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Lal, D Gallup, C D Somayajulu, BLK et al.

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Records of cosmogenic radionuclides ¹⁰Be, ²⁶Al and ³⁶Cl in corals: First studies on coral erosion rates and potential of dating very old corals

Devendra Lal, ^{1,*} Christina D. Gallup, ² Bhamdipati L. K. Somayajulu, ³ Loïc Vacher, ¹ Mark W. Caffee, ⁴ Anthony J. T. Jull, ⁵ Robert C. Finkel, ⁶ Robert C. Speed, ^{7,†} and Amos Winter ⁸

Scripps Institution of Oceanography, Geosciences Research Division, La Jolla, CA 92093, USA
 Department of Geological Sciences and Large Lakes Observatory, University of Minnesota Duluth, *Duluth, MN 55812, USA
 Physical Research Laboratory, Navrangpura, Ahmedabad, 380 009, India
 PRIME Lab, Purdue University, 525 Northwestern Avenue, West Lafayette, IN 47907-2036, USA
 NSF Arizona Accelerator Mass Spectrometer Laboratory, Department of Geosciences, University of Arizona, Tucson, AZ 85721, USA
 Center for Accelerator Mass Spectrometry, Lawrence Livermore National Laboratory, Livermore, CA 94550, USA
 Department of Earth System Science, University of California, Irvine, CA 92697, USA
 Department of Marine Sciences, University of Puerto Rico, Mayaguez, 00680, Puerto Rico

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Abstract—We present results of measurements of cosmogenic ¹⁰Be, ²⁶Al and ³⁶Cl, and the indigenous (intrinsic) concentrations of the stable elements Be, Al and Cl in 120–200 kyr old corals from Barbados and Puerto Rico. The concentration levels of these radionuclides in the corals lie in the range 10⁴ to 10⁸ atoms/g. A comparison of the measured nuclide concentrations with those expected to be produced in the corals by nuclear interactions of energetic cosmic radiation shows that (i) the radionuclides ²⁶Al and ³⁶Cl are derived from in situ cosmic ray interactions in the corals after their formation, but that (ii) the radionuclide ¹⁰Be owes its provenance in the coralline lattice primarily due to incorporation of dissolved beryllium in seawater in the lattice structure of the corals. *Copyright* © 2005 Elsevier Ltd

We discuss production rates and potential uses of cosmogenic radionuclides in corals and the implications of the measurements reported here on the concentration of the cosmogenic radionuclides $^{10}\text{Be},\,^{26}\text{Al}$ and $^{36}\text{Cl}.$ We show that the latter two radionuclides serve as gauges of coral terrace erosion rates, whereas the cosmogenic ^{10}Be is suitable for determining the ages of old corals, of ages exceeding a few million years, up to $\sim\!10$ myr. The erosion rates of the corals range from 0.7 to 5 \times 10^{-3} cm/yr, corresponding to an appreciable surface loss after aerial exposure: 1–3 m since the last interglacial and $\sim\!8$ m since the penultimate interglacial.

1. INTRODUCTION

Corals serve as unique archives of past chemical history of the oceans, past seawater temperatures, and sea levels. They serve as high resolution recorders of paleoenvironments. Trace element (e.g., Sr, Ba, Cd, Mn) concentrations and isotopic ratios, δ ¹⁸O, δ ¹³C, in surface waters (Fairbanks and Dodge, 1979; Shen et al., 1992; Schrag, 1999) have been used to infer valuable "related" and "independent" information on climatic changes in the past millennium (Beck et al., 1992; Shen et al., 1992). An interesting application of coral studies has been to study the effect of the ENSO system of the tropical ocean, which governs global climatic changes (Cole et al., 1993; Druffel, 1997; Cobb et al., 2003). Corals also provide information on sea level changes (Gallup et al., 1994; Cutler et al., 2003) and yield valuable information on the effect of changes in sea level on marine trace element chemistry (Stoll and Schrag, 1998).

For each of the applications listed above, coral stratigraphy is relevant and dating is critical. Coral stratigraphy results in part from the zonation of species with water depth in coral reefs. In the Caribbean, this zonation is well documented (Goreau, 1959) and has been used to infer original water depth of ancient coral reefs drowned due to sea level rise (Fairbanks, 1989) or uplifted by tectonic uplift (Matthews, 1973). The stratigraphy of uplifted coral terraces also results from the effects of sea level change, tectonic uplift, and erosion. Sea level studies aim to unravel these effects to isolate the sea level record and thus require a well documented and understood stratigraphy.

Uranium-series methods are the primary resource for dating corals. The methods rely on the disequilibrium between parent and daughter isotopes (²³⁸U: ²³⁴U and ²³⁰Th; ²³⁵U: ²³¹Pa), where ²³⁰Th/²³⁸U and ²³¹Pa/²³⁵U activities start at zero in the coral skeleton and increase to secular equilibrium values with time and ²³⁴U/²³⁸U activity starts above secular equilibrium and decays back to secular equilibrium with time. The ingrowth of ²³⁰Th and ²³¹Pa provide chronometers, while the decay of ²³⁴U provides a check for closed-system behavior. ²³⁴U does not provide a third chronometer because, whereas the modern seawater ²³⁴U/²³⁸U activity is known (Chen et al., 1986), the past value is constrained but not known (Edwards et al., 2003). The shortcomings of U-series methods are the potential for open-system behavior during the diagenesis of the aragonitic coral skeleton and the limited time range of application. In principal, corals can be dated to ~600,000 yr (Stirling et al., 2001) but, in practice, diagenesis often limits application to the last \sim 200,000 yr. Identifying corals that have remained a closed system, and thus have reliable ages, involves 1) screening samples for alteration to calcite, 2) cross checking the ²³⁰Th (and ²³¹Pa where available) ages with the amount of

^{*} Author to whom correspondence should be addressed (dlal@ucsd.edu).

[†] Deceased.

Table 1. Expected in situ production rates of long-lived cosmogenic radionuclides in corals at sea level (geomagnetic latitudes ${\geq}60^{\circ}$), arranged in order of decreasing half-lives.

Radionuclide	Half-life	Principal target element in coral	Nuclide production rate (references) ^b (atoms/g coral/y)
¹⁰ Be	1.5 my	Oxygen, carbon	8.1 (1,2)
²⁶ Al	0.7 my	Calcium	$\sim 0.55 (2)$
³⁶ Cl	0.3 my	Calcium	21.6 (3,4)
¹⁴ C	5730 y	Oxygen	16 (2,5)
³⁹ Ar	269 y	Calcium	~30 (2)
³² Si	~150 y	Calcium	$\sim 1.0 (2)$

^a The list excludes ⁴¹Ca and ³⁸Ar, which may find useful applications as cosmogenic tracers.

²³⁴U decay, and 3) checking for stratigraphic consistency within an outcrop (e.g., Gallup et al., 2002).

In this paper we present results of our studies of the cosmogenic radionuclides ¹⁰Be, ²⁶Al and ³⁶Cl, and the concentrations of the stable elements Be, Al and Cl in U-series dated corals from Barbados and Puerto Rico. Our results augment the records contained in fossil corals. The primary goal of this study is to determine the usefulness of cosmogenic radionuclides to ascertain erosion rates and ages of coral reef terraces. Accurate assessment of erosion rates is expected to result in improved stratigraphy in sites where fossil corals have been collected for sea level studies. To date, there exist no radiometric methods of dating corals older than ~600,000 yr. A by-product of our studies is the realization that the coral ¹⁰Be/ ⁹Be ratio has the potential to serve as a chronometer for determining the ages of "old" (3–10 myr) corals.

2. PRODUCTION RATES OF USEFUL COSMOGENIC RADIONUCLIDES IN CORALS

Long-lived radionuclides expected to be produced in corals in easily measurable amounts are listed in Table 1, along with their estimated production rates. Table 1 lists the production rates at sea level, and geomagnetic latitudes, $\geq 60^{\circ}$. For 10 Be and 26 Al, the scaling factors for other altitudes and latitudes can be obtained by using the scaling factors given by Lal (1991). For 36 Cl altitude scaling, especially for altitudes below sea

level, one has to take into account the changes in the flux of slow muons (Stone et al., 1996, 1998; Heisinger et al., 2002); 36 Cl production rates can be estimated using these studies. The production rates of 10 Be, 26 Al and 36 Cl in corals at the respective latitude and altitude (Table 2) can be obtained by multiplying the nuclide production rates in Table 1 for latitudes \geq 60° by factors of 0.833, 0.795, 0.804 and 0.807 for PR-3B, NU1493, NU1494 and WANC-93-1, respectively.

As seen in Table 1, corals that contain the relatively high mass-number element Ca offer the possibility of studying a number of commonly studied cosmogenic radionuclides of mass number <40 (39 Ar, 36 Cl, 32 Si, 14 C, 26 Al, and 10 Be), with half-lives ranging between 1.5 × 10 2 to 1.5 × 10 6 yr. Not discussed in Table 2 are the radionuclide 41 Ca (expected to be produced by thermal neutron capture in Ca), and the stable nuclides, 3 He, 21 Ne and 38 Ar (expected to be produced in high energy neutron interactions with Ca), which may prove useful as tracers. By way of comparison, in quartz (SiO₂), a mineral commonly studied in geomorphology, three radionuclides, 14 C, 26 Al, and 10 Be, and two stable nuclides, 3 He and 21 Ne, are produced. Although numerous radionuclides are produced in corals, they are exposed at low altitudes, where cosmogenic production rates are low.

