

Regeneration of Silicate in the Ocean

I. The Japan Sea as a Model of Closed System*

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Abstract: Regeneration of silicate in the Japan Sea, an example of semi-closed sea, was studied. In the Japan Sea Proper Water the apparent regenerative ratio of the nutrients was determined to be:

$$\Delta O : \Delta C : \Delta N : \Delta P : \Delta Si = -289 : (116) : 14.3 : 1 : 81.$$

It was assumed that the dissolved silicate present in sea water is grouped into three fractions; 1) *preformed* silicate of conservative nature, 2) *oxidative* silicate which dissolves in oxidation process of organisms with consumption of oxygen, and 3) *non-oxidative* silicate which dissolves without oxygen consumption. The dissolution rate of *non-oxidative* silicate in the Japan Sea Proper Water was estimated to be $0.07 \mu\text{g-at. Si/l/yr}$ from the data of ΔAOU values and assumed rates of oxygen consumption. This dissolution rate of *non-oxidative* silicate agreed with that obtained in the deep Pacific by the vertical advection diffusion model by KIDO and NISHIMURA (1972).

1. Introduction

The behavior of biochemical change of organic matter in the ocean can be elucidated by assuming a closed system and measuring the change of water properties during the time-course.

The Japan Sea, a model of semi-closed sea, is thought to provide such a system. The deep water which is called the Japan Sea Proper Water is of uniform character as to temperature and salinity, and occupies a greater part of the total volume, *i.e.* 90%. Since all the straits connecting the Japan Sea to outer seas are very shallow, about a hundred meters, direct exchange of the deep water with other marginal seas is not possible. It has been considered that such a uniform water originates from the surface water found in winter in the northern area of the sea along the continent (UDA, 1934). In a closed system, the amount of change of biogenic elements due to decomposition of organic matter can be estimated by tracing biochemical and inorganic alteration of the water during the circulation course.

There have been a great deal of works on

the relation between the concentrations of nutrients and the amount of oxygen consumption. In normal open oceans the oxidative atomic ratio proposed by REDFIELD, KETCHUM and RICHARDS (1963),

$$\Delta O : \Delta C : \Delta N : \Delta P = -276 : 106 : 16 : 1$$

is agreeably accepted by several workers (RICHARDS, 1958; PARK, 1967; STEFÁNSSON, 1968; ALVAREZ-BORREGO *et al.*, 1972). The concentration of dissolved silicate, however, varies greatly in its ratios to phosphate and nitrate as pointed out by SVERDRUP, JOHNSON and FLEMING (1942). SCHOTT and EHRHARDT (1969) determined the oxidative ratio to be $\Delta\text{Si}/\Delta\text{P}=7.3$ in the Northwestern North Sea. STEFÁNSSON (1968) found a non-linear correlation between phosphate and silicate in the Northern Irminger Sea. STEFÁNSSON observed the value of 4.9-19.7 for $\Delta\text{Si}/\Delta\text{P}$ in water mass having phosphate concentrations of 0.2-1.1 $\mu\text{g-at./l}$ and value of 16 in water mass having phosphate concentrations higher than 0.8 $\mu\text{g-at./l}$. The latter value is in agreement with those of RICHARDS (1958) for intermediate layer of the Western North Atlantic and of BROENKOW

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(1965) for the Costa Rica Dome in the Eastern Tropical Pacific. In the Gulf of Carpentaria, KIDO (1970) obtained $\Delta Si/\Delta P=6$ as the oxidative ratio. SUGIURA and CHAITIAMVONG (1964) also reported the non-linear correlation between oxygen and silicate in the Northern Frontal Region of Kuroshio. Furthermore, according to CALVERT and PRICE (1971), at the upwelling region in the Benguela Current, the oxidative ratio of nutrients including the silicate was quite different from those observed in normal open oceans.

Thus, there are still many problems to be solved as to the behavior of silicate and other nutrients in the regeneration process. The object of this report is to study the mode of regeneration of silicate in the Japan Sea as a closed system.

