

TEMPORAL VARIATIONS OF RADIOCARBON RESERVOIR AGES IN THE SOUTH PACIFIC OCEAN DURING THE HOLOCENE

G S Burr^{1,2,3} • C Vance Haynes⁴ • Chuan-Chou Shen⁵ • Fred Taylor⁶ • Yu-Wei Chang⁵ • J W Beck² • Vicki Nguyen² • Weijian Zhou¹

ABSTRACT. This article discusses the magnitude and rate of change of radiocarbon reservoir ages from the surface ocean in the South Pacific during the Holocene. ¹⁴C reservoir ages are calculated from paired U/Th and ¹⁴C measurements. Seventeen pairs of coral dates were determined from samples collected on Rendova and Tetepare Islands, in the Solomon Islands, and from Espiritu Santo Island, Vanuatu. The samples are all Holocene in age, with ²³⁰Th ages ranging from about 400 to 9400 BP. Samples were collected as drill cores or surface outcrops. About half of the surface samples appear to have incorporated modern carbon through postdepositional recrystallization. Two of the core samples were also affected by carbon exchange. The Holocene ¹⁴C reservoir ages observed in this data set show stable values for the last 3000 yr, and substantial variability from 5000–6000 BP (~100 to ~950 ¹⁴C yr). Persistent low values (<200 ¹⁴C yr) were observed for samples from 7000–8000 BP. We attribute these variations to temporal changes in lateral advection and vertical mixing, and possibly to local environmental conditions related to the interplay between sea-level rise and episodic uplift, characteristic of all the coral localities.

INTRODUCTION

A marine radiocarbon reservoir age is the age difference, in ¹⁴C years, between carbon in the ocean and the contemporaneous atmosphere. Marine ¹⁴C reservoir ages are known to vary in time and space and depend especially on the proximity of upwelling regions (vertical mixing) and prevailing surface ocean circulation pathways (lateral advection). Variations in surface ocean circulation are capable of producing changes in ¹⁴C reservoir ages on seasonal, annual, and longer timescales. Corals that grow near the ocean's surface preserve a record of these changes, by fixing ¹⁴C from dissolved inorganic carbon (DIC) in seawater as they incorporate carbon into their skeletons (Nozaki et al. 1978; Druffel 1981; Druffel and Linick 1987). Since corals can be independently dated with U/Th, they can be used to determine surface ocean ¹⁴C reservoir ages at different times in the past (Paterne et al. 2004; McGregor et al. 2008; Burr et al. 2009; Yu et al. 2010; Komugabe et al. 2014). Although our knowledge of regional ¹⁴C reservoir ages has improved substantially in recent years, we still know very little about temporal changes from site to site. This study presents some preliminary data that allow us to examine temporal variability in the Southwest Equatorial Pacific.

STUDY AREAS AND SAMPLING

Rendova Island and Tetepare Island are part of the New Georgia Group of the Solomon Islands (Figure 1). They are situated just north of a prominent subduction zone where the Australian Plate is being subducted beneath the Pacific Plate. This region has experienced a dramatic neotectonic reversal since the late Quaternary, marked initially by hundreds of meters of subsidence and followed by abrupt, rapid uplift since the Last Glacial Maximum (LGM). At these sites, neotectonic uplift kept pace with, or exceeded, sea-level rise since the LGM (Mann et al. 1998; Taylor et al. 2005). As a result, Holocene corals are exposed above sea level at some locations, and we collected a number of these for study. We collected surface samples from Tetepare Island (8°42'S, 157°25'E) and Rendova Island (8°42'S, 157°7'E) and we also collected surface samples using a drill rig to core into the reef rocks buried beneath the surface where we encountered additional Holocene corals. A few of the samples studied here were collected from Espiritu Santo Island, in Vanuatu (Figure 1), where

1. Chinese Academy of Sciences, Institute of Earth Environment, Xi'an, China (PRC).

2. University of Arizona, Physics Department, Tucson, AZ 85721-0081, USA.

3. Corresponding author. Email: burr@email.arizona.edu.

4. University of Arizona, School of Anthropology, University of Arizona, Tucson, AZ 85721, USA.

5. National Taiwan University, High-Precision Mass Spectrometry and Environmental Change Laboratory (HISPEC), Department of Geosciences, Taipei, Taiwan (ROC).

6. Institute for Geophysics, J.J. Pickle Research Campus, Bldg. 196, 10100 Burnet Rd. (R2200), Austin, TX 78758-4445, USA.

a similar neotectonic setting produced uplifted Holocene corals as well. We also collected a single coral sample from Finschhafen, Morobe Province, on the north coast of Papua New Guinea (PNG). This sample was used to test the feasibility of extracting organic carbon separately from inorganic carbon in a single specimen, using pyrolysis.