³⁹Ar and ³²Si offer the possibility of measuring coral erosion rates over short periods of time (< 500 yr), in situations where recent appreciable coral denudation may be expected. The in situ produced ¹⁴C offers the possibility of measuring erosion rates over the past 10,000 yr. It may seem that measurement of ¹⁴C will be foiled by the incorporation of dissolved ¹⁴C from seawater and the ubiquitous presence of organic matter in corals. However, in situ ¹⁴C forms mostly ¹⁴CO (Lal et al., 2000; Lal and Jull, 2001), making it possible to distinguish the in situ ¹⁴C from seawater ¹⁴C and organic matter ¹⁴C, which would be extracted in the form of ¹⁴CO₂ (Handwerger et al., 1999)

3. SAMPLES AND METHODS

We present measurements of 3 radionuclides, 10 Be, 26 Al and 36 Cl, in corals from Puerto Rico and Barbados. Puerto Rico has a stable coastline (in the Quaternary); one coral was collected from the exposed last interglacial reef, which grew $\sim 125,000$ yr ago when sea level was ~ 6 m higher than today. Barbados is an uplifting coastline; one coral was collected from the last interglacial terrace at ~ 70 m elevation and two corals were collected from the penultimate interglacial terrace, one

Table 2. Physical data on corals.

Sample	Location	Species	Elevation a.s.l. (m)	Coral age (kyr)	Sampling depth (cm)	Reference ^a
PR-3B	Puerto Rico substage 5e (18° 04.7′ N; 67° 53.5′ W)	Montastraea faveolata	4.1	127.5 ± 1.4	50	1, 2
NU-1493	West Barbados, Gays Cove (stage 5e) NU (13° 18.2′ N; 59° 35.3′ W)	Acropora palmata	70 ± 2	128 ± 2	9–12	3
NU-1494	West Barbados, Cave Hill substage 7.1, Wilcox (13° 8.4' N; 59° 37.9' W)	Acropora palmata	92 ± 2	190–200	6–10	3
WANC-93-1 (Wanstead-C)	S.E.Coast Barbados (13° 40.7′, 59° 37.7′ W)	Siderastrea	79	200 ± 1.5	Surface	4

^a 1: Winter et al. (2003); 2: Watanabe et al. (2002); 3: Speed and Cheng (2004); 4: Gallup et al. (1994).

^b 1: Nishiizumi et al. (1989); 2: present work; 3: Stone et al. (1996); 4: Stone et al. (1998); 5: Lal and Jull (1994).

¹⁰Be conc. (atoms/g) Intrinsic ¹⁰Be/⁹Be ratio Sample^a Sample weight (g) Intrinsic ⁹Be conc. (g/g) $6.47 \pm 0.08 \times 10^{-9}$ PR-3B 50.16 1.05×10^{-7} $4.55 \pm 0.06 \times 10^7$ 5.73×10^{-9} $2.76 \pm 0.07 \times 10^{-8}$ NU-1493a 26.80 $1.06 \pm 0.03 \times 10^{7}$ 8.52×10^{-9} $1.98\,\pm\,0.06\,\times\,10^{-8}$ NU-1493b $1.13 \pm 0.03 \times 10^{7}$ 54.53 8.52×10^{-9} $2.48 \pm 0.13 \times 10^{-8}$ NU-1493c 13.36 $1.41 \pm 0.07 \times 10^{7}$ 1.66×10^{-7} $9.30 \pm 0.11 \times 10^{-9}$ NU-1494a $1.03 \pm 0.01 \times 10^{8}$ 36.06 8.52×10^{-9} $2.13 \pm 0.20 \times 10^{-8}$ $1.21 \pm 0.11 \times 10^7$ NU-1494b 28.06 9.71×10^{-8} $5.88 \pm 0.08 \times 10^{-9}$ $3.82 \pm 0.05 \times 10^{7}$ WANC-93-1a 73.57 1.60×10^{-9} $2.42 \pm 0.17 \times 10^{-8}$ WANC-93-1b 14.00 $2.58 \pm 0.19 \times 10^{6}$ 2.71×10^{-9} WANC-93-1c 29.00 $2.31 \pm 0.09 \times 10^{6}$ $1.27 \pm 0.05 \times 10^{-8}$

Table 3. Measured ${}^{9}\text{Be}$ and ${}^{10}\text{Be}$ concentrations in coral samples. Statistical errors cited are 1σ values.

of which is from the reef crest at 92 m and the other from the fore-reef at 79 m. The physical data on the corals, including their locations, ages and sampling depths, are given in Table 2. Each of the corals was collected from the exposed horizontal surface of a coral terrace and oriented to show which direction was up. Each of the samples is also quite large, extending 6-70 cm below the exposed surface: sample PR-3B from Puerto Rico is a drill core taken from a large head coral and the Barbados samples were taken with a hammer and chisel from the tops of road cuts into coral terraces. The ages of PR-3B (Winter et al., 2003) and NU-1493 are from U-Th ages of the samples themselves; the comparison of the ²³⁰Th ages with the ²³⁴U/²³⁸U activities shows only minimal evidence for open system behavior, suggesting that the ages are accurate to within a few thousand years (e.g., Gallup et al., 1994; Thompson and Goldstein, 2005). Samples NU-1494 and WAN-C-93-1 have not been dated directly by U-Th methods; the ages are inferred from reliable dates from corals within the same terrace complex (Gallup et al., 1994).

Although the ages of formation of corals are known (Table 2), the duration of their free exposure (unshielded by seawater) to cosmic radiation are not known precisely. We can however estimate plausible durations of free exposure for the corals studied based on sea level chronology. The last interglacial corals were submerged until sea level fell at the end of MIS 5e. The best estimate for the end of the last interglacial high sea level stand of \sim + 6 m comes from Australia (Stirling et al., 1998), where there is evidence that coral growth continued, though not robustly, until 116 \pm 1 ka. The best evidence for sea level drop after this comes from Barbados, where a coral grew 20 m below modern sea level at 113.1 ± 0.7 kyr (Cutler et al., 2003). Therefore, PR-3B and NU-1493 have been exposed to cosmic radiation since they emerged between 112 and 117 ka ago (114.5 \pm 2.5 kyr). The emergence of the penultimate interglacial corals is constrained by the youngest penultimate interglacial coral, which is recorded by a Barbados coral as 191.7 ± 1.6 kyr (Edwards et al., 1997), and the drop from the high stand of -6 to 9 m to below -18 m by 189.7 ± 1.5 kyr, as recorded by a Bahamian speleothem (Bard et al., 2002). Therefore, NU-1494 and WANC-93-1 have been exposed to cosmic radiation since between 193.3 and 188.2 kyr (190.8 \pm 2.5 kyr).

X-ray diffraction studies by Winter et al. (2003) show that PR-3B aragonite has undergone little or no diagenesis. Our studies of NU-1493 also show essentially no diagenesis. However, NU-1494 and WANC-93-1 show considerable diagenesis effects, $\sim\!20\%$ and $\sim\!80\%$ (\pm 5%) calcite in the two cases, respectively.

Subsamples for radionuclide measurements of 20–100 g were taken with a stainless steel chisel. They were taken from the portions of the coral exhibiting the cleanest looking coral skeleton, away from the generally dirty exposed surface portion. The depth(s) of each subsample below the exposed surface are given in Table 2. The coral samples were first ground to 100 micron size using a titanium mortar. The samples were washed to remove adhering fine dust. Samples were cleansed of detrital materials using the procedures discussed earlier (Dong et al., 2001). ~15%–20% of the sample was then slowly dissolved using 5%–10% nitric acid in large volumes of water to remove any adsorbed Be and Al. The dried coral powder was then processed for AMS measurement of ¹⁰Be, ²⁶Al and ³⁶Cl using standard radiochemical procedures (¹⁰Be: Gu et al., 1996; ²⁶Al: Kohl and Nishiizumi, 1992; ³⁶Cl: Stone et al., 1996). The concentrations of ¹⁰Be

were measured at the NSF AMS Facility at the University of Arizona at Tucson; those of ²⁶Al and ³⁶Cl were measured at the Center for Accelerator Mass Spectrometry, Lawrence Livermore National Laboratory at Livermore.

We expect that the cleansing procedure should effectively remove any adhering detrital particles in the coralline matrix, and also desorb garden variety ¹⁰Be, ²⁶Al and ³⁶Cl. One would expect that the surfaces where the garden variety ¹⁰Be and ²⁶Al are adsorbed would also be easily accessible to acid dissolution. This follows from consideration of the facts that Be and Al are very particle active, and they would be adsorbed on outer surfaces of grains during percolation of meteoric waters. If this is a reasonable expectation, we should be able to effectively cleanse the corals of garden variety ¹⁰Be and ²⁶Al. We do not expect any problem with meteoric ³⁶Cl, as it should easily get removed during washing of the coralline matrix.

The concentrations of 10 Be, 26 Al and 36 Cl were measured after adding nominally 3 mg, 2 mg and 3 mg carriers of Be, Al and Cl, respectively. In all cases we measured the intrinsic Be, Al and Cl concentrations (by "intrinsic" we mean the amounts present in the coralline lattice) in aliquots of the dissolved sample using ICP-OES. Statistical errors in measurements of intrinsic concentrations are smaller than \pm 10% in most cases. In the case of radionuclide concentrations, statistical errors include those arising from the background in the AMS and from chemical blanks. (Errors cited in elemental and radionuclide concentrations are 1σ values). These measurements permitted determination of intrinsic 10 Be/ 9 Be, 26 Al/ 27 Al and 36 Cl/ Cl ratios in the corals.

