

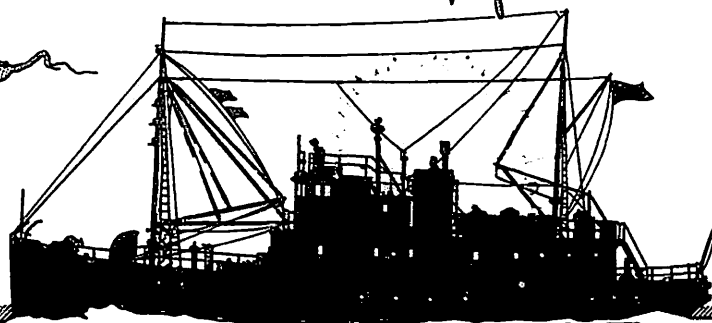
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Technical Reports  
Nos. 174, 175, 176,  
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RICHARD H. FLEMING  
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SOME CONSEQUENCES OF THE DECOMPOSITION  
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AN ANOXIC FJORD

BY FRANCIS A. RICHARDS, JOEL D. CLINE, WILLIAM W. BROENKOW,  
AND LARRY P. ATKINSON

# SOME CONSEQUENCES OF THE DECOMPOSITION OF ORGANIC MATTER IN LAKE NITINAT, AN ANOXIC FJORD<sup>1</sup>

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William W. Broenkow, and Larry P. Atkinson*  
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## ABSTRACT

Observations in Lake Nitinat, an anoxic fjord on Vancouver Island, British Columbia, indicate that the large accumulations of ammonia, carbonates, phosphates, silicates, and sulfides in the deep water are the result of oxidative and fermentative decomposition of organic matter of planktonic origin, the reduction of sulfate ions, hydrolytic or other non-oxidative release (in the case of silicates), and the solution of carbonates (which also increases the alkalinity). Ammonia, sulfides, and silicates accumulate in the sulfide zone in direct proportion to each other, but some of the phosphate is probably released from the organic matter earlier than the other components, and some of the phosphate may be precipitated onto the bottom. Methane was observed in the anoxic waters, suggesting that some decomposition takes place by anaerobic fermentation. The concentrations of ferrous and sulfide ions are probably controlled by the solubility of ferrous sulfide. The vertical distribution of sulfides can be described by a mathematical model that can be simplified to one dimension because horizontal advective and diffusive terms can be neglected.

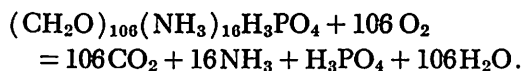
## INTRODUCTION

In several of his papers, Redfield (1934, 1942, 1958) has related the changes in concentration of nitrogen, carbon, and phosphorus compounds accompanying biological processes in the marine environment to the average ratios in which these elements occur in marine organisms. He has also shown that the consumption of dissolved oxygen from the water is statistically related to these changes in a relatively fixed proportion. These concepts have led to stoichiometric models of the ratios in which inorganic forms of nitrogen, phosphorus, and carbon are bound by photosynthesis and again released to the water by respiration and decomposition. The accompanying production and consumption of dissolved oxygen is an integral part of these models.

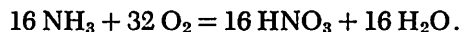
The above models have been based on statistically average plankton material in which the ratio C:N:P = 106:16:1, by

<sup>1</sup>Contribution No. 372 from the Department of Oceanography, University of Washington. This work was supported in part by Office of Naval Research Contract Nonr 477(37), Project NR083-012 and National Science Foundation Grant G19784.

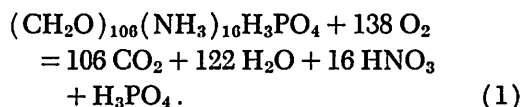
atoms. This ratio has been used by Richards (1965, in press) to construct a model of average organic matter in the sea having the empirical formula  $(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}\text{H}_3\text{PO}_4$ . The biochemical oxidation of this material would be completed, at the expense of dissolved oxygen, according to the equation



Ammonia is a transient form in oxygen-bearing seawater, and is ultimately biochemically oxidized to nitrate by processes that can be represented thus:



Adding the above equations gives



This equation provides the ratios in which concentrations of dissolved oxygen, total carbon dioxide, nitrate, and phosphate ions would change when organic matter having the proposed composition was completely decomposed in the marine environment. Enough tests of the model have been made

TABLE 1. Concentration of methane at Station 3, June 1965

Depth (m)	CH <sub>4</sub> (μg-at./liter)
30	0
40	20
50	30
60	50
90	50
100	60
110	70
120	60
130	50

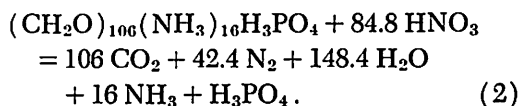
to show that it is a reasonable representation of these processes in large areas of the ocean (Stefánsson and Richards 1963; Broenkow 1965; Sugiura and Yoshimura 1964; Sugiura 1965).

The assumptions of the above model are not always fulfilled because 1) large departures exist from the assumed average composition of the plankton (Riley 1951, 1956) and 2) the rates of regeneration of phosphorus, nitrogen, and carbon may not be uniform with the result that the reactions do not go to completion or are not completed simultaneously. The admixture of waters containing preformed nutrients, as defined by Redfield (1942), can obscure the model relationships.

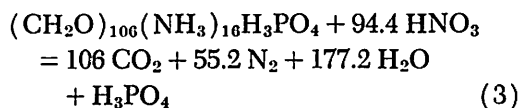
The model referred to above can apply only as long as free dissolved oxygen is available in the water. This is generally the case in the open ocean; Redfield (1958) has shown that the balance of nature is such that in the freely circulating parts of the ocean, the oxygen demand is somewhat more than met by the solution of air and by photosynthetic production. This is because the amount of organic matter that can be formed is limited by the availability of nutrients. However, this is not the case in certain marine environments (that Redfield calls nutrient traps) where the circulatory replenishment of oxygenated water is limited, or the biochemical oxygen demand is unusually high, or both. These environments become anoxic; they are usually semi-enclosed basins or fjords. The Black Sea, Dramsfjord in Norway, the Gulf of Cariaco and the Cariaco Trench in the Caribbean

Sea off Venezuela, Kaeo Bay in Indonesia, and Saanich Inlet and Lake Nitinat on Vancouver Island in British Columbia are examples of these environments (Richards and Vaccaro 1956; Richards 1965, in press).

