Abstract

The content of uranium was determined for sea water samples collected on board M. S. SOYA on her cruises from Japan to Antarctica during the fifth and sixth Japanese Antarctic Research Expeditions (1960-61, 1961-62) and in the Drake Passage on board S. S. CAPITAN CANEPA of the Argentine Navy Hydrographic Service during the TRIDENTE-3 cruise (Feb.-Mar., 1963).

Uranium was analyzed by the fluorometric method using transmission type fluorometer after separation by solvent extraction and fusion with sodium fluoride.

The analytical results showed that the uranium content in surface water respectively ranged from 2.7 to 3.2×10^{-6} g/l in the Indian Ocean Basin of the Antaratic, Ocean, 2.7 to 3.5×10^{-6} g/l in the Drake Passage, 2.5 to 3.5×10^{-6} g/l in the Indian Ocean and 2.5 to 3.3×10^{-6} g/l in the South China Sea. Judging from the mean value of 0.5×10^{-13} g/l for radium in the Indian Ocean (PETTERSSON[1], 1955; KOCZY and SZABO[2], 1962) the ratio of radium to uranium may be 4 to 6 per cent of the secular equilibrium amount.

Introduction

A number of investigators have studied the content and the interrelationship of radioelements in ocean waters and bottom sediments (JOLY[3], 1908; PETTERSSON[4], 1937; FØYN and others[5], 1939; PIGGOT and URRY[6], 1939; RONA and URRY[7], 1952; HOLLAND and KULP[8], 1954; GOLDBERG and KOIDE[9]; 1962; MIYAKE and SUGIMURA[10], 1963).

However, little is known on radioactive elements in sea waters near Antarctica.

As to the uranium content in the oceanic waters, RONA et al[11] (1956) and WILSON et al[12] (1960) gave an average value of 3.3×10^{-6} g/l for the eastern North Pacific and the North Atlantic. NAKANISHI[13] (1952) reported the average value of 2.8×10^{-6} g/l in the region of the Kuroshio Current, and MIYAKE and SUGIMURA[10] (1963) gave an average value of 3.4×10^{-6} g/l of uranium for Kuroshio and adjacent waters off Japan. In the Indian and the Southern Oceans, BARANOV and KHRISTIANOVA[14] (1959) reported a rather lower average value, 2.3×10^{-6} g/l, in waters collected during the cruise of the Second Russian Complex Antarctic Expedition (Feb.-Mar., 1956). It is of interest to examine whether or not the content of uranium in the Indian and the Southern Ocean waters is lower than those in other ocean waters.

The present authors intend to report on the content of uranium in sea waters which were collected in the Indian Ocean, Indian Ocean Basin of the Antarctic Ocean, the Drake Passage and also in the South China Sea.

The result of determination will be given below with a brief discussion from the viewpoints of radioactive equilibrium and geochemistry.

1. Collection of samples

Water samples were collected on board the M. S. SOYA (3,500 tons) on her cruises from Tokyo to the Syowa Base, Antarctica, during the fifth and sixth Japanese Antarctic Research Expeditions (JARE-5, Dec. 1960-Apr. 1961; JARE-6, Nov. 1961-Apr. 1962). Other water samples were collected aboard the S. S. CAPITAN CANEPA (700 tons) of the Argentine Navy Hydrographic Service in the Drake Passage along the transection from Tierra del Fuego to the South Shetland

