98. *Non-Destructive $^{226}Ra/^{238}U$ dating of Quaternary Corals by Gamma-Spectrometry*

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Introduction. Since Barnes *et al.* (1956) proposed the uranium-ionium (^{230}Th) method of dating, many works have been performed for dating of fossil corals (Komura and Sakanoue, 1967; Bloom *et al.*, 1974; Ku *et al.*, 1974; and see the references therein). The ^{230}Th method has a potential to estimate the absolute age back to about 300000 years. This method is one of the most reliable methods for a sample older than a few ten thousand years, since the half-life of ^{14}C limits the applicable age back to about 40000 years.

In order to determine ^{230}Th age, activity ratios of $^{230}Th/^{234}U$ and $^{234}U/^{238}U$ must be measured. Alpha spectrometry has usually been performed to measure these isotopes. On the other hand, measurement of ^{230}Th can be made indirectly by its daughter nuclide ^{222}Rn by assuming radioactive equilibrium between ^{230}Th and ^{226}Ra (^{222}Rn) (Nydal, 1975). If this assumption is acceptable, the ^{230}Th can also be measured by ^{214}Pb, ^{214}Bi and ^{210}Pb, the amount of which can be determined by γ-spectrometry. Furthermore, ^{238}U concentration can be determined by measuring low energy γ-rays from its daughter nuclide ^{234}Th. In this report, the non-destructive $^{226}Ra/^{238}U$ method is proposed for the dating of fossil corals by γ-spectrometry using a germanium detector Ge(Li) and a low energy photon spectrometer (LEPS). The non-destructive dating method has advantages over the conventional ones in that the elaborate and time-consuming chemical procedures are unnecessary and no change in the chemical state occurs in the sample analyzed, hence, the same sample can be used for further investigation after the non-destructive measurement.

Method of measurement. Five coral samples which range in age from present-day to Late Pleistocene, but retain their entire initial aragonite mineralogy were selected to test the applicability of the proposed method. Sample descriptions are given in Table I. The

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Table I. Coral samples measured by non-destructive $^{226}Ra/^{238}U$ dating method

Sample	Suggested age	^{14}C-date ($\times 1000$ y)	^{230}Th-date ($\times 1000$ y)	Sample location and stratigraphic unit	Reference
CK-M1	Present-day	——	——	Kikai, Fore-reef slope, 8 m below MSL	
N-2723	Late Holocene	3.95 ± 0.09	——	Kikai, Raised Coral Reef	(a)
CK-19	Latest Pleistocene	——	41 ± 2	Kikai, Araki Limestone	(b)
GH-3	Late Pleistocene	27.5 ± 0.7	——	Minami-daito, Kaigunbo Limestone	(c)
GH-1	Late Pleistocene	>37.8	——	Minami-daito, Kaigunbo Limestone	(c)

(a) Ota *et al.*, Geographical Rev. Japan, vol. 51, p. 109 (1978).
(b) Konishi *et al.*, Proc. Second Intern. Coral Reef Symp., vol. 2, p. 595 (1974).
(c) Konishi *et al.*, Proc. Japan Acad., vol. 54B, p. 516 (1978).

ages suggested for two fossil corals from Minami-daito are partly based on the oxygen isotope analysis of the associated molluscs (Konishi *et al.*, 1978). The coral samples were crushed by a hammer and powdered in an agate mortar. The powdered sample of 37 to 54 grams was compressed to a disc shape of 50 mm diameter and wrapped by thin Saran sheet. Then it was sealed in a polyethylene bag to prevent the loss of gaseous nuclide ^{222}Rn. Two types of heavily shielded germanium detectors, the detection efficiencies of which are carefully calibrated by mock-up sources containing known amounts of natural uranium, ^{22}Na, ^{137}Cs and KCl, were used for γ-ray measurements. Low energy γ-rays from ^{234}Th (63 and 93 keV) were measured by a LEPS detector with 32 mm$\phi\times$10 mm thick. The γ-rays from

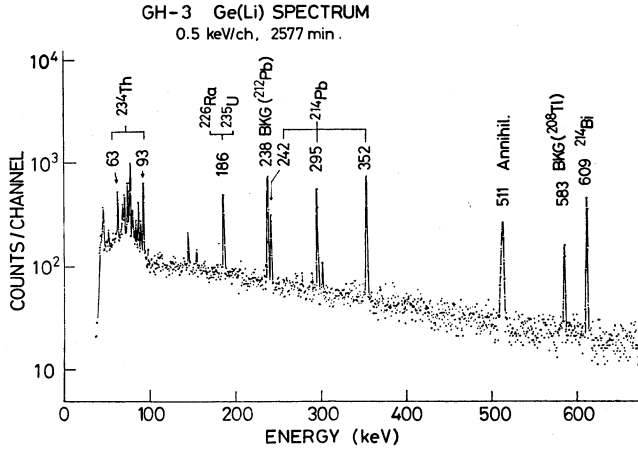

Fig. 1. Ge(Li) spectrum of sample GH-3.

