INTERACTIONS OF BIOGENIC OPAL, SEDIMENT, AND SEAWATER
IN THE CENTRAL EQUATORIAL PACIFIC

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By

David Crockett Hurd

Dissertation Committee

Keith Chave, Chairman
James Andrews
Brent Gallagher
Arthur Hubbard
Robert Buddemeier

We certify that we have read this dissertation and that in our opinion it is satisfactory in scope and quality as a dissertation for the degree of Doctor of Philosophy in Oceanography.

Dissertation Committee

Keith E. Chave

Chairman

Arthur Hubbard

James E. Andrews

Robert W. Buddemeier

Brent Gullay

ABSTRACT

The solution rate of biogenic opal in near-surface sediments in the Central Equatorial Pacific is three to eight orders of magnitude lower than similar acid-cleaned samples. Iron, magnesium, and calcium alumino-silicates may be the minerals which are forming on the surface of the opal and reducing its solution rate. The scale height of the system studied suggests that diffusive and not advective processes are primarily responsible for the removal of dissolved silica in sediments. Solution budget calculations for this area suggest that 90 to 99 per cent of the biogenic opal produced in surface waters dissolves before reaching the sediment-water interface; an additional amount dissolves within the sediment and diffuses into bottom waters leaving 0.05 to 0.15 per cent of the original amount of opal produced by organisms in the sedimentary record. The relative solution potential of the upper 1000 m of the water column varies by more than an order of magnitude from the Antarctic to the Equator and may have a pronounced effect on the accumulation rate of biogenic opal in underlying sediments.

TABLE OF CONTENTS

	Page
ABSTRACT	111
LIST OF TABLES	vi
LIST OF FIGURES	vii
CHAPTER I. INTRODUCTION	1
CHAPTER II. METHODS	3
CHAPTER III. RESULTS AND CONCLUSIONS	8
Qualitative Discussion of Field Data	8
Possible Alteration of Biogenic Opal	10
Uptake of Dissolved Silica by Authigenic Mineral Formation	11
Formation of Inorganic Surface Layer	14
Absence of Biogenic Opal	17
Qualitative Model of Opal Dissolution in Sediments	18
Mathematical Modeling of Dissolved Silica Gradients in the Sediments	18
Relative Importance of Diffusive and Advective Effects	18
Description of Variables in Mathematical Model	20
Application of Mathematical Model to Real Sediment Data	26
Comparison of Rate Constants from Model with Laboratory Data	31
Geochemical Implications	39
Flux of Dissolved Silica across the Sediment-Water Interface	39
Calculation of Solution Budget for Water and Sediment Columns	40

Relative Solution Potential of the Upper 1000 m of the Water Column as a Function of Latitude	45
Biological Considerations	48
Conclusions	50
APPENDIX A	53
APPENDIX B	61
APPENDIX C	69
BIBLIOGRAPHY	72

LIST OF TABLES

Table		Page
1	Station Data, R/V MAHI Cruise 1970, Leg 4, Guam to Guam	5
2	Semi-quantitative Mineral Analysis of Whole Sediment Using X-ray Diffraction and Smear Slides	13
3	Variables and Calculated Data Relating to Equation (5).	27
4	Surface Area in m^2/gm versus Depth in the Core for the Greater than 44μ Size Fraction of the Sediment	30
5	List of Variables and Calculated Data Relating to the Estimation of the Heterogeneous Solution Rate Constant for Biogenic Opal in the Sediment	32
6	Listing of Variables and Fluxes for Dissolved Silica from each Station	42
7	Difference in the Net Absorbances of Several Minerals under the Conditions of the Method	59

LIST OF FIGURES

Figure		Page
1	Station locations in the area of study	4
2	Concentration of dissolved silica versus depth for several of the stations studied	9
3	Scanning electron microscope photographs of authigenic mineral growth on the surface of a radiolarian . .	16
4	Average per cent opal (W/V) in the upper 40 cm of the sediment, per cm ³ of interstitial water versus k ₂ S, the combined solution rate constant and surface area term	29
5	Heterogeneous solution rate constant of acid-cleaned biogenic opal as a function of pH at 3 ± 1°C . . .	33
6	Heterogeneous solution rate constant of acid-cleaned biogenic opal as a function of pH at 23 ± 1°C . . .	34
7	Solubility of biogenic opal as a function of pH and temperature	35
8	Variation of relative solution potential, amorphous silica production, and per cent amorphous silica in the sediment, as a function of latitude along 170°W longitude	46
9	Standard curve of net absorbance (absorbance - reagent blank) versus weight per cent opal in standard clay mixtures	56

CHAPTER I

INTRODUCTION

Studies of dissolved silica concentrations and gradients in the interstitial waters of modern deep-sea sediments reveal much about the chemical reactions of biogenic opal, and of silicate minerals in general. They also further test the validity of models that have been proposed concerning long-term pH and dissolved silica control in the oceans (Sillén, 1967; Broecker, 1971; Mackenzie et al., 1966; Holland, 1972).

Although several thousands of dissolved silica analyses have been done on deep-sea sediment interstitial waters in the last 30 to 40 years, only a few hundred have been done on water squeezed from the sediment at the in situ bottom temperature of 1° to 3°C. Fanning and Pilson (1971) have shown that as the temperature of squeezing increases from 3°C to 21° to 23°C, the dissolved silica concentrations in a sediment sample may increase 40 to 60 per cent. Their observation indicates that previous statements (Bischoff et al., 1970; Fanning et al., 1969; Harriss et al., 1966; Siever et al., 1965) concerning the saturation of interstitial waters with respect to amorphous silica (ca. 1000 μM dissolved silica at 3°C; Alexander et al., 1953; Siever, 1962; Hurd, 1972) may be in doubt because most of their samples were processed at temperatures greater than 1° to 3°C.

This work will attempt to answer the following questions from both a physical-chemical and geochemical point of view:

- 1) What reactions control the concentration and rate of release of dissolved silica in sediments?
- 2) Are present mathematical models describing the change in the concentration of dissolved silica with depth in a sediment as a function of the relative rates of supply and removal adequate; if not, how may these models be realistically improved?
- 3) What are the dissolution kinetics of the dissolution of acid-cleaned biogenic opal in seawater at different values of temperature and pH; how do the dissolution kinetics of the acid-cleaned opal in seawater relate to those of opal in deep-sea sediments?
- 4) What are the fluxes of dissolved silica from the surfaces of the sediments studied; how do these fluxes relate in magnitude to the amount of solution occurring in the water column above the sediment?
- 5) What possible effects do the changes in the temperature and pH of the upper 1000 m of the water column have on the stability of descending siliceous tests?

CHAPTER II

METHODS

Aboard the R/V MAHI in the fall of 1970, near-surface sediments were sampled at 13 stations using free-fall or boomerang coring devices. Three to five cores were taken at each of the locations shown in Fig. 1 and Table 1. The cores were brought on board within 2 to 3 hours after the release of the corers from the ship and stored at ca. 3°C for one day. They were then cut into 10-cm sections and squeezed in a refrigerator at $3 \pm 1^\circ\text{C}$. The sediment squeezers were of the all plastic type (Reeburgh, 1967) in which gas pressure (at no time greater than 100 lbs/in²) acting on a rubber diaphragm compresses the sediment and forces the interstitial water through filters into a sample bottle. The expressed water was immediately analysed for dissolved silica (Strickland and Parsons, 1969).

A portion of each of the squeezed sediment samples was dried at 110°C and finely ground. Calcium carbonate was determined by the volume of CO₂ gas released when a given weight of sample was treated with dilute HCl at 25°C, 1 atm pressure (Hulsemann, 1966). The volume of gas obtained was then compared with a standard curve showing volume of gas released versus weight of A.R. calcium carbonate added.

The terms biogenic opal and amorphous silica have been used by different authors to describe the same substance (Iler, 1955; Siever, 1962; Jones, 1969; Huang and Vogler, 1972; Lisitzin, 1972; Heath,

Figure 1. Station locations in the area of study.

Table 1. Station Data, R/V MAHI Cruise 1970, Leg 4, Guam to Guam

Station Number	Location		Water Depth	Micropaleontological age
	Latitude	Longitude	meters	of radiolarians, upper 20 cm of core
90	2°46'N	145°39'E	4525	Holocene-Pleistocene
91	1°52'N	151°31'E	4810	Holocene-Pleistocene
92	0°31'S	161°49'E	4250	Holocene-Pleistocene
93	8°07'N	174°24'W	6000	Holocene-Pleistocene
94	11°37'N	163°20'W	5160	Eocene with upper Miocene contam.
95	9°58'N	163°40'W	4335	upper Miocene-lower Pliocene
96	4°59'N	168°00'W	5400	mixed Holocene and upper Miocene
97	2°39'N	176°56'W	5400	upper Miocene
98	3°02'N	174°55'E	5000	Pliocene
99	3°46'N	171°20'E	4280	Holocene-Pleistocene
100	5°33'N	164°34'E	4670	Holocene-Pleistocene
101	8°43'N	154°35'E	5300	Holocene-Pleistocene
102	11°38'N	148°05'E	5710	Holocene-Pleistocene

in press). In this study the two terms will be used interchangeably, with the choice of term depending on the particular reference cited. A number of methods for determining opal in soils and deep-sea sediments have been presented in the last 15 years (Bezrukov, 1955; Calvert, 1966; Chester et al., 1968; Weaver et al., 1968; Jones, 1969). The method used in this study is an improvement of earlier wet-chemical methods, in that an internal standard made up of silicate minerals is used to correct for dissolved silica release when a sample containing them is analysed. The experimental details and a discussion of the method are given in Appendix A.

The weight per cent organic carbon in each sediment sample was determined on freeze-dried samples by a modified method of Strickland and Parsons (1969). A portion of the freeze-dried sample (0.5 to 0.7 gm) is suspended in 250 cm³ of low-organic carbon water with ultrasonics and two 5 cm³ aliquots are placed in glass ampules; phosphoric acid and potassium persulfate are added and the inorganic carbon removed by passing nitrogen gas through the sample; the ampule is then sealed with a torch, autoclaved for about 1 hour; the amount of CO₂ released when the organic carbon is oxidized is estimated by flushing the ampule with nitrogen gas and passing the gas mixture through a non-dispersive infrared absorption gas analyser.

Weight per cents of sediment greater than 44 μ and less than 4 μ sizes were determined by standard sieving and pipetting techniques (Folk, 1965). Porosity, per cent water and the grain density (grndns) of the sediment were determined on one of the duplicate cores from each station by the Hawaii Institute of Geophysics core

lab. Values for the above determinations versus depth for each core are listed in Appendix B.

