Chemical Studies of the Western Pacific Ocean. VI. The Vertical Variation of Minor Constituents of the "Kurosio" Region. Part 2.

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Silicate. Silicon is assimilated by diatoms in the upper water layer in the ocean; therefore, its concentration in such layers is smaller and it increases gradually with depth. Thus in the Atlantic water, H. W. Harvey(1) gave 0.05–0.1 mg. Si per litre at the surface, 0.17 mg. at 1,000 m. and 0.50 mg. at 3,000 m. According to H. Wattenberg,(2) deep sea water less affected by diatoms contains 0.8–1.2 mg. Si per litre. It is of interest to note that the waters of the east side of the Pacicfic Ocean contain a larger quantity of silicon than the Atlantic; thus the content of silicon in the former waters often attains the value as high as 0.3–0.9 mg. Si per litre even at the surface.

The author determined the vertical variation of silicate in the "Kurosio". The analytical results by the Diénert-Wandenbulcke's method show that the silicate content in the region of this ocean current is much smaller than that of the Californian-Current, flowing along the eastern coast of the Pacific.

Such difference can be easily explained when we consider that the Californian-Current is a cold one with an upwelling turbulent motion, while the "Kurosio" is a warm current with a large vertical stability.

In Table 1 and Fig. 1, the average values of milligram Silicon per litre at various depths are given.

Table 1. The Vertical Variation of Silicate.

Depth (m.)	Si (mg./l.)	Depth (m.)	Si (mg./l.)
0	0.13	300 – 400	0.93
25	0.21	400 – 500	1.21
50	0.15	500 – 600	1.26
100	0.20	600 – 700	1.77
100 – 150	0.46	700 – 800	2.01
150 – 200	0.52	800 – 900	2.05
200 – 250	0.68	900 – 1000	2.28
250 – 300	0.74		

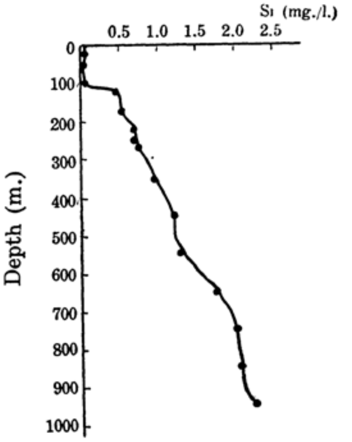

Fig. 1. The Vertical Variation of Silicate.

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(1) H. W. Harvey, "Biological Chemistry and Physics of Sea Water", 50, Cambridge (1928).

(2) H. Wattenberg, *Z. anorg. allgem. Chem.*, **236** (1938), 339.

A similar vertical variation of silicate was seen in the "Tusima-Current" in the Japan Sea. This similarity is easily understood when we consider that the "Tusima-Current" is one of the branches of the "Kurosio".

Phosphate. As it is the case with silicate and nitrogen compounds, phosphate is essential to marine organisms, and as the concentration of this compound in sea water is small, it often acts as an important limiting factor to the growth of plankton.

Thus the content of phosphate varies very much with the depth and the location, and it shows a marked annual variation.

The average amount of phosphate in sea water has been found about 1–60 γ P per litre, and in general, deeper water contains more phosphate than the shallower. According to H. Wattenberg,(3) in the open sea, the maximum of phosphate occurs just below the intermediate oxygen minimum. Now, as stated in the foregoing paper, there was no intermediate oxygen minimum in the "Kurosio" in the range of 1,000 m. from the surface, no wonder if we did not find any distinct maximum of phosphate.

Table 2 and Fig. 2 give the result of the phosphate analyses by the Denigés-Atkins' method which were carried out in the "Korosio" region.

Table 2. The Vertical Variation of Phosphate.

Depth (m.)	P (γ/l.)	Depth (m.)	P (γ/l.)
0	2.0	300– 400	10.0
25	0.8	400– 500	12.5
50	1.6	500– 600	11.8
100	1.3	600– 700	15.7
100–150	4.2	700– 800	13.0
150–200	3.5	800– 900	17.8
200–250	6.3	900–1000	11.7
250–300	8.0		

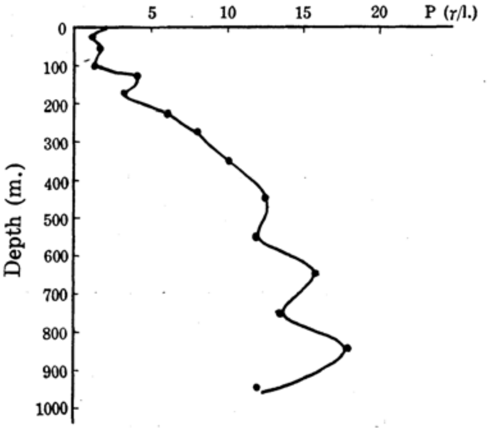

Fig. 2. The Vertical Variation of Phosphate.

