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RADIOCARBON DATING OF DEEP-SEA CORALS

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ABSTRACT. Deep-sea corals are a promising new archive of paleoclimate. Coupled radiocarbon and U-series dates allow ¹⁴C to be used as a tracer of ocean circulation rate in the same manner as it is used in the modern ocean. Diagenetic alteration of coral skeletons on the seafloor requires a thorough cleaning of contaminating phases of carbon. In addition, 10% of the coral must be chemically leached prior to dissolution to remove adsorbed modern CO₂. A survey of modern samples from the full $\Delta^{14}\text{C}$ gradient in the deep ocean demonstrates that the coralline CaCO₃ records the radiocarbon value of the dissolved inorganic carbon.

INTRODUCTION

The radiocarbon content of dissolved inorganic carbon (DIC) in seawater is an important tool for constraining the rate of deep-water circulation. GEOSECS observations constrain the mean overturning time of the ocean to be about 800 years (Stuiver et al. 1983). At any one site in the ocean, considerations of both mixing and in-situ aging are important in determining the seawater $\Delta^{14}\text{C}$. In the modern western Atlantic for instance, there is a 100‰ range in $\Delta^{14}\text{C}$, but only about 150 years worth of aging (equivalent to about 20‰) since the water last was at the surface (Broecker and Peng 1982). In addition to mixing, $\Delta^{14}\text{C}$ ventilation age calculations from radiocarbon are complicated by the addition of nuclear bomb produced ¹⁴C during the era of atmospheric testing. Some early measurements of surface waters help constrain the pre-bomb values (Bien et al. 1960; Broecker 1963; Fonselius and Ostlund 1959), but there are virtually no measurements from the deep where bomb radiocarbon can be seen today. A variety of tracer based methods have been used to “unmix” this bomb influence in newly formed deep waters (Broecker 1979; Broecker et al. 1985), but direct reconstructions are not available. Similar to the way surface corals and mollusks constrain pre-bomb surface water values to be uniformly –50‰ between 40°N and 40°S (Bard 1988; Druffel and Linick 1978), deep-sea corals could provide a map of natural radiocarbon before the bomb contamination.

Studies of fossil corals (Bard et al. 1993; Edwards et al. 1993) and varved sediments (Hughen et al. 1998) constrain the $\Delta^{14}\text{C}$ of the surface ocean and atmosphere for the past 30,000 years. Corals provide unique calibration points because they contain enough Uranium to make independent ²³⁰Th dates on the exact same material used to generate ¹⁴C ages. These combined measurements provide strong constraints on both changes in cosmogenic nuclide production rate and changes in the fluxes of carbon between active reservoirs. Rapid increases in past atmospheric $\Delta^{14}\text{C}$ are occasionally associated with a large-scale decrease in deep-water production rate (Stocker and Wright 1996), thus providing some of our best information about past ocean overturning rates.

More direct measurements of past deep-water circulation rate have been limited to comparisons between contemporaneous benthic and planktonic foraminifera (Broecker et al. 1990; Duplessy et al. 1989; Shackleton et al. 1988). Recently, deep-sea corals have been used as a new archive of past deep ocean $\Delta^{14}\text{C}$ itself (Adkins et al. 1998; Goldstein et al. 2001; Mangini et al. 1998). Similar to

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surface corals, coupled ^{230}Th and ^{14}C dates in these samples provide a direct measurement of past seawater $\Delta^{14}\text{C}$ that is not model dependent. Calculation of past circulation rates from this data are constrained by the same problems of mixing and in-situ aging that modern measurements face (Adkins and Boyle 1999). With a large enough sample set in both space and time, one could potentially use deep-sea corals to create paleo $\Delta^{14}\text{C}$ maps similar to the modern GEOSECS data.

However, two important questions must be addressed before there is widespread use of deep corals as paleo $\Delta^{14}\text{C}$ archives. We need both an exhaustive study of the analytical techniques involved and a modern "core top" calibration. The latter point addresses the question "Do the corals record the radiocarbon value of the DIC in which they grow?" This is fundamentally about the coral's biomineralization itself. The first point addresses the question "Can we recover skeletal $\Delta^{14}\text{C}$ from past samples regardless of the radiocarbon's origin?" This is a question of cleaning techniques and analytical precision. Both points are examined in this paper.

METHODS

Physical and Chemical Cleaning

Cleaning methods are designed to remove contaminating carbon sources that accumulate both while the specimen is on the sea floor and while it is stored on land after collection. Black, organic carbon rich crusts that form in-situ on fossil corals after death have been described in our earlier work (Cheng et al. 2000). These crusts are diagenetic iron and manganese oxides that can trap significant amounts of detrital aluminosilicates. In addition, modern corals frequently have deposits of organic matter trapped between septa. Both of these phases can be removed with mechanical and chemical cleaning steps designed to attack an organic coating bound to the aragonite. The following procedure is based on one developed for trace metals in surface corals by Shen and Boyle (Shen and Boyle 1988).

Prior to chemical cleaning, all evidence of endolithic activity is drilled out to remove any possible reprecipitation of CaCO_3 by boring worms or sponges on the surface. Water rinses and scrubbing with a brush remove sediment from inside the coral and between the septa. Samples are then immersed in a 50/50 mixture of 30% H_2O_2 and 1N NaOH and ultrasonicated for 15 minutes. This oxidizing solution step is repeated several times. Occasionally, samples are again scrubbed with a brush to promote removal of the black crusts in small sheets. Oxidizing solution steps are repeated until there is very little black crust or polyp organic matter left on the sample. However, this process often leaves a brownish/orange organic stain on the CaCO_3 . Quick dips (30 seconds to 2 minutes) in a 50/50 mixture of 30% H_2O_2 and 1% HClO_4 effectively remove this stain. The danger is that this perchloric acid step also dissolves about 5–10% of the sample. Small siphons for spent cleaning solutions and plastic racks to hold samples aid in the mechanics of the cleaning process. After the dilute perchloric step, samples are rinsed thoroughly with clean distilled water.

