Dissolution Rates of Silica from Diatoms Decomposing at Various Temperatures

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Abstract

In a study of silica dissolution from diatoms, the rate coefficient (K) h^{-1} of raw diatom cells was estimated as 4 to 5 times smaller than that of the acid-digested siliceous skeletons. The dissolution rate coefficient at early stage (K_1) can be predicted as a function of temperature (T °C): $\ln K_1 = \alpha + \beta\, T$, where α is the frequency factor depending on the properties of diatom species, ranging from -7.35 to -10.38, and the temperature coefficient β is 0.0833 for all species. Activation energies were calculated to be 1.37 to 1.38 Kcal mol^{-1}. This equation suggests that the rate coefficient K_1 increases by a factor of 2.27 for each 10 C° rise in temperature. This equation will also be applied to a new approach for the fate and behavior of biogenous silica settling through a water column by introducing the term temperature into a model.

Introduction

The silica balance in the oceans has been studied by numerous workers (e.g. Harriss, 1966; Gregor, 1968; Calvert, 1968; Burton and Liss, 1968) but it still needs further study. The uptake of silica by diatoms and other siliceous organisms and their postmortem dissolution play an important role in controlling the silica budget of the oceans and the abundance of siliceous ooze in bottom sediments. Before reaching the sea floor, the bulk of the diatomaceous silica produced in the euphotic zone dissolves in the water column, and the diatoms which reach the sea floor intact are subjected to further dissolution both before and after burial. It is, therefore, important to study the dissolution rate for various kinds of siliceous organisms.

The dissolution of silica from the skeletons of various diatoms, radiolarians and sponge spicules and their mixtures has been extensively studied (Jørgensen, 1955; Lewin, 1961; Grill and Richards, 1964; Kamatani, 1969;

Hurd, 1972; Lawson et al., 1978; Kamatani and Riley, 1979; Kamatani et al., 1980). In spite of the fact that the kinetic approach gives an important clue for evaluating the silica cycle in the oceans, such studies have long been hampered by the difficulties posed by heterogeneous reactions. However, some scientists (Hurd, 1972; Wollast, 1974; Lawson et al., 1978) have tried to model the mechanisms using a first order equation proposed by O'Connor and Greenberg (1958) and Van Lier et al. (1960). Kamatani et al. (1980) reexamined the kinetics by studying the dissolution rate of acid-washed siliceous skeletons and concluded that if the amount of skeletons was more than required for saturation of the water with respect to amorphous silica, the dissolution followed a first order reaction, but when the skeletons were not in excess the kinetics of dissolution appeared to be more complex. Kamatani et al. also developed an equation taking the rate of change of surface area into account. On the other hand, Kamatani and Riley (1979) have proposed a pseudo first order equation which seems to provide a simpler analysis in the case where the skeletons were not present in excess.

Except for several experiments, no systematic information of dissolution rates and dissolution sequences of different diatom species have been published. To fill this gap, laboratory experiments were conducted on living diatom assemblages. The present note is mainly to provide data for the rate coefficients of the dissolution of the skeletons of living diatoms using the simple equation of Kamatani and Riley (1979). In addition to this, the rate coefficients were recalculated from data obtained by previous workers. These results provide a clearer picture of the behavior and the fate of different diatom skeletons in the oceans than the approaches of previous workers.

Materials and Methods

Two different diatom assemblages were collected from the surface water in Tokyo Bay by net sampler. In the sample

collected in March, 1978 *Eucampia zoodiacus* dominated and *Coscinodiscus gigas* in the sample of October, 1978. Microscopic examination showed the presence of only a small amount of nonbiogenic silica, such as clay minerals in both samples, but the amount was considered to be negligible for the purposes of the present study.

Dissolution experiments were carried out using near-surface water (33.84‰ S, pH = 8.0) from Sagami Bay, Japan. The water was filtered through a 0.45 μm Millipore filter and was found to contain 0.04 mg SiO_2 l^{-1}. An appropriate amount of diatom assemblage (ca 30–50 mg SiO_2) was suspended in one liter of the filtered sea water. The suspension was stored in polyethylene bottles, and the bottles were kept in a thermostated dark-cabinet throughout the experimental period. At intervals, small aliquots of the sample were removed and centrifuged. The supernatant was decanted and used for the analysis of silica dissolved from the skeletons. During the first 10-d incubation, the samples were aerated with oxygen daily in order to maintain aerobic condition. After this period, aeration was carried out only when the sample was collected for experiments.