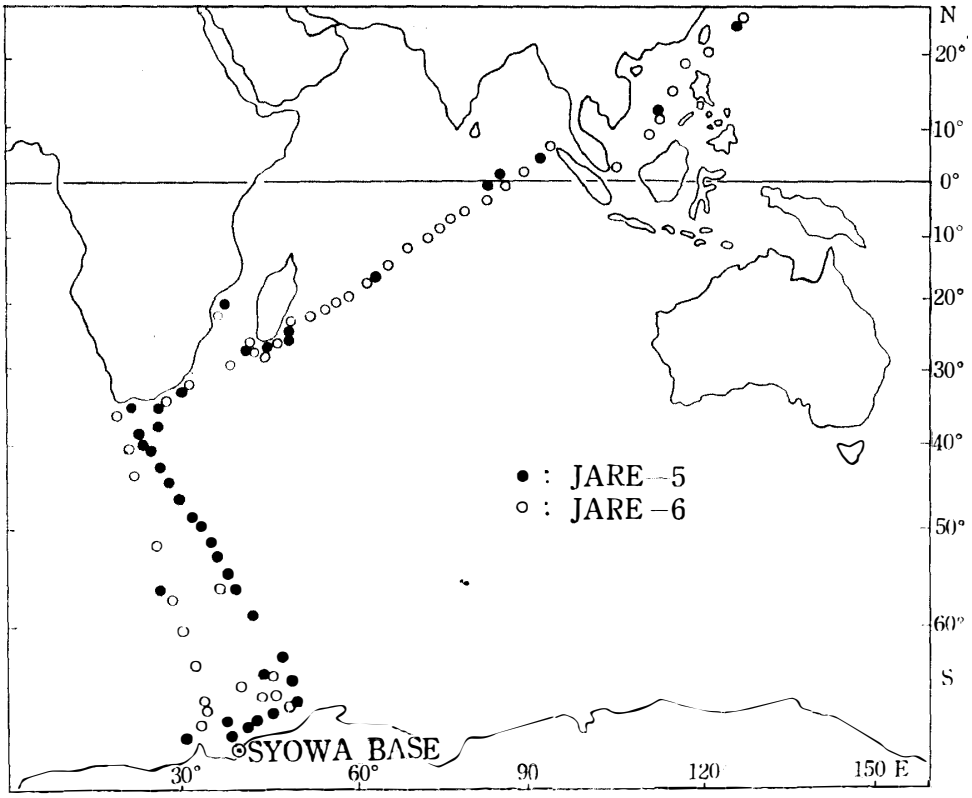

Fig. 1. Location of water samples during the cruise of JARE–5 and JARE–6.

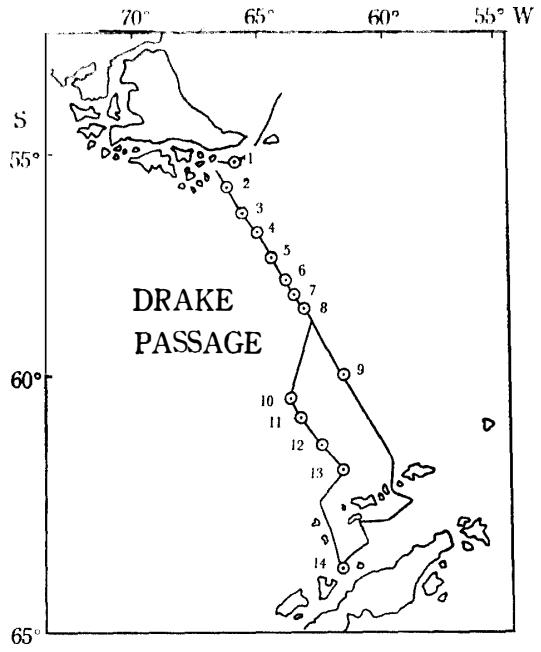

Fig. 2. Location of water samples in the Drake Passage.

Islands of Antarctica during the TRIDENTE-3 cruise (Feb.-Mar., 1963).

The samples were collected either with Nansen bottles or by direct syphoning through polyvinyl tubing. Phytoplanktons and other suspended matters were filtered off by a Millipore filter (HA type) or by a fine glass filter. After the addition of nitric acid samples were stored in glass bottles. Bottles were rinsed with dilute hydrocholric acid, distilled water and then sea water prior to filling. No significant difference in the uranium content was found between filtered and unfiltered samples when they were acidified after sampled. Locations of sampling sites are shown in Figs. 1 and 2.

2. Method of analysis

The microquantities of uranium present in samples were determined fluorometrically by using a fused mixture with sodium fluoride.