CHAPTER III

RESULTS

Qualitative Discussion of Field Data

Before any specific mathematical models are applied to the data, a general inspection of the dissolved silica gradients and their final concentrations in the cores should be made to estimate the complexity of the system. Figure 2 shows typical gradients from several of the stations. The vertical and horizontal lines through each data point show the length of core squeezed and the standard deviation of the dissolved silica determination, respectively. The curve connecting each set of data points was generated by a computer best-fit of these points; it will be discussed in more detail in another section of this study (Description of Variables in Mathematical Model).

Two observations are clear from the figure: (1) Since most of the changes in concentration occur within 30 to 40 cm of the surface of the sediment, the 1-m length of core used here should be sufficient for this type of study. (2) None of the final concentrations at the bottom of the cores are more than 50 to 60 per cent of the saturation value of opal at 3°C, i.e., ca. 1000 μM . This second observation suggests that one or more of the following are at work: (a), the biogenic opal has undergone some chemical change in crystal structure towards a more stable, less soluble form (quartz, tridymite, or cristobalite); (b), authigenic reactions are occurring which are

Figure 2. Concentration of dissolved silica versus depth profiles for several of the stations studied. Station number is given beside each array of points. Curves drawn by computer best-fit using equation (5).

consuming the dissolved silica as fast as it is produced; (c), an inorganic reaction product has formed on the surface of the solid and is effectively halting the release of dissolved silica; or (d), no biogenic opal is present and the dissolved silica concentration is being controlled by other silica-containing minerals. Let us examine each of the foregoing in turn.

Possible Alteration of Biogenic Opal

X-ray diffraction of dried sediment samples from each core showed small peaks in the $4.04 \text{ \AA}$ area of several of the samples, possibly indicating tridymite or cristobalite. Since this value also is in the general range of several plagioclase feldspars which may also be present, no positive identification could be made. Quartz was found in all samples, both by X-ray diffraction and by microscopic examination of smear slides. However, Rex and Goldberg (1959) indicate such quartz is largely detrital, more than likely resulting from aeolian transport. In any case, as shown by Stöber (1967), the dissolution rate constant of vitreous silica (i.e., amorphous silica gel which has been dehydrated and fused by firing) is more than ten times that of cristobalite, tridymite or quartz. Since the rate of dissolution of opal has also been suggested to be a function of its water content (Huang and Vogler, 1972), biogenic opal should dissolve even faster than the vitreous silica because the opal has a higher water content.

Therefore, under the same conditions of temperature, degree of

undersaturation of solution, and surface area of solid per unit volume of solution, biogenic opal should dissolve much faster than the other above-mentioned silica minerals. In addition, the dissolved silica concentrations below 30 to 40 cm in the cores of this study are greater than or equal to the saturation values of quartz and cristobalite at this temperature (Heath, in press). Finally, sieved, acid-cleaned samples of radiolarians from all of the surface sediments studied gave dissolved silica saturation values at 23°C that equaled that of amorphous silica, even though several of the stations contained Eocene age radiolarians (Table 1; Theyer, 1972). The hypothesis that the crystal structure of the biogenic opal in the first meter of sediment has changed to a more stable, less soluble form which controls its solubility does not therefore appear justified. In addition, since the lower portions of the cores studied are super-saturated with respect to the other silica minerals discussed, these minerals cannot be a source of dissolved silica to the interstitial waters.

Uptake of Dissolved Silica by Authigenic Mineral Formation

Helgeson et al. (1969) and Helgeson and Mackenzie (1970) present theoretical logarithmic activity diagrams which describe the existence of solid mineral phases as a function of the activities of hydronium ions, silica molecules, and the dissolved cations Ca^{+2} , Mg^{+2} , Na^{+} , and K^{+} . Unfortunately these workers gave no confidence limits for any of the stability fields, and such diagrams are therefore only

useful as semi-quantitative guidelines in general situations.

Bearing this limitation in mind, the diagrams are seen to imply that at the in situ pH and temperature of deep-sea sediments (6.9 to 7.3, 1° to 3°C) the following minerals are in near-equilibrium with dissolved silica: sodium plagioclase feldspar, kaolinite, potassium orthoclase feldspar, magnesium and sodium montmorillonite, leonhardite, sepiolite and talc. All but the last three have been qualitatively identified by X-ray diffraction analysis in a number of the cores studied. The results of these analyses are given in Table 2. The existence of the minerals in the sediments suggests that they possibly are a sink for dissolved silica. However, data from other areas using oxygen and hydrogen (Savin and Epstein, 1970) and strontium (Dash, 1969) isotopic analysis of pelagic silicate minerals suggest that, in detrital minerals, no wide-scale transformation (with the exception of ion exchange) is occurring in Recent sediments. The minerals montmorillonite, phillipsite, clinoptilolite, heulandite, harmotome, and the ferromanganese suite which forms manganese nodules, are presently forming within the sediment, but these reactions generally result from the alteration of volcanic ash and basalt (Rex, 1967; Dasch, 1969; Morgenstein, 1967; Bonatti and Nayudu, 1965; Keller, 1970). Therefore, if authigenic reactions are consuming dissolved silica as fast as it is being released from the biogenic opal, the rate of release must be extremely slow.

Table 2. Semi-quantitative Mineral Analysis of Whole Sediment Using X-ray Diffraction and Smear Slides

Station	X-ray diffraction, whole sample				X-ray diffraction, less than 4 μ size fraction			Smear slide, whole sample
	Ca, Na-spar	K-spar	Qtz	Zeol.	Montmor.	Illite	Kaolinite	Volcanic glass
90	x		x		x	xx	x	x
91	x		x		x	xx	x	x
92								
93	x	x?	x		x	xx	x	
94	xx	x	x	xx	x	x	x	
95	x	x?	x		x	xx	x	
96	x		x		x	xx	x	x
97	x		x		xx	x	x	x
98	x		x		x	xx	x	x
99			x		x	xx	x	
100	x		x		x	xx	x	x
101	x	x	x		x	xx	x	xx
102	xx	x?	x		x	xx	x	xx

x = present; xx = relatively abundant

Formation of Inorganic Surface Layer

In those sediments under study characterized by noticeable manganese nodule formation (Stations 94, 95, 96, 98 and 101), many of the spongy-structured radiolarians are iron-stained. Lewin (1961) reported that pre-treatment of acid-cleaned diatoms with various metal ions at pH values near those in interstitial waters inhibits solution rates. The pH_{zpc} (the pH at which the surface of a solid in solution has no net charge) for amorphous silica is 2; above that value the surface charge becomes increasingly negative because of the dissociation of the silanol groups at the solid's surface. This negative charge then becomes more effective as a cation complexor, as Iler (1955) and Stumm and Morgan (1970) have pointed out. Dugger et al. (1964) determined the free energy of the complex formation reaction

and found that these values showed a strong inverse relationship with the log of the first hydrolysis constant of each ion. The implications of the latter are that the SiO^- and OH^- groups react similarly toward the same metal ion; i.e., those metal ions which hydrolyse readily at a particular pH may also be complexed by the silica surface at nearby pH values. Using metal ion distributions as given by Dugger et al. for the above reaction at pH 7 and 5°C, the following ions were found to be strongly bound to the silica

surface (i.e., at least half of the available silanol groups would be complexed by these metal ions at their concentrations in seawater if each were the only complexable ion in solution): Ca^{+2} , Mg^{+2} , Al^{+2} , Fe^{+3} , La^{+3} , Cr^{+3} , Th^{+3} , and UO_2^{+2} . The above theoretical evidence (Dugger et al.) and laboratory evidence (Lewin) then suggest that it is quite possible for inorganic ions to be absorbed to the surface of the opal and that such absorption can reduce the solution rate of the opal. Three additional observations lend credence to the concept of the inorganic layer: (1) Samples of biogenic opal from station 96 in this study were cleaned by sieving and heating with dilute HCl at 60°C in an ultrasonic bath for one hour. The opal was then dissolved in HF and analyzed by the Hawaii Institute of Geophysics Geochemistry Lab for transition elements. Iron, manganese, copper and zinc were found in the ppm range and above. Whether or not these elements are actually within the matrix of the test is not known at this time; if they are, the sedimentation of siliceous tests may provide a more rapid removal mechanism for transition elements from surface waters. In any case, it may be that as the biogenic opal dissolves, an incongruent solution process occurs yielding metal oxide or disordered metal silicates at the surface of the solid. (2) In fact, minerals have been found growing on the surface of radiolarian tests from sediments near the area of study. One of the sediment samples from east of the Line Islands (Lat. 8°16'N, Long. 155°51'W) was treated by sieving and washing three to four times with distilled water. Several of the remaining radiolarians were analysed by scanning electron microscopy. Figure 3 shows one

600X

6000X

Figure 3. Scanning electron microscope photographs of authigenic mineral growth on the surface of a radiolarian.

of the radiolarians with one or more unidentified minerals on its surface. While these minerals do not completely cover the surface, their presence suggests that the opal surface does accept authigenic mineral formation. (3) Recent studies by Christ et al. (1972) on the determination of the activity-product constant of well-crystallized sepiolite suggests a value of $10^{-41.8}$ at 0°C. Assuming an activity coefficient of 1 for the dissolved silica molecule, 0.36 for Mg^{+2} (Garrels and Christ, 1965), the formula $(Mg^{+2})^2(H_4SiO_4)^3(OH^-)^4$ for sepiolite, and a pH of 6.9-7.3 at 1-3°C for the interstitial waters of the sediments and the final concentrations of dissolved silica at the bottom of each core, 12 of the 13 cores studied are then at equilibrium with sepiolite. The mineral may form readily on the surface of the opal since an earlier discussion suggested that conditions in the sediment were favorable for Mg^{+2} absorption. Once formed, such a layer would reduce the solution rate of the opal.

Absence of Biogenic Opal

All of the samples in this study showed biogenic opal was present throughout the cores. Its presence was determined chemically and by microscopic examination of smear slides. Therefore, it would appear that biogenic opal is the probable major source of dissolved silica in sediments.

Qualitative Model of Opal Dissolution

The general model we now propose is as follows: as soon as it is deposited, biogenic opal begins to interact with the sediment. A porous reaction layer commences to form on the surface of the opal; this layer allows release of dissolved silica from the opal but at a rate much lower than acid cleaned opal dissolving at in situ temperature and pH conditions. The layer continues to accrete until a steady state is reached in which dissolved silica released from the opal is either completely taken up by authigenic silicates or the reaction layer becomes thick enough to halt the release of dissolved silica. Below this level in the sediment, interstitial dissolved silica concentrations remain constant until equilibrium conditions are altered by changes in temperature or by the conversion of opal to one of the more stable forms of silica.

