[RADIOCARBON, VOL. 15, NO. 1, 1973, P. 68-74]

HAWAII INSTITUTE OF GEOPHYSICS RADIOCARBON DATES I

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INTRODUCTION

The radiocarbon dating laboratory of the University of Hawaii was established with joint support of the Hawaii Institute of Geophysics, the Water Resources Research Center, the Department of Chemistry, and the Graduate Division. The laboratory is located in the Hawaii Institute of Geophysics, on the ground floor of a four-story concrete building, and contains two separate radiocarbon counting systems.

1. Gas proportional counter

The sample counter has a volume of ca. 850 cc, is built from a silvered quartz tube with nylon end-plugs and a 0.05 mm stainless steel anode wire. The guard counter is an annular, 9-wire, gas-proportional counter with plexiglas end-pieces and an aluminized plexiglas wall. Counting array is surrounded by, in order, one cm stainless steel, 3 cm Hg, one cm stainless steel, and 15 cm old iron (the breech section of an 8-in. 1945 howitzer).

The sample is converted to methane (Buddemeier *et al.*, 1970). Sample pressure is controlled by reference to a modified Wallace and Tiernan pressure gauge (Model 62A-2B-0120). The guard counter is filled with tank methane at the same pressure as the sample; to date, all determinations have been at a pressure of 2 atm, absolute.

A Power Designs 1556A HV power supply provides a negative 4660 v to the walls of both counters; this operates both sample and guard counters on their proportional plateaus. Charge-sensitive preamplifiers transmit the pulses to a Smith-Root Model 200 4-channel anticoincidence scaling unit. Channels monitored are: I) net sample above the upper discriminator; II) net sample between upper and lower discriminator; III) gross sample above lower discriminator; and IV) guard. Discriminators are adjusted empirically for optimum standard/background ratio; Channel II provides the sample count, Channel I monitors radon contamination, and the difference between Channel III and the sum of I and II represents the sum of cosmic ray count rate plus background; the relative constancy of this rate provides a simple check on the counting characteristics of the sample gas. Channel II triggers a Simplex printing time clock every 100 counts; Chauvenet's criterion for rejection of statistical data is applied to the resulting printout before final calculation.

Samples are measured in 2 one-day counts, at least one week apart. If the 2 counts differ by >1 standard deviation, the sample is counted a 3rd time. A normal counting sequence consists of an 8-day cycle containing 1 background, 3 samples, 1 NBS oxalic acid standard, and 3

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more samples. Background samples are prepared by dry combustion of coal. All samples are aged at least 2 weeks to eliminate radon contamination.

For geophysical samples, δC^{14} values are reported; dates are based on the 5568 yr half-life. All values are reported with an error of one standard deviation, including the statistical uncertainty in the observed counting rate of the unknown and the uncertainty in the background and standard counting rates. For the samples cited below, the average of 11 background determinations was 1.96 ± 0.05 cpm and the average value of 95% of net NBS oxalic acid activity, based on 13 measurements, was 8.04 ± 0.10 cpm. In both cases, individual counts were distributed statistically around the mean, and 4-sample running averages revealed no significant trends.

Almost complete is a 2nd counter, similar to the 1st but with .025 mm anodes and a 10 kv power supply to permit measurements at higher pressures. Under development is a stable isotope laboratory which will permit determinations of δC^{13}.

2. Liquid scintillation counter

Since 1967, the Water Resources Research Center has used a Beckman LS-100 liquid scintillation counter to monitor "bomb" tritium and radiocarbon in Hawaiian natural waters. The instrument and procedures have been modified to a dating level. Variable discriminators, a variable high voltage control, and 5 cm of lead shielding above the counting chamber were added. Benzene is synthesized from sample CO_2 by the method of Noakes *et al.* (1965) and is counted in shortened Beckman low-background glass counting vials. Samples are diluted to a total net weight of 6.000 g with reagent grade benzene, also serving as background benzene.

Counting vials show slight variations in inherent background levels; relative values of these vials have been well established. A normal radiocarbon count consists of 2 backgrounds, 2 NBS oxalic standards, one "hot" efficiency check standard, and 6 samples, all cycled at 50 min. intervals for at least a week. Background values are determined by multiplying the background monitor samples by the appropriate vial ratios. Except for long-term accumulation of these ratios, each counting cycle is a self-contained set of determinations, permitting alternation of radiocarbon and tritium determinations without extensive recalibration.