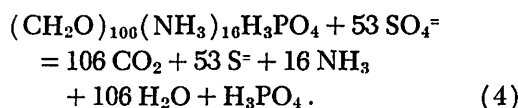
A model has been proposed by Richards (1965, in press) for the decomposition of organic matter in anoxic marine environments, where nitrate and nitrite ions supply the oxygen consumed by the biochemical oxidation of organic matter as long as they are available; when they are completely (or nearly completely) consumed, sulfate reduction can ensue. The first part of the model is represented by the equation:



This equation ignores the intermediate reduction of nitrate to nitrite, and does not show the possible oxidation of ammonia at the expense of nitrate which may or may not take place during this stage. If it does, the equation



might be expected to describe the relationships. Sulfate reduction can be represented by the equation



The observations reported in this paper have been made to examine a natural system in terms of its adherence to, or departures from the above model, and to describe other features arising from the anoxic decomposition of organic matter.

The authors wish to acknowledge the inspiration that the career of Alfred C. Redfield has given them, personally and in his writings. We wish also to acknowledge the help of Dr. Kilho Park, who carried out the methane analyses given in Table 1 and chromatographic CO<sub>2</sub> analyses in the field, and the assistance of our colleagues in the

department, particularly L. A. Codispoti, M. Healy, D. R. Kester, R. A. Kletsch, Meredythe Meller, R. Overstreet, R. W. Riley, D. Robare, and Edwyna von Gal.

#### METHODS AND MATERIALS

Observations of temperature, salinity, dissolved oxygen, inorganic phosphate, nitrate ions, nitrite ions, ammonia, reactive silicate, pH, alkalinity, total carbon dioxide, free dissolved nitrogen, dissolved methane, dissolved hydrogen, and of sulfides and other reduced forms of sulfur have been made in Lake Nitinat on two occasions.

*Temperature* was observed using standard deep-sea reversing thermometers.

*Salinity* was determined from conductivity measurements and by Knudsen titrations.

*Dissolved oxygen* was determined in the field using the Winkler titration and by analyses of gas samples extracted from the water by the methods of Broenkow (1963) using Scholander's (1947) apparatus and methods.

*Dissolved nitrogen* was determined by the gasometric method used for dissolved oxygen (above).

*Inorganic phosphate* was determined by the ascorbic acid-potassium antimonyl tartrate method of Murphy and Riley (1962) as modified by Strickland and Parsons (unpublished).

*Nitrate ions* were determined by a modification of the hydrazine reduction method of Mullin and Riley (1955*b*).

*Nitrite ions* were determined by the method described by Barnes (1959).

*Reactive silicate* concentrations were determined by the method of Mullin and Riley (1955*a*), modified by using  $\text{Na}_2\text{SiF}_6$  as a primary standard and in other minor details.

*pH* was determined using either a Beckman Model G or Corning Model 12 pH Meter, after bringing the samples to a temperature near 20°C.

*Titration alkalinity* was determined by the method of Anderson with Robinson (1946) and by a modification of the method of Gast and Thompson (1958) in

which standard acid was added to the sample and the excess back-titrated electrometrically to a pH of 7.00 after the liberated  $\text{CO}_2$  was purged from the sample with nitrogen.

*Total carbon dioxide* was calculated from the alkalinity and pH using the tables and equations of Buch (*in* Barnes 1959). It was also determined by the gasometric methods referred to under the sections on dissolved oxygen and nitrogen, and by the gas chromatographic method of Swinnerton, Linnenbom, and Cheek (1962*a,b*).

*Methane and hydrogen*: Hydrogen was detected and semiquantitatively estimated by gas chromatographic analyses of gas samples extracted from the water by the method used for dissolved nitrogen. Methane was similarly estimated, but it was also determined by a modification of the methods of Swinnerton et al. (1962*a,b*).

*Ammonia* was determined by the method of Richards and Kletsch (1964).

*Soluble and particulate iron* were determined according to the method described by Strickland and Parsons (1960). Particulate iron was determined on the residue remaining on a Millipore<sup>®</sup> 0.45  $\mu$  filter after filtration of a 1-liter water sample. The soluble iron was determined using 100-ml subsamples of the filtrate.

*Total reduced sulfur compounds* ( $\text{H}_2\text{S}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SO}_3^{2-}$ ) were determined by adding an excess of iodine to a seawater sample followed by back titration of the excess iodine to the starch endpoint (Kolthoff 1929). Thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ) and sulfite ( $\text{SO}_3^{2-}$ ) were tested for by adding excess zinc carbonate to another aliquot and removing the precipitated zinc sulfide by filtration, followed by iodometric titration.

*Calcium* concentrations were determined by the method of Pate and Robinson (1958) and were corrected for strontium using the strontium-chlorinity ratio 0.0007.

Samples were taken in all-plastic (high impact polyvinyl chloride) and rubber samplers built from a modification of the Emsworth design of Carruthers, Stubbings, and

<sup>2</sup> Registered trademark, Millipore Filter Corporation, Bedford, Massachusetts.

