

DISSOLUTION RATES OF SILICA
SOURCES IN SEA WATER

A Thesis
Presented to
Virginia Institute of Marine Science
The College of William and Mary in Virginia

In Partial Fulfillment
Of the Requirements for the Degree of
Master of Arts in Marine Science

by
Carol A. Lake

1972

APPROVAL SHEET

This thesis is submitted in partial fulfillment of
the requirements for the degree of

Master of Arts

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ACKNOWLEDGMENTS

The writer wishes to express her appreciation to William MacIntyre and Craig Smith for their guidance and criticism throughout this study. The author also is indebted to Robert Byrne, David Kranbuehl, and John Ziegler for their careful reading and criticism of the manuscript.

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ABSTRACT

Three clay minerals and a biogenic silica source were dissolved in synthetic sea water. The rate of dissolution and the final steady state concentration of each silica source were determined. The relative rates were used as a basis for determining what controls the dissolved silica concentration in the ocean. Since the biogenic silica dissolved about 100 times faster than the clay minerals, it is proposed that biogenic silica controls the ocean's dissolved silica concentration.

It is also postulated from general trends in oceanic data that the probable control of the ocean's silica concentration is the mixing and circulation of waters originating from areas of biogenic silica deposits.

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INTRODUCTION

The concentration of silica in sea water and the control of this concentration are subjects of much discussion. Most of the controversy has arisen in the attempt to explain the reason why the river's concentration of dissolved silica is about 13 ppm (parts per million) and that of the ocean is substantially less, i.e. 1-5 ppm. Numerous workers have tried to explain this difference by a silica budget of the ocean by tabulating the silica sources and sinks.

A controversy has arisen regarding the mechanism of removal of the dissolved silica from the ocean waters which gives the lower concentrations relative to the river water. This question is extremely important because the removal mechanism is considered to control the silica concentration in the ocean. On the one side Harris (1966), Calvert (1968), and Gregor (1968) feel the silica is removed by the deposition of marine organism frustules composed of silica.

Burton (1968), Garrels and MacKenzie (1966) disagree, and believe the following "reverse weathering" mechanism:
$$\text{amorphous-Al-silica} + \text{SiO}_2 + \text{cations} \rightleftharpoons \text{Cationic-amorphous-Al-silica}$$
explains the dissolved silica concentration in the oceans.

Previous work has used the following information to solve the problem of the control of the silica concentration:

- 1) the supposed equilibrium solubility of the silica sources,
- 2) the final concentration of dissolved silica released,
- 3) the input rate of dissolved silica of the rivers, and
- 4) depositional rate of the diatom frustules. In this study the rates of hydrolysis of several silica sources have been determined. Silicates which dissolve most rapidly should suppress the dissolution rate of other silicates and thereby control free silicate concentration.

The final observed concentrations in this study provide a check on the "equilibrium" silicate concentration of other workers.

METHODS AND MATERIALS

The apparatus used consisted of two polyethylene vessels (1.75 liter capacity) immersed in a large water bath which maintained the vessel contents at 20 ± 0.5 C. The reaction solution was stirred with a teflon magnetic bar driven by a magnetic stirrer located below the bath. The reaction vessels contained a small valve through which samples of the solution were removed.

Three clay minerals were used in this study - montmorillonite #25, illite #36, and kaolinite #7. These clays were American Petroleum Institute Clay Mineral Standards Project No. 49, distributed by Ward's Natural Science Establishment, Inc. The clays were crushed using an agate mortar and pestle and then passed through a 64μ sieve. This particle size was representative of the size of suspended and deposited clay and silt in the ocean environment, i.e. particles 64μ are classified clay or silt.

To insure that the water used in this study would be essentially silica free, i.e. 0.3 ppm SiO_2 , water was collected directly from a tin-lined water still. This water was used in the reaction solutions, in solutions for the analysis of dissolved silica, and in washing and rinsing equipment. To minimize contamination of the reaction solution by silica from sources other than the clay minerals, all equipment in

contact with the solution was either teflon or polyethylene. Synthetic sea water was prepared according to Lyman and Fleming (1940) using reagent grade chemicals.

The experimental procedure was as follows for each clay mineral: 7.5 g of 64μ clay mineral was added to 1.5 liters of synthetic sea water. The reaction vessel was submerged into the water bath and stirring begun. At selected time intervals, an aliquot of 12.5 ml was removed from the solution and filtered using a Nalgene 0.2μ plain membrane filter unit to remove suspended clay mineral. The filtrate was then analyzed for dissolved silica by forming the reduced silicomolybdate complex and measuring its concentration photometrically on the Beckman DU as described in Strickland and Parsons (1968). Two runs were made on each clay mineral.

The biogenic silica was obtained from live cultures of Phaeodactylon triconutum, a diatom found in coastal waters. Five twenty-liter cultures were gravity-filtered. The organisms were scraped and washed off the filter pad with a small amount of acetone. The excess water and acetone were vacuum filtered from the organisms which were then stored in a freezer for ten days. To remove all organic material from the frustules, the diatoms were treated twice with 100% nitric acid, first for three hours, then filtered, and secondly for eighteen hours, then filtered. The silica was washed with water and acetone, then

dried in a 120°C. oven. 0.339 gram of biogenic silica was obtained. This silica was not crushed or passed through a sieve because whole frustules predominate in the marine environment.

The silica was evenly divided so that two dissolution runs could be made. The experimental procedure was the same as described above for the clay minerals with the exception that only one liter of synthetic sea water was used.

The dissolution reactions were stopped when an apparent steady state concentration had been reached.

RESULTS

The final concentrations of dissolved silica released are the following: 1.65 ppm SiO_2 from kaolinite, 2.93 ppm from illite, 4.46 ppm from montmorillonite, and 88.7 ppm from biogenic silica (Tables 1-4). Values for the clays are comparable to those of Garrels and MacKenzie (1965) for kaolinite and illite, but these authors found two to four times higher silica concentrations for montmorillonite than were observed in this work. The biogenic silica results agree with those of Kamatani (1971).