4. RESULTS OF MEASUREMENTS OF COSMOGENIC RADIONUCLIDES, ¹⁰BE, ²⁶AL, AND ³⁶C IN CORALS

4.1. ¹⁰Be

Measured $^9\mathrm{Be}$ and $^{10}\mathrm{Be}$ concentrations are presented in Table 3. Statistical errors in $^{10}\mathrm{Be}$ measurements are <4% in most cases; in two of the cases the errors are 7%–9%. The $^{10}\mathrm{Be}$ concentrations (Table 3) lie in the range of 2.3×10^6 – 1.0×10^8 atoms/g coral, varying by $\sim\!2$ orders of magnitude. The intrinsic $^9\mathrm{Be}$ concentrations lie in the range of 1.6×10^{-9} – 1.6×10^{-7} g Be/ g coral, and vary by $\sim\!2$ orders of magnitude, similar to and in step with the variation in $^{10}\mathrm{Be}$ concentrations. Intrinsic $^{10}\mathrm{Be}/^9\mathrm{Be}$ ratios in the samples analyzed fall in a narrower range, between $\sim\!6\times10^{-9}$ and 3×10^{-8} atoms $^{10}\mathrm{Be}/$ atoms $^{9}\mathrm{Be}/$ atoms $^{9}\mathrm{Be}/$ atoms $^{9}\mathrm{Be}/$ atoms $^{9}\mathrm{Be}/$ atoms $^{9}\mathrm{Be}/$ atoms $^{9}\mathrm{Be}/$

Results of multiple determinations of ⁹Be and ¹⁰Be in three coral samples are seen to lie outside statistical errors in some cases, especially in the case of the two NU-1494 subsamples, which differ by an order of magnitude, and in one of the three WANC-93-1 subsamples (WANC-93-1-a), which also is deviant by an order of magnitude. The range of ¹⁰Be/⁹Be ratios is smaller than the spread in ⁹Be and ¹⁰Be concentrations. This is

^a a, b, c represent subsamples taken from the same bulk sample.

Sample	Sample wt. (g)	Intrinsic Al conc. (g/g)	²⁶ Al concentration (atoms/g)	Intrinsic ²⁶ Al/Al ratio
PR-3B	50.16	3.14×10^{-8}	$1.9 \pm 1.18 \times 10^4$	$2.7 \pm 1.69 \times 10^{-11}$
NU-1494	36.06	4.13×10^{-6}	$1.8 \pm 4.7 \times 10^4$	$2.0 \pm 5.1 \times 10^{-14}$
WANC 03 1a	73 57	3.53×10^{-7}	$6.1 + 2.3 \times 10^3$	$7.7 + 2.0 \times 10^{-13}$

Table 4. Measured Al and ²⁶Al concentrations in three corals.

not surprising since Be in the coral lattice is primarily derived by incorporating dissolved ⁹Be and ¹⁰Be species present in the seawater; changes is the ¹⁰Be/⁹Be ratio between samples could reflect numerous factors.

Measurements of 10 Be and 9 Be concentrations were reported previously for two coral samples and several samples of a 460 m coral reef by Bourlès et al. (1984). The 9 Be concentrations in the reef ranged between 10^{-9} – 10^{-8} g Be/ g coral. The 10 Be/ 9 Be ratios in the reef samples of expected ages of \leq 3 ma ranged between $\sim 10^{-7}$ and 10^{-6} . Two measurements of intrinsic 9 Be in corals gave values of 1– 2×10^{-9} g Be/ g coral (Dong et al., 2001). We discuss the implications of the coral 9 Be and 10 Be data in Section 6.

4.2. ²⁶Al

The results of measurements of $^{26}\mathrm{Al}$ in three coral samples are presented in Table 4. Unlike the $^{10}\mathrm{Be/^9Be}$ ratios, the $^{26}\mathrm{Al/^{27}Al}$ ratios in the samples were close to the limit of detection $\sim 5 \times 10^{-15}$, resulting in large statistical uncertainties of ~ 40 and 60% in two of the samples. For the third sample (NU-1494), the measured $^{26}\mathrm{Al}$ concentration has a large statistical uncertainty, partly because of the smaller sample size. The intrinsic $^{27}\mathrm{Al}$ concentrations in the three samples range between $\sim 3 \times 10^{-8}$ and 4×10^{-6} g $^{27}\mathrm{Al/g}$ coral. The intrinsic $^{26}\mathrm{Al/^{27}Al}$ ratios in the samples range between $\sim 8 \times 10^{-13}$ and 3×10^{-11} atoms $^{26}\mathrm{Al/atoms}$ $^{27}\mathrm{Al}$.

Measurements of 26 Al and 27 Al concentrations were reported earlier for 2 coral samples from a core in a lagoon by Bourlès et al. (1984), and of 27 Al for 2 coral samples by Dong et al. (2001). Bourlès et al. (1984) reported values of 2.6×10^3 and 1.4×10^4 atoms 26 Al /g for the two samples; the corresponding values of 27 Al were 1.5×10^{-6} and 1.7×10^{-6} g 27 Al/g coral. Dong et al.(2001) reported values of 0.23×10^{-6} and 0.82×10^{-6} g 27 Al/g for two coral samples. We discuss the implications of the coral 26 Al and 27 Al data in Section 6.

4.3. ³⁶Cl

The ^{36}Cl concentrations in the four coral samples are presented in Table 5. Statistical errors in ^{36}Cl measurements range between 5 and 16%, except in the case of WANC-93-1d where the statistical uncertainty is 44%. The intrinsic $^{36}\text{Cl/Cl}$ ratios lie between $\sim 4 \times 10^{-15}$ and 1.5×10^{-13} . The AMS detection limit for the $^{36}\text{Cl/Cl}$ ratio is $\sim 5 \times 10^{-16}$. The intrinsic $^{36}\text{Cl/Cl}$ ratios should be considered only as lower limits (Table 5) since it is difficult to remove all of the seawater occluded Cl in the coralline matrix.

5. INTERPRETATION OF DATA ON COSMOGENIC ¹⁰BE, ²⁶AL, AND ³⁶CL IN CORALS

Cosmogenic ¹⁰Be, ²⁶Al and ³⁶Cl owe their origin in corals to: (i) in situ production by nuclear interactions inside the

coralline matrix, and (ii) incorporation of dissolved ¹⁰Be, ²⁶Al and ³⁶Cl in seawater in the lattice structure of the corals. We first consider the expected concentrations of these radionuclides produced in situ in the CaCO₃ matrix of the corals, exposed for a period of T (yr) above sea level. A part of the cosmogenic production would be expected to occur when the coral is growing just below sea level. In corals exposed for >100 kyr above sea level, as is the case for the samples analyzed, below-sea-level production can be neglected. The production rate estimates in Table 1 include muon contributions at sea level, and apply for all the coral samples analyzed since they were exposed close to sea level.

A fraction of the cosmogenic radionuclide production in corals is expected to occur from capture of muons in Ca, C and O. In the case of ³⁶Cl, neutron capture in ³⁵Cl is significant for intrinsic Cl concentrations exceeding 100 ppm. For an intrinsic Cl concentration of 100 ppm Cl, we estimate that the production rate at sea level and high geomagnetic latitudes is estimated to be 2.6 atoms ³⁶Cl/g coral/yr (Lal and Peters, 1967), which amounts to 12% of the production of ³⁶Cl by energetic neutrons. At greater depths in the coral, the fast neutron production rate of ³⁶Cl decreases exponentially as in Eqn. 1, but the thermal neutron production rate monotonically increases to a depth of $\sim 30~{\rm g\cdot cm^{-2}}$ (Phillips et al., 2001), and then decreases following the absorption of the (parent) high energy neutrons. However, it is not known whether the intrinsic Cl measured in the corals is truly in the coralline matrix, or whether this is the amount which we were not able to remove from the coral during the chemical purification steps. We will use the data from multiple determinations of ³⁶Cl and Cl concentrations in the same sample to evaluate the source of Cl in the samples (see Section 6.2).