The suspended particulate silica which was collected on a 0.45 μm Millipore filter was fused with anhydrous sodium carbonate in a platinum crucible. After dissolving the cake in distilled water, a portion of the solution was analysed for silica. Reactive silicate in solution was determined by a colorimetric method described elsewhere (Kamatani, 1971).

Acid-washed siliceous skeletons were subjected to similar experiments for comparison with raw ones.

Results

For an approach to the dissolution of biogenous silica, a simple first order reaction equation was applied for estimating the overall dissolution rate coefficient (Kamatani and Riley, 1979); $dC/dt = -K$ $(C_0 - C)$ and the integration gives $Kt = -\ln((C_0 - C)/C_0)$, in which K is termed a "rate coefficient h^{-1}" is not a true kinetic equation, but simply a formula for calculating K from the initial concentration of biogenous silica (C_0) per unit volume of solution and concentration at some subsequent time t(C). This equation is essentially similar in form with that proposed by Nelson and Goering (1977) who used the term V_{dis} instead of K. It should be noted that K includes a term relating to the effective surface area of siliceous skeletons, because, in contrast to the acid-washed skeletons, those of living diatoms used in the present studies were protected with organic films. Thus it is impossible to evaluate the effective surface area of the skeletons; the effective surface area changes in time because of the bacterial decomposition of the protecting organic films. The rate coefficient, K (or V_{dis}) seems to be valuable for comparison with the specific uptake rate of silica by diatom to determine the balance between gains and losses of particulate silica (Nelson and Goering, 1977).
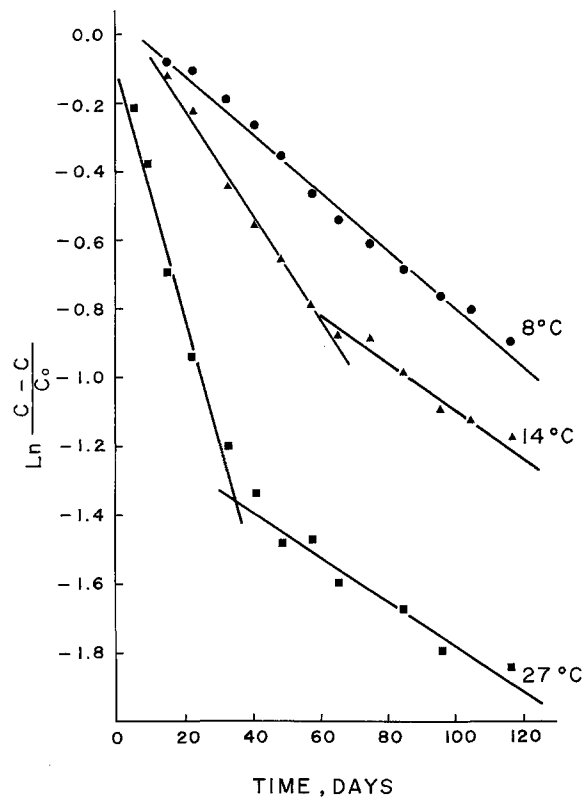

Fig. 1. *Eucampia zoodiacus*. Dissolution of siliceous skeletons as a function of time at various temperatures