Mathematical Modeling of Dissolved Silica Gradients in the Sediments

Relative Importance of Diffusive and Advective Effects

Before we begin discussion of the actual mathematical model, the relative importance of diffusive and advective processes must be considered. A dissolved substance can be transferred from interstitial waters to bottom waters in one of two ways: (a) by molecular diffusion, along a concentration gradient of the dissolved substance; (b) by compaction of the sediments with depth and the

resultant expression of water from these sediments (an advective process). The process of diffusion has been compared with those of advection by determining the scale height of the system concerned (Lerman, 1971). The scale height is defined as the ratio of the diffusion coefficient D in $\text{cm}^2 \text{sec}^{-1}$ to the sedimentation rate U in cm sec^{-1} . This ratio produces a length in cm which is characteristic for a given system. If the only changes in concentration of a dissolved substance occur over distances from the sediment-water interface which are small relative to the scale height of the system, then diffusive processes are primarily responsible for removal of the dissolved substance from the sediment. Alternatively if the concentration gradient extends over distances greater than the scale height, then the advective processes (of water removal by sediment compaction) are more important. For example, if we assume a D range of 1 to $10 \times 10^{-6} \text{cm}^2 \text{sec}^{-1}$ (Duursma and Bosch, 1970) and a U range of 1 to $10\text{mm}/1000$ years (Lisitzin, 1972) for most open-ocean sediments, then the scale height range is about 30 to 3000 meters. Obviously, changes in concentration of dissolved silica which occur in the upper 30 to 40 cm of the sediment result primarily from diffusive processes. Furthermore, the porosities determined for each core were essentially constant and did not decrease with depth, again indicating that substances are not being expressed from the sediment by compaction at rates comparable to those by diffusion.

Description of Variables in Mathematical Model

Several mathematical models have been proposed to describe the diffusion of dissolved substances to and from sediments (Crank, 1957; Duursma and Bosch, 1970; Anikouchine, 1967; Tzur, 1971; Lerman and Weiler, 1970). The terms in these proposed equations describe changes in the concentration of a dissolved substance with depth in the core as a function of the sedimentation rate, the change in porosity with depth in the core, the rate at which the dissolved substance is being supplied or consumed within the core; and the apparent diffusion coefficient of the substance. These equations further assume that: the sedimentation rate is constant; the sediments are homogeneous in structure and uniform in mineral and chemical composition; the chemical reactions supplying dissolved substance obey first-order kinetics; the apparent diffusion coefficient is constant; and there is lateral homogeneity in the sediment so that a one-dimensional treatment is adequate. A further assumption for this study is that biogenic opal is the source of the dissolved silica in the interstitial water and is constantly dissolving. This last assumption is reasonable since none of the cores used in this study were saturated with respect to amorphous silica, yet all contained some of the mineral.

The following discussion concerns equations originally suggested by Crank (1957) and later modified by Anikouchine (1967). The distribution of dissolved silica with depth in a core, as a function of removal by diffusion and supply by solution of biogenic

opal, is described by:

$$\frac{C_z - C_F}{C_0 - C_F} = \exp [z(k_1/D)^{1/2}] \quad (2)$$

where C_0 , C_z , and C_F are the dissolved silica concentrations, in moles cm^{-3} , at depths zero, Z , and the bottom of the core (Z is the distance from the sediment-water interface in cm, and increases negatively downward); k_1 is the apparent first-order rate constant describing the solution of the most readily soluble silica-containing mineral, in sec^{-1} ; and D is the apparent diffusion coefficient of the dissolved silica molecule, in $\text{cm}^2 \text{sec}^{-1}$.

In fitting the data of this study to the above equation, an estimate had to be made of C_0 . The concentration of dissolved silica below 4500 m for the Central Equatorial Pacific is $150 \pm 5 \mu\text{M}$ (Bogoyavlensky, 1967); since other samplings of near-bottom waters in the Pacific (Culberson, 1972) and Atlantic (Fanning and Schink, 1969) have shown no consistent increase in dissolved silica to within $\frac{1}{2}$ m of the sediment-water interface, this value will be used for C_0 .

The diffusion coefficient of the silicate molecule in the interstitial waters of sediments is a function of temperature, solution viscosity, any exchange reaction the molecule may have with the sediment, and the tortuosity or mean free path per unit length perpendicular to the sediment-water interface traveled by the molecule. It is assumed that changes in temperature and solution viscosity in the upper meter of sediments are too small to affect

the diffusion coefficient calculations in this work. If the surfaces of the minerals in the sediment are not saturated with respect to their ability to adsorb dissolved silicate, there will then be a net retardation of the molecules as they diffuse through the sediment, and the apparent diffusion coefficient will have an even smaller value (Duursma and Bosch, 1970; Manheim, 1970). However, if the sediments are saturated there will be no net retardation effect; for an individual molecule to react with any surface it must in effect dislodge another dissolved silica molecule. Experiments are currently underway to determine the magnitude of this retardation effect; however, the following calculations assume no net retardation. Wollast and Garrels (1971) have determined that the self-diffusion coefficient of dissolved silica in seawater at 25°C is $1.0 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$, and Manheim (1970) has suggested that at 0°C this value is halved. Turk (1972) using resistivity measurements in clays has derived the following empirical relationship:

$$\log (D_{\text{sed}}/D_{\text{sol}}) = 0.0165 (\text{porosity}) - 1.65 \quad (3)$$

where D_{sed} and D_{sol} are the diffusion coefficients in the sediment of a given porosity and in free solution in $\text{cm}^2 \text{ sec}^{-1}$, and porosity is in per cent. It is suggested that the above equation corrects the apparent diffusion coefficient for tortuosity in most pelagic sediments for the following reason: for a given sediment the porosity gives the volume percentage of sediment which is occupied

by liquid; if the solid is fine grained and uniformly dispersed throughout the liquid, then diffusion along a concentration gradient through this liquid will be hindered to an extent proportional to the number of particles obstructing the mean free path of the diffusing substance; as the porosity decreases, the tortuosity or extra distance the diffusing substance must travel around the obstructing particles will increase; since most of the pelagic sediments in this study contain large amounts of fine-grained material (see Appendix B), equation (3) should be realistic in its correction of the diffusion coefficient for tortuosity in terms of porosity.

The first order congruent solution of amorphous silica is described by the equation

$$dC/dt = k_2 (C_{\text{sat}} - C_{\text{sol}}) S \quad (4)$$

where k_2 is the first order rate-constant in cm sec^{-1} ; C_{sat} and C_{sol} are the concentrations of a solution saturated at a particular temperature and pH, and the solution being observed at time t in moles cm^{-3} ; and S is the surface area of the solid per unit volume of solution in cm^{-1} (O'Connor and Greenberg, 1958). Since this equation also describes the solution rates of biogenic opal (Hurd, 1972), the k_1 of equation (2) equals the $k_2 S$ in equation (4); i.e., k_1 must implicitly contain a surface-area-per-unit-volume term because the solution of a solid is a heterogeneous reaction. Equation (2) is then replaced by the following equation, in which all

of the terms have been previously defined:

$$\frac{C_Z - C_F}{C_O - C_F} = \exp [Z(k_2 S/D)^{1/2}] \quad (5)$$

In equation (5), however it is assumed that one of the variables controlling the rate of diffusion of dissolved silica from the sediments, $(C_O - C_F)$, is equal to an analogous expression in equation (4), $(C_{sat} - C_{sol})$, which controls the dissolution rate of opal in seawater. This assumption is valid only if $C_F = C_{sat}$. However, in the sediments of this study the mean $(C_O - C_F)$ difference is 270 μM , while the mean $(C_{sat} - C_{sol})$ difference (assuming $C_{sat} = 1000 \mu\text{M}$ and $C_{sol} = C_F$) is 580 μM , or about twice the $(C_O - C_F)$ value. While this difference will not affect calculations relating to the flux of dissolved silica across the sediment-water interface, estimations of the k_2 for opal in the sediment may be in error by a factor of two.

It should also be noted that the geometric configurations of the tests of silica-secreting organisms in general and radiolarians in particular can be quite complex. It is intuitively obvious that the BET-measured specific surface area (Weiler et al., 1965) of the tests may be much larger than the effective area available for solution; the inner portions of spongy-structured radiolarians will dissolve less rapidly because of over-lapping diffusion halos resulting from hindrance of solution flow through the structure.

Thus, the value of k_2 for the radiolarian mixture must be larger by some amount than for opal of the same type but of a more regular geometrical structure, i.e., rods, plates, or spheres.

Furthermore, if D is a function of temperature, viscosity, porosity, and ion exchange reactions; and S is a function of the species of plant or animal skeleton, degree of dissolution, and weight per cent opal per unit volume of interstitial water; and k_2 is a function of temperature, pH, type of opal and covering or layer on the surface of the opal in the sediment, these three "constants" in equation (5) are indeed complex variables, and each must be differentiated or integrated separately to arrive at an equation similar to equation (5). It may be observed here that such an exercise is of academic interest only and not related to the cores studied for the following reason:

Physical and mineralogical properties such as porosity, the specific surface area of the biogenic opal, the weight of opal per unit volume of sediment, and the solution rate constant of the opal are not constant with depth in a core nor do these properties appear to vary with depth in any consistent fashion. This amount of variation puts limits of accuracy on the order of $\pm 50\%$ for any one calculation. While ideal sediment types with constant productivities in the waters above the sediments and constant sedimentation rates may exist, they were not evident in this study.

The data in Appendix B for dissolved silica versus depth Z were

fitted to equation (5) in the following manner: theoretical curves for each station were generated by substituting values for k_2S/D , and the sum of the absolute differences between real and artificially generated data points obtained. The value of k_2S/D giving the least absolute sum was chosen as the best fit. The values of k_2S/D and the estimated apparent diffusion coefficient for each station are given in Table 3.