This cleaning process removes about 10% of the total coral weight. Immediately prior to dissolution, a second acid wash removes an additional 5–75% of the cleaned mass. This step is designed to reduce adsorbed modern CO_2 that accumulates during sample storage (Burr et al. 1992). For the second acid wash, pre-weighed samples are dipped into 6N HCl for 15–60 seconds followed by rinses in two separate beakers of deionized H_2O . After drying for several minutes in a 60 °C oven, the samples are cooled and reweighed to determine the percent of sample removed. Samples are then crushed in an agate mortar and pestle to facilitate dissolution in the reaction flasks. All equipment for handling coral samples is cleaned with 10% HCl prior to use.

Dissolution and Graphitization

Dissolution is carried out in specially designed finger flasks that contain a side arm for the phosphoric acid reservoir. Crushed samples are transferred to the acid cleaned flask with filter paper and care is taken not to spread fine CaCO_3 on the flask walls. Approximately 2 mL of 85% H_3PO_4 is added to the side arm with a cleaned Pasteur pipette. The flask is connected to a vacuum line using an 18/9 o-ring ball/socket joint and evacuated. Once the pressure has dropped, the sample reaction vessels are closed, removed from the line and tilted to allow the H_3PO_4 to spill out of the side arm and react with the coral sample. After reacting overnight, the samples are extracted on a vacuum line through two dry ice/isopropyl alcohol water traps. The purified sample is expanded into a known volume and measured with a MKS Baratron Type 122A absolute pressure gauge. Two milliliters of CO_2 gas are isolated for AMS analysis and about 4.6% (usually about 0.1–0.3 mL at STP) of the residual is saved for $\delta^{13}\text{C}$ determination. All excess is frozen into a glass tube. The tube is flame sealed and stored. $^{13}\text{C}/^{12}\text{C}$ ratios were determined at the Woods Hole Oceanographic Institution.

Graphitization of the 2 mL CO_2 sample for AMS analysis follows the method of Vogel (Vogel et al. 1987). Graphite samples are pressed into targets and measured for their $^{14}\text{C}/^{13}\text{C}$ ratio at the Lawrence Livermore National Lab Center for Accelerator Mass Spectrometry (CAMS). The corrected fraction modern (F) is reported as described by Donahue et al. (1990). The “old” oxalic acid standard is normalized to 1950 and a $\delta^{13}\text{C}$ value of -19‰ and the sample is normalized to a $\delta^{13}\text{C}$ of -25‰ . With these adjustments the radiocarbon age is given by (Stuiver and Polach 1977; Donahue et al. 1990):

$$\text{Radiocarbon age} = \tau \ln F$$

where τ is the Libby mean life of 8033 years. The measured fraction modern, F_m , is converted to the true fraction modern (F) by accounting for the blank introduced during graphite formation:

$$F = F_m (1+f) - f$$

where f is the fraction modern of a ^{14}C -free calcite sample that is processed exactly the same way as the coral samples.

Leaching Experiments

There is considerable evidence that surface corals have a significant component of adsorbed modern CO_2 on their skeletons (Burr et al. 1992). But deep-sea corals are generally not porous; they have a smaller surface area to volume ratio and are less susceptible to modern contamination. We designed several leaching experiments to test for the presence of adsorbed CO_2 . In each case we placed the unleached coral sample, with an excess of phosphoric acid, inside a reaction flask. Periodically the evolved CO_2 gas was removed and purified as described above. Smaller amounts of gas were collected at the beginning of the experiment and larger portions were collected at the end, sometimes after several days of sitting in the reaction vessels. Several different types of samples were used for these tests. JFA 20c is a *Desmophyllum cristagalli* with a U-series age of $65,455 \pm 246$ years (Cheng et al. 2000). This age corresponds to an F of 0.0003. Both cleaned and untreated pieces of this ^{14}C -dead sample were processed. We also dissolved successive fractions from calcite blanks that were acidified in HCl immediately prior to the experiment as described above. For this test some samples were crushed in a mortar and pestle prior to dissolution and some were not.

RESULTS

All calcite blanks from a 5-year period are listed in Table 1. The total standard deviation in F corresponds to an age detection limit of ~44,000 ^{14}C years. Rather than use this overall average, samples are blank corrected using the calcites from their same graphitization run. Only the data from August 1995 shows a small deviation from the routine CAMS backgrounds.

Table 1 Calcite blank data. The variance of the measured fraction modern over this five-year time period corresponds to a maximum radiocarbon age of >44,000 years.

Date	UCID	CAMS	Wt. (mg)	CO ₂ Gas (ml)		F _m	error (1 σ)	
	#	#		Total	AMS			
March 1995	663	19384	52	10.36	1.35	0.0028	0.0002	
	664	19385	42	9.76	1.30	0.0027	0.0003	
August 1995	1006	22458	82	18.12	1.30	0.0066	0.0006	
	1012	22459	61	10.77	1.37	0.0066	0.0004	
August 1996	1535A	30195	47	11.35	1.98	0.0025	0.0002	
	1535B	30196	47	11.35	2.06	0.0024	0.0002	
March 1997	2059	36256	274	61.33	1.93	0.0025	0.0002	
	2056	36259	65	13.63	1.93	0.0015	0.0002	
May 1997	2205			2.45	1.99	Sample Lost		
	2206	39264		2.08	1.93	0.0040	0.0003	
	2207	39265		3.56	1.96	0.0026	0.0001	
	2208	39266	65.5	6.94	1.95	0.0024	0.0001	
	2209	39267		2.41	1.97	0.0024	0.0003	
	2210	39268		1.61	1.53	0.0040	0.0001	
	2211	39269		5.59	1.96	0.0031	0.0002	
	2212	39270	82.5	9.41	1.95	0.0024	0.0002	
	May 2000	3214	66007		6.5	1.5	0.0027	0.0001
		3250	66006		10.13	1.5	0.0033	0.0001
3786		66010				0.0036	0.0001	
July 2000	3978	66008		10.24	1.54	0.0025	0.0001	
	3224	66955		10.36	1.51	0.0009	0.0001	

Average	0.0031
Std Deviation	0.0014

Results from leaching experiments are presented in Table 2 and Figure 1 (figures begin on page 574). Neither crushed nor uncrushed calcite shows a trend in the fraction modern of the successive fraction removed (higher fraction number), and all data fall within the long-term range for all blanks (Figure 1A). The pre-dissolution HCl wash clearly removes any adsorbed modern CO₂ from these types of samples. Similar results for ^{14}C -dead *D. Cristagalli* are shown in Figure 1b. There is some evidence for adsorbed CO₂ in samples that have been dissolved less than 5%. All other cleaned samples, not affected by leaks in the finger flasks (see Discussion), have the same fraction modern within experimental error.

