Seasonal Variations of Minor Chemical Constituents in the Waters of the Zunan-Kuroshio Region. II. Silicate Contents of Sea Water and Changes in Quality of the Kuroshio*

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Introduction

In the previous paper1), the author has studied the problem concerning variations of nitrate and phosphate contents in the waters of the Kuroshio region. The present paper deals with the seasonal variations of silicate contents of water in connection with the changes in quality of the Kuroshio. Although silicate has been regarded as one of the most essential nutrient salts for marine organisms, especially for diatoms, together with phosphate and nitrate, it differs from the other nutrient salts in respect to circulation, the magnitude of the concentration and the physiological significance for organisms.

The author previously made a chemical study on Omura Bay2) (Nagasaki prefecture, Japan), reporting that, contrary to general expectation, silicate contents of sea water in the estuary of the Kôri river were lower than in the adjacent areas. In this case, however, the physico-chemical state of silicon-compounds colorimetrically determined has not been made clear.

Later, a number of studies were conducted by various authors as to the state of silicon-compounds colorimetrically estimated3)4), changes in silicate coloration when sea water was diluted with natural fresh water5) and the state of silicon-ccompounds in hot springs and land waters6), yielding valuable results.

Although a decisive conclusion has not been reached up to now, it is probable that the most part of silicon-compounds in the oceanic waters may be in a colorimetrically measurable state7), seasonal variations of which were mainly considered in this paper, not referring to the state of silicon-compounds.

Materials and the Analytical Method

The following discussions are based upon the data obtained for the samples collected from the oceanographical stations illustrated in Fig. 1 of the previous report during the period from January 1950 to Feburuary 1951. The analyses of the samples were carried out as soon as possible after

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1) R. Fukai, This Bulletin, **25**, 323 (1952).

2) R. Fukai, M. Osako and H. Hamada, *Oceanogr. and Meteorol., Nagasaki Marine Observatory,* **3**, No. 3 (1949) (in Japanese).

3) F. Aoki, *J. Chem. Soc. Japan*, **71**, 634 (1950); **72**, 15 (1951).

4) T. Okura, *J. Chem. Soc. Japan*, **72**, 927 (1951).

5) A. Saeki, *J. Oceanogr. Soc. Japan*, **5**, 41 (1949); **6**, 39 (1950).

6) I. Iwasaki, T. Katsura & T. Tarutani, This Bulletin, **24**, 227 (1951).

7) T. Chow and R. J. Robinson, *Anal. Chem.*, **25**, 646 (1953).

collections either on board ship or on the land, depending on the sea conditions in each observation cruise.

For the analysis was adopted the Dienert-Wandenbulcke's method in which the yellow color of silicomolybdate was developed by addition of ammonium molybdate solution and sulfuric acid. Although further reduction of silicomolybdate by stannous chloride provides the more sensitive method[8]), the ordinary method was followed with regard to conditions on board ship. For the color comparison were used the color standard of buffered potassium chromate solution containing borax and improved Hehner tubes with the length of 25 cm., or Beckman's spectrophotometer at a wave length of 380 mμ. Checking experiments were made as to the changes in concentration of silicate which occurred during the standing period of the samples, proving that no change was recognized unless water samples were kept in contact with the glass walls of containers.[9])

Results and Discussions

In order to examine the seasonal variations of silicate in the region under study, it is necessary to distinguish the variations in the surface layers (0–200 m.) from the fluctuations of vertical distributions. The former may be related to prevalence or decline of coastal water masses; and the latter to vertical mixing of water strata due to mechanical disturbance and vartical diffusion.

1. Variations in the Surface Layer.— Variations of silicate contents in the surface layers (0–100 m. and 100–200 m. layers) with those of chlorinity (in 0–100m. layer) at Stations 3 and 6 are shown in Figs. 1 and 2, respectively. The values plotted in the figures are the integral mean values for each water layer.

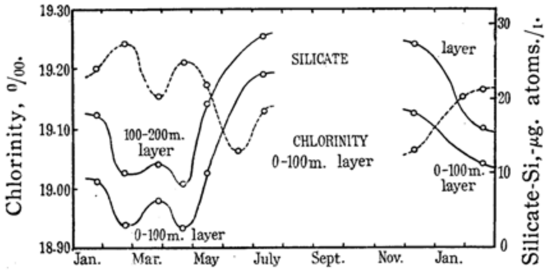

Fig. 1. Seasonal variations of silicate and chlorinity in the surface layers at Station 3. Solid curves: silicate. Broken curves: chlorinity.

From the figure, it is readily noted that chlorinities of the waters in the region decreased in summer, while they increased in winter. It seems to be a remarkable fact that the decrease at Station 6, which is located within the main current of the Kuroshio and is not likely to be affected immediately by land waters, is larger than that at Station 3 located in the mixing region of the Kuroshio with coastal water masses. This may suggest that the decrease in chlorinity of the Kuroshio itself ought to take place before the Kuroshio flows into the region under consideration.