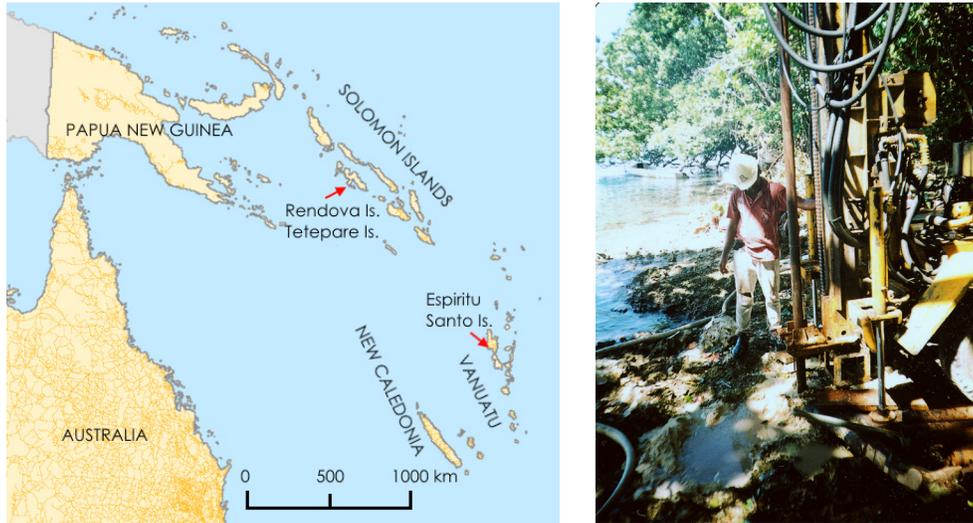


Figure 1 (a) Study site. Samples were collected from Rendova Island and Tetepare Island in the Solomon Islands; and from Espiritu Santo Island in Vanuatu. Modified from the “Oceania map,” Global Roads Open Access Data Set (gROADS), v1 (1980–2010). Center for International Earth Science Information Network, Columbia University. (b) Drill core samples collected for this study (in the Solomon Islands) were collected using a truck-mounted drill that was shipped to the site by boat. Michael Rahe (pictured) operated the drill.

ANALYTICAL METHODS

^{14}C ages of the corals were determined by accelerator mass spectrometry (AMS). The corals were visually inspected for signs of recrystallization. To remove possible surface contamination from the corals, they were processed in the laboratory using selective dissolution (Burr et al. 1992). In this procedure, a minimum of 25 mg of coral was placed in a vacuum vessel and evacuated to $<10^{-3}$ Torr. A few mL of phosphoric acid was introduced into the vessel while under vacuum, and the coral began to dissolve. When about half of the coral remained, the CO_2 produced in the reaction was pumped away and discarded. The vessel was again isolated and the dissolution was allowed to continue. The CO_2 produced from the second dissolution step was then dried in a dry ice/isopropyl alcohol cold trap and collected with liquid nitrogen. The CO_2 was converted to graphite by reduction over iron using standard procedures at the Arizona AMS lab, and measured in the AMS (Burr and Jull 2010).

For the U/Th dating, each fossil coral was gently crushed into segments, and physically cleaned with ultrasonic methods (Shen et al. 2008). Chipped segments, 0.9–1.2 g, for each fossil coral were picked for U/Th chemistry (Shen et al. 2003). Uranium and thorium isotopic measurements were conducted on a multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS), Thermo Electron Neptune, at the High-Precision Mass Spectrometry and Environment Change Laboratory (HISPEC), Department of Geosciences, National Taiwan University (Shen et al. 2012). A triple-spike, ^{229}Th - ^{233}U - ^{236}U , isotope dilution method was employed to correct for mass bias and determine all uranium and thorium isotopic and concentration values. All errors of isotopic data and dates given in Table 1 are quoted with two standard deviations (2σ), unless otherwise noted.

Table 1 Uranium and thorium isotopic composition and ^{230}Th ages measured by MC-ICP-MS.

Sample ID	Weight (g)	^{238}U (ppb)	^{232}Th (ppt)	$\delta^{234}\text{U}$ measured ^d	$^{230}\text{Th}/^{238}\text{U}$ activity ^b	$[\frac{^{230}\text{Th}}{^{232}\text{Th}}]$ ppm ^c	^{230}Th age uncorrected	^{230}Th age corrected ^{b,d}	$\delta^{234}\text{U}$ initial corrected ^e
AA42088	0.1382	2147.4 ± 1.6	107.4 ± 5.0	148.5 ± 1.5	0.004255 ± 0.000019	1405 ± 66	405.3 ± 1.9	404.1 ± 2.0	148.7 ± 1.6
AA42089	0.1353	2033.0 ± 1.5	105.6 ± 5.1	146.0 ± 1.3	0.004250 ± 0.000017	1351 ± 66	405.7 ± 1.7	404.5 ± 1.8	146.1 ± 1.3
AA42089	0.1633	2005.4 ± 1.9	62.3 ± 4.3	148.5 ± 1.9	0.004230 ± 0.000020	2249 ± 154	402.9 ± 2.0	402.2 ± 2.1	148.6 ± 1.9
AA42089	average						403.5 ± 1.4	403.5 ± 1.4	147.4 ± 1.8
AA42091		2635.0 ± 5	201 ± 10	147.0 ± 2.0	0.0811 ± 0.0004		7995 ± 42	7992 ± 42	150.4 ± 2.1
AA42092	0.1546	2263.7 ± 1.5	26.8 ± 4.5	146.3 ± 1.1	0.009964 ± 0.000022	13,918 ± 2342	953.0 ± 2.3	952.9 ± 2.3	146.7 ± 1.1
AA42092	0.1236	2346.8 ± 2.1	24.9 ± 5.6	150.3 ± 2.0	0.009964 ± 0.000022	15,516 ± 3512	949.8 ± 2.7	949.6 ± 2.7	150.7 ± 2.0
AA42092	average						951.5 ± 1.8	951.5 ± 1.8	148.7 ± 2.8
AA42100	0.0964	2624.4 ± 2.7	30.9 ± 7.2	144.0 ± 2.2	0.09422 ± 0.00025	131,865 ± 30,796	9356 ± 32	9356 ± 32	147.8 ± 2.3
AA42101	0.1263	2504.3 ± 3.8	175.8 ± 5.5	140.3 ± 3.3	0.06773 ± 0.00016	15,906 ± 500	6669 ± 26	6668 ± 26	143.0 ± 3.4
AA42106	0.0933	2899.5 ± 4.5	2804 ± 10	130.5 ± 2.5	0.11342 ± 0.00035	1933.8 ± 8.5	11,506 ± 46	11,484 ± 47	134.8 ± 2.6
AA42108	0.1215	2123.5 ± 2.2	648.1 ± 5.8	138.7 ± 2.5	0.07662 ± 0.00019	4139 ± 38	7586 ± 26	7579 ± 26	141.7 ± 2.5
AA42109	0.0994	3510.5 ± 5.3	115.9 ± 7.0	144.9 ± 3.1	0.02235 ± 0.00008	11,163 ± 676	2149.1 ± 9.9	2148.4 ± 9.9	145.7 ± 3.1
AA42110	0.1077	2776.1 ± 4.2	549.9 ± 6.6	140.5 ± 3.0	0.09496 ± 0.00023	7904 ± 96	9464 ± 36	9459 ± 36	144.3 ± 3.1
AA42112	0.0978	3057.4 ± 5.4	861.9 ± 7.2	143.6 ± 2.8	0.02437 ± 0.00009	1427 ± 13	2351 ± 11	2345 ± 11	144.5 ± 2.8
AA42115	0.0965	2152.2 ± 3.9	3731 ± 11	140.2 ± 2.8	0.02979 ± 0.00018	283.4 ± 1.8	2886 ± 19	2846 ± 28	141.3 ± 2.9
AA42116	0.1173	3241.7 ± 5.3	2011.9 ± 7.1	141.6 ± 2.9	0.03263 ± 0.00014	866.9 ± 4.6	3160 ± 16	3146 ± 18	142.9 ± 2.9
AA42117	0.1061	3215.1 ± 5.0	1401.2 ± 6.9	140.7 ± 2.7	0.04940 ± 0.00014	1869.1 ± 10.3	4824 ± 18	4814 ± 19	142.6 ± 2.7
AA42122	0.1017	2797.6 ± 4.4	41,273 ± 230	139.8 ± 2.7	0.05991 ± 0.00071	67.0 ± 0.9	5881 ± 73	5539 ± 186	142.0 ± 2.7
AA42139	0.1035	2830.9 ± 4.8	282.8 ± 6.7	147.3 ± 2.6	0.05217 ± 0.00015	8611 ± 207	5070 ± 19	5068 ± 19	149.4 ± 2.7
AA21140	0.0970	2361.3 ± 3.2	16.2 ± 7.2	142.7 ± 2.5	0.05487 ± 0.00016	131,526 ± 58,094	5361 ± 20	5361 ± 20	144.9 ± 2.6
AA21141	0.1228	2362.0 ± 3.0	26.8 ± 5.7	142.2 ± 2.3	0.06303 ± 0.00013	91,552 ± 19,360	6183 ± 18	6182 ± 18	144.7 ± 2.3