The modern calibration data set is listed in Table 3. Uranium series ages for these corals are reported in Table 4. Data were collected and ages calculated as described in Cheng et al. (2000). Corrected ages and age errors are given relative to 1950 (years BP) and include a correction for unsupported ^{230}Th using the ^{232}Th data. ^{14}C replicates of the same CO₂ gas graphitized separately always agree within 2 σ . A modern coral standard of *Porites sp.* run many times over the course of this study gives a value of 0.9461 ± 0.0025 , well within the long-term average from the UCI lab.

Table 2 Radiocarbon data from all leaching experiments. Errors are 1 σ .

Fraction Number	UCID #	CAMS #	Start wt. (mg)	CO ₂ Gas (ml)		Fraction Modern	error
				Total	AMS		
<i>JFA 20c Top</i>							
1	2039	36240	301.1	2.77	1.87	0.0119	0.0008
2	2040	36241		5.58	1.95	0.0084	0.0008
3	2041	36242		7.70	1.92	0.0077	0.0008
4	2042	36243		9.56	1.93	0.0066	0.0008
5	2043	36244		4.85	1.92	0.0097	0.0008
<i>JFA 20c Bottom I</i>							
1	2044	36245	231.8	2.78	1.62	0.0178	0.0009
2	2045	36246		4.09	1.90	0.0120	0.0009
3	2046	36247		7.28	1.93	0.0109	0.0009
4	2047	36248		9.13	1.93	0.0110	0.0008
5	2048	36249		30.55	1.94	0.0218	0.0009
<i>JFA 20c Bottom II</i>							
1	2049	36250	226.6	2.48	1.68	0.0174	0.0010
2	2050	36251		4.36	1.94	0.0118	0.0008
3	2051	36252		10.59	1.92	0.0132	0.0009
4	2052	36253		11.26	1.93	0.0160	0.0008
5	2053A	36254		22.75	1.91	0.0248	0.0008
5	2053B	36255			1.93	0.0240	0.0008
<i>Calcite Uncrushed</i>							
1	2205		65.5	2.45	1.99	Lost during graphitization	
2	2206	39264		2.08	1.93	0.0040	0.0003
3	2207	39265		3.56	1.96	0.0026	0.0001
4	2208	39266		6.94	1.95	0.0024	0.0001
<i>Calcite Crushed</i>							
1	2209	39267	82.5	2.41	1.97	0.0024	0.0003
2	2210	39268		1.61	1.53	0.0040	0.0001
3	2211	39269		5.59	1.96	0.0031	0.0002
4	2212	39270		9.41	1.95	0.0024	0.0002
<i>JFA 62.1 Top</i>							
1	2197	39255	87.8	1.95	1.87	0.6852	0.0030
2	2198	39256		4.56	1.98	0.6837	0.0027
3	2199	39257		4.65	1.97	0.6840	0.0032
4	2200	39258		9.26	1.95	0.6799	0.0029
<i>JFA 62.1 Bottom</i>							
1	2201	39259	48.5	1.66	1.57	0.6777	0.0029
2	2202	39260		2.8	1.88	0.6757	0.0030
3	2203	39261		3.44	1.96	0.6776	0.0030
4	2204	39262		3.02	1.95	0.6790	0.0032

Table 3 Modern “core top” calibration data set

ID	UCID	CAMS #	Depth (meters)	Lat	Long	Species	Cal Age (years)	err	¹⁴ C Age	err	Δ ¹⁴ C	error	DIC Δ ¹⁴ C	err
85080	655	19373	990-1150	43.47S	150.29E	D. cristagali	34	10	1000	50	-113	6	-115	20
47413	654	19372	421	50.38S	167.38E	D. cristagalli	37	4	590	40	-67	5	-62	8
48740.1	1020	22462	1420-1470	48°41'N	10°54'W	D. cristagalli	139	9	720	50	-70	6	-70	10
86873.1	1018	22460	1112	25°53'S	5°44'E	St. campaniformis	331	115	1400	60	-126	14	-120	8
91545.2	1003	22446	1510-1600	21°18'S	36°18'E	St. nobilis	407	35	1550	50	-134	7	-125	10
BI-103-3	1013	22454	1355	18°N	157°W	E. rostrata	688	14	2710	50	-224	5	-230	12
JFA 47.1	1021	22463	1790-1803	48°10'S	148°16'E		850	24	2190	50	-156	6	-150	20
94069.1	3222	66899	710	30°31'S	178°39'W	D. cristagalli	986	10	1530	30	-69	4	-70	8
<i>Samples without U-series Ages</i>														
48518	1023	22465	1420-1470	48°41'N	10°54'W	S. variabilis			640	50	-77	6	-70	10
47373	1022	22464	2010-2100	49°51'S	178°35'E	F. impensum			1420	50	-162	5	-164	8
93177.3	999	22442	4100	34°43'N	123°4'W	F. marenzelleri			2020	50	-222	5	-230	10
83522	1004	22447	1760	21°31'S	81°31'W	Caryophyllia sp.			2210	50	-241	5	-210	10

Table 4 Uranium series data. Only the data for new corals are shown. Errors are 2σ and ages are at the time of measurement. Age uncertainties are calculated from the ^{232}Th concentration and the error on the $^{230}\text{Th}/^{238}\text{U}$ activity as described in Cheng et al. (2000a). Half-lives for ^{230}Th and ^{234}U are the most recent as reported in Cheng et al. (2000b).