The plots of $\ln((C_0 - C)/C_0)$ as a function of time are expected to make a linear relationship but actually show curvature corresponding to a decrease in rate of dissolution (Figs. 1 and 3). The curvature makes it difficult to assess the rate of dissolution. The curvature was then divided into two segments by the ratio of the slopes for various time intervals, and the rate coefficients K_1 and K_2, corresponding to the first and second stages were calculated from the mean slope.
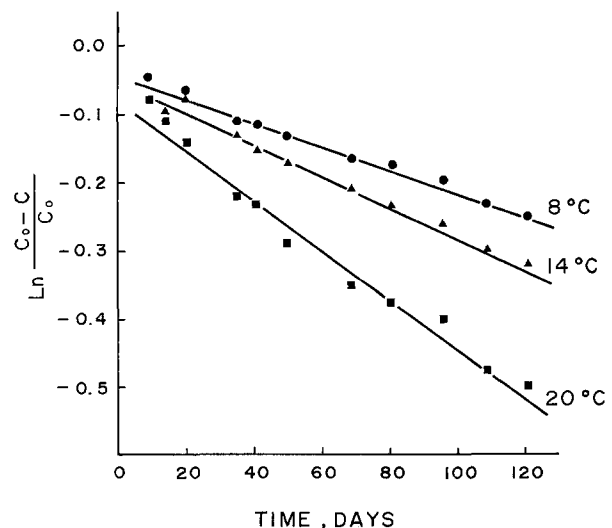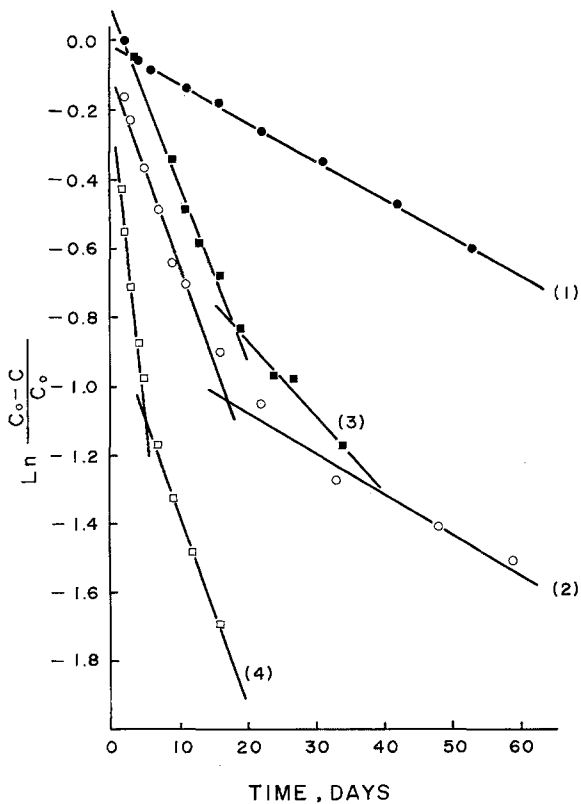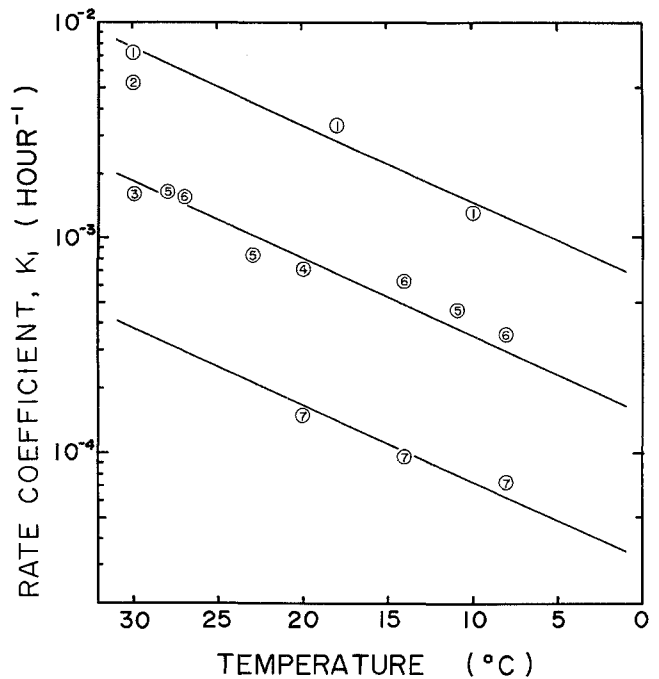

Fig. 2. *Coscinodiscus gigas*. Dissolution of siliceous skeletons as a function of time at various temperatures

TIME , DAYS

Fig. 3. Dissolution of silica from acid-cleaned siliceous skeletons and diatoms decomposing as a function of time. The numbers in parentheses correspond to the following treatments; (1): untreated *Coscinodiscus gigas,* (2): acid-cleaned skeletons of *C. gigas,* (3): untreated *Eucampia zoodiacus,* (4): acid-cleaned skeletons of *E. zoodiacus.* These experiments were carried out under shaking condition (120 strokes min^{-1}) at 20 °C

Fig. 4. Rate coefficients (K_1) plotted as a function of temperature. The numbers in circles correspond to the sample numbers in Tables 1 and 2

The experimental results for *Eucampia zoodiacus,* which were carried out at three different temperatures, are illustrated in Fig. 1. The run at 27 °C showed a transitional stage of the rate of dissolution around the 30th day, corresponding to the loss of about 75% of the siliceous skele-

tons. On the other hand, the sample run at 8 °C released silica at a slow rate and no clear change of the dissolution rate was observed throughout the experimental period. It can be seen from Fig. 2 that the dissolution of silica from *Coscinodiscus gigas* proceeds at a slow rate for the temperatures studied, and even at the end of the 20 °C experiment (120th day) the released silica is calculated to be only 40%. The rate coefficients calculated from each slope in Figs. 1 and 2 are shown in Table 1, where the rate coefficients at the second stage show to be 2.2 to 5.6 times smaller than those at the first stage.