U-Th chemistry (Shen et al. 2003) was performed on 28 July 2011 for AA42100-AA42139 and AA21140 & AA21141. Instrumental analyses were performed on MC-ICP-MS (Shen et al. 2012). Analytical errors are 2σ of the mean.

^a $[\frac{^{238}\text{U}}{^{235}\text{U}}] = [137.77 (\pm 0.11\%) (\text{Heiss et al. 1999})]$; $\delta^{234}\text{U} = (\frac{^{234}\text{U}/^{238}\text{U}}{\text{activity}} - 1) \times 1000$.

^b $[\frac{^{230}\text{Th}}{^{238}\text{U}}]_{\text{activity}} = 1 - e^{-\lambda_{230}T} + (\frac{^{234}\text{U}}{^{238}\text{U}})_{\text{measured}} / 1000 (\lambda_{230} - \lambda_{234}) (1 - e^{-\lambda_{230}T - \lambda_{234}T})$, where T is the age. Decay constants are $9.1705 \times 10^{-6} \text{ yr}^{-1}$ for ^{230}Th , $2.8221 \times 10^{-6} \text{ yr}^{-1}$ for ^{234}U (Cheng et al. 2013), and $1.55125 \times 10^{-10} \text{ yr}^{-1}$ for ^{238}U (Jaffey et al. 1971).

^cThe degree of detrital ^{230}Th contamination is indicated by the $[\frac{^{230}\text{Th}}{^{232}\text{Th}}]$ atomic ratio instead of the activity ratio.

^dAges are quoted relative to chemistry date (28 July 2011), and have been adjusted using an estimated atomic $^{230}\text{Th}/^{232}\text{Th}$ ratio of 4 ± 2 ppm (Shen et al. 2008).

^e $\delta^{234}\text{U}_{\text{initial corrected}}$ was calculated based on ^{230}Th age (T), i.e. $\delta^{234}\text{U}_{\text{initial}} = \delta^{234}\text{U}_{\text{measured}} \times e^{234T}$, where T is the corrected age.

Pyrolysis. As a proof of concept exercise, we subjected the PNG coral sample to a pyrolysis technique that leaves an organic-rich residue (Haynes et al. 1966). ^{14}C measurements determined from paired carbonate and organic material form the foundation for most of what we know about ^{14}C reservoir ages in the South Pacific (Petchey et al. 2004, 2005, 2008, 2009). These values rely on careful screening to insure that the carbonate and organic components are coeval (Ascough et al. 2005). Although our focus is on paired U/Th and inorganic ^{14}C measurements, we describe the pyrolysis method and a preliminary result in the hopes that this approach can find broader application where only ^{14}C measurements are available.

The pyrolysis procedure is as follows: (1) the sample was gently crushed and sieved; (2) about 20 g of sieved sample was placed in a Vycor[®] pyrolysis tube and evacuated; (3) the tube with sample was heated to 610°C for about 1 hr to polymerize the organic carbon; (4) after cooling the sample was removed and acidified with HCl; (5) the solution was then rinsed repeatedly until neutral, and centrifuged to isolate the residue; (6) at which point the residue was dried in an oven. The dried residue was combusted to produce CO_2 and reduced to graphite for AMS analysis.