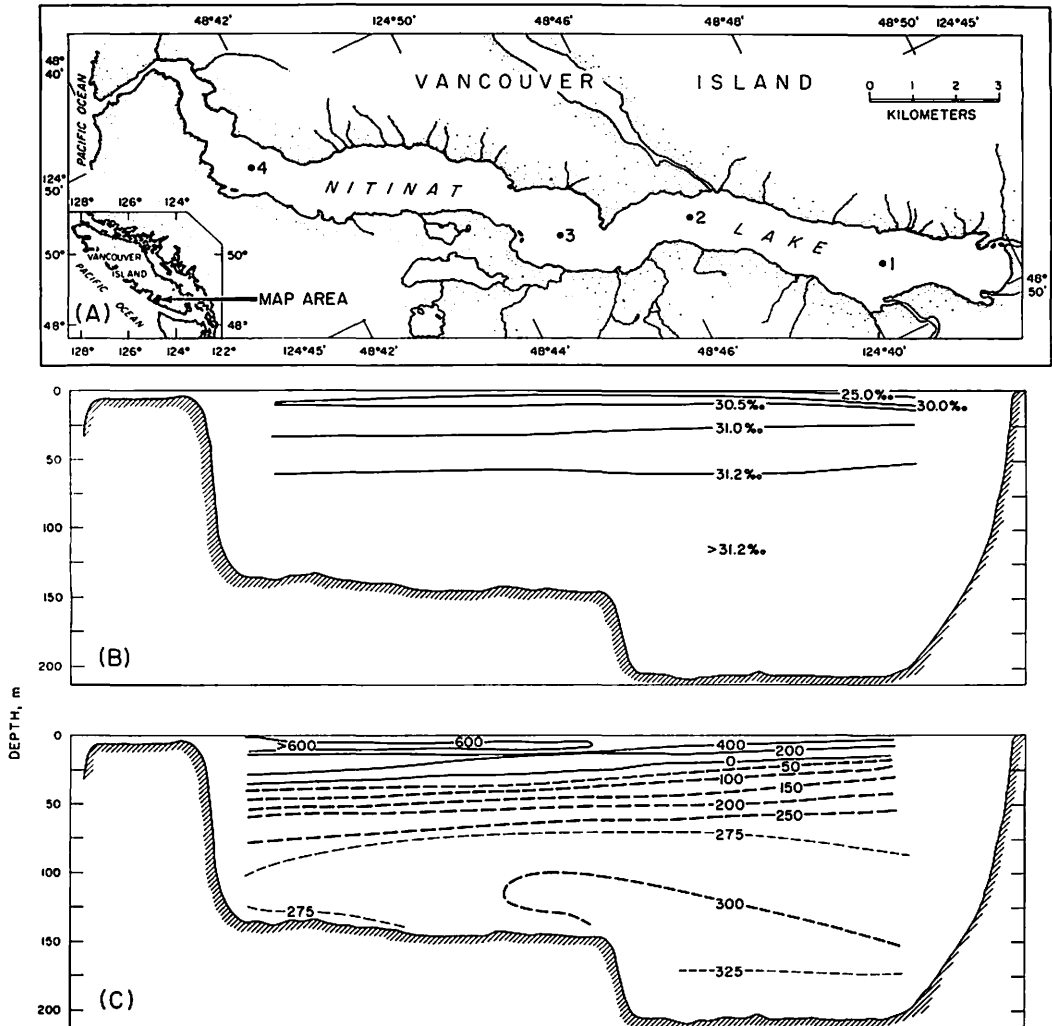


FIG. 1. A. Station plan, Lake Nitinat June 1964 and June 1965. B. Distribution of salinity (%). C. Distribution of oxygen ( $\mu\text{g-at./liter}$ )—and hydrogen sulfide ( $\mu\text{g-at./liter}$ )—June 1965.

Lawford (1950). The samples for nitrate, phosphate, and silicate were frozen in polyethylene bottles for subsequent analysis in the laboratory. Ammonia samples were frozen in glass bottles after acidifying to a  $\text{pH}$  value of about 3. Samples for gas extraction were refrigerated in special glass containers; a small amount of a paste made of solid  $\text{HgCl}_2$  and distilled water was added to them at the time of collection.

#### OBSERVATIONS

The data to be used in this paper arise from visits to Lake Nitinat made in June

1964 and June 1965 aboard the *RV Hoh* of the University of Washington.

Lake Nitinat is an anoxic fjord on southwestern Vancouver Island, British Columbia (Fig. 1A). It is about 23 km long by 1.2 km wide (Northcote, Wilson, and Hurn 1964). The fjord is highly stratified and nearly cut off by a long, shallow (4 m) entrance from the open Pacific Ocean. A strong halocline exists by virtue of freshwater influxes, but salinities close to those of full seawater are found from depths of about 40 m to the bottom at about 200 m (Fig. 1B).

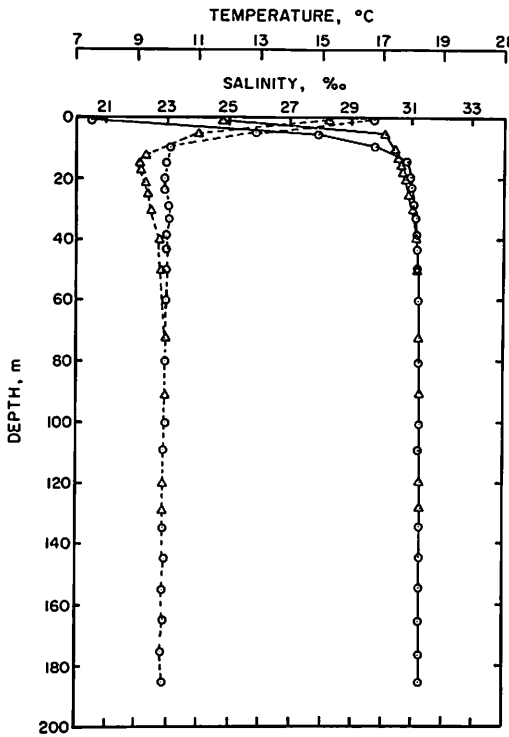


FIG. 2. Vertical distributions of temperature---and salinity---at Stations 1 (○) and 3 (△) June 1965.