As shown in Table 2 and Fig. 2, the surface water contains almost a negligible amount of phosphate. The concentration increases with the depth in a rather complicated manner; however, as a whole the phosphate content of the "Kurosio" water seems to be somewhat lower than that of other oceanic waters. The maximum value was only 25 γ P per litre.

Boron. In a previous paper,(4) the present author determined volumetrically the borate content of the surface water from the western

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(3) H. Wattenberg, *Ann. Hydr.*, **65** (1937) September Beiheft.

(4) This Bulletin, **14** (1939), 55.

part of the North Pacific Ocean. In that paper, the author calculated the chlorinity ratio of boron without taking into account the density of water; therefore the obtained values were slightly higher than actual ones. If a proper attention is paid in regards to the density of water, as it was done in some later determination by the author, the value of the chlorinity ratio is in quite a good agreement with Th. G. Thompson's analysis. (0.0222 and 0.0228 instead of 0.0228 and 0.0234)

The vertical variation of boron in sea water was recently studied by Th. G. Thompson and his collaborators(5) in the eastern coast of the North Pacific Ocean. According to their results, the curve of the boron chlorinity ratio did not show any remarkable vertical change, except a minimum at a depth of about 25 m. and a peculiar maximum at a depth of about 800 m.

The present study was started in order to prepare the data of analyses of the samples from the western coast of the Pacific for the comparison with the eastern ones. The analytical procedure was the same as was reported in the previous paper. Seventy-seven selected samples from various depths were analyzed. In Table 3, the average concentration of boron expressed in number of milligrams of boron per kilogram of sea water is given.

Table 3. The Vertical Variation of Boron.

Depth (m.)	B (mg./kg.)	Depth (m.)	B (mg./kg.)
0	4.61	400 – 500	5.24
25	4.33	500 – 600	4.86
50	4.67	600 – 700	5.28
100	4.83	700 – 800	5.56
200	5.00	800 – 900	5.32
300 – 400	5.07	900 – 1000	5.44

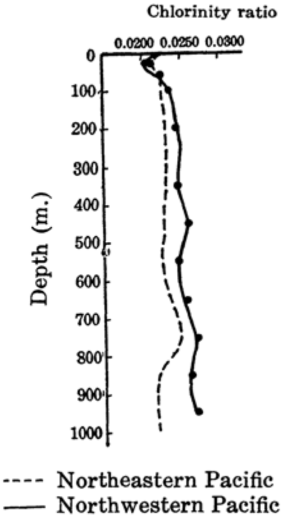

Fig. 3. The Vertical Variation of Boron.

As shown in Table 3, in spite of the gradual diminution in chlorinity with increasing depth, the concentration of boron increases slightly. In Fig. 3 the vertical variation of the chlorinity ratio of boron (the value milligram atom boron divided by the chlorinity) in the "Kurosio" is compared with the results by Th. G. Thompson and his collaborators. The difference between the two curves is probably due to some difference in the nature of the two oceanic currents which were dealt with in the foregoing paragraph.

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(5) Th. G. Thompson, I. Igelsrud and B. M. G. Zwicker, *Am. J. Sci.*, [5], **35** (1938), 47.

Copper. The biochemistry of copper is one of the most interesting problem at present,⁽⁶⁾ inasmuch as it has been known that various marine animals, for instance oysters, contain much copper in their shells and flesh. It is also notable that copper is an essential constituent of haemocyanin, the blood pigment of many marine invertebrates.

The copper content of the sea water, however, is not yet clearly determined, because of the lack of a reliable process for its micro-analysis.

Recently, H. Meyer⁽⁷⁾ determined the copper content of a sample of sea water with Pulfrich's stufen-photometer using sodium-diethyl-dithiocarbamate as a reagent, and found that the sea water contains 6 to 26 γ Cu per litre. After H. Meyer, K. Kalle and H. Wattenberg⁽⁸⁾ using the same method reported 3 to 12 γ Cu per litre in surface waters collected by the observation ship "Meteor" during the German North Atlantic Expedition (1938).

