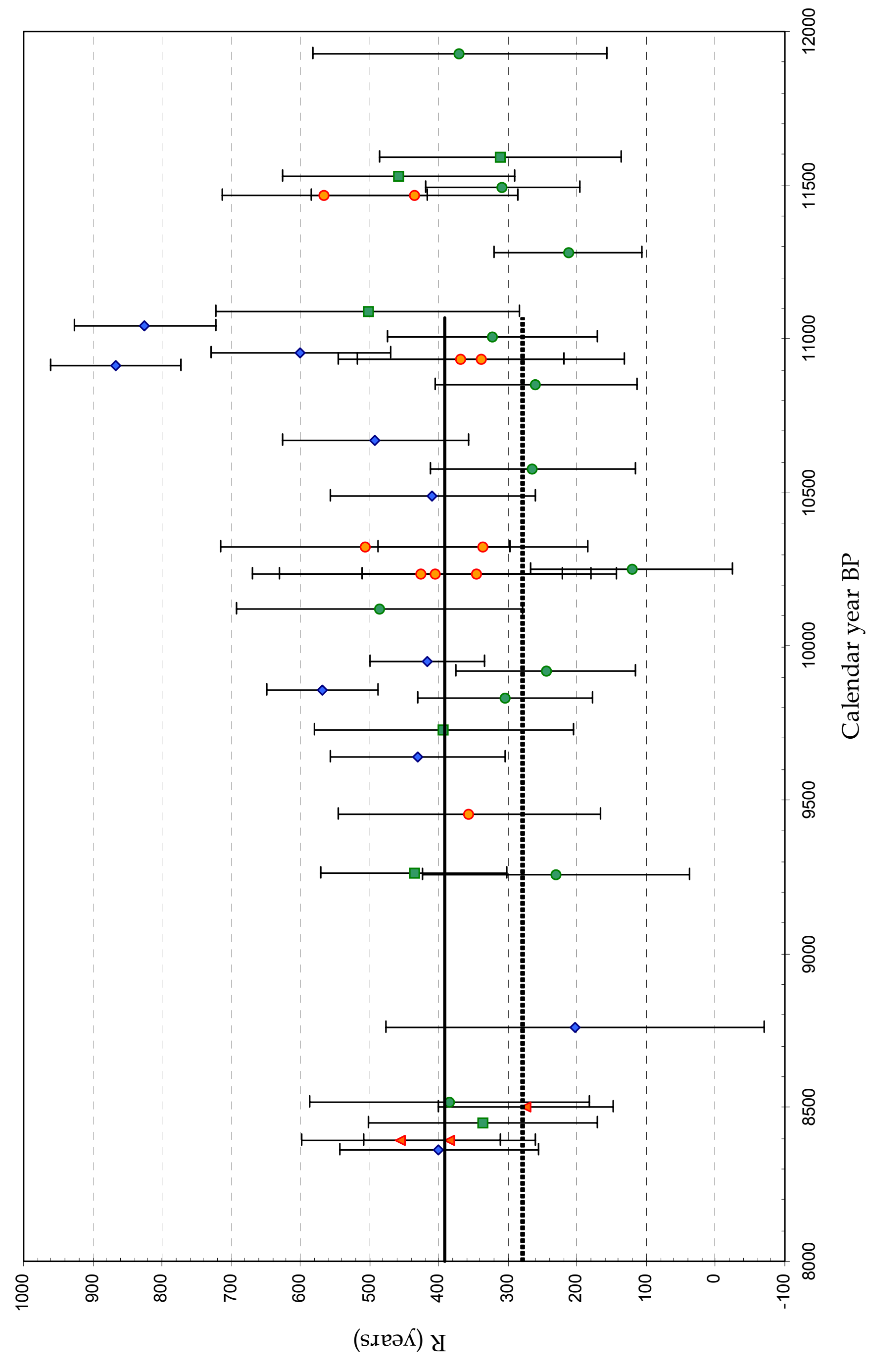

Figure 4 Sea surface reservoir ages (difference between coral and atmospheric ^{14}C ages [Stuiver at al. 1998] of similar calendar ages). Black and dotted lines correspond to the weighted mean *R* value of the Marquesas and Tahiti corals. Same references as Figure 2.