To each sample, 200-500 m*l*, was added 10 m*l* of a mixture in a ratio 3 : 2 : 5 of concentrated nitric acid, aluminum nitrate solution (950 mg Al $(NO_3)_3$/m*l*) and ammonium hydrogen phosphate solution (12 mg $(NH_4)_3$ HPO_4/m*l*). After boiled for ten minutes to decompose carbonate anionic complex of uranium, aluminum phosphate was precipitated at pH 6 by adding ammonium hydroxide. Uranium was coprecipitated with the hydroxide precipitate.

The precipitate containing uranium was separated by filtration and ignited in a porcelain crucible at 450°C-500°C in an electric oven. The residue was dissolved in 10 m*l* solution of HNO_3-acidified aluminum nitrate (a solution containing 900 g of Al $(NO_3)_3 \cdot 9H_2O$ in 500 m*l* of 1 : 10 HNO_3) playing the role of solvent and salting-out agent. The solution was transferred into a test tube with a glass stopper.

Uranium was extracted with 10 m*l* of ethylacetate. The ethylacetate solution was made pass through a dried filter paper. A 2 m*l* portion of the ethylacetate solution was ignited and evaporated in a platinum dish (1.5″ diameter) containing 1 m*l* of distilled water to avoid creaping of ethylacetate during the evaporation. To the residue in the platinum dish, 2 g of flux (fused and pluverized mixture of K_2CO_3, Na_2CO_3 and NaF of a ratio 45.5 : 45.5 : 9 by weight) was added and fused for 20 minutes at 650°C in an electric oven (a specially designed double-rotating type electric oven).

The cake obtained from rapid cooling of the fused material was stored in a desiccator. The intensity of fluorescence due to the uranium contained in sodium fluoride under the irradiation of ultraviolet lamp was measured at the wave length of 555 mμ with a transmission-type fluorometer (AOYAMA[15], 1961).

The uranium content in the reagents used for the determination was checked. The result showed that the total blank was below 0.01 ppm.

3. Results and discussion

The results of analyses of the uranium in surface ocean waters are given in Tables 1-3. The vertical profiles are shown in Table 4.

Table 1. Uranium in surface water of the Antarctic Ocean.

A. Samples from JARE-5.

Date of collection	Location S	Location E	Temp. (°C)	Chlorinity (‰)	Uranium ($\times 10^{-6}$ g/l)
Jan. 2, 1961	50°16.5′	32°57′	—	18.72	2.9
3	51°53′	34°36′	2.0	18.81	3.0
3	53°35.5′	36°16.5′	1.7	18.76	2.8
4	55°22′	38°01.5′	1.4	18.79	3.1
4	57°11′	39°52′	0.2	18.71	2.9
5	59°01′	41°50.5′	0.0	18.64	3.1
5	63°53′	43°52′	0.2	18.63	2.7
6	62°43.5	45°57.5′	−0.3	18.72	3.0
6	64°33.5′	48°00′	−0.2	18.85	2.8
7	66°19.5′	49°14.5′	−1.4	18.31	2.9
8	66°47.5	44°55′	−1.5	18.66	2.8
8	67°42.5′	40°54′	−1.0	18.45	2.8
15	67°05′	40°29′	0.2	18.53	3.0
16	67°16′	37°13′	−0.2	18.62	3.1
Feb. 27	68°13′	38°44′	−1.4	18.48	2.8
Mar. 3	68°32′	30°10′	−0.2	18.93	3.0
7	57°03.5′	26°08.5′	1.7	18.82	3.0