Discriminator and voltage settings were selected for maximum stability of radiocarbon count rate with respect to system variations (Polach, 1969). Typically, values for 95% of net NBS oxalic acid activity are ca. 7.65 cpm/g carbon and for background, ca. 6.30 cpm for a 6 g blank. Standard deviations of all activities are estimated by counting statistics and by calculating standard deviations of the average of separate count intervals; the larger value is used for ($\pm 1\sigma$) uncertainties.

Unless stated otherwise, ground water activities were determined

https://doi.org/10.1017/S0033822200058604 Published online by Cambridge University Press

on the liquid scintillation counter; other activities with the gas proportional counter.

ACKNOWLEDGMENTS

We gratefully acknowledge the invaluable advice of A. W. Young, University of Washington and H. A. Polach, Australian National University, on equipment design and laboratory procedures. A. Puccetti, A. Barres, and C. Hosokawa assisted in sample preparation. The support and encouragement of G. P. Woollard, L. S. Lau, K. E. Chave, R. G. Inskeep and R. L. Pecsok made development of the laboratory possible. This date list is the Hawaii Institute of Geophysics Contribution No. 446, Water Resources Research Center Cooperative Contribution No. 3.

SAMPLE DESCRIPTIONS

I. CORALS AND CORALLINE ALGAE

Samples are analyzed by x-ray diffraction; contents of > a few % calcite are noted. Samples are prepared by adding 3 N HCl to coral chips in a system purged with CO_2-free tank N_2. CO_2 is trapped with liquid nitrogen; if size permits, the 1st 10 to 15% of the gas evolved is discarded to reduce possible surface contamination. Since pre-bomb zero age of ocean surface water is approx. zero without δC^{13} correction and since coral carbonate is close to isotopic equilibrium with the water, uncorrected ages are reported for species grown at or near sea level; δC^{14} (‰) values are reported for all samples.

Interlaboratory check sample

HIG-1. Great Barrier Reef, Australia

14,045 ± 335
12,095 B.C.
$\delta C^{14} = -826 \pm 7$‰

Specimen dated by Isotopes, Inc. at 13,600 ± 200; subm. by H. H. Veeh, described by Veeh and Veevers (1970). *Comment*: agreement is adequate; U-Th age of 17,000 ± 1000 yr has been reported.

Eniwetok series

Samples are from 3 sites: reef flat (11° 25′ 59″ N Lat, 162° 23′ 30″ E Long); algal ridge (11° 25′ 5″ N Lat, 162° 23′ 41″ E Long) and groove and spur system on reef front (11° 25′ 29″ N Lat, 162° 23′ 45″ E Long), Eniwetok Atoll, Marshall Is. Sites lie on a transect running WNW to ESE and centered ca. 1 km NE of Muti I. All samples coll., id. and subm. May-June 1971 by S. V. Smith and R. A. Kinzie, Univ. Hawaii.

HIG-2. Algal ridge-1

4420 ± 140
2470 B.C.
$\delta C^{14} = -423 + 10$‰

Large coral head cemented in matrix of algal-coral rubble limestone. Base of coral ca. 50 cm below surface of algal ridge pavement; surface approx. at present MSL. *Comment*: age should be of cementation of algal ridge pavement.

4980 ± 150
HIG-3. Reef flat-1 **3030 B.C.**
$\delta C^{14} = -462 \pm 10‰$

Base of coral head (*Acropora*) cemented into reef flat pavement by *Halimeda* sandstone. Ca. 1 m below present MSL. *Comment*: dates deposition, maximum age of cementation of reef flat pavement.

3960 ± 135
HIG-4. Reef flat-2 **2010 B.C.**
$\delta C^{14} = -389 \pm 10‰$

Flakes of loosely to moderately cemented *Halimeda* separated from a chunk of reef flat pavement, from 5 to 7 cm below pavement surface; ca. −1 m. *Comment* (S.V.S.): appears shallow and relatively unaltered; may date most recent marine cementation on reef flat.