Table 1. Rate coefficients of silica dissolution from diatoms decomposing at various temperatures

Sample No.	Species	Temperature (°C)	Initial concentration of biogenous silica (mg l^{-1})	Rate coefficient (h^{-1})	
				K_1	K_2
6	*Eucampia zoodiacus* (20 – 100)**	8	41.1	3.5×10^{-4}	–
		14	41.1	6.3×10^{-4}	2.9×10^{-4}
		27	41.1	1.5×10^{-3}	2.7×10^{-4}
7	*Coscinodiscus gigas* (150 – 300)**	8	29.8	7.3×10^{-5}	–
		14	29.8	9.6×10^{-5}	–
		20	29.8	1.5×10^{-4}	–
*	*Eucampia zoodiacus* (acid-cleaned)	20	48.9	2.1×10^{-3}	9.2×10^{-4}
		20	48.8	7.5×10^{-3}	2.4×10^{-3}
*	*Coscinodiscus gigas* (acid-cleaned)	20	42.5	4.7×10^{-4}	–
		20	44.9	2.3×10^{-3}	4.9×10^{-4}

* These experiments were carried out under shaking condition (120 strokes min^{-1})
** The figures in parentheses show the length of apical axis in μm (Kokubi, 1965; Yamaji, 1977)

Table 2. Rate coefficients of silica dissolution from diatoms decomposing at various temperatures

Sample No.	Species	Temperatur (°C)	Initial concentration of biogenous silica (mg l^{-1})	Rate coefficient (K_1) (h^{-1})	Reference
1	*Skeletonema costatum* (18 – 35)**	10	2.43	1.3×10^{-3}	Kamatani (1969)
		20	2.43	3.4×10^{-3}	
		30	2.43	7.2×10^{-3}	
2	*Cheatocerous gracilis* (4 – 7)**	30	3.30	5.3×10^{-3}	Kamatani (1969)
3	*Thalassiosira decipiens* (12 – 40)**	30	3.24	1.6×10^{-3}	Kamatani (1969)
4	Centric diatom	20	31.5	7.1×10^{-4}	Grill and Richards (1964)
5	Diatom assemblages	11	38.6	4.6×10^{-4}	Lawson et al. (1978)
		23	29.3	8.4×10^{-4}	
		28	10.7	1.7×10^{-3}	

** The figures in parentheses show the length of apical axis in μm (Kokubo, 1965; Yamaji, 1977)

It will be noted from Fig. 3 that there is considerable difference in the rate of dissolution between the acid-washed skeletons and those of living diatoms. By removing the organic films the rate coefficient (K_1) of *Coscinodiscus gigas* increased about 5 times and that of *Eucampia zoodiacus* ca 3.6 times (see Table 1). This suggests that the skeletons of living diatoms are protected from dissolution by organic or inorganic films to some degree and that the available surface area for dissolution must increase by removing the protective coatings. Fig. 3 also shows that shaking has a positive effect on the dissolution rate. The fact shows that diffusion was the rate controlling factor in this process. It therefore implies that the degree of diffusion induced by current in the oceans must have a great effect on the dissolution of particulate silica, particularly in the surface waters where a stronger current usually prevails than in the deeper waters.

Compared with the present studies, the rate coefficients re-calculated from data obtained by previous workers are summarized in Table 2 and illustrated in Fig. 4. This figure will give clues as to the relative preservation of diatoms falling in the water column as well as of skeletons buried in sediments.

Discussion

One purpose of this report is to provide data for the rate of dissolution of diatoms decomposing over a certain range of temperatures. One of the most interesting results is that the rate of dissolution differed from one species to another and the rate coefficients ranged over one order of magnitude, i.e. from 3.5×10^{-3} h^{-1} for *Skeletonema costatum* to 1.5×10^{-4} h^{-1} for *Coscinodiscus gigas* (at ca 20 °C, Fig. 4). This difference is considered to be mostly due to the physicochemical characteristics of siliceous skeletons and also to the organic or inorganic matter protecting the skeletons. Hecky et al. (1973) showed that

the decomposition of the organic materials associated with the cell walls varies from one species to another. This suggests that the rate of bacterial attack on the films may differ from one species to another and may control to some degree the rate of dissolution of the skeletons.

The results also show that the rate of dissolution decreases gradually as dissolution proceeds. This phenomenon could be ascribed to selective dissolution, which was supported by microscopical evidence (Kamatani and Riley, 1979): in the process of getting thinner, delicate parts of siliceous skeletons dissolve more rapidly than those which are robust, and a portion which has a rough surface becomes smoother. The decrease in specific surface area resulting from this latter process may well account for the fall observed in the rate of dissolution. The dissolution mechanism of siliceous skeletons which are protected with organic films is very difficult to interpret, but we can stress from the above results that in the natural environment the more fragmented siliceous skeletons, which would be found in deeper water, may dissolve more slowly than the skeletons which have a rapidly dissolving layer on the outside, usually found in surface waters.