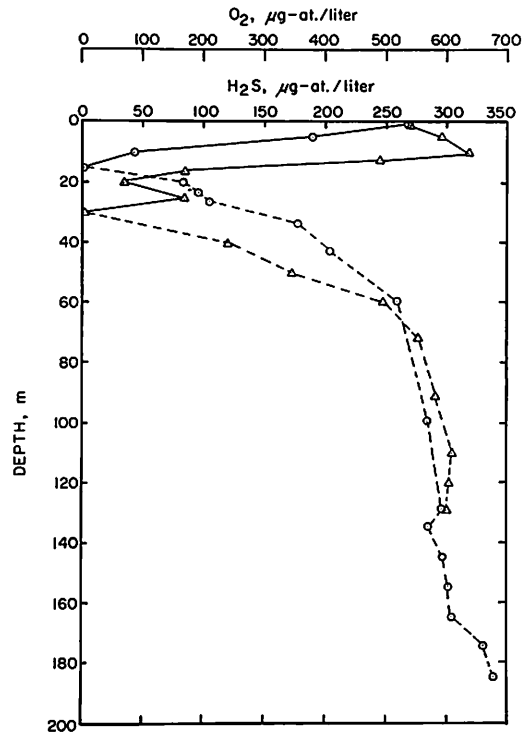


FIG. 3. Vertical distributions of dissolved oxygen---and hydrogen sulfide---at Stations 1 (○) and 3 (△) June 1965.

The vertical distributions of phosphate, silicate, and ammonia clearly demonstrate the extraordinary accumulation of these products of organic decomposition. The concentrations of phosphate, silicate, and ammonia in the deep waters of the fjord equal or exceed those found in the near-bottom waters of the Black Sea at depths of nearly 2,000 m (Richards 1965). The nitrate and nitrite distribution show maxima above 20 m, but there was no evidence of the presence of nitrate or nitrite ions in the sulfide-bearing water, from which dissolved oxygen was also absent. Titration alkalinities in the sulfide zone were larger than expected for normal seawater.

Methane was detected, gas chromatographically, in the anoxic waters. The method used was only semiquantitative, but the approximate concentrations observed at Station 3 on 20 June 1965 are shown in Table 1.

Hydrogen was detected by gas chromatography in samples taken in 1964, but not in any taken in 1965. No hydrogen was found in samples from the oxygenated zone, and maximum concentrations in the anoxic zone were about 100  $\mu\text{g-at./liter}$ .

No information on seasonal variations is available. Observations made in 1964 were essentially like those in 1965. The distributions of the various chemical variables are shown in Figs. 2 through 9.

#### DISCUSSION

The data will be examined in terms of the stoichiometric model referred to above, departures from the model, and possible explanations of the departures. Other features of the anoxic system will be commented on.

The consumption of free, dissolved oxygen is assumed to be the difference between observed oxygen concentrations and

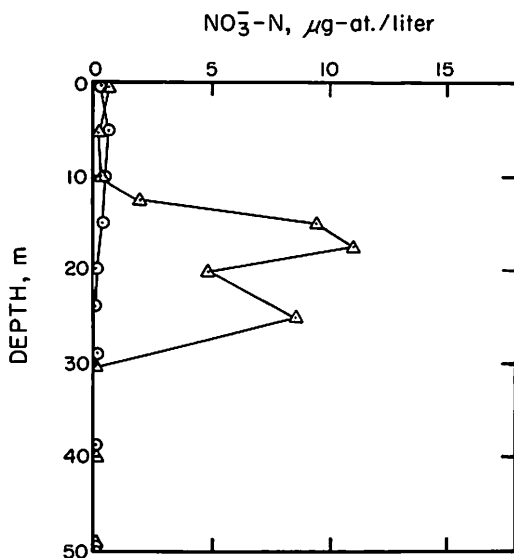


FIG. 4. Vertical distribution of inorganic nitrate-nitrogen at Stations 1 (○) and 3 (△) June 1965.

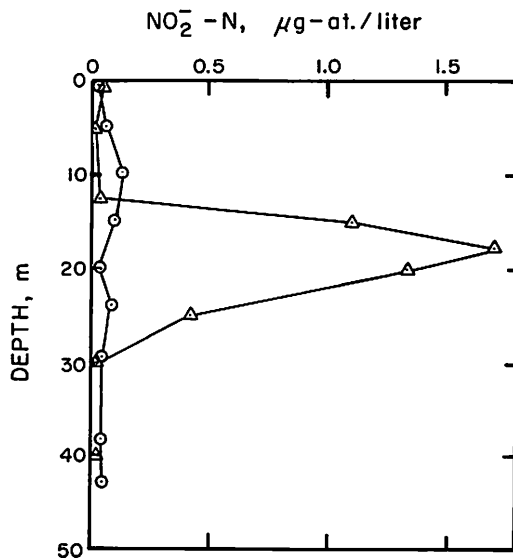


FIG. 5. Vertical distribution of inorganic nitrite-nitrogen at Stations 1 (○) and 3 (△) June 1965.

the amount of oxygen that would be dissolved in seawater having the *in situ* temperature and salinity, when equilibrated with a standard atmosphere of water-saturated air at the sea surface. The solubility data of Truesdale, Downing, and Lowden (1955) have been used, although these are probably somewhat in error (Green 1965). Each molecule of oxygen so consumed is equivalent to two atoms of oxidation equivalents.

The dissolved nitrogen estimates indicate that the production of free N<sub>2</sub> by denitrification is quantitatively of minor importance in Lake Nitinat. The volumes of residual gases estimated by the Scholander (1947) method exceeded those to be expected from the solution of air by the amount accounted for by methane (Table 1) plus an amount of free nitrogen equivalent to about 30 to 50 µg-at./liter of nitrate-nitrogen (equations 2 and 3). The oxidation equivalent to this amount of free nitrogen produced by denitrification (90 to 150 µg-at./liter) is small compared to the oxidation equivalents (up to more than 1,300 µg-at./liter) arising from sulfate reduction. This is in contrast to conditions in Dramsfjord, the Cariaco

Trench, and Saanich Inlet, in which denitrification appears to be relatively more important (Richards 1965).

The amount of sulfate reduction was estimated from determinations of total reduced sulfur compounds. Tests for thio-sulfate and sulfate were negative (the limit of detection for the sum of these ions was 10 µmoles/liter). Thus, the total reduced sulfur is assumed to be only hydrogen sulfide, although small, undetected quantities of free sulfur, tetrathionate (S<sub>4</sub>O<sub>6</sub><sup>2-</sup>) ions, and so on, may have been present. Each atom of sulfur present in the sulfide form is assumed to have yielded four atoms of oxygen (equation 4).