To determine the rate of dissolution of a silica source into sea water, a rate law following this general formula is used: (Helgeson, 1971)

$$\frac{dm}{dt} = kt^w \quad (1)$$

where k is the rate constant, $\frac{dm}{dt}$ is the rate of change of the activity of the aqueous species, H_4SiO_4 (the dissolved silica), t is time, and w is the exponent which depends on the reaction. Since the concentrations of H_4SiO_4 in this study are so low, the molarity is used instead of the activity.

To find the rate constant for each silica source, a

computer program (Table 5) is used to calculate k from the integrated form of equation (1).

Integrated forms:

$$\int dm = \int kt^w dt \quad w \neq -1$$

$$m_2 - m_1 = \frac{k}{w+1} (t_2^{w+1} - t_1^{w+1})$$

$$k = (m_2 - m_1)(w+1)/(t_2^{w+1} - t_1^{w+1}) \quad (2)$$

$$\int dm = \int kt^w dt \quad w = -1$$

$$m_2 - m_1 = k (\ln t_2 - \ln t_1)$$

$$k = (m_2 - m_1)/(\ln t_2 - \ln t_1) \quad (3)$$

In the program, a value k is calculated for each w value from +2.0 to -2.0 by intervals of 0.25, i.e. w = +2.0, +1.75, +1.50, ... -1.75, -2.0. The Delc and Delt calculated are either from consecutive values of m and t or offset by 2, i.e. $m_3 - m_1$, $m_4 - m_2$, depending on the number of samples taken. For montmorillonite and biogenic silica less samples were taken so consecutive values of m and t are used in the calculations of k.

By inspection, several w+1 values for each silica source are chosen which yield fairly constant k values and a simple linear regression is run on the computer for each set of t^{w+1} and m values. The best w+1 value is that which has the highest correlation coefficient obtained from the linear regression (Table 6). After obtaining the w+1 value, the rate constant for each silica source is

computed from the slope of the linear regression equation (Table 6).

The best $w+1$ value for each of the clay minerals is 0.25; therefore, the rate law which is applicable is $\frac{dm}{dt} = kt^{-.75}$. The best $w+1$ value for biogenic silica is -0.25 and its rate law is $\frac{dm}{dt} = kt^{-1.25}$. In Figures 1-4 the linear regression equation and experimental points are plotted for each silica source.

As a test of the accuracy of this approach in choosing the best $w+1$ value, the kinetic data of the hydrolysis of feldspar (Table 7) of Wollast (1967) is also used in both programs. Wollast proposes that the initial dissolution step is diffusion-controlled, i.e. $w = -0.5$. If the first six sets of data are used in both programs, the best w value is found to be -0.5. If all of Wollast's data is used in the analysis, the best w value is -0.75 (that found for the clay minerals in this study) (Table 8).

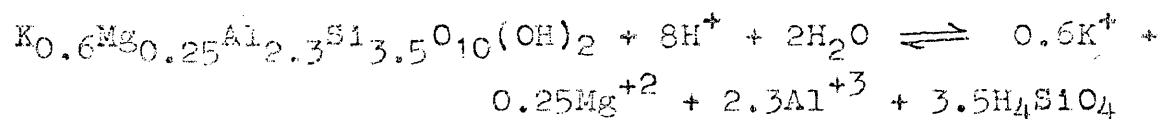
DISCUSSION

In this analysis of the data, a strictly kinetic and somewhat empirical approach has been taken. Previous work in this field has been mainly concerned with the final, "equilibrium" concentration of dissolved silica and with studies of the control of the silica concentration in the ocean using this equilibrium concentration and other geochemical considerations.

Even though it is generally thought that the silica concentration in the deep ocean is at a steady state rather than in equilibrium, in studies of this nature, the principles of thermodynamic equilibrium have been used to interpret the kinetic data. For example, in the kinetic work using feldspar, Helgeson (1971) proposed a mechanism by which (1) the rate limiting step in the hydrolysis involved a diffusional transfer of material from the reactant mineral (feldspar) through a surface layer of reaction products (H-feldspar, gibbsite, kaolinite) out into the bulk solution and (2) precipitation of reaction products by an equilibrium process. Also O'Connor and Greenberg (1958) in their kinetic work on the solution of quartz assumed (1) that equilibrium was reached

between the solid silica and silicic acid: $\text{SiO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{H}_4\text{SiO}_4$ and (2) that the silicic acid deposited by condensation reacts back on to the surface of the silica. In both examples, the interpretation of the kinetic data was made after assuming some mechanism by which the silica source dissolved and precipitated after equilibrium was reached. Assumption of the mechanism for the simple amorphous silica-distilled water system may have been valid but the mechanism proposed for the feldspar system was tenuous.

In the case of hydrolysis of clay minerals, e.g. illite, a simple mechanism is implied by writing this equation,



$$K_{\text{eq}} = \frac{[\text{K}^+]^{0.6} [\text{Mg}^{+2}]^{0.25} [\text{Al}^{+3}]^{2.3} [\text{H}_4\text{SiO}_4]^{3.5}}{[\text{H}^+]^8}$$

This equation indicates that illite is precipitated once equilibrium is reached, an unlikely event because the conditions under which illite is originally formed are vastly different from those in this simplified ocean environment. Therefore application of equilibrium principles to the kinetic data in this study is invalid. It is more likely that a steady state is reached in which (1) illite hydrolyzes to silicic acid and cations, (2) as the steady state is reached, the reaction product precipitates as amorphous

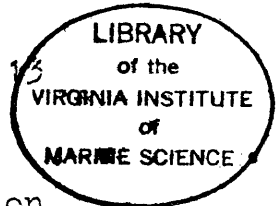
silica containing various cations - the content of which is quite variable depending only on its own immediate ion environment at the time of precipitation-, and (3) this precipitate may redissolve contributing to the dissolved silica concentration or may be metastable and alter itself to some other lower, free energy state.

