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The Uranium Content and the Activity Ratio $^{234}U/^{238}U$ in Marine Organisms and Sea Water in the Western North Pacific*

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Abstract: The uranium content and activity ratio $A^{234}U/A^{238}U$ were determined in open ocean water, marine plankton, marine algae and sea water in the environment in which plankton and algae live. The average uranium content of $3.34 \pm 0.28 \times 10^{-6}$ g/l and the average activity ratio of 1.13 ± 0.04 were obtained in open ocean water. The uranium contents in plankton and algae were respectively from 1.7 to 7.8×10^{-7} g/g and 0.4 to 23.5×10^{-7} g/g on dry basis with the respective concentration factors of 48 to 260 and 10 to 733. The activity ratio in plankton and algae ranged from 1.07 to 1.18 which coincided well with those in the environmental sea water.

1. Introduction

Concerning the uranium content in sea water in the western North Pacific, NAKANISHI (1951) reported the average values of 1.86×10^{-6} g/l and 2.87×10^{-6} g/l in the Kuroshio region at the surface and depth below 500 m respectively. MIYAKE and SUGIMURA (1964) gave the average of 3.4×10^{-6} g/l in the Kuroshio and mixing area of Kuroshio and Oyashio. They found that there are considerable variations of about 25% in uranium concentration in water with location and depth. Later, MIYAKE, SUGIMURA and UCHIDA (1966) gave the same average content of uraninm and reconfirmed the variation in uranium content in sea water as in the previous study.

They suggested that the variation in the content of uranium in sea water might be related to biological activities in the marine hydrosphere. In this respect, it is interesting to note that KOCZY, TOMIC and HECHT (1957) reported that the lower uranium content in the upper layer in the Baltic Sea might be attributed to the sorption of uranium to organic debris during their settling to the sea bottom. On the other hand, the remarkable enrichment in marine biota of some metallic elements existing in minute quantity in sea water has been reported. Therefore, it may be possible that the content of uranium in sea water is affected by the presence of organic matter.

With respect to the activity ratio of $^{234}U/^{238}U$ in sea water, the anomaly from the radioactive equilibrium of about 10 to 20 per cent was reported by several researchers (THURBER, 1964; KOIDE and GOLDBERG, 1965; BLANCHARD, 1965; UMEMOTO, 1965; MIYAKE, SUGIMURA and UCHIDA, 1966; VEEH, 1968).

The average ratio of 1.09 ± 0.05 with small fluctuations with location and depth was reported in the western North Pacific by MIYAKE, SUGIMURA and UCHIDA (1966).

Up to now, the results of several studies have beeh reported on the uranium content in calcareous marine organisms and fish-meat, but no available data can be found on the content of uranium and its isotopic abundance in marine plankton and algae.

The present report will give the results of study on the concentration and isotopic ratio of uranium in sea water, marine plankton and marine algae in the western North Pacific and on the coast of Japan.

2. Samples and analytical methods

Samples of open ocean waters in the western North Pacific were obtained during the eleventh cruise of the Japanese Expedition to the Deep Sea (JEDS-XI, May to June, 1967) on board the research vessel M. S, Ryofu-maru II (1,599

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ton) along the longitudinal section of 151°E. Locations of water sampling are shown in Fig. 1.

Nine samples of marine plankton were collected in the area of the western North Pacific off Japan. Immediately after the collection of samples, the neutralized formaline solution was added to prevent decomposition. Location of plankton sampling are also shown in Fig. 1. Taxonomical descriptions on plankton samples are given in Table 1. Twelve samples of non-planktonic algae were collected on the coast of the Sagami Bay and the Tokyo Bay. Samples were packed in polyethylene bags and stored in a refrigerator. To study relationships between the uranium content and the isotopic ratio in marine organisms and sea water, the samples of environmental sea water were collected. The method of analysis of uranium in sea water is the same as described by MIYAKE, SUGIMURA and UCHIDA (1966).

Fig. 1. Map of western North Pacific near Japan, showing locations of sampling sites.