Comparison of the ^{14}C Ages and $\Delta^{14}C$ Values from the Marquesas and Vanuatu with Previous Marine and Atmospheric ^{14}C Record

Between 3000 cal yr and 11,500 cal yr, the ^{14}C ages are very reproducible within each coral (Table 1). Using an *R* value of 400 yr, the estimates of the difference between the absolute and ^{14}C ages are in agreement with previous determinations (Stuiver et al. 1998; Burr et al. 1998; Edwards et al. 1993; Bard et al. 1993, 1998) (Figures 2, 5, 6). Beyond 11,500 cal yr, 2 corals dated at 12,000 and ~15,100 cal yr, however, present scattered ^{14}C values.

The 2 sub-samples of coral specimen DR1183(2) dated at 12,000 cal yr gave significantly different ^{14}C ages at the 95% confidence level (Table 1), with the marine or atmospheric $\Delta^{14}C$ values of these 2 sub-samples varying by some 50‰. Two slabs from a single coral specimen (DR 1183 and DR 1183[1]) were dated each at ~15,100 cal yr by the $^{230}Th/U$ method and were sub-sampled for the ^{14}C dating (Figure 7). While the 2 $^{230}Th/U$ dates are very similar, the ^{14}C dates by contrast are highly scattered (Figures 2, 5, 6; Table 1). The ^{14}C ages of the sub-samples within each slab present the same range of variations from approximately 12,800 to ~13,400 yr, corresponding to marine $\Delta^{14}C$ values of 250 ± 35‰ to 160 ± 55‰ (2 σ), respectively. They are all within error (2 σ) of the marine and atmospheric INTCAL98 values (Stuiver et al. 1998) (Figures 5, 6). Only the upper $\Delta^{14}C$ values at ~310‰, corresponding to the youngest ^{14}C ages, are consistent with those of the atmospheric ^{14}C record from Lake Suigetsu (Kitagawa and van der Plicht 2000) (Figures 2, 4, 5). Similarly, at 12,000 cal yr, only the largest $\Delta^{14}C$ value (Figures 5, 6) agrees well with those of the ^{14}C INTCAL98 calibration record (Stuiver et al. 1998) and with those from the Lake Suigetsu ^{14}C record (Kitagawa and van der Plicht 2000). Therefore, the addition of modern carbon either during the different steps of AMS ^{14}C dating procedure and/or during recrystallization processes with seawater seems unlikely. This is also attested by the very low content of magnesian (Mg) calcite in the corals. The initial $^{234}U/^{238}U$ ratios of all the corals analyzed are very similar to that of sub-modern corals at ~145‰ (in Delanghe et al. 2002) and within ±5‰ of the modern seawater values (Henderson et al. 1999; Delanghe et al. 2002) (Table 1). The detrital Th contents are very low. Thus, little post-depositional alteration or recrystallization of the primary coralline aragonite has taken place. In-situ dissolution processes alone may also be ruled out, as the U concentrations of these 2 corals, DR1183(2) and DR1183(1)/DR1183, are among the largest of the measured ones (Table 1). Therefore, the $^{230}Th/U$ dates may be considered as most likely valid.

The anomalous ^{14}C data at ~12,000 and ~15,000 cal yr would be the low $\Delta^{14}C$ values, and thus the old ^{14}C ages when compared to the determined atmospheric ones from Lake Suigetsu (Kitagawa and van der Plicht 2000) (Figures 2, 6). This may be related to a subtle submarine diagenesis, which would include here dissolution of old carbonates and secondary Mg-calcite precipitation. Due to organic matter degradation, coral pore waters have a lower pH than that of open reef waters (Enmar et al. 2000) that may favor dissolution of carbonates. Secondary precipitation of aragonite and/or Mg-calcite micrites or needles of some 10 µm often fill voids in skeleton pores of sub-marine fossil corals (Enmar et al. 2000) (Figure 3). A 10% result in weight of secondary crystallization deriving from old ^{14}C-depleted carbonates would account for the anomalously old ^{14}C ages at 15,100 cal yr and 5% at 12,000 cal yr. Such a parallel contamination by "old" marine uranium with $^{234}U/^{238}U$ activity of 1.1, close to the value found in last interglacial corals at the time of deposition, would lead to a slight decrease of the $\delta^{234}U_{initial}$ from the value of 149 to ~144‰. This may explain the slightly lower $\delta^{234}U_{initial}$ values of these 2 corals with respect to those of the other corals, although the difference is not significant at the 95% confidence level (Table 1). However, this represents a very extreme case, and in the marine environment, the diagenetic changes in corals with recrystallization and secondary aragonite or Mg-calcite precipitation within seawater are usually related to increasing $\delta^{234}U_{initial}$ values (Bar-Matthews et al. 1993).