In this kinetic treatment of the data, the mechanism by which the silica sources dissolve and reprecipitate need not be stated explicitly; however, the k and w values obtained for each source can be interpreted meaningfully. It will be initially assumed that the rate determining step of the hydrolysis of clay minerals is diffusion controlled. The amount of silicic acid brought into solution during the time interval dt is given by

$$\frac{dm}{dt} = \frac{DeA(M - m)}{Wl} \quad (4)$$

where e is effective directional porosity, M is concentration of silicic acid on the surface of the clay mineral, m is concentration of silicic acid in solution, A is the surface area of the clay, D is the diffusion coefficient of silicic acid, and W is the mass of water in the system. This treatment is essentially that of Helgeson (1971), but l is represented here simply as the distance between the surface layer of the clay to the bulk solution. Integrate the equation yields

$$m = kt^{\frac{1}{2}} \quad (5)$$



where $k = \frac{AD^{\frac{1}{2}}eM}{W}$. To determine the rate of the reaction,

$\frac{dm}{dt}$, equation (5) is differentiated to give $\frac{dm}{dt} = kt^{-\frac{1}{2}}$.

Since the exponent of t is -0.75 for the clay minerals rather than -0.50 (as ascribed to a solely diffusion controlled reaction), the rate of dissolution is probably not completely diffusion controlled. Since the concentration of silicic acid seems to level off at some final value, it is reasonable to assume the silicic acid is being removed from solution by some mechanism. Whether the precipitate is amorphous silica or amorphous silica containing specific or varying ratios of cations, whether the precipitate is forming on the original clay mineral or not, and whether the precipitate is playing a major role in maintaining the final concentration of silicic acid in solution by redissolving are questions which cannot be answered by this experiment.

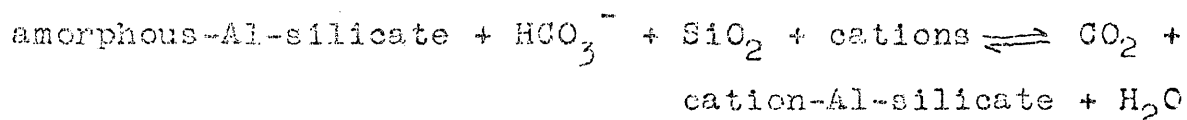
Even though there are these uncertainties in the exact interpretation of the rate constant, k, and the w value, one can compare the rate constants of the different clay minerals since their w values are equal. Assuming a diffusion controlled hydrolysis, k is proportional to $eAD^{\frac{1}{2}}$. In the experimental procedure, the number and surface area of the clay particles should be approximately the same for each of the clay minerals. The grams of clay in each run were the same and the grinding and sieving should

higher k values - 100 times greater than that of montmorillonite. It is not strictly valid to compare directly the rate constant of the biogenic silica to those of the clay minerals since the rate controlling step may be different and comparison of the surface area and particle number of the two systems would be difficult. Even with these theoretical reservations, it seems justifiable to compare the rates of the clay minerals and biogenic silica dissolution since in this experiment (1) the surface area of both is as nearly representative of what is found in the ocean environment as possible and (2) the particle number is probably higher in the clay mineral experiment (7.5 grams vs. 0.17 gram of biogenic silica), tending to shift the comparable rate constant of biogenic silica even higher, especially if both dissolutions are somewhat diffusion controlled.

The comparison of dissolution rates is pertinent to the discussion of what controls the dissolved silica concentration in the ocean, i.e. whether it is controlled by biogenic silica or clay minerals. Harriss (1966), Gregg (1968), Burton (1968), and Calvert (1968) have used similar geological explanations to resolve these questions. Each has calculated a silica budget for the ocean in which is estimated the supply and removal of oceanic silica from various sources. On this basis, each decides whether

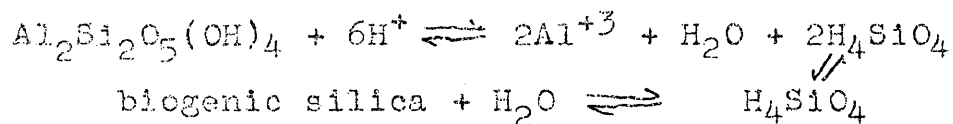
the ocean is in a steady state (Gregor, 1968; Burton, 1968; Calvert, 1968) or not (Harriss, 1966) and whether the silica concentration is controlled by biological activity (Harriss, 1966; Gregor, 1968; Burton, 1968) or by inorganic reactions involving silicate minerals (Calvert, 1968). For example, in Calvert's silica budget (Table 9), the rivers supply most of the silica to the ocean and biological activity, in the form of primary production (formation of diatoms) and deposition of biogenic silica, remove the silica from the ocean. He concludes that, since the amount of silica deposited as skeletons and tests is close to that supplied by rivers, (1) biological activity controls the concentration of silica in the sea, (2) the ocean is in an approximately steady state with respect to silica, and (3) the amount of silica removed by inorganic reactions is small.

The inorganic reactions mentioned above have been proposed by Garrels and MacKenzie (1965) and MacKenzie (1966, 1967) to be the main control of the silica concentration in the ocean. They propose a "reverse weathering" reaction of dissolved silica with degraded aluminosilicate minerals.



In their experiments silicate minerals release silica to silica-deficient sea water and abstract silica from silica-enriched sea water. Therefore, they conclude that silicate minerals exert a major control on the concentration of dissolved silica in the oceans.

While these budgets may accurately describe the silica input and output of the ocean, they do not answer the question of what controls the dissolved silica concentration in the ocean. It is not the quantity of solid material which is added or removed (as indicated by the silica budgets) that is important in determining what controls the dissolved species concentration, but rather the rate at which the solid dissolves. For example, in the deep ocean floor where both clay mineral and biogenic silica deposits are found, the comparison of the dissolution rate of the silica sources is the most salient concern as to the control of dissolved silica. Since the biogenic silica dissolves about 100 times faster than the clay minerals, then the concentration of silica released from the biogenic silica would suppress further dissolution of the clay minerals in a steady state system.



Garrels and MacKenzie (1965) assert that clay minerals are a major controller of silica in the oceans since the

average concentration of silica in the ocean is approximately 2-5 ppm or 30-80 μ moles H_4SiO_4 per liter, the concentration released by the clay minerals.