In situ production of ¹⁰Be in corals by neutrons and muons is not significant because the seawater occluded ¹⁰Be far exceeds the in situ produced ¹⁰Be. In the case of ²⁶Al, its concentration in the corals is expected to be primarily due to in situ production by high energy neutrons. In this case, the in situ production rate of ²⁶Al within the coralline matrix at a depth, x (cm) is given by the function P(x):

$$P(x) = P(0)e^{-\mu \rho x}$$
 (1)

where P(0) is the radionuclide production rate at the exposed coral surface (x = 0); μ and ρ are the absorption coefficient for energetic nuclear active particles of the cosmic radiation (g⁻¹.cm²) and the mean density of the coralline matrix (g.cm⁻³) respectively (Lal, 1991). (The absorption mean distance (1/ μ) is taken to be 160 g.cm⁻² and the density of coralline matrix is taken as 2.7 g.cm⁻³). After cosmic ray irradiation for a period of T years, the number of ²⁶Al atoms, N(x, T) per g coralline matrix, eroding at a constant rate, ε (cm/yr) is given by (Lal, 1991):

Sample ^a	Sample wt. (g)	Intrinsic Cl conc. (g/g) ^b	³⁶ Cl conc. (atoms/g)	Intrinsic ³⁶ Cl/Cl ratio ^b
PR-3B	50.16	2.63×10^{-4}	$1.96 \pm 0.11 \times 10^{5}$	$4.39 \pm 0.25 \times 10^{-15}$
NU-1493	26.48	4.20×10^{-4}	$9.53 \pm 1.55 \times 10^{5}$	$1.34 \pm 0.22 \times 10^{-13}$
NU-1494	36.06	1.78×10^{-4}	$2.76 \pm 0.13 \times 10^{5}$	$9.13 \pm 0.42 \times 10^{-14}$
NU-1494	36.06	1.78×10^{-4}	$2.05 \pm 0.24 \times 10^{5}$	$6.78 \pm 0.80 \times 10^{-15}$
	Average, NU-1494		$2.40 \pm 0.27 \times 10^{5}$	$7.85 \pm 1.00 \times 10^{-14}$
WANC-93-1a	73.57	1.61×10^{-4}	$2.84 \pm 0.20 \times 10^{5}$	$1.04 \pm 0.07 \times 10^{-13}$
WANC-93-1d	31.47	6.28×10^{-4}	$3.17 \pm 1.40 \times 10^{5}$	$2.97 \pm 1.31 \times 10^{-14}$
	Average, WANC-93-1		$3.00 \pm 1.41 \times 10^5$	$6.68 \pm 2.98 \times 10^{-14}$

Table 5. Measured Cl and 36 Cl concentrations in four corals. Statistical errors cited are 1σ values.

$$N(x,T) = N(x,0)e^{-\lambda T} + \frac{P(0)}{\lambda + \mu\rho\varepsilon}e^{-\mu\rho x}(1 - e^{-(\lambda + \mu\rho\varepsilon)T}) \quad (2)$$

In Eqn. 2, the first term on the right hand side gives the contribution to radionuclide concentration arising from incorporation of the corresponding dissolved species in the seawater during formation of the coralline matrix, with N(x,0) being the initial 'dissolved' radionuclide concentration at t=0. As discussed below, it is possible to place reasonable limits on the initial nuclide concentration from estimates of the concentration of the radionuclide and the element in the seawater, and the concentration of the element in the coralline matrix. The second term on the right hand side in Eqn. 2 is the expected number of 26 Al after exposure of the coralline matrix for a time period of T years; it assumes that the nuclide concentration is not affected by exchange with the environment.

If N(x, 0), P(0), and T are known, the rate of erosion is easily obtained using iterative methods to solve Eqn. 2. Eqn. 2 does not yield simple equations for the functional behavior of the sensitivity of erosion rate to uncertainties in the cosmogenic production rate, P, or the exposure duration, T. We have calculated the fractional uncertainty in erosion rate, $(d\varepsilon/\varepsilon)$, as functions of (dT/T) and (dP/P). Figure 1 shows these calculations for 6 values of T $(10^3, 10^4, 3 \times 10^4, 10^5, 3 \times 10^5 \text{ and } 10^6 \text{ yr})$. Uncertainties in ε are functions of erosion rate and exposure duration. The ratio, $d\varepsilon/\varepsilon$, is more sensitive to uncertainties in P, relative to uncertainties in T.

Assuming that the measured intrinsic Cl concentrations in the coral samples are truly the amounts present in the coralline matrix, we have estimated the coral erosion rates in the following manner. The expected in situ 36 Cl production at depth, x (cm), after cosmic ray exposure for T years is estimated taking into account the actual depth dependence in the total 36 Cl production rate, due to fast and thermal neutrons, $P_{total,}$ as a function of depth:

$$N(x,T) = \int_{0}^{T} P(x+\varepsilon t)e^{-\lambda t}dt$$
 (3)

In the above equation, erosion rate is assumed to be constant as in Eqn. 2. The rate of production of 36 Cl by high energy neutrons is given in Table 1. The corresponding thermal neutron production rate of 36 Cl is taken to be 2.6×10^{-2} atoms 36 Cl /g coral /ppm Cl /yr, as stated earlier.

6. INFORMATION BASED ON COSMOGENIC RADIONUCLIDES ¹⁰BE, ³⁶CL, AND ²⁶AL

6.1. Information Based on ¹⁰Be

The measured ^{10}Be concentrations in the corals are much greater than those expected from in situ production. The maximum expected in situ ^{10}Be concentration in the corals, corresponding to an exposure age of $\sim\!150$ kyr and 'zero' erosion rate is $\sim\!1\times10^6$ atoms $^{10}\text{Be/g}$ coral. This value is $\sim\!40\%$ of the lowest ^{10}Be concentrations in two WANC-93-1 subsamples, and $\sim(1\text{--}10)~\%$ of the ^{10}Be concentrations in other samples. The more realistic expected in situ ^{10}Be concentration of WANC-93-1-c, taking into account the coral erosion rate (Table 6; 5×10^{-3} cm/yr), is $\sim\!10^4$ atoms $^{10}\text{Be/g}$ coral, which corresponds to $\sim\!0.4\%$ of the measured ^{10}Be concentrations in the two low concentration WANC-93-1-b and c samples.

The absolute ¹⁰Be concentrations in the four coral samples vary by a factor of ~ 50 (Table 3). The exposure ages of the corals are within a narrow range, 125-200 kyr, suggesting that most of the 10Be in the coral is not in situ produced. This conclusion is buttressed by the observation that the concentrations of ¹⁰Be and intrinsic ⁹Be (Fig. 2) are well correlated, as would be expected if they are both derived from dissolved 10Be and ⁹Be species in seawater. The ¹⁰Be/⁹Be ratios are within a narrow range, 6×10^{-9} to 3×10^{-8} , relative to the much larger range in ¹⁰Be concentrations (range of 50×). These ratios are quite consistent with those observed in seawater (Kusakabe et al., 1987; Ku et al., 1990; Kusakabe et al., 1990). There is a systematic trend in the ¹⁰Be/⁹Be ratios (which range between 4×10^{-8} and $\sim 2 \times 10^{-7}$) along advective flow lines (Ku et al., 1990) from surface N. Atlantic (4 \times 10⁻⁸) to surface Pacific (2×10^{-7}) . The corals studied in this investigation are from the W Atlantic Ocean. The reported 10Be/9Be values (Ku et al. 1990) for the nearest site in the Atlantic ocean is for the N. Atlantic (33⁰-42⁰ N latitude and 63⁰-77⁰ W longitude); the ratios range from 2 to 6×10^{-8} . The ratios in corals utilized for this work (Table 3) overlap the observed range in seawater, but are definitely lower by factors of \sim 2–5. One would expect appreciable differences between ¹⁰Be/⁹Be ratios in seawater surrounding islands and coastal regions vis-à-vis open-ocean waters, due to relatively larger fluxes of detrital Be in near island/coastal waters. Dissolution of detrital particles would cause preferential increase in dissolved ⁹Be concentration in

^a a, d represent subsamples taken from the same bulk sample.

^b The intrinsic ³⁶Cl/Cl ratios should be considered only as lower limits since it is expected that the intrinsic Cl concentrations would definitely include some occluded Cl in the coralline matrix, which could possibly be removed only if the coral was very finely ground. Our samples were ground to sub-100-μm size.

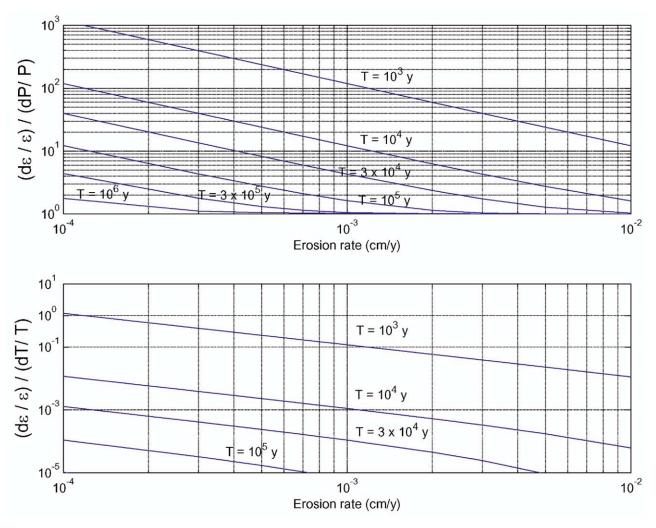


Fig. 1. (top) Theoretical ratios of fractional uncertainties in estimated erosion rates and nuclide production rates (Eqn. 2), with N(x,0) = 0) plotted as a function of erosion rate for discrete exposure periods, $T = 10^3$, 10^4 , 3×10^4 , 10^5 , 3×10^5 and 10^6 yr). (bottom) Theoretical ratios of fractional uncertainties in estimated erosion rates and exposure periods.

seawater, which lowers 10 Be/ 9 Be ratios. The data plotted in Figure 2 are consistent with these expectations, both on the large scatter in 10 Be concentrations and the narrow range in 10 Be/ 9 Be ratios in corals. We note here that dissolved 9 Be/Ca ratios in N. W. Atlantic surface seawater, $(1-7) \times 10^{-7}$ (Kusakabe et al., 1990), are of the same order as the measured 9 Be/Ca ratios in corals, although much lower ratios, 4×10^{-9} , are observed in some samples (Table 3).