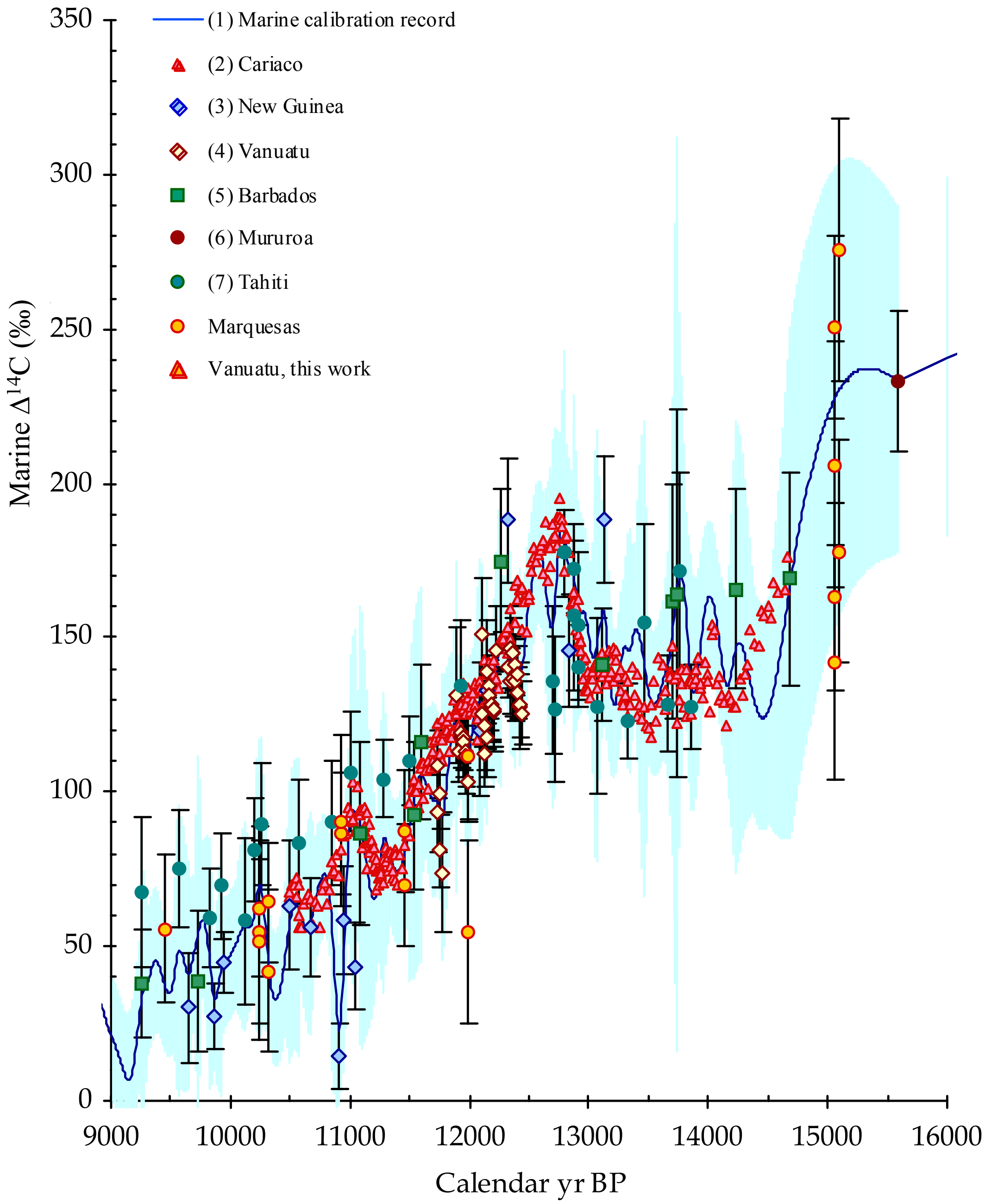

Figure 5 Marine $\Delta^{14}C$ changes at the 2-σ confidence level as a function of calendar ages. The blue envelope figured out the 2-σ error of the marine INTCAL98 $\Delta^{14}C$ values. (1) Stuiver et al 1998; (2) Hughen et al. 2000; (3) Edwards et al. 1993; (4) Burr et al. 1998; (5, 6, 7) Bard et al. 1993, 1998. Same references as Figure 2.