Rather than an average concentration, one should consider the variation of the silica concentration in the ocean below the photic zone. (In the photic zone the silicate is controlled by living organisms, e.g. diatoms, and is not pertinent to this discussion.) In areas of known diatomaceous and biogenic silica deposits, the concentration of dissolved silica is significantly above that of the average, 5ppm. Considering the data collected from various parts of the ocean, it is evident that high concentrations are found at great depths near Antarctica (Table 10) (Discovery Reports, 1947), (Table 13) (Capurro, 1961) and near the equator in the Pacific where radiolarian-derived biogenic silica deposits are found (Table 11) (Bruneau, et al., 1948). Even at intermediate depths near Antarctica, the concentration is quite high (higher than most parts of the world). These concentrations can be expected if one considers the circulation and mixing of the Circumpolar Current and the Antarctic Bottom Water (AAB) which flows over the biogenic silica deposits (Gordon, 1971).

Though concentrations as high as obtained in this experiment have only been found during the OE and Discov-

ery II cruises (Tables 10 and 13), the lower values could be due to the swift Antarctic bottom currents which are evidenced by the numerous manganese nodule formations and ripple marks found in this region by the Eltanin cruises (Goodell, 1971), i.e. it is impossible to reach the high concentrations because the water is not in contact with the deposits long enough.

The only region which is consistently low in silica concentration is the North Atlantic Ocean. Here the North Atlantic Deep and Bottom Water (NAD&B) originates around Greenland and Norway where there is a lack of abundant siliceous deposits. Therefore one would expect low silica concentrations (Table 12) (Bruneau, 1948). In the south Atlantic Ocean where there is mixing between the NAD&B and the AAB, higher concentrations are found. One can almost delineate the northern-most boundary of the AAB (Table 10); however, such identification of water masses is tenuous since there is continual mixing of the AAB upwards, diluting its silica concentration.

Water in the Pacific and Indian Oceans results from mixing of the Circumpolar Current, AAB, and NAD&B. Concentrations higher than those of the Atlantic Ocean are found (Table 11). This could be due to enrichment either from the AAB and Circumpolar Current or from areas of siliceous, biogenic deposits known to exist in equatorial

Pacific and Indian Oceans.

Therefore as evidenced by the general trends denoted in this data, the probable control of the ocean's silica concentration is the mixing and circulation of waters originating from areas of biogenic silica deposits - the source of dissolved silica.

FUTURE WORK

Additional experiments which could further the understanding of the dissolution mechanism of clay minerals and biogenic silica are the following: (1) X-ray studies of the silica source before, during and after the dissolution to determine the extent of structural changes and form of the depositing silica after a steady state has been reached, (2) dissolution studies inside a semi-permeable membrane to determine the precipitate which might form outside the membrane after the steady state has been reached, and (3) monitoring the change in cation concentration during the dissolution. Also high pressure dissolution rate studies would be of interest since the high pressures which exist on the ocean floor could alter these dissolution rates.

APPENDIX 1

TABLE 1
 DISSOLVED SILICA CONCENTRATION
 VERSUS TIME FOR KAOLINITE

Time (hours)	Micromoles of H_4SiO_4 /liter	
	Run 1	Run 2
2.0	1.3	1.2
4.0	3.0	2.3
7.0	4.3	2.9
24.2	7.6	7.7
33.5	9.3	10.2
51.8	10.3	10.5
78.6	15.4	15.8
100.3	16.7	16.0
124.1	18.6	18.6
147.9	20.3	21.0
358.8	28.3	27.4
433.9	29.5	26.2
507.0	28.4	27.7

Average of last six values = 27.9
 27.9 micromoles = 1.65 ppm SiO_2

TABLE 2
 DISSOLVED SILICA CONCENTRATION
 VERSUS TIME FOR MONTMORILLONITE

Time (hours)	Micromoles of H_4SiO_4 /liter	
	Run 1	Run 2
1.5	28.0	-
3.0	29.8	30.5
22.8	52.3	53.0
28.5	55.6	55.0
47.6	64.6	64.5
71.5	66.5	72.7
95.3	77.9	72.7
118.7	73.9	71.7
169.7	75.9	76.2
190.7	75.4	75.2

Average of last four values = 75.7
 75.7 micromoles = 4.46 ppm SiO_2

TABLE 3
DISSOLVED SILICA CONCENTRATION
VERSUS TIME FOR ILLITE

Time (hours)	Micromoles of H_4SiO_4 /liter	
	Run 1	Run 2
2.2	11.5	10.5
15.2	14.7	14.5
8.8	16.4	16.6
22.4	23.8	22.5
33.3	27.1	26.4
48.4	30.0	27.5
75.5	33.0	33.7
96.3	36.9	40.0
152.3	35.9	32.0
173.7	39.7	35.7
241.3	39.0	36.5
361.3	49.9	44.5
505.5	55.3	48.6
722.6	50.2	49.5

Average of last six values = 49.7
49.7 micromoles = 2.93 ppm SiO_2

TABLE 4
 DISSOLVED SILICA CONCENTRATION
 VERSUS TIME FOR BIOGENIC SILICA

Time (hours)	Micromoles of H_4SiO_4 /liter	
	Run 1	Run 2
2.0	115.0	188.8
5.0	308.8	476.3
28.0	1268.0	1252.0
49.8	1328.0	1402.0
96.0	1422.0	1378.0
129.0	1478.0	1328.0
214.5	1478.0	1528.0
504.0	1552.0	1458.0