Our conclusion, namely that most of the ¹⁰Be in coral samples derived from dissolved beryllium in seawater, is supported by the results of Bourlès et al. (1984), who measured ¹⁰Be and ⁹Be in several samples of a 460 m coral reef of age 6.5 myr. Their measured values of ¹⁰Be concentrations and ¹⁰Be/⁹Be ratios, corrected for ¹⁰Be decay, are similar to those we observed (Table 3). However the scatter in the ¹⁰Be/⁹Be ratios of Bourlès et al. (1984) is much larger than those we observed. Note that we can compare the results of Bourlès et al. (1984) with ours since the two data sets primarily refer to the ¹⁰Be occluded from seawater (and not to in situ produced ¹⁰Be).

A potentially significant feature of the observed distribution

in ¹⁰Be/⁹Be ratios in corals (Table 3) is that it suggests a potential method of determining ages of 'old' corals. The measured ¹⁰Be/⁹Be ratios in relatively young corals (compared to half-life of ¹⁰Be), show that we are able to remove adsorbed garden-variety ¹⁰Be (meteoric ¹⁰Be adsorbed after aerial exposure), and that we are primarily measuring intrinsic ¹⁰Be and ⁹Be concentrations in the coralline matrix (as seen from the linear regression between ¹⁰Be and ⁹Be in Fig. 2). If it can be assumed that the relative ratio of concentrations of Be isotopes was not altered during any subsequent diagenetic changes in the coral, the measured ratio ¹⁰Be/⁹Be in an old coral can be used to determine its age.

If the mean 10 Be/ 9 Be ratio in the coral at the time of formation is R_0 , the age of a coral can be obtained by using the conventional age dating equation:

$$R = R_0 e^{-\lambda T} \tag{4}$$

In Eqn. (4), R is the measured 10 Be/ 9 Be ratio in a coral of age T, and λ is the disintegration constant of 10 Be. For small

Table 6. Estimated erosion rates of corals based on in situ ³⁶Cl and ²⁶Al and corresponding uncertainties arising from uncertainties in P and T (P is the nuclide production rate and T is the coral exposure age).

	Erosion ra	ate (cm/y)	Sensitivity of erosion rate to:		
Sample ^a	$^{36}\text{Cl}^{\text{b}}$	²⁶ Al	±10% P change	±10% T change	
PR-3B	$2.60 \pm 0.25 \times 10^{-3}$ (6.10 \pm 0.35 \times 10^{-3})	$3.70 \pm 11.9 \times 10^{-3}$	±11%	±0.6%	
NU-1493	$7.18 \pm 2.14 \times 10^{-4}$ $(1.96 \pm 0.38 \times 10^{-3})$	c	±14%	±11%	
NU-1494	$\begin{array}{c} (1.90 \pm 0.36 \times 10^{-3}) \\ 4.50 \pm 0.52 \times 10^{-3} \\ (6.81 \pm 0.52 \times 10^{-3}) \end{array}$	_	±10%	<< ±0.2%	
WANC-93-1a	$(0.81 \pm 0.32 \times 10^{-3})$ $4.27 \pm 0.31 \times 10^{-3}$ $(6.10 \pm 0.44 \times 10^{-3})$	$2.12 \pm 0.83 \times 10^{-3}$	±10%	<< ±0.2%	
WANC-93-1d	$\begin{array}{c} (0.10 \pm 0.44 \times 10^{-}) \\ 4.75 \pm 0.21 \times 10^{-3} \\ (1.18 \pm 0.48 \times 10^{-2}) \end{array}$	_	±10%	$<< \pm 0.2\%$	

^a a, d represent subsamples taken from the same bulk sample.

uncertainties in the initial ratio, R_0 , the uncertainty in the estimated age, $dT = (dR_0/R_0)/\lambda$. Therefore a 1% uncertainty in R_0 results in an absolute uncertainty of 2.17×10^4 yr in the age. For larger uncertainties in R_0 , the absolute error in age, $\Delta T = \log_e(K)/\lambda$, independent of the coral age; K is the ratio of 'true' and 'assumed' values of initial $^{10}Bef^9Be$ ratios.

In the present set of measurements, the mean value of R_0 ($^{10}\text{Be/}^9\text{Be}$ ratios) based on 8 measurements in 3 relatively young corals (Table 3) is: $1.7 \pm 0.8 \times 10^{-9}$. The cited uncertainty in R_0 corresponds to 1σ uncertainty of 1.1 myr in the coral age, independent of its true age. Thus with the present uncertainties in the initial $^{10}\text{Be/}^9\text{Be}$ ratio, one can determine ages of corals older than 3 myr within uncertainties of <30%.

It is apparent from the multiple determinations made on the same coral (Table 3) that for dating an old coral, one has to make several measurements on different samples from the coral to ascertain the variability in both ⁹Be concentrations and ¹⁰Be/⁹Be ratios. More research is needed to establish the range of variations in initial 10Be/9Be ratios We may mention here the results of von Blanckenburg et al. (1996) for ¹⁰Be/⁹Be ratios in ferromanganese crusts in the N. Atlantic and Pacific Oceans, which show a very narrow range of $(0.4-0.6) \times 10^{-7}$ and $(1.0-1.6) \times 10^{-7}$, respectively. These data refer to ratios in waters of depth >200 m, where lesser variability would be expected. Results of Carcaillet et al. (2004) for authigenic ¹⁰Be/⁹Be ratios in sedimentary sequences from the Portuguese margin (NE. Atlantic) covering the past 300 kyr led them to the conclusion that the ratios remained within a narrow range except during geomagnetic excursions.

6.2. Information Based on ³⁶Cl and ²⁶Al

The measured isotopic abundance ratios in the cases of 36 Cl and 26 Al are much larger than those expected if these radionuclides were primarily derived in the coralline matrix from dissolved species in the seawater. In the case of 36 Cl, the seawater 36 Cl/Cl ratio is lower than that which can be measured using AMS, $\sim 10^{-15}$. Adopting atmospheric production rate of 36 Cl (Lal and Peters, 1967), we estimate for the steady state

natural (in the period before testing of nuclear weapons) 36 Cl/Cl seawater ratio, a value of 1.22×10^{-16} . The measured 36 Cl/ Cl ratios range between $\sim 4 \times 10^{-15}$ and 1.5×10^{-13} , significantly larger than that expected from dissolved Cl isotopes in seawater.

The measured 26 Al / 27 Al ratios in seawater samples of <900 m depth (Kusakabe et al., 1987; Ku et al., 1995) lie in the range of \sim n × (10^{-15} – 10^{-14}), with 1 < n < 10. The measured 26 Al / 27 Al ratios in two corals, ignoring NU-1494 where the errors are huge, are 7.7×10^{-13} and 2.7×10^{-11} (Table 4), greater than that expected from dissolved Al isotopes in seawater. We therefore make the plausible assumption that both 36 Cl and 26 Al in the coral samples we analyzed are primarily due to their in situ production during their exposure above sea level.

Results of Bourlès et al. (1984) gave values of 4×10^{-16} and 8×10^{-17} for 26 Al / 27 Al ratios in 2 corals. These ratios are lower than those in seawaters (Kusakabe et al., 1987; Ku et al., 1995); nevertheless they support our conclusion that the 26 Al in the coral samples we analyzed is primarily due to its in situ production during its exposure to cosmic radiation above sea level. The larger 26 Al / 27 Al ratios in our data set arise due to the fact that the corals were exposed to cosmic radiation for ~ 100 kyr above sea level.

We will now estimate coral erosion rates based on estimated exposure durations for the four coral samples (Section 3: 114.5 \pm 2.5 kyr for PR-3B and NU-1493, and 190.8 \pm 2.5 kyr for NU-1494 and WANC-93-1). These differ by <13% and <5% from the coral formation ages, for PR-3B and NU-1493 and NU-1494 and WANC-93-1, respectively. An uncertainty is therefore introduced in the erosion estimates since we are neglecting the cosmic ray exposure of corals below sea level, whereby erosion rates would be underestimated. The effect of this neglect can be seen in Table 6, where we present estimates of uncertainties introduced in the erosion estimates for corresponding uncertainties in cosmic ray exposure duration.

In Table 6, we present estimated erosion rates of corals based on mean free cosmic ray exposure durations of 114.5 ± 2.5 kyr and 190.8 ± 2.5 kyr for PR-3B and NU-1493, and NU-1494

^b In the case of ³⁶Cl based erosion rates, we have presented two values. Erosion_rate-1 estimate assumes that the measured ³⁶Cl was produced entirely from interaction of high energy neutrons with Ca. Erosion_rate-2 estimate (values given within parentheses) assumes that ³⁶Cl was produced additionally from neutron capture in ³⁵Cl in the coralline matrix.

^c Dash indicates no data.