The plankton sample was subjected to centrifugation and residual water remaining in the sample was removed as possible by pressing with filter paper. The sample was dried in an air bath at 110°C followed by ashing in an electric oven at 500°C to 550°C in the oxygen atmosphere. The algal sample washed with sea water *in situ* was dried in an air bath at 110°C followed by ashing in a nickel crusible. The ashed sample was digested with hot concentrated hydrochloric acid and nitric acid successively, and the residue was treated with a mixed solution of hydrofluoric acid and nitric acid. The solutions were combined and a known amount of ^{232}U (an α-emitter of 5.3 MeV) was added as a tracer for determining the yield of the chemical separation. The solution was dried up and the residue was dissolved in 100 m*l* of 10 M hydrochloric acid followed by an anion exchange separation. Uranium adsorbed on the resin (Dowex 1×8 of Cl form, 50 to 100 mesh)

Table 1. Taxonomy of marine plankton.

Sample designation	Location N	Location E	Taxonomy
Diatom I	33°20′	136°32′	diatoms(卅), dinoflagellates(tr), chaetognaths(tr), copepods(tr), radiolarians(tr)
Diatom II	Maizuru Bay		diatoms(only); *Skeletonema costatum*(卅), *Chaetoceros affinis*(卅), *Coscinodiscus lineatus*(tr)
Diatom III	35°03′	139°24′	diatoms(only); *Nitzschia seriata, Skeletonema costatum, Chaetoceros affinis, Ch. distans*
Copepoda	40°–42°	142°–145°	copepods(卅)
Euphausiacea	33°09′	139°43′	euphausids(卅), amphipods(+), larvae of fish(+)
Thaliacea	32°32′	137°32′	thalids(卅, *Doliolum denticultum*), copepods(+), radiolarians(tr), chaetognaths(tr)
Composite I	35°56′	135°20′	diatoms(卅, *Rhizosolenia styliformis* variations), euphausids(卄)
Composite II	33°28′	139°19′	copepods(卅), diatoms(卄), chaetognaths(+)
Composite III	33°55′	137°37′	copepods and their eggs(卅), diatoms(卄). chaetognaths(+), radiolarians(+)

was eluted with 100 ml of 0.1 M hydrochloric acid. After extracting iron with isopropyl ether, the aqueous layer was dried up, and the residue was taken into 100 ml of a mixed solution of 6 M hydrochloric acid and methanol (1:4). Further purification of uranium was carried out by an anion exchange resin (Dowex 1×8 of Cl form, 50 to 100 mesh) in the medium of the mixed solution in the presence of 200 mg of ascorbic acid. Uranium was subsequently eluted with 100 ml of 1 M hydrochloric acid and the effluent was dried up with concentrated perchloric acid to decompose a trace of organic matter.

The residue containing ^{232}U of about 500 cpm was transferred into a counting disk with a small amount of hydroshloric acid, and the chemical yield was determined by the α-activity with a 2-pi gas flow counter. Then, the residue on the disk was dissolved into 49 ml of 0.1 M hydrochloric acid and 1 ml of 0.05 % aqueous solution of Arsenazo-III (2, 7-Bis (azo-2) phenyl arsono-1, 8-dihydroxy-naphthalene-3, 6-disulfonic acid disodium salt) was added to the solution. The absorption of light by the uranium complex compound was measured at the wave-length of 660 mμ in a 100 mm cell 30 minutes after the addition of the reagent. When samples contain only a few cpm of ^{232}U, the yield was determined by the α-ray spectrometry.

The recovery of uranium in the above procedure was 87.2±8.9 % with the range from 76.5 to 96.8 %.

As to the standard, the uraninite, which was produced in the Schwaltzwalder mine in U.S.A., was used in which the activity ratio of $^{234}U/^{238}U$ of 1.003±0.006 was obtained. An example of α-spectrum of uranium isotopes in a marine organisms is shown in Fig. 2.