Average of last four values = 1504.0
 1504 micromoles = 88.7 ppm SiO_2

TABLE 5

COMPUTER PROGRAM USED TO DETERMINE K

Dimension T(40), C(40)

```

7 READ (2,1) N, ULIMIT, STEP, IOSET
  N = N*2
1 FORMAT (I5, F5.0, F5.0, I5)
  NN = N-IOSET
  K = (ULIMIT * 2.0)/STEP + 1.0
  READ (2,2) (T(I), T(I+1), C(I), C(I+1)), I = 1,N,2)
2 FORMAT (F10.0, F10.0, F5.0, F5.0)
  DO 4 I = 1, K
    OMEGA = ULIMIT - (I-1) * STEP + 1
    WRITE (5,6) OMEGA, IOSET
    IF (OMEGA) 8,9,8
9 DO 11 J = 1, NN
  L = J + IOSET
  DELC = C(L) - C(J)
  DELT = ALOG (T(L)) - ALOG(T(J))
  FK = DELC/DELT
  WRITE (5,10) FK
10 FORMAT (' K =' F10.3)
11 CONTINUE
  GO TO 4
8 DO 5 J = 1, NN
  L = J + IOSET
  DELC = (C(L) - C(J)) * OMEGA
  DELT = T(L)**OMEGA - T(J)**OMEGA
  FK = DELC/DELT
5 WRITE (5,3) FK
3 FORMAT (' K=' F10.3)
6 FORMAT (' OMEGA=' F10.5, ' OFFSET=' I3)
4 CONTINUE
  GO TO 7
END

```

TABLE 6
DATA FROM PROGRAMS

Silica source	w	k(1)	Correlation Coefficient	Linear Regression Eq.(2)
kaolinite	-0.75	2.05	0.99	$y = -9.44 + 8.21x$
	-0.50	0.67	0.98	$y = 1.49 + 1.33x$
montmorillonite	-0.75	5.93	1.00	$y = 1.21 + 23.72x$
	-0.50	2.82	0.99	$y = 23.42 + 5.63x$
illite	-0.75	2.50	0.98	$y = 1.18 + 10.99x$
	-0.50	0.90	0.96	$y = 13.58 + 1.80x$
biogenic silica	-1.25	598.0	-0.98	$y = 2144.5 - 2390.7x$
	-1.00	615.5(3)	0.94	$y = 103.8 + 615.5x$

(1) $k = \text{slope times } (w+1)$, slope is that of the linear regression equation

(2) $y = \text{concentration of } H_4SiO_4$, $x = \text{time}$

(3) slope = k in this calculation

TABLE 7

KINETIC DATA OF WOLLAST FOR DISSOLUTION OF FELDSPAR

Time (hours)	Silica concentration (mg/l.)
2	0.1
6	0.8
11	1.0
24	3.4
48	5.5
72	6.8
95	6.7
144	7.1
200	8.1

TABLE 8

DATA FROM PROGRAMS USING WOLLAST'S DATA

w	Correlation Coefficient	Linear Regression Equation
-0.75(1)	0.98	$y = -5.57 + 4.14x$
-0.50(1)	0.99	$y = -1.67 + 1.00x$
-0.75(2)	0.98	$y = -4.24 + 3.42x$
-0.50(2)	0.96	$y = -0.30 + 0.66x$

(1) Using the first six sets of data

(2) Using all the data

TABLE 9
CALVERT'S SILICA BUDGET

	grams of SiO ₂ /year
Supply	
Streams	4.3×10^{14}
Submarine weathering	0.03×10^{14}
Submarine volcanism	0.0003×10^{14}
Total	4.3303×10^{14}
Removal	
Primary production (corrected for solution of diatom tests)	$0.77 - 16.1 \times 10^{14}$
Deposition of siliceous sediments	
Antarctic	3.0×10^{14}
Pacific subarctic	0.2×10^{14}
Equatorial Pacific	0.005×10^{14}
Bering Sea	0.10×10^{14}
Okhotsk Sea	0.15×10^{14}
Gulf of California	0.15×10^{14}
Total	3.605×10^{14}

TABLE 10
 SILICA CONCENTRATION IN WATERS
 FROM TIP OF AFRICA TO ANTARCTICA

Position	Depth(meter)	Si(mg.atom/meter ³)
33°54'S, 01°46.5'E (south west tip of Africa)	100	0.8
	150	0.9
	200	1.2
	300	1.8
	390	2.8
	580	6.8
	780	16.4
	980	24.9
	1470	46.4
	1970	43.5
	2270	42.4
	2720	43.0
	3180	43.5
3630	50.4	
4090	65.1	
36°01.8'S, 00°04.3'E	100	1.4
	150	1.8
	200	1.9
	300	2.1
	400	3.7
	600	7.5
	800	13.4
	990	25.6
	1490	46.7
	1980	51.3
	2480	48.6
	2980	47.3
	3470	57.7
3970	78.6	
4470	80.3	

TABLE 10
(continued)

Position	Depth(meter)	Si(mg.atom/meter ³)
45°01.3'S, 00°33.7'E	100	4.3
	150	4.5
	200	7.5
	300	10.7
	400	17.8
	600	28.4
	800	39.1
	1000	54.7
	1490	62.8
	1970	64.9
	2470	67.2
	2970	78.2
	3460	93.4
3960	100.8	
59°23.8'S, 00°09.3'E	100	75.8
	150	100.0
	200	108.6
	300	111.9
	400	111.9
	580	111.9
	780	111.9
	960	111.9
	1460	111.9
	1970	108.6
	2480	102.7
	2980	108.6
	3480	108.6
3980	108.6	
4470	105.6	

TABLE 10
(continued)

Position	Depth(meter)	Si(mg.atom/meter ³)
64°31.9'S, 00°28.6'E	100	86.2
	150	90.4
	200	90.4
	300	90.4
	390	90.4
	580	97.4
	780	100.0
	980	102.7
	1480	105.6
	1990	108.6
	2490	108.6
	2990	108.6
3490	108.6	
3380	108.6	
66°06.5'S, 06°45.6'W	100	79.0
	150	86.2
	200	97.4
	300	97.4
	390	97.4
	590	100.0
	790	105.6
	990	108.6
	1480	108.6
	1970	108.6
	2450	108.6
	2950	105.6
	3460	105.6
3960	108.6	
4460	108.6	