Table 2 Radiocarbon and ^{230}Th ages before present (BP) and ^{14}C reservoir ages.

Sample ID	Site	Type	$\delta^{13}\text{C}$ (‰) ^a	^{14}C age (^{14}C yr BP) ^b	^{230}Th age (cal BP) ^c	^{230}Th age (^{14}C yr BP) ^d	Reservoir age (R) (^{14}C yr BP) ^e
AA42088	Rendova Island, Sol. Is.	surface	-1.3	799 ± 28	343.0 ± 2.0	395 ± 8	404 ± 29
AA42089	Rendova Island, Sol. Is.	surface	-0.6	738 ± 38	343.0 ± 1.4	395 ± 8	343 ± 39
AA42091	Rendova Island, Sol. Is.	surface	-0.6	7340 ± 59	7941 ± 42	7142 ± 54	198 ± 80
AA42092	Rendova Island, Sol. Is.	surface	-0.3	1436 ± 39	891.0 ± 1.8	972 ± 9	464 ± 40
AA42100	Tetepare Island, Sol. Is.	surface	-0.7	8177 ± 54	9295 ± 32	8330 ± 35	-153 ± 64
AA42101	Tetepare Island, Sol. Is.	surface	0.0	5353 ± 66	6607 ± 26	5823 ± 12	-470 ± 69
AA42108	Rendova Island, Sol. Is.	core	-1.7	6833 ± 37	7518 ± 26	6678 ± 29	156 ± 64
AA42109	Rendova Island, Sol. Is.	core	-2.4	2532 ± 70	2087 ± 10	2153 ± 14	380 ± 71
AA42110	Rendova Island, Sol. Is.	core	-2.3	8688 ± 60	9398 ± 36	8413 ± 26	276 ± 65
AA42112	Rendova Island, Sol. Is.	core	-0.6	2549 ± 42	2284 ± 11	2223 ± 16	327 ± 45
AA42115	Rendova Island, Sol. Is.	core	-1.0	2816 ± 52	2785 ± 28	2735 ± 35	81 ± 63
AA42116	Rendova Island, Sol. Is.	core	0.9	3399 ± 46	3085 ± 18	2983 ± 26	417 ± 53
AA42117	Rendova Island, Sol. Is.	core	-0.8	3955 ± 45	4753 ± 19	4185 ± 35	-230 ± 57
AA42122	Rendova Island, Sol. Is.	core	3.1	5763 ± 59	5478 ± 186	4798 ± 126	966 ± 139
AA42139	Tasmaloum Is., Vanuatu	surface	0.6	4699 ± 66	5007 ± 19	4463 ± 21	237 ± 69
AA21140	Tasmaloum Is., Vanuatu	surface	-0.2	4638 ± 46	5300 ± 20	4615 ± 48	23 ± 66
AA21141	Tasmaloum Is., Vanuatu	surface	0.0	5461 ± 52	6121 ± 18	5363 ± 26	99 ± 58

^a $\delta^{13}\text{C}$ measurements were performed using a conventional isotope ratio mass spectrometer.

^bBefore present (AD 1950). A ^{14}C yr is calculated as $-8033\ln F$ and implies a half-life of 5568 yr (Donahue et al. 1990). Uncertainties are 1σ .

^cU/Th ages cal BP. Uncertainties are 2σ .

^dCalendar ages converted graphically to ^{14}C yr using the SHCal13 data set. Uncertainties are 1σ .

^eThe reservoir age, $R(t)$ = the ^{14}C age of coral - ^{14}C age of the contemporaneous atmosphere. The ^{14}C age of the atmosphere is taken as the ^{230}Th age of the coral converted to ^{14}C yr. Uncertainties are propagated for both the ^{14}C and ^{230}Th ages and are quoted at 1σ .

RESULTS

The ^{14}C ages and calculated ^{14}C reservoir ages are given in Table 2. We quote these values in ^{14}C years by definition. Since we report both ^{14}C and calendar ages, we use “BP” alone to signify calendar years before present (AD 1950) and “ ^{14}C yr BP” to signify ^{14}C years before present. The ^{14}C values for the corals were taken to be representative of the surface ocean at the time the coral

grew. We assumed that the ^{230}Th ages were equivalent to calendar ages, within the uncertainties of the measurements. In order to compute ^{14}C reservoir ages, the ^{230}Th dates ($\pm 2\sigma$) were converted to ^{14}C yr BP following the reverse of the procedure normally used to convert ^{14}C dates to calendar dates (atmospheric ^{14}C age). This was performed graphically using the SHCal13 data set, appropriate for the Southern Hemisphere (Hogg et al. 2013). This procedure yielded a range of possible ^{14}C dates and the median was taken as the contemporary ^{14}C age of the atmosphere for a particular sample. The calculated range was assumed to represent a $\pm 2\sigma$ variance. Once the ^{230}Th ages were converted to ^{14}C yr, the reservoir effect R , was calculated as

$$R(\text{location, time}) = \text{marine } ^{14}\text{C age} - \text{contemporaneous atmospheric } ^{14}\text{C age} \quad (1)$$

Uncertainties in R include both analytical uncertainties and uncertainties in the ^{14}C calibration curve. All of the sites are from low-lying islands and we expect that any recrystallization of the corals would incorporate relatively modern carbon from seawater or groundwater. Hence, we interpret negative ^{14}C reservoir ages (or those within 1σ of zero) as evidence of postdepositional carbon exchange. This was especially prevalent among surface samples (4 of 9 total). The corals that were sampled by drilling were less affected (2 of 8 total), but not immune to postdepositional alteration.

