Studies on the Dating Methods for Quaternary Samples by Natural Alpha-Radioactive Nuclides

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I-1 Introduction

In the history of the Earth, the creation of the human civilization may be the most interesting and important event. It may afford the important contribution to our understandings both on the Earth's and man's history to know the circumstances and the absolute date of the evolution of the human race.

The discovery of radioactivity, which appeared as one of the leading actor of science at the end of nineteenth century, not only upset the conception of the elements, but also by efforts of a great many scientist realized the dream of utilizing atomic energy. It was soon after the discovery of the radioactivity that the constancy of the radioactive decay drew the attention of scientist as a natural clock.

The exsistence of the relationship between the lead content and the geological ages of the uranium minerals (Boltwood, 1907) had become the first cognition of the usefulness of the radioactivity as a tool for the dating of geological formation. Though in following year Strutt proposed the He/U method for dating of uranium minerals, the theoretical foundation was not given until discovery of the displacement law by Soddy and Russell (1922). According to this law, the uranium isotopes ^{238}U and ^{235}U and the thorium isotope ^{232}Th decay through series of short-lived daughters to stable lead isotopes ^{206}Pb, ^{207}Pb and ^{208}Pb, respectively. Fig. 1 shows these three
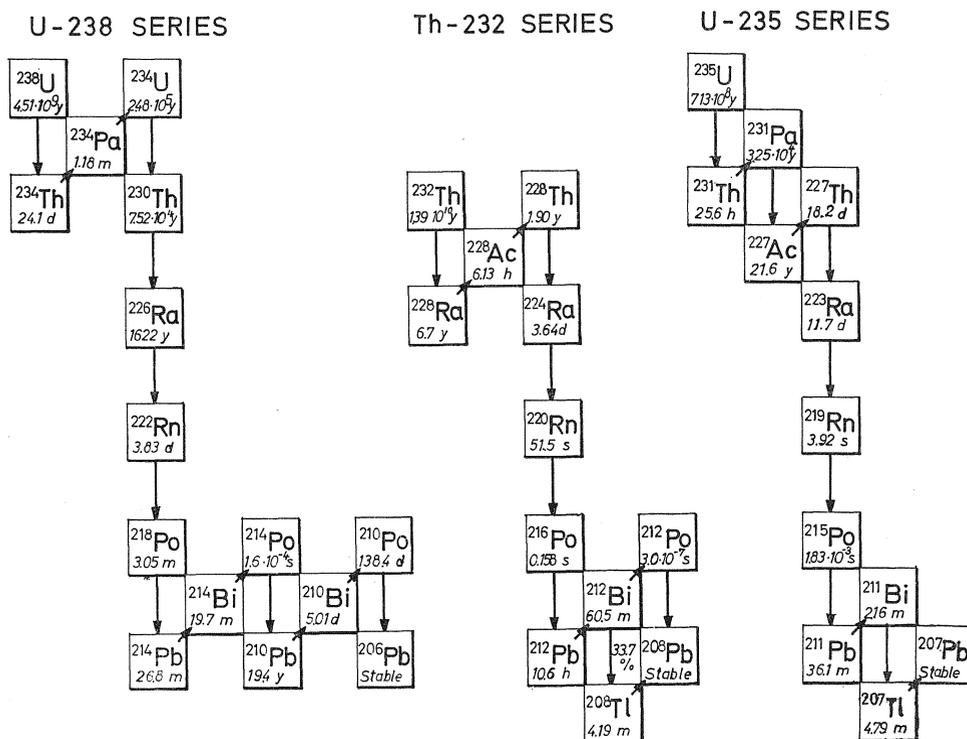
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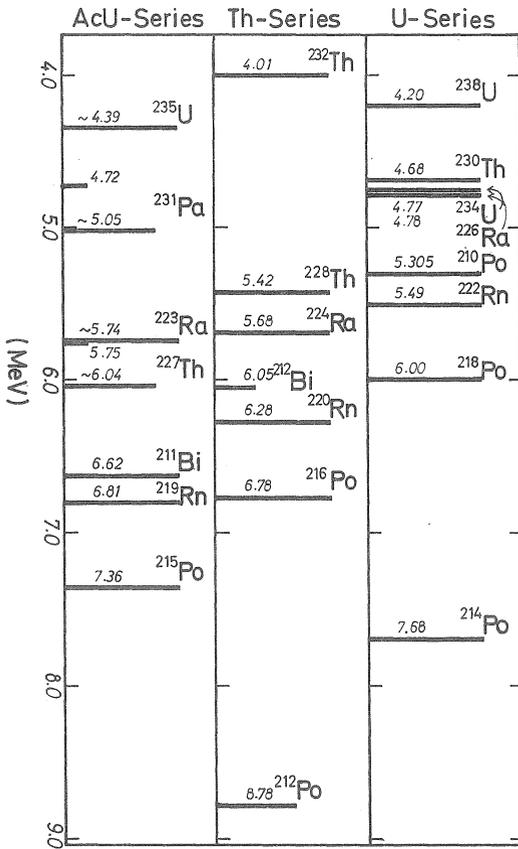
Fig. 1 b. Alpha Particle Energies of the Decay Chain Members

natural radioactive decay series (Fig. 1 a) together with the alpha particle energies of the members in these chain series (Fig. 1 b).

By the invention and the developments of mass spectrometric techniques, the dating method using long lived radioactive isotopes other than uranium and thorium had made great advances. They are ^{87}Rb-^{87}Sr method (Ahrence, 1947), ^{40}K-^{40}Ar method (Aldrich and Nier, 1948), ^{187}Re-^{187}Os method (Herr and Merz, 1958), ^{40}K-^{40}Ca method (Polevaya et al., 1958) etc.. In spite of the wide applications of these dating methods, their availabilities were limitted to the sample older than several million years because of the long half-lives of the parent nuclides. So, the dating method applicable for Quaternary age was sought extensively.

The problem of Quaternary age determination was solved by an unexpected method based on the cosmogenic radioactive carbon isotope ^{14}C(1), which is produced at constant rate in the upper atmosphere by ^{14}N (n, p) ^{14}C reaction. Radiocarbon produced from the nitrogen in the atmosphere is soon oxidized to $^{14}CO_2$ and mixed with non-radioactive CO_2 in air, and then the circulation of the radiocarbon among the atmosphere, hydrosphere and biosphere begins. Once ^{14}C is fixed in the organisms or geological formations containing carbon, the change in specific activity of ^{14}C will indicate the time from the end of the exchange of carbon between the sample and its environments, unless the carbon exchange occurs during the sample preservation. As the carbon is one of the most important constituent of the organic materials and has high abundance in nature, ^{14}C dating method is applicable nearly all of the samples containing carbon. However, the relatively short half-life of ^{14}C (5730 yr) limits the available range of this method back to about 40,000 years, and the gap between million years determined by mass spectrometric methods and several ten thousand years by radiocarbon method still remained to be filled with other useful method for dating.

I-2 History of the Excess ^{230}Th (Ionium) and ^{231}Pa (Protactinium) Methods for Pleistocene Dating

From the view point of half-lives, ^{230}Th (75,200 yr) and ^{231}Pa (32,480 yr) are very attractive for Pleistocene age determination. This was pointed out first by Khlopin (2) for the age determination of secondary uranium minerals, but had not been realized for a long time because of the difficulty of the direct determination of ^{230}Th or ^{231}Pa. The fact discovered by Joly (1908) that the radium content in sea sediment core is much greater than that in terrestrial materials, was reaffirmed by Piggot and Urry (3) in 1942, and this became the initiation of the excess ^{230}Th method (the use of ^{230}Th decay in sample) for Pleistocene dating of sea sediments. This method had been improved greatly by the direct determination of ^{230}Th (4) and by the advances of the apparatuses for alpha spectrometric measurement. Though many works have been carried out in this direction, the accumulation of the analytical data showed the possibility of the migration of ^{230}Th itself in and out the sample and the excess ^{230}Th method was sometimes proved to be erroneous for the dating of the sedimentation rate of the sea sediments.

On the other hand, the use of ^{231}Pa as a tool for age determination was put into practice only recently by Rosholt (5) in 1961, because of the extremely low concentration of ^{231}Pa in natural samples and of its trouble behaviours in chemical treatment. Recently several investigations as to the excess ^{231}Pa method (the use of ^{231}Pa decay in the sample) were carried out by the scientists mainly in U. S. A. and USSR. Sarma (6) investigated the accumulation rate of the deep sea sediment by using excess ^{231}Pa and ^{230}Th methods and confirmed the usefulness of the ratio ^{231}Pa/^{230}Th for dating. Further investigation by Sackett et al. (7) showed that the excess protactinium method affords much more reliable data than the excess ^{230}Th method, if the data obtained by these two methods were compared with radiocarbon data.

I-3 History of the Deficient ^{230}Th and ^{231}Pa Methods for Pleistocene Dating

Since Barns et al. (8) had shown the possibility of using the degree of the deficiency of ^{230}Th with respect to its parent ^{234}U as an age indicator for coral cuttings of Pacific atoll, many works have been made. Sackett (9) analyzed many marine carbonates and obtained the good agreement of the ^{230}Th ages with radiocarbon ages. Further studies by Tatsumoto and Goldberg (10) emphasized the contribution of initial ^{230}Th and proposed the ^{232}Th content as an indicator for correction.

In 1955, Cherdyntsev (11) made an important discovery that the activity ratio of ^{234}U/^{238}U is not unity and ^{234}U anomaly occurs rather commonly in natural conditions. The author pointed out the need of correction for age calculation by the ^{230}Th growth method. In this respect Cherdyntsev (12) made an age determination of the fossil bones collected from the remains of ancient civilization (Kostenki, Molodovo, cave Kudaro, etc.) and obtained very useful results for archaeological studies.

They had used the simple thorium isotope method using the ratio $^{230}Th/^{234}Th$ instead of direct determination of ^{234}U activity and the other method using the ratio $^{227}Th/^{234}Th$ instead of $^{231}Pa/^{235}U$. They also suggested the possibility of the dating method using the decay of ^{234}U (248,000 yr).

Thurber (13) confirmed the exsistence of ^{234}U anomaly also in sea water and marine carbonates and proposed the $^{234}U/^{238}U$ dating method, which may be applicable back to about one million years. The ratio $^{234}U/^{238}U$ obtained from many sea water samples showed all good agreement within the range of statistical error ($r=1.15\pm0.02$), which may be taken as the initial $^{234}U/^{238}U$ ratio in all sort of marine carbonate samples.

Though Rosholt et al. (14), Sackett and Potratz (15) had suggested the use of $^{231}Pa/^{235}U$ ratio for cross checking the reliability of ^{230}Th dating method, the activity of ^{231}Pa was too small to be measured accurately without developing the detector with very low background activity and with high counting efficiency. Accordingly, other criteria had to be sought to confirm the assumption of the closed system for ^{230}Th dating method. Broecker (16) and Blanchard (17) studied many corals and molluskan shells collected from various regions in the world. Based on the analytical results of U/Ca, Ra/Ca and uranium series disequilibrium in the sample, they emphasized that the $^{226}Ra/^{230}Th$ ratio was very useful criterion for confirmation of the closed system. Recently, deficient ^{230}Th dating have been applied to various materials as follows;

Fossil bones (18-20), Travertine (19,22), Peat bogs (21,23),

Marine and non-marine mollusks (18-20,22,24-30).

I-4 Other Possible Methods for Pleistocene Dating

In addition to the methods mentioned above, uranium-herium method, which was advanced greatly by Fanale and Schaeffer (31), the methods using cosmogenic radionuclides such as ^{36}Cl (3.1×10^5yr) (32), ^{26}Al (7.4×10^5 yr) (33), and ^{10}Be (2.5×10^6 yr) (34), and fission track method developed by Price and Walker (35) have the possibility for the dating of Pleistocene epoch. However, all other methods except uranium-herium and fission track methods seem not so promising, because the extremely low abundances of these
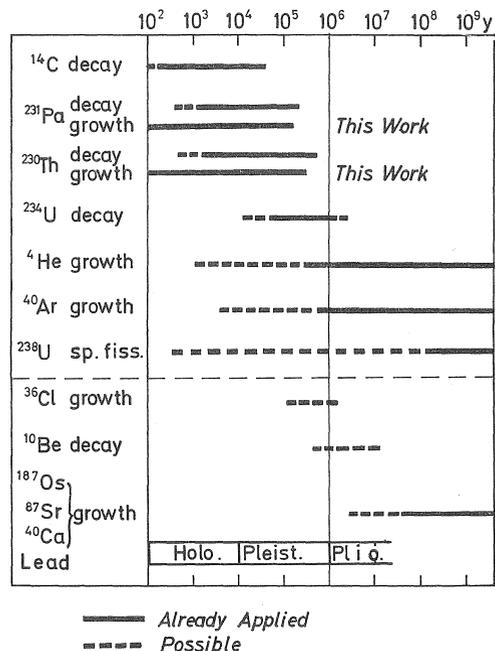
Fig. 2 Radioactive Dating Methods Applicable for Quaternary Period

cosmogenic radionuclides in nature make it difficult to obtain the reliable analytical results of these nuclides.

In Fig. 2, all the methods discussed above are summalized.

I-5 Purposes of This Work

The principal purposes of this work are followings :

    i. To establish the simple and reliable analytical method for uranium, thorium and protactinium in carbonate sample.

    ii. To develope for the first time the deficient protactinium method as an age indicator, and to confirm the limit and the availability of this method for Pleistocene dating.

    iii. To apply ^{230}Th and ^{231}Pa methods for dating of marine carbonate samples collected from Ryukyu Islands, in order to obtain some informations about the climatic circumstances in Pleistocene epoch.

    iv. The preliminary evaluation of the validity of the stalagmite for dating by ^{230}Th/^{234}U and ^{234}U/^{238}U methods.

II. Theory of the Deficient ^{230}Th and ^{231}Pa Methods for Pleistocene Dating

II-1 General

There are three fundamental requisites to be satisfied for the sake of obtaining a reliable age by deficient ^{230}Th and ^{231}Pa methods. They are as follows.

    i. There exsists measurable amount of uranium in the sample.

    ii. It is desirable that no initial ^{230}Th and ^{231}Pa exsist in the sample at the time of living, fossilizing or mineralizing of the sample. If these nuclides exsist initially in the sample, the amounts of them should be negligibly small comparing with that accumulated by the radioactive decay in the sample during the exsistence, or the initial values can be corrected by appropriate means.

    iii. There are no migration of parent uranium isotopes and/or their daughters after the deposition of the sample. In other words, during the exsistence of the sample, there occured no action to alter the isotopic composition except by the processes of radioactive decay and growth.

The first condition was satisfied in any samples analyzed as shown afterward, because of relatively high abundance of uranium in marine or terrestrial materials. The order of the uranium contents were $0.x$ to 3 ppm for coral samples, $0.0x$ to 2 ppm for *Tridacna* shell samples and $0.0x$ to $0.x$ ppm for stalagmite sample, therefore, the appropriate quantities of uranium were assured by taking sufficient amounts of sample.

The second condition is the most important one for the deficient ^{230}Th and ^{231}Pa methods. However, it seems as a matter of course considering the differences of uranium, thorium and protactinium in the chemical behaviours. Whereas uranium is very soluble by forming carbonate or sulfate complexes ($[UO_2(CO_3)_2]^{2-}$, $[UO_2(CO_3)_3]^{4-}$, or $[UO_2(SO_4)_2]^{2-}$, $[UO_2(SO_4)_3]^{4-}$) in the presence of carbonate or sulfate ions in sea or ground water, thorium and protactinium are scarcely soluble in such conditions. As they are hydrolyzed to forming hydroxide colloids or have large tendencies to be adsorbed to the colloidal materials, these elements will soon deposit with particulate matter in the water. Hence, the separation of parent uranium from its daughter nuclides may occur in natural conditions. This was confirmed by studying the contents of uranium, thorium and protactinium in sea water (36) and natural waters (37). Furthermore, the experiments on the relative leachabilities of these elements (38) proved the separation of uranium from its daughters in very mild conditions, which might exsist in natural conditions.

The third condition is also important for dating, because either the migrations of parent uranium isotopes or that of their daughter nuclides distorts the age estimation by the ratios of ^{230}Th/^{234}U and ^{231}Pa/^{235}U, and sometimes may make it impossible to estimate the age of the sample. The criterions for ascertaining the good preservation of the sample are listed as follows:

i.   Sample has 100% aragonitic structure (meta-stable state of calcium carbonate). Exsistence of calcite structure (stable state of calcium carbonate) indicates the possibility of alteration, except for the sample which secretes initially calcium carbonate as calcite structure. This can be proved by X-ray diffraction analysis or by the chemical examination using $Co(NO_3)_2$ as testing reagent.

ii. There are no observational proof of weathering such as the chalky structure or colour changes.

iii. Homogeneous distribution of the micro-components such as uranium and its daughters, strontium, magnesium, etc. in carbonate sample. This can be examined by emission spectroscopy, electron micro analysis, activation analysis, activation autoradiography, etc..

iv. Agreement of the ages estimated by several independent methods such as ^{226}Ra/^{234}U, ^{230}Th/^{234}U, ^{234}U/^{238}U, ^{231}Pa/^{235}U, ^{231}Pa/^{230}Th, He/U, ^{14}C methods etc..

If these conditions are satisfied in the sample analyzed, age calculation becomes possible by using the relationships among parent uranium isotopes and their daughter nuclides as described below.

II-2 Significance of the Uranium Isotopic Ratio ^{234}U/^{238}U

As pointed out in I-3, the uranium isotopic ratio ^{234}U/^{238}U has important meanings in uranium series disequilibrium method of dating, therefore, it seems very

useful to consider the significance of the ratio of ^{234}U/^{238}U in geochemical studies of the uranium isotopes. Let us consider at first the general aspect of uranium isotopic ratio ^{234}U/^{238}U, and then discuss several special cases. If we assume the model case illustrated in Fig. 3 that the uranium having ^{234}U/^{238}U ratio of r_0 constantly inflows into a system (for example, a basin) and these uranium isotopes decay or are removed out from the system (for example, depositional removal) according to their half-lives or to the residence time (τ), respectively, the relation between parent ^{238}U and its daughter ^{234}U can be expressed as follows:

$$dN_8/dt = a - (\lambda_8 + p)\, N_8 \tag{1}$$

$$dN_4/dt = b + \lambda_8 N_8 - (\lambda_4 + p)\, N_4 \tag{2}$$

where N_8, N_4 : number of atoms of ^{238}U and ^{234}U,

a, b : constants, which denote the amounts of ^{238}U and ^{234}U (in atom number) introduced in a given system,

λ_8, λ_4 : decay constants of ^{238}U and ^{234}U, respectively,

p : removal constant of uranium (depositional constant) which is equal to the reciprocal of the residence time (τ) of uranium in a given system.