2. Analytical methods

Inorganic phosphate and nitrate concentrations were determined by the methods by STRICKLAND and PARSONS (1968). Reactive silicate was determined by the method of KATO and KITANO (1966) with a slight modification by KIDO (1970). Analyses of these nutrients were made on board immediately after sampling by Dr. S. NISHIZAWA and his colleagues. The other numerical data have been presented in the cruise report of *Hakuho-Maru* KH-70-4 Cruise (Ocean Research Institute, 1970).

3. Sample collection

The sea water samples were collected with 2-liter teflon-coated Nansen bottles on the R/V *Hakuho-Maru* of the Ocean Research Institute, University of Tokyo during the KH-70-4 Cruise (July 29-Sept. 1, 1970). Locations of the oceanographic stations are shown in Figure 1.

4. Results and discussion

Generally the upper water of the Japan Sea is divided into two water masses; the one is of relatively high temperature and high salinity of the warmer sector along the Japan Islands, and the other is of relatively low temperature and low salinity of the colder sector along the Korean Peninsula and Siberia. In Figure 2, the open circles (St. 5) and solid circles (St. 2 and

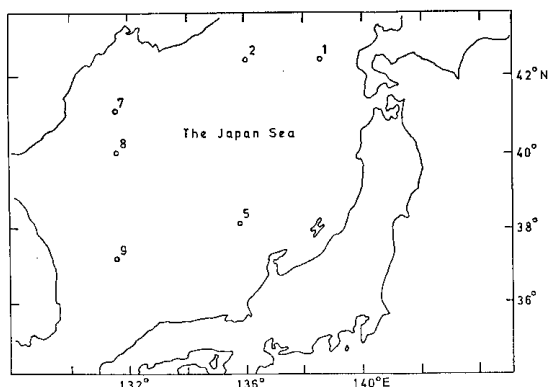


Fig. 1. Sampling stations by *Hakuho-Maru* KH-70-4 Cruise. St. 1, 42°29'N, 138°29'E; St. 2, 42°28'N, 135°57'E; St. 5, 38°13'N, 135°44'E; St. 7, 41°10'N, 131°28'E; St. 8, 40°06'N, 131°31'E and St. 9, 37°18'N, 131°30'E.

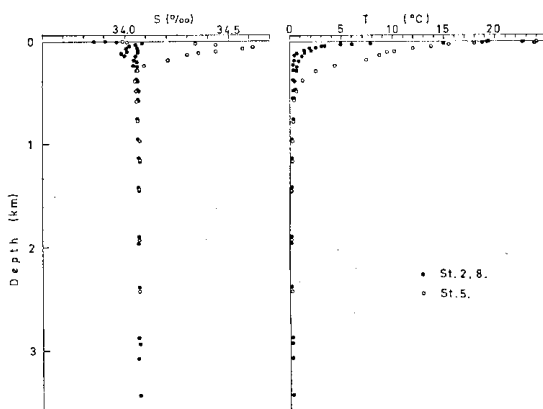


Fig. 2. Vertical profiles of salinity and temperature.

St. 8) are representatives of the warmer and colder sectors, respectively. In the Japan Sea Proper Water identified by the density greater than $\sigma_t=27.35$, the conservative properties are remarkably uniform (Figure 2), but the non-conservative properties such as oxygen and nutrients do not show uniformities and indicate gradual decrease or increase with depth (Figures 3 and 4).

As stated above, the Japan Sea Proper Water is thought to be of a single origin. Therefore, the oxidative ratios of biogenic elements under the degradation process may be obtained from the relationships between the nutrient concen-

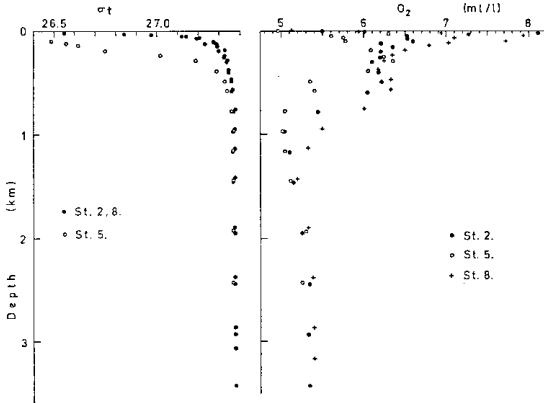


Fig. 3. Vertical profiles of σ_t and dissolved oxygen.