The maxima in the distributions of nitrate and nitrite (Figs. 4 and 5) apparently are caused by the release of these nutrients by bacterial decomposition of organic matter at the expense of free oxygen in the upper layer and by bacterial denitrification in the oxygen-deficient layer below. Denitrification processes apparently are confined to a very thin zone near the sulfide-oxygen interface where the downward diffusive flux of nitrate and nitrite are just balanced by denitrification. There

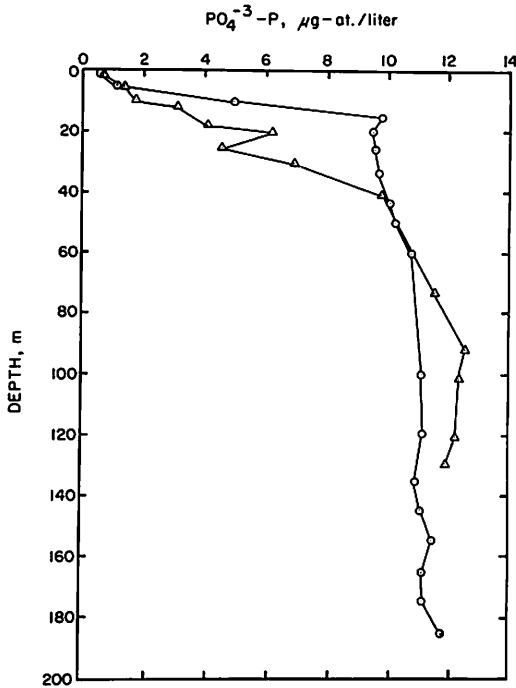


FIG. 6. Vertical distribution of inorganic phosphate-phosphorus at Stations 1 (O) and 3 (Δ) June 1965.

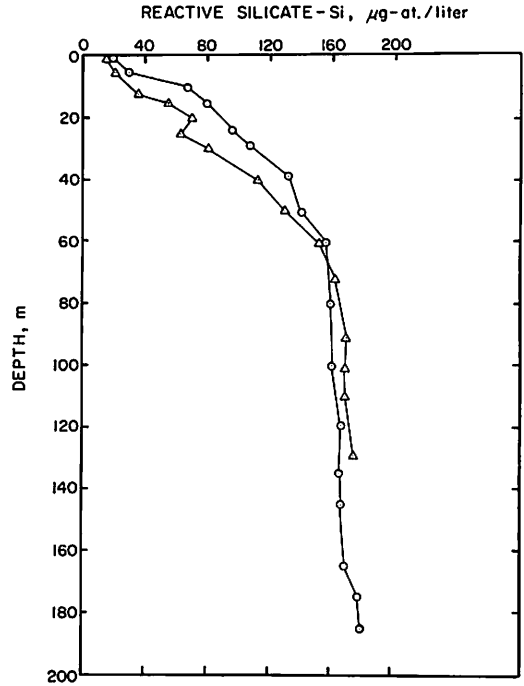


FIG. 7. Vertical distribution of reactive silicate-silicon at Stations 1 (O) and 3 (Δ) June 1965.

are insufficient data from this zone to test the validity of equations (2) and (3), and only the relationships in equation (4) will be examined. The relatively large nitrite maxima observed just above the sulfide zone appears to represent an intermediate step in the reduction of nitrate to free  $N_2$  (Brandhorst 1959; Richards 1965).

#### *Model relationship*

According to the model, the relationships in Table 2 should exist among the various products of organic decomposition and the equivalents of oxygen consumed, and these should be reflected in the correlation between the concentrations of the various decomposition products in discrete samples from the fjord and the slopes of the regression lines. The most important correlations in the data can be summarized as follows:

1) There is good correlation between the concentration of ammonia and the total reduced sulfur compounds in the sulfide-bearing waters (Fig. 10). The slope of

the line shown was determined by the method of least squares and is not significantly different from that predicted by the model,  $\Delta H_2S : \Delta NH_3 = 53 : 16$  (3.3 : 1). This gives confidence in the model, at least insofar as this process is concerned.

2) There is a high degree of linear relationship between the concentration of reactive silicate and oxidation equivalents (Fig. 11). Although the regeneration of silicates is not considered in the model, this correlation may be used to help evaluate the quality of the data. Richards (1958) and Stefánsson and Richards (1963) have observed silicate and phosphate concentrations in natural environments that, in limited strata, appear to be linearly related or nearly so. Grill and Richards (1964) observed the concurrent release of silicate and phosphate from phytoplankton decomposing in the dark in a laboratory experiment; during an intermediate time period, these elements seemed to be released in a

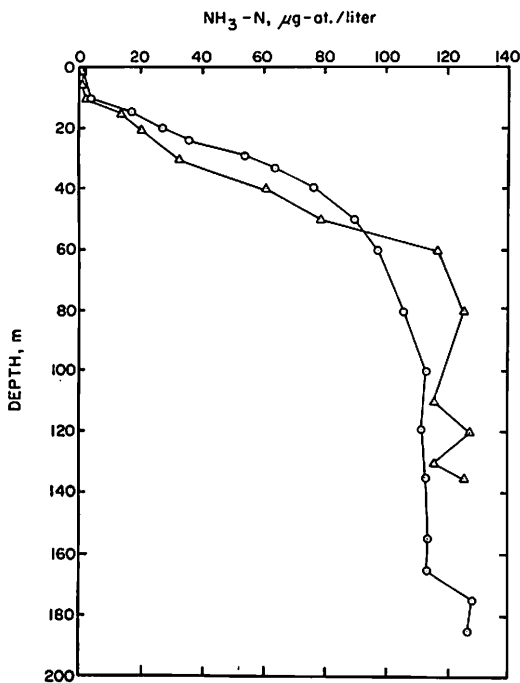


FIG. 8. Vertical distribution of ammonia-nitrogen at Stations 1 (○) and 3 (△) June 1965.