Pyrolysis

The carbonate age determined for the PNG sample (AA30268) = $10,952 \pm 60$ ^{14}C yr, with a $\delta^{13}\text{C}$ value of -2.1% . The organic residue age of the sample (AA104395) = 9076 ± 53 ^{14}C yr, with a $\delta^{13}\text{C}$ value of -21.0% . The starting weight of the coral was 24.24 g. This produced a residue of 49 mg after acidification, and when combusted the residue was found to contain 1.12 mg of carbon.

DISCUSSION

As a starting point for understanding marine ^{14}C reservoir ages in the South Pacific, we can say that at any given time the surface ocean can be remarkably uniform over large regions. For example, Burr et al. (2009) compiled results from corals and sponges from the 1940s and 1950s to calculate an average ^{14}C reservoir effect for the Western Equatorial Pacific of 322.1 ± 8.6 ^{14}C yr (2σ). The low variance of this value is impressive, given the fact that the samples included in the average were collected and measured independently by several groups. Western Equatorial Pacific sites included the Solomon Islands (Guilderson et al. 2004; Schmidt et al. 2004), Vanuatu (Fallon et al. 2003; Burr et al. 2009), and Papua New Guinea (Burr et al. 2009). A ^{14}C reservoir age gradient was observed from east to west across the Equatorial South Pacific, following the South Equatorial Current (Figure 2). This surface current carries relatively ^{14}C -depleted water from the east towards the west. The highest ^{14}C reservoir ages identified for the Equatorial Pacific are found in the east, from the Galapagos Islands (450 ± 16 ^{14}C yr, 2σ), where active upwelling occurs (Druffel 1981). Intermediate values were observed in the central South Pacific, with an average ^{14}C reservoir age of 361 ± 8.2 ^{14}C yr (2σ).

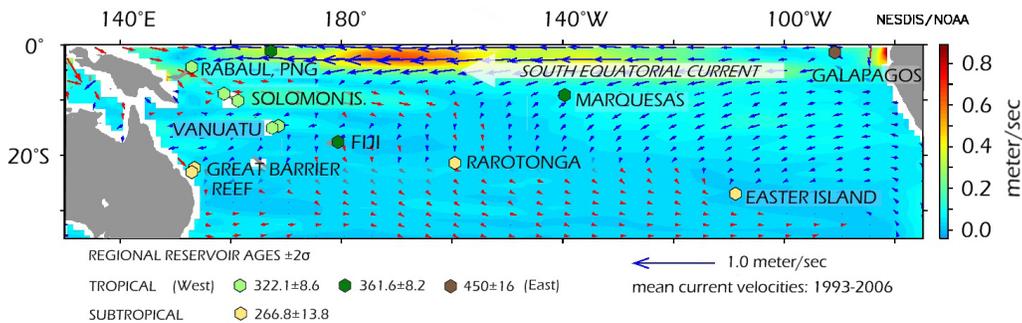


Figure 2 Summary plot of 1940s and 1950s ^{14}C reservoir ages determined from corals showing average surface currents in the South Pacific (Bonjean and Lagerloef 2002). Reproduced from Burr et al. (2009); data sources given in the text.

These sites include Nauru (Guilderson et al. 1998), Fiji (Toggweiler et al. 1991), and the Marquesas (Burr et al. 2009). The lowest ^{14}C reservoir ages were found within the subtropical gyre, far from the influence of upwelling (Figure 5). Subtropical sites included the Great Barrier Reef (Druffel and Griffin 1993, 1995, 1999), Rarotonga (Guilderson et al. 2000), and Easter Island (Burr et al. 2009).

McGregor et al. (2008) used paired U/Th and ^{14}C measurements to study Holocene changes in the ^{14}C reservoir effect on the north coast of Papua New Guinea. They identified a reduced reservoir age of 185 ± 30 ^{14}C yr from 7220–5850 BP, as compared to a modern value of 420 ^{14}C yr. They attributed this change to a northerly displacement of the Intertropical Convergence Zone, which strengthened tradewinds at that time, enhancing air-sea gas exchange and lowering the reservoir age. They suggested that an increase in El Niño activity from 5850 to 5420 BP facilitated a return to more modern reservoir age values. The results of McGregor et al. (2008), recalculated with the SHCal13 database, are plotted alongside our reservoir age results in Figure 3. For the limited number of points available, the results show reasonable consistency. The main features of this plot are the very large change in reservoir age around 5000–6000 BP, a period of low reservoir ages around 7000 BP, and relatively stable values since at least 3000 BP. The large increase in reservoir age at 5000–6000 BP is ~ 800 ^{14}C yr, and occurred within 500 calendar years. Holocene reservoir age variations of this magnitude are not known to occur in the Equatorial Pacific, but have been reported during the Late Pleistocene (Paterne et al. 2004). Reservoir ages as high as 1290 ^{14}C yr have been reported from coastal Peru in the early to mid-Holocene, where active coastal upwelling occurs (Fontugne et al. 2004). The low values observed in our data around 7000 BP are consistent with the results of McGregor et al. (2008), and stable reservoir ages for the past several thousand years agree with the findings of Petchey et al. (2009) and Petchey and Ulm (2012).