By integrating the Eqs. (1) and (2), the solutions of (3) and (4) can be obtained if we give N_8^0 and N_4^0 as the initial values of N_8 and N_4 in a given system considered here;

INFLOW $r_0 = \dfrac{b\lambda_4}{a\lambda_8}$

DEPOSIT or OUTFLOW

$$r = \frac{\lambda_4 N_4}{\lambda_8 N_8}$$
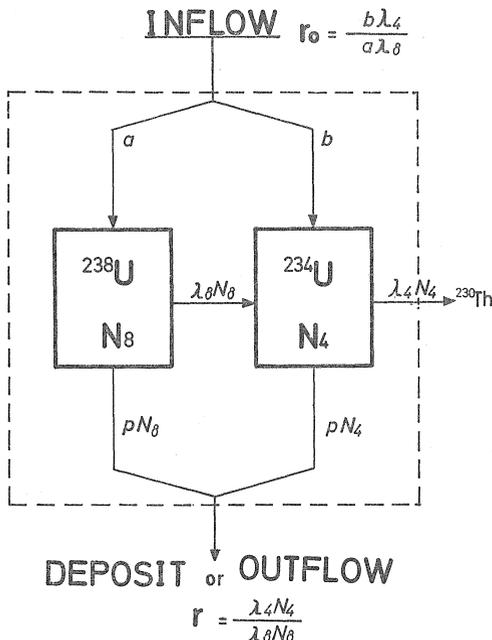
Fig. 3 Model of the Introduction and the Removal of the Uranium Isotopes for a System

$$N_8 = \{a/(\lambda_8 + p)\}\{1 - e^{-(\lambda_8 + p)t}\}$$
$$+ N_8^0\, e^{-(\lambda_8 + p)t} \tag{3}$$

$$N_4 = \{b/(\lambda_4 + p)\}\{1 - e^{-(\lambda_4 + p)t}\}$$
$$+ \{a\lambda_8/(\lambda_8 + p)(\lambda_4 + p)\}$$
$$\{1 - e^{-(\lambda_4 + p)t}\}$$
$$- \{a\lambda_8/(\lambda_8 + p)(\lambda_4 - \lambda_8)\}$$
$$\{e^{-(\lambda_8 + p)t} - e^{-(\lambda_4 + p)t}\}$$
$$+ \{N_8^0\, \lambda_8/(\lambda_4 - \lambda_8)\}\{e^{-(\lambda_8 + p)t}$$
$$- e^{-(\lambda_4 + p)t}\}$$
$$+ N_4^0\, e^{-(\lambda_4 + p)t} \tag{4}$$

Eqs. (3) and (4) indicate the atom numbers of ^{238}U and ^{234}U at the given time t after the beginning of the uranium introduction. The complicate general equations given above can be simplified by assuming the special cases, which may be probable in natural conditions. They are the following cases.

Case (I) Both introduction and removal of uranium isotopes except for the radioactive decay do not occur, namely the requisite condition for the closed system. This may be held in well preserved marine carbonates (such as coral, molluskan shells, oolites, etc.), secondary uranium minerals, peat bogs, fossil bones (carbonitized), etc..

Now, a, b and p in Eqs. (3) and (4) are put to be zero, (and $\lambda_8 \doteqdot 0$), simplified equations of (5) and (6) can be obtained.

$$N_8 = N_8^0 \tag{5}$$

$$N_4 = (N_8^0 \lambda_8 / \lambda_4)(1 - e^{-\lambda_4 t}) + N_4^0 e^{-\lambda_4 t} \tag{6}$$

Then, the activity ratio $r = {}^{234}U/{}^{238}U$ at time t is expressed as follows if we put the initial ${}^{234}U/{}^{238}U$ ratio as $r_0 = N_4^0 \lambda_4 / N_8^0 \lambda_8$

$$r = 1 - (r_0 - 1) e^{-\lambda_4 t} \tag{7}$$

or $$(r - 1)/(r_0 - 1) = e^{-\lambda_4 t} \tag{8}$$

Case (II) The depositional removal of uranium is negligibly small compared with the amounts of the introduction. This case was assumed to be true for the dating of the lake formation of Issyk-Kul and Chatyr-kul in Kirgizskaya USSR (39), which had been believed to be formed in late Pleistocene epoch, and the reasonable data were obtained. As N_8^0, N_4^0 and p in Eqs. (3) and (4) can be neglected, simplified solutions of N_8 and N_4 are given as follows.

$$N_8 = at \tag{9}$$

$$N_4 = a\lambda_8 t / \lambda_4 + (b - a\lambda_8 / \lambda_4)(1 - e^{-\lambda_4 t})/\lambda_4 \tag{10}$$

Since $b\lambda_4 / a\lambda_8$ can be substituted by r_0, the value r is expressed as Eq. (11) (the activity ratio of uranium isotopes in the case of constant introduction),

$$r = 1 + (r_0 - 1)(1 - e^{-\lambda_4 t})/\lambda_4 t \tag{11}$$

or $$(r - 1)/(r_0 - 1) = (1 - e^{-\lambda_4 t})/\lambda_4 t \tag{12}$$

Case (III) The deqositional removal of uranium is geochemically balanced with the amounts of the uranium introduced into a given system (a basin), namely, the case of stationary state. This is perhaps held in ocean water system. In this case, the solution yields the residence time of uranium in a given basin. According to the assumption made just above, we can consider dN_8/dt and dN_4/dt in original equations (1) and (2) as zero, therefore, a and b are expressed as follows.

$$a = (\lambda_8 + p) N_8 \tag{13},$$

$$b = (\lambda_4 + p) N_4 - \lambda_8 N_8 \tag{14}.$$

If the residence time of uranium has the value comparable to the half-life of ${}^{234}U$, namely, the order of 10^5 years, we have the simplified r value of

$$r = 1 + (r_0 - 1) p / (\lambda_4 + p) \tag{15},$$

or $$(r - 1)/(r_0 - 1) = p/(\lambda_4 + p) \tag{16}.$$

Consequently, the residence time (τ) of uranium can be calculated from the next equation:

$$\tau = 1/p = (r_0 - r)/(r - 1) \times 1/\lambda_4 = (r_0 - r)/(r - 1) \times T_{1/2}/0.693 \tag{17},$$

where $T_{1/2}$ denotes the half-life of ^{234}U.

If activity ratio $^{234}U/^{238}U$ introduced by rivers into the ocean is assumed to be $r_0 = 1.30$, the residence time of about 3.6×10^5 yr can be obtained. This result does not contradict the value recognized today (5×10^5 yr).

Variations of the $(r-1)/(r_0-1)$ values given by Eqs. (8), (12) and (16) are shown in Fig. 4 respectively, the sample age t or the residence time being taken on abscissa.
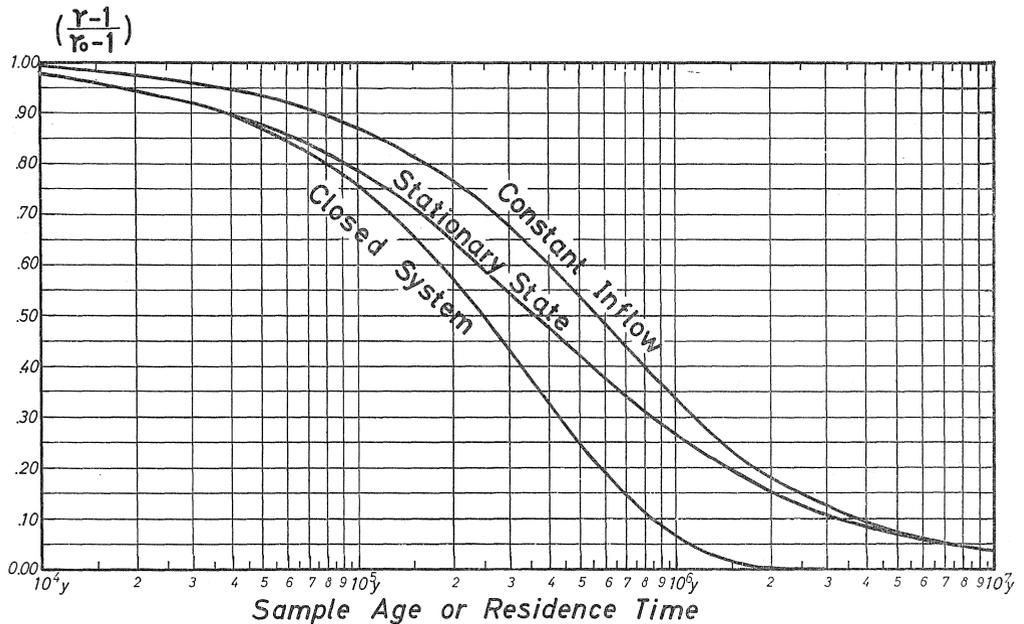
Fig. 4   Change in $(r-1)/(r_0-1)$ Values for the Special Cases of   (ⅰ)   Closed System, (ⅱ)   Constant Inflow and   (ⅲ)   Stationary State

II-3   Relation Between ^{230}Th and Uranium Isotopes ^{234}U and ^{238}U

As the difference of half-lives between ^{230}Th and its direct precursor ^{234}U is relatively small, the ratios of ^{230}Th to parent uranium isotopes change with time somewhat more complicatedly than the ratio ^{231}Pa to ^{235}U does. By assuming r_0 as the initial value of $^{234}U/^{238}U$ and r as its value at time t, the ratios $^{230}Th/^{238}U$ and $^{230}Th/^{234}U$ are expressed as Eqs. (18)~(21):

$$^{230}Th/^{238}U = 1 - e^{-\lambda_0 t} + (r_0 - 1)(e^{-\lambda_4 t} - e^{-\lambda_0 t}) \times \lambda_0/(\lambda_0 - \lambda_4) \tag{18}$$

$$= 1 - e^{-\lambda_0 t} + (r - 1)\{1 - e^{-(\lambda_0 - \lambda_4)t}\} \times \lambda_0/(\lambda_0 - \lambda_4) \tag{19},$$

$$^{230}Th/^{234}U = (1 - e^{-\lambda_0 t})/r + (1 - 1/r)\{1 - e^{-(\lambda_0 - \lambda_4)t}\} \times \lambda_0/(\lambda_0 - \lambda_4) \tag{20},$$

$$= 1 - e^{-\lambda_0 t} + (1 - 1/r)[\{1 - e^{-(\lambda_0 - \lambda_4)t}\} \times \lambda_0/(\lambda_0 - \lambda_4)$$

$$- (1 - e^{-\lambda_0 t})] \tag{21},$$

where λ_4 and λ_0 denote the decay constants of ^{234}U and ^{230}Th.
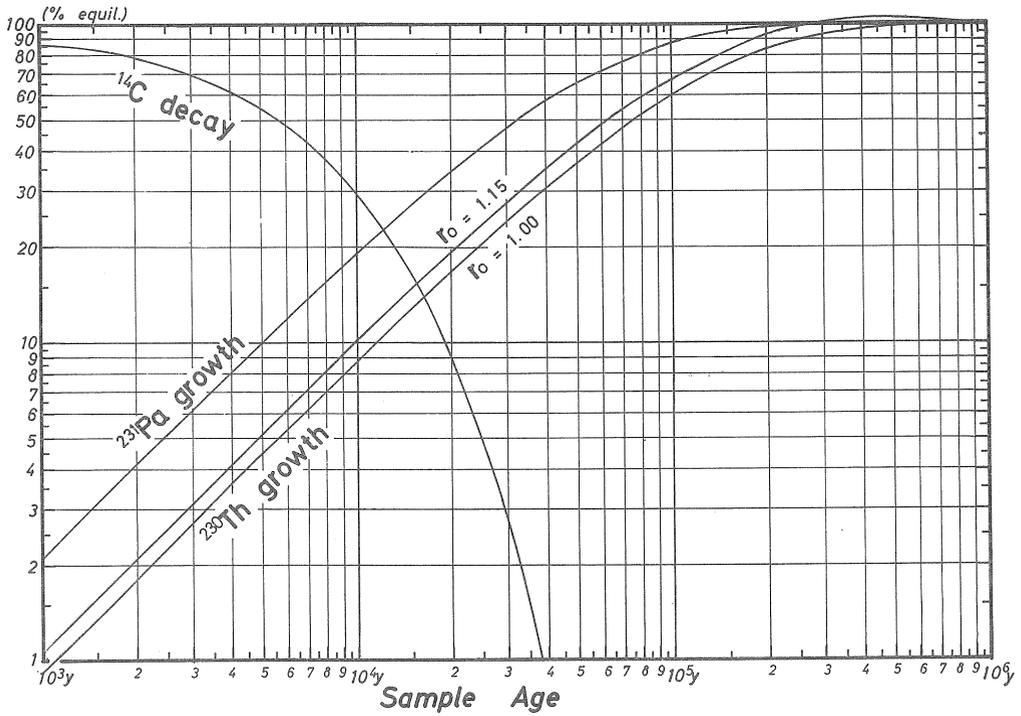
Fig. 5   Theoretical Growth Curves of ^{230}Th and ^{231}Pa
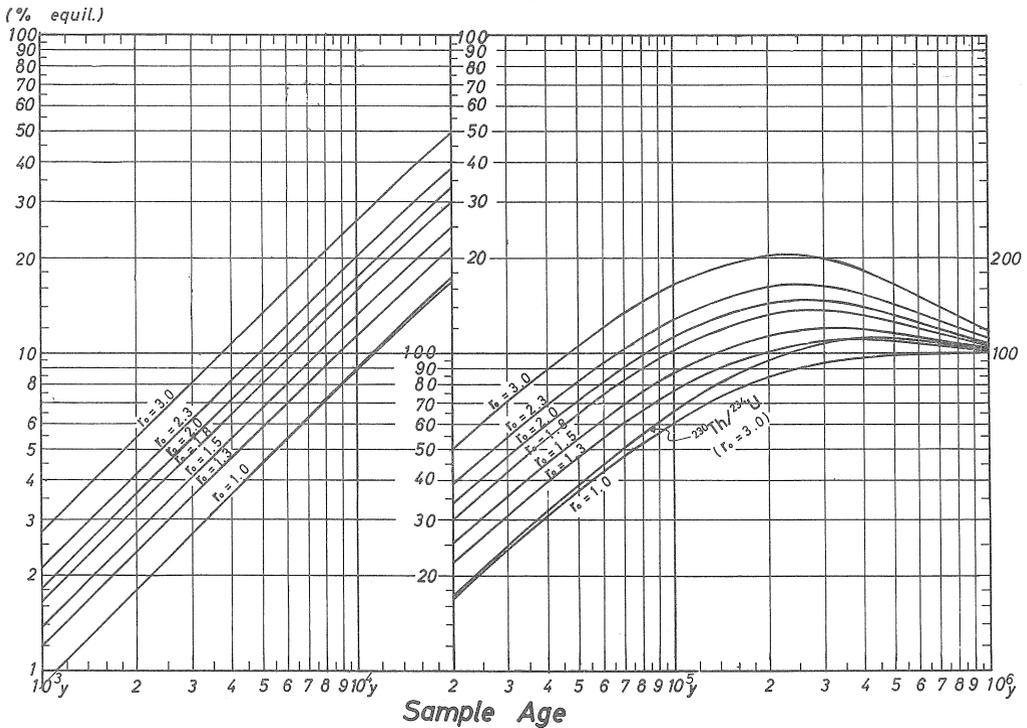
Fig. 6   Contribution of r_0 Values to the Growth of ^{230}Th/^{238}U Ratio

Fig. 5 shows the change of ^{230}Th/^{238}U ratio with sample age in the case of $r_0 = 1.00$ or 1.15, which is most probable value for the marine carbonate samples as analyzed in this work. In Fig. 6, the various growth curves of ^{230}Th/^{238}U ratio are illustrated for different r_0 values together with the growth curve of ^{230}Th/^{234}U of $r_0 = 3.00$. Furthermore, for convenience, the deviations from the simplest equation of $^{230}Th/^{234}U = 1 - e^{-\lambda_0 t}$ are calculated in two ways and shown in Fig. 7: (i) the relative correction factors by which the measured ^{230}Th/^{234}U of a given sample should be devided to obtain a corrected ^{230}Th/^{234}U value to be used in the above mentioned simple equation, (ii) the absolute excess in per cent, which should be substracted from the measured ^{230}Th/^{234}U (% equil.) value to obtain a corrected ^{230}Th/^{234}U value.
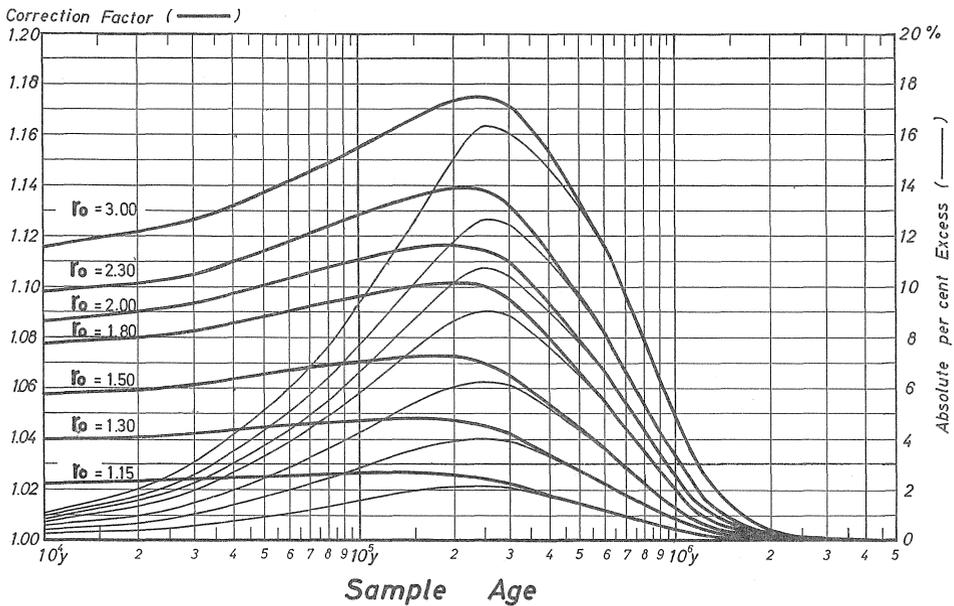
Fig. 7   Deviation from the Simplest Equation $^{230}Th/^{234}U = 1 - e^{-\lambda_0 t}$

II-4   Relation Between ^{231}Pa and Its Parent ^{235}U

Different from the case of ^{230}Th, the relation between ^{231}Pa and its parent ^{235}U is very simple, because the half-life of the intermediate nuclide ^{231}Th (UY) $(T_{1/2} = 25.6h)$, is short enough to consider its activity to be always in equilibrium with its parent's. So, the relation is expressed as following equation without considering the activity of the intermediate nuclide,

$$^{231}Pa/^{235}U = 1 - e^{-\lambda_1 t} \tag{22},$$

where λ_1 denotes the decay constant of ^{231}Pa.