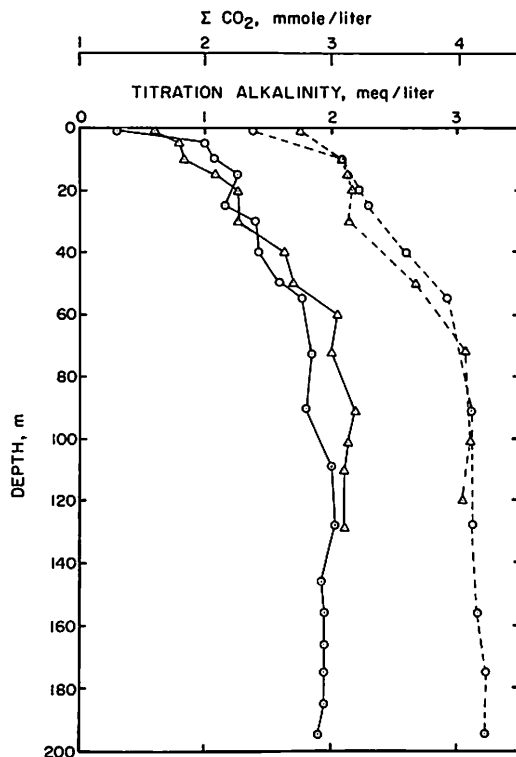


FIG. 9. Vertical distributions of total carbon dioxide—and titration alkalinity—at Stations 2 (○) and 3 (△) June 1965.

ratio of  $\Delta\text{Si} : \Delta\text{P}$  of 23 : 1 (by atoms), but the overall ratio from the beginning of the experiment until near the end was close to the 16 : 1 ratio that Richards (1958) suggested occurred in several strata of the western North Atlantic Ocean and Caribbean Sea waters. During both the stage in which free  $\text{O}_2$  is the oxygen source and during sulfate reduction, the oxidation equivalents consumed should be linearly related to the phosphate concentration by equations (1) and (4), so it follows that oxidation equivalents and silicates should be linearly related. In Lake Nitinat, the ratio  $\Delta\text{oxidation equivalents} : \Delta\text{SiO}_4 = 16 : 1$  (Fig. 11).

There is no reason to believe that the regeneration of phosphate and silicate are related through oxidative processes; it is more likely that both are simply regenerated by reactions that follow first order reaction kinetics (Grill and Richards 1964).

The point of this discussion is simply to suggest that the data are good, that silicate and ammonia have accumulated as would be expected, and one would also expect phosphate ions to have accumulated in concentrations related simply to ammonia concentrations in the sulfide-bearing waters and to the oxidation equivalents in the whole system. Such is not the case (Fig. 12), so explanations of the correlations involving phosphate will require that processes not included in the model be considered.

3) The relationships between phosphate concentrations and oxidation equivalents and ammonia concentrations (Figs. 12 and 13) depart markedly from those predicted by the model. Two features of the relationship between oxidation equivalents and phosphate concentrations in Fig. 12 disagree with the model. First, the slope of the relationship in the anoxic zone is  $\Delta\text{oxidation equivalents} : \Delta\text{PO}_4^{-3} = 285 : 1$  rather

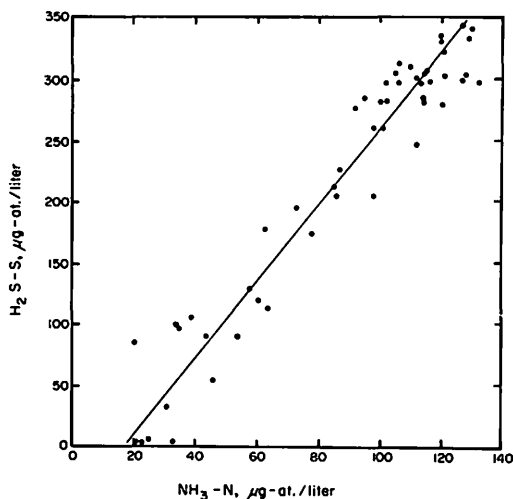


FIG. 10. Hydrogen sulfide vs. ammonia-nitrogen June 1965. Computed slope of line is  $\Delta S : \Delta NH_3 = 50.2 : 16$ .

than 212 : 1 as predicted by the model. Second, there is a marked discontinuity in the relationship at the boundary between the oxygenated and anoxic zones. Moreover, the relationship between the ammonia concentrations and phosphate concentrations is  $\Delta NH_3 : \Delta PO_4^{-3} = 22 : 1$  rather than the predicted 16 : 1.

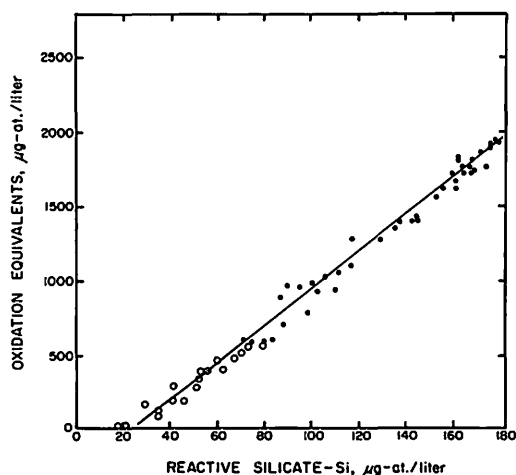


FIG. 11. Oxidation equivalents vs. reactive silicate-silicon June 1965. Computed slope of line is  $\Delta \text{oxidation equivalents} : \Delta Si = 16 : 1$ . Open circles represent data from oxygenated zone, solid dots represent data from anoxic zone.

Because the sulfide-ammonia relationship agrees with the model, it appears that both ammonia and oxidation equivalents (oxidation equivalents in the anoxic zone vary as four times the sulfide concentration, because the oxygen consumption is practically uniform and presumably the amount of denitrification is constant and small in the anoxic zone) behave according to the model. Thus, it seems that phosphate is the anomalous variable.