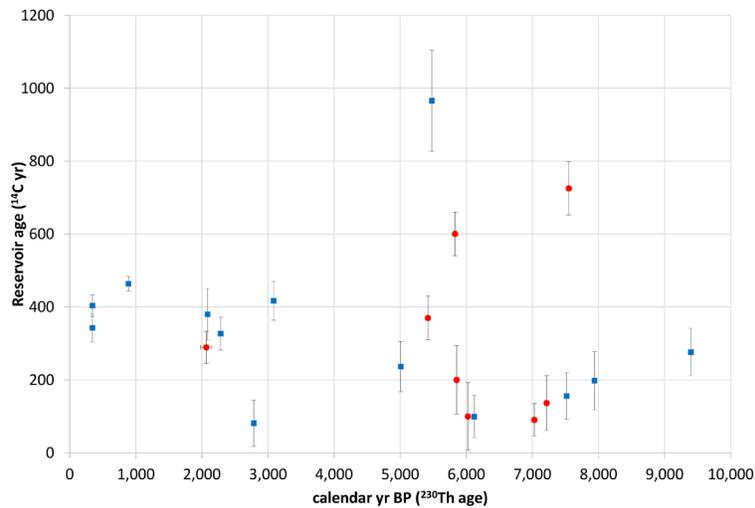


Figure 3 Southwest Pacific ^{14}C reservoir ages from paired U/Th and ^{14}C measurements on coral. Reservoir ages from McGregor et al. (2008) were recalculated with the SHCal13 data set, using the procedure described in the text. Their ^{14}C ages were an average of conventional and AMS results, where both were reported. McGregor et al. data are shown as red circles; results from this study are shown as blue squares. All results are plotted with 1σ error bars.

The rate of change of the ^{14}C reservoir age is controlled by horizontal advection and vertical mixing processes. This was shown by Druffel and Griffin (1993, 1999) for corals from the Great Barrier Reef. They produced the longest continuous South Pacific ^{14}C record currently available, from a

coral that grew on Abraham Reef (22°S, 153°E). The Abraham Reef results are complemented by a second record from Heron Island (23°S, 152°E). Taken together, these records trace South Pacific ^{14}C variability since AD 1635. Their data set is shown in Figure 4, recalculated as reservoir ages using the method described above (SHCal13 data set). The Great Barrier Reef values show a persistent change in the ^{14}C reservoir age on a timescale of decades. During the 18th century, for example, the reservoir age dropped by about 200 ^{14}C yr (Figure 4). Superimposed on this trend are very rapid changes, with a frequency of a few years. These can exceed 100 ^{14}C yr in amplitude, as is observed in the late 17th century by a sharp decrease and subsequent increase of ~ 150 ^{14}C yr within ten calendar yr. This trend is also observed further south, in the Tasman Sea, from paired U/Th and ^{14}C measurements of black corals that lived from AD 1910 to 1960 (Komugabe et al. 2014).

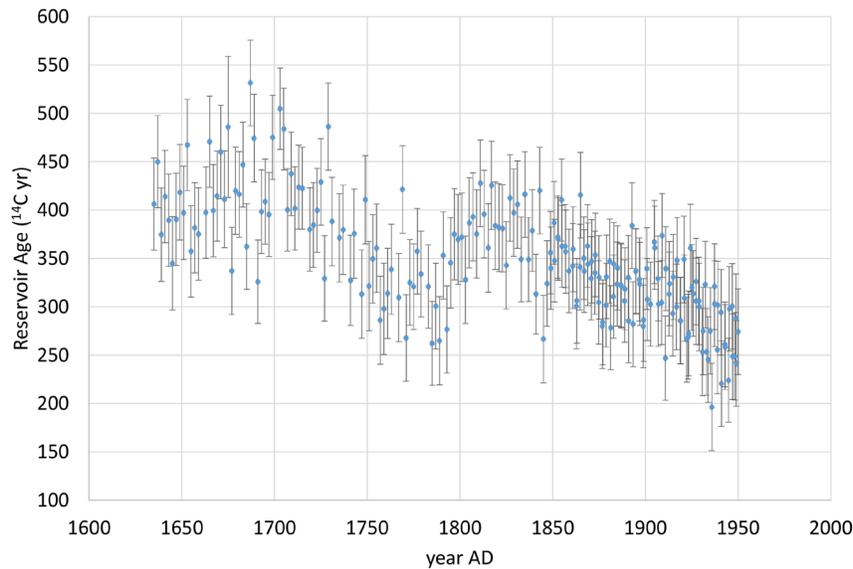


Figure 4 Radiocarbon reservoir ages calculated from ^{14}C records from Abraham Reef and Heron Island, Australia (data from Druffel and Griffin 1993, 1999). Errors are 1σ . Reservoir ages were calculated with the SHCal13 data set.

Other continuous records have been published for the Central Equatorial Pacific by Zaunbrecher et al. (2010), using a number of annualized time series that reach back to about AD 940. Their study adopted the same strategy employed here, with paired ^{230}Th dates and ^{14}C measurements for corals from Christmas Island (2°N, 157°W) and Palmyra Island (6°N, 162°W). Their data show a gradual reduction of the ^{14}C reservoir age from about 480 ^{14}C yr in the 10th century to a recent value of about 300 ^{14}C yr. As with the Great Barrier Reef data, they also observe substantial reservoir age changes that occur on a timescale of years. For example, at Palmyra Island, in the 13th century the ^{14}C reservoir age decreased by about 120 ^{14}C yr over a 10-yr period (AD 1240–1250), and then rapidly increased by 180 ^{14}C yr a few decades later (AD 1280–1290). Zaunbrecher et al. (2010) also documented significant seasonal variability in the reservoir effect that can exceed 100 ^{14}C yr.