B. Samples from JARE-6.

Date of collection	Location S	Location E	Temp. (°C)	Chlorinity (‰)	Uranium ($\times 10^{-6}$ g/l)
Dec. 21, 1961	57°39′	37°02′	0.8	18.86	2.9
23	64°32′	44°38′	−1.5	18.77	3.0
29	65°00′	40°19.5′	−0.2	18.82	3.0
30	65°43′	42°53.5′	−1.0	18.76	3.0
Jan. 3, 1962	65°26′	46°00′	−1.6	18.69	3.1
4	65°48.8′	49°02.8′	−1.2	18.77	3.0
Feb. 15	67°33′	33°35′	−1.6	18.85	3.0
16	65°58′	33°33′	−0.2	18.98	2.9
16	66°17.5′	33°30.5′	−0.7	18.89	3.2
17	63°33′	31°50′	1.0	18.64	3.0
18	60°27′	30°23′	1.0	18.66	2.8
19	57°59′	29°05.5′	2.2	18.77	3.3
21	52°21′	25°27′	2.0	18.85	3.0

C. Samples from the Drake Passage.

Station	Location S	Location W	Temp. (°C)	Chlorinity (‰)	Uranium ($\times 10^{-6}$ g/l)
1	55°06′	66°07′	8.9	18.03	2.8
2	55°50′	66°05′	6.5	18.85	3.3
3	56°30′	65°33′	5.4	18.90	3.3
4	55°52′	65°01′	5.9	18.86	2.7
5	57°27′	64°19′	5.0	18.90	3.0
6	58°00′	63°50′	4.0	18.84	3.0
7	58°25′	63°20′	3.5	18.79	3.2
8	58°28′	63°10′	2.2	18.83	3.0
9	60°00′	61°25′	1.2	18.75	3.0
10	60°32′	63°34′	2.0	18.80	3.2
11	60°56′	63°08′	1.8	18.76	3.1
12	61°28′	62°20′	1.2	18.77	3.5
13	61°58′	61°30′	1.1	18.70	3.1
14	64°00′	61°41′	0.6	18.69	3.1

Table 2. Uranium in surface waters of the Indian Ocean.

A. Samples from JARE-5.

Date of collection		Location S	Location E	Temp. (°C)	Chlorinity (‰)	Uranium ($\times 10^{-6}$ g/l)
Dec.	3, 1960	03°57′(N)	92°09′	29.0	19.04	3.0
	5	01°01′(N)	85°23′	28.1	19.45	2.9
	15	24°39′	48°40′	24.4	19.48	3.1
	16	26°34′	44°28′	26.3	19.49	3.1
	29	35°53′	19°24′	20.5	19.67	3.2
	29	37°18′	20°28′	20.0	19.63	2.9
	30	38°54.5′	21°44′	19.0	19.55	3.2
	30	40°26.5′	23°00.5′	16.0	19.59	2.9
	31	42°07′	24°27.5′	14.7	19.50	3.3
	31	43°46′	26°00.5′	9.4	19.21	2.9
Jan.	1, 1961	45°26′	27°48′	6.7	18.81	3.0
	1	47°07.5′	29°35′	—	18.79	2.9
	2	48°43.5′	31°17′	—	18.73	2.9
Mar.	21	34°48′	21°33′	—	19.61	3.1
	22	33°56′	26°18′	—	19.56	3.3
	23	32°51′	29°42′	24.4	19.61	3.3
	26	27°53.5′	41°35′	26.8	19.61	3.1
	28	25°16′	47°52′	28.9	19.59	3.1
Apr.	4	16°00′	63°15′	28.0	19.17	3.0
	10	01°51′	83°37′	29.0	19.20	3.1