As the direct determination of ^{235}U is very difficult, its activity is usually calculated from the ^{238}U activity by assuming the constancy of the ratio ^{235}U/^{238}U

in natural uranium. From their atomic abundance ratio 1/138 and each half-life, the value of 1/21.7 is generally accepted for this calculation. Hence. the activity ratio $^{231}Pa/^{235}U$ is calculated by the formula given below:

$$^{231}Pa/^{235}U = 21.7 \times (^{231}Pa/^{238}U)_{A\cdot R\cdot} = {}^{231}Pa/^{238}U \text{ (equivalent unit)}.$$

In Fig. 5, the growth curve of ^{231}Pa is illustrated together with the growth and decay curves of ^{230}Th and ^{14}C.

II-5 Relation Between ^{231}Pa and ^{230}Th

The ratio $^{231}Pa/^{230}Th$ has the interesting meaning for the age determination using the uranium and actinium series disequilibrium, since this ratio offers the important informations about the secondary alterations of the sample as discussed later. Furthermore, the ratio $^{231}Pa/^{230}Th$ becomes one of the indicators to examine the reliability of the estimated age by comparing the ages obtained from independent three methods, i. e., ^{230}Th, ^{231}Pa and $^{231}Pa/^{230}Th$ methods. However, this ratio depends largely on the ratio $^{234}U/^{238}U$ or on the exsistence of initial ^{231}Pa or ^{230}Th in original sample, and shows very complicated feature in applying deficient ^{231}Pa and ^{230}Th methods.

Whereas the $^{231}Pa/^{230}Th$ ratio in excess ^{230}Th and ^{231}Pa methods is expressed by a simple equation such as Eq. (24), this ratio in deficient methods has complicated form as expressed by a general formula of Eq. (25):
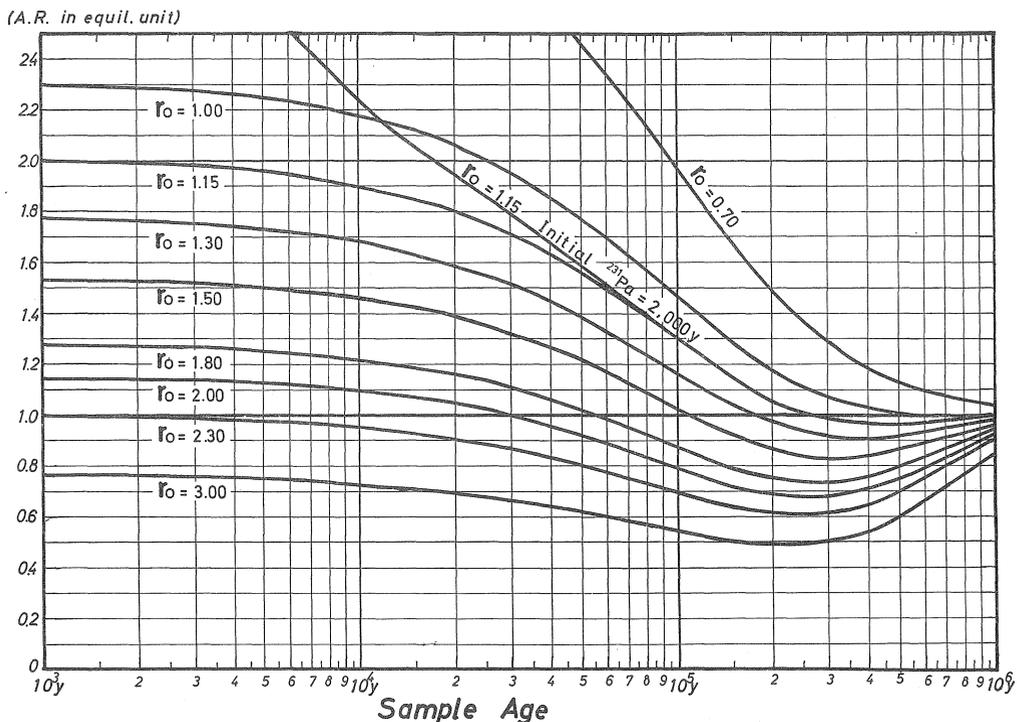
Fig. 8 Change in $^{231}Pa/^{230}Th$ Ratio versus Sample Age for Various r_o Values

i.   excess ^{231}Pa and ^{230}Th method,

$$(^{231}Pa)_{ex}/(^{230}Th)_{ex} = (^{231}Pa^0)_{ex}/(^{230}Th^0)_{ex} \times e^{-(\lambda_1 - \lambda_0)t} \qquad (24),$$

ii.   deficient ^{231}Pa and ^{230}Th method,

$$^{231}Pa/^{230}Th = (^{231}Pa/^{235}U)/(^{230}Th/^{238}U) = (Eq.22)/(Eq.\ 18) \qquad (25).$$

In Fig. 8, ^{231}Pa/^{230}Th to time relationship (Eq. 25) are illustrated for various r_0 values. As seen from this figure, the ratio ^{231}Pa/^{230}Th defined by Eq. (25) falls from 2. 31 to 1.00 at $r_0 = 1.00$ However, when the initial ^{234}U/^{238}U ratio (r_0) increases, this ratio shows somewhat such strange feature that the value initially decreases and then increases to the equilibrium value 1.00. Besides the complicated feature of the ratio ^{231}Pa/^{230}Th, the difficulty of precise determination of ^{231}Pa activity limits the application of this method, but the importance of this ratio for cross-checking the estimated ages must be still emphasized here.

II-6   Other Useful Relations for Age Calculation

In addition to the relations discussed above, the isotopic ratios ^{230}Th/^{234}Th, ^{227}Th/^{234}Th, and ^{226}Ra/^{238}U are also very useful for the age calculation. They are related to their parent isotopes as follows:

$$^{230}Th/^{234}Th = {}^{230}Th/^{238}U \qquad (26),$$

$$^{227}Th/^{234}Th = {}^{231}Pa/^{238}U = (^{231}Pa/^{235}U) \ (\text{equivalent unit}) \qquad (27)$$

and $$^{226}Ra/^{238}U = {}^{230}Th/^{238}U - (e^{-\lambda_0 t} - e^{-\lambda_6 t})\lambda_0/(\lambda_6 - \lambda_0)$$
$$- (r-1)\{\lambda_0\lambda_0 e^{-\lambda_0 t}/(\lambda_0 - \lambda_4)(\lambda_6 - \lambda_4)$$
$$- \lambda_0\lambda_4 e^{-\lambda_4 t}/(\lambda_0 - \lambda_4)(\lambda_6 - \lambda_4)$$
$$- \lambda_6\lambda_0 e^{-\lambda_6 t}/(\lambda_6 - \lambda_4)(\lambda_6 - \lambda_0)\} \qquad (28),$$

where λ_4, λ_0 and λ_6 denote the decay constant of ^{234}U, ^{230}Th and ^{226}Ra, respectively. When sample age is greater than 10^4 years, Eq. (28) must practically agree with ^{230}Th/^{238}U given by Eq. (18), unless the migration of radium occur during the time t, because the half-life of ^{226}Ra (1,622 yr) is relatively short in comparison with that of ^{230}Th.

This ratio becomes one of the useful criteria to examine the validity of the age estimation (16, 17) as pointed before, although the ratio ^{226}Ra/^{238}U cannot afford any information about the secondary alteration that might have occured more than several thousand years ago.

III   Apparatuses and Chemicals

III-1   Apparatuses

Electric Centrifuge: Model-FT9S, Kubota Seisakusho Co., Ltd..

Radiation Detectors:

i.   Gamma-Scintillation Detector: well type NaI (Tl) crystal, $1\frac{3}{4}'' \times 2''$,

Scaler ; TEN 1000 scaler, Model SA-230, Kobe Kogyo Co., Ltd.

ii. GM Counter : End-window type GM tube with $2''$ diameter, Aloka, Model GM-5006, window thickness $2.4 \sim 2.6$ mg/cm^2, BG 28 30 cpm.

iii. Alpha-Scitillation Detector : ZnS (Ag) crystal with $2''$ diameter, Scaler : Aloka, Model TDC-1, Nihon Musen Co., Ltd.

iv. Double Gridded Ionization Chamber : Model No. 4, Osaka Denpa Co., Ltd. Resolution Power : 1.8% (FWHM) for ^{232}U, BG : $0.02 \sim 0.04$ cpm/($0.4 \sim 0.5$) MeV region, Counting Efficiency : 2π (assumed).

v. 100 Channel Pulse Height Analyzer : Model AN-100, Kobe Kogyo Co., Ltd.

III-2 Chemicals

All chemicals are the guaranted reagent except for the organic reagent Di-iso-Butyl Ketone (DIBK) and Tri-iso-Octyl Amine (TIOA).

Acids : HCl, HNO$_3$, HClO$_4$, HF, H$_2$SO$_4$, H$_2$C$_2$O$_4$ and their mixtures,

Salt Solutions : $2M$ HCOONH$_4$, $4N$NaCl, 10 mg/ml Fe^{3+} carrier solution, Saturated AlCl$_3$ solution in $8N$HCl,

Organic Reagents for Solvent Extraction : DIBK pre-equilibrated with $8N$HCl, TIOA (Farmine-T, Kao Soap Co., Ltd.) 5% xylene solution.

Ion Exchange Resins :

Anion Exchange Resin : Dowex-1$\times$8, $200 \sim 400$ mesh, Oxalate Form

As the resin obtained commercially is not pure enough to be used as it is, the resin was swelled up in hydrochloric acid solution and washed in a glass column sufficiently with $8N$HCl until the yellowish effluent disappear. After washing with distilled water, the resin was converted to oxalate form by passing sufficient amount of $0.5M$ H$_2$C$_2$O$_4$ solution.

Cation Exchange Resin : Dowex-50$\times$8, $100 \sim 200$ mesh, H-form

The cation exchange resin was purified by hydrochloric acid just in the same manner as the case of an anion exchanger.

Ion Exchange Column :

The ion exchange column was made of hard glass and shaped as shown in Fig. 9. A corrosive effect of hydrofluoric acid on glass is negligible at the concentration of fluoric acid used in this work ($0.1N$). Though flow rate was not controlled especially in any case, it was nearly constant ($0.1 \sim 0.2$ ml/min in anion exchange, $0.4 \sim 0.5$ ml/min in cation exchange).
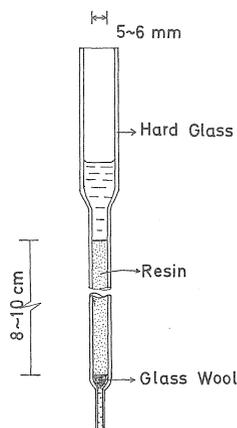
Fig. 9 Ion Exchange Column

IV Samples

IV-1 Purposes of Analysis

The Quaternary coral limestones that remain in Ryukyu Islands can be classified into three or four members according to the geological view points. Particularly in Kikai-jima, these members have been investigated in detail by Schlanger and Konishi (40) and tentative discrimination was made as (i) Raised Coral Reefs, (ii) Araki Limestones, (iii) Upper Member of Ryukyu Limestones and (iv) Lower Member of Ryukyu Limestones. It is well known that the growth and the propagation of coral depend greatly on the temperature in sea water, in other words, on the climatic change of the Earth (warm or cold). Neighboring Ryukyu Islands is the present north boundary of reef forming coral dwelling, therefore, the climatic conditions seem to have influenced more critically on the growth and the propagation of the coral in this region than that in tropical area and the coral limestones are the foot-prints of the warm periods in ancient ages. Hence, an age determination of these four members of coral limestones will make it possible to obtain many important informations about the change of the temperature in sea water in this region of Pacific Ocean during Pleistocene epoch. And this may afford the lock to solve the ages and the periods of the glacial advances and withdrawals in late Pleistocene.

Besides the coral samples, *Tridacna* shells and a stalagmite were analyzed, too, in order to examine their validities as the radioactive dating sample by deficient ^{230}Th and ^{231}Pa methods.

Water samples were also analyzed for ^{234}U/^{238}U ratio and their uranium contents.

Fig. 10 shows the geographic locations of the sample analyzed in this work.

IV-2 Sample Descriptions

Stratigraphic positions and the detailed sample locations of the Kikai-jima samples are shown in Figs. 11 and 12, respectively.

Coral samples except CK 7, CK 9, CK 10 and CO 1, have all aragonitic structure. Absence of calcite structure in the sample was confirmed by means of X-
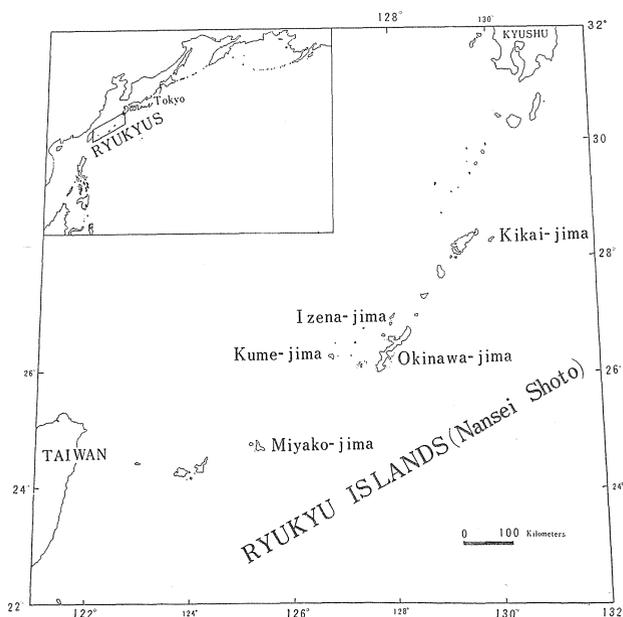
Fig. 10 Geographic Locations of the Analytical Samples
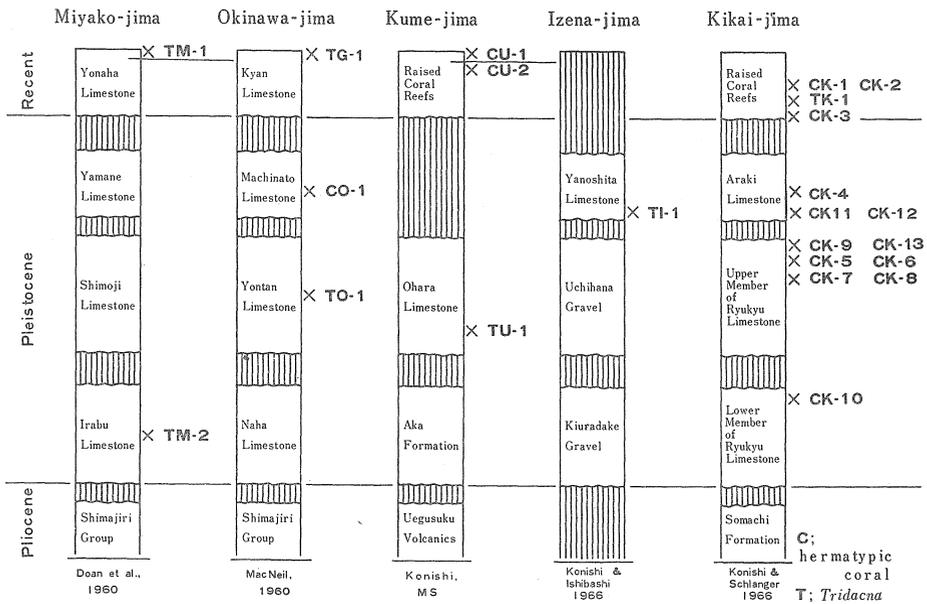
Fig. 11 Stratigraphic Positions of the Coral and *Tridacna* Samples

ray diffraction analysis and no visual al-
terations such as weathering or colour
changes could not be observed in these
samples.   Samples were collected from
the each member of these limestones in
order to estimate the absolute ages of
these coral formations. They are listed
in Table 1.