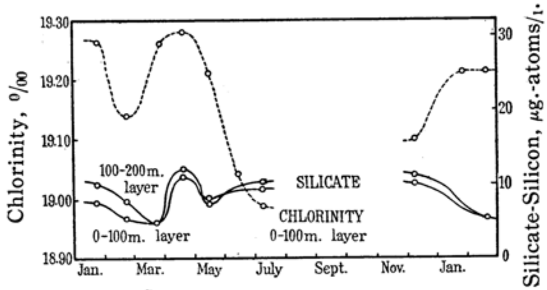

Fig. 2. Seasonal variations of silicate and chlorinity in the surface layers at Station 6. Solid curves: silicate. Brokenc curves: chlorinity.

Silicate contents tend to increase in summer and decrease in winter, being contrary to the variations in chlorinity. This inverse proportionality is remarkable at Station 3. Although the relationship may indicate that silicate contents fluctuate in accordance with the prevalence or decline of coastal water masses, quantitative correlations do not exist.

Now, let us assume that the maximum chlorinity of 19.30‰ represents the normal chlorinity of water in the Zunan-Kuroshio region and that the normal sea water of the region is only mixed up with the fresh water; moreover, let us define the mixing percentage of fresh water, M_f, as follows;

$$M_f = \frac{[\mathrm{Cl}]_n - [\mathrm{Cl}]_s}{[\mathrm{Cl}]_n} \times 100 \qquad (1)$$

where $[\mathrm{Cl}]_n$ is the normal chlorinity, namely 19.30% in this case, and $[\mathrm{Cl}]_s$ is the chlorinity in summer.

The values of mixing percentage calculated from the equation 1 did not exceed 2% as shown in Table I. On the basis of the mixing percentage and silicate contents of sea water in summer, silicate contents of assumed fresh water were computed as shown in the last column of Table I. Among these values, the one for July 1950 is three times higher than the mean value for river waters in Japan. This may indicate that the variations of silicate contents in the surface layers are not controlled only by direct invasion of terrestrial water, even at Station 3, located relatively coastward.

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[8]) A. B. Carlson and C. V. Banks, *Anal. Chem.*, **24**, 472 (1952).

[9]) R. Fukai, *J. Oceanogr. Soc. Japan*, in press.

TABLE I

ESTIMATED SILICATE CONTENTS OF FRESH WATERS

	$\Delta Cl^0/_{00}$	Percentage of fresh water mixed	Si in sea water µg.-at./l.	Estimated Si of fresh water mg.-at./l
Station 3				
May 1950	0.13	0.7	9.7	0.5
July ,,	0.17	0.9	27	2.5
Station 6				
May 1950	0.09	0.5	8.2	1.2
July ,,	0.31	1.6	9.3	0.3

As the other origin of *excess silicate* in sea water, the following may be considered:

(1) the silicate-rich substratum,

(2) the decomposition processes of abundant populations of diatoms in summer,

(3) a water mass having high silicate content and low chlorinity.

Among these cases, the former two can hardly be accepted, since the Kuroshio is a stably stratified and origotrophic water mass of the southern origin. Therefore, the last case should be most probable. It cannot be immediately concluded, however, where the origin of a mixing water mass is.

In the variations of silicate and chlorinity, the conditions are quite different between Stations 3 and 6. This suggests that the causes of the variations are not the same at these stations. Whereas it is probable that the variations in the main current of the Kuroshio are being affected by the water of southern origin such as the adjacent water to Formosa or the water of the East China Sea, the effect of the Oyashio might be taken into consideration as the cause of the variation at Station 3, since the Oyashio from the northern areas of the N. W. Pacific prevails along the coastal region of Japan in summer months.

In order to estimate the silicate content of a water mass of northern or southern origin which is likely to mix with the Kuroshio, the mixing percentage of water masses is computed by using the following equation, defining the normal chlorinity of each water mass from the data previously obtained[10,11];

$$M=\frac{[\mathrm{Cl}]_n-[\mathrm{Cl}]_s}{[\mathrm{Cl}]_n-[\mathrm{Cl}]_m}\times 100. \qquad (2)$$

The notations in Eq. 2 are the same as in Eq. 1, except that $[\mathrm{Cl}]_m$ designates the postulated chlorinity for the mixing water mass.

From the values in Table II, it may be concluded that the actual circumstances are not explained so far as only the mixing of different sea waters is concerned. Consequently, the mixing with both fresh and sea water must be taken into consideration.

TABLE II

ESTIMATED SILICATE CONTENTS OF WATER MASSES MIXED WITH THE KUROSHIO

(July 1950)

Water mass	Cl $^0/_{00}$ of water mixed	Mixing percentage	Estimated Si of water mixed µg.-at./l.	Si found in the Kuroshio µg.-at./l.
Northern				
Station 3	18.35	17.9	130	30
Station 6	18.35	32.6	20	30
Southern				
Station 3	17.50	9.4	250	—
Station 6	17.50	17.2	30	—

As described above, the variations of silicate contents in the surface layer are complicated. Nevertheless, it is noteworthy that silicate which appears to originate primarily from land waters is related to the changes in quality of the oceanic water mass such as the Kuroshio.