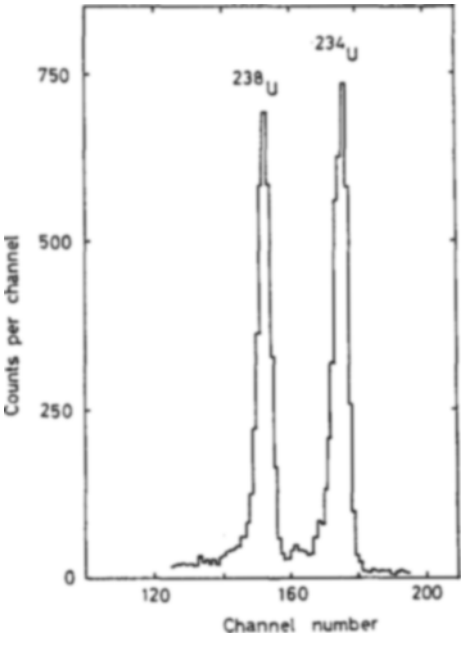

Fig. 2. α-spectrum of uranium isotopes in *Sargassum patens*. Counting period: 1385 minutes. $A^{234}U/A^{238}U$: 1.14±0.03.

3. Results and discussion

The results of analyses of uranium in open ocean water are summarized in Tables, 2, 3, and 4 and Figs. 3 and 4. Uranium content in surface water was uniform within the analytical errors, but in deep waters there was a considerable variation in the uranium content. The weighted average content of uranium in open ocean water was $3.34\pm0.28\times10^{-6}$ g/l ranging from 2.9 to 3.7×10^{-6} g/l. The mean value is in agreement with the previous values by MIYAKE and SUGIMURA (1964) and MIYAKE, SUGIMURA and UCHIDA (1966) in the western North Pacific,

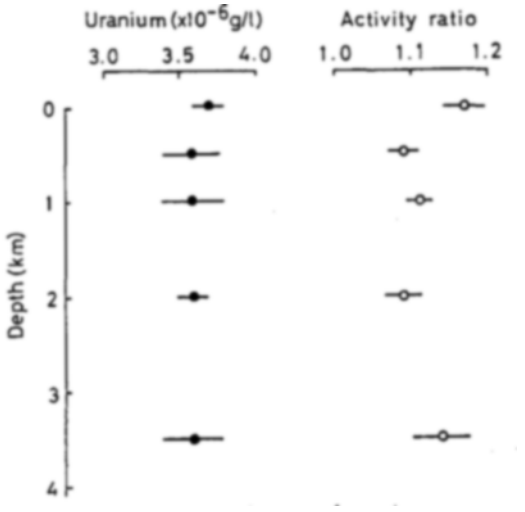

Fig. 3. Vertical distribution of uranium content and activity ratio of $A^{234}U/A^{238}U$ in the western North Pacific water. Location: JEDS-11, J-1, 32°32′N, 137°34′E. Depth: 4035 meters. Date of collection: May 19, 1967.

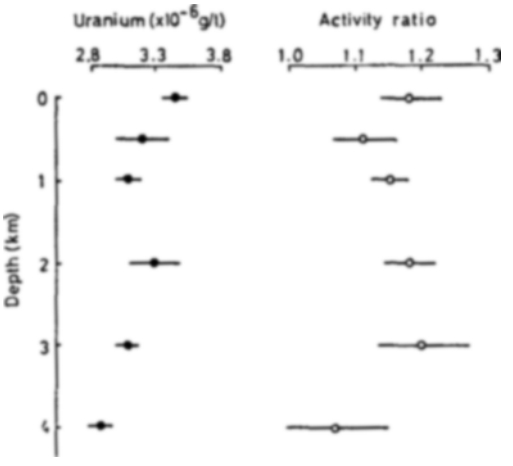

Fig. 4. Vertical diftribution of uranium content and activity ratio of $A^{234}U/A^{238}U$ in the western North Pacific water. Location: JEDS-11, J-3, 31°00'N, 136°26'E. Depth: 4280 meters. Date of collection: May 21, 1967.

and by RONA *et al.* (1956), WILSON *et al.* (1960) and THURBER (1964) in the Atlantic and the eastern North Pacific.