Application of Mathematical Model to Real Sediment Data

Before a k_2 for opal in sediments can be obtained we must first understand the implications of equation (4) with respect to the k_2S/D term in equation (5). In equation (4) the solution rate is a function of the rate constant, the degree of saturation of the solution and the surface area of the solid per unit volume of solution. If the surface area is doubled but the other factors are held constant then the solution rate will double; by the same token if the amount of solid per unit volume of solvent is doubled the rate will also double. This concept can be applied to sediments by analyzing the sediment solid phase for opal and correcting for the volume of sediment taken up by the solid phase by using the sediment porosity. This calculation yields weight per cent opal per unit volume of interstitial water; the solution rate of opal in the sediment should be proportional to this value assuming that the k_2 and the specific surface area for the opal are the same in all of the sediments. Under these same conditions a plot of weight per cent biogenic opal

Table 3. Variables and Calculated Data Relating to Equation (5)

Station	K_2 S/D Ratio, 10^{-3} cm^{-2}	Apparent D, $10^{-5} \text{ cm}^2 \text{ sec}^{-1}$	K_2 S, 10^{-8} sec^{-1}	Depth in sediment above which 90% of the opal solution occurs, cm.
90	26	$0.31 \pm .03$	$8 \pm .8$	15
91	26	$0.31 \pm .03$	$8 \pm .8$	15
92	6	* $0.18 \pm .02$	* $1 \pm .1$	30
93	15	$0.39 \pm .04$	$6 \pm .6$	19
94	6	* $0.37 \pm .04$	* $2 \pm .2$	30
95	41	$0.17 \pm .03$	7 ± 1.4	12
96	70	$0.36 \pm .05$	25 ± 4.0	9
97	21	$0.39 \pm .04$	8 ± 1.0	16
98	105	$0.31 \pm .05$	33 ± 6.0	7
99	31	$0.18 \pm .01$	$6 \pm .3$	13
100	11	$0.28 \pm .04$	$3 \pm .4$	22
101	165	$0.28 \pm .07$	46 ± 12.0	6
102	31	$0.25 \pm .06$	8 ± 2.0	13
	mean 43	mean $0.29 \pm .04$	mean 12 ± 1.7	mean 16

*Estimated value; physical properties not determined on core

per unit volume of interstitial water versus the $k_2 S$ term for each suspension should be linear because an increase in the amount of suspended solid could only increase the value of S . Figure 4 shows such a plot for the stations of this study. In this figure the weight percentages, porosity, and grain density were obtained from data in Appendix B; $k_2 S$ values were obtained by multiplying the $k_2 S/D$ ratio for each station in Table 3 by its corresponding apparent diffusion coefficient. The vertical and horizontal lines through each point represent the standard deviations of the weight per cent opal and $k S$ ratios respectively.

Figure 4 shows a fair degree of spreading in the data points. One possible reason for this spread is seen in Table 4; i.e., the average specific surface area of the size fraction studied is about $115 \text{ m}^2 \text{ gm}^{-1}$, but the range of values within a single core and from one core to the next may be as much as 30 to $300 \text{ m}^2 \text{ gm}^{-1}$. It should be noted that washing the sediment with distilled water or dilute HCl increases the specific surface area (Weiler et al., 1965) perhaps by removing minerals adsorbed to the surface of the opal which are blocking its pore structure. It appears to us that the larger surface area is more realistic for our estimations of k_2 in the sediment since all of the surface of the opal is a source of dissolved silica, even though it may be covered with a solution-inhibiting layer. Assuming that the specific surface area for all size fractions of opal is the same and that a realistic value of S for each station may be obtained by multiplying the averaged specific surface areas for each station by the weight of opal per unit volume of interstitial

Figure 4. Average per cent opal (W/V) in the upper 40 cm of the sediment, per cm^3 of interstitial water versus k_2S , the combined solution rate constant and surface area term.

Table 4. Surface area in m^2/gm versus depth in the core for the greater than 44μ size fraction of the sediment. Samples were obtained by sieving sediments from several depths in each core and measuring the specific surface area of the radiolarians and diatoms in the greater than 44μ size fraction by nitrogen adsorption; samples having more than 1 per cent calcium carbonate were washed with dilute HCl; those with microscopically obvious contaminants were not run.

Station	Depth in core (cm)					
	0-10	10-20	20-30	30-40	40-50	50-60
90		113 $\pm$ 5		25 $\pm$ 3	19 $\pm$ 3	
91		100 $\pm$ 10		124 $\pm$ 5	92 $\pm$ 8	
92	*289 $\pm$ 20	*314 $\pm$ 20		*151 $\pm$ 10		
93		156 $\pm$ 10	114 $\pm$ 5			65 $\pm$ 10
94						
95		*111 $\pm$ 10	* 91 $\pm$ 10	* 82 $\pm$ 7		
96		117 $\pm$ 10		92 $\pm$ 3	72 $\pm$ 4	
97	110 $\pm$ 5	80 $\pm$ 3				43 $\pm$ 4
98		32 $\pm$ 3		52 $\pm$ 5	65 $\pm$ 5	
99		*223 $\pm$ 15	*350 $\pm$ 20		*300 $\pm$ 20	
100	33 $\pm$ 3		29 $\pm$ 5		53 $\pm$ 3	
101						
102						

* Sample treated with dilute HCl to remove carbonates.

water, the data in Table 5 result. In this table also are estimates of the rate constant k_2 which were obtained by dividing the value of $k_2 S$ for each station by our above estimate of S . The two order of magnitude range of these calculated k_2 values suggests that the above mentioned spread of data-points in Figure 4 must be a combined surface area and rate constant effect. Some similar process may be controlling the over-all solution of opal in these sediments, however, since seven of the ten cores in Table 5 have k_2 values within one standard deviation of the estimated mean k_2 value for these cores.

Comparison of Rate Constants from Model with Laboratory Data

When acid-cleaned biogenic opal from a deep water sediment sample (Lat. $9^{\circ}16'N$, Long. $155^{\circ}51'W$) was dissolved in buffered seawater and 0.7M NaCl solutions as a function of temperature and pH, the data shown in Figures 5, 6 and 7 result. The details of this procedure are given in Appendix C. The data in Figure 5 suggest that at the in situ pH and temperature of deep-sea sediments (6.9 to 7.3, 1 to $3^{\circ}C$) the k_2 of this material is in the range 3 to 6×10^{-9} cm sec $^{-1}$, a difference of three orders of magnitude from the mean k_2 of Table 4!

The following arguments may help to clarify this incongruity:

1) If the tests were close-packed, the apparent k_2 of the opal in the sediment would be reduced (Greenberg, 1957; Hurd, 1972), because overlapping diffusion halos would reduce the value of the term $(C_{sat} - C_{sol})$ in equation (4). However, if such were the case, the solution would still eventually become saturated with respect to

Table 5. List of Variables and Calculated Data Relating to the Estimation of the Heterogeneous Solution Rate Constant for Biogenic Opal in the Sediment

Station	Average specific area, greater than 44 μ size fraction, upper 40 cm	Average amount of opal in the upper 40 cm of the sediment	Estimated heterogeneous solution rate constant, k_2
	(cm^2/mg)	(mg/cm^3)	(10^{-3} cm/sec)
90	700 $\pm$ 350	23	50 $\pm$ 35
91	1100 $\pm$ 100	27	30 $\pm$ 5
92	2500 $\pm$ 500	38	1 $\pm$.3
93	1350 $\pm$ 300	43	8 $\pm$ 4
94			
95	1000 $\pm$ 150	30	20 $\pm$ 5
96	1050 $\pm$ 200	80	40 $\pm$ 15
97	950 $\pm$ 200	25	40 $\pm$ 15
98	400 $\pm$ 100	55	100 $\pm$ 35
99	2850 $\pm$ 500	11	20 $\pm$ 10
100	300 $\pm$ 40	28	32 $\pm$ 18
101			
102			
range = 1 to 100, mean = 34 $\pm$ 14

Figure 5. Heterogeneous solution rate constant of acid-cleaned biogenic opal as a function of pH at $3 \pm 1^\circ\text{C}$. Note lesser values of k_2 in seawater at increasing pH values relative to the 0.7 M NaCl solutions.

Figure 7. Solubility of biogenic opal as a function of temperature and pH.

amorphous silica. This saturation level was not observed in any of our cores.

2) Quite small amounts of metal ions are sufficient to completely cover the surface of the opal present in the sediment. Iler (1955) implies that Fe^{+3} or Al^{+3} ions take up about as much room as an Si atom when incorporated into the amorphous silica structure. Since there are about four Si atoms per $\text{m}\mu^2$, there must be about 4×10^{14} per cm^2 . The average surface area of 32 mg of opal from a cm^3 of the sediments studied is about $2.9 \times 10^{14} \text{ cm}^2$; therefore, there are about 12×10^{18} atoms of Si on the surface of the opal. This corresponds to 2×10^{-5} moles of Si, and a like amount of Fe^{+3} or Al^{+3} if the entire surface is to be covered. In fact, much less may be needed to effectively halt silica release, since only a portion of the surface is negatively charged in sediment conditions. Moreover, not all of the above-mentioned ions must be in solution at once, nor must just a single ion be the adsorbed agent for an effective layer to be formed; ions diffusing through interstitial waters or being released in the process of mineral alteration within the sediments are also possible ion sources since the inhibiting layer need not be formed instantaneously upon contact with the sediment.

3) Adsorption of organic molecules to the surface of the opal (Iler, 1955; Stumm and Morgan, 1970) may be occurring in the sediment; however, at the present time no data are available for the percentages of organic carbon in sediments which are adsorbed to the surfaces as molecules as compared with the amounts which are in particulate form. Much work is needed in this area. In any case, since organic

carbon per se generally decreases with depth in the cores studied as seen in Appendix B, the solution retarding effects of adsorbed organic molecules would be expected to diminish with time rather than increase.

Garrels (1972) has suggested an interesting and plausible extension of the inorganic coating concept: if the covering on the surface of the opal is an authigenic silicate, then the silica release rate from the opal will decrease as this layer thickens or more completely covers the surface of the opal. For the steady state situation (values of C_F for a particular core) the rate of growth of the authigenic mineral equals the rate of dissolution of opal. When the release rate of dissolved silica becomes extremely low, the dissolved silica concentration in the interstitial water approaches the equilibrium value for the authigenic mineral. But for the mineral to form, its activity product must be exceeded. If the mineral formed is not pH dependent and forms at some interval between C_0 and C_F , then the dissolved silica versus depth curve must go through a maximum and return to the dissolved silica value at which the activity product was exceeded. Such a curve was not seen in our cores, but they may be too shallow for this silica concentration reversal to occur. If the mineral formed is pH dependent, and tends to form in seawater as the pH increases, then the activity product of such a mineral may be constant with depth in a core: since pH tends to decrease with depth (because of the oxidation of organic matter), and dissolved silica tends to increase, these two opposite changes in activity would tend to hold the activity product constant.

The mineral formed on the opal near the surface of the sediment would be stable deeper into the core and the dissolved silica concentrations would not have to change below the C_F value. Sepiolite may be a mineral of this type as suggested by earlier activity product calculations.