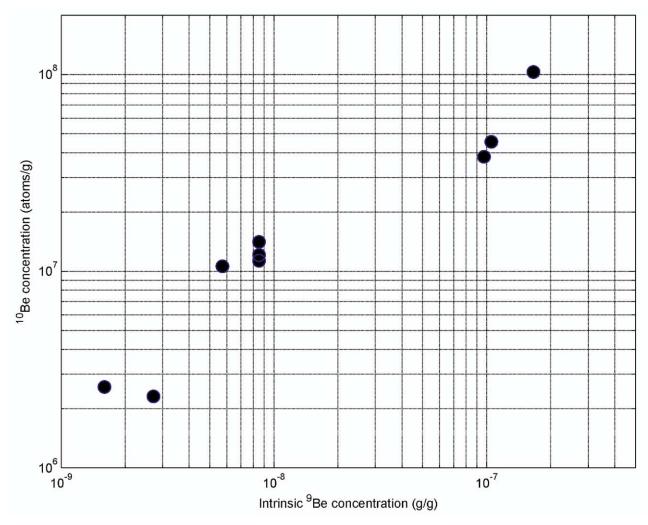


Fig. 2. Measured ¹⁰Be concentrations are plotted against measured intrinsic ⁹Be concentrations for the nine coral samples in Table 3.

and WANC-93-1, respectively. In the case of ³⁶Cl, we give two erosion rate values in each case, arising from the uncertainty as to whether ³⁶Cl was produced by neutron capture in ³⁵Cl in the coralline matrix, in addition to its production by the interaction of high energy neutrons with Ca. This uncertainty arises from the fact that we do not know whether the measured intrinsic Cl in the coral samples was indeed present in the coralline matrix originally or was added later during subaerial exposure. "Erosion_rate-1" estimates are based on the assumption that the measured intrinsic Cl concentration represents recently occluded Cl from pore water, and that therefore it does not contribute to ³⁶Cl production in the coralline matrix. "Erosion-_rate-2" estimates (values given within parentheses in Table 6) are based on the assumption that the measured intrinsic Cl concentration was initially present in the coralline matrix, and that therefore it does contribute to ³⁶Cl production. The two estimates differ by ~30% in the case NU-1494 and WANC-93-1, but in the case of PR-3B and NU-1493, the Erosion-_rate-2 estimates are about two times greater. If we were unable to clean the corals effectively and most of the measured Cl is

recent, then Erosion_rate-1 would be appropriate. The presence of recently occluded Cl is not unexpected, as the high surface area of coral skeletons makes it very difficult to clean them thoroughly.

An examination of the 36Cl and Cl concentration data reveals some clues about the effectiveness of our efforts to remove Cl from the pores of the coral. Two subsamples of WANC-93-1, WANC-93-1a and WANC-93-1d, show very different Cl concentrations, 160 ppm and 680 ppm, respectively (Table 5). The two samples have nearly the same ³⁶Cl concentrations. However, because of the large differences in their intrinsic Cl concentrations, one obtains very different Erosion_rate-2 values for these subsamples: 6.10×10^{-3} and 1.18×10^{-2} cm/yr, respectively. This result suggests that most of the measured Cl concentrations represent pore water occluded Cl, which is not present in the coralline matrix. This inference is consistent with the observation of Budd and Land (1990) who documented Cl concentrations of 40 ppm in pore water in a similar tropical coastal setting (the Bahamas) right after the rainy season.

In view of the foregoing, we conclude that the more reliable erosion rate estimates in the case of 36 Cl are the Erosion_rate-1 estimates. The 26 Al-based erosion rate estimate for WANC-93-1, which has however a statistical uncertainty of \sim 40%, is not inconsistent with its Erosion_rate-1 estimate.

In Table 6, we have also presented the uncertainties in the estimated erosion rates for a ± 10% uncertainty in the exposure time, T, which corresponds to 13 kyr in the case of PR-3B and NU-1493, and 20 kyr in the cases of NU-1494 and WANC-93-1-a. Only in the case of NU-1493, which exhibits a much lower erosion rate, \sim 7 \times 10⁻⁴ cm/yr, the deduced uncertainty in erosion rate is comparable to the corresponding uncertainty in T. For other samples that have erosion rates of $2-5 \times 10^{-3}$ cm/yr, a \pm 10% uncertainty in T corresponds to \leq 1% uncertainty in the erosion rate. In Table 6 we also present uncertainties in estimated erosion rates arising from any uncertainties in the production rates, P of the radionuclides ³⁶Cl and ²⁶Al. Again, the sample NU-1493 displays higher sensitivity to uncertainty in P. Thus, we note that the erosion rate of NU-1493 has an additional uncertainty (over and above the statistical uncertainties in measurements given in column 2 in Table 6 of about \pm 20%, considering uncertainties of \pm 10% in P and T. For the other 3 samples the additional uncertainties due to uncertainties in P and T, are about \pm 10%–11%.

One can now calculate the total amount of erosion implied by our data to have occurred at each sample location since it emerged above sea level (Table 6). The amount of erosion since the last interglacial is close to 3 m for Puerto Rico, compared to less than a meter in Barbados coral NU-1493. However, the erosion in Barbados coral NU-1494 since the penultimate interglacial is significant, ~ 8 m, suggesting, if alteration is not a factor, that much of this erosion occurred between the penultimate and last interglacial periods.

7. DISCUSSION

7.1. Significance of Erosion Rates

Subaerial coral erosion rates are relevant to carbonate platform development models and to fossil-coral sea level studies. Modeling studies of reef accumulation as part of carbonate platform development during the Quaternary (Paulay and McEdward, 1990; Galewsky et al., 1996) rely on published coral erosion rates to estimate the balance between the effects of tectonics, sea level, and erosion on the morphology of reef terraces. Sea level studies aim to extract the sea level signal out of this balance. Much of late-Quaternary sea level change has been reconstructed from uplifted corals in locations such as Papua New Guinea (Stein et al., 1993; Cutler et al., 2003) and Barbados (Gallup et al., 1994; Gallup et al., 2002). Sea level records from tectonically uplifting coastlines are constructed by 1) identifying reef-crest coral species in growth position, 2) dating them with U-series methods, 3) determining how much the sample has been raised tectonically by multiplying its age by the uplift rate, and 4) subtracting the amount of uplift from the sample's current elevation to calculate its initial sea level relative to present. Coral reefs formed during the last interglacial period make an excellent reference point for determining uplift rates because sea level was ~6 m above present sea level at the time, meaning that last interglacial reefs can be found

exposed on stable coastlines around the world. Coral reef crests accrete upward during rising sea level and outward during periods of stable sea level. In Barbados, the dominant reef-crest coral is Acropora palmata, which grows within 5 m of sea level. In a fossil coral reef-crest deposit, each sample of Acropora palmata that died on the reef crest grew within 5 m of sea level and provides a sea level marker. In this way, erosion of overlying reef crest material removes potential sea level data, but does not negate the sea level information contained in the remaining section of the deposit. However, erosion does remove stratigraphy that provides important context for the samples collected. The new constraint on erosion of the last interglacial terrace in Barbados provides a good example. The youngest coral dated from the last interglacial terrace in Barbados is ~124 ka (Gallup et al., 1994; Edwards et al., 1997) and most of the dates are \sim 130 ka, despite the fact that the last interglacial lasted until 116 ka (Stirling et al., 1998). This raises the question whether the effective sample ages have all been shifted to older ages by diagenesis: either younger material was eroded off the top or younger material was eroded off the front of the terrace. Our new constraint from ³⁶Cl data indicates that less than a meter of material has been eroded off the top of the terrace, consistent with the early last interglacial ages and an outwardly accreting reef during a relatively stable last interglacial sea level (or a slowly eroding surface to balance the ~ 0.5 m/ka uplift), suggesting that significant back-cutting erosion has occurred.

7.2. Comparison with Published Erosion Rates

Subaerial erosion of Pleistocene reef systems has been quantified previously in two main ways: 1) through the amount of accommodation space made for Holocene reefs in atoll systems and 2) by direct in situ measurements. The atoll studies have the advantage of averaging over a glacial-interglacial cycle. These studies are based on drill core from atolls that penetrate the upper Holocene reefs and the underlying last interglacial reefs. The vertical thickness of the Holocene reef accretion is a result of how much the last interglacial reef subsided and eroded, leaving room for Holocene growth. After correction for the last interglacial reef's initial + 6 m height and for subsidence, erosion rates have been calculated for Muroroa (0-0.017 mm/yr; Labeyrie et al., 1969), for Enewetak (8.2–20.2 \times 10⁻³ cm/yr; Sackett and Potratz, 1963), and for Tarawa (1.1– 14.6×10^{-3} cm/yr; Marshall and Jacobson, 1985). The same approach was used to estimate an erosion rate of $7-14 \times 10^{-3}$ cm/yr from drill core from the Great Barrier Reef (Marshall and Davies, 1984).

In contrast, several studies have used direct measurements of surface erosion by micro-erosion meter to measure erosion rates over a period of 12 to 24 months. Trudgill (1976) measured deflation of exposed reef surfaces on Aldabra atoll and found mean rates of $9-51\times10^{-3}$ cm/yr. Spencer (1985) used similar methods, but with more measurements per site, on exposed Pleistocene reefs of Grand Cayman, West Indies, and found erosion rates of 11 to 69×10^{-3} cm/yr.

The difference between the results of these two approaches is significant and is best exhibited by comparing the amount of erosion each implies since the last interglacial period. The drill core studies suggest from 0 to 1 m to \sim 20 m erosion; the

micro-erosion meter studies suggest from 10 m to 70 m! Our results agree with the lower range of the drill core studies and are consistent with observations of exposed last interglacial reefs on Barbados. Many sites around the island exhibit wavecut notches just above the reef-crest deposits (Johnson, 2001), marking the sea level during the last interglacial period. Twenty to 70 m of erosion would likely have destroyed these features. Our results suggest that short-term direct measurements over estimate erosion rates by an order of magnitude.

7.3. Diagenesis

We have noted above that two of the four corals analyzed; NU-1494 and WANC-93-1 are diagenetically altered. Although the total number of samples analyzed in the present study is small, this gives us an opportunity to comment on the time when the alteration may have occurred in the samples. We take advantage of the fact that during diagenesis, the expected changes in the Be and Cl isotopic composition of the corals are expected to be quite different, in view of their chemical behaviors.