Similar situations as the case of
coral can be considered in the growth
and propagation of *Tridacna*, however,
the difficulty in finding out the fossil
Tridacna shells appropriate for dating
makes it hard to utilize them as an age
indicator of the limestone formation.
The *Tridacna* shell samples are listed
in Table 2. TM 1 and TG 1 were ana-
lyzed to obtain the initial values of
^{230}Th/^{234}U and ^{231}Pa/^{235}U in Modern
sample.   Among the samples, TU 1 and
TM 2 contain some calcite structure in
the outer bulb of the shell. Therefore, both aragonite and calcite part were analyzed
in order to investigate the influence of the phase change on isotopic ratios among
parents and daughter nuclides.
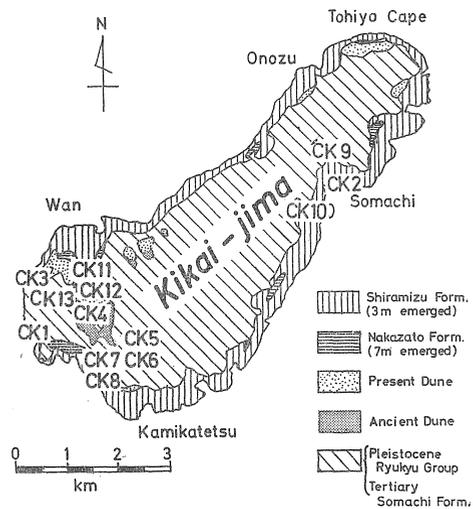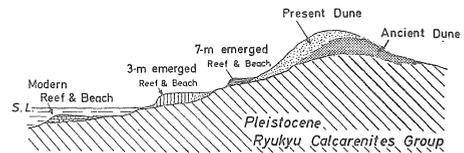
Fig. 12 Sample Location in Kikai-Jima (55)

Table 1 List of Coral Samples

Code Number	Sample Number	Geographic Unit	Elevation	Sample Locations	Species
CU 1	60–12–9	Recent (lived)	— 25m	Between Naka-bishi and Uku-bishi, Kume	*Favia speciosa*
CU 2	65—9–21	Raised Coral Reef	5m	Ohara, Kume	*Coelovia rustica*
CK 1	65–12–20–7–3	Raised Coral Reef	2m	W. of Araki, S. Kikai	
CK 2	65–12–22–1–2	Raised Coral Reef	3~4m	Komiya, S. of shrine, Shiomichi, C. Kikai	*Gconiastrea retiformis*
CK 3	65–12–24–6–2	Raised Coral Reef	4~5m	SWW. of Nakazato, W. Kiaki	
CK 4	66–5–10–2–1	Araki Limestones	27m	150m NW. of Araki, S. Kikai	
CK 5	65–12–23–6–2	Upper Limestone Member	43m	750m N. of Kamikatetsu, S. Kikai	*Acanthastrea echinata*
CK 6	65–12–23–6–1	Upper Limestone Member	43m	750m N. of Kamikatetsu, S. Kikai	*Favites favosa*
CK 7	64–7–20b	Upper Limestone Member	40m	500m N. of Kamikatetsu, S. Kikai	
CK 8	66–5–12–3	Upper Limestone Member	40m	500m N. of Kamikatetsu, S. Kikai	
CK 9	65–12–22–8–4	Upper Limestone Member	50m	500m NW. of Shiomishi, C. Kikai	
CK 10	65–12–21–2–1	Older Limestone	150m	750m E. of Shiramidzu, C. Kikai	*Favia magnistella*
CK 11	66–5–10–14–1	Top of the Upper Limestone Member	18m	700m SW. of Nakazato, W. Kikai	
CK 12	66–5–10–14–2	Top of the Upper Limestone Member	18m	750m SW. of Nakazato, W. Kikai	
CK 13	66–5–10–12–1	Upper Limestone Member	28m	800m N. of Araki, W. Kikai	
CO 1	64–12–4–5	Machinato Limes-tone (Nagamo Quarry)	20m	Minatogawa, S. Okinawa	

Table 2 List of *Tridacna* Sample

Code Number	Geographic Unit	Elevation	Sample Locations
TM 1	Recent (lived)	0m	Drift on beach, Ogami-jima
TG 1	Recent	0m	Drift on beach, Miyagi-jima
TK 1	Recent	2m	Collected in Raised Coral Reefs, W. of Araki, S. Kikai
T I 1	Yanoshita Limestone	high tide	Yanoshita-jima
TO 1	Yontan Limestone (Sobe Quarry)		Nakagami, Okinawa-jima
TU 1	Ohara Limestone	40m	Kitahara, W. Kume
TM 2	Irabu Limestone	4m	Koganeokaisaki, 1.2Km NW of Hisamatsu, C. Miyako

Stalagmite sample having diameter of 18 cm near the root was collected in the cave at Ike-jima very near by Okinawa-jima. Surface of it is brown and cocentric many rings are observed in cross section of the sample.

The waters were sampled at the following places: cave "Yuhi", mouth of Taibo River and Shioya Bay (Okinawa-jima) and Tsukumo Bay (Noto-Peninsula).

V. Analytical Procedures

V-1 Sample Decomposition

Except for several samples, sample blocks of about $20 \sim 40$ grams were carefully selected from the sample of coral and *Tridacna* shell still in aragonitic structure and were dissolved in $200 \sim 300$ ml of $6N$ $HNO_3 + 0.05N$ HF mixed acid in a 500 ml polypropylene beaker. The tracer solutions of [234]Th, [233]Pa and [232]U (which may contain small amount of [228]Th and its daughter nuclides in the course of storing) were added to the sample solution to know the chemical yields in the separation and purification procedure. The solution was then heated under an infra red lamp and left for several days to attain the isotopic exchange equilibrium between tracer and the isotopes in sample. If this solution contained significant amounts of undissolved matter, then it was filtered off by passing through a filter paper (No 5C, Toyo Roshi Co., Ltd.), and the residue was decomposed together with the filter paper, initially by heating with conc. H_2SO_4 and thereafter with conc. $HClO_4 +$ conc. HNO_3. The resultant solution was evaporated to dryness, taken in $8N$HCl$+0.1N$HF mixture and put together with the original solution.

In the case of stalagmite sample, about 100 grams of block samples was taken and decomposed in the same manner as the case of coral samples, because of its very low uranium content and of the exsistence of phosphate ion that interfere the recovery of the thorium isotopes.

V-2 Initial Concentration of Radioactive Elements with Hydroxide Precipitation

After an attainment of the isotopic exchange equilibrium, the solution was transferred to conical beaker made of glass, and boiled to expel dissolved carbonate ions in the solution and the hydroxide of iron was precipitated by passing ammonia gas free from CO_2. As the high ionic strength of the solution makes the efficiency of the coprecipitation worse, especially the coprecipitation yield of uranium isotopes, bioled water was added to dilute the solution, and large excess of ammonia gas was blowed into the solution for the sake of better coprecipitation of the trace elements.

The hydroxide precipitate containing uranium, thorium, protactinium and many other radioactive decay products was separated by centrifugation in a polyethylene centrifuge tube and then dissolved in 20 ml of $8N$ HCl solution. The resultant solution which contains organic matter and small amount of calcium ion as well as the radioactive elements, was transferred to the conical beaker used previously for the

initial hydroxide precipitation, and evaporated to dryness on the hot plate. About 5 ml of conc. H_2SO_4 was added to the residue and heating was continued to convert all the salts to sulfate until the white fume of SO_3 ceased to come out. If the blackish thick matter appeared during the heating, heating was suspended and then 5 ml of conc. $HClO_4$ and conc. HNO_3 were added carefully along with the wall of the beaker, and the heating was resumed to decompose the organic matter until the solution dried up. The residue was dissolved in about 150 ml of dilute HCl by boiling the solution long time. If the insoluble matter still remained in the solution, the suspended matter was filtered off by passing the solution through the filter paper (No 5C) and washed sufficiently with $8N$HCl$+0.1N$HF solution. This residue was usually discarded, because the quantity of the radioactive elements adsorbed on the filter paper was negligibly small except in the case of dealing with stalagmite sample.

In the case of stalagmite sample, thorium isotopes were adsorbed strongly to the undissolved residue, therefore, carbonate fusion was carried out to decompose the residue completely. After cooling the fusion products, it was taken up with $3N$HCl and added to the original solution.

The solution thus processed was boiled and the hydroxide precipitation was repeated twice and finally washed with the boiled water containing ammonia gas to remove chloride ion.

All the procedures were controlled by means of gamma countings.

V-3 Initial Separation of Radium, Thorium, Protactinium and Uranium by Anion Exchange Method

The hydroxide precipitate thus obtained was dissolved in $0.5M$ $H_2C_2O_4$ solution as small quantity as possible (usually about 5 ml), and the resultant solution of yellowish green coloured was passed through an oxalate form anion exchange column (41), which retains uranium, thorium, protactinium, iron and polonium and permits radium, actinium, lead and alkaline earth elements to pass through. After washing the column with 5 column volumes of $0.5M$ $H_2C_2O_4$ solution, thorium, protactinium, and uranium were eluted stepwise from the column by passing 6 column volumes of $8N$ HCl, 4 column volumes of $8N$ HCl$+$ $0.1N$ HF and finally 10 column volumes of $6N$ HCl $+1N$ $HClO_4$ mixture. Elution diagram of these procedures is shown in Fig. 13,
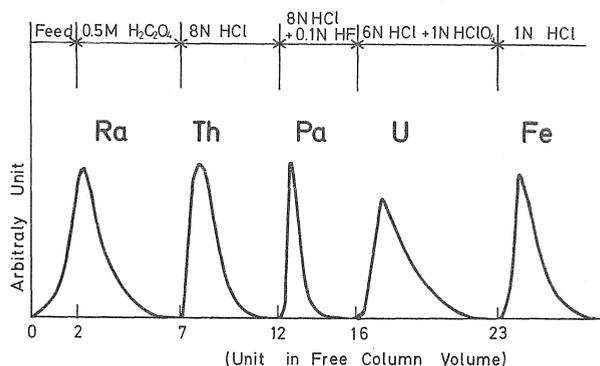
Fig. 13 Elution Diagram of Ra, Th, Pa, U and Fe from Anion Exchange Resin Column

which was obtained by a model experiment using the radioactive tracer of [224]Ra, [234]Th, [233]Pa, [237]U and [59]Fe.

In the first step of thorium elution, an yellowish green band of oxalate complex of iron (III), $[Fe(C_2O_4)_3]^{3-}$, is converted to brown chloride complex and the iron band expands twice the initial width. Though widening of iron band occurs also in the last step of uranium elution, elution of iron does not take place. If the hydroxide precipitate was dissolved in $8N$ HCl solution, because of the exsistence of impurities that could not be dissolved in oxalic acid solution, the column operation was begun from the step of thorium elution.

All the procedures were controlled by gamma countings and gamma spectrometry of each fraction. Detection of the mutual contamination of thorium and protactinium is possible by means of gamma spectrometry even in the case of $300:1$ and $1:4$ in beta activity ratios between them (42).

Although the chemical behaviours of polonium in the anion exchange procedure was not studied in detail, preliminary experiments indicated that polonium would be still retained on the anion exchange resin together with the carrier iron, since polonium could not be found in any fraction of eluate. If this expectation is correct, polonium will be recovered from the column separately from iron by the fractional elution using appropriate concentration of nitric acid.

Anode(Pt Wire)

Bakelite Cap

Electrolytic Cell (Polyethylene Tube)

Packing(Polyethylene)

Cell Holder (Brass)

Cathode (Stainless Steel Plate)

0 1 2 3 4 cm
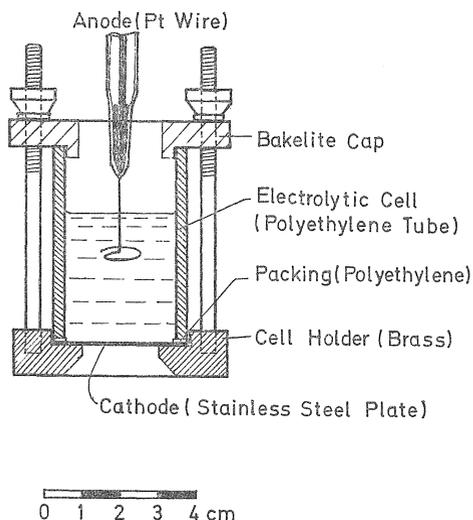
Fig. 14 Electrodeposition Cell

Each fraction thus obtained were submitted to the final purification from the interferring elements for the electrodeposition process by means of cation exchange or solvent extraction techniques.

V-4 Purification and Electrodeposition of Thorium Isotopes

The thorium fraction which contains oxalic acid driven out by hydrochloric acid and small quantity of calcium, was transferred to 50 ml beaker and treated with conc. HNO_3+conc. $HClO_4$ solution to decompose oxalic acid. White residue containing calcium salt was taken up with 5 ml of $3N$ HCl solution and passed through a cation exchange column (43) (H-form) which adsorbs selectively thorium, and other impurities pass through this column. Thorium was eluted from the column with 10 ml of $0.5M$ $H_2C_2O_4$ solution. Oxalic acid in thorium fraction was decomposed by heating with conc. $HClO_4$+conc. HNO_3 mixture as before, and the solution was evaporated to dryness.

Radiochemically purified thorium was taken up with 5 ml of $0.5N$ HCl solution by heating calmly on the hot plate, and then 1 ml of $0.5M$ $H_2C_2O_4$, 4ml of $4N$ NaCl and 0.8 ml of $2N$ $HCOONH_4$ solutions were added (44). The solution thus prepared was transferred to a polyethylene electrodeposition cell (6 cm height of polyethylene tubing with out-side diameter of 3.4 cm and inside diameter of 2.8 cm). A stainless steel disc having diameter of 3.5 cm served as the cathod, whereas a platinum wire as an anode. The vertical section of the electrodeposition cell is illustrated in Fig. 14. Thorium was electrodeposited for $2\sim3$ hours at constant current of 0.5 A. After an electrodeposition, stainless steel cathode was rinsed sufficiently with distilled water, and dried under an infra red lamp. The electrodeposited plate was counted under a $2''$ end-window type GM tube to determine the chemical yield of thorium isotopes. The overall chemical yield varied from 10 to 85 per cent (mean value 45%).

V-5 Purification and Electrodeposition of Protactinium Isotopes

Purification of protactinium was carried out by a solvent extraction technique using DIBK-HCl system (45). To the protactinium fraction obtained by an anion exchange procedure, 2 ml of $AlCl_3$ saturated solution in $8N$ HCl was added to mask the fluoride ion, and protactinium was extracted with 4 ml of DIBK by shaking vigorously for 2 minutes. After the centrifugation, an organic phase was transferred to another polyethylene tube, and the extraction with 4 and 2 ml of DIBK were repeated to assure the complete transfer of protactinium to organic phase. Protactinium in organic phase was washed with 4 ml of $8N$ HCl and finally stripped to aqueous phase with 4 ml of $0.5N$ HCl solution.

An electrodeposition of protactinium fraction was carried out by entirely the same manner as the case of thorium, in chemical composition of electrolytes and also in conditions of electrodeposition, instead of the method recommended before (46). Overall chemical yields of protactinium varied from 10 to 75 per cent (mean value 40%).

V-6 Purification and Electrodeposition of Uranium Isotopes

The uranium fraction usually did not need the further purification. However, in the case that the amount of the residue after the evaporation of the uranium fraction was considerably large, solvent extraction procedure was carried out by using the TIOA-HCl system as follows. The residue was dissolved in 5 ml of $8N$ HCl solution and uranium was extracted with 3 ml of TIOA. Extraction was repeated twice with 3 ml of TIOA and the uranium in organic phase was washed several times with $8N$ HCl solution. Finally uranium was back extracted to aqueous phase with 5 ml of $0.1N$ HCl solution and the solution was evaporated to dryness with conc. H_2SO_4+ conc. HNO_3 to decompose any organic matter mixed with.

a

Sample

← $6N$ HNO_3 + $0.05N$ HF
← ^{232}U, ^{234}Th, ^{233}Pa (Spike)
(heat)

residue (filtering) filtrate

— 1. c. H_2SO_4
— 2. c. $HClO_4$ + c. HNO_3

← Fe^{3+} carrier (10 mg)
(boil)
← NH_3 gas
(centrifuge)

sup. (discard)　ppt.

— dil. HCl
(evap.)
— 1. c. H_2SO_4
— 2. c. $HClO_4$ + c. HNO_3
(evap.)
— $1N$ HCl
← NH_3 gas } × 2
(centrifuge)

sup. (discard)　ppt. (wash)

— $0.5M$ $H_2C_2O_4$

(Anion exchange)

b

(Anion exchange)

Dowex-1 × 8
Oxalate form

1. $0.5M$ $H_2C_2O_4$
→ Ra, Ac, Pb

2. $8N$ HCl
→ Th *

3. $8N$ HCl + $0.1N$ HF
→ Pa **

4. $6N$ HCl + $1N$ $HClO_4$
→ U ***

c

*

← c. $HClO_4$ + c. HNO_3
(evap.)
← $3N$ HCl

(cation exchange)

Dowex-50 × 8
H-form

(washing)
$3N$ HCl
(elution)
$0.5M$ $H_2C_2O_4$

Th

← c. $HClO_4$ + c. HNO_3
(evap.)

(Electrodep.)

d

**

← $AlCl_3$ (satd. in $8N$ HCl)
← DIBK
(shake)

aq. (c.f.)　org.

← DIBK

aq.　org.

(washing)
← $8N$ HCl × 2
(stripping)
← $0.5N$ HCl

aq. (evap.)　org.

Pa

(Electrodep.)

e

***

(evap.)
← $8N$ HCl
← TIOA
(shake)

aq.　org.

← TIOA

aq.　org.

(washing)
← $8N$ HCl × 2
(stripping)
← $0.1N$ HCl

aq. (evap.)　org.

U

(Electrodep.)

Fig. 15　Analytical Scheme of the Carbonate Sample

The uranium thus purified was taken up with 2 ml of $2N$ HClO$_4$ under the heating, and 2.5 ml of $2M$ HCOONH$_4$ solution and 10 ml of distilled water were added to make up the electrolytic solution, instead of the method developed by Hashimoto and Sakanoue (47). The solution thus prepared was transferred into the electrodeposition cell and uranium was electrodeposited on a stainless steel plate for about 3 hours at a constant current of 0.4 A. Overall chemical yield of uranium isotopes varied from 20 to 70 per cent (mean value 40%).

All the purification methods described above are shown schematically in Fig. 15.