There are two factors that should be kept in mind with regard to the ^{14}C reservoir age results presented here. The first is postdepositional alteration. Corals that are exposed to water at the surface are susceptible to recrystallization that can involve significant exchange with modern carbon. We attempted to mitigate this problem by the use of selective dissolution, but 4 of 9 surface samples produced negative reservoir ages, and 2 of 8 core samples were also affected. However, the addition

of modern carbon can only lower reservoir ages, and cannot explain elevated values. Hence, we have no reason to doubt the large mid-Holocene variability observed in Figure 3. A second factor is the local environment in which the coral lived. We know that our corals grew at, or near, sea level when they were alive, but we do not know if they were lagoonal, part of a fringing reef, or part of a patch reef surrounded by deep water. However, a study of hardwater lagoonal effects on reservoir age (Petchey and Clark 2011) suggests that such changes in local environment should be minimal. Expanding the number of sites across the South Pacific to achieve a consensus picture of temporal ^{14}C reservoir age variations as described here would solve both of these issues.

CONCLUSIONS

Holocene ^{14}C reservoir ages for the Southwest Pacific are seen to vary on subannual, multiannual, and decadal timescales. The largest deviations we observe occur during the mid-Holocene, as reflected in corals from Papua New Guinea and the Solomon Islands. A period of lower ^{14}C reservoir ages is seen around 7000 BP, in accord with the observations of McGregor et al. (2008). Stable ^{14}C reservoir ages are observed for the past several thousand years. Corals offer the possibility of constructing a marine calibration curve for the Holocene that would be independent of model calculations.

ACKNOWLEDGMENTS

We thank the native population of Vanuatu and the Solomon Islands who welcomed us during the sampling of the corals studied here. We thank Michael Rahe in particular for his efforts in drilling the Rendova Island cores. We wish to acknowledge the support of the National Science Foundation towards drilling and sampling: ESH -OCE-9503256 and OCE0202549. U-Th dating was supported by the Taiwan Ministry of Science and Technology (MOST) (103-2119-M-002-022).

REFERENCES

- Ascough P, Cook G, Dugmore A. 2005. Methodological approaches to determining the marine radiocarbon reservoir effect. *Progress in Physical Geography* 29(4):532–47.
- Bonjean F, Lagerloef GSE. 2002. Diagnostic model and analysis of the surface currents in the Tropical Pacific Ocean. *Journal of Physical Oceanography* 32(10):2938–54.
- Burr GS, Jull AJT. 2010. Accelerator mass spectrometry for radiocarbon research. In: Beauchemin D, Matthews DE, editors. *The Encyclopedia of Mass Spectrometry Volume 5, Elemental and Isotope Ratio Mass Spectrometry*. Amsterdam: Elsevier. p 656–69.
- 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 JW, Corrège T, Cabioch G, Taylor FW, Donahue DJ. 2009. Modern and Pleistocene reservoir ages inferred from South Pacific corals. *Radiocarbon* 51(1):319–35.
- Cheng H, Edwards RL, Shen C-C, Polyak VJ, Asmerom Y, Woodhead J, Hellstrom J, Wang YJ, Kong XG, Spötl C, Wang XF, Alexander EC. 2013. Improvements in ^{230}Th dating, ^{230}Th and ^{234}U half-life values, and U-Th isotopic measurements by multi-collector inductively coupled plasma mass spectrometry. *Earth and Planetary Science Letters* 371–372:82–91.
- Donahue DJ, Linick TW, Jull AJT. 1990. Isotope-ratio and background corrections for accelerator mass spectrometry radiocarbon measurements. *Radiocarbon* 32(2):135–42.
- Druffel EM. 1981. Radiocarbon in annual coral rings from the eastern tropical Pacific. *Geophysical Research Letters* 8(1):59–62.
- Druffel ERM, Griffin S. 1993. Large variations of surface ocean radiocarbon: evidence of circulation changes in the Southwestern Pacific. *Journal of Geophysical Research* 98(C11):20,249–59.
- Druffel ERM, Griffin S. 1995. Regional variability of surface ocean radiocarbon from southern Great Barrier Reef corals. *Radiocarbon* 37(2):517–24.
- Druffel ERM, Griffin S. 1999. Variability of surface ocean radiocarbon and stable isotopes in the southwestern Pacific. *Journal of Geophysical Research* 104(C10):23,607–13.
- Druffel EM, Linick TW. 1978. Radiocarbon in annual coral rings of Florida. *Geophysical Research Letters* 5(11):913–6.
- Fallon SJ, Guilderson TP, Caldeira K. 2003. Carbon isotope constraints on vertical mixing and air-sea CO_2 exchange. *Geophysical Research Letters* 30(24):2289, doi:10.1029/2003GL018049.
- Fontugne M, Carré M, Bentaleb I, Julien M, Lavallée D. 2004. Radiocarbon reservoir age variations in the south Peruvian upwelling during the Holocene. *Radiocarbon* 46(2):531–7.