In the case of ¹⁰Be, if the coral had recrystallized early on while still in seawater, recrystallization would not be expected to impart any significant change in Be isotope concentrations. However if the coral recrystallized sometime after it emerged from seawater (~ 190 kyr B.P. for NU-1494 and WANC-93-1), it could have picked up large amounts of ¹⁰Be from meteoric waters (relative to ⁹Be) resulting in very high ¹⁰Be/⁹Be ratios. Since this is not the case, one would be inclined to postulate that the two corals underwent diagenesis early on before emerging from seawater. However, if both ¹⁰Be and ⁹Be are not mobilized during diagenesis, the alteration could have occurred at any time. We do not see any notable differences in the ¹⁰Be/⁹Be ratios or the ¹⁰Be or ⁹Be concentrations in these corals from the two unaltered corals: PR-3B and NU-1493.

The element Cl is expected to be much more mobile than Be and consequently it is expected to be affected much more by diagenesis. If diagenesis occurred after emergence of the coral from seawater, one may expect that the intrinsic Cl concentration of Cl would be lower for altered corals. The ³⁶Cl based erosion rates determined from the two unaltered corals, PR-3B and NU-1493 are 2.60 \pm 0.25 \times 10 $^{-3}$ and 7.18 \pm 2.14 \times 10 $^{-4}$ cm/yr, respectively, compared to $4.50 \pm 0.52 \times 10^{-3}$ and 4.27 \pm 0.31 \times 10⁻³ cm/yr for the altered corals NU-1494 and WANC-93-1, respectively. There are two ways to interpret these data: 1) the similarity in erosion rates determined from samples PR-3B, NU-1494, and WANC-93-1 suggests that the two altered corals are in line with regional erosion rates and have not lost ³⁶Cl as a result of diagenesis, or 2) the low erosion rate determined from NU-1493 reflects the true local erosion rate, which may imply that the two altered corals have lost ³⁶Cl as a result of diagenesis, resulting in artificially high erosion rates. If the first scenario is correct, this would imply that the calcite alteration happened early, before or within several thousand years of emergence. Early conversion is in conflict with a study by Matthews (1968) on Barbados, where he argued that the transformation of fossil corals from aragonite to calcite takes several hundred thousand years of subaerial exposure, and with field observations that the presence of calcite is rare in samples younger than 100 kyr and common in samples older than 200 kyr. However, it should be noted that the annual rainfall of Barbados and Puerto Rico are virtually identical (51" and 52", respectively), suggesting that the erosion rates should be very similar. Testing the two very different interpretations will require further measurement of last interglacial corals from the region and of unaltered penultimate interglacial corals from Barbados and the region, if available.

8. CONCLUSIONS

We have presented results of measurements of cosmogenic radionuclides 10Be, 26Al and 36Cl and their stable elements in the coralline matrix of 127-200 kyr old corals from Barbados and Puerto Rico. Based on multiple determinations of ¹⁰Be and ⁹Be concentrations in four coral samples, and from a comparison with its theoretically expected in situ production by cosmic radiation, we show that the data are consistent with the incorporation of the bulk of the observed ¹⁰Be in the coralline matrix during its formation from the dissolved 10Be and 9Be in ocean water. A plot of ¹⁰Be concentrations against ⁹Be concentrations shows a linear correlation suggesting temporal variability in the dissolved ¹⁰Be and ⁹Be concentrations in the waters where the corals grew. The principal variability is ascribed to variation in ⁹Be concentration, since the variability in the ¹⁰Be/⁹Be ratio is smaller by an order of magnitude than that in ⁹Be concentrations. Further, the ¹⁰Be/⁹Be ratios are lower but consistent with those measured in seawater, since detrital fluxes in the waters surrounding islands are expected to lower the open ocean

In distinction with the case of ¹⁰Be, we show that the concentrations of the two radionuclides ³⁶Cl and ²⁶Al in the coralline matrix owe primarily to their in situ production by cosmic ray irradiation. The results on in situ produced ³⁶Cl reported here have sufficient accuracy to obtain erosion rates of coral surfaces (Table 6). However, in the case of in situ produced ²⁶Al, the measurements errors are large at present, whereby erosion rate could be calculated in the case of two corals only. We have determined the sensitivity of the estimated erosion rates to uncertainties in both the cosmogenic production rates and exposure duration (Table 6).

Clearly, further research is needed to examine the effects of diagenetic alteration on the concentrations of Be and Cl isotopes in the coral. Future studies should also emphasize measurements of 1) modern corals to assess variability in partitioning of ¹⁰Be and ⁹Be present in coralline matrix, as well as 2) check on the effectiveness of cleaning methods for ancient corals. Based on the present limited data, it appears that the concentrations of Be isotopes may not be significantly affected during alteration! If this be the case, 10Be/9Be ratios may be useful for dating old corals of up to 10 myr age. Based on the presently observed scatter in ¹⁰Be/⁹Be ratios (~50%), which defines the uncertainty in the initial ¹⁰Be/⁹Be ratio, we conclude that the absolute error in coral age determination is ~ 1 myr, independent of the coral age. Therefore, with the presently observed scatter in the limited Be isotope data, it should be possible to determine ages of corals older than 3 myr within uncertainties of <30%. However, we believe that with improved chemical procedures for cleaning the coralline matrix, it may be possible to narrow down the range in the scatter of ¹⁰Be and ⁹Be concentrations.

In conclusion, the results of studies of cosmogenic radionuclides ¹⁰Be, ²⁶Al and ³⁶Cl in corals have proved very valuable and promise to further extend the value of corals as a geophysical/ geochemical archive. Measured erosion rates of the corals studied agree with indirect measurements of subaerial coral erosion rates, but are an order of magnitude lower than those based on direct measurements of surface erosion using a microerosion meter over periods of 12 to 24 months. Present radionuclide based erosion rates correspond to appreciable surface loss, of ~3 m in Puerto Rico since the last interglacial and ~8 m in Barbados since the penultimate interglacial, assuming no artifacts from coral diagenesis. Finally, we show that the cosmogenic ¹⁰Be is potentially useful for dating old corals of ages exceeding a few million years.

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REFERENCES

- Bard E., Antonioli F., and Silenzi S. (2002) Sea-level during the penultimate interglacial period based on a submerged stalagmite from Argentarola Cave (Italy). *Earth Planet. Sci. Lett.* **196**, 135– 146.
- Beck J. W., Edwards R. L., Ito E., Taylor F. W., Recy J., Rougerie F., Joannot P., and Henin C. (1992) Sea-surface temperature from coral skeletal strontium calcium ratios. *Science* 257, 644–647.
- Budd D. A. and Land L. S. (1990) Geochemical imprint of meteoric diagenesis in Holocene ooid sands, Schooner Cays, Bahamas: Correlation of calcite cement geochemistry with extant groundwaters. *J. Sediment. Petrol.* 60, 361–378.
- Bourlès D., Raisbeck G. M., Yiou F., Loiseaux J. M., Lieuvin M., Klein J., and Middleton R. (1984) Investigation of the possible association of ¹⁰Be and ²⁶Al with biogenic matter in the marine environment. *Nucl. Instr. Methods Phys. Res.* B5, 365–370.
- Carcaillet J., Bourles D. L., Thouveny N., and Arnold M. (2004) A high resolution authigenic ¹⁰Be/ ⁹Be record of geomagnetic moment variations over the last 300 ka from sedimentary cores of Potugese margin. *Earth Planet. Sci. Lett.* **219**, 397–412.
- Chen J. H., Edwards R. L., and Wasserburg G. J. (1986) ²³⁸U, ²³⁴U and ²³²Th in seawater. *Earth Planet. Sci. Lett.* **80**, 241–251.
- Cobb K. M., Charles C. D., Cheng H., and Edwards R. L. (2003) El Nino/Southern Oscillation and tropical Pacific climate during the last millennium. *Nature* 424, 271–276.
- Cole J. E., Fairbanks R. G., and Shen G. T. (1993) Recent variability in the southern oscillation—Isotopic results from a Tarawa Atoll coral. *Science* 260, 1790–1793.
- Cutler K. B., Edwards R. L., Taylor F. W., Cheng H., Adkins J., Gallup C. D., Cutler P. M., Burr G. S., and Bloom A. L. (2003) Rapid sea-level fall and deep-ocean temperature change since the last interglacial period. *Earth Planet. Sci. Lett.* 206, 253–271.
- Dong W., Lal D., Ransom B., Berger W., and Caffee M. W. (2001) Marine biogeochemistries of Be and Al: A study based on cosmogenic ¹⁰Be, Be and Al in marine calcite, aragonite and opal. *Proc. Indian Acad. Sci. Earth Planet. Sci.* **110**, 95–102.
- Druffel E. R. M. (1997) Geochemistry of corals: Proxies of past ocean chemistry, ocean circulation and climate. *Proc. Natl. Acad. Sci. U* S A 94, 8354–8361.
- Edwards R. L., Cheng H., Murrell M. T., and Goldstein S. J. (1997) Protactinium-231 dating of carbonates by thermal ionization mass spectrometry: Implications for quaternary climate change. *Science* **276**, 782–786.