VI Measurements

Chemical yields of thorium and protactinium isotopes through all the procedure including the coprecipitation, anion exchange, purification and electrodeposition were determined by beta countings using a 2″ end-window type GM counter, whereas that of uranium was determined by means of alpha spectrometry. Alpha spectrometries were carried out by using Double Gidded Ionization Chamber (48) with very low back ground activity and with high counting efficiency. In Fig. 16, the apparatus used for alpha spectrometry is shown. Energy resolution of this chamber was measured by using uranium isotope ^{232}U (E=5.318 MeV 68%, 5.261 MeV 32%) and apparent value of 1.8~2.0 per cent in the unit of FWHM (full width of half maximum) was obtained.
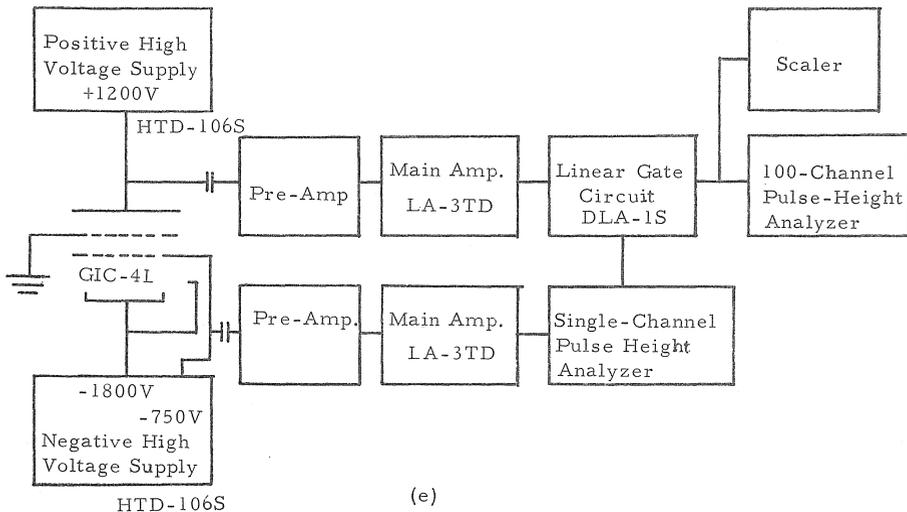
Fig. 16 Alpha Counting System
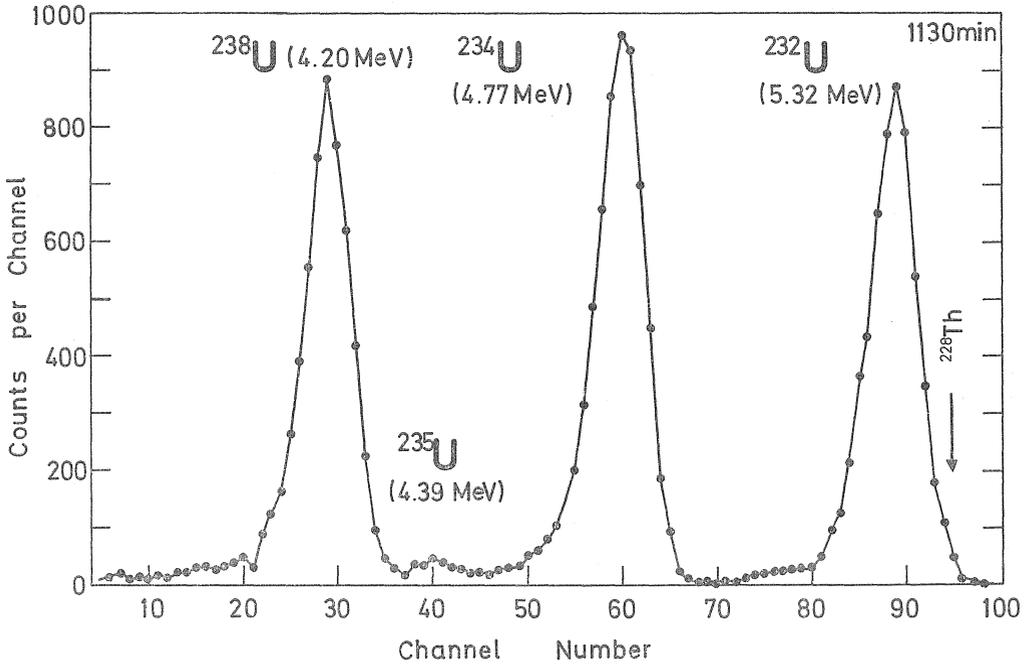
Fig. 17 Alpha Spectrum of Uranium Fraction (Stalagmite Sample SC)
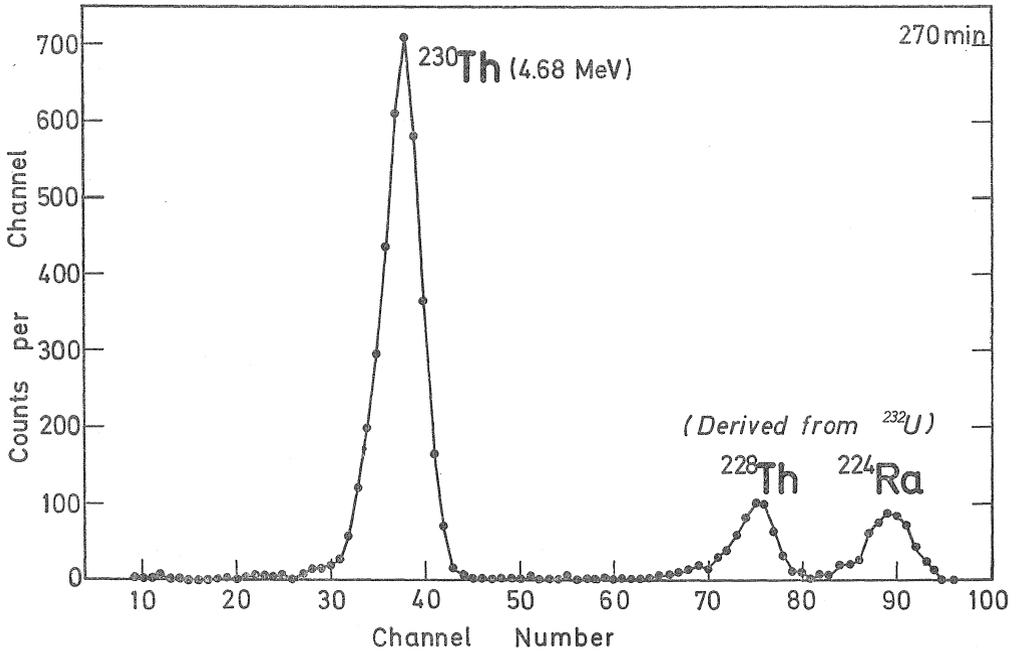
Fig. 18 Alpha Spectrum of Thorium Fraction (Coral Sample CK 10)
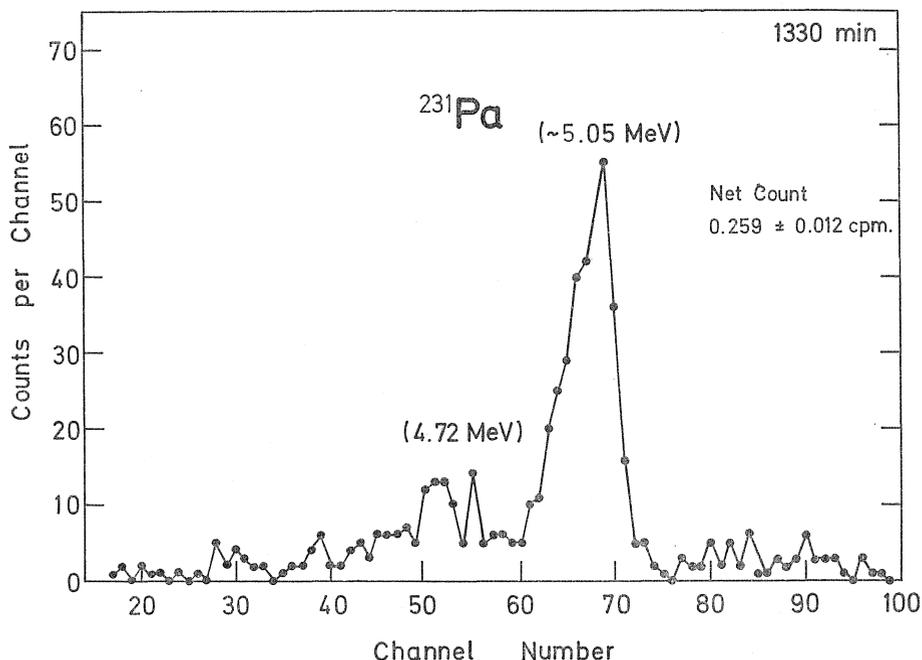
Fig. 19 Alpha Spectrum of Protactinium Fraction (Coral Sample CK 11)

Activities of ^{234}U and ^{238}U in the sample were calculated from the sums of countings in 20 and 18 channel ranges, respectively. The above mentioned channel ranges were chosen so as to give the ^{234}U/^{238}U ratio of the old uraninite sample to be 1.00 ± 0.01, at the condition of 20 keV/channel, and absolute quantities of ^{234}U and ^{238}U were calculated using recovered ^{232}U activity. The activities of thorium and protactinium isotopes were calculated from the sums of countings in $\sim$22 and $\sim$27 channel ranges, respectively. The typical alpha spectra of the uranium, thorium and protactinium fractions are shown in Figs. 17, 18 and 19. Counting time ranged from several hours to several days according to the level of the activities of the counting sources. Countings were continued so that the statistical errors of counting were settled within 2% for ^{234}U/^{238}U ratio and ^{230}Th, and 5% for ^{231}Pa.

VII Results and Discussion

VII-1 Uranium Assay

In order to verify the validity of the alpha spectrometric analysis of uranium using ^{232}U as uranium tracer, the uranium concentration in *Tridacna* shell samples was analyzed also by fluorimetric analysis for comparison. The sample solution which contains 10~15 grams of sample per 100 ml of acid solution (HNO$_3$+HF) was divided into two fractions of 300~500 ml and 5 ml for alpha spectrometry and fluorimetric analysis, respectively. The analytical results are given in Table 3 together with

the data obtained from the different blocks of the same sample for the sake of examining the homegeneity of the uranium distribution in a shell.

Table 3   Analytical Results of Uranium Content in *Tridacna* Shells
(Comparison of the Analytical Methods)

Sample	The Same Solution from a Sample		Other Blocks of a Sample	
	232U*	Fluorimetry**	232U*	Activ. Anal.***
TM 1	ppm 0.040±0.004	ppm 0.04	ppm 0.082±0.003	ppm 0.15
T I 1	0.28 ±0.01	0.26	—	0.73
TO 1	0.37 ±0.01	0.31	—	1.38
TM 2	1.21 ±0.03	0.70	1.11 ±0.03****	1.48
TU 1	—	—	{ 0.58 ±0.02 { 2.06 ±0.06****	{ 0.23, 0.14, { 0.26, 0.79 { 1.63****

* : Alpha Spectrometric Analysis Using ^{232}U as Uranium Tracer
** : Fluorimetric Analysis by Ohashi, Atomic Fuel Co.
*** : Activation Analysis by Osawa and Abe, Kanazawa Univ.
**** : Uranium Contents of Recrystallized Part (Calcite Part)

As known from this table, the results of alpha spectrometric analysis agree quite well with that of fluorimetry except the case of TM 2. This fact indicates the reliability of the alpha spectrometric method using ^{232}U as uranium tracer. It is also known from this table including the results of activation analysis (44) that the uranium concentration in a *Tridacna* shell is far from homogeneity even if the blocks were taken from the very near part in the same sample. This fact gives an interesting biological problem as to the mechanism of the trace element introduction in a shell. Though the alpha spectrometric analysis cannot discuss the detailed variety of the uranium concentration in micro scale because of its low sensitivity (at least several microgram of uranium is needed), it is evident that the distribution of uranium in a shell is heterogeneous also in fairly macro scale.

In this respect, a very interesting study was reported recently by Lahoud et al. (49). They investigated the uranium distribution in the shell samples collected from various environment (fresh water, brackish and marine), by using newly developed technique of fission track method, and obtained some interesting regularities about the uranium content and distribution: (i) uranium concentration in molluscan shell differs conspicuously by the environment of the mollusc dwelling, (ii) uranium concentration in a shell differs very widely by the position of the same sample, i.e. external valve surface contains more uranium than internal valve surface, and the fructured surface contains by far little amount of uranium than external and internal valve surfaces.

It is well known that the migration of the trace elements may occur during the change of crystal structure. In the case of fossil carbonate samples, this will be recognized as the change from the metastable aragonite to stable calcite form. The results of TM 2 and TU 1 indicate the enrichment of uranium at the time of recrystallization, that is, calcite part contains more uranium than aragonitic part.

As suggested already above, it must be emphasized that the study of the distribution of the trace elements in micro scale is very important to recognize the correlation between biological action and the trace elements introduction during the growth or after the death of organisms. Activation analysis, fission track technique and the activation autoradiography, which is developed by Sakanoue et al. (50), seem very promising to investigate the distribution of the trace elements in very small scale, because of their high sensitivities and/or easiness for performance.

Besides the diffrences of the uranium distribution in a shell, the variety of uranium content among the same species of mollusca must be pointed out. It is very interesting that the uranium content in *Tridacna* shell tends to increase from geologically younger sample (TM 1, 0.04 ppm) to older one (TM 2, 1.21 ppm). Similar results have been reported by Blanchard (51) and Stearns et al. (28) for uranium and by Lowenstam (52) for strontium in fossil molluscs. These facts may be explained by assuming that some trace elements are introduced not at the time during the growth of the organisms, but at the time of degradation of the organic matter in their structures.

VII-2 Analytical Results of Coral Samples

Analytical results given in Figs. 20, 21 and 24 are expressed as the activity ratios of $^{234}U/^{238}U$, $^{230}Th/^{234}U$ (% equil.) and $^{231}Pa/^{235}U$ (% equil.). Here, the activity ratio $^{231}Pa/^{235}U$ was calculated from the activity ratio of $^{231}Pa/^{238}U$ by assuming the activity ratio of ^{235}U to ^{238}U as 1:21.7. In the right hand two columns, the ages calculated from $^{230}Th/^{234}U$ and $^{231}Pa/^{235}U$ ratios are given, although these data are not submitted to any correction as to initial ^{230}Th and ^{231}Pa as discussed below. Analytical results of different blocks of the same sample are distinguished by the subscript a, b and c.

Fig. 20 shows the analytical results of coral samples. All the samples listed above CK 10 are remained still in aragonitic structure. As known from this figure, ^{231}Pa ages show considerably good agreement with the ages of ^{230}Th method, and the $^{234}U/^{238}U$ ratios do not contradict to their initial ratios of 1.15~1.14 recognized as their ratio in sea water. Particularly, the sample having the ages of 40~70 thousand years (CK 4, CK 8, CK 5 and CK 13) give completely the same ages between these two independent methods within the statistical errors, and other independent method using $^{231}Pa/^{230}Th$ can also be applied by assuming the initial $^{234}U/^{238}U$ ratio as 1.15.

However, ^{231}Pa method seems to give systematically somewhat older ages than ^{230}Th method for relatively younger samples of less than ten thousand years, for

	U (ppm)	Activity ratio (• $\frac{Th\text{-}230}{U\text{-}234}$: ○ $\frac{Pa\text{-}231}{U\text{-}235}$: ✕ $\frac{U\text{-}234}{U\text{-}238}$)		Ages (×10³y) Th-230 method	Pa-231 method
CU 1	2.85	1.3±0.2 / 1.5±0.2 / 7.4±1.5		(1.6±0.2)	(3.6±0.8)
CU 2	3.12	3.3±0.1		3.7±0.2	
CK 1 a / b	2.86 / 2.74	5.9±0.3 18±3 / 5.2±0.2 16±1		6.6±0.3 / 5.8±0.2	9.4±2.0 / 8.1±0.6
CK 2	2.54	6.3±0.3 17±3		7.1±0.3	8.8±1.5
CK 3	2.58	7.1±0.3 21±2		8.0±0.3	11.0±1.0
CK11	2.92	31.4±1 68.6±4		44±2	54±6
CK12	3.01	33.3±1		44±2	
CK 4	3.06	34±1 67±4		45±2	52±6
CK 8	3.70	37±1 63±5		49±2	46±5
CK 5 a / b	2.78 / 3.34	43±2 74±4 / 41±3		60±3 / 57±5	62±7
CK 6 a / b / c	2.94 / 3.18 / 3.52	54±2 84±6 / 39±2 80±4 / 40±1 81±3		81±5 / 53±4 / 56±2	84±14 / 91±17 / 79±15
CK13	2.99	45.4±1.5 75.9±3.0		66±3	67±6
CK10 a / b	1.83 / 1.35	110±4 110±7 / 120±5 108±7		> 200 [>500]	
CK 7	1.53	53±1 91±6		80± 3	110± 40
CO 1	0.75	73±3 106±7		140±10	>120
CK 9	0.77	116±4 146±9		[250~80]	

$\left(\frac{Th\text{-}230}{U\text{-}234}\right)$ % Act $\left(\frac{Pa\text{-}231}{U\text{-}235}\right)$ % Act   [ ] $\frac{U\text{-}234}{U\text{-}238}$ Age

Fig. 20 Analytical Results of Coral Samples

		U contents (ppm)	Activity ratio		
TM 1 a / b	0.04 ±0.004 / 0.08 ±0.003		17± 3 1.5± 0.3 / 4.2±0.4 1.23±0.02		
TG 1	0.294 ±0.009		1.6±0.05 6.3±1.4 1.15±0.015		
TK 1	0.32 ±0.01		8.4±0.6 1.15±0.02		
TI 1	0.28 ±0.01		121± 5 1.06±0.02		
TO 1	0.37 ±0.02		118± 5 160± 30 1.02±0.02		
TU 1 Arag / Cal	0.58 ±0.02 / 2.06 ±0.06		111± 4 140±10 1.00±0.02 / 98.4±3.2 99±6 0.99±0.014		
TM 2 Arag / Cal	1.21 ±0.03 / 1.11 ±0.03		91± 4 131± 3 1.04±0.02 / 150±4 87±7 1.00±0.02		