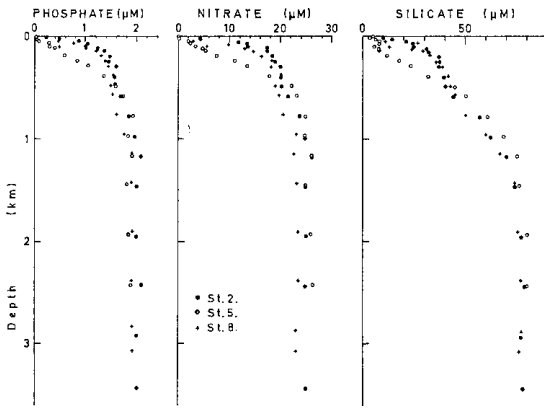


Fig. 4. Vertical profiles of phosphate, nitrate and silicate.

trations and AOU (apparent oxygen utilization) which is defined as the difference between the oxygen concentration observed and the concentration in equilibrium with the normal atmosphere at the *in situ* temperature and salinity. In Figure 5, the relationships of nutrients versus AOU are shown. Each regression line calculated by the method of least squares has a slope of $\Delta P/\Delta AOU=1/289$, $\Delta N/\Delta AOU=14.3/289$ and $\Delta Si/\Delta AOU=81/289$ in atoms, and the following relation is obtained:

$$\Delta AOU : \Delta C : \Delta N : \Delta P : \Delta Si \\ = 289 : (116) : 14.3 : 1 : 81$$

The figure in parentheses is a calculated value

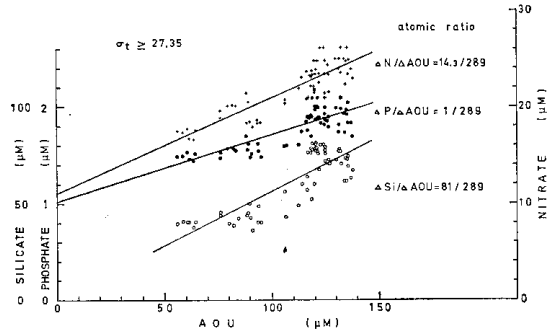


Fig. 5. Nutrient-AOU relationship in the Japan Sea Proper Water.

obtained by the way of REDFIELD *et al.* (1963). Compared to the oxidative ratio proposed by REDFIELD *et al.* (1963),

$$\Delta AOU : \Delta C : \Delta N : \Delta P = 276 : 106 : 16 : 1$$

and the ratio by RICHARDS (1958),

$$\Delta AOU : \Delta C : \Delta N : \Delta P : \Delta Si \\ = 270 : (103) : 16 : 1 : 16$$

the ratio among phosphate, nitrate and oxygen in the Japan Sea Proper Water is in fairly good agreement with those in the literatures, but the characteristic of the Japan Sea Proper Water is of the high ratio of silicate regeneration. The value of silicate is rather comparable to that of the deep Pacific reported by TSUNOGAI (1972),

$$\Delta O : \Delta C : \Delta N : \Delta P : \Delta Si \\ = -289 : 125 : 12 : 1 : 120$$

who estimated the ratio by the vertical advection-diffusion model. TSUNOGAI (1972) ascribed this high ratio to the delayed regeneration of silicate from the silicious tests of marine organisms. BROECKER (1971) demonstrated that the concentrations of the elements, Si, P, and C, in sea water are almost certainly influenced by the behavior of particulate debris produced by living organisms. Thus, the high value found in the Japan Sea Proper Water is also thought to be the result of delayed regeneration of silicate from the biogenic particulate debris.