B. Samples from JARE-6.

Date of collection	Location S	Location E	Temp. (°C)	Chlorinity (‰)	Uranium ($\times 10^{-6}$ g/l)
Nov. 24, 1961	07°44′	75°42′	27.6	19.12	2.9
29	20°34′	57°56′	25.6	19.48	3.0
Dec. 3	27°51′	41°50′	23.8	19.71	3.3
7	35°01′	22°35′	20.1	19.62	3.0
Feb. 23, 1962	44°46′	22°38′	11.0	19.14	2.9
24	41°27′	21°07′	15.0	19.41	3.3
25	37°04′	19°31′	21.0	19.58	3.2
Mar. 8	33°51′	26°40′	23.7	19.47	3.2
9	32°33′	30°12′	23.7	19.61	3.1
11	29°36′	38°04′	26.0	19.72	3.1
12	27°13′	42°05′	27.0	19.66	3.2
13	26°06′	45°42′	27.0	19.45	3.4
14	24°38′	48°44′	27.5	19.38	3.1
15	22°54′	52°22′	27.8	19.34	3.0
16	21°25′	56°19′	27.8	19.46	3.0
17	19°23′	59°39′	28.0	19.20	3.5
18	17°03′	62°51′	28.3	19.18	3.0
19	14°37′	66°14′	29.0	18.89	2.5
20	12°20′	69°55′	29.0	19.02	3.1
21	10°01′	73°01′	29.2	18.94	2.9
22	07°31′	76°19′	29.0	18.95	3.1
23	05°24′	79°27′	29.0	18.94	3.2
24	02°55′	82°54′	29.0	18.90	3.0
25	00°21′	86°24′	29.1	18.92	2.8
26	02°07′(N)	89°49′	29.3	18.94	3.1

Table 3. Uranium in surface waters of the South China Sea.

Date of collection	Location N	Location E	Temp. (°C)	Chlorinity (‰)	Uranium ($\times 10^{-6}$ g/l)
Nov. 16, 1960	24°36′	126°32′	26.6	19.17	3.1
20	12°46′	113°52′	—	18.09	3.0
Nov. 6, 1961	16°32′	117°58′	27.6	18.59	2.9
10	03°29′	105°40′	28.0	18.36	2.7
19	05°04′	93°31′	28.2	17.85	2.8
Apr. 7, 1962	09°31′	111°04′	27.0	18.69	3.0
8	11°39′	113°45′	27.9	18.70	2.9
9	15°45′	116°50′	28.0	18.83	2.5
10	18°38′	119°32′	26.5	18.93	3.2
11	21°17′	121°56′	25.8	19.05	3.3
13	26°43′	128°36′	22.0	19.23	3.3

Table 4. Vertical distribution of uranium in the Southern Ocean.

A. Sampling site: 68°13′ S, 38°44′ E (Feb. 27, 1961).

Depth (m)	Temp. (°C)	Chlorinity (‰)	Uranium ($\times 10^{-6}$ g/l)
0	−1.4	18.48	2.8
500	1.08	19.18	2.9
1000	0.47	19.20	2.8
1500	0.11	19.20	3.1

B. Sampling site: 65°00′ S, 40°19.5′ E (Dec. 29, 1961).

Depth (m)	Temp. (°C)	Chlorinity (‰)	Uranium ($\times 10^{-6}$ g/l)
0	−0.3	18.82	3.0
10	−0.20	18.87	2.9
50	−1.03	18.88	3.0
100	−1.62	18.97	2.8
193	1.21	19.18	2.8
392	1.42	19.21	2.9
597	1.21	19.22	3.0
985	0.82	19.20	3.5
1498	0.47	19.19	3.3
1992	0.26	19.19	3.3
2489	0.07	19.20	3.2

C. Sampling site: 58°28′ S, 63°10′ W (Mar. 9, 1963).

Depth (m)	Temp. (°C)	Chlorinity (‰)	Uranium ($\times 10^{-6}$ g/l)
0	2.20	18.82	3.0
48	2.31	18.80	3.0
96	1.18	18.87	3.0
192	0.90	18.91	3.0
384	1.85	19.05	2.9
693	2.26	19.16	3.5
932	2.11	19.19	3.3
1420	1.79	19.24	3.5
1903	1.42	19.26	3.4

D. Sampling site : 60°00′ S, 61°25′ W (Mar. 10, 1963).

Depth (m)	Temp. (°C)	Chlorinity (‰)	Uranium ($\times 10^{-6}$ g/l)
0	1.20	18.75	3.0
180	0.72	18.95	3.1
360	1.95	19.14	3.0
770	1.99	19.15	3.2
1820	1.18	19.17	3.3

It can be seen in Table 1 that the uranium in sea waters collected in the sea areas where the westerly wind drift current prevails have a range of 2.7 to 3.5×10^{-6} g/l, averaging 3.0×10^{-6} and 3.1×10^{-6} g/l respectively for Cape Town to Antarctica and for the Drake Passage. Uranium in the South China Sea ranged from 2.5 to 3.3×10^{-6} g/l, averaging 3.0×10^{-6} g/l.