The weighted average activity ratio of $^{234}U/^{238}U$ in sea water was 1.13 ± 0.04 ranging from 1.07 to 1.20, which is slightly higher than that given by MIYAKE, SUGIMURA and UCHIDA (1966), while it is slightly lower than that by other researchers (THURBER, 1964; KOIDE and GOLDBERG, 1965; and UMEMOTO, 1965).

The results of analyses of uranium in marine organisms and the environmental sea water are shown in Tables 5 and 6.

The concentration of uranium in plankton ranged from 1.7 to 7.8×10^{-7} g/g on the dry basis. The average contents in phyto- and zooplankton were respectively $6.9\pm1.0\times10^{-7}$ g/g and $2.6\pm0.9\times10^{-7}$ g/g. In the composite samples

Table 2. Uranium content and activity ratio of $A^{234}U/A^{238}U$ in surface water in the western North Pacific.

Station	Location N	Location E	Water temp. °C	Salinity ‰	Uranium $\times10^{-6}$g/l	Activity ratio $A^{234}U/A^{238}U$
RY-3120	40°00′	150°58′	6.4	33.059	2.6±0.1*	1.12±0.02**
RY-3124	39°57′	151°02′	15.3	34.477	3.4±0.1	1.14±0.06
RY-3129	35°00′	151°02′	21.6	34.852	3.5±0.2	1.19±0.04
RY-3131	32°59′	151°06′	22.1	34.792	3.7±0.1	1.11±0.04
RY-3134	30°00′	150°56′	21.9	34.862	3.5±0.1	1.16±0.06
RY-3139	24°58′	151°00′	25.3	34.985	3.7±0.1	1.18±0.05
20-A	25°00′	148°45′	27.2	34.906	3.7±0.1	1.09±0.03
20-B	25°06′	148°44′	27.9	34.926	3.5±0.1	1.18±0.05
JEDS-XI, J-1	32°32′	137°34′	22.0	34.847	3.7±0.1	1.17±0.03
JEDS-XI, J-2	31°45′	136°57′	22.7	34.967	3.5±0.1	1.08±0.03
JEDS-XI, J-3	31°00′	136°26′	23.7	35.043	3.5±0.1	1.17±0.05
JEDS-XI, J-10	33°55′	137°37′	20.8	34.339	3.5±0.1	1.07±0.04
JEDS-XI, J-11	35°03′	139°24′	21.7	34.560	3.6±0.1	1.09±0.03

* Estimated range of analytical error
** Counting error

Table 3. Vertical distribution of uranium content and activity ratio of $A^{234}U/A^{238}U$ in the western North Pacific water.
Location: 32°32′N. 137°34′E (JEDS-XI, J-1)
Depth : 4035 m

Depth m	Water temp. °C	Salinity ‰	Uranium $\times10^{-6}$g/l	Activity ratio $A^{234}U/A^{238}U$
0	22.0	34.847	3.7±0.1*	1.17±0.03**
500	15.3	34.659	3.6±0.2	1.09±0.02
1000	4.6	34.282	3.6±0.2	1.11±0.02
2000	2.1	34.591	3.6±0.1	1.09±0.03
3500	(1.5)	(34.70)	3.6±0.2	1.14±0.04

* Estimated range of analytical error
** Counting error

Table 4. Vertical distribution of uranium content and activity ratio of $A^{234}U/A^{238}U$ in the western North Pacific water.
Location: 31°00'N, 136°26'E (JEDS-XI, J-3)
Depth : 4280 m

Depth m	Water temp. °C	Salinity ‰	Uranium $\times10^{-6}$ g/l	Activity ratio $A^{234}U/A^{238}U$
0	23.7	35.034	3.5±0.1*	1.18±0.05**
500	14.1	34.573	3.2±0.2	1.11±0.05
1000	4.7	34.301	3.1±0.1	1.15±0.03
2000	2.1	34.595	3.3±0.2	1.18±0.04
3000	1.6	34.671	3.1±0.1	1.20±0.07
4000	(1.6)	(34.60)	2.9±0.1	1.07±0.08

* Estimated range of analytical error
** Counting error

Table 5. Uranium content and activity ratio of $A^{234}U/A^{238}U$ in dried marine plankton and environmental sea water.