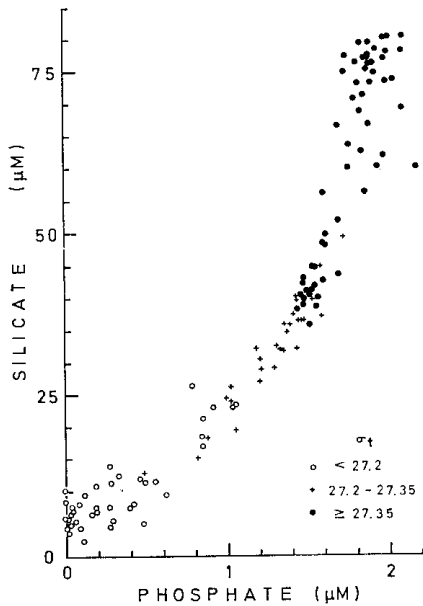


Fig. 6. Phosphate-silicate relationship in the Japan Sea.

As shown in Figure 6, the silicate shows an exponential increase against the phosphate, compared to the linear relationship between the phosphate and nitrate (Figure 7). In Table 1, the ratio of $\Delta\text{Si}/\Delta\text{P}$ at three σ_t levels are shown. The value of $\Delta\text{Si}/\Delta\text{P}=16$ given to the water of σ_t less than 27.2 is identical with that by RICHARDS (1958), BROENKOW (1965) or STEFÁNSSON (1968), and is close to $\Delta\text{Si}/\Delta\text{P}=22$ by STEFÁNSSON and RICHARDS (1963), or GRILL and RICHARDS (1964). This suggests that phosphate and silicate have approximately the same regenerative pattern at least in the earlier stage of degradation in the normal ocean.

SVERDRUP, JOHNSON and FLEMING (1942) first presented a relationship between oxygen depletion and nutrient concentration, that is:

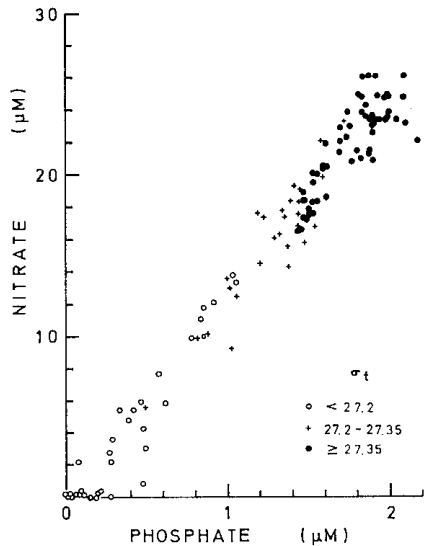


Fig. 7. Phosphate-nitrate relationship in the Japan Sea.

$$\begin{aligned} &\text{Nutrient concentration at a depth} \\ &= V + (\text{constant}) \times (\text{O}_2 \text{ depletion}) \end{aligned}$$

where V is the amount of a nutrient which has existed in the water that sinks from the surface. REDFIELD *et al.* (1963) developed this concept and denoted the first and second terms of the above equation as “preformed” and “oxidative”, respectively. As demonstrated in the foregoing section, the phosphate-silicate relationship in the Japan Sea does not show a linear correlation, and it is difficult to employ the above concept as it is.

In a chemical sense, oxidation is not involved in the formation of phosphate and silicate, but oxygen is consumed at the decomposition process of organic matter containing phosphate and silicate. The silicate produced by such an oxidative decomposition is denoted as *oxidative*

Table 1. The slopes of $\Delta\text{N}/\Delta\text{P}$ and $\Delta\text{Si}/\Delta\text{P}$ of the regression lines at three σ_t levels.

σ_t	No. of samples	$\Delta\text{N}/\Delta\text{P}$	No. of samples	$\Delta\text{Si}/\Delta\text{P}$
<27.2	41	13.1	41	16
27.2-27.35	30	13.2	29	30
≥27.35	61	14.3	62	81
Whole water column		13.6		

silicate, Si_{ox} . The silicate by the dissolution process without oxygen consumption is denoted as *non-oxidative* silicate, $Si_{n,ox}$ which is added as the third term in the calculation of the total dissolved silicate.