- Guilderson TP, Schrag DP, Kashgarian M, Southon J. 1998. Radiocarbon variability in the western equatorial Pacific inferred from a high-resolution coral record from Nauru Island. *Journal of Geophysical Research – Oceans* 103(C11):24,641–50.
- Guilderson TP, Schrag DP, Goddard E, Kashgarian M, Wellington GM, Linsley BK. 2000. Southwest subtropical Pacific surface water radiocarbon in a high-resolution coral record. *Radiocarbon* 42(2):249–56.
- Guilderson TP, Schrag DP, Cane MA. 2004. Surface water mixing in the Solomon Sea as documented by a high-resolution coral ^{14}C record. *Journal of Climate* 17(5):1147–56.
- Haynes CV Jr, Damon PE, Grey DC. 1966. Arizona radiocarbon dates VI. *Radiocarbon* 8:1–21.
- Heiss GA, Dullo W-C, Joachimski MM, Reijmer JJG, Schuhmacher H. 1999. Increased seasonality in the Gulf of Aqaba, Red Sea, recorded in the oxygen isotope record of a *Porites lutea* coral. *Senckenbergiana Maritima* 30(1–2):17–26.
- Hogg AG, Hua Q, Blackwell PG, Niu M, Buck CE, Guilderson TP, Heaton TJ, Palmer JG, Reimer PJ, Reimer RW, Turney CSM, Zimmerman SRH. 2013. SHCal13 Southern Hemisphere calibration, 0–50,000 years cal BP. *Radiocarbon* 55(4):1889–903.
- Jaffey AH, Flynn KF, Glendenin LE, Bentley WC, Essling AM. 1971. Precision measurement of half-lives and specific activities of ^{235}U and ^{238}U . *Physical Review C* 4(5):1889–906.
- Komugabe AF, Fallon SJ, Thresher RE, Eggins SM. 2014. Sea surface reservoir ages from deep-sea black corals. *Deep-Sea Research II* 99:207–12.
- Mann P, Taylor FW, Lagoe MB, Quarles A, Burr G. 1998. Accelerating late Quaternary uplift of the New Georgia Island Group (Solomon island arc) in response to subduction of the recently active Woodlark spreading center and Coleman seamount. *Tectonophysics* 295(3–4):259–306.
- McGregor HV, Gagan MK, McCulloch MT, Hodge E, Mortimer G. 2008. Mid-Holocene variability in the marine ^{14}C reservoir age for northern coastal Papua New Guinea. *Quaternary Geochronology* 3(3):213–25.
- Nozaki Y, Rye DM, Turekian KK, Dodge RE. 1978. ^{13}C and ^{14}C variations in a Bermuda coral. *Geophysical Research* 5:825–8.
- Paterne M, Ayliffe LK, Arnold M, Cabioch G, Tisnerat-Laborde N, Hatté C, Douville E, Bard E. 2004. Paired ^{14}C and $^{230}\text{Th}/\text{U}$ dating of surface corals from the Marquesas and Vanuatu (sub-equatorial Pacific) in the 3000 to 15,000 cal yr interval. *Radiocarbon* 46(2):551–66.
- Petchev F, Clark G. 2011. Tongatapu hardwater: investigation into the ^{14}C marine reservoir offset in lagoon, reef and open ocean environments of a limestone island. *Quaternary Geochronology* 6(6):539–49.
- Petchev F, Ulm S. 2012. Marine reservoir variation in the Bismarck region: an evaluation of spatial and temporal change in ΔR and R over the last 3000 years. *Radiocarbon* 54(1):45–58.
- Petchev F, Phelan M, White P. 2004. New ΔR values for the southwest Pacific Ocean. *Radiocarbon* 46(2):1005–14.
- Petchev F, Green R, Jones M, Phelan M. 2005. A local marine reservoir correction value (ΔR) for Watom Island, Papua New Guinea. *New Zealand Journal of Archaeology* 26:29–40.
- Petchev F, Anderson A, Zondervan A, Ulm S, Hogg A. 2008. New marine ΔR values for the South Pacific Subtropical Gyre region. *Radiocarbon* 50(3):373–97.
- Petchev F, Allen MS, Addison D, Anderson A. 2009. Stability in the South Pacific surface marine ^{14}C reservoir over the last 750 years: evidence from American Samoa, the southern Cook Islands and the Marquesas. *Journal of Archaeological Science* 36(10):2234–43.
- Schmidt A, Burr GS, Taylor FW, O'Malley J, Beck JW. 2004. A semiannual radiocarbon record of a modern coral from the Solomon Islands. *Nuclear Instruments and Methods in Physics Research B* 223–224:420–7.
- Shen C-C, Cheng H, Edwards RL, Moran SB, Edmonds HN, Hoff JA, Thomas RB. 2003. Measurement of attogram quantities of ^{231}Pa in dissolved and particulate fractions of seawater by isotope dilution thermal ionization mass spectroscopy. *Analytical Chemistry* 75(5):1075–9.
- Shen C-C, Li K-S, Sieh K, Natawidjaja D, Cheng H, Wang X, Edwards RL, Lam DD, Hsieh Y-T, Fan T-Y, Meltzner AJ, Taylor FW, Quinn TM, Chiang H-W, Kilbourne KH. 2008. Variation of initial $^{230}\text{Th}/^{232}\text{Th}$ and limits of high precision U-Th dating of shallow-water corals. *Geochimica et Cosmochimica Acta* 72(17):4201–23.
- Shen C-C, Wu C-C, Cheng H, Edwards RL, Hsieh Y-T, Gallet S, Chang C-C, Li T-Y, Lam DD, Kano A, Hori M, Spotl C. 2012. High-precision and high-resolution carbonate ^{230}Th dating by MC-ICP-MS with SEM protocols. *Geochimica et Cosmochimica Acta* 99:71–86.
- Taylor FW, Mann P, Bevis MG, Edwards RL, Cheng Hai, Cutler KB, Gray, SC, Burr GS, Beck JW, Phillips DA, Cabioch G, Récy J. 2005. Rapid feature uplift and subsidence caused by impinging bathymetric features: examples from New Hebrides and Solomon Arcs. *Tectonics* 24(6):TC6005.
- Toggweiler JR, Dixon K, Broecker WS. 1991. The Peru upwelling and the ventilation of the South Pacific thermocline. *Journal of Geophysical Research* 96(C11):20,467–97.
- Yu K, Hua Q, Zhao J-X, Hodge E, Fink D, Barbetti M. 2010. Holocene marine ^{14}C reservoir age variability: evidence from ^{230}Th -dated corals in the South China Sea. *Paleoceanography* 25:PA3205.
- Zaunbrecher LK, Cobb KM, Beck JW, Charles CD, Druffel ERM, Fairbanks RG, Griffin S, Sayani HR. 2010. Coral records of central tropical Pacific radiocarbon variability during the last millennium. *Paleoceanography* 25:PA4212.