ID	^{238}U (ppb)	^{232}Th (ppt)	$\delta^{234}\text{U}$ (measured)	$^{230}\text{Th}/^{238}\text{U}$ (activity)	Age (years BP)	$\delta^{234}\text{U}$ (initial)
86873.1	4191 \pm 11	1039 \pm 27	146.5 \pm 5.2	0.00473 \pm 0.00013	284 \pm 115	146.6 \pm 5.2
91545.2	4952 \pm 4	371 \pm 44	146.5 \pm 1.4	0.00464 \pm 0.00008	356 \pm 35	146.6 \pm 1.4
BI-103-3	5553 \pm 4	154 \pm 27	145.1 \pm 1.1	0.00733 \pm 0.00007	641 \pm 14	145.4 \pm 1.1
JFA 47.1	4706 \pm 3	227 \pm 48	145.9 \pm 1.2	0.00912 \pm 0.00010	802 \pm 24	146.2 \pm 1.2
94069.1	4070 \pm 5	65 \pm 3	145.6 \pm 1.3	0.01038 \pm 0.00008	936 \pm 10	146.0 \pm 1.3

DISCUSSION

Leaching Experiments

The ^{14}C -dead deep-sea coral, sample JFA 20c, shows some effect of modern CO_2 contamination in the initial fraction of CO_2 leached. Carbon from the first 5–10% of the coral sample is slightly elevated in its fraction modern (Figure 1B). This effect occurs in both the cleaned and untreated samples. *D. cristagalli* samples must be washed in acid prior to dissolution to avoid this problem. The effect is not as large as that for surface corals where acid treatments of up to 50% mass loss did not remove all of the modern contamination (Burr et al. 1992). This large difference between porous surface corals and relatively dense deep-sea specimens is not surprising and is probably due to their different surface area to volume ratios.

There is also a clear effect of the cleaning procedure on the radiocarbon age. Untreated samples with intact black crusts (gray points in Figure 1b) are always elevated in their fraction modern relative to the cleaned piece from the same sample (black points in Figure 1b). As we used phosphoric acid to acidify our samples, it is unlikely that the contaminating carbon phase is something other than CaCO_3 . Removing the black crusts eliminates reduced organic carbon, but this is not easily hydrolyzed in the H_3PO_4 . Contaminating CaCO_3 probably comes from secondary precipitates that are somehow protected or promoted by the formation of black crusts. The difference between gray and black points in Figure 1b is not due to adsorbed modern CO_2 as its effect is removed in the first fraction leached. Cleaning fossil samples prior to radiocarbon age determination is crucial to determining the correct $\Delta^{14}\text{C}$ of past water masses.

In both the calcite and coral leaching experiments there is evidence for a small modern CO_2 blank in the preparation lines, and a larger contamination from leaks in the o-ring seals (Figure 1). The leak source, however, is only apparent in samples that sat for several days while they reacted. These samples are marked with dashed circles around the data points. The rate of sample dissolution slowed considerably during the leaching experiments and stopped altogether for the cleaned sample of JFA 20c. These last fractions sat in the reaction vessel for several days and are clearly contaminated. Actual samples for measuring past $\Delta^{14}\text{C}$ are never exposed to this long delay and are unaffected by leaks in the reaction flask.

There is clear evidence for a small contamination from modern CO_2 in the gas handling lines themselves, but only for the smallest samples. This effect is evident by plotting a sample's fraction modern versus its size (Figure 2). ^{14}C -dead samples should show no trend in their measured fraction modern as a function of amount of CaCO_3 reacted, but the individual fractions from our leaching

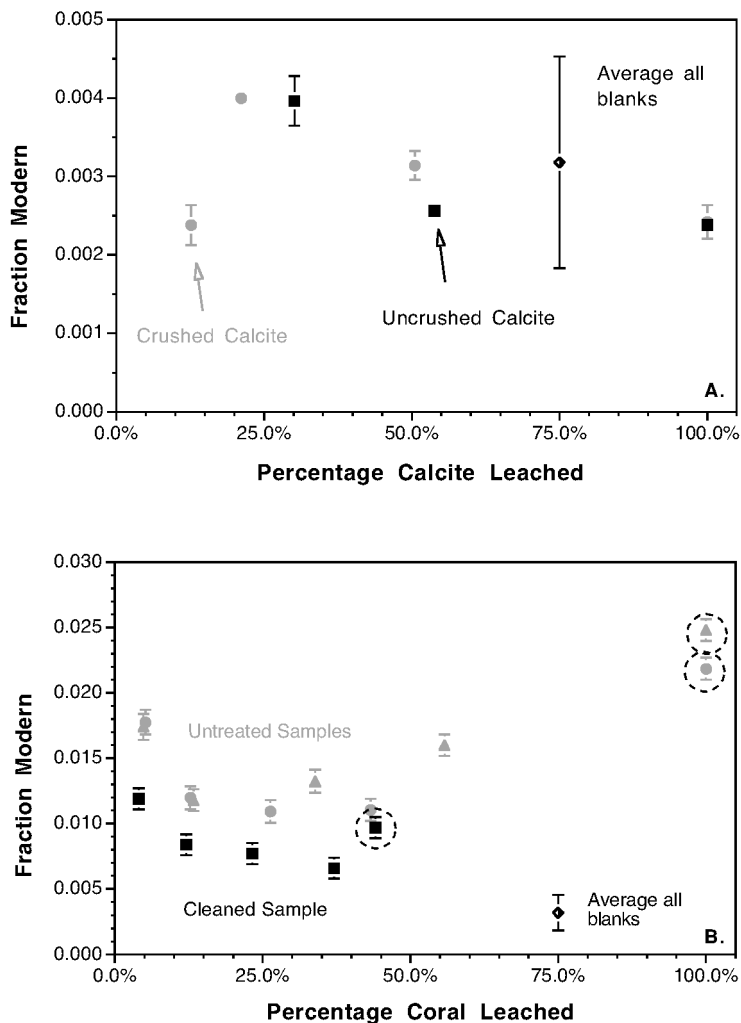


Figure 1 ^{14}C -dead CaCO_3 leaching experiment results. A. Calcite results for samples both crushed (gray circles) and not crushed (black squares) prior to dissolution. B. *D. cristagalli* sample JFA 20c results for both cleaned (black squares) and untreated (gray circles and triangles) samples. Dotted circles around the last point in each series indicate contamination from a leak in the reaction flasks (see Discussion). In both figures the half-filled diamond is the average and 1σ standard deviation of all blanks in Table 1.

experiments do show larger ^{14}C values for samples below about 2–3 mL of CO_2 . The effect is larger for coral samples than for calcites, but our paleo $\Delta^{14}\text{C}$ sample sizes are always larger than the 2–3 mL threshold.