Sample	U in organisms		U in sea water		CF* (dry)
	$\times10^{-7}$ g/g	$A^{234}U/A^{238}U$	$\times10^{-6}$ g/l	$A^{234}U/A^{238}U$	
Phytoplankton					
Diatom I	—	1.11±0.05***	3.04±0.06**	1.08±0.03***	—
Diatom II	7.8 ±0.8**	1.15±0.05	3.02±0.06	1.16±0.04	260
Diatom III	5.92±0.11	1.18±0.03	3.55±0.08	1.09±0.03	167
Zooplankton					
Copepoda	—	1.18±0.04	2.88±0.06	1.19±0.03	—
Euphausiacea	1.7 ±0.2	1,10±0.10	3.52±0.07	1.16±0.03	48
Thaliacea	3.47±0.06	1.18±0.03	3.47±0.14	1.17±0.05	94
Composite					
Composite I	7.6 ±0.8	1.10±0.04	3.02±0.06	1.16±0.04	250
Composite II	5.4 ±0.6	1.14±0.06	3.40±0.07	1.13±0.03	160
Composite III	6.42±0.10	1.13±0.04	3.49±0.06	1.07±0.04	184

* Concentration factor
** Estimated range of analytical error
*** Counting error

of phyto- and zooplankton an average of 6.5± 0.9×10^{-7} g/g was obtained.

The contents of uranium in nonplanktonic algae showed a wide range of variation from 0.04×10^{-6} g/g, dry in *Gymnogongrus flabelliformis* to 2.35×10^{-6} g/g, dry in *Ishige okamurai*. There is a tendency that uranium is enriched more in some species of *Phaeophyceae* than *Phodophyceae* and *Chlorophyceae*. Within the same genus, for example among four species of *Sargassum*, two of *Gloiopeltis* and two of *Ishige*, a small difference in the uranium content was observed. The concentration factors on the dry basis of marine organisms ranged from 48 to 260 in plankton, and 10 to 733 in nonplanktonic algae.

In order to assess the effect of plankton on the concentration of uranium in sea water, e following calculation was done. In the first place, an uptake rate of uranium by plankton population was estimated under the following assumptions, *i.e.* the uranium content in phytoplankton is 7×10^{-7} g/g, dry, the uranium content in surface water is 3.5×10^{-6} g/l, the primary production rate is 80 gC/m²/y, and the carbon content in phytoplankton is 25 %. The result of calculation shows that 2.2×10^{-4} g/m²/y of uranium is taken up into the marine bioshere by the primary production. This corresponds to 0.06 % of the total content of uranium in the euphotic zone of 100 m thickness. This result shows that a change in uranium content in sea

Table 6. Uranium content and activity ratio of $A^{234}U/A^{238}U$ in dried marine algae and environmental sea water.