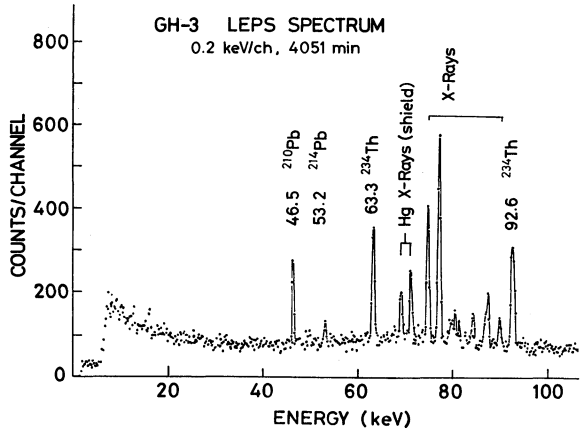

Fig. 2. LEPS spectrum of sample GH-3.

^{214}Pb (295 and 352 keV) and ^{214}Bi (609, 1120 and 1764 keV) were measured by a coaxial type Ge(Li) detector having 82 cm^3 of active volume and 16% of efficiency relative to 7.6 cm×7.6 cm NaI(Tl) detector at 25 cm for 1332 keV. The coral samples were measured for 2 to 7 days. Examples of the spectra taken by the Ge(Li) and LEPS detector are shown in Figs. 1 and 2.

Result and discussion. The results of non-destructive $^{226}Ra/^{238}U$ dating are summarized in Table II. The estimated ages are calculated by assuming the initial activity ratios of $^{234}U/^{238}U$, $^{230}Th/^{238}U$ and $^{226}Ra/^{238}U$ to be 1.15, 0.015 and 0.015, respectively. The errors in the table are due only to counting statistics. As shown by comparison of Tables I and II, the ages determined by the present method are consistent with those estimated by ^{14}C and ^{230}Th methods except GH-3. Oxygen isotope analysis of associated gastropods (Konishi *et al.*, 1978) indicates that the sea surface stood high, close to the present level, during deposition of the Kaigunbo Limestone, and eliminates the possible assignment to Late Wisconsin time as suggested by the ^{14}C date for GH-3.

In order to obtain a reliable $^{226}Ra/^{238}U$ age, initial values of $^{234}U/^{238}U$, $^{230}Th/^{238}U$ and $^{226}Ra/^{238}U$ must accurately be known. These

Table II. Results of non-destructive $^{226}Ra/^{238}U$ dating method

Sample	Weight (g)	^{238}U (ppm)	^{226}Ra (dpm/g)	$^{226}Ra/^{238}U$ (% equil.)	Estimated age (×1000 y)
CK-M1	42.8	3.66±0.12	0.037±0.014	1.4±0.6	0
N-2723	49.2	2.80±0.15	0.079±0.012	3.8±0.6	4.2± 0.8
CK-19	48.5	2.64±0.13	0.777±0.041	40.1±2.8	48 ± 8
GH-3	37.1	2.71±0.22	1.42 ±0.02	71.3±5.8	110 ±14
GH-1	54.0	3.14±0.12	1.61 ±0.02	69.7±4.0	105 ±11

values can be experimentally measured by analyzing present-day corals. For the $^{234}U/^{238}U$ ratio, the value of 1.15, which is the average of 28 present-day corals measured by Omura (1976), is adopted. Sakanoue *et al.* (1967) obtained the value of 0.014 ± 0.002 as the initial $^{230}Th/^{234}U$ ratio for the coral sample collected in Kikai. A similar attempt has been made by Omura (1976), who obtained initial $^{230}Th/^{234}U$ ratios ranging from 0.0026 to 0.056 (average value $\simeq$0.015). The value of 0.015 adopted in the present work is based on the above values. The initial ^{226}Ra problem is serious only for a sample younger than 10000 years because of the relatively short life of ^{226}Ra. It seems reasonable to consider that radium is incorporated by corals in nearly the same radium-to-calcium ratio as that in sea water (Broecker, 1963). According to Moore and Krishnaswami (1972), present-day corals collected in Jamaica contained about 5 dpm (disintegration per min) of ^{226}Ra per 100 g of coral sample, which agrees with our value of 3.7 ± 1.4 dpm/100 g-coral obtained from sample CK-Ml. If one assumes the average concentrations of uranium and radium in corals to be 3 ppm and 4 dpm/100 g-coral, respectively, the initial $^{226}Ra/^{238}U$ ratio becomes 0.018. So, the initial value of 0.015 appears to be reasonable.

The accuracy of age estimation by non-destructive $^{226}Ra/^{238}U$ dating method may be greatly improved by using a detector with higher detection efficiency and lower background. The large diameter of the LEPS detector, for example, 50 mmϕ with a thickness of 15–20 mm seems to be most suitable for non-destructive dating. By using such a LEPS detector, low energy γ-rays from ^{234}Th and ^{210}Pb and even from ^{214}Pb can be measured simultaneously with high detection efficiency and the age is simply calculated from $^{210}Pb/^{234}Th$ and $^{214}Pb/^{234}Th$ activity ratios.

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