345 ± 100
HIG-5. Groove and spur-1 **A.D. 1605**
$\delta C^{14} = -42 \pm 12‰$

Piece of coral rubble 2 to 13 cm below surface of large piece of limestone blasted from side of spur, at −2 to 3 m. Matrix above and beside sample consists of encrusting coralline algae; coral-algal rubble is below. *Comment* (S.V.S.): age suggests latest portion of spur and groove system history is constructional or combined constructional-erosional.

170 ± 100
HIG-6. Groove and spur-2 **A.D. 1780**
$\delta C^{14} = -21 \pm 12‰$

Coralline algal layer ca. 6 cm below HIG-5. *Comment*: age agrees with HIG-5 and supports comment.

Glover's Reef, British Honduras

1945 ± 115
HIG-7. Glover's Reef-1 **A.D. 5**
$\delta C^{14} = -215 \pm 11‰$

Coral (*Diploria strigosa*) from Glover's Reef, British Honduras (11° 28′ N Lat, 87° 27′ W Long), embedded in sandy phosphate rock ca. 30 cm below surface and ca. 1.6 m above present MSL. Coll. and subm. 1971 by K. E. Chave, Univ. Hawaii; id. by K.E.C. and F. R. Fosberg, Smithsonian Inst. *Comment* (K.E.C.): suggests date of deposition of phosphate rock on a coral atoll presently with neither birds nor roosting sites.

Deep-water coral series

To determine whether to use either "bomb" C^{14} or conventional radiocarbon dating to study growth rates and carbon sources of Hawaiian pink corals, samples of *Corallium secundum* were dredged from a coral bed ca. 8 km E of Makapuu Pt., Oahu (21° 12′ N Lat, 157° 32′ W Long), from depth 400 m. Samples were alive, and grew on a carbonate surface

swept by rapid bottom currents. Coll., id., and subm. by R. W. Grigg, Univ. Hawaii.

HIG-8. Pink coral-1 $\delta C^{14} = -42 \pm 15‰$

Tips of branches coll. August, 1970, and estimated to be 2 yr old. Diluted to 82.0% sample.

HIG-9. Pink coral-2 $\delta C^{14} = -55 \pm 12‰$

Material drilled from centers of 3 large coral trunks coll. 1968 and 1969. Diam. from 2.4 to 3.5 cm; inner 1 cm sampled from each and drillings combined.

General Comment: difference of activity is questionable, but if so, it is expected as a result of bomb C^{14} penetration into the intermediate water layer. Both activities are lower than expected from the water profile given below, which suggests that either the coral's source of skeletal carbon or its immediate environment is different from that assumed. Investigations are continuing.

II. OCEAN WATER

Station Gollum is in 4760 m of water 47 km N of Oahu (22° 10′ N Lat, 150° 00′ W Long), a site of various geochemical and oceanographic studies since 1969 (Gordon, 1970). C^{14} profiles were taken several times a year to observe rate of penetration of excess C^{14} into the intermediate water; the profile below was measured first for comparison with the deep water coral results given above. Samples were taken with a 60 L water sampler (Young *et al.*, 1969), aliquots analyzed for total CO_2 and salinity, and CO_2 stripped out as described by Fairhall *et al.* (1971).

TABLE 1

Sample no.	Date	Depth	δC^{14}(‰)
HIG-10	1 Apr. 70	Surface	+276 ± 15
HIG-11	"	300 m	+ 92 ± 13
HIG-12	"	500 m	− 49 ± 10
HIG-13	"	800 m	− 87 ± 12
HIG-14	"	1500 m	−123 ± 12

III. VOLCANIC ENVIRONMENTS

Kilauea Ohia series

These samples are initial results from a long-term study designed to use magmatic (dead) CO_2 as a tracer for volcanic product distribution (Chatters *et al.*, 1969) and to estimate total volcanic emission on the basis of CO_2 dilution contours. Samples coll. on a grid around Kilauea volcano on Hawaii I., and, unless otherwise specified, are of recent growth shoots of ubiquitous *Metrosideros* tree. Samples <3 mos old (Lamoreaux and Porter, 1971, Dept. Botany, Univ. Hawaii, *oral commun.*).