The resulting equation is:

$$Si_{obs} = Si_{pre} + Si_{ox} + Si_{n,ox}$$

where Si_{obs} is the observed concentration of dissolved silicate, and Si_{pre} is the concentration of the *preformed* silicate. This equation is analogous to the expression of PARK (1967), and $Si_{n,ox}$ corresponds to his Si_{inorg} .

As the nitrate and phosphate concentrations are of linear relationship to AOU (Figure 5), the preformed nitrate and phosphate concentrations are obtained to be $11 \mu\text{g-at./l}$ and $1.0 \mu\text{g-at./l}$ by extrapolation of the lines. The concentrations of preformed silicate corresponding to the phosphate ($1.0 \mu\text{g-at./l}$) and nitrate ($11 \mu\text{g-at./l}$) are sought to be 23 and $18 \mu\text{g-at./l}$ from Figures 6 and 8, respectively, provided that the water representing the preformed silicate is the same water representing the preformed phosphate or nitrate. Then, $21 \mu\text{g-at./l}$ is given to the Si_{pre} as an average.

Representative vertical profiles of the conservative and non-conservative properties in the northern part of the Japan Sea in winter are

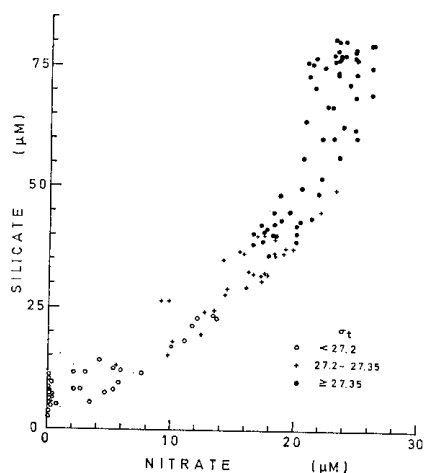


Fig. 8. Nitrate-silicate relationship in the Japan Sea.

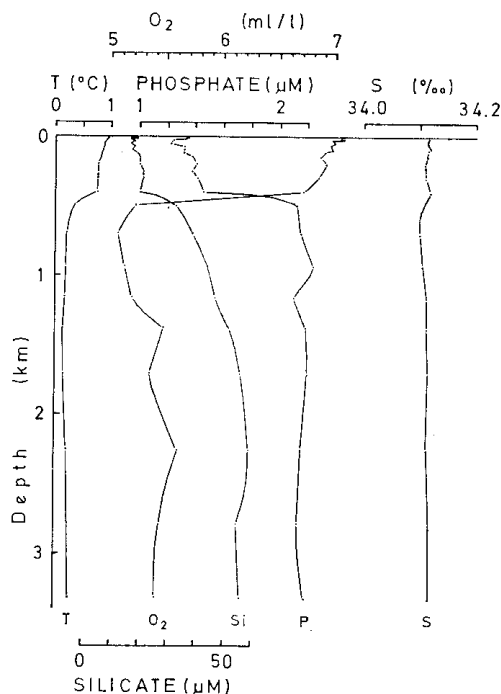


Fig. 9. Vertical profiles of salinity, temperature, dissolved oxygen, phosphate and silicate at St. 26 ($42^{\circ}08'N$, $136^{\circ}04'E$) on Feb. 27th in 1966 given by Maizuru Marine Observatory (1966).

shown in Figure 9. The value of each property is almost uniform down to the depth of 400 m by vigorous convective mixing. Such a sea water that have relatively higher values of density and nutrient concentrations settles down and supplies the Japan Sea Proper Water in the northern part of the Japan Sea in winter. Consequently, each average value of nutrients in the upper water corresponds to so-called *preformed* nutrient. The silicate concentration in the upper water, about $20 \mu\text{g-at./l}$, is in good agreement with $21 \mu\text{g-at./l}$ given to the Si_{pre} mentioned above.

If we assume that $Si:AOU$ ratio ($\Delta Si/\Delta AOU = \Delta Si/\Delta P \times \Delta P/\Delta AOU = 16/289$) in surface water is kept in deeper water, Si_{ox} is written as $(16/289) \times (AOU)$ (Table 1). Then, the concentration of $Si_{n,ox}$ is calculated from the following equation:

$$Si_{n,ox} = Si_{obs} - 21 - \frac{16}{289} \times AOU$$

The $Si_{n,ox}$ is a function of age of the water, providing that the dissolution rate is constant.