In addition, the following calculations suggests that the apparent k_2 for opal in marine sediments may be even lower than previously estimated. If it is assumed that the expression $k_2(C_{\text{sat}} - C_{\text{sol}})^S$ gives the solution rate of biogenic opal, and that the surface area of the opal per unit volume of interstitial water remains constant while half of the opal in the sediment dissolves, then using average values of k_2S and $(C_{\text{sat}} - C_{\text{sol}})$ in Table 3 and from Appendix B,

$$\begin{aligned} k_2S(C_{\text{sat}} - C_{\text{sol}}) &= (12 \times 10^{-8} \text{ sec}^{-1})(1000 - 400 \text{ } \mu\text{moles cm}^{-3}) \\ &= 2.3 \times 10^{-6} \text{ moles cm}^{-3} \text{ yr}^{-1} \end{aligned}$$

Since the average sediment studied contained about 5×10^{-4} moles of opal per cm^3 of sediment, it would only require 100 years for half of the opal (below the depth of removal by diffusion) to be dissolved and converted to another silicate mineral. But the very presence of the opal and the lack of authigenic mineral formation denies this rapid a conversion rate. Therefore, the k_2S value of the opal in the sediment (below the depth of removal by diffusion) must be six to eight orders of magnitude smaller than the acid-cleaned opal value

under similar conditions. By the same taken, those values of k_2S estimated in Table 5 must be the average value for k_2S as it decreases from the sediment-water interface to below the depth of removal by diffusion. Only detailed sampling for dissolved silica and weight per cent opal in the sediment over small intervals in undisturbed cores, and solution rate work on these samples can elucidate the above contradiction in k_2S values.

Geochemical Implications

Flux of Dissolved Silica across the Sediment-Water Interface

Calculations involving the residence time of dissolved silica in the oceans also require estimates of the dissolved silica flux from deep-sea sediments into bottom waters. The following discussion gives estimates of the flux of dissolved silica from the cores studied. In this discussion it is assumed that k_2 , S , and D in equation (5) are constant in a given core (at least until $C_Z = C_F$), that D can be estimated from equation (3), and that C_0 and C_F are known, giving the dissolved silica boundaries; re-arrangement of equation (5) and differentiation with respect to Z gives:

$$\begin{aligned} \text{Flux, moles/cm}^2/\text{sec} &= -D(dC/dZ) = \\ &= -(k_2SD)^{1/2}(C_0 - C_F)\exp(Z(k_2S/D)^{1/2}) \end{aligned} \quad (6)$$

When $Z = 0$, this equation gives the total flux of dissolved silica

across the sediment-water interface. Since Z increases negatively downward, the exponential term in (6) varies from 1 at $Z = 0$ to zero at $Z = -\infty$. The sediment depth above which 90% of the dissolved silica which is removed by diffusion occurs may be obtained by setting the exponential term equal to 0.1, inserting the calculated estimate of $k_2 S/D$ from Table 3 and solving for Z . This depth for each core is given also in Table 3. The mean depth for the samples studied is only 16 cm, suggesting that most of the solution of the biogenic opal in these sediments occurs at quite shallow depths; future studies of dissolved silica and weight per cent opal in cores must be done over much smaller intervals if the model is to be realistically expanded.

Calculation of Solution Budget for Water and Sediment Columns

Solution of biogenic opal produced in the upper 200 to 300 m of the ocean can occur throughout the water column as the test descends, and as we have shown, in the upper few cm of the sediment. In calculating a biogenic opal solution budget, the amounts of opal originally produced by the organisms and the amount which is buried below the depth of removal by solution and diffusion will be used as boundary conditions. Thus,

$$\begin{aligned} & (\text{Amount Produced by Organisms}) - (\text{Amount Below Removal Depth}) \\ &= (\text{Amount Dissolving in Water Column}) + (\text{Amount from Sediment} \\ & \quad \text{by Diffusion}) \end{aligned}$$

The amount of opal per unit time which is removed from the sediment by diffusion for each core is given in Table 6, along with other pertinent data for equation (6). The amount removed by diffusion plus the amount accumulating below the level of removal must equal the amount of opal reaching the sediment-water interface. This latter amount when subtracted from the amount produced by the organisms gives the amount of opal dissolved in the water column.

Absolute rates of biogenic opal accumulation were estimated for each station by averaging the amount of opal (moles per cm^3 of sediment converted from weight per cent data in Appendix B) below the 90 per cent solution level, and multiplying this value by the estimated sedimentation rate (Lisitzin, 1972) in $\text{cm}/1000$ yrs giving moles opal/ $\text{cm}^2/1000$ yrs. The production of opal by organisms in the upper layers of the ocean was estimated from Lisitzin's data (1972). By comparing the absolute accumulation rate with biogenic production for each station we can see that very little of the biogenic opal produced by organisms remains in the sedimentary record -- on the average only 0.05 to 0.15 per cent! Also comparison of the sum of the flux across the sediment-water interface and the absolute accumulation rate with the amount of opal produced by organisms shows that the range of solution in the water column is 55 to 99.7 per cent, with an average of 92 to 99 per cent. These values substantiate the hypothesis that most of the solution of biogenic opal occurs in the water column as evidenced by the field data of Lisitzin (1972); his data suggest that 90 to 99 per cent of the solution

Table 6. Listing of variables and fluxes for dissolved silica from each station

Station	$C_o - C_f$	$(k_2 SD)^{1/2}$	Flux of dissolved silica at Z=0
	$(10^{-7} \text{ moles/cm}^3)$	(10^{-7} cm/sec)	$(10^{-3} \text{ moles/cm}^2/10^3 \text{ yr})$
90	2.90	5 ± 1	4.6
91	3.00	5 ± 1	4.7
92	3.00	$1.4 \pm .3$	1.3
93	2.65	4.9 ± 1	4.1
94	2.50	2.7 ± 3	2.1
95	2.60	$3.5 \pm .6$	2.9
96	3.25	9.5 ± 2	9.7
97	3.85	5.8 ± 1.4	7.0
98	2.80	3.2 ± 1	2.8
99	2.50	$3.9 \pm .4$	3.1
100	2.35	$2.9 \pm .3$	2.1
101	2.30	11.5 ± 3	*8.3
102	1.20	$1.4 \pm .4$	.5
		mean	4.1

*Volcanic Ash

Table 6 (continued). Listing of variables and fluxes for dissolved silica from each station

Station	Absolute accumulation rate of opal (10^{-3} moles/ 10^3 yr)	Estimated Sedimentation Rate (mm/ 10^3 yr)	Estimated Surface Productivity (10^{-3} moles/cm ² / 10^3 yr)
90	.27	10	15-150
91	.28	8	15-150
92	.21	5	150-400
93	.07-.14	1-2	150-400
94	.03-.06	1-2	15-150
95	.1-.2	1-2	150-400
96	.4-.6	6-8	400-800
97	.5-.7	8-12	400-800
98	.2-1	2-10	150-400
99	.1-.4	2-10	150-400
100	.1-.4	2-10	150-400
101	.1-.2	6-10	15-150
102	.08-.13	6-10	15-150
mean	.2		mean 136-365

process occurs in the water column and that only 0.05 to 1 per cent of the original amount of opal produced by organisms remains in the sedimentary record. However, the amorphous silica production figures of Lisitzin for Equatorial regions may be too high by as much as an order of magnitude for the following reasons: 1) While it is assumed that diatoms are responsible for the primary production of organic carbon (from which the biogenic opal production numbers are estimated) nannophytoplankton may also play an important role (Watt, 1971); 2) Radiolarians are a major biogenic opal source in Equatorial regions but are on a secondary trophic level -- their production of biogenic opal must require more overall carbon fixation than diatoms; 3) The relative turnover rates for organic carbon and silica are not known for radiolarians and diatoms; while Lisitzin assumes an equal turnover rate, a slower turnover rate of silica relative to organic carbon will result in a lower biogenic opal production rate. If the overall production of biogenic opal is much smaller than the estimates given in Table 5, then a much greater role in the recycling of silica in the oceans will be played by diffusion of dissolved silica from sediments.

In comparing the flux of dissolved silica from the sediments with the absolute accumulation rate, it appears that an order of magnitude decrease in the amount of biogenic opal per cm^3 of sediment must occur between the sediment-water interface and the 90 per cent solution depth. We suggest that such trends are not obvious in Appendix B because of the relatively large sampling intervals chosen. Future

studies will analyse this problem in more detail.

Relative Solution Potential of the Upper 1000 m of the Water Column as a Function of Latitude

Because most of the biogenic opal produced by organisms is dissolved in the water column, it is important to determine whether all water masses behave similarly with respect to their ability to dissolve biogenic opal. From Figs. 5 and 6 one would intuitively suspect that low-temperature, low-pH waters would be less aggressive toward opal than warmer, higher-pH waters. This is graphically substantiated in Fig. 8, where the potential solution characteristics of the upper 1000 m of the water column are graphed as a function of latitude. The assumptions and method of calculating the solution potentials are:

(1) The solution rates for acid-cleaned biogenic opal in stirred seawater solutions are directly proportional to the solution rates of radiolarians and diatoms falling through the water column.

(2) A linear relationship exists between $\ln k_2$ and $1/\text{temp}$ (Greenberg, 1957) and between C_{sat} and T (Alexander *et al.*, 1954).

(3) The temperature, pH, and dissolved silica data as a function of depth along 170°W Lat. (Horibe, 1970) represent typical oceanic values.

(4) The values of C_{sat} at $3 \pm 1^\circ$ and $23 \pm 1^\circ\text{C}$ represent actual oceanic values.

(5) The same amount of solid with the same specific surface

Figure 8. Variation of relative solution potential, amorphous silica production, and per cent amorphous silica in the sediment, as a function of latitude along 170°W longitude.

area is used for all depths allowing a cancellation of the surface area term in equation (4).

(6) There is no change in solubility of the biogenic opal with increase in pressure in the first 1000 m, nor is there any resulting effect of pressure on the rate constant.

(7) For each latitude the product of the rate constant, (adjusted for pH and temperature) and $C_{\text{sat}} - C_{\text{sol}}$, (C_{sat} adjusted for temperature) is plotted as a function of depth to 1000 m. The integral of each curve is then divided by the integral of the curve computed for Lat. 65°S, since this latitude had the lowest relative solution potential. The resulting values give the potential solution characteristics of a given column of water relative to the same depth of water at 65°S.

Also plotted in this figure are the annual production rates of biogenic opal by organisms in $\text{gm/m}^2/\text{yr}$ (Lisitzin, 1972) and the amorphous silica distribution in the surface sediment, as percentage of the weight of dry, carbonate-free sediment (Lisitzin, 1972).