We also successively dissolved the top and bottom pieces of a Holocene aged coral to test the top/bottom age reversals found in deglacial corals by Adkins et al. (1998). Sample JFA 62.1 was dredged from 1420 m on the Pluto Seamount in the eastern basin of the North Atlantic. This sample has black crusts like the deglacial samples, but grew during a time when we do not expect rapid changes in the deep $\Delta^{14}\text{C}$ of DIC. As such, the top to bottom age difference should only reflect the

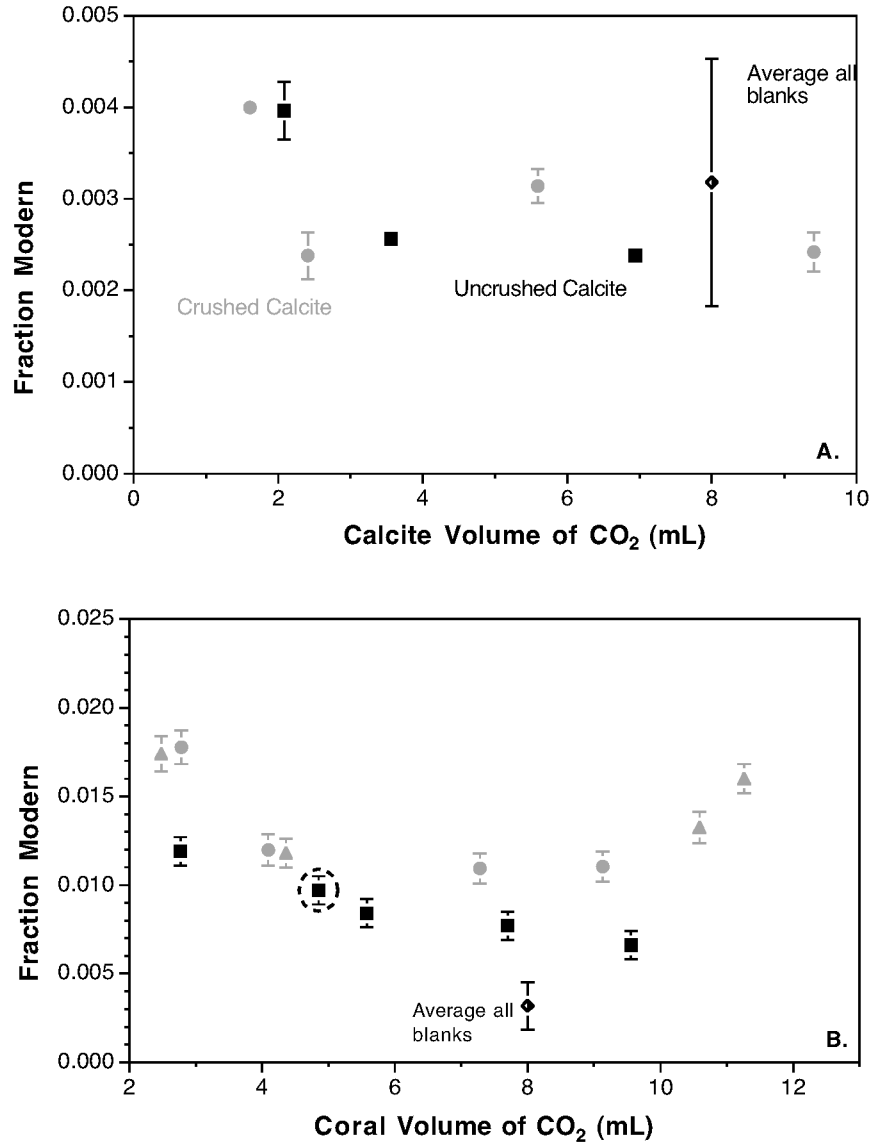


Figure 2 The same data as in Figure 1 but plotted against sample size instead of percentage removed. Symbols are as described in Figure 1. Higher fraction modern values for the smallest samples indicate a contribution from modern carbon in the preparation lines (see text).

coral's mean extension rate. Figure 3 illustrates that there is a clear difference in the ages of the top and bottom pieces (70 ± 28 yr) and that there is no difference between successive acid treatments of the same piece. Unlike the deglacial corals in Adkins et al. (1998) this sample is younger at the top than at the bottom. Age "reversals" between the top and bottom of a single coral are therefore representative of a change in the seawater DIC at that site during the coral's lifetime. The 70 ± 28 -yr age difference implies a mean growth rate of ~ 0.7 mm/yr, in good agreement with the U-series derived mean growth rates of several modern *D. cristagalli* (Cheng et al. 2000).