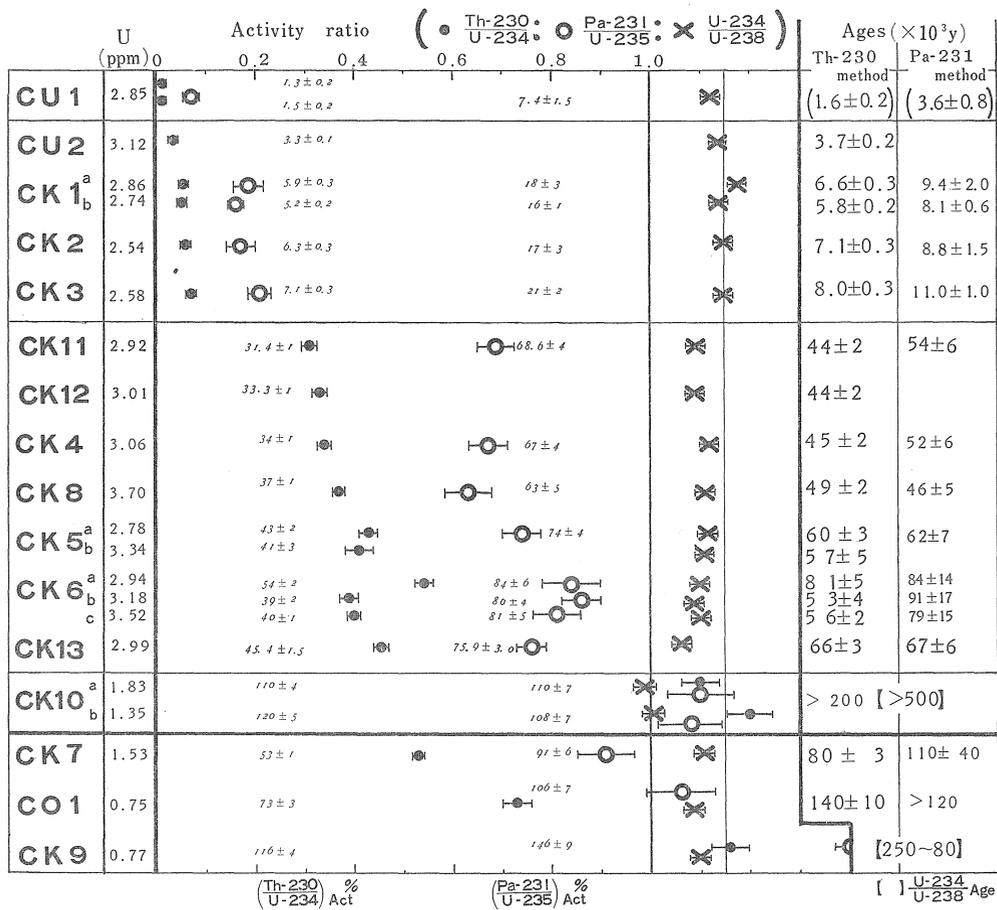$\left(\frac{Th\text{-}230}{U\text{-}234}\right)$ % Act $\left(\frac{Pa\text{-}231}{U\text{-}235}\right)$ % Act $\left(\frac{U\text{-}234}{U\text{-}238}\right)$ % Act
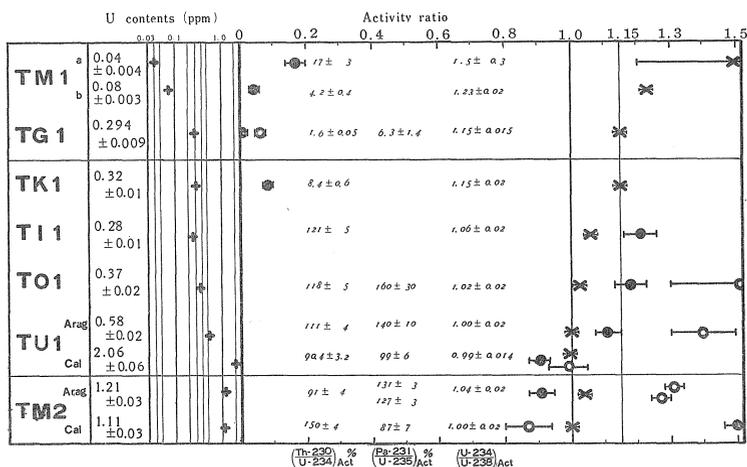
Fig. 21 Analytical Results of *Tridacna* Shell Samples

examples CU 2, CK 1, CK 2 and CK 3. This discrepancy is considered to be derived from the following two causes:

(ⅰ) Contamination with external ^{231}Pa, most probable source being the imperfection of ^{231}Pa removal from ^{232}U tracer,

(ⅱ) Exsistence of initial ^{231}Pa introduced into the coral body during its growth. But, the former cause (ⅰ) was found to be negligibly small by the blank experiment and by the experimental determination of ^{231}Pa in the great amounts of ^{232}U tracer (about 2×10^4 dis/min). Therefore, the latter cause (ⅱ) that initial ^{231}Pa exceed the amount of initial ^{230}Th become more probable. The analytical results of modern coral sample (CU 1) seems to prove this assumption to be correct.

Contents of initial ^{230}Th and ^{231}Pa are $(1.3 \sim 1.5) \pm 0.2 \%$ equil. and $7.4 \pm 1.5 \%$ equil. with respect to their parent uranium isotopes ^{234}U and ^{235}U, respectively, and these values may be taken as the initial ratios of ^{230}Th/^{234}U and ^{231}Pa/^{235}U to correct the ages obtained directly from the ratios of ^{230}Th/^{234}U and ^{231}Pa/^{235}U in the sample.

If the coral cannot distinguish thorium and protactinium from parent uranium in the processes of introduction of these heavy elements, the initial isotopic ratios of ^{230}Th/^{234}U and ^{231}Pa/^{235}U in coral sample will have the same value with the ratios of these isotopes in sea water, in which the coral had grown.

Concerning to the uranium and thorium series inequilibrium in sea water, Moore and Sackett (53) have reported the value of 0.05% equil. for ^{230}Th and 0.2% equil. for ^{231}Pa against the expectation of the author of this paper, while Kuznetsov et al. (54) obtained the values of $1 \sim 4 \%$ equil. for ^{230}Th and $5 \sim 7 \%$ equil. for ^{231}Pa from many water samples collected from near equatorial region in Pacific Ocean. The latter values just corresponds to the ratios expected and agree with the analytical results of modern coral sample.

The discrepancy between the results of Moore et al. and Kuznetsov et al. may be explained by the difference of analytical method, namely, the former analyzed the purely dissolved ^{230}Th and ^{231}Pa in sea water after centrifugation away the particle matter, whereas the latter determined the total amounts of ^{230}Th and ^{231}Pa in sea water without any treatment before analysis.

If the assumption as to the exsistence of initial ^{231}Pa and ^{230}Th are valid, not only the discrepancy of about 2,000 years between ^{231}Pa and ^{230}Th ages is explained very smartly, but also the correction by initial ^{231}Pa and ^{230}Th becomes possible for any marine carbonate samples. But for older samples, exsistence of initial ^{231}Pa and ^{230}Th does not cause significant errors for age calculations, because of relatively small contribution from initial values in comparison with the statistical errors of measurements.

In Table 4, corrected ^{231}Pa and ^{230}Th ages are given by assuming the initial ratios of ^{231}Pa/^{235}U and ^{230}Th/^{234}U as $7.4 \pm 1.5 \%$ equil. and $1.4 \pm 0.2 \%$ equil., respectively.

Tadle 4   Corrected ^{230}Th and ^{231}Pa Ages of Coral and *Tridacna*

Sample	^{230}Th Ages (10^3 yr)	^{231}Pa Ages (10^3 yr)	(^{231}Pa Age)/(^{230}Th Age)
CU 1	0.0±0.2	0.0±0.8	—
CU 2	2.1±0.3	—	—
CK 1a	5.0±0.4	5.8±2.1	1.16±0.43
1b	4.2±0.3	4.5±1.0	1.07±0.25
CK 2	5.5±0.4	5.2±1.7	0.94±0.21
CK 3	6.4±0.4	7.4±1.3	1.16±0.21
CK 11	39±2	50±6	1.27±0.15
CK 12	42±2	—	—
CK 4	44±2	48±5	1.09±0.12
CK 8	47±2	42±5	0.89±0.14
CK 5a	59±5	59±7	1.00±0.13
5b	56±5	—	—
CK 6a	79±5	80±14	1.01±0.19
6b	52±4	87±17	1.67±0.33
6c	54±2	75±15	1.39±0.28
CK 13	64±3	63±6	0.99±0.11
TG 1	0.00±0.06	0.0±0.7	—
TK 1	7.75±0.75	—	—

Assumed Initial Values (in % equil.)
    Coral: ^{230}Th=1.5±0.2, ^{231}Pa=7.4±1.5
    Tridacna : ^{230}Th=1.59±0.05, ^{231}Pa=6.3±1.4

As known from the Table 4 and Fig 22, agreement of ^{231}Pa ages with ^{230}Th ages bocomes better than before.

Radiocarbon data reported by Mii and Kigoshi (55) for the sample taken from the same stratigraphic position as CK 1, CK 2, and CK 3 gives nearly the consistent ages of 6,630± 150 yr for coral (GaK 454) and 4,370 ±130 yr for *Tridacna* shell (GaK 452). On the other hand, although too younger age of 27,200±1,200 yr for echinoid sample (GaK 455) is reported for the age of the similar stratigraphic member with the samples CK 8, CK 5 and CK 6, the ages

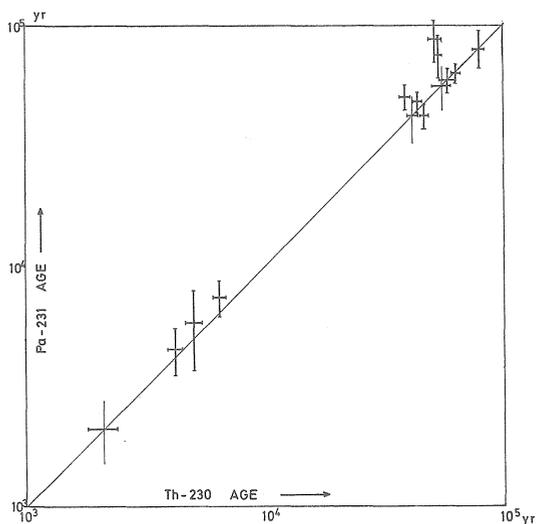Fig. 22 Correlation between corrected Pa–231
        ages and Th–230 ages

obtained by ^{230}Th and ^{231}Pa methods (55~65×10^3 yr) are considered to be more reliable, because the contamination with recent ^{14}C is very probable for such an old carbonate sample.

The oldest coral sample CK 10, which was collected from the lower members of Ryukyu Limestones known as Hyakunodai Limestone, contains some calcite structure and the analytical data shows the impossibility of the age calculation both by ^{230}Th and ^{231}Pa methods, because the contents of daughter nuclides exceed their equilibrium values with their parents. Only the equivocal age of more than 500 thousand years is estimated from the ^{234}U/^{238}U ratio. Uranium content of CK 10 is considerably small (1.83 and 1.35 ppm) compared with the content of non-recrystallized coral samples (about 3 ppm). This fact suggests the preferential leaching of uranium during the phase change from aragonite to calcite. Analytical results of CK 7, CO 1 and CK 9, which are almost in calcite structure, also show such circumstances. For these recrystallized samples, it is characteristic that the uranium content is considerably lower than that in the normal sample and that the daughter nuclides generally exceed their equilibrium values.

Analyses for the samples indicated by the sign a, b and c, were carried out to examine the reproducibility of th analytical method and to know the homogeneity of the radioactive elements in coral. Though good agreement was obtained for the samples CK 1 and CK 5 not only in uranium content but in ages, the results of CK 6 and CK 10 showed large difference in these values. This might not be explained by the analytical error accompanied with this method.

These disagreements, particularly in age of the sample CK 6, may be caused by the heterogenous distribution of radioactive elements including the possibility of the migration of parent uranium, even if any change of crystalline form could not be confirmed by the X-ray diffraction analysis. Probable age of CK 6 is considered to be the same that of CK 5 (55~59×10^3 yr).

VII-3 Analytical Results of *Tridacna* Shell Samples

In Fig. 21, the analytical results of *Tridacna* shell samples are summarized. Differing from the case of coral samples, age calculation by ^{230}Th and ^{231}Pa could not be applied except for very young samples of TM 1 (Modern), TG 1 (Modern) and TK 1 collected from the Raised Coral Reefs. Although any alteration in their crystal structure is observed, activities of daughter nuclides mostly exceed their equilibrium values with the parent uranium isotopes, and only the relative age assignments are possible from the ratio ^{234}U/^{238}U by assuming their initial ratio as 1.15 and no differential leaching or addition of two uranium isotopes occurred.

As discussed above, large amounts of recent samples of TM 1 (30 gram and 190 gram) and TG 1 (552 gram) were analyzed to obtain the reliable initial activity ratios of ^{230}Th/^{234}U and ^{231}Pa/^{235}U. Among these three samples, TG 1 gives the results which agree with the results obtained from the recent coral sample CU 1,

supporting the validity of the assumption made above. They are $1.59 \pm 0.05\%$ equil. for initial $^{230}Th/^{234}U$ ratio and $6.3 \pm 1.4\%$ equil. for initial $^{231}Pa/^{235}U$ ratio. On the other hand, TM 1 gives extraordinaly higher ratio of initial $^{230}Th/^{234}U$ (TM 1a, $17 \pm 3\%$ equil., TM 1b, $4.2 \pm 0.4\%$ equil.) than expected values of $1\sim2\%$ equil.

This discrepancy can be explained if the absolute value of ^{230}Th content (dpm) per unit weight of sample are compared, i. e.,

TM 1a　　0.007 ± 0.002　dis/min/g,
TM 1b　　0.0038 ± 0.0003　dis/min/g,
TG 1　　　0.0040 ± 0.0001　dis/min/g.

From the same order values of ^{230}Th content among the samples, it is known that the large $^{230}Th/^{234}U$ ratios in modern *Tridacna* shell (TM 1a and TM 1b) are caused by their extremely low uranium content (TM 1a, 0.040 ppm; TM 1b, 0.082 ppm) compared with the content of uranium in TG 1 (0.3 ppm). Therefore, it is more preferable to discuss by using the absolute disintegration rate per unit weight of sample instead of the ratio $^{230}Th/^{234}U$ solely. This may perhaps be held in the case of ^{231}Pa, though any information could not be obtained in this work.

According to the reasons discussed above, it may be more reliable to consider the initial ^{230}Th and ^{231}Pa contents as 1.59 ± 0.05 and $6.3 \pm 1.4\%$ equal. for the ordinary samples containing uranium about 0.3 ppm. Therefore, the age of the only sample (TK 1) that could be determined by $^{230}Th/^{234}U$ method, is considered as $7,750 \pm 750$ yr instead of the apparent age of 9,500 yr. The corrected age does not contradict to the age of the coral sample (CK 1) taken from the same stratigraphic position.

Analyses were carried out for both the aragonitic and calcite parts of the older samples TU 1 and TM 1, so as to investigate the influences of diagenesis (aragonite to calcite). As discussed in VII-1, the most noticable fact may perhaps be the increase of the uranium content in older samples. The values of 0.58 and 2.06 ppm for the sample TU 1 and 1.21 and 1.11 ppm for TM 2 are larger than the ordinary uranium content in *Tridacna* shell samples. This fact indicates the secondary introduction of uranium into the shell. Abnormal ratios between parent uranium and their daughters are obtained as a matter of course for these altered samples. For these samples, age should not be calculated, even if the $^{230}Th/^{234}U$ ratio would not attain its equilibrium value. For example, though the sample TM 2 arag. gave the value of 91 ± 4 % equil for $^{230}Th/^{234}U$, age estimation could not be carried out, since the activity of ^{231}Pa exceeding about 30 % over the equilibrium value indicated the secondary alteration of the sample.

Therefore, it must be emphasized again here that the ^{230}Th to ^{231}Pa ratio serves as one of the most reliable criterion for judging the validity of the age estimation, because the anomalous changes in isotopic composition occuring more than several thousand years ago could not have any print on the ratio $^{226}Ra/^{230}Th$ of the sample.
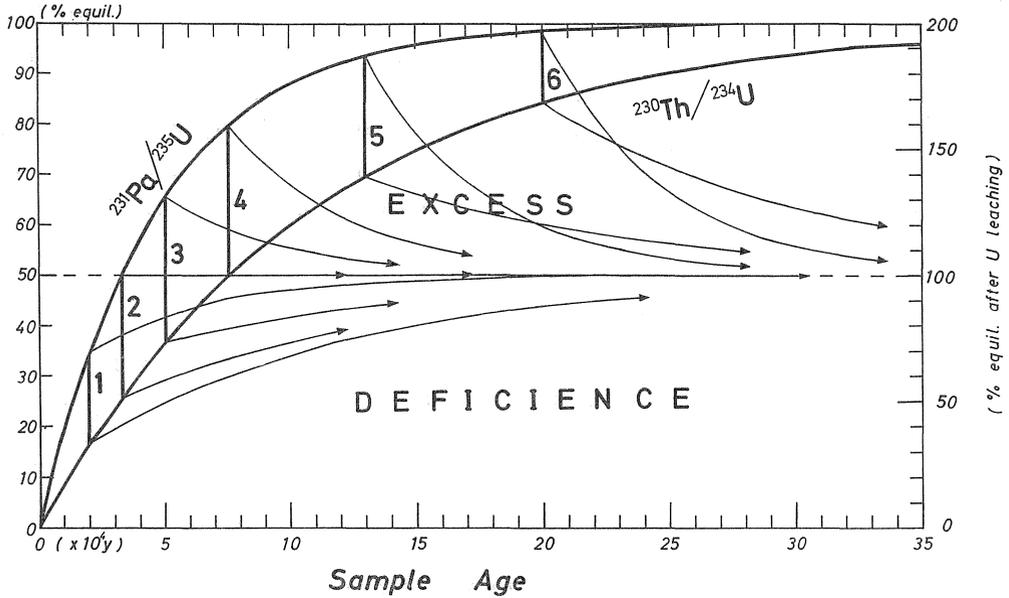
Fig. 23 Influence of the Uranium Leachig to the Growth and Decay Properties of ^{231}Pa and ^{230}Th

A mechanism that causes the excess ^{231}Pa or ^{230}Th, is shown schematically in Fig. 23, by assuming the preferential leaching of uranium during the secondary alteration. In making the figure, assumption was made that the 50 % of uranium was preferentially leached away from the sample without disturbing the contents of ^{230}Th and ^{231}Pa of the sample, and that the time needed for leaching was negligibly shorter than the time of exsistence of the sample, since, for example, the large excess of daughter nuclides was observed in the case of the sample CK 9. Abnormal cases may be approximately explained by this simple mechanism of uranium leaching. The actual cases found in coral and *Tridacna* shell samples seem to correspond to the following groups: (case numbers correspond to the numbers in Fig. 23)

$$\begin{array}{ll}
\text{CK 7} \dotfill & \text{Case 1,} \\
\text{CO 1, TM 2 }_{arag.} \dotfill & \text{Case 3,} \\
\text{CK 9, CK 10, TO 1, TU 1 }_{arag.} \dotfill & \text{Case 5 or 6.}
\end{array}$$

Though, the age and the time of leaching can be estimated, theoretically, on the basis of these assumption by using the ^{234}U/^{238}U ratio and ^{231}Pa/^{230}Th ratio as an age indicator, the probability of fractional leaching of ^{234}U and ^{238}U, and the lack of the method to determine the accurate ratio of ^{234}U/^{238}U, limit the application of this method. Furthermore, the leaching of uranium may not occur in natural conditions such a simple mechanism as assumed here.