The large phosphate gradient observed at the depth of the oxygen-sulfide boundary (Fig. 6) is unlike the gradients of silicate (Fig. 7) and ammonia (Fig. 8) at these depths, and plots of phosphate vs. silicate and ammonia show discontinuities similar to that in Fig. 12. These observations suggest that phosphate is regenerated disproportionately to silicate and ammonia in the upper part of the anoxic zone. If this were the case, less particulate phosphate would find its way to the bottom of the anoxic zone and higher than predicted  $\Delta \text{oxidation equivalents} : \Delta PO_4^{-3}$  and  $\Delta NH_3 : \Delta PO_4^{-3}$  ratios would result.

This discontinuity could also be caused by the presence of about  $3 \mu\text{g-at./liter}$  of preformed phosphate in the deeper waters of the lake. If that were the case, the high  $\Delta \text{oxidation equivalents} : \Delta PO_4^{-3}$  ratio must be caused by some process other than those accounted for by the model. One such process might be the inorganic precipitation of calcium phosphate,  $Ca_3(PO_4)_2$ , from the near-bottom waters. To determine if inorganic precipitation is possible, the ion product of calcium phosphate was computed as follows:

The true phosphate ion,  $PO_4^{-3}$ , concentration was calculated using the empirical apparent dissociation constants of phosphoric acid given by Sendroy and Hastings (1927). These were corrected for temperature using the equations of Bates and Acree (1943) and Bates (1951) and extrapolated from the data compiled by Farr (1950). Thus, the first, second, and third apparent dissociation constants,  $K_1'$ ,  $K_2'$ , and  $K_3'$  at 10C are

TABLE 2. Ratios of changes, by atoms, of the products of organic decomposition predicted by the stoichiometric model

	During decomposition at the expense of free oxygen	During denitrification		During sulfate reduction
		with concurrent oxidation of $\text{NH}_3$	without oxidation of $\text{NH}_3$	
$\Delta\text{Oxygen Equivalents}:\Delta\text{P}$	276:1	254.2:1	283.2:1	212:1
$\Delta\text{NO}_3^-:\Delta\text{P}$	16:1	—	—	—
$\Delta\text{S}^{2-}:\Delta\text{NH}_3$	—	—	—	53:16
$\Delta\text{S}^{2-}:\Delta\text{P}$	—	—	—	53:1
$\Delta\text{Oxygen Equivalents}:\Delta\text{CO}_2$	276:106	254.2:106	282.2:106	212:106
$\Delta\text{CO}_2:\Delta\text{P}$	106:1	106:1	106:1	106:1
$\Delta\text{CO}_2:\Delta\text{NH}_3$	—	—	106:16	106:16

$$pK_1' = 2.09 - 0.5\sqrt{\mu},$$

$$pK_2' = 7.25 - 1.25\sqrt{\mu}, \text{ and}$$

$$pK_3' = 12.67 - 2.25\sqrt{\mu},$$

where  $\mu$  is the ionic strength of the solution. Assuming  $\mu = 0.64$  ( $\text{Cl} = 17.29\%$ ), and using the data in Table 3, the calcium phosphate ion product was found to vary from  $3.4$  to  $7.3 \times 10^{-24}$  moles<sup>5</sup> liter<sup>-5</sup>. The apparent solubility product of calcium phosphate was estimated from the following equation of Sendroy and Hastings (1927):

$$pK_{sp}' = 30.95 - \frac{17.40\sqrt{\mu}}{1 + 1.48\sqrt{\mu}} \text{ at } T = 38\text{C}, \quad (5)$$

where  $K_{sp}' = 2.1 \times 10^{-24}$  moles<sup>5</sup> liter<sup>-5</sup>. This indicates that the waters deeper than about 20 m are approximately 170% saturated with calcium phosphate. Because the relationship in equation (5) was determined at 38C, the estimated degree of supersaturation is somewhat conservative. We do not imply that  $\text{Ca}_3(\text{PO}_4)_2$  is precipitating in this environment, but as Dietz, Emery, and Shepard (1942) have suggested, the degree of supersaturation of tricalcium phosphate may be related to the deposition of certain phosphorite minerals.

4) The relationship between total carbon dioxide and ammonia in the anoxic zone is shown in Fig. 14. The least squares slope of the line is  $\Delta\text{CO}_2 : \Delta\text{NH}_3 = 141 : 16$ , and differs significantly from the 106 : 16 ratio predicted by equation (4). Titration alkalinity values in Lake Nitinat are about 1 meq/liter higher than "normal" seawater (Harvey 1955), increasing from ca. 2.2

meq/liter at 20 m to over 3.2 meq/liter in the deep water (Fig. 9). The alkalinity contributed by sulfide ions ranges from nil to ca. 0.30 meq/liter. Phosphate, silicate, and borate ions will also contribute to the alkalinity, while ammonium ions will diminish it. The silicate contribution is probably negligible, while the contributions of phosphate, sulfide, and borate to the alkalinity of a sample from 100 m at Station 3 (1965) are estimated to be 0.024, 0.268, and 0.005 meq/liter, respectively. The carbonate alkalinity of the sample, estimated independently from the gas chromato-

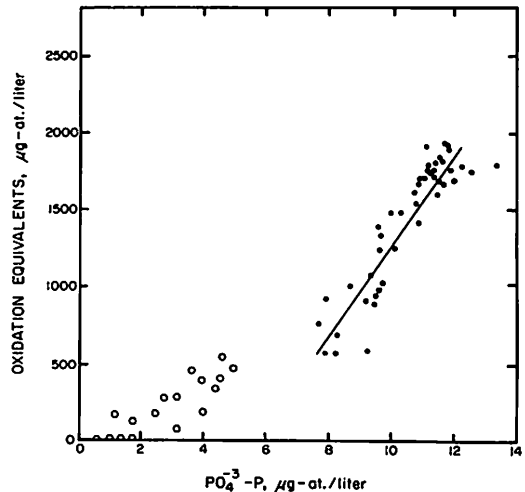


FIG. 12. Oxidation equivalents vs. inorganic phosphate-phosphorus June 1965. Open circles represent data from oxygenated zone, solid dots represent data from anoxic zone. Computed slope of anoxic data is  $\Delta\text{oxidation equivalents} : \Delta\text{PO}_4^{3-} = 285 : 1$ .