The corals dated at ~12,000 and ~15,100 cal yr were sampled in the same dredge (DR1183: 8°45.5′S; 140°03.8′W) and would reflect local and brief changes of the seawater chemical composition in the vicinity of Marquesas. Seasonal to annual variability of ^{14}C ages, which can be

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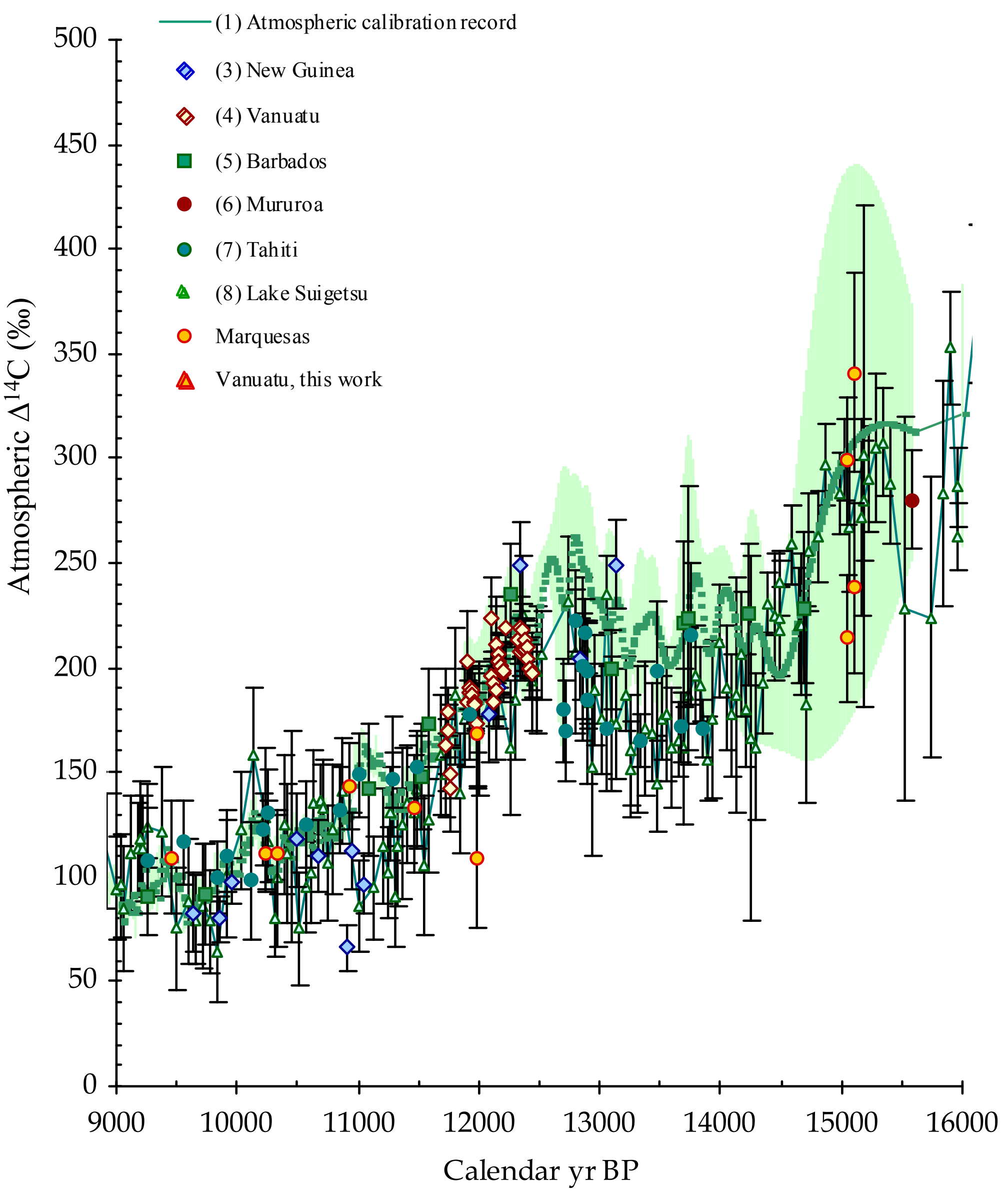