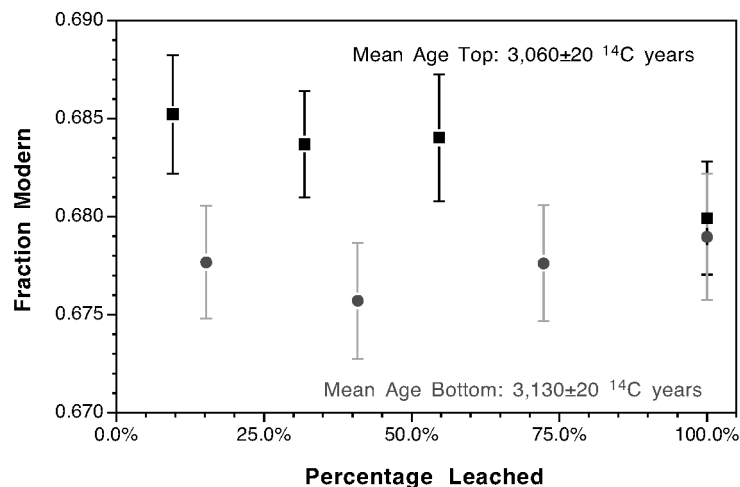


Figure 3 Stepwise dissolution experiment results for sample JFA 62.1, a *D. cristagalli* from 1400 m deep in the northeast Atlantic Ocean. The top of the coral is younger than the bottom by 70 ± 28 yr. This difference corresponds to a mean extension rate of ~ 0.7 mm/yr.

Calibration Data Set

Our modern coral calibration is shown in Figure 4. Samples were initially determined to be “modern” by inspection of the quality of the septa and the lack of endolithic activity. Water $\Delta^{14}\text{C}$ values for all coral samples are estimated from nearby GEOSECS stations. Coral ^{14}C data for these samples fall on or below the 1:1 line in Figure 4. Falling below this line indicates that a coral is older than the water in which it grew. By measuring the U-series age of these “too old” samples, we can correct for the time between the date the coral stopped growing and the day we measured its age. In all cases where we made both ^{230}Th and ^{14}C dates (black squares), the samples came back onto the 1:1 line. An example of how we determine the water $\Delta^{14}\text{C}$ is shown in Figure 5. This sample from the South Pacific is nearly 1000 years old and lies at the modern (mid 1970s) depth of bomb ^{14}C penetration, as indicated by the tritium data. The fact that our old coral point lies on the mid-’70s $\Delta^{14}\text{C}$ trend supports the ^3H conclusion that the bomb ^{14}C influence is small below 550 m (Broecker et al. 1985).

The data in Figure 4 are a clear demonstration that within analytical error deep-sea corals, from a variety of genera, are excellent recorders of the $\Delta^{14}\text{C}$ of the dissolved inorganic carbon (DIC) in which they grow. Modern looking samples may have spent considerable time dead on the sea floor and/or in sample drawers before being measured, but this effect can be accurately and precisely determined. As several of our samples in this set are hundreds of years old (Table 3) and were clean enough to be called “modern”, the black crusts, at least in the modern ocean, do not seem to form immediately after the coral’s death.

The 1:1 correspondence between coral $\Delta^{14}\text{C}$ and seawater DIC $\Delta^{14}\text{C}$ is strong evidence that inorganic carbon is the sole source of skeletal CaCO_3 . However, we can more quantitatively use the data in Figure 4 to test what fraction of a coral’s skeleton can come from metabolic CO_2 . These organisms are essentially filter feeders, eating the available detritus that washes over them. Several of the specimens in Figure 4 grew when this food source was contaminated by bomb ^{14}C . The elevated level of $\Delta^{14}\text{C}$ in this organic matter relative to the surrounding DIC (Griffin and Druffel 1989) pro-

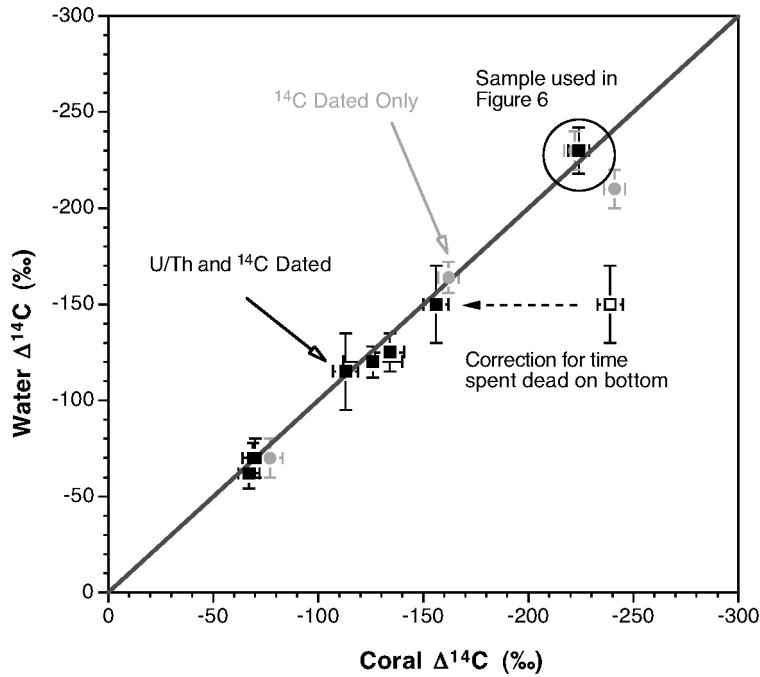


Figure 4 Modern calibration of ¹⁴C in deep-sea corals. Water data are estimated from nearby GEOSECS stations. Corals are measured as described in the text. Gray circles are samples with only ¹⁴C dates. Black squares are samples with both ¹⁴C and ²³⁰Th dates. The open black square shows how a ¹⁴C date is transformed into the Δ¹⁴C at the time of death by correction with a ²³⁰Th age. All samples fall on a 1:1 line, indicating that corals are an excellent archive of seawater Δ¹⁴C. The circled sample is the coral used in the percent metabolic CO₂ calculation (see Figure 6 and text).

vides a test of how much organically derived CO₂ is fixed into the skeletal aragonite. We can write the radiocarbon mass balance equation for a coral’s skeleton as follows:

$$(\text{Fraction Respired CO}_2)(\Delta^{14}\text{C of Food}) + (1 - \text{Fraction Respired CO}_2)(\Delta^{14}\text{C of DIC}) = \text{Skeleton } \Delta^{14}\text{C}$$