Concerning the Indian Ocean waters, it is well known that the current system changes periodically from season to season. Therefore, rather uniform distribution of uranium can be expected due to mixing of waters in both horizontal and vertical directions at least down to the depth of thermocline. Our result for uranium in the Indian Ocean waters gave a value 2.8 to 3.3×10^{-6} g/l (averaging 3.1×10^{-6} g/l). No significant difference in the uranium content could be determined from waters of other oceans.

BARANOV and KHRISTIANOVA[14] (1959) determined the uranium content in sea waters by the luminescence method developed by KUZNETSOV and AKINOVA[16] (1958) in which uranium was coprecipitated from sea waters with methyl violet. They gave values of uranium respectively 2.7×10^{-6} g/l in the areas from Cape Town to Antarctica, 2.0×10^{-6} g/l from the Antarctic to Bengal Bay, 2.7×10^{-6} g/l in the southwestern part of the Indian Ocean and 1.8×10^{-6} g/l in the southern, northern and central parts of the Indian Ocean. According to the recalculation by SUGIMURA[17] (1964) using data of BARANOV and KHRISTIANOVA[14], the overall average value of the uranium content in the Indian and the Southern Ocean waters is 2.3×10^{-6} g/l. This value is twenty or thirty per cent lower than our results. For example, near Bengal Bay, a few of our stations were located very closely to the Russian stations of 1956. But, as far as the uranium content is concerned, our values ranged from $2.8-3.2\times10^{-6}$ g/l, considerably higher than those of BARANOV et al (1.4 to 2.0×10^{-6} g/l). The disagreement may be attributable to the procedure of treatment of samples and the rate of recovery in the method used by BARANOV et al.

In the Oceanic waters, uranium may form a stable anionic carbonate complex and take the hexavalent oxidation state. However, during the storage of waters, deposition or adsorption of uranium may occur sometimes due to a change in the oxidation state.

As far as the present knowledge goes, it can be concluded that the content of uranium in the Indian Ocean waters is not different from other ocean waters.

In the Southern Ocean, vertical distribution of uranium was determined in the samples from two stations near Lützow-Holm Bay of Antarctica and from two stations in the Drake Passage.

At the station of 68°13′ S, 38°44′ E, the content of uranium is 2.8×10^{-6} g/l at the surface and 3.1×10^{-6} g/l at a depth of 1,500 m. Down to 1,000 m depth, the content of uranium showed little variation. On the other hand, at the station of 65°00′ S, 40°19.5′ E, a minimum uranium content was found at a depth of about 100 m and the content gradually increased downward from that depth. The highest content 3.5×10^{-6} g/l was observed at the 1,000 m depth.

At the stations in the Drake Passage (St. 8: 58°28′ S, 63°10′ W; St. 9: 60°00′ S, 61°25′ W), a minimum content was found at the depth of about 200 m increasing with depth.

It can be seen in Table 4 and Fig. 3 that the vertical distribution of uranium in the Southern Ocean waters is apparently correlated with the stratification of chlorinity. Generally speaking, the uranium content increased below the layer of higher chlorinity than 19.1–19.2. Below the depth of 500 m or 600 m, the content of uranium increased up to 3.5×10^{-6} g/l from the surface value of 2.8 to 3.0×10^{-6} g/l. A similar distribution was reported by G. KOCZY[18] (1950) from the Tropical and the South Pacific, and by MIYAKE and SUGIMURA[10] (1963) from