TABLE 11
 SILICA CONCENTRATION IN WATERS
 ACROSS THE EQUATORIAL PACIFIC

Position	Depth(meter)	SiO ₂ (μg-atoms/l.)
9°14'N, 109°39'W	110	23.8
	160	25.8
	345	36.8
	447	49.0
	651	65.6
	905	83.6
11°39'N, 114°15'W	95	23.8
	143	31.2
	291	36.8
	390	41.8
	584	62.4
	777	81.2
	969	102.8
	1453	103.6
	2421	112.6
	3390	144.6
3874	134.8	
17°46'N, 126°51'W	142	7.6
	190	24.8
	287	37.8
	379	52.4
	474	57.8
	771	85.8
	970	108.4
	1445	103.6
	2397	150.0
	3350	165.6
3826	165.6	
4398	162.8	

TABLE 12
 SILICA CONCENTRATION IN WATERS
 OF THE MIDDLE AND NORTH ATLANTIC OCEAN

Position	Depth(meter)	SiO ₂ (μg-atoms/l.)
0°30'N, 25°38'W	1348	26.9
	1827	21.8
	2785	36.0
	3240	39.9
	3261	40.9
0°27'N, 27°45'W	1326	25.5
	2741	36.0
	3551	43.1
	3670	40.3
	3691	38.2
0°57'N, 29°49'W	1411	22.1
	2354	26.9
	2772	37.0
	2804	37.7
	2816	37.0
0°39'N, 32°10'W	1451	20.4
	1924	18.5
	2891	29.8
	3712	32.1
	3833	33.2
	3854	32.4

TABLE 13

SILICA CONCENTRATION IN THE ANTARCTIC WATERS

Position	Depth(meter)	SiO ₂ (mg-atom/l.)
65°30.2'S, 20°07.4'E	104	42.67
	207	51.67
	319	51.00
	534	60.50
	810	56.30
	1176	64.00
	2142	66.67
	3140	63.83
	4132	66.33
60°01.2'S, 20°00.0'E	98	34.17
	220	48.33
	362	53.00
	466	67.83
	870	75.00
	1226	70.83
	1548	85.00
	2038	85.00
	2970	82.00
	3895	89.17
	4420	79.67
5164	75.00	
62°48.3'S, 20°00.5'E	105	31.17
	197	42.50
	400	69.17
	854	57.50
	1010	55.67
	2577	63.17
	3024	64.50
	3925	67.83
	4420	66.67