Sample	U in organisms		U in sea water		CF* (dry)
	$\times 10^{-7}$ g/g	$A^{234}U/A^{238}U$	$\times 10^{-6}$ g/l	$A^{234}U/A^{238}U$	
Chlorophyceae					
Ulva conglobata	2.3 ±0.2**	1.09±0.03***	2.86±0.06**	1.08±0.04***	79
Phodophyceae					
Porphyra tenera	1.6 ±0.2	1.10±0.07	2.39±0.05	1.12±0.07	67
Gloiopeltis furcata	1.8 ±0.2		3.21±0.06	1.12±0.03	56
G. complanata	1.9 ±0.2	1.07±0.06	3.21±0.06	1.12±0.03	59
Phaeophyceae					
Hizikia fusiforme	7.0 ±0.7	1.10±0.04	2.86±0.06	1.08±0.04	240
Ishige okamurai	23.5 ±2.4	1.14±0.02	3.21±0.06	1.12±0.03	733
I. foliacea	17 ±2	1.08±0.03	3.21±0.06	1.12±0.03	530
Sargassum patens	3.92±0.07	1.14±0.03	3.21±0.06	1.12±0.03	122
S. ringgoldianum	3.57±0.05	1.15±0.05	3.21±0.06	1.12±0.03	111
S. fulvellum	2.3 ±0.2	1.10±0.05	3.21±0.06	1.12±0.03	72
S. horneri	5.5 ±0.6	1.17±0.03	3.21±0.06	1.12±0.03	170
Gymnogongrus flabelliformis	0.4 ±0.1	—	3.21±0.06	1.12±0.03	10

* Concentration factor ** Estimated range of analytical error *** Counting error

water due to the fluctuation of the uptake rate by living organisms from year to year or place to place may be small.

In the second place, the uranium content in the organic substances dissolved in sea water is considered.

In order to assess the effect of organic substances on the content of uranium in sea water, a following equation is considered.

$$r=f\frac{A_b}{A_w}$$

where r is the ratio of the amount of uranium respectively in the organic and inorganic forms. f is a concentration factor of uranium in organic substances, A_b and A_w are the amounts of organic substances and sea water in the euphotic zone respectively. It is assumed that the total amount of organic substances in the ocean is about 8 kg/m^2 on an average, in which 3 kg/m^2 is present in the euphotic zone of 100 m thickness. By taking the concentration factor (on dry basis) of uranium of about 200 in phytoplankton and also assuming that uranium content in the organic substances is approximately the same as in photoplankton, r can be estimated as follows.

$$r=200\times 3/10^5=6\times 10^{-3} \text{ or } 0.6\,\%$$

As well known, there is a wide fluctuation in the content of the organic substances according to seasons and locations, with a factor of up to about 5. Therefore, it may be possible to consider that there will be a variation in uranium content in sea water up to a few per cent due to the biological effect.

With respect to the isotopic ratios of uransum in marine plankton, the average value of $A^{234}U/A^{238}U$ of 1.14±0.03 was obtained with a range from 1.10 to 1.18. The observed ratios in plankton are in good agreement with those in the environmental sea water within an error in measurement except for one diatom sample. The sample collected at the Sagami Bay which consisted mostly of *Chaetoceros*, seemed to enrich the lighter isotope of uranium (1.18±0.03) in ralative to *in situ* sea water (1.09±0.03). The activity ratios in nonplanktonic algae ranged from 1.07 to 1.17 with the average value of 1.11±0.03. No significant difference on the ratio was observed between algae and sea water. These results show that there is little biological fractination of uranium isotopes by marine biota.

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北太平洋西部海域の海産生物および海水中のウラン含量とウラン同位体 $^{234}U/^{238}U$ 比について

三宅泰雄　杉村行勇　前田　勝

要旨　北太平洋西部海域の外洋水，海洋プランクトン，海藻およびプランクトンや海藻採取海域の海水中のウラン含量と，ウラン同位体比 ($^{234}U/^{238}U$) を測定した．海水の平均ウラン含量は，3.34×10^{-6} g/l で，平均同位体比は，1.13 である．プランクトンと海藻のウラン含量は，それぞれ $1.7\text{-}7.8\times10^{-7}$ g/g と $0.4\text{-}23.5\times10^{-7}$ g/g であり，ウランの濃縮係数は，それぞれ，48-260 と 10 から 733 になる．ウラン含量は，褐藻類に高く，最も高い含量を示すのは，いしげである．海藻やプランクトンの $^{234}U/^{238}U$ 比は，1.07 から，1.18 で，この値は，試料採取地域の海水の $^{234}U/^{238}U$ 比と一致している．