While within the error bars all of our data falls on a 1:1 line between DIC Δ¹⁴C and coral Δ¹⁴C, the circled data point in Figure 4 falls about 8‰ above the line. Sample number 93177.3 is a *Fungia-cyathus marenzelleri* that was picked alive from 4100 m in the sub-tropical north-east Pacific (very close to Station M, 34°50’N, 123°00’W) on 20 October 1992. By adopting a water to coral difference of 10‰ and using a water Δ¹⁴C value of -230‰, we can rewrite the above equation:

$$\Delta^{14}\text{C of Food} = 10 / (\text{Fraction Respired CO}_2 - 230)$$

This function is plotted in Figure 6 for a range of fractions of respired CO₂ in the skeleton. Using data on the Δ¹⁴C of suspended and sinking particulate organic carbon (POC) from almost exactly the same location as the coral (Druffel et al. 1996), we can constrain the maximum respired CO₂ our data allows in the skeleton. The oldest food source, suspended POC, gives a maximum value of about 8%. Within the errors of our AMS measurements and the estimates of bottom water Δ¹⁴C of DIC, the skeletons of deep-sea corals are drawn entirely from ambient inorganic carbon. There is room in the data for a maximum of 8% of the skeleton to be of a respired origin. This result has

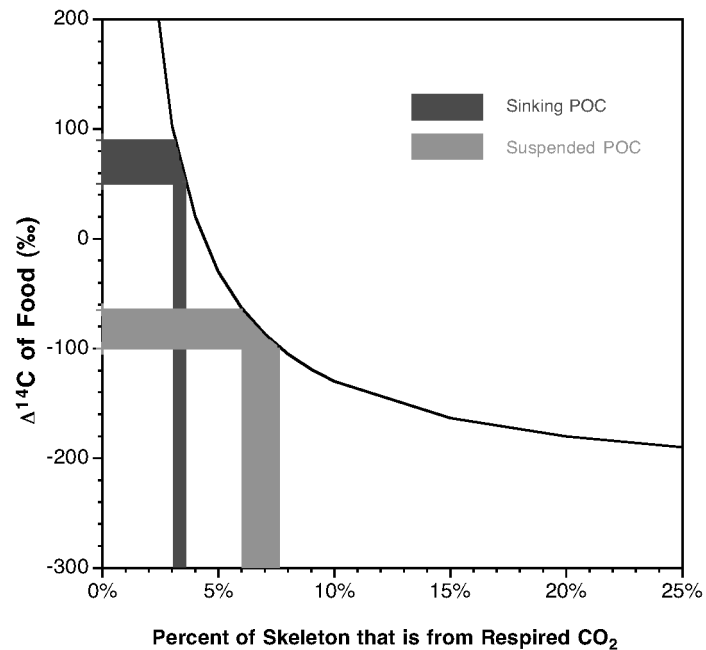
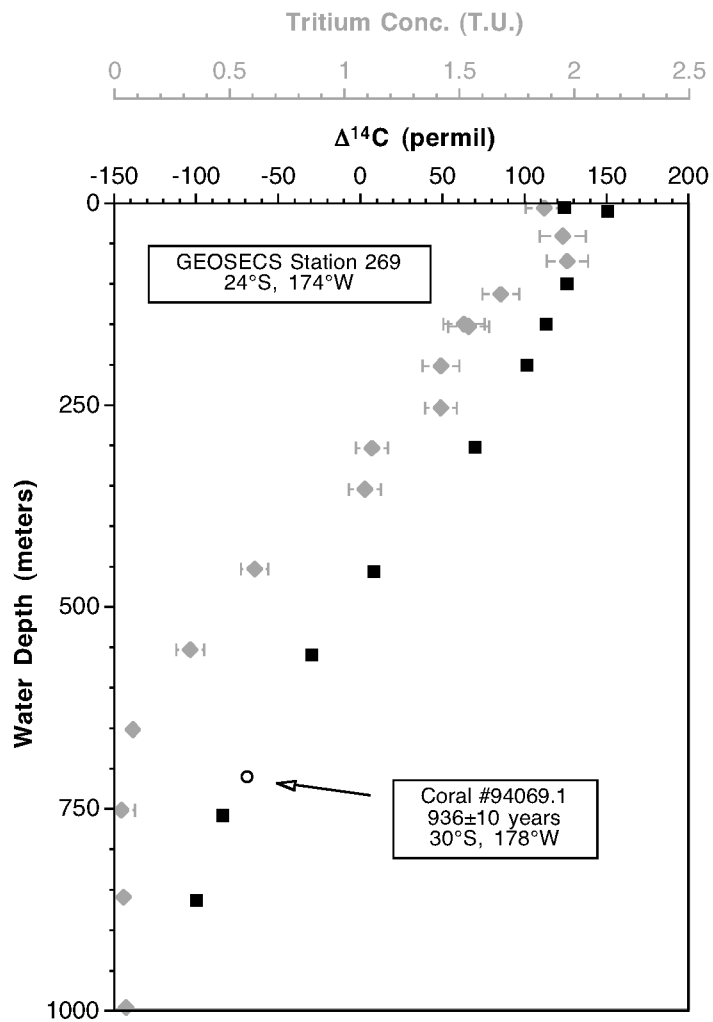


Figure 6 (above) Results of the metabolic carbon calculation described in the text. The black line describes all possible combinations of the fraction of skeletal carbon that is from the coral's food source and the $\Delta^{14}\text{C}$ of that source. Particulate data from a nearby hydrographic station shows that at most 8% of the skeleton could be from suspended particulate organic carbon (POC). Within error the sample used to make the black line lies on the 1:1 modern calibration line, so that 0% respired carbon in the skeleton is also a possibility.

Figure 5 (left) Example of water $\Delta^{14}\text{C}$ estimation for use in Figure 4. Sample 94069.1 lies on the trend in the modern $\Delta^{14}\text{C}$ profile. At this depth in the mid-1970s the influence of bomb ^3H was negligible.

important implications for the mechanism of coral calcification when there are not photosymbionts to feed dissolved organic carbon to the polyp.