The relative age of water was calculated indirectly from the amount of oxygen consumption and the estimated oxygen consumption rate. PACKARD, HEALY and RICHARDS (1971) estimated the rate of oxygen consumption in sea water by measuring the activity of the respiratory electron transport system in plankton in the Eastern Tropical Pacific Ocean. The oxygen utilization rate (R : $\mu\text{l-O}_2/\text{l/yr}$) below 500 m was given as follows:

$$R_z = 3.2 - 0.47z$$

where z was a depth in kilometers. Taking a depth of 3 km as an example, $2 \mu\text{l-O}_2/\text{l/yr}$ is calculated from the above equation. On the other hand, MUNK (1966) gave the rate of 2.7–5.3 $\mu\text{l-O}_2/\text{l/yr}$ in the North Pacific at 1–4 km in depths, and TSUNOGAI (1972) 1–2 $\mu\text{l-O}_2/\text{l/yr}$ at 3 km in the deep Pacific. The rate estimated from the equation by PACKARD *et al.* (1971) agrees fairly well with Munk and Tsunogai's estimations. We used the Packard *et al.*'s equation for the calculation of the oxygen consumption rate at each depth in the Japan Sea Proper Water.

The oxygen utilization rate in deep sea water is generally related to the amount of oxidizable organic matter. According to NAKAJIMA (1973), the areal mean concentration of seston by dried weight ranges 0.1–0.3 mg/l in the Japan Sea and the Kuroshio area (21°N–30°N, 132°E), 0.1–0.4 mg/l in the Western North Pacific (10°N–28°N, 142°E), and 0.1–2.3 mg/l in the Oyashio area (42°N, 146°E). Consequently, the amounts of oxidizable organic matter in the Japan Sea and the Pacific seem to be of the same order of magnitude, and it may be valid to apply the oxygen utilization rate calculated from the Packard *et al.*'s equation to the deep water in the Japan Sea as a first approximation.

By using the data of the Japan Sea Proper Water at the continental side (Sts. 1, 2, 7 and 8), the relation between $\Delta Si_{n,ox}$ and the relative age of the water is plotted in Figure 10. The resulting dissolution rate of $Si_{n,ox}$ was $0.072 \pm 0.008 \mu\text{g-at.Si/l/yr}$ at the 95% confidence level.

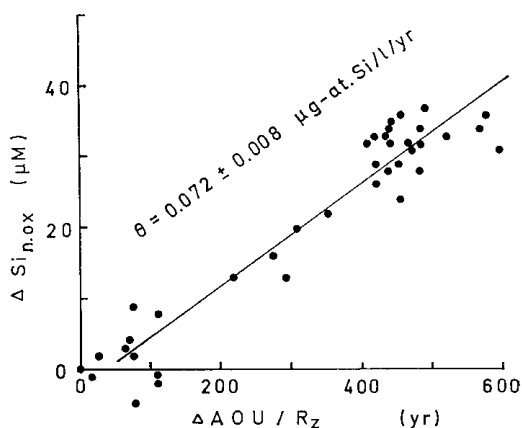


Fig. 10. Dissolution rate of *non-oxidative* silicate in the Japan Sea Proper Water at continental side (Sts. 1, 2, 7 and 8). The rate was calculated at the 95% confidence level.

This value is in good agreement with that of KIDO and NISHIMURA (1972), who estimated the dissolution rate of $Si_{n,ox}$ to be $0.06 \pm 0.02 \mu\text{g-at.Si/l/yr}$, applying the vertical advection-diffusion model to the distribution of the dissolved silicate in the wide area of the deep Pacific from 51°N to 6°S along the 170°W line.