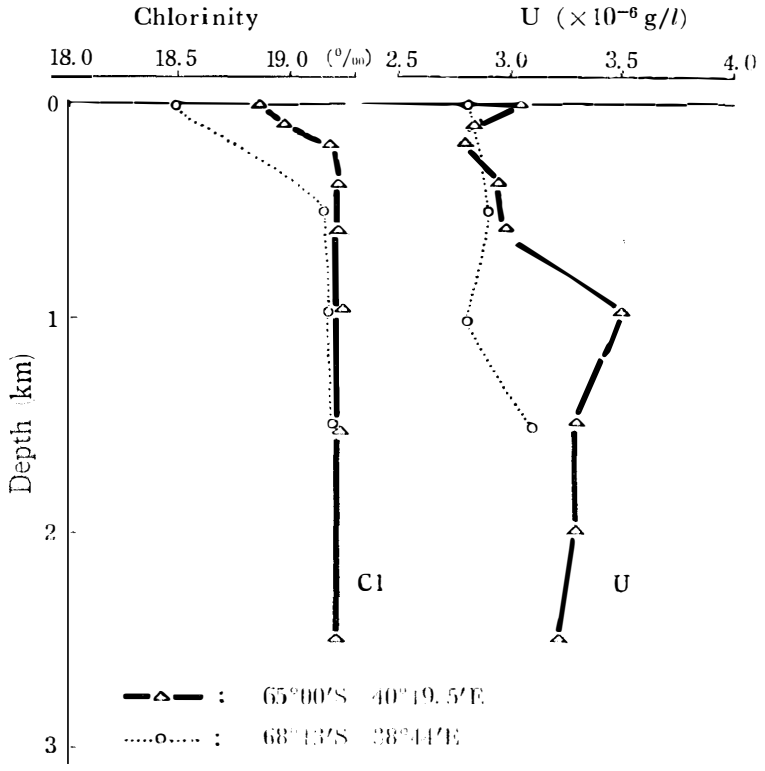

Fig. 3. Vertical distribution of uranium off Lützow-Holm Bay.

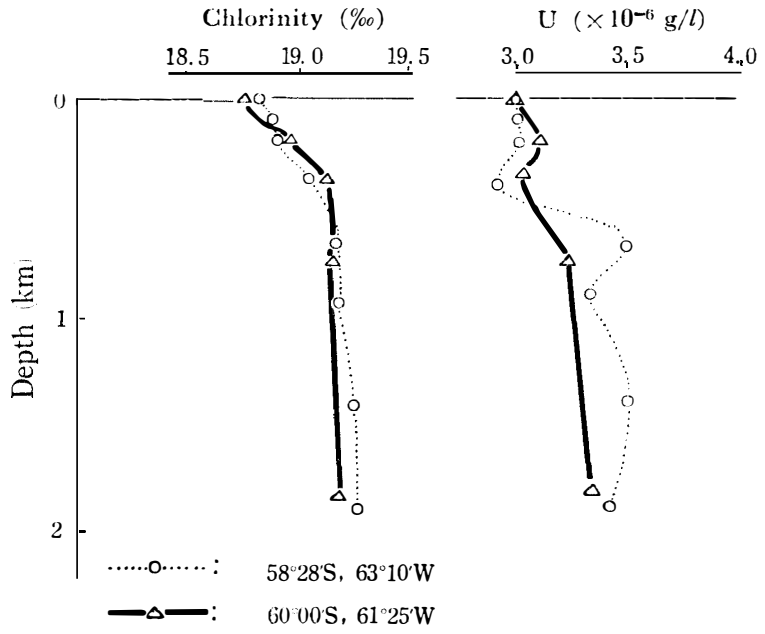

Fig. 4. Vertical distribution of uranium in the Drake Passage.

the western North Pacific.

Concerning the relationship between contents of uranium and radium, it is well known that in sea water uranium surpasses radium with respect to the radioactive equilibrium between two radioelements.

Judging from the value 0.5×10^{-13} g/*l* for radium in the Indian Ocean (PETTERSSON[1], 1955; KOCZY and SZABO[2]; 1962) and from the observed value of uranium 2.5 to 3.5×10^{-6} g/*l*, the radium content may be equivalent to only 4-6% of that in the secular equilibrium.