APPENDIX 2

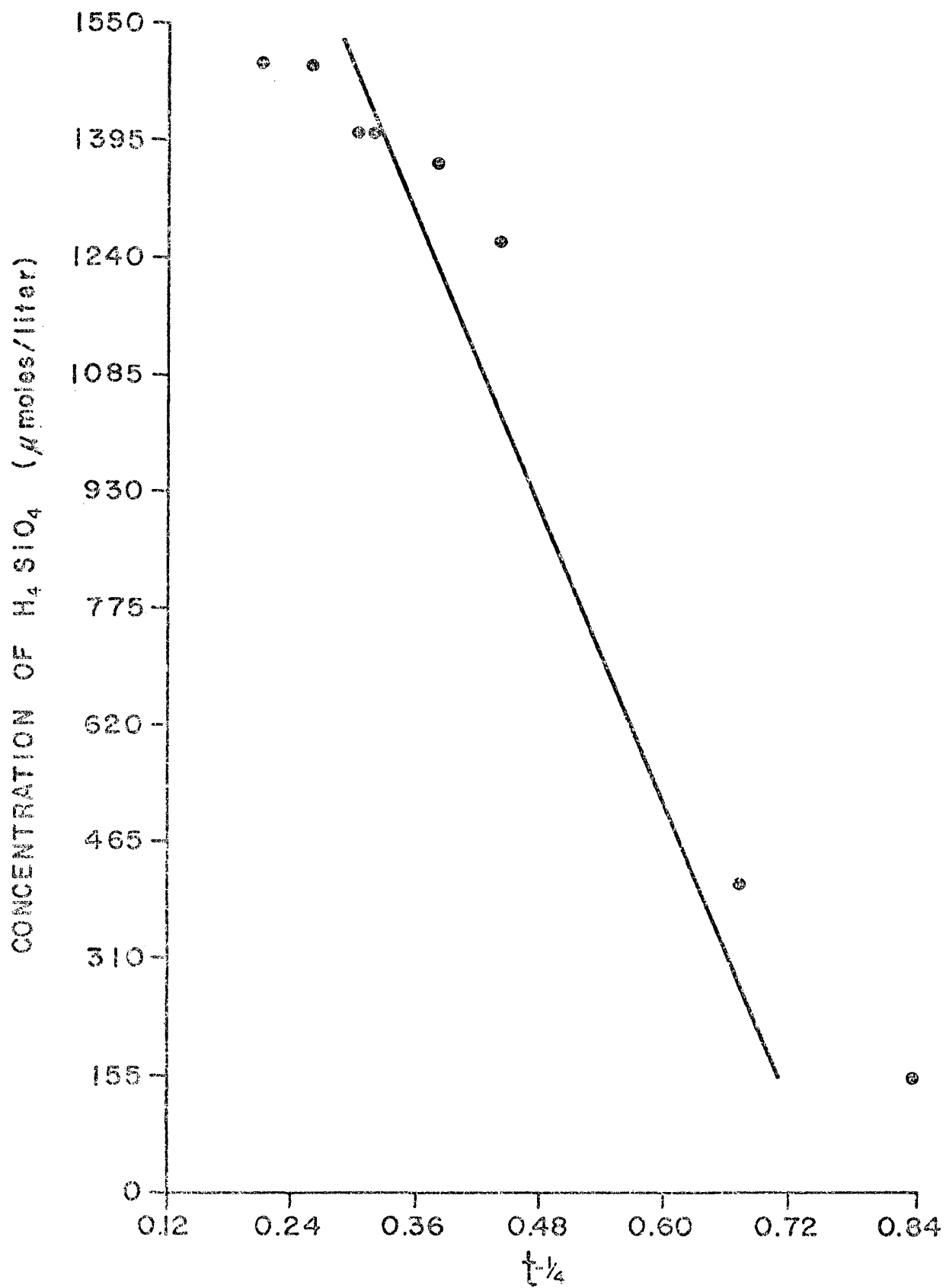


Figure 1. Theoretical Line Compared with Experimental Points for Biogenic Silica

Figure 2. Theoretical Line Compared with Experimental Points for Kaolinite

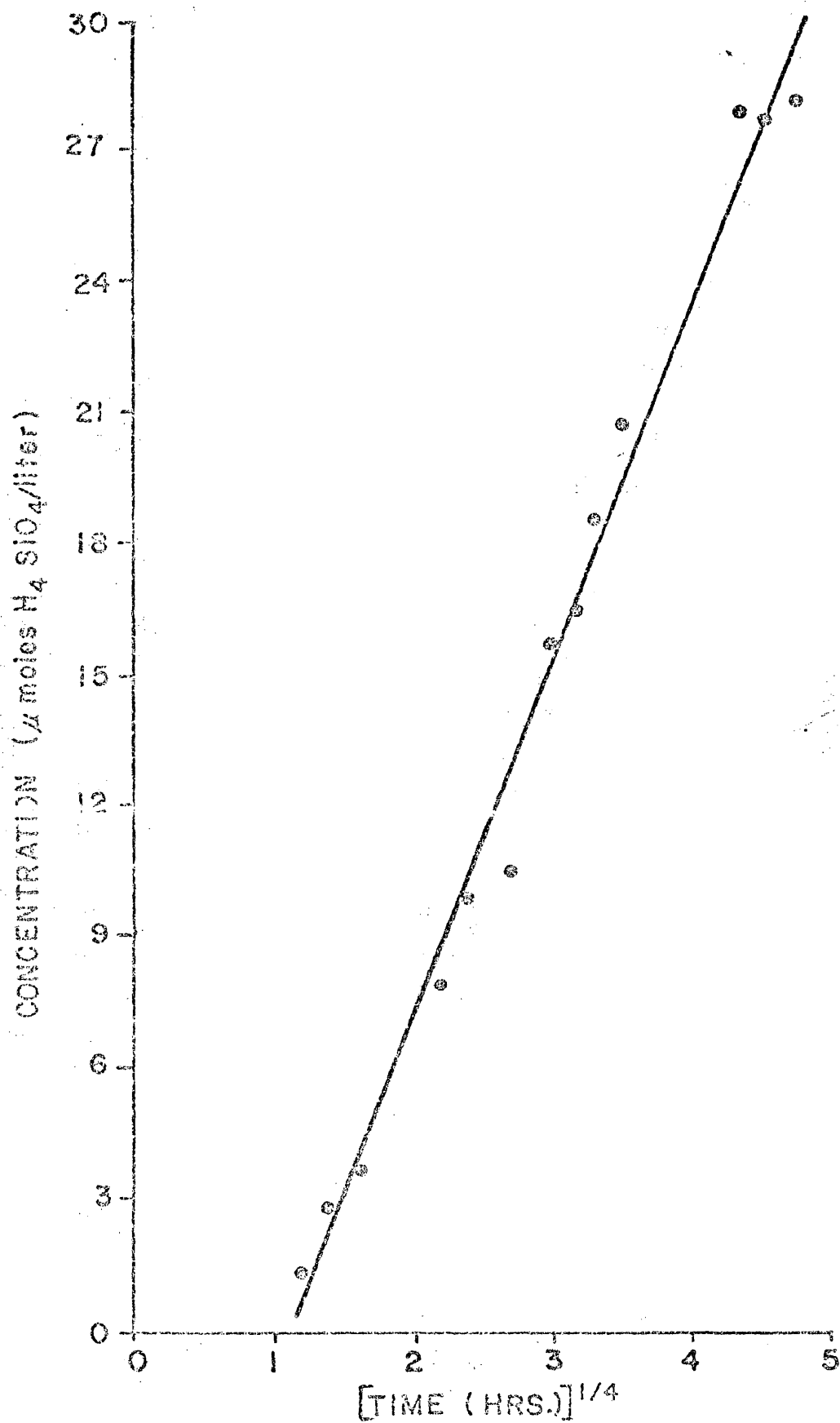


Figure 3. Theoretical Line Compared with Experimental Points for Illite.