Since all of these estimations have been done only with the surface water, it will be of interest to investigate the vertical variation of copper in the open sea.

Results of the Analyses. Diethyl-dithiocarbamate method was adopted. 0.5 c.c. of the reagent solution (0.1%) was added to each 30 c.c. of a sample, and the colour thus developed was compared with the standard copper solution in an artificial sea water.

Seventy-seven samples collected from various depths in the "Kurosio" region were analyzed. From the analytical results obtained, we can see that the copper content of the surface water from the "Kurosio" region is from trace to 30 γ Cu per litre which is in a good agreement with the results of the above mentioned authors.

It is noteworthy that the concentration of copper increases evidently with the depth and the highest values attained was as high as a hundred times that of the surface water. But, lately it became clear that there is a fear of contamination in so far as Nansen's water-bottles are used for sampling of water below the surface. Then, in the first place, it seems to be necessary to collect the samples of water with bottles completely free from copper. Further study will be done in near future.

Fluoride. Of the halogens in sea water, fluorine is the third in abundance. In 1850, Forchhammer first called attention to the presence of this element and reported that the sea water contains 0.7 mg. fluorine per litre. The results of Forchhammer and his successors are all incredible because of the inherent difficulty in the methods of determining minute quantities of fluoride in the presence of other salts.

Recently Th. G. Thompson and H. J. Taylor⁽⁹⁾ determined the

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(6) Dittmar, "Challenger" Reports. "Physics and Chemistry". Vol. 1. (1884); Phillips, *Marine Biol. Pap. Carnegie Inst.*, **9** (1917), 9; Hiltner and Wichmann, *J. Biol. Chem.*, **38** (1919), 205; Rose and Bodansky, *ibid.*, **44** (1920), 99; Phillips, *Papers Marine Biology.*, **18** (1922), 97; Orton, *Fish. Invest. London* (2), No. 3, (1924), *ibid.*, No. 4; Gaarder, Bergens Museums Arbok, (1932), Naturvidenskapelig rekke, Nr. 3; Atkins, *Marine Biol. Ass. Journ.*, N. S., **18** (1932), 193; Plytherch, *Ecol. Monogr.*, **4** (1934), 47; Riley, *J. Marine Research*, **1** (1937), 60; Webb, *Sci. Proc. Royal Dublin Soc.*, **21** (1937), 505.

(7) H. Meyer, *Ann. Hydr.*, **66** (1938), 325.

(8) K. Kalle and H. Wattenberg, *Naturwiss.*, **26** (1938), 1.

(9) Th. G. Thompson and H. J. Taylor, *Bull. Nat. Research Council*, **85** (1932), 136.

fluorine content of sea water colorimetrically using alizarine-sulphonate and zirconium nitrate, and found that 1.4 mg. of fluorine is present per litre when the chlorinity is 35‰. This is at the present, the most reliable value for the concentration of fluoride in sea water.

The author tried to investigate the vertical variation of fluorine in sea water by this recent analytical method. The analytical result shows that the average value of the fluorine is 1.3 mg. F per litre when the salinity is about 34.6‰, which is in a good agreement with the value of Th. G. Thompson and H. J. Taylor.

In Table 5, the average values of fluorine corresponding to each depth are given.

Table 4. The Vertical Variation of Fluorine.

Depth (m.)	F (mg./l.)	Depth (m.)	F (mg./l.)
0	1.31	400– 500	1.36
25	1.32	500– 600	1.33
50	1.34	600– 700	1.28
100	1.20	700– 800	1.31
200	1.30	800– 900	1.30
300 – 400	1.38	900–1000	1.28

Differing from other minor elements, fluorine shows no appreciable vertical variation in its concentration. Then, fluorine, a scanty element in sea water, seems to be quite indifferent to biological action.

Summary.

The vertical variation of silicate, phosphate, borate, copper and fluoride in the region of the "Kurosio" were studied.

In conclusion, the author wishes to express his hearty thanks to Professor T. Okada, Director of the Central Meteorological Observatory of Japan, for his kind guidance and permission of publishing this report. He is also indebted to Mr. H. Matui, for his earnest assistance throughout this work.

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