Acknowledgements

The authors express their deep appreciation to Professor Y. MIYAKE, Tokyo Kyoiku Daigaku (the Tokyo University of Education), for his helpful suggestions and encouragement, and are greatly indebted also to Dr. Y. SUGIMURA, Meteorological Research Institute, for his valuable criticism and suggestions. Only through the efforts of the scientific staff of the JARE-5, JARE-6 and TRIDENTE-3, especially those of Drs. H. MEGURO, K. WATANUKI, Y. SUGIMURA and S. FUKASE, was the sampling possible

References

1) Pettersson, H. (1955): Manganese nodules and oceanic radium. Papers Marine Biology and Oceanography (Suppl. Vol. 3, Deep Sea Res.), Pergamon Press, Lodon, 335–345.
2) Koczy, F. F. and B. Szabo (1962): Renewal time of bottom water in the Pacific and Indian Oceans. Jour. Oceanogr. Soc. Japan., 20th Ann., 590–599.
3) Joly, J. J. (1908): On the radium content of deep sea sediments. Phil. Mag., **16,** 190–197.
4) Pettersson, H. (1937): Das Verhältnis Thorium zu Uran in den Gesteinen und im Meer. Sitzber. Akad. Wiss. Wien, Math.-Naturw. Kl., **127,** 400a.
5) Føyn, E., B. Karlik, H. Pettersson and E. Rona (1939): The radio-activity of sea water. Göteborgs Kgl. Vetenskaps-Vitterhets samhäll Handl., Ser. B 6, No. 12, 44.
6) Piggot, C. S. and W. D. Urry (1939): The radium content of ocean bottom core. Jour. Wash. Acad. Sci., **29,** 405–415.
7) Rona, E. and W. D. Urry (1952): Radioactivity of ocean sediments-8. Amer. Jour. Sci,. **250,** 241–262.
8) Holland, H. D. and J. L. Kulp (1954): a) The mechanism of removal of ionium and radium from the oceans. Geochim. Cosmochim. Acta, **5,** 214–222.
   b) The transport and deposition of uranium ionium and radium in rivers, oceans and ocean sediments. ibid., **5,** 197–213.
9) Goldberg, E. D. and M. Koide (1962): Geochronological studies of deep sea sediments by the Io/Th method. Geochim. Cosmochim. Acta, **26,** 417–450.
10) Miyake, Y. and Y. Sugimura (1963): Uranium and radium in the western North Pacific waters. Trans. Amer. Geophys. Union, **44,** 59 (abstract), and also Koji Hidaka Sixtieth Years Anniversary Paper, Tokyo (in press).
11) Rona, E., L. O. Gilpatrick and L. M. Jeffrey (1956): Uranium determination in sea waters Trans. Amer. Geophys. Union, **37,** 697–701.
12) J. D. Wilson, R. K. Webster, G. W. C. Milner, G. A. Barnett and A. A. Smales (1961): Anal. Chim. Acta, **23,** 505.
13) Nakanishi, M. (1951): Fluorometric microdetermination of Uranium V. Bull. Chem. Soc. Jap., **24,** 36–38.
14) Baranov, V. I. and L. A. Khristianova (1959): Radioactivity of the waters of the Indian Ocean. Geochemistry, 765–769 (English translation).
15) Aoyama, Y. (1961): The microdetermination of uranium by transmission type fluorometer. Jour. Chem. Soc. Japan., **82,** 336–339 (in Japanese).
16) Kuznetsov, V. I. and T. G. Akinova (1958): Organic coprecipitate; Communication-8, Coprecipitation of uranium for its determination in sea waters. Zh. Anal. Khimi., 79–82.
17) Sugimura, Y. (1964): Natural radioelements in the ocean. (a review), Jour. Jap. Chem., **18,** 89–101.
18) Koczy, G. (1950): Weitere Uranbestimmungen und Meerwasserproben. Osterr. Akad. Wiss. Math.-naturw. Kl., Sitzber., Abt. IIa, **158,** 113–121.

(*Manuscript received Abril 15, 1964*)