This figure suggests that strictly from a physical-chemical point of view, the percentage of amorphous silica (which is presumed to be primarily biogenic opal) is a function of both productivity and the solution potential of the upper 1000 m of the water column. In the Antarctic where productivity is high and relative solution potential low, large amounts of amorphous silica exist in the sediment; however, where intermediate productivity and high relative solution potential coincide (10 to 20°S Lat.) a low amount of

amorphous silica may result.

Biological Considerations

Solution rates of tests in the water column below 1000 m, where changes in temperature and dissolved silicate changes are both small, are a function of the specific surface area or surface to volume ratio of the test, and any protective coating which may be still on the test. Since the amount of opal dissolving with depth in the water column is small in comparison with the amount already present in dissolved form, an open system model may be used for solution estimates. Under these conditions there should be a definite relationship between the following parameters: the initial size and specific surface area of an organism's test, the depth of the water column, the average solution rate over the length of the water column, and whether the test is found in both surface waters and surface sediments.

In dealing with biogenic minerals, a number of variables other than strictly chemical and physical ones enter into the solution model. Radiolarians, diatoms, and silicoflagellates are found throughout the water column, but are concentrated in the upper 200 m (Lisitzin, 1970), while siliceous sponges are benthic. Schrader (1971) has recently shown that grazing by copepods on diatoms produces fecal pellets which both increase the rate of fall and inhibit solution by an enclosing membrane. Although most of the pellets appear to have disintegrated at 500 m depth, whether by bacterial decomposition of the membrane or secondary grazing by other

animals (Grill, 1970) such a mechanism transports silica from an extremely active zone of solution to a relatively passive one. Grazing also has adverse effects on test preservation (Grill, 1970). Mechanical breakage of the test caused by mastication increases specific surface area, and chemical breakdown during digestion of the protoplasm removes material responsible for producing and protecting the test, both factors tending to increase the rate of solution of the test.

While grazing is reported to be the primary method of removal of siliceous organisms from the euphotic zone, a portion of the population may descend because of changes in the specific gravity of the organism, as a result of turbulence (Riedel and Aberdeen, 1957), or nutrient depletion (Kozlova and Mukhina, 1967; Raymont, 1963). The viability of radiolarians, diatoms, and silicoflagellates with respect to changes in light, temperature, pressure, and nutrients in the oceans is not well understood; it has been suggested that once organisms have sunk below the oceans' surface layers they may still remain viable for several months (Lisitzin, 1970). Radiolarians in particular have been collected alive in the whole length of the water column (Riedel and Aberdeen, 1957).

When the test has reached the sediment-water interface, active solution continues. The burrowing and foraging of benthic animals serves at least two purposes: the organic content and nutrient level of sediment passing through the but of an organism is even further reduced, and the sediment is re-suspended into the water directly

above the sea-floor, allowing more surface area to be available for solution during settling.

Conclusions

1. Although biogenic amorphous silica is the most soluble silica-containing mineral in the sediment, none of the interstitial waters studied were saturated with respect to this mineral. Implications are that other silicate minerals are active in regulating dissolved silica concentrations. Furthermore, comparison of the heterogeneous solution rate-constant of acid-cleaned biogenic opal with that extracted from equation (5) indicates that the solution of biogenic opal may be as much as three to six orders of magnitude slower in the sediments. Below the depth of the concentration gradients, solution of biogenic opal must be at least six to eight orders of magnitude slower than the acid-cleaned standard.

2. Because of the strong negative charge on the silica surface, the following ions would be strongly adsorbed at in situ sediment conditions: Ca^{+2} , Mg^{+2} , Al^{+3} , Fe^{+3} , Sc^{+3} , Cr^{+3} , Th^{+3} , and UO_2^{+2} . It is therefore likely that iron, magnesium, and calcium aluminosilicates may be the minerals forming on the silica surface and reducing the release rate of dissolved silica.

3. Since the scale height of the system is large (diffusion/sedimentation = 30 to 3000 m) compared to the depth at which dissolved silica concentrations generally become constant (30 to 40 cm), removal of dissolved silica results primarily from diffusive effects.

4. The following parameters are suggested as controlling the distribution of dissolved silica versus depth in a core:

- a. The net rate of release of dissolved silica from the most readily soluble silicate mineral; this release is in turn related to the surface area of the dissolving mineral per unit volume of interstitial water, the degree of saturation of the solution with respect to the solubility of this mineral, and the apparent heterogeneous solution-rate constant of the mineral.
- b. The apparent diffusion coefficient of the dissolved silica molecule in the sediment; this coefficient is related to the tortuosity or mean free path length traveled by the diffusing molecule per unit length of sediment, and to any interaction this molecule may have with the surfaces of the minerals in the sediment.

5. Solution budget calculations suggest that, for the Central Equatorial Pacific, 92 to 99 per cent of the biogenic opal produced in surface waters by organisms dissolves before it reaches the sediment. Of the amount reaching the sediment, nearly all dissolves as well--only 0.05 to 0.15 per cent of the opal produced at the surface remains in the sedimentary record.

6. The relative solution potential of the upper 1000 m of the water column is a function of its average temperature, pH, and dissolved silica concentration, and varies with latitude along the 170°W Long. line studied. Below 1000 m, the relative solution

potentials of the world's oceans are within 10 to 12 per cent of one another, for a given length of water column.

APPENDIX A

Wet chemical determination of opal in deep-sea sediments

INTRODUCTION

Geochemical calculations involving silica balance in the oceans require accurate determinations of the amount of opal present in the oceanic sediments; methods presently available for such determinations are subject to a variety of interferences.

The amount of opal present in a sample is often overemphasized in smear-slide determinations by the open lattice-work of radiolarians and diatoms. Also, because of the low specific gravity of opal (2.2 as compared with 2.6-2.7 for carbonates and quartz, 2.8-2.9 for the clays) the area per cent estimate obtained may overemphasize the amount of opal present. Earlier investigators (Chester et al., 1968; Calvert, 1966) in their attempt to obtain weight per cent values used X-ray diffraction and infra-red techniques, but both of these procedures suffer from the disadvantages of strong palagonite interference (Tj. van Andel, 1970, personal communication). Russian investigators refer to the method of Bezrukov (1955), and his paper mentions a double extraction with 5% Na_2CO_3 of the sediment sample, but gives no further details. An extraction technique of this type has been investigated and developed at the University of Hawaii and found to provide reliable weight per cent values for opal in deep-sea sediments in the presence of several silica-containing minerals studied.

OUTLINE OF METHOD

Twenty milligrams of finely ground, oven-dried sediment is added to 125 ml of 5% Na_2CO_3 solution and agitated for 5 hours in a constant temperature bath maintained at 85°C. The mixture is centrifuged and a 1 ml aliquot of the supernatant is diluted to 25 ml with distilled water and analysed for reactive silicate according to the method of Strickland and Parsons (1968). All reaction containers, centrifuge tubes, and graduated cylinders were of polyethylene or polypropylene. The resulting absorbance value of the colored solution is compared to a standard curve prepared by mixing varying percentages of opal with an artificial sediment standard (10% quartz, 45% illite, 35% montmorillonite, 10% kaolinite). This particular mixture (Griffin *et al.*, 1968) was chosen as being representative of the area in which we are interested, the Central Equatorial Pacific. An example of a standard curve is given in Figure 9. Net absorbance of the sample rather than the actual amount of silica leached from the sample is used in the curve because of its linear relationship with weight per cent opal in the sample.

Carbonate minerals in the sample do not interfere and act as dilutants, but a constant weight of carbonate-free sample (e.g., 20 mg) is required for use with the standard curve; the net absorbance based on a carbonate-free sample must then be corrected back to a whole sediment value.

Figure 9. Standard curve of net absorbance (absorbance - reagent blank) versus weight per cent opal in clay standard mixtures.

$$\begin{array}{l} \text{Net absorbance of opal} \\ \text{in carbonate-free sample} \end{array} = \frac{100}{\% \text{ carbonate}} \cdot (\text{net absorbance}) \quad (7)$$

This net absorbance is then compared with the standard curve to give weight per cent opal on a carbonate-free basis. The whole sediment value is obtained by the formula:

$$\begin{array}{l} \text{Weight per cent opal} \\ \text{in whole dry sediment} \end{array} = (100 - \% \text{ carbonate}) (\% \text{ opal in carbonate-free sediment}) \quad (8)$$

A total of 116 sediment samples were analysed, forty of them in duplicate. The precision of the method is given by: weight per cent opal $\pm 5.8/n^{1/2}$, where n refers to the number of determinations done on a single sample, and 5.8 is two standard deviation units. As discussed by Strickland and Parsons (1968), this statistical procedure gives about 95% confidence.

To account for variations in reaction conditions, clay-standard and opal mixtures should be run with each set of determinations.

SELECTION OF REACTION CONDITIONS

The rate of solution of opal increases with increasing temperature and pH, the pH dependence being more noticeable above pH 7 (Siever, 1962; Alexander *et al.*, 1954; Okamoto *et al.*, 1957;

Langston et al., 1964). Conditions of high temperature and pH also accelerate attack on other silica-containing minerals (Langston et al., 1964); however, their rate of solution is much slower than that of opal. This difference between the rate of solution of these other minerals and that of opal forms the basis of the method described here.

Kaolinite, illite, quartz, montmorillonite, palagonite, and biogenic opal were used in the silica solution experiments. The kaolinite, illite, and montmorillonite were American Petroleum Institute standards obtained from the University of Hawaii Soils Department; the quartz, from the University of Hawaii Geology Department; and the palagonite, from M. Morgenstein, Hawaii Institute of Geophysics. The biogenic opal was a mixture of radiolarians, diatoms, and sponge spicules, separated from Central Pacific (Lat. 8°N, Long. 156°W) pelagic sediments in our lab by sieving with a 62 μ sieve, washing in an ultrasonic bath in 1N HCl, re-sieving, and drying at 100°C for several hours. The resulting opal standard contained no microscopically obvious impurities.

For the method to be reliable the following criteria must be satisfied:

1. All minerals used other than the opal must release silica much more slowly than the opal.
2. The amount of silica released by any silica-containing mineral under the conditions of the method must be a function only of the weight of the sample.

Table 7 shows that these criteria are met for samples of

Table 7. Difference in the Net Absorbances of Several Minerals under the Conditions of the Method

Mineral	Sample wt (mg)	Net absorbance
Palagonite	20.6	.124
Palagonite	10.5	.068
Illite	20.3	.030
Illite	10.7	.018
Quartz	20.5	.010
Quartz	10.5	.006
Montmorillonite	20.0	.104
Montmorillonite	10.1	.050
Kaolinite	20.1	.026
Kaolinite	9.9	.009
Biogenic opal	20.1	.830
Biogenic opal	16.0	.705
Biogenic opal	12.1	.545
Biogenic opal	7.9	.333
Biogenic opal	4.1	.171

kaolinite, illite, quartz, montmorillonite, palagonite, and biogenic opal. As seen under the conditions of the method, the net absorbance of the reactive silicate released by a particular mineral is a linear function of the amount of that mineral added. The data also show the rate at which silica-containing minerals other than opal are dissolved under constant experimental conditions.