From Fig. 4, the data plots between ln K_1 and temperature would be expected to be linear for all diatoms. Activation energies were calculated using the Arrhenius equation to be 13 700–13 800 cal mol^{-1}. From this we can make a simple predictive equation for the rate coefficient K_1 h^{-1} as a function of temperature:

$$\ln K_1 = \alpha + \beta\, T,$$

where α is the frequency factor depending on the properties of the diatom species, β is the temperature coefficient calculated from the slope of the line, and T is temperature in degree celsius. According to the calculation based on Fig. 4, α ranges from -7.35 to -10.38, and β is 0.0833 for all samples. Consequently we can say that the rate coefficient K_1, independent of species, increases by approximately 2.27 for each 10 C° rise in temperature. The above

equation should be valuable for estimating the decomposition rate and the fate of diatoms falling in a water column over a wide temperature range.

Information on sinking rate in addition to the rate of dissolution is required for the estimation of the proportion of diatom silica produced in the euphotic zone which may dissolve in transit through the water column. The sinking behaviour of diatom cell strongly depends on the shape and the size (Munk and Riley, 1952; Lerman et al., 1974). Arrayed in order of sinking rate of decreasing, for particles 5 μm in diameter: plate > cylinder > sphere; for those 50 μm: cylinder $\sim$ plate > sphere; while for 500 μm particles: cylinder > sphere > plate. The diagram of Lerman et al. suggests that a settling velocity of particle with a volume equivalent to a sphere differs over two orders of magnitude. Extrapolating to phytoplankton, very narrow cells of plate-shaped diatoms such as species of genera Eucampia and Climacodium would sink more rapidly than cylinder-shaped forms such as species of genera Rhizosolenia and Guinardia of similar size, but shows an opposite tendency as the size increases (Smayda, 1970). Data on in situ diatom density is as important as shape in determining sinking rate, but its density is not known to any precision. It is, therefore, very difficult to estimate accurately the sinking rate. However, one of the major aims of this report is to carry out order-of-magnitude calculations for the decomposing diatom skeletons in the oceans. Fig. 4 shows the evidence that the smaller diatom has a higher rate coefficient than the larger one: an initially large particle with a slow dissolution rate travels rapidly through the water column without a noticeable change in size, while a small particle with a faster rate of dissolution undergoes substantial loss in size over a short distance. The mean sinking rate of diatoms, except large ones such as the genus Coscinodiscus, is less than 1 m d^{-1} (Smayda, 1970). Assuming the rate coefficient in surface waters to be 5×10^{-4} h^{-1}, the siliceous skeletons lose about 90% of their silica before reaching 200 m, and if the rate coefficient is 1×10^{-3} h^{-1} the skeletons were dissolved completely within 100 m. Actually, the sinking rate of siliceous skeletons in a water column decreases gradually as the skeletons become smaller in size during the course of dissolution. Accordingly the diatom skeletons must become naturally buoyant at a shallower depth than was expected. Gilbert and Allen (1943) reported that diatom cell numbers decreased up to 400 times at the 300-m level relative to their numbers at the surface in the Gulf of California. A similar decrease of diatom cells with depth was also observed in the surface waters of the Antarctic (Kozlova and Mukhina, 1967).

In dealing with the rate of dissolution of diatom skeletons in a water column, a number of factors in addition to the simple physical and chemical ones mentioned above should be taken into consideration. One of them is zooplankton grazing; the diatom cells which are eaten by zooplankton would of course be excreted in the fecal pellets and this would provide further complications. The mean sinking rate of fecal pellets, ranging from 10 to $\sim$ 1000 m d^{-1}, was calculated to be approximately 150 m d^{-1} (Osterberg et al., 1963; Smayda, 1969; Wiebe et al., 1976; Turner, 1977; Honjo and Roman, 1978). Using a rate coefficient of dissolution of 10^{-4} h^{-1}, the diatom skeletons of which the sinking rate are accelerated by fecal transport lose only a few per cent of their silica before reaching the sea floor at a depth of 3 000 m. Fecal pellets therefore play the primary role as conveyers of intact diatom skeletons to the bottom layer. The rate coefficient of dissolution in the sediment from the central part of the Bering Sea was calculated to be between 6.9×10^{-9} and 2.7×10^{-8} h^{-1} (Kamatani and Riley, 1979) which is at least 3 orders of magnitude smaller than the rate coefficient expected from Fig. 4.

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