2. Variations below the Subsurface Layer.—The variations of silicate below the subsurface layer cannot be discussed simply. In general, vertical distributions of silicate contents tend to have parallel correlations with those of phosphate above a depth of 1000 m. In the Kuroshio region, phosphate contents reach the maximum at a depth of about 1000 m., while silicate contents increase continuously.

In Fig. 3 is given the relationship between silicate and phosphate contents above the maximum layer of phosphate, together with the data obtained as to the water samples

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[10] R, Fukai, This Bulletin, in press (1954).

[11] Y. Matsudaira and S. Inoue, *J. of Oceanography, Imperial Marine Observatory, Kobe, Japan,* 705 (1939).

collected from the Aleutian region. Points in the figure were plotted on the basis of the annual mean values for each of the constituents. A close linear correlation was obtained from these values, although the data for each month were considerably fluctuated. The mean value of Si : P was 28. On the other hand, no linear correlations recognized as to the points for the Aleutian region.

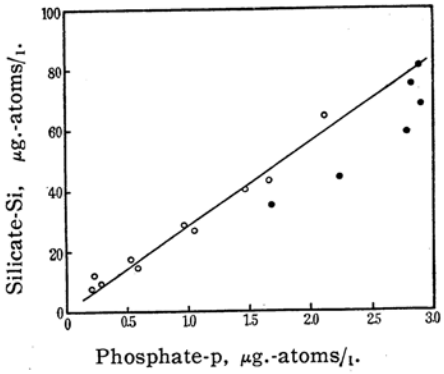

Fig. 3. Relationship between silicate and phosphate. Circles: for the Kuroshio region. Dots: for the Aleutian region.

Deviations from the mean ratio of Si : P in the Kuroshio region are especially large in the upper layers. Although relatively close values were obtained as to the waters below subsurface layers, the values tend to fluctuate due to mixing with the waters of deeper layers.

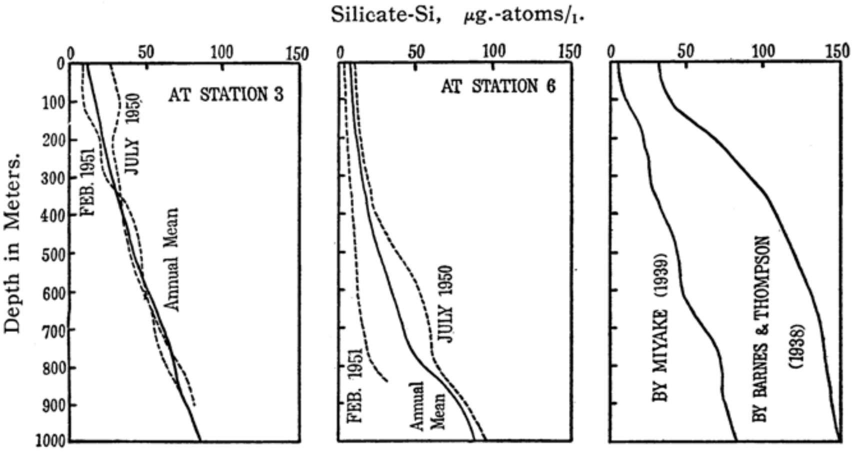

Fig. 4. Vertical distributions of silicate.

In Fig. 4 are shown the annual mean vertical distributions of silicate and examples of vertical distribution for summer and winter. For a comparison, the vertical distributions obtained by various investigators[12] from the North Pacific were added.

Although the causes for the fluctuation of vertical distributions are not obvious, it should be noted that the whole water column tends to become uniform at Station 6 in winter, suggesting that the mixing with the waters of the substratum due to convection process which may be acting as the controlling factor.

Summary

Seasonal variations of silicate have been considered in the present paper on the basis of the data obtained from the observations carried out from January 1950 to February 1951.

The variations of silicate in the surface layers tend to have an inverse proportionality with those of chlorinity, increasing in summer while decreasing in winter. It is not sufficient to consider that the cause of the variations merely lies in the mixing either with fresh waters from the coast of Japan or with a water mass having low chlorinity and high silicate content. The actual circumstances may probably be caused by the overlapping effect of these two causes.

Although the fluctuation of vertical distributions of silicate below subsurface layer was also complicated, a close linear correlation between annual mean silicate contents and those of phosphate was obtained, to be expressed as the Si : P ratio of 28. However, the vertical distributions fluctuated considerably in the course of time, tending to become uniform in winter.

As the conclusion, it may be estimated that the vertical and lateral mixing of water

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[12] Y. Miyake, This Bulletin, **14**, 467 (1939); C. A. Barnes & T. G. Thompson, "Univ. of Washington Publ. in Oceanogr.", **3**, No. 2 (1938).

masses is the prevailing factor for the variations of silicate in the region under consideration.

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