DISCUSSION

The chemical formula for opal is $\text{SiO}_2 \cdot n \text{H}_2\text{O}$, where the weight per cent water varies between 4 and 10 per cent (Searle et al., 1959). This amount of variation implies that the accuracy of any opal determination could be no better than $\pm 3\%$. Since the age and type of opal may affect its water content, opal from the particular area of study should be used as the standard for that area. The solution rates may also be affected by the previous history of the organisms and by varying combinations of inorganic constituents in the sediments (Lewin, 1961).

Recently, amounts of up to a few per cent cristobalite have been found in Pacific sediments; however, cristobalite should give no interference since its silica solution rate is even slower than that of quartz (Langston et al., 1964).

The method outlined above is fast and reliable, and does not suffer the interferences suffered by previous methods. Up to 35 samples a day are being analysed in our labs.

APPENDIX B

Physical, chemical and geological properties
related to solution and diffusion in deep-sea
sediments in the Central Equatorial Pacific

STATION 90.

RED CLAY...HEAVY MOTTLING 12-32, 56-66 CM...BANDING IN 1 CM INTERVALS, 32-46 CM

DEPTH IN CORE, CM	DISS. SiO2 MICRO MOLAR	WT. % OPAL	WT. % CaCO3	WT. % NON-BIOG.	WT. % ORG. C	WT. % GT 44	WT. % LT 4	WT. % WATER	% POROSITY GRNDS	OPAL,GM/CM3 WHOLE SED.	
5.	340.	5.	1.3	94.	0.37	0.5	81.0	66.	85.	2.8	0.020
15.	365.	8.	0.8	91.	0.30	3.5	77.0	70.	90.	3.4	0.028
25.	365.	6.	1.7	92.	0.30	5.5	76.0	71.	88.	2.6	0.019
35.	410.	5.	2.4	93.	0.27	5.4	76.0	68.	85.	2.6	0.019
45.	430.	3.	2.8	94.	0.20	5.2	80.0	65.	87.	3.3	0.013
55.	410.	6.	0.8	93.	0.23	3.4	82.0	66.	86.	3.0	0.025
65.	440.	5.	0.3	95.	0.16	1.2	84.0	69.	88.	3.0	0.018
75.	440.	3.	0.1	97.	0.22	0.7	82.0	67.	86.	2.7	0.012
85.	430.	5.	0.1	95.	0.25	0.6	76.0	65.	86.	3.0	0.022
MEAN	403.	5.	1.1	94.	0.27	2.9	79.	67.	87.	2.9	0.020
STD	37.	2.	1.0	2.	0.05	2.2	3.	2.	1.	0.3	0.005

STATION 91.

RED CLAY...MEDIUM MOTTLING 26-33, 81-114 CM...BAND EDGES AT 65,69,79 & 90 CM

DEPTH IN CORE, CM	DISS. SiO2 MICRO MOLAR	WT. % OPAL	WT. % CaCO3	WT. % NON-BIOG.	WT. % ORG. C	WT. % GT 44	WT. % LT 4	WT. % WATER	% POROSITY GRDNDS	OPAL,GM/CM3 WHOLE SED.	
5.	350.	9.	0.5	90.	0.30	3.7	82.0	74.	90.	2.8	0.026
15.	375.	7.	0.5	92.	0.25	1.8	77.0	72.	90.	3.0	0.021
25.	388.	6.	0.5	93.	0.18	3.6	83.0	70.	88.	2.8	0.021
35.	425.	5.	0.5	94.	0.20	2.7	83.0	72.	89.	2.8	0.016
45.	430.	6.	0.5	94.	0.22	1.5	85.0	69.	85.	2.4	0.022
55.	455.	6.	0.4	94.	0.21	0.8	86.0	66.	85.	2.8	0.025
65.	435.	7.	0.4	93.	0.17	1.0	84.0	67.	86.	2.7	0.027
75.	450.	7.	0.4	93.	0.16	1.4	80.0	67.	87.	3.0	0.028
85.	440.	6.	0.4	94.	0.14	1.0	83.0	70.	88.	2.9	0.021
MEAN	416.	7.	0.5	93.	0.20	1.9	83.	70.	87.	2.8	0.023
STD	37.	1.	0.1	1.	0.05	1.1	3.	3.	2.	0.2	0.004

STATION 92.

CALCAREOUS GLOBIGERINA OOZE...MOTTILING AND BANDING NOT DETERMINED

DEPTH IN CORE, CM	DISS. SiO2 MICRO MOLAR	WT. % OPAL	WT. % CaCO3	WT. % NON-BIOG.	WT. % ORG. C	WT. % GT 44	WT. % LT 4	WT. % WATER	% POROSITY GRNONS (ESTIMATED)		OPAL,GM/CM3 WHOLE SED.
5.	225.	5.	79.0	16.	0.18	14.3	69.0	47.	73.	2.7	0.036
15.	360.	4.	79.0	17.	0.11	24.1	55.0	47.	73.	2.7	0.029
25.	385.	4.	76.0	20.	0.14	15.9	72.0	47.	73.	2.7	0.029
35.	415.	3.	83.0	14.	0.13	17.6	68.0	47.	73.	2.7	0.022
45.	445.	2.	81.0	17.	0.12	20.7	51.0	47.	73.	2.7	0.015
55.	445.	2.	84.0	14.	0.0	25.4	20.0	47.	73.	2.7	0.015
65.	445.	2.	81.0	17.	0.10	24.6	42.0	47.	73.	2.7	0.015
75.	445.	6.	67.0	27.	0.11	11.7	70.0	47.	73.	2.7	0.044
85.	450.	8.	69.0	23.	0.12	14.9	67.0	47.	73.	2.7	0.058
MEAN	402.	4.	77.7	18.	0.11	18.8	57.	47.	73.	2.7	0.029
STD	74.	2.	6.0	4.	0.05	5.1	17.	0.	0.	0.0	0.015

STATION 93.

RED CLAY...HEAVY MOTTILING 52-71 CM...BAND EDGES AT 3,5,15,16,67,71,94,96 & 98 CM

DEPTH IN CORE, CM	DISS. SiO2 MICRO MOLAR	WT. % OPAL	WT. % CaCO3	WT. % NON-BIOG.	WT. % ORG. C	WT. % GT 44	WT. % LT 4	WT. % WATER	% POROSITY GRNONS		OPAL,GM/CM3 WHOLE SED.
5.	300.	23.	0.1	77.	0.25	3.4	80.0	81.	96.	4.0	0.040
15.	355.	25.	0.1	75.	0.23	2.9	82.0	79.	93.	2.9	0.052
25.	375.	10.	0.1	84.	0.23	1.3	83.0	78.	91.	2.6	0.036
35.	395.	12.	0.1	88.	0.16	0.7	87.0	77.	92.	3.0	0.028
45.	400.	15.	0.1	85.	0.20	0.4	87.0	77.	93.	3.3	0.036
55.	395.	13.	0.1	87.	0.18	1.2	84.0	79.	93.	2.9	0.027
65.	410.	15.	0.1	85.	0.27	0.7	86.0	82.	94.	2.9	0.026
75.	425.	13.	0.1	87.	0.12	0.2	89.0	54.	78.	2.8	0.082
85.	415.	15.	0.1	85.	0.17	0.1	91.0	54.	76.	2.6	0.092
MEAN	386.	16.	0.1	84.	0.21	1.2	85.	74.	90.	3.0	0.047
STD	38.	5.	0.0	5.	0.06	1.2	4.	11.	7.	0.4	0.025

STATION 94.

RED CLAY...MOTTILING AND BANDING NOT DETERMINED

DEPTH IN CORE, CM	DISS. SiO2 MICRO MOLAR	WT. % OPAL	WT. % CaCO3	WT. % NON-BIOG.	WT. % ORG. C	WT. % GT 44	WT. % LT 4	WT. % WATER	% POROSITY GRNONS (ESTIMATED)	OPAL,GM/CM3 WHOLE SED.	
5.	255.	13.	0.3	87.	0.16	33.0	52.0	80.	92.	2.7	0.028
15.	295.	13.	0.2	87.	0.09	26.4	60.0	80.	92.	2.7	0.028
25.	325.	13.	0.3	87.	0.07	18.4	61.0	80.	92.	2.7	0.028
35.	365.	15.	0.3	85.	0.04	14.1	63.0	80.	92.	2.7	0.032
45.	365.	15.	0.3	85.	0.02	12.7	65.0	80.	92.	2.7	0.032
55.	380.	10.	0.3	90.	0.05	0.7	82.0	80.	92.	2.7	0.022
65.	390.	9.	0.3	91.	0.07	3.2	77.0	80.	92.	2.7	0.019
75.	405.	12.	0.3	88.	0.0	2.0	86.0	80.	92.	2.7	0.026
85.	400.	12.	0.3	88.	0.01	1.2	84.0	80.	92.	2.7	0.026
MEAN	353.	12.	0.3	87.	0.06	12.4	70.	80.	92.	2.7	0.027
STD	51.	2.	0.0	2.	0.05	11.8	12.	0.	0.	0.0	0.004

STATION 95.

CALCAREOUS GLOBIGERINA OOZE CHANGING TO RED CLAY...MOTTILING 32-42 CM...BAND EDGES AT 19,40 & 70 CM

DEPTH IN CORE, CM	DISS. SiO2 MICRO MOLAR	WT. % OPAL	WT. % CaCO3	WT. % NON-BIOG.	WT. % ORG. C	WT. % GT 44	WT. % LT 4	WT. % WATER	% POROSITY GRNONS	OPAL,GM/CM3 WHOLE SED.	
5.	335.	1.	83.0	16.	0.12	33.3	44.0	42.	66.	2.6	0.009
15.	355.	1.	86.0	13.	0.06	31.4	46.0	43.	68.	2.8	0.009
25.	380.	3.	66.0	31.	0.06	24.0	44.0	49.	72.	2.6	0.022
35.	405.	6.	57.0	37.	0.04	21.3	47.0	53.	77.	2.8	0.038
45.	405.	8.	11.0	81.	0.03	17.9	58.0	45.	70.	2.7	0.066
55.	420.	14.	4.9	81.	0.02	20.3	44.0	43.	67.	2.7	0.123
65.	420.	7.	4.3	89.	0.02	21.6	26.0	43.	68.	2.8	0.062
75.	400.	7.	2.8	90.	0.02	20.1	32.0	40.	65.	2.8	0.067
85.	405.	7.	3.8	89.	0.02	18.7	27.0	40.	65.	2.8	0.069
MEAN	392.	6.	35.4	59.	0.04	23.2	41.	44.	69.	2.7	0.052
STD	29.	4.	36.7	33.	0.03	5.5	10.	4.	4.	0.1	0.037

STATION 96.