Figure 6 Atmospheric $\Delta^{14}C$ changes at the 2-σ confidence level as a function of calendar ages. The green envelope figured out the 2-σ error of the atmospheric INTCAL98 $\Delta^{14}C$ values. (8) Lake Suigetsu record (Kitagawa and van der Plicht 2000). Same references as Figure 2.

approached from our random sampling, was observed in modern banded coral samples from the Pacific Ocean (Brown et al. 1993; Druffel and Griffin 1993; Guilderson and Schrag 2001). Such variability was attributed to changes in the extent and intensity of the equatorial Pacific upwelling. However, this natural ^{14}C variability did not exceed 10–15‰ (Druffel and Griffin 1993), which is significantly lower than the $\Delta^{14}C$ changes we observed in the fossil Marquesas corals. Thus, causes of the variation of the ^{14}C ages in these corals remain a puzzling question.

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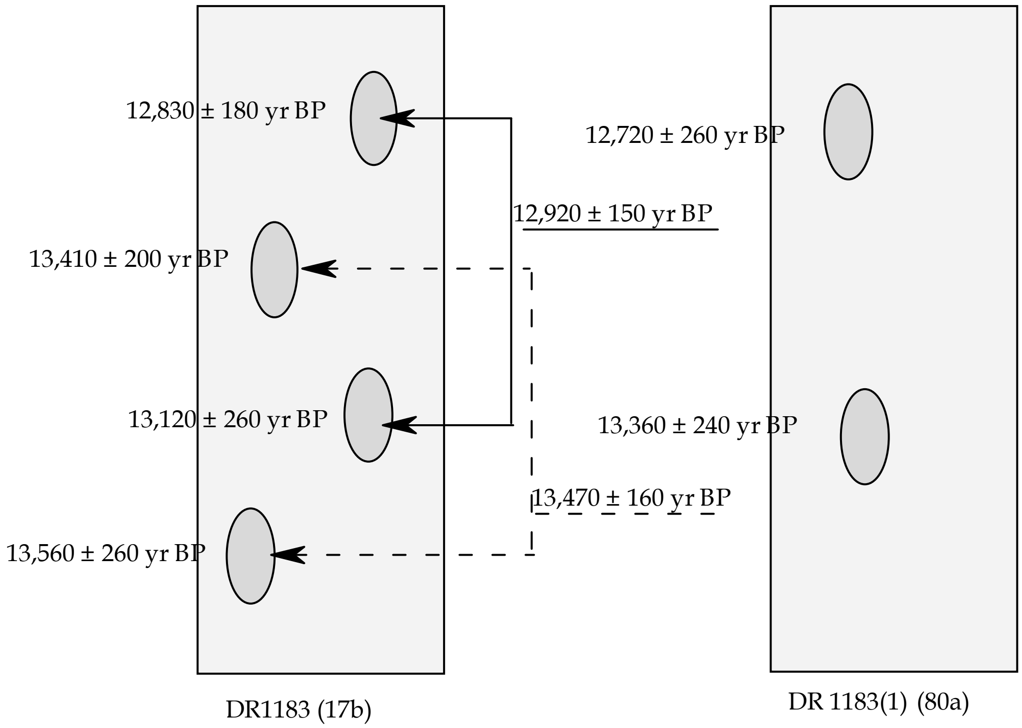

Figure 7 Sketch of 2 slabs, DR1183 and DR1183(1), of the same coral which was sub-sampled for AMS ^{14}C dating. The weighted mean of the ^{14}C ages and the weighted 2 σ from DR1183 (Table 1) are underlined.

CONCLUSION

Paired ^{14}C and $^{230}Th/U$ dating of corals from the Marquesas and Vanuatu provide additional estimates of the difference between the absolute and ^{14}C ages of marine biogenic materials. These estimates are in agreement with those determined in previous studies between 3000 and 11,500 cal yr (Edwards et al. 1993; Stuiver et al. 1998; Bard et al. 1990a, 1993, 1998; Burr et al. 1998; Hughen et al. 2000; Kitagawa and van der Plicht 2000). Over this time interval, the reservoir age of the surface waters from the Marquesas differ by 100 yr from *R* values of corals from Tahiti. This is compatible with previous suggestions that variations of *R* exist in the Pacific Ocean (Stuiver et al. 1998; Goslar et al. 2002).