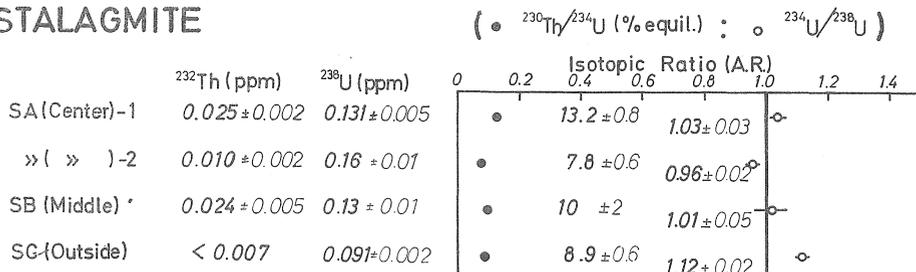**VII-4** Analytical Results of Stalagmite and Water Samples.

In Fig. 24, the analytical results of stalagmite and the water samples are illus-

trated by the same manner as the results of coral and *Tridacna* shell samples. Stalagmite sample was divided into four sections of SA 1 (Central part), SA 2 (Central part, just upper part of SA 1), SB (Middle part) and SC (Outside part). These four blocks were analyzed for their $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ ratios to examine their validity for dating sample. As known from this figure, contents of uranium and thorium vary considerably wide range of factor $2\sim4$, and the ratios $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ do not obey the theoretical changes of these values, which may be expected by assuming the constant growth rate of stalagmite without the migration of radioactive elements in it.

These abnormal ratios between parents and daughter nuclides, probably, due to the complicate mechanism of the stalagmite formation. In the repeated process of the recrystallization, parent uranium will migrate by forming the carbonate complex with carbonate ions that exsist sufficiently in its environment. Another cause may be the exsistence of the impurities, which are introduced at the time of the formation of brownish yellow coloured ring. And the relatively large content of ^{232}Th (0.02 ppm) will be explained not by the introduction through purely chemical processes of disso-lution and deposition, but by the simultaneous introduction with the impurities in detrital form.

Although the exact age estimation could not be made for this sample, apparent maximum age of 15×10^3 years was obtained from the ratio $^{230}Th/^{234}U$ of the central part SA 1 without the correction by initial ^{230}Th introduced with ^{232}Th.
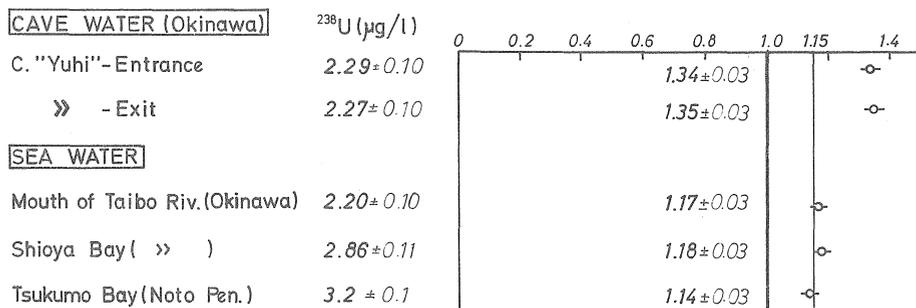

Fig. 24 Analytical Results of Stalagmite and Water Samples

Ground water of cave "Yuhi" and several coastal sea water of Okinawa and Noto Peninsula were also analyzed for their uranium content and $^{234}U/^{238}U$ ratios. As known from Fig. 22, cave water samples give considerably large amounts of uranium (2.3 microgram/liter) and relatively high $^{234}U/^{238}U$ ratio of $1.33 \sim 1.34$. Since the source of uranium in cave water sample is considered to be the limestone bed, through which the ground water has passed, high $^{234}U/^{238}U$ ratio will be caused by the preferential leaching of daughter nuclide ^{234}U compared with parent ^{238}U, because the $^{234}U/^{238}U$ ratio in the limestone bed composed of marine deposited calcium carbonates is considered to have at most the same value of sea water (1.15).

The preferential leaching of daughter nuclide may be due to the recoil effect of alpha and beta decay processes, which makes ^{234}U more leachable than parent ^{238}U, as assumed firstly by Cherdyntsev (11) to explain the anomalous $^{234}U/^{238}U$ ratio in natural uranium samples.

Three samples of coastal sea water give the activity ratios of $^{234}U/^{238}U$ 1.17 ± 0.03, 1.18 ± 0.03 and 1.14 ± 0.03. These values do not contradict to the data reported by many authors (13, 56~59).

VIII   Discussions on the Causes of Error

> Errors expected to be brought into this dating method are classified into following four groups. Those are (i) pipetting error or the uncertainty of the concentration of ^{232}U spiked, (ii) impurities in the tracer solution, (iii) counting statistics and (iv) contamination of the sample with foreign materials. Those factors are discussed below.

VIII-1   Pipetting Error and the Absolute Activity of ^{232}U

Pipetting of thorium and protactinium tracer was carried out by using the ultra micro pipettes (Shibata Rikagaku Kikai Co., Ltd. or Beckmann Co., Ltd.) whose capacities are 0.05 and 0.20 ml, and the error derived from the reproducibility of pipetting is assumed to be within 3 per cent including the geometrical differences of the mounting of the standard sources, whereas the uranium tracer ^{232}U was added to the sample by using the measuring pipette so as to add the adequate amounts of ^{232}U according to the uranium content in the analytical solutions.

An absolute counting rate of ^{232}U spiked was determined from the activity of the standard source prepared from an aliquot of ^{232}U stock solution. In this case, the ^{232}U stock solution had been purified in advance from daughter muclides which may grow up with the half-life of 1.9 year (^{228}Th) owing to an alpha decay of ^{232}U. Considering the tailing of the alpha spectrum obtained by the evaporated standard source, ^{232}U activity was calculated from the sum of the counts in the range from 3.5 to 5.32 MeV.

Besides the direct measurement of ^{232}U activity mentioned above, it was determined by using other uranium tracer ^{237}U (half-life, 6.75 days, beta and gamma ray emitter) (47). In this case, ^{237}U (inevitably contains target uranium with the ratio

of $^{234}U/^{238}U = 0.20 \pm 0.01$) was mixed with an aliquot of ^{232}U stock solution and the purification of uranium was carried out by means of an anion exchange method after the attainment of isotopic exchange equilibrium. Then, the purified uranium was electrodeposited on a stainless steel plate as the same manner described before. After the determination of the chemical yield of uranium by the beta counting of the recovered ^{237}U, alpha spectrometry was carried out. The peak area of ^{232}U (from 4.80 to 5.32 MeV region) was computed and normalized by the chemical yield. The ^{232}U activity thus determined agreed very well with the value obtained from the evaporated source within 2 per cent. Hence, the errors derived from pipetting, geometrical difference of mounting and the counting statistics were assumed not to exceed 3 per cent for uranium tracer ^{232}U.

As the tailing effect cannot be neglected both for the electrodeposited and eva- porated sources, an absolute quantity of uranium may be somewhat lower than that of real one. However, such effect will not interfere the caluculation of the ratios of $^{230}Th/^{234}U$ and $^{231}Pa/^{235}U$, since tailing effect may also exsist in the alpha spectra of all nuclide studied in this work.

VIII-2 Impurities in Tracer Solution

i) ^{231}Pa in ^{232}U

As the uranium tracer ^{232}U was prepared by the neutron irradiation of ^{231}Pa by $^{231}Pa\ (n,\gamma)^{232}Pa \xrightarrow[1.31\,d]{\beta-} {}^{232}U$ reaction (60), the contamiantion of ^{232}U with target ^{231}Pa is most probable and critical problem, because the ^{231}Pa activity is extremely small in natural sample. That is, this activity never exceed the value 1/21.7 of the ^{238}U activity unless the geochemical processes that enrich protactinium or leach out parent uranium might occur. This sort of contamination is more critical for the dating of younger samples than for that of older ones. If the activity ratio of $^{231}Pa/^{232}U$ in tracer solution and that of $^{232}U/^{238}U$ are assumed as 10^{-3} and 1.0, respectively, activity of protactinium in tracer solution corresponds to about 2.2% of the equilibrium value with parent ^{235}U (this value corresponds to about 1,000 year background) and causes a serious error for the age determination of the sample younger than ten thousand years. The uranium tracer used in this work was purified by three cycles of solvent extraction and two cycles of anion exchange and absence of ^{231}Pa in ^{232}U tracer solution was ascertained by means of alpha spectrometry using ^{233}Pa as protactinium tracer, therefore, the possibility of ^{231}Pa contamination from the uranium tracer spiked could perfectly avoided.

ii) ^{230}Th and Uranium in ^{234}Th

^{234}Th was prepared by the milking technique from its parent ^{238}U by means of cation exchange (43) and solvent extraction methods. In this case, a complete removal of uranium is the most critical problem and, furthermore, the contribution of ^{230}Th growing up simultaneously with ^{234}Th must also be considered, because the activity of

^{230}Th increases linearly with time, whereas that of ^{234}Th has attained the saturation. The relation between ^{230}Th and ^{234}Th is described as Eq. (29):

$$^{230}\text{Th}/^{234}\text{Th} = (^{234}\text{U}/^{238}\text{U})\lambda_0 t/(1 - e^{-\lambda_4 t})e^{-\lambda_4 T} \ (29), \tag{20}$$

where λ_0, λ_4: decay constants of ^{230}Th and ^{234}Th,

t: the period between the time of the uranium (cow) purification and the time of milking,

T: the time elapsed after the preparation of thorium tracer ^{234}Th.

By assuming ^{234}U/^{238}U$=1.0$, t and T as ten and three half-lives of ^{234}Th (24.1 days), the value of 4.8×10^{-5} is obtained as the activity ratio of ^{230}Th/^{234}Th. Accordingly, the contribution of ^{230}Th in thorium tracer cannot be neglected when ^{234}Th is prepared from aged uranium or aged ^{234}Th is used as thorium tracer. These troubles can be avoided by using the depleted uranium (with low ^{234}U/^{238}U ratio) for cow and by taking t and T in Eq. (29) as small as possible.

iii). ^{233}U, ^{231}Pa and Thorium Isotopes ^{232}Th and ^{230}Th in ^{233}Pa

^{233}Pa was produced from neutron irradiated ^{232}Th by ^{232}Th (n, γ) ^{233}Th $\xrightarrow[23.3m]{\beta^-}$ ^{233}Pa reaction, and purified by solvent extraction using DIBK-HCl system (45) or by adsorption and desorption technique using SiO_2 or glass powder as adsorbent (44). In the case of ^{233}Pa tracer, the contaminating nuclides which must be considered are ^{232}Th as the target material, ^{231}Pa produced together with ^{233}Pa from ^{230}Th in ^{232}Th, and ^{233}U accumulated by the decay of ^{233}Pa. Among these nuclides, ^{232}Th and ^{231}Pa are considered as the same manner as the case of ^{234}Th and can be proved not to cause serious errors.

However, ^{233}U has somewhat critical problem that the alpha particle energy of ^{233}U (4.82 MeV) is nearly the same as that of ^{234}U (4.77 MeV) and may interfere the determination of the ^{234}U/^{238}U ratio. The increase of ^{233}U activity and the decrease of ^{233}Pa activity are related as follows:

$$^{233}\text{U}/^{233}\text{Pa} = (e^{\lambda_{3p} t} - 1)\lambda_{3u}/\lambda_{3p} \tag{30}$$

where λ_{3u} and λ_{3p} denote the decay constant of ^{233}U and ^{233}Pa, respectively, and t—— the time after the preparation of ^{233}Pa tracer.

If t is assumed to be five half-lives of ^{233}Pa (27,4 days), the value of 1.4×10^{-5} is obtained as the activity ratio of ^{233}U/^{233}Pa. This value increases exponentially with time and may cause a little error in determination of ^{234}U/^{238}U ratio when very small quantity of uranium is analyzed. Hence, ^{233}Pa must be purified at times to remove ^{233}U accumulated in the ^{233}Pa stock solution.

VIII-3 Counting Errors

In the radioactive dating, counting errors are generally the most important determinant in the error of the estimated age. And the factors that contribute to these errors may be classified into next three groups.

i) The level of radioactivity of the counting source (it is better to have as much activity as possible in respect to counting statistics).

     * The quantity of the sample that determines the amounts of parent uranium,

     * The age of the sample that determines the amounts of the daughter nuclides.

     * The overall chemical yields of uranium, thorium and protactinium.

ii) Counting apparatuses for alpha spectrometry.

     * Counting efficiency : Ionization chamber (2π) is better than Semiconductor ($<2\pi$).

     * Background activity: (The following data are reported)

                  Semiconductor ($0.00X$ cpm)

                  $<$Double-gridded Ionization Chamber ($0.0X$ cpm)

                  $<$Single-gridded Ionization Chamber ($0.X$ cpm)

     * Resolution power : Semiconductor ($0.3 \sim 0.8\%$ FWHM) is better than Gridded Ionization Chamber ($1 \sim 2\%$ FWHM).

iii) Measuring time (Though the long measuring time is desirable to obtain the total counts with less relative statistical error, the drift of measuring condition and background activity must be also taken care in this case)

Refering to these factors, the theoretical limit of the applicabilities of the deficient ^{230}Th and ^{231}Pa dating methods are examined. Because the background activity of the counting system limits the determinable amounts of ^{230}Th and ^{231}Pa on the counting plate, it seems most useful to consider at first the lowest limit of the age obtainable in this method, when the background activity and the measuring time are given.

If the background activity, the measuring time and the lowest limit of detection be b cpm, t minutes and four times of the standard deviation (σ) of the background activity (cpm) respectively, the next equation is obtained from the law of the counting statistics :

$$\text{Limit of detection (cpm)} \quad = 4\,\sigma$$
$$= 4\,(bt/t^2)^{1/2} = 4\,(b/t)^{1/2} \qquad (31).$$

As b and t are usually $0.02 \sim 0.04$ cpm and 3,000 minutes in this experiment, the lowest limit of detection becomes $0.010 \sim 0.014$ cpm. By using 0.014 cpm as the detection limits of ^{230}Th and ^{231}Pa activities, the relation between total amounts of uranium in the analytical sample and the lowest limits of the age determination by deficient ^{230}Th and ^{231}Pa methods can be expressed by the following equations :

$$\text{For } ^{230}\text{Th} \cdots\cdots\cdots\cdots 0.014 = \frac{0.735}{2} \times [U] \times 0.5 \times (1 - e^{-\lambda_0 T_0}) \qquad (32),$$

$$\text{For } ^{231}\text{Pa} \cdots\cdots\cdots\cdots 0.014 = \frac{0.735}{2 \times 21.7} \times [U] \times 0.5 \times (1 - e^{-\lambda_1 T_1}) \qquad (33),$$

where $[U]$: total amount of uranium in the analytical sampl (μg),

λ_0, λ_1: decay constants of ^{230}Th and ^{231}Pa,

T_0, T_1: the lowest limits of the age obtainable by ^{230}Th and ^{231}Pa methods, respectively,

0.014: limit of detection (cpm),

0.735: counting rate for 1 μg uranium by 2π geometry counting,

21.7 : the activity ratio of ^{238}U/^{235}U in natural uranium sample,

0.5 : assumed as the chemical yields of thorium and protactinium isotopes, in practice, this value varies in the range from 0.8 to 0.1.

If $\lambda_0 T_0$ and $\lambda_1 T_1$ are sufficiently small compared with 1 (T_0, $T_1 < 10^3$ yr), Eqs. (32) and (33) have very simple forms and the lowest limits of age are estimated by

$$T_0 = 0.0763/\lambda_0 [U] = 0.110 \times (T_{1/2})_0/[U] = 8.3 \times 10^3/[U] \text{ (year)} \tag{34},$$

$$T_1 = 0.110 \times 21.7 \times (T_{1/2})_1/[U] = 7.8 \times 10^4/[U] \text{ (year)} \tag{35}.$$

where $(T_{1/2})_0$ and $(T_{1/2})_1$ denote the half-lives of ^{230}Th and ^{231}Pa, respectively If the sample contains 100 μg of uranium, about 80 and 800 years are obtained as the lowest limits of ages in deficient ^{230}Th and ^{231}Pa methods, respectively. The minimum statistical errors in the estimated age may be the same order with these values, if the above mentioned conditions are assumed.

Relation between total uranium content and the lowest limits of the age determinable is shown graphically in Fig. 25. Though the device to lower the background activity of the measuring apparatus and to prolong the measuring time will enable to lower the age limit, effect of them are only proportional to the square root of $1/b$ and t. So, in order to obtain more reliable age of the younger sample, it is more effective to analyze the larger amounts of the sample with high chemical yields.
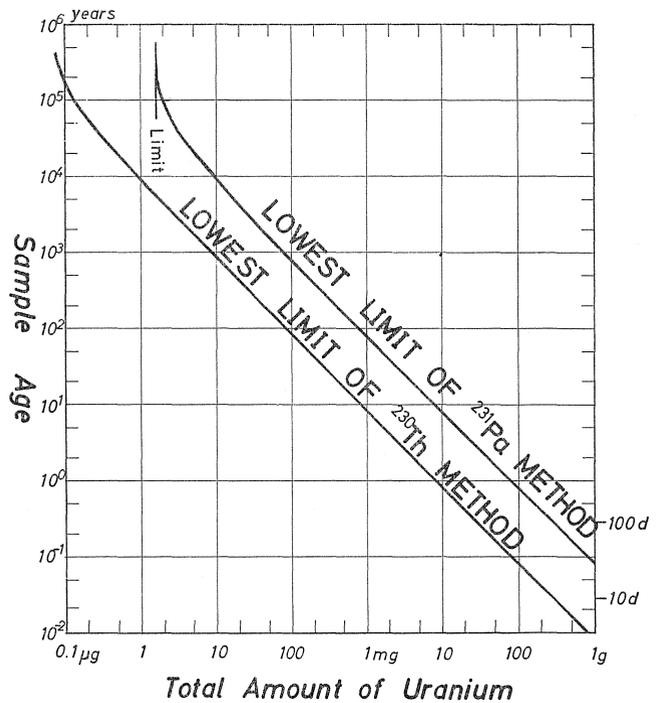

Fig. 25   Available Limits of the Deficient ^{230}Th and ^{231}Pa Methods

VIII-4   Contamination

Three main causes are considered as the source of the contamination. Those are

(i) exsistence of initial ^{230}Th and ^{231}Pa as discussed before in VII-2, (ii) contamination with the foreign materials such as clay that will contain ^{230}Th and ^{231}Pa in equilibrium amounts with parent uranium, (iii) experimental contaminations from reagents, glasswares, ion exchange resins and electro-deposition cell, etc..