CONCLUSION

Before reliable ^{14}C ages can be collected, fossil deep-sea corals must be cleaned of their black crusts and endolithic activity. Immediately prior to graphitization, these samples must have at least 10% of their mass acid leached to remove the effect of adsorbed modern CO_2 . Once these precautions are taken, it is clear that deep-sea corals record the $\Delta^{14}\text{C}$ of the DIC in which they grow. At most, 8% of the skeleton can come from respired CO_2 . Coupled with U-series ages this makes deep-sea corals a promising new archive of paleo-ventilation rates. When there is no change in bottom water $\Delta^{14}\text{C}$ during a coral's lifetime, the ^{14}C age difference between the top and the bottom reflects the mean skeletal extension rate.

REFERENCES

- Adkins JF, Boyle EA. 1999. Age screening of deep-sea corals and the record of deep North Atlantic circulation change at 15.4 ka. In: Abrantes F, Mix A, editors. *Proceedings of the Sixth International Conference on Paleoceanography*. Elsevier. Forthcoming.
- Adkins JF, Cheng H, Boyle EA, Druffel ERM, Edwards L. 1998. Deep-sea coral evidence for rapid change in ventilation of the deep North Atlantic 15,400 years ago. *Science* 280:725–8.
- Bard E. 1988. Correction of accelerator mass spectrometry ^{14}C ages measured in planktonic foraminifera: paleoceanographic implications. *Paleoceanography* 3: 635–45.
- Bard E, Arnold M, Fairbanks R, Hamelin B. 1993. ^{230}Th - ^{234}U and ^{14}C ages obtained by mass spectrometry on corals. *Radiocarbon* 35(1):191–9.
- Bien GS, Rakestraw NW, Suess HE. 1960. Radiocarbon concentration in Pacific Ocean water. *Tellus* 12:436–43.
- Broecker WS. 1963. $^{14}\text{C}/^{12}\text{C}$ ratios in surface ocean water. *Nuclear Geophysics* 1963:138–49.
- Broecker WS. 1979. A revised estimate for the radiocarbon age of North Atlantic Deep Water. *Journal of Geophysical Research* 84:3218–26.
- Broecker WS, Klas M, Clark E, Trumbore S, Bonani G, Wolfli W, Ivy S. 1990. Accelerator mass spectrometric measurements on foraminifera shells from deep sea cores. *Radiocarbon* 32(2):119–33.
- Broecker WS, Peng T-H. 1982. *Tracers in the sea*. Eldigio Press.
- Broecker WS, Peng T-H, Ostlund G, Stuiver M. 1985. The distribution of bomb radiocarbon in the ocean. *Journal of Geophysical Research* 90:6953–70.
- 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.
- Cheng H, Adkins JF, Edwards RL, Boyle EA. 2000. U-Th dating of deep-sea corals. *Geochemica et Cosmochimica Acta* 64:2401–16.
- Donahue DJ, Linick TW, Jull AJT. 1990. Isotope ratio and background corrections for accelerator mass spectrometry radio carbon measurements. *Radiocarbon* 32(2):135–42.
- Druffel ERM, Linick TW. 1978. Radiocarbon in annual coral rings of Florida. *Geophysical Research Letters* 5(11):913–6.
- Druffel ERM, Bauer JE, Williams PM, Griffin S, Wolgast D. 1996. Seasonal variability of particulate organic radiocarbon in the northeast Pacific Ocean. *Journal of Geophysical Research* 101: 20,543–52.
- Duplessy J-C, Arnold M, Bard E, Juillet-Leclerc A, Kallel N, Labeyrie L. 1989. AMS ^{14}C study of transient events and of the ventilation rate of the Pacific intermediate water during the last deglaciation. *Radiocarbon* 31(3):493–502.
- Edwards LR, Beck WJ, Burr GS, Donahue DJ, Chappell JMA, Bloom AL, Druffel ERM, Taylor FW. 1993. A large drop in atmospheric $^{14}\text{C}/^{12}\text{C}$ and reduced melting in the Younger Dryas, documented with ^{230}Th ages of corals. *Science* 260:962–7.
- Fonselius S, Ostlund G. 1959. Natural radiocarbon measurements on surface water from the North Atlantic and the Arctic Sea. *Tellus* 11:77–82.
- Goldstein SJ, Lea DW, Chakraborty S, Kashgarian M, Murrell MT. 2001. Uranium-series and radiocarbon geochronology of deep-sea corals: implications for Southern Ocean ventilation rates and the oceanic carbon cycle. *Earth and Planetary Science Letters* 193: 167–82.
- Griffin S, Druffel ERM. 1989. Sources of carbon to deep-sea corals. *Radiocarbon* 31(3): 533–43.
- Hughen KA, Overpeck JT, Lehman SJ, Kashgarian M, Southon J, Peterson LC, Alley R, Sigman DM. 1998. Deglacial changes in ocean circulation from an extended radiocarbon calibration. *Nature* 391:65–8.
- Mangini A, Lomitschka M, Eichstadter R, Frank N, Vogler S, Bonani G, Hajdas I, Patzold J. 1998. Coral provides way to age deep water. *Nature* 392:347–8.
- Shackleton NJ, Duplessy J-C, Arnold M, Maurice P, Hall MA, Cartlidge J. 1988. Radiocarbon age of the last

- glacial Pacific deep water. *Nature* 335:708–11.
- Shen GT, Boyle EA. 1988. Determination of lead, cadmium and other trace metals in annually-banded corals. *Chemical Geology* 67:47–62.
- Stocker TF, Wright DG. 1996. Rapid changes in ocean circulation and atmospheric radiocarbon. *Paleoceanography* 11:773–96.
- Stuiver M, Polach HA. 1977. Reporting of ^{14}C data. *Radiocarbon* 19(3):355–63.
- Stuiver M, Quay PM, Ostlund HG. 1983. Abyssal water carbon-14 distribution and the age of the world oceans. *Science* 219:849–51.
- Vogel JS, Nelson DE, Southon JR. 1987. ^{14}C background levels in an accelerator mass spectrometry system. *Radiocarbon* 29:323–33.