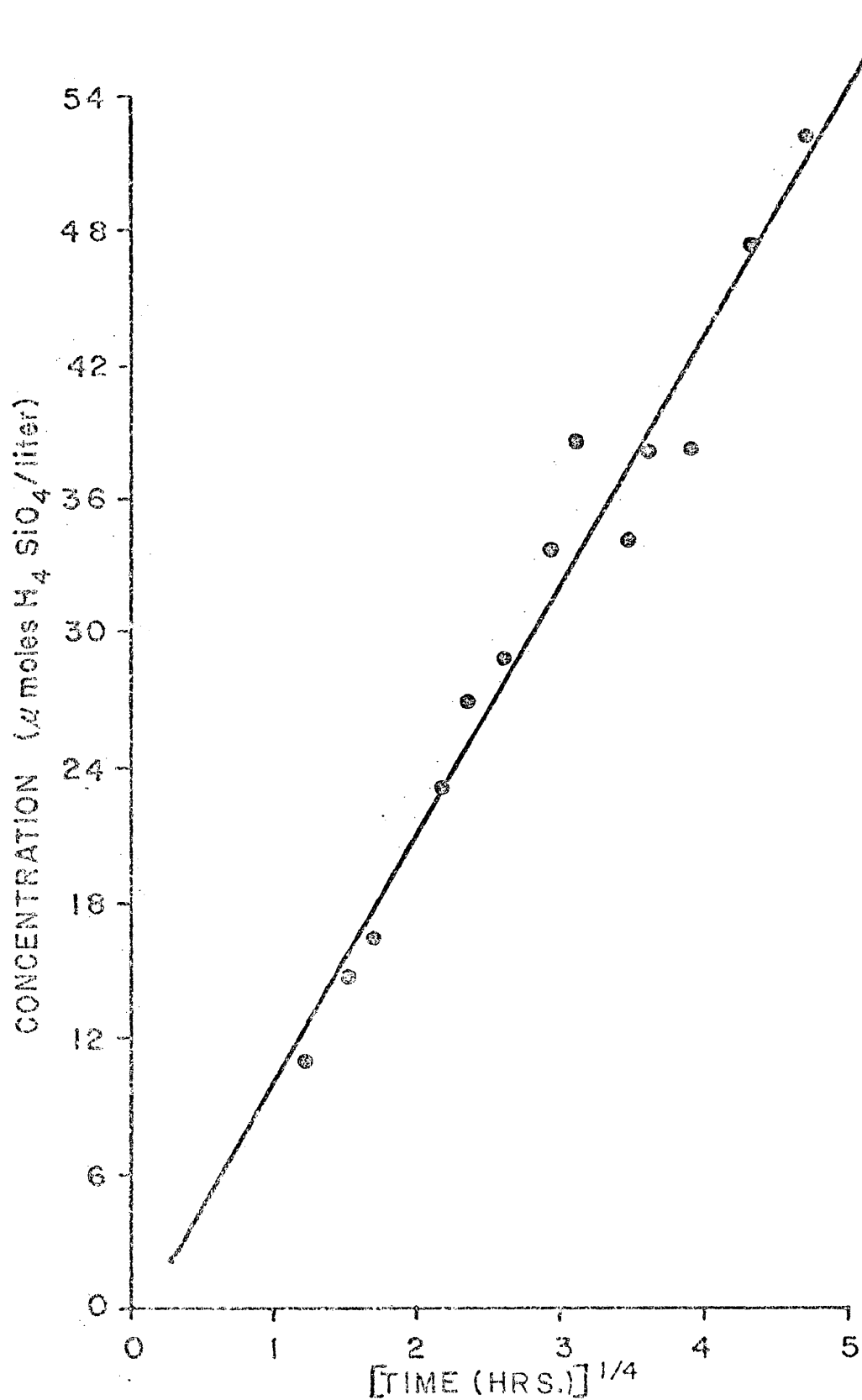
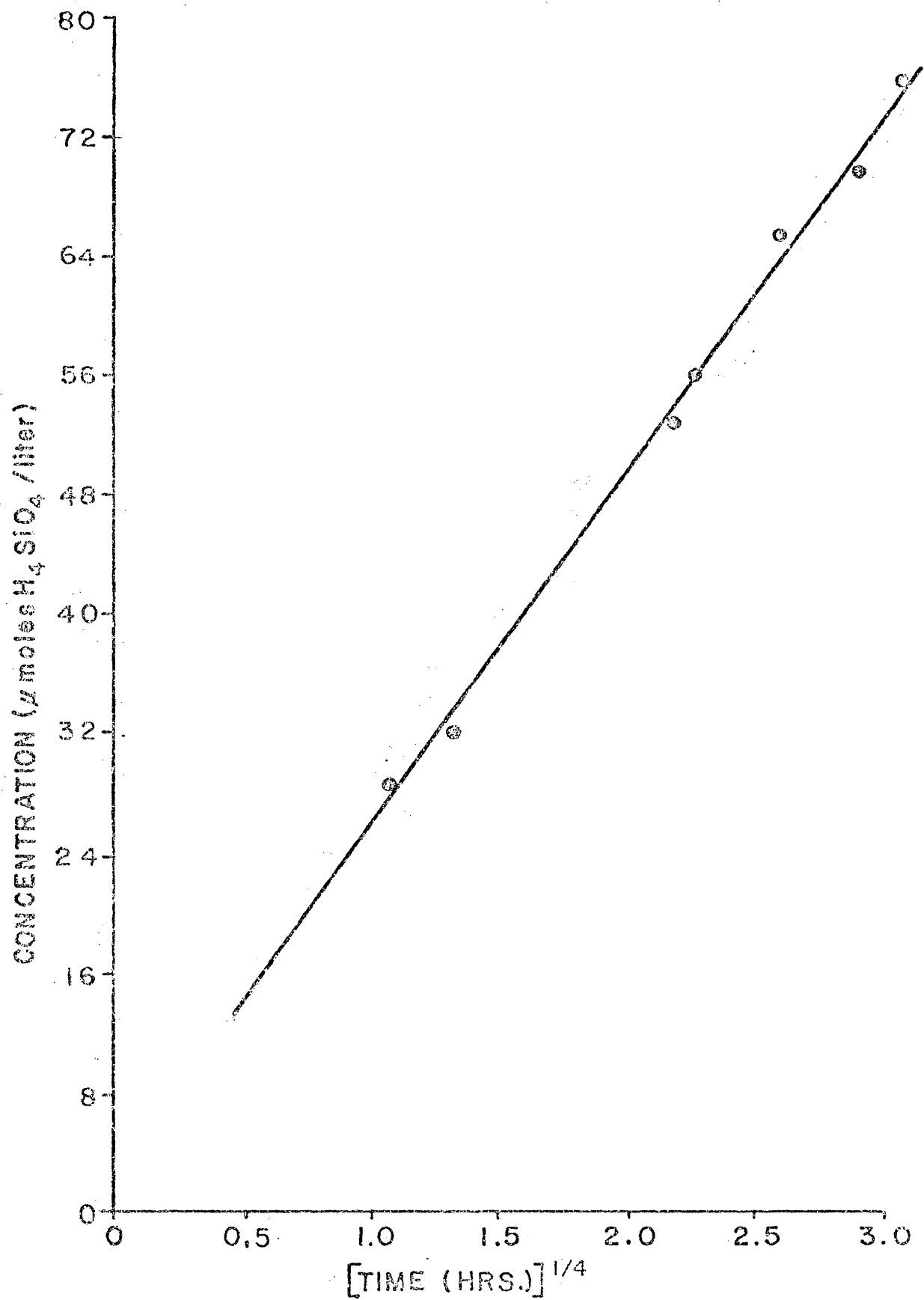


Figure 4. Theoretical Line Compared with Experimental Points for Montmorillonite



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