The source (i) can be corrected by the analysis of large amounts and numbers of modern sample, or by the appropriate correction methods such as ^{232}Th content as indicator (10).

As the sources (ii) and (iii) can also be avoided by a careful experiment, these factors are not discussed here.

For example, a typical data sheet of the coral sample CK 5 is given in Table 5.

Table 5 Exampe of the Data Sheet

	Radioactive Dating by ^{230}Th and ^{231}Pa Methods			No. CK 5	
Sample	Classific.	Upper Limestone Member			
	Location	Kamikatetsu, S. Kikai			
	Date	65–12–23–6–2			
Analytical Data					
	Date	66–1–28			
	Weight	37.6g			
	Dissoln.	HNO_3+HF			
	Tracer	UX1 (0.10ml), Pa (0.40ml), U–232 (15.5cpm)			
	Sepn. Method. Fe(III) coppt. Ionex				
Electrodeposition		U	Th		Pa
	Date	66–2–2	66–2–2		66–2–2
	Chem. Yield		45.7 ± 0.6		36.8 ± 0.5(%)
GIC Measurement					
	Date	66–2–9	66–2–9		66–2–11
	Meas. Time	1,320	321		1,410 (min)
	Counts/Ch	^{238}U 7,021/19	^{230}Th 2,787/24	^{231}Pa 806/28	
		^{234}U 7,860/21	^{232}Th 178/22		
		^{232}U 2,809/23			
Results	U–238	39.6±1.1 (cpm)	^{234}U/^{238}U	1.12±0.02 (A.R.)	
	U–234	44.3±1.1 (cpm)	^{230}Th/^{234}U	42.9±1.7 (%equil.)	
	Th–230	19.0±0.4 (cpm)	^{231}Pa/^{235}U	73.5±3.8 (%equil.)	
	Pa–231	1.34±0.06(cpm)	^{230}Th/^{232}Th	18 (A.R.)	
	Th–232	1.05±0.08(cpm)	U concn.	2.87±0.06(ppm)	
			Th concn.	0.23±0.02(ppm)	
Estimated Ages					
	^{234}U/^{238}	(80±60)×10^3 (y)			
	^{230}Th/^{234}U	(59±3) //			
	^{231}Pa/^{235}U	(59±7) //			
	^{231}Pa/^{230}Th	(56±13) //			

IX Comparison of Results with Other Data

We can consider that the ages obtained from Ryukyu Limestones indicate the warm periods in late Pleistocene epoch in this region of Pacific Ocean. From the ^{230}Th data, they are presumed to be $5\sim7\times10^3$ yr for Raised Coral Reefs, 40×10^3 yr for the beginning of the warm period and $40\sim45\times10^3$ yr for Araki Limestones and $55\sim65\times10^3$ yr for Upper Limestone Membere, respectively. However, reliable data was not obtained for Lower Member of Ryukyu Limestones.
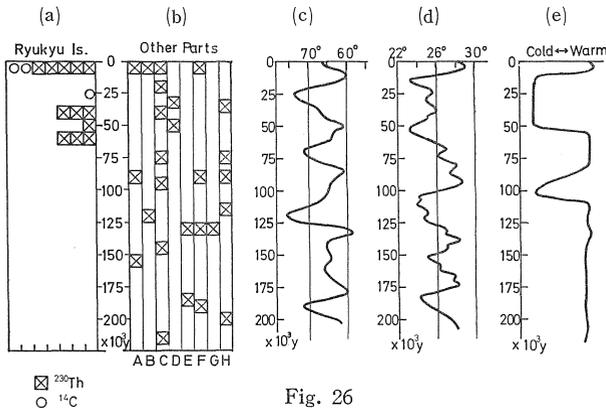

Fig. 26

Comparison of the Analytical Data with Other Data

In Fig. 26, the data obtained by this work are shown together with other data based on fossil carbonate samples (17, 24~30, 53, 61) (Fig. 26b), solar insulation curve (62) (Fig. 26 c), $^{18}O/^{16}O$ temperature (63) (Fig. 26 d) and paleontologic climate (64) (Fig. 26 e) estimated from the data by deep sea sediment core samples. As seen from this figure, Ryukyu Limestone seems to give somewhat younger ages than expected from $^{18}O/^{16}O$ temperature or paleontologic climate, and to correspond rather to solar insulation curve with minimum value at about 50×10^3 yr before present.

The comparison of the sample age with the elevation above present sea level gives very interesting information that the sea level stands higher in ancient sea. Sea levels are becoming higher in the order, that is, 0 m for the present one, $2\sim5$ m for $5\sim7\times10^3$ yr B.P., $20\sim30$ m for $40\sim45\times10^3$ yr B. P. and $40\sim45$m for $55\sim65\times10^3$ yr B. P. as shown in Fig. 27.

Since the period of $10\sim40\times10^3$ yr range was considered to be in the last glacial age (Würm) and the sea level would have the minimum value at about $20\sim30\times10^3$ yr B.P. Therefore, the sea level near Kikai-jima might have varied along the dotted line curves in Fig.27 during last seventy thousand
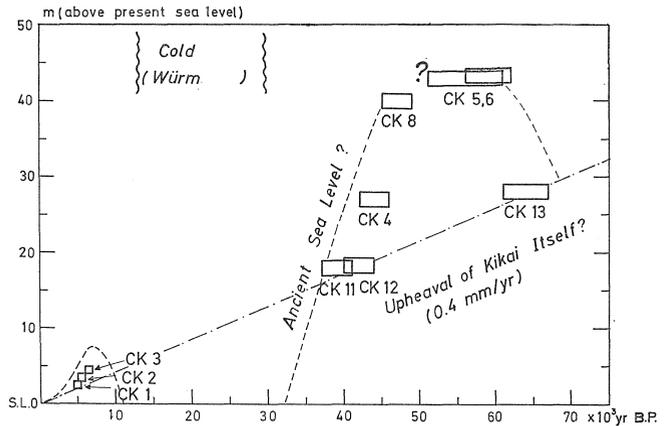

Fig. 27 Presumed Ancient Sea Level near Kikai-Jima without any consideration of tectonic movement other than simple upheaval.

years unless the geological upheaval of Kikai-jima had occurred during this period. If the simple upheaval of Kikai-jima had been occurring during this period without any other tectonic movement, it will be given by the chain formed line $(- \cdot - \cdot)$ which indicates approximately the mean upheaval rate of 0.4 mm/yr. Even in this case the change of sea level must be considered to explain the ages of some samples (CK 4, CK 8 CK 5 and CK 6).

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References

(1) Anderson, E.C., Libby, W.F., Weinhous, S., Reid, A.F., Kirshenbaum, A.V. and Grosse, A.V., Natural radiocarbon from cosmic radiation, Phys. Rev. 72 931(1947).

(2) Khlopin, V.G., Dokl. Akad. Nauk SSSR (1926) 178.

(3) Piggot, C.S. and Urry, W.D., Radioactivity of ocean sediments. IV, The radium content of sediments of the Cayman trough, Am. Jour. Sci. 240 1 (1942).

(4) Issac, N. and Piciotto, E., Ionium determination in deep-sea sediments, Nature 171 742 (1953).

(5) Rosholt, J.N., Emiliani, C., Geiss, J., Koczy, F.F. and Wangersky, P.J., Absolute dating of deep-sea cores by the [231]Pa/[230]Th method, J. Geol. 69 162 (1961).

(6) Sarma, T.P., Dating of marine sediments by ionium and protactinium methods, Ph. D thesis, Carnegie Inst. Tech. (1964).

(7) Sackett, W.M., Broecker, W.S. and Thurber, D.L., The geochemistry of [231]Pa and the dating of pelagic sediments, Annual Rept. AEC Contact AT (30–1) (1965).

(8) Barns, J.W., Lang, E.J. and Potratz, H.A., Ratio of ionium to uranium in coral limestones, Science 124 175 (1956).

(9) Sackett, W.M., Ionium-uranium ratios in marine deposited calcium carbonates and related materials, Ph. D thesis, Washington Univ. (1958).

(10) Tatsumoto, M. and Goldberg, E.D., Some aspects of the marine geochemistry of uranium, Geochim. Cosmochim. Acta 17 201 (1959).

(11) Cherdyntsev, V.V., Tr. III sessii komissii po opredeleniyu absolyutnogo vozrasta, Izv. Akad, Nauk SSSR (1955).

(12) Cherdyntsev, V.V., Vopr. geologii antropogena. K VI kongressy INQUA GIN AN CCCP, p266 (1961)

(13) Thurber, D.L., Anomalous [234]U/[238]U in nature, J. Geophys. Res. 67 4518 (1962).

(14) Rosholt, J.N. and Antal, P.S., Evaluation of the [231]Pa/U, [230]Th/U methods for dating Pleistocene carbonate rocks, USGS Profess. Paper 450–E, Article 209 E101–E111 (1963).

(15) Sackett, W.M. and Potratz, H.A., Subsurface geology of Eniwetok atoll, Dating of carbonate rocks by ionium and uranium ratios, USGS Profess. Paper 260–BB (1963).

(16) Broecker, W.S., A preliminary evaluation of uranium series inequilibrium as a tool for absolute age measurement on marine carbonates, J. Geophys. Res. 68 2817 (1963).

(17) Blanchard, R.L., Uranium series disequilibrium in age determination of marine calcium carbonates, Ph. D thesis, Washington Univ., St. Louis, Mo. (1963).

(18) Cherdyntsev, V.V., Kazachevsky, I.V. and Kuzmina, E.A., Isotopic composition of uranium and thorium in supergene zone. Studies on the fossil bone and shell of molluscs, Geokhimiya (1963) 254.

(19) Cherdyntsev, V.V., Kazachevsky, I.V. and Kuzmina, E.A., Age of the Pleistocene carbonate formation by isotopes of thorium and uranium, Geokhimiya (1965) 1085.

(20) Alokseev, V.A., Kazachevsky, I.V. and Cherdyntsev, V.V., Izd. Akad. Nauk SSSR, Absolute geochronology of Quaternary period (1964).

(21) Cherdyntsev, V.V., Malyshev, V.I. and Kazachevsky, I.V., Isotopic composition of uranium and thorium in supergene zone. Study of peat bog substances, Geokhimiya (1964) 399.

(22) Cherdyntsev, V.V., Kazachevsky, I.V, Kislitsina, G.I., Kuzmina, E.A.. and Kind, N.V., Non-equilibrium uranium in carbonate deposits and their age determination, Geokhimiya (1966) 139.

(23) Titaeva, N.A., On the possibility of the absolute age determination of organic sediments by the ionium method, Geokhimiya (1966) 1183.

(24) Kaufman, A. and Broecker, W.S., Comparison of ^{230}Th and ^{14}C ages for carbonate materials from lakes Lahontan and Bonneville, J. Geophys, Res. **70** 4039 (1965).

(25) Thurber, D.L., Broecker, W.S., Potratz, H.A. and Blanchard, R.L., Uranium series ages of Pacific atoll coral, Science **149** 55 (1965).

(26) Broecker, W.S. and Thurber, D.L., Uranium series dating of corals and oolites from Bahaman and Florida Key limestones, Science **149** 58 (1965).

(27) Osmond, J.K., Carpenter, J.P. and Windom, H.L., ^{230}Th/^{234}U ages of the Pleistocene corals and oolites of Florida, J. Geophys. Res. **70** 1843 (1965).

(28) Stearns, C.E. and Thurber, D.L., ^{230}Th/^{234}U dates of late Pleistocene marine fossils from the Mediterranean and Moroccan littorals, Quaternaria **7** 29 (1965).

(29) Richards, H.G. and Thurber, D.L., Pleistocene age determination from California and Oregon, Science **152** 1091 (1966).

(30) Veeh, H.H., ^{230}Th/^{238}U and ^{234}U/^{238}U ages of Pleistocene high sea level stand, J. Geophys. Res. **71** 3379 (1966).

(31) Fanale, F. and Shaeffer, O., The herium-uranium ratios for Pleistocene and Tertiary fossil aragonites, Science **149** 312 (1965).

(32) Shaeffer, O.A. and Davis, R., ^{36}Cl in nature, New York Acad. Sci. Ann. **62** 105 (1955).

(33) Rightmire, R.A., Kohman, T.P. and Hinterberger, H., Über die Halt-wertzeit des langlebigen ^{26}Al, Z. Naturforschung **13a** 847 (1958).

(34) Merrill, J.R., Lyden, E.F.X., Honda, M. and Arnold, J.R., The sedimentary geochemistry of the beryllium isotopes, Geochim. Cosmoshim. Acta **18** 108 (1960).

(35) Price. P.B. and Walker, R.M., Observation of fossil particle tracks in natural mica, Nature **196** 732 (1962).

(36) Sackett, W.M., Protactinium–231 content of ocean water and sediments, Science **132** 1761 (1960).

(37) Syromyatnikov, N.G., "Migratsiya isotopov urana, radia i toria i interpretatsiya radioaktivnikh anomaly", Izd. Akad. Nauk Kaz. SSR, (1961).

(38) Starik, I.E., "Osnovi Radiokhimii", Izd. Akad. Nauk SSSR, pp. 185–199 (1960).

(39) Chalov, P.I., Tuzova, T.V. and Musin, Ya, A., The isotopic ratio ^{234}U/^{238}U in natural waters and use of it in nuclear geochronology, Geokhimiya (1965) 405.

(40) Schlanger, S.O. and Konishi, K., Contrasting bryozan content of Pleio-Pleistocene to Present day carbonates from Guam, Mariana Islands, and Kikai-jima, Ryukyu Islands, and its regional implications, Proc, 11 th Pacific Sci. Congr., Tokyo 435 (1966).

(41) Komura, K. and Sakanoue, M., Consecutive anion exchange separation of radium, thorium, protactinium and uranium from an iron carrier, Japan Analyst **16** 114 (1967).

(42) Sakanoue, M. and Onishi, K., Consecutive determination of ^{234}U/^{238}U ratio, ^{231}Pa and ^{230}Th(^{228,232}Th) in natural samples, Abstract of papers, The 17th Annual Meeting of Chem. Soc. Japan 2E06, 106 (1964).

(43) Goldberg, E.D. and Koide, M., Geochronological studies of deep sea sediment by ionium/thorium method, Geochim. Cosmochim. Acta **26** 417 (1962).

(44) Abe, M., The separation and the determination of some nuclides produced by neutron irradiation of uranium and thorium and their application to activation analysis and neutron dosimetry, M.S thesis, Kanazawa Univ. (1967).

(45) Sakanoue, M., Osawa, M., Sakai, T. and Ishida, K., Radiochemical studies on the separation and determination of protactinium, J. At. Energy Soc. Japan **6** 503 (1964).

(46) Sakanoue, M., Takagi, T. and Maeda, M., Studies of the adsorption and electrodeposition of protactinium, Radiochimica Acta 5 607 (1966).

(47) Hashimoto, T. and Sakanoue, M., Basic studies on the production of enriched uranium-237 and the measurement of its specific activity, Sci. Rept. Kanazawa Univ. 11 49 (1966).

(48) Doke, T., A new method for the reduction of alpha-ray background in a gridded ionization chamber, Can. J. Phys. 40 607 (1962).

(49) Lahoud, J.A., Miller, D.S. and Friedman, G.M., Relationship between depositional environment and uranium concentration of molluscan shells, J. Sed. Petrol. 36 541 (1966).

(50) Sakanoue, M., Konishi, K. and Komura, K., Stepwise determination of thorium, protactinium and uranium isotopes and their application for geochronological studies, IAEA symposium on Radioactive Dating and Methods of Low-level Counting at Monaco, SM 87/28 (1967).

(51) Blanchard, L., Relationship between uranium and radium in coastal marine shells and their environment, J. Geophys. Res. 70 2911 (1965).

(52) Lowenstam, H.A., "Sr/Ca ratio of skeletal aragonites from the recent marine biota at palau and from fossil Gastropods", Isotopic and Cosmic Chemistry (Craig, H., Miller, S.L. and Wasserburg, G.J.), North Holland Pub, Co., Amsterdam, 114 (1964).

(53) Moore, W.S. and Sackett, W.M., Uranium and thorium series inequilibrium in sea water, J. Geophys. Res. 69 5401 (1964).

(54) Kuznetsov, Yu. V., Simonyak, Z.N., Eleizarova, A.N. and Lisitsin, A.P., Content of protactinium and thorium isotopes in ocean water, Radiokhimiya 8 455 (1966).

(55) Mii, H. and Kigoshi, K., Radiocarbon dating of the ancient beach and coastal dune deposits, Kikai Island, Amami. ^{14}C age of Quaternary deposits in Japan XXXVIII, Earth Sci. 82 43 (1966).

(56) Blanchard, R.L., ^{234}U/^{238}U ratio in coastal marine waters and calcium carbonates, J. Geophys. Res. 70 4055 (1965).

(57) Koide, M, and Goldberg, E.D., "Uranium-234/uranium-238 ratios in sea water", Progress in Oceanography vol. 3 (Sears, M.), Pergamon, London, 173 (1965).

(58) Umemoto, S., ^{234}U/^{238}U in sea water from Kuroshio region, J. Geophys. Res. 70 5326 (1965).

(59) Miyake, Y., Sugimura, Y. and Uchida, T., Ratio ^{234}U/^{238}U and the uranium concentration in sea water in the western north Pacific, J. Geophys. Res. 71 3083 (1966).

(60) Sakanoue, M. and Komura, K., The preparation of carrier-free U-232 and the estimation of various nuclides produced by the neutron irradiation of Pa-231, J. Nucl. Sci. Technol. 3 249 (1966).

(61) Thurber, D.L. and Broecker, W.S., An evaluation of absolute ages for the elevated marine terraces of the Palos Verdes hills area based on uranium series inequilibrium in mollusks, Nucl. Sci. Abstract 19 2777 (1965).

(62) Brouwer, J. and van Woerkom, A.J.J., Climatic change, Harvard Univ. Press, 318 (1958).

(63) Emiliani, C., Pleistocene temperatures, J. Geol. 63 538 (1955).

(64) Erickson, D.B., Ewing, M. and Wollin, G., The Pleistocene epoch in deep sea sediments, Science 146 723 (1964).