- Edwards R. L., Gallup C. D., and Cheng H. (2003) Uranium-series dating of marine and lacustrine carbonates. Rev. Mineral. Geochem. 52, 363–405.
- Fairbanks R. G. (1989) A 17,000-year glacio-eustatic sea-level record: Influence of glacial melting rates on the Younger Dryas event and deep-ocean circulation. *Nature* 342, 637–642.
- Fairbanks R. G. and Dodge R. E. (1979) Annual Periodicity of the O-18-O-16 and C-13-C-12 ratios in the coral *Montastrea annularis*. Geochim. Cosmochim. Acta 43, 1009-1020.
- Galewsky J., Silver E. A., Gallup C. D., Edwards R. L., and Potts D. C. (1996) Foredeep tectonics and carbonate platform dynamics in the Huon Gulf, Papua New Guinea. *Geology* 24, 819–822.
- Gallup C. D., Edwards R. L., and Johnson R. G. (1994) The timing of high sea levels over the past 200,000 years. Science 263, 796–800.
- Gallup C. D., Cheng H., Taylor F. W., and Edwards R. L. (2002) Direct determination of the timing of sea level change during Termination II. Science 295, 310–313.
- Goreau T. F. (1959) The ecology of Jamaican coral reefs I. Species composition and zonation. *Ecology* 40, 67–89.
- Gu Z. Y., Lal D., Liu T. S., Southon J., Caffee M. W., Guo Z. T., and Chen M. Y. (1996) Five million year Be-10 record in Chinese loess and red-clay: Climate and weathering relationships. *Earth Planet.* Sci. Lett. 144, 273–287.
- Handwerger D. A., Cerling T. E., and Bruhn R. L. (1999) Cosmogenic C-14 in carbonate rocks. *Geomorphology* 27, 13–24.
- Heisinger B., Lal D., Jull A. J. T., Kubik P., Ivy-Ochs S., Knie K., and Nolte E. (2002) Production of selected cosmogenic radionuclides by muons: 2. Capture of negative muons. *Earth Planet. Sci. Lett.* 200, 357–369.
- Johnson R. G. (2001) Last interglacial sea stands on Barbados and an early anomalous deglaciation timed by differential uplift. J. Geophys. Res. 106, 11543–11551.
- Kohl C. P. and Nishiizumi K. (1992) Chemical isolation of quartz for measurement of in-situ-produced cosmogenic nuclides. *Geochim. Cosmochim. Acta* 56, 3583–3587.
- Ku T. L., Kusakabe M., Measures C. I., Southon J. R., Cusimano G., Vogel J. S., Nelson D. E., and Nakaya S. (1990) Beryllium isotope distribution in the western north-Atlantic—A comparison to the Pacific. *Deep-Sea Res. A Oceanogr. Res. Papers* 37, 795–808.
- Ku T. L., Wang L., Luo S., and Southon J. R. (1995) ²⁶Al in seawater and ²⁶Al/¹⁶Be as paleo-flux tracer. *Geophys. Res. Lett.* 22, 2163– 2166.
- Kusakabe M., Ku T. L., Southon J. R., Vogel J. S., Nelson D. E., Measures C. I., and Nozaki Y. (1987) Distribution of Be-10 and Be-9 in the Pacific Ocean. *Earth Planet. Sci. Lett.* 82, 231–240.
- Kusakabe M. K., T-L Southon J. R., and Measures C. I. (1990) Beryllium isotopes in the ocean. *Geochem. J.* **24**, 263–272.
- Labeyrie J., Lalou C., and Delibrias G. (1969) Etude des treansgressions marines sur l'atoll de Mururoa par la datation des differents niveaux de corail. *Cah. Pac.* **13**, 59–68.
- Lal D. (1991) Cosmic-ray labeling of erosion surfaces—In-situ nuclide production-rates and erosion models. *Earth Planet. Sci. Lett.* **104**, 424–439.
- Lal D. and Peters B. (1967) Cosmic ray produced radioactivity on the earth. In *Handbuch der Physik*, Vol. 46/2 (ed. S. Flugge), pp. 551–612. Springer-Verlag.
- Lal D. and Jull A. J. T. (1994) Studies of cosmogenic in-situ (CO)-C-14 and (CO₂)-C-14 produced in terrestrial and extraterrestrial samples—Experimental procedures and applications. *Nucl. Instruments Methods Phys. Res. B Beam Interactions Mater. Atoms* 92, 291–296.
- Lal D., Jull A. J. T., Burr G. S., and Donahue D. J. (2000) On the characteristics of cosmogenic in-situ ¹⁴C in documented GISP2 Holocene ice samples. *Nucl. Instr. Methods Phys. Res. B*172, 623– 631.
- Lal D. and Jull A. J. T. (2001) In-situ cosmogenic C-14: Production and examples of its unique applications in studies of terrestrial and extraterrestrial processes. *Radiocarbon* 43, 731–742.
- Marshall J. F. and Davies P. J. (1984) Last interglacial reef growth beneath modern reefs in the southern Great Barrier Reef. *Nature* 307, 44-46.
- Marshall J. F. and Jacobson G. (1985) Holocene growth of a mid-Pacific atoll: Tarawa, Kiribiti. *Coral Reefs* **4**, 21–28.

Matthews R. K. (1968) Carbonate diagenesis—Equilibration of sedimentary mineralogy to subaerial environment—Coral cap of Barbados West Indies. J. Sediment. Petrol. 38, 1110–1119.

- Matthews R. K. (1973) Relative elevation of late Pleistocene high sea-level stands: Barbados uplift rates and their implications. *Quat. Res.* **3,** 147–153.
- Nishiizumi K. W., E. L. Kohl C. P., Lal D. Arnold J. R. Klein J., and Middleton R. (1989) Cosmic ray production rates of ¹⁰Be and ²⁶Al in quartz from glacially polished rocks. *J. Geophys. Res. Atm.* 94, 17907–17916.
- Paulay G. and McEdward L. R. (1990) A simulation model of island reef morphology: The effects of sea level fluctuations, growth, subsidence and erosion. *Coral Reefs* 9, 51–62.
- Phillips F. M., Stone W. D., and Fabryka-Martin J. T. (2001) An improved approach to calculating low-energy cosmic-ray neutron fluxes near the land/atmosphere interface. *Chem. Geol.* 175, 689– 701.
- Sackett W. M. and Potratz H. A. (1963) Dating of carbonate rocks by ionium-uranium ratios. In *Subsurface geology of Eniwetok Atoll*, Vol. 260-BB (ed. S. O. Schlanger), pp. 1053–1065. Geol. Soc. Am. Prof. Pap.
- Schrag D. P. (1999) Rapid analysis of high-precision Sr/Ca ratios in corals and other marine carbonates. *Paleoceanography* 14, 97–102.
- Shen G. T., Cole J. E., Lea D. W., Linn L. J., McConnaughey T. A., and Faibanks R. G. (1992) Surface ocean variability at Galapagos from 1936–1982: Calibration of geochemical tracers in corals. *Pale-oceanography* 7, 563–588.
- Speed R. C. and Cheng H. (2004) Evolution of marine terraces and sea level in the last interglacial, Cave Hill, Barbados. *Geol. Soc. Am. Bull.* 116, 219–232.
- Spencer T. (1985) Weathering rates on a Caribbean reef limestone: Results and implications. *Mar. Geol.* **69**, 195–201.
- Stein M., Wasserburg G. J., Aharon P., Chen J. H., Zhu Z. R., Bloom A. L., and Chapell J. (1993) TIMS U series dating and stable

- isotopes of the last interglacial event at Papua New Guinea. *Geochim. Cosmochim. Acta* **57**, 2541–2554.
- Stirling C. H., Esat T. M., Lambeck K., and McCulloch M. T. (1998) Timing and duration of the last interglacial: Evidence for a restricted interval of widespread coral reef growth. *Earth Planet. Sci. Lett.* 160, 745–762.
- Stirling C., Esat T., Lambeck K., McCulloch M., Blake G., Lee D.-C., and Halliday A. (2001) Orbital forcing of the marine isotope stage 9 interglacial. *Science* **291**, 290–293.
- Stoll H., M. and Schrag D. P. (1998) Effects of Quaternary sea level cycles on strontium in seawater. *Geochim. Cosmochim. Acta* 62, 1107–1118.
- Stone J. O., Allan G. L., Fifield L. K., and Cresswell R. G. (1996) Cosmogenic chlorine-36 from calcium spallation. *Geochim. Cosmochim. Acta* 60, 679–692.
- Stone J. O. H., Evans J. M., Fifield L. K., Allan G. L., and Cresswell R. G. (1998) Cosmogenic chlorine-36 production in calcite by muons. *Geochim. Cosmochim. Acta* 62, 433–454.
- Thompson W. G. and Goldstein S. L. (2005) Open-system coral ages reveal persistent sub-orbital sea-level cycles. *Science* **308**, 401–404.
- Trudgill S. T. (1976) The subaerial and subsoil erosion of limestones on Aldabra atoll, Indian ocean. Z. Geomorphol. Suppl. 26, 201–210.
- von Blanckenburg F., O'Nions R. K., Belshaw N. S., Gibb A., and Hein J. R. (1996) Global distribution of beryllium isotopes in deep ocean water as derived from Fe-Mn crusts. *Earth Planet. Sci. Lett.* 141, 213–226.
- Watanabe T., Winter A., Oba T., Anzai R., and Ishioroshi H. (2002) Evaluation of the fidelity of isotope records as an environmental proxy in the coral Montastraea. *Coral Reefs* 21, 169–178.
- Winter A., Nyberg J., Oba T., Lundberg J., Schrag D., and Taggart B. (2003) Orbital control of lower latitude seasonality during the Eemian. *Geophys. Res. Lett.***30**, 10–14.