HURD (1972) investigated the factors affecting dissolution rate of biogenic opal in sea water. It is interesting to compare the rate estimated by us with the experiment made by HURD. The first order equation adopted by him is as follows:

$$dC/dt = k_2(C_{sat} - C_{sol})S$$

Based on his experimental data at 3°C and stirred condition, we estimated the dissolution rate in the Japan Sea Proper Water to be $6 \mu\text{g-at.Si/l/yr}$, by using the value of $0.07 \mu\text{g-at.Si/cm}^3$ in the Japan Sea Proper Water (C_{sol}) and the value of 0.01/cm for the surface area of the solid per unit volume of solution (S). The latter was calculated from the specific surface area of $60 \text{ m}^2/\text{g}$ given by HURD and the mean concentration of particulate silica of $16 \mu\text{g-SiO}_2/\text{l}$ in the upper water of the Japan Sea (KIDO, 1973). The dissolution rate calculated according to HURD, $6 \mu\text{g-at.Si/l/yr}$, is 2 orders of magnitude higher than the value, $0.07 \mu\text{g-}$

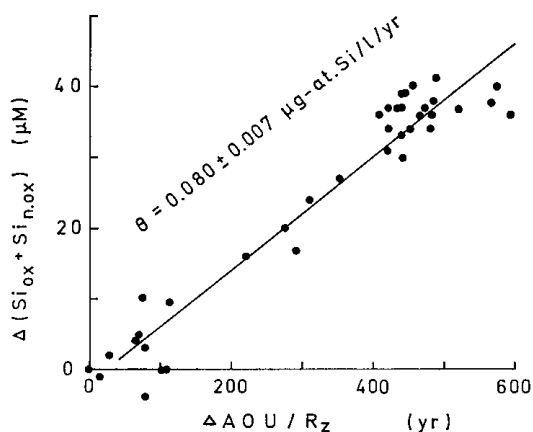


Fig. 11. Total dissolution rate of silicate in the Japan Sea Proper Water at continental side (Sts. 1, 2, 7 and 8). The rate was calculated at the 95 % confidence level.

at.Si/l/yr, given in this paper. Although it is hard to interpret this large discrepancy, perhaps one reason is the pre-cleaning of the surface of biogenic opal in his experiment, because the surface of particulates in the sea seems to be coated with organic matter and the coating may prevent the dissolution of silica from the surface. Another reason may be ascribed to the estimation of the specific surface area of particulates in the sea.

The total dissolution rate of silicate including the oxidative silicate was estimated to be $0.080 \pm 0.007 \mu\text{g-at.Si/l/yr}$ at the 95 % confidence level (Figure 11). The dissolution rate of $\text{Si}_{n,ox}$ accounts for 90 % of the total dissolution ($\text{Si}_{ox} + \text{Si}_{n,ox}$). Therefore, it should be noted that the silicate expressed in the term $\text{Si}_{n,ox}$ plays an important role in the silicate concentration in deep water. Such a fact was also recognized in the deep Pacific by PARK (1967), and KIDO and NISHIMURA (1972). The contribution of Si_{ox} is small, but its role cannot be ignored in subsurface and intermediate waters, where the oxygen consumption rate is large and the nutrients increase abruptly.

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海洋におけるケイ酸塩の再生

I. 閉鎖系モデルとしての日本海

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要旨: 半閉鎖海の一例として, 日本海におけるケイ酸塩の再生を調べた. 日本海固有水における栄養塩類のみかけの再生比は次のように決定された.

$$\Delta O : \Delta C : \Delta N : \Delta P : \Delta Si = -289 : (116) : 14.3 : 1 : 81$$

海水中に存在する溶存ケイ酸は, 三つの部分に分類されると仮定した. 1) 保存成分的性格の *preformed* Si, 2) 酸素消費に伴う有機物の酸化過程で溶解する *oxidative* Si, および 3) 酸素消費を伴わないで溶解する

non-oxidative Si である.

ΔAOU 値のデータおよび推定した酸素消費速度をもとに, 日本海固有水における *non-oxidative* Si の溶出速度を $0.07 \mu\text{g-at. Si}/1/\text{yr}$ と見積った. この *non-oxidative* Si の溶出速度は, 城戸・西村 (1972) が鉛直移流・拡散モデルを用いて太平洋深層水について求めたものとよく一致する.