Among all the corals analyzed, 2 of them from the Marquesas dated at ~12,000 and ~15,000 cal yr present scattered ^{14}C ages during the period of coral growth. Such variability may be related to rapid changes of the ^{14}C content of the surface waters around the Marquesas or to a subtle submarine diagenesis. Additional coupled ^{14}C and $^{230}Th/U$ dating of corals from the Pacific should refine our knowledge of the extent and magnitude of these rapid changes in surface ^{14}C in this region, and will be important in understanding the underlying mechanism responsible for such fluctuations.

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REFERENCES

Arnold M, Bard E, Maurice P, Duplessy JC. 1987. C-14 dating with the Gif sur Yvette Tandetron accelerator: status report. *Nuclear Instruments and Methods in Physics Research B* 29:120–3.

Arnold M, Bard E, Maurice P, Valladas H, Duplessy JC. 1989. ^{14}C dating with the Gif-sur-Yvette Tandetron accelerator: status report and study of isotopic fractionation in the sputter ion source. *Radiocarbon* 31(3): 284–91.

Bard E. 1988. Correction of accelerator mass spectrometry ^{14}C ages measured in planktonic foraminifera: paleoceanographic implications. *Paleoceanography* 3: 635–45.

Bard E, Arnold M, Fairbanks RG, Hamelin B. 1990a. Calibration of the ^{14}C timescale over the past 30,000 years using mass spectrometric U-Th ages from Barbados corals. *Nature* 345:405–10.

Bard E, Hamelin B, Fairbanks RG, Zindler A, Arnold M, Mathieu G. 1990b. U/Th and ^{14}C ages of corals from Barbados and their use for calibrating the ^{14}C timescale beyond 9000 years BP. *Nuclear Instruments and Methods in Physics Research B* 52:461–8.

Bard E, Arnold M, Fairbanks RG, Hamelin B. 1993. ^{230}Th-^{234}U and ^{14}C ages obtained by mass spectrometry on corals. *Radiocarbon* 35(1):191–9.

Bard E, Arnold M, Mangerud J, Paterne M, Labeyrie L, Duprat J, Mélières M, Sonstegaard E, Duplessy JC. 1994. The North Atlantic atmosphere-sea surface ^{14}C gradient during the Younger Dryas climatic event. *Earth and Planetary Science Letters* 126:275–87.

Bard E, Arnold M, Hamelin B, Tisnerat-Laborde N, Cabioch G. 1998. Radiocarbon calibration by means of mass spectrometric $^{230}Th/^{234}U$ and ^{14}C ages of corals: an updated database including samples from Barbados, Mururoa and Tahiti. *Radiocarbon* 40:1085–92.

Bar-Matthews M, Wasserburg GJ, Chen JH. 1993. Diagenesis of fossil coral skeletons: correlation between trace elements, textures and $^{234}U/^{238}U$. *Geochemica et Cosmochimica Acta* 57:257–76.

Beck JW, Richards DA, Edwards RL, Silverman BW, Smart PL, Donahue DJ, Hererra-Osterheld S, Burr GS, Calsoyas L, Jull AJT, Biddulph D. 2001. Extremely large variations of atmospheric ^{14}C concentration during the Last Glacial period. *Science* 292:2453–7.

Burr GS, Edwards RL, Donahue DJ, Druffel ERM, Taylor FW. 1992. Mass spectrometric ^{14}C and U-Th measurements in coral. *Radiocarbon* 34(3):611–8.

Burr GS, Beck WJ, Taylor FW, Recy J, Edwards LR, Cabioch G, Corrège T, Donahue DJ, O'Malley JM. 1998. A high-resolution radiocarbon calibration between 11,700 and 12,400 calendar years BP derived from ^{230}Th ages of corals from Espiritu Santo island, Vanuatu. *Radiocarbon* 40(3):1093–1105.

Cabioch G, Ayliffe LK. 2001. Raised coral terraces at Malakula, Vanuatu, southwest Pacific, indicate high sea level during marine isotope stage 3. *Quaternary Research* 56:357–65.

Druffel ERM, Griffin S. 1993. Large variations of surface ocean radiocarbon: evidence of circulation changes in the southwestern Pacific. *Journal of Geophysical Research* 98:20,249–59.

Edwards RL, Beck JW, Burr GS, Donahue DJ, Chappell JMA, Bloom AL, Druffel ERM, Taylor FW. 1993. A large drop in atmospheric $^{14}C/^{12}C$ and reduced melting in the Younger Dryas, documented with ^{230}Th ages of corals. *Science* 260:962–8.