SILICEOUS RADIOLARIAN OOZE...MOTTLING AT 40-105 CM...BAND EDGE AT 71 CM

DEPTH IN CORE, CM	DISS. SiO2 MICRO MOLAR	WT. % OPAL	WT. % CaCO3	WT. % NON-BIOG.	WT. % ORG. C	WT. % GT 44	WT. % LT 4	WT. % WATER	% POROSITY GRDNDS	OPAL, GM/CM3 WHOLE SED.
5 (sample missing) 0.		0.	0.0	100.	0.0	0.0	0.0	0.	0.	0.0
15.	440.	30.	0.1	70.	0.19	9.5	56.0	78.	93.	0.068
25.	465.	28.	0.1	72.	0.14	13.0	48.0	77.	91.	0.067
35.	475.	25.	0.1	75.	0.11	16.8	45.0	77.	93.	0.060
45.	465.	28.	0.1	72.	0.09	16.0	50.0	76.	89.	0.071
55.	475.	13.	0.1	87.	0.07	11.4	50.0	76.	89.	0.033
65.	475.	15.	0.1	85.	0.06	17.8	41.0	79.	92.	0.032
75.	465.	10.	0.2	90.	0.04	22.2	44.0	80.	92.	0.020
85.	475.	13.	0.1	87.	0.06	28.1	42.0	79.	92.	0.027
MEAN	415.	18.	0.1	82.	0.08	15.0	42.	69.	81.	0.042
STD	156.	10.	0.0	10.	0.06	8.0	16.	26.	30.	0.025

STATION 97.

SILICEOUS RADIOLARIAN OOZE...MOTTLING AT 37-38, 51-60 & 81-115 CM...BAND EDGES AT 42, 91 & 109 CM

DEPTH IN CORE, CM	DISS. SiO2 MICRO MOLAR	WT. % OPAL	WT. % CaCO3	WT. % NON-BIOG.	WT. % ORG. C	WT. % GT 44	WT. % LT 4	WT. % WATER	% POROSITY GRDNDS	OPAL, GM/CM3 WHOLE SED.
5.	405.	22.	0.1	78.	0.34	8.3	56.0	77.	90.	0.053
15.	410.	10.	0.1	90.	0.39	4.2	65.0	76.	92.	0.026
25.	430.	0.	0.1	100.	0.34	1.5	54.0	78.	91.	0.0
35.	465.	8.	0.0	92.	0.35	1.0	57.0	80.	94.	0.016
45.	475.	29.	0.0	71.	0.02	2.1	84.0	81.	94.	0.054
55.	495.	15.	0.0	85.	0.01	2.7	85.0	81.	93.	0.027
65.	510.	27.	0.0	73.	0.03	6.1	81.0	82.	93.	0.047
75.	540.	27.	0.0	73.	0.06	7.7	78.0	82.	95.	0.046
85.	530.	30.	0.0	70.	0.07	9.0	78.0	83.	94.	0.050
MEAN	473.	19.	0.1	81.	0.08	4.7	71.	80.	93.	0.035
STD	50.	11.	0.0	11.	0.10	3.1	13.	3.	2.	0.019

STATION 98.

CALCAREOUS GLOBIGERINA OOZE CHANGING TO SILICEOUS RADIOLARIAN OOZE...MOTTLING AT 55-105 CM...BAND EDGES AT 20,24

DEPTH IN CORE, CM	DISS. SiO2 MICRO MOLAR	WT. % OPAL	WT. % CaCO3	WT. % NON-BIOG.	WT. % ORG. C	WT. % GT 44	WT. % LT 4	WT. % WATER	% POROSITY GRNONS	OPAL,GM/CM3 WHOLE SED.	
5.	375.	8.	51.0	41.	0.18	13.0	61.0	64.	84.	2.9	0.036
15.	395.	9.	60.0	31.	0.17	20.0	52.0	64.	84.	2.8	0.040
25.	410.	11.	60.0	29.	0.08	44.0	29.0	59.	80.	2.6	0.057
35.	430.	11.	52.0	37.	0.18	16.0	57.0	63.	83.	2.5	0.049
45.	420.	14.	4.6	81.	0.16	23.0	61.0	70.	88.	2.9	0.049
55.	430.	18.	25.0	57.	0.09	16.0	51.0	68.	86.	2.6	0.068
65.	430.	38.	0.8	61.	0.01	28.0	40.0	79.	92.	2.7	0.080
75.	425.	38.	0.6	61.	0.01	30.0	42.0	80.	92.	2.6	0.078
85.	430.	40.	0.6	59.	0.44	41.0	33.0	79.	92.	2.5	0.085
MEAN	416.	21.	28.3	51.	0.10	25.7	47.	69.	87.	2.7	0.060
STD	19.	14.	27.3	17.	0.07	11.1	12.	8.	4.	0.2	0.018

STATION 99.

CALCAREOUS GLOBIGERINA AND COCCOLITH OOZE...MOTTLING AT 51-97 CM...BAND EDGES AT 30,51,60,65 & 76 CM

DEPTH IN CORE, CM	DISS. SiO2 MICRO MOLAR	WT. % OPAL	WT. % CaCO3	WT. % NON-BIOG.	WT. % ORG. C	WT. % GT 44	WT. % LT 4	WT. % WATER	% POROSITY GRNONS	OPAL, GM/CM3 WHOLE SED.	
5.	320.	1.	89.0	10.	0.17	35.0	44.0	53.	76.	2.7	0.006
15.	350.	1.	88.0	11.	0.16	28.0	53.0	47.	72.	2.8	0.008
25.	375.	1.	97.0	2.	0.13	31.0	49.0	46.	71.	2.7	0.008
35.	395.	1.	89.0	10.	0.14	25.0	47.0	44.	70.	2.8	0.009
45.	405.	6.	89.0	5.	0.10	33.0	58.0	45.	73.	3.2	0.052
55.	425.	5.	78.0	17.	0.13	20.0	54.0	48.	73.	2.8	0.038
65.	400.	4.	80.0	16.	0.12	18.0	57.0	49.	74.	2.8	0.030
75.	405.	3.	88.0	9.	0.07	29.0	48.0	49.	75.	2.9	0.022
85.	400.	3.	89.0	8.	0.07	30.0	47.0	46.	73.	3.0	0.025
MEAN	386.	3.	87.4	10.	0.12	27.7	51.	47.	73.	2.9	0.022
STD	33.	2.	5.5	5.	0.04	5.7	5.	3.	2.	0.2	0.016

STATION 102.

RED CLAY...MOTTILING AT 84-103 CM...BAND EDGES AT 84 & 90 CM

DEPTH IN CORE, CM	DISS. SiO2 MICRO MOLAR	WT. % OPAL	WT. % CaCO3	WT. % NON-BIOG.	WT. % ORG. C	WT. % GT 44	WT. % LT 4	WT. % WATER	% POROSITY GRANDS	OPAL,GM/CM3 WHOLE SED.	
5.	230.	7.	0.3	93.	0.11	21.0	46.0	65.	86.	3.1	0.030
15.	250.	1.	0.2	99.	0.08	12.0	53.0	60.	82.	2.8	0.005
25.	250.	1.	0.1	99.	0.06	8.1	63.0	60.	81.	2.7	0.005
35.	260.	1.	0.1	99.	0.08	7.1	63.0	62.	83.	2.7	0.005
45.	270.	2.	0.2	98.	0.06	5.6	66.0	60.	83.	2.9	0.010
55.	270.	3.	0.2	97.	0.08	8.7	60.0	48.	64.	1.8	0.020
65.	270.	2.	1.5	97.	0.06	5.6	59.0	70.	95.	6.2	0.007
75.	270.	2.	4.0	94.	0.04	3.7	63.0	58.	77.	2.3	0.010
85.	270.	2.	0.8	97.	0.04	2.3	68.0	68.	88.	3.1	0.008
MEAN	260.	2.	0.8	97.	0.07	8.2	60.	61.	82.	3.1	0.011
STD	14.	2.	1.3	2.	0.02	5.6	7.	6.	8.	1.2	0.008

APPENDIX C

Laboratory techniques involved in obtaining the
data shown in Figures 5 and 6.

The same weight of biogenic opal was dissolved in a constant volume of seawater and the dissolved silica monitored with time. The biogenic opal samples were obtained from the upper 80 cm of the sediment at Lat. 8°N, Long. 156°W. The sediment sample was sieved and the greater than 62 μ size fraction saved. This fraction was washed with hot dilute HCl, placed in an ultra-sonic cleaner for 30 minutes, re-sieved, and the greater than 62 μ size fraction washed with distilled water and dried at 100°C for one hour. Examination of a smear slide of the material at 400x showed no obvious impurities. The seawater used was a near-surface sample from Lat. 19°N, Long. 159°W, whose initial dissolved silica concentration was 15 μ M. The opal-seawater mixtures (20 mg opal + 30 ml seawater) were contained in 2 oz polycarbonate centrifuge tubes with polypropylene caps. A standard curve consisting of a reagent blank, a seawater blank, and 500, 1000, 1500, and 2000 μ M H_4SiO_4 standards was run each time samples were taken. Because of the high silica concentrations each sample was diluted 1:25 with distilled water before the analysis was begun. In order to maintain a constant solid to solution ratio, samples of the suspension were removed at periodic time intervals and the solid phase removed by filtration through a Swinnex filter; the filter used had no effect on the concentration of dissolved silica passing through it. In order to maintain a constant pH in each of the samples, varying ratios of Trizma-HCl and Trizma Base (reagent grade forms of (tris (hydroxymethyl)aminomethane hydrochloride) and (tris(hydroxymethyl)aminomethane)) were added to the solutions and the pH monitored with a Thomas combination electrode. As shown

in Fig. 6, this buffer may increase the solution rate of the biogenic opal by ca. 50 per cent. The stirring was accomplished by placing the tubes on a Scientific Industries multipurpose rotator, adjusting the rotator face to a 45° angle and using the lowest speed, 12 RPM. The specific surface area of the opal used was $60 \text{ m}^2/\text{gm}$ as determined by nitrogen adsorption (Weiler et al., 1965).

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