HIG-15. Kilauea I-8a $\delta C^{14} = -7 \pm 13‰$

Coll. 13 April 1971 in Sulfur Banks area of Volcano Natl. Park (19° 26′ 2″ N Lat, 155° 15′ 51″ W Long). Trees were on a bank above and ca. 3 m downwind of an active fumarole. Moderate to heavy vegetation, noticeable warmth and moisture and some vegetation damage from fumarolic gases. Alt. 2600 m.

HIG-16. Kilauea I-11 $\delta C^{14} = +462 \pm 16‰$

Coll. 14 April 1971 on Mauna Loa Summit trail NW of Kilauea (19° 30′ N Lat, 155° 25′ W Long). Area sparsely wooded, dry. Alt. 4100 m.

General Comment: HIG-16 should be relatively free of volcanic effects, but is at alt. of trade-wind inversion and may not fully represent unperturbed conditions at alt. of volcano. HIG-15 is depleted ca. 32‰ relative to HIG-16, suggesting an equivalent apparent age of ca. 3000 yr under pre-bomb conditions.

IV. HAWAIIAN GROUND WATER

Well, shaft, and spring water samples are regularly analyzed for radiocarbon, tritium, and chemical content for both geochemical research and water resource evaluation. These samples are from tunnels or shafts in the Koolau range on Oahu I. The geologic environment is almost exclusively basaltic, and heavily compartmented by dikes. Ground surfaces have abundant vegetation and virtually no human modification. The area receives large amounts of rain and is one of the major recharge area for Oahu's ground water. In Table 2, H is the approx. vertical distance between the tunnel and the overlying surface. Coll. by T. H. Hufen.

TABLE 2

Sample no.	Tunnel	Date	$H_{(m)}$	δC^{14}(‰)
HIG-17	Nuuanu	15 Nov. 71	20	+135 ± 16
HIG-18	Manoa	19 Nov. 71	40	+ 14 ± 14
HIG-19	Palolo	11 Sept. 71	60	+ 28 ± 16
HIG-20	Waihee	1 Nov. 71	80	− 19 ± 15
HIG-21	Luluku	18 Oct. 71	100	− 14 ± 14
HIG-22	Haiku	28 Sept. 71	260	− 47 ± 13

General Comment: HIG-19 contains no measurable tritium, HIG-20 yields a tritium count on the margin of significance; the others definitely contain bomb tritium. Results suggest the pre-bomb zero-age activity of ground water originating in the Koolau range is ca. −15‰. This supports assumptions that this area will have both rapid flow rates for water and a rapid turnover of soil carbon.

https://doi.org/10.1017/S0033822200058604 Published online by Cambridge University Press

References

Buddemeier, R. W., Young, A. Y., Fairhall, A. W., and Young, J. A., 1970, Improved system of methane synthesis for radiocarbon dating: Rev. Sci. Instruments, v. 41, p. 652-654.

Chatters, R. M., Crosby, J. W., and Engstrand, L. G., 1969, Fumarole emanations: their influence on carbon-14 dates: Circ. 32, Coll. Engineering, Research Div. Washington State Univ., Pullman, Washington.

Fairhall, A. W., Buddemeier, R. W., Yang, I. C., and Young, A. W., 1971, Radiocarbon in the sea: USAEC rept. HASL-242, p. I-35—I-78.

Gordon, D. C., 1970, Chemical and biological observations at Station Gollum, an oceanic station near Hawaii, Jan. 1969 to June 1970: Hawaii Inst. of Geophysics tech. rept. HIG-70-22.

Noakes, J. E., Kim, S. M., and Stipp, J. J., 1965, Chemical and counting advances in liquid scintillation age dating: Radiocarbon and tritium dating, 6th internatl. conf. Proc., Pullman, Washington, p. 68-92.

Polach, H. A., 1969, Optimisation of liquid scintillation radiocarbon age determinations and reporting of ages: Atomic Energy in Australia, v. 12, no. 3, p. 21-28.

Veeh, H. H. and Veevers, J. J., 1970, Sea level at −175 m off the Great Barrier Reef 13,600 to 17,000 years ago: Nature, v. 226, p. 536-537.

Young, A. W., Buddemeier, R. W., and Fairhall, A. W., 1969, A new 60-liter water sampler built from a beer keg: Limnol. and Oceanog., v. 14, p. 634-637.