Enmar R, Stein M, Bar-Matthews M, Sass E, Katz A, Lazar B. 2000. Diagenesis in live corals from the Gulf of Aqaba. I. The effect on paleo-oceanography tracers. *Geochimica et Cosmochimica Acta* 64:3123–32.

Franck N, Paterne M, Ayliffe L, van Weering T, Henriet JP, Blamart D. 2004. Eastern North Atlantic deep-sea corals: tracing upper intermediate water $\Delta^{14}C$ during the Holocene. *Earth and Planetary Science Letters* 219:297–309.

Goslar T, Arnold M, Tisnérat-Laborde N, Hatté C, Paterne M, Ralska-Jasiewiczona M. 2000. Radiocarbon calibration by means of varves versus ^{14}C ages of terrestrial macrofossils from Lake Gościąż and Lake Perespilno, Poland. *Radiocarbon* 42(3):335–48.

Guilderson TP, Schrag DP. 1998. Abrupt shift in subsurface temperatures in the tropical Pacific associated with changes in El Niño. *Science* 281:240–3.

Henderson GM, Slowey NC, Haddad GA 1999. Fluid flow through carbonates platforms: constraints from $^{234}U/^{238}U$ and Cl- in Bahamas pore-waters. *Earth and Planetary Science Letters* 169:99–111.

Hughen KA, Overpeck JT, Lehman SJ, Kashgarian M, Southon J, Peterson LC, Alley R, Sigman DM. 1998. Deglacial changes in ocean circulation from an extended radiocarbon calibration. *Nature* 391:65–8.

Hughen KA, Overpeck JT, Lehman SJ, Kashgarian M, Southon J, Peterson LC. 1998. A new ^{14}C calibration data set for the last deglaciation based on marine varves. *Radiocarbon* 40(1):483–94.

Kitagawa H, van der Plicht J. 1998. Atmospheric radiocarbon calibration to 45,000 yr BP: Late Glacial fluctuations and cosmogenic isotope production. *Science* 279:1187–90.

Kitagawa H, van der Plicht J. 2000. Atmospheric radiocarbon calibration beyond 11,900 cal BP from Lake Suigetsu laminated sediments. *Radiocarbon* 42(3): 369–80.

Nadeau MJ, Grootes PM, Voelker A, Bruhn F, Duhr A, Oriwall A. 2001. Carbonate ^{14}C background: does it have multiple personalities? *Radiocarbon* 43(1):169–76.

Priess K. 1997. La croissance des *Porites spp.* du groupe lobata-lutea-solida (scléractiniaires massifs) dans le lagon de Mayotte (NO Canal de Mozambique). Etude sclérochronologique [PhD dissertation]. Université de la Méditerranée. 170 p.

Schleicher M, Grootes PM, Nadeau MJ, Schoon A. 1998. The carbonate ^{14}C background and its components at the Leibniz AMS facility. *Radiocarbon* 40(1):85–93.

Siani G, Paterne M, Michel E, Sulpizio R, Sbrana A, Arnod M, Haddad G. 2001. Mediterranean sea surface radiocarbon reservoir age changes since the Last Glacial Maximum. *Science* 294:1917–20.

Sikes E, Samson CR, Guilderson TP, Howard WR. 2000. Old radiocarbon ages in the southwest Pacific Ocean during the last glacial period and deglaciation. *Nature* 405:555–9.

Stirling CH, Esat TM, McCulloch MT, Lambeck K. 1995. High-precision U-series dating of corals from Western Australia and implications for the timing and duration of the last Interglacial. *Earth and Planetary Science Letters* 135:115–30.

Stuiver M, Reimer PJ, Bard E, Beck WJ, Burr GS, Hughen KA, Kromer B, McCormac G, van der Plicht J, Spurk M. 1998. INTCAL98 radiocarbon age calibration, 24,000–0 cal BP. *Radiocarbon* 40(3):1041–83.

Voelker AHL, Sarnthein M, Grootes PM, Erlenkeuser H, Laj C, Mazaud A, Nadeaeu MJ, Schleicher M. 1998. Correlation of marine ^{14}C ages from the Nordic Seas with the GISP2 isotope record: implications for ^{14}C calibration beyond 25 ka BP. *Radiocarbon* 40(1):517–34.

Yokoyama Y, Esat TM, Lambeck K, Fifield LK. 2000. Last ice age millennial scale climate changes recorded in Huon Peninsula corals. *Radiocarbon* 42(3):383–401.