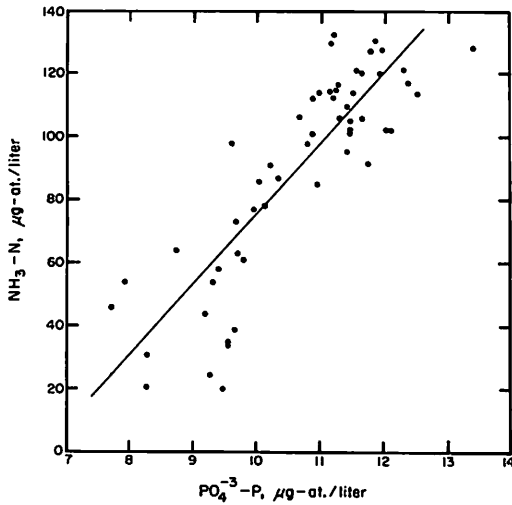


FIG. 13. Ammonia-nitrogen vs. inorganic phosphate-phosphorus in the anoxic zone June 1965. Computed slope of the line is  $\Delta\text{NH}_3 : \Delta\text{PO}_4^{3-} = 22 : 1$ .

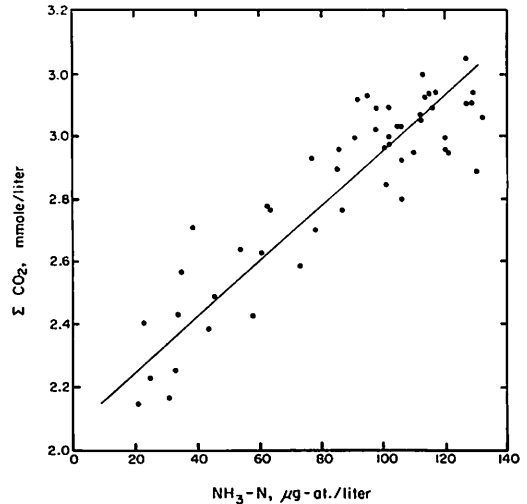


FIG. 14. Total carbon dioxide vs. ammonia-nitrogen in the anoxic zone June 1965. Computed slope of the line is  $\Delta\text{CO}_2 : \Delta\text{NH}_3 = 141 : 16$ .

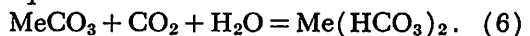
graphically determined total  $\text{CO}_2$ , was 2.962 meq/liter, and the contribution of ammonia (as estimated from the dissociation constant given by Hodgman 1959) would be  $-0.117$  meq/liter:

Carbonate alkalinity	=	2.96 meq/liter
Phosphate alkalinity	=	0.02 meq/liter
Sulfide alkalinity	=	0.27 meq/liter
Borate alkalinity	=	0.01 meq/liter
		—————
		3.26 meq/liter
Ammonia alkalinity	=	$-0.12$ meq/liter
		—————
Titration alkalinity	=	3.14 meq/liter.

The titration alkalinity as measured was 3.12 meq/liter. If the specific alkalinity of

“normal” seawater is taken as 0.123 (Harvey 1955, p. 161), the alkalinity of the Lake Nitinat sample should have been 2.125 meq/liter ( $\text{Cl} = 17.28\%$ ) before any accumulation of organic decomposition products began. The organic decomposition processes have therefore contributed 1.017 meq/liter to the alkalinity, of which 0.840 meq/liter is carbonate alkalinity which, at the ambient  $\text{pH}$ , would essentially all be as  $\text{HCO}_3^-$  ions. It is probable that any contribution to the alkalinity made by organic acids (ignored in the above calculation) is not measurable by titration because the original and final  $\text{pH}$  of the sample was near 7.

The excesses of carbon dioxide can arise from three sources: a) the  $\text{CO}_2$  evolved as a result of the oxidative processes described in the model, b) the  $\text{CO}_2$  of fermentative origin (to be discussed below), and c) the solution of carbonates according to the equation



The simple production of  $\text{CO}_2$  in the system by means of a) and b) above will not contribute to the alkalinity, and the  $\text{CO}_2$  produced by these processes must enter reactions analogous to equation (6) for the

TABLE 3. Distribution of total inorganic phosphate-phosphorus ( $\mu\text{g-at./liter}$ ), calcium (millimoles/liter), observed calcium-chlorinity ratio ( $\text{gm/gm}$ ), and  $\text{pH}$  at Station 3, June 1964

Depth (m)	$\text{PO}_4^{3-}\text{-P}$ ( $\mu\text{g-at./liter}$ )	Ca (mmole/liter)	Ca/Cl ( $\text{gm/gm}$ )	pH
5	1.35	8.95	0.0315	8.16
20	3.42	9.18	0.0212	7.53
29	8.90	9.39	0.0214	7.42
54	9.66	9.43	0.0214	7.24
69	10.68	9.43	0.0214	7.16
99	11.27	9.48	0.0215	7.17
129	11.45	9.45	0.0214	7.18

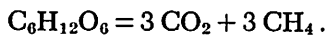
TABLE 4. Distributions of pH, total hydrogen sulfide, and soluble and particulate iron at Station 3, June 1965

Depth (m)	pH	$\Sigma\text{H}_2\text{S}$ ( $\mu\text{g-at./}$ liter)	Soluble iron ( $\mu\text{g-at./}$ liter)	Particulate iron ( $\mu\text{g-at./}$ liter)
0	7.85	0	0.18	4.9
5	7.81	0	0.04	2.6
10	7.85	0	0.02	2.8
12.5	7.76	0	0.02	3.4
15	7.40	0	0.04	3.0
17.5	7.39	0	0.09	2.5
20	7.23	0	0.04	2.8
25	7.34	0	0.09	2.0
30	7.25	4*	0.07	2.4
40	7.16	120	0.28	2.2
50	7.18	174	0.17	1.8
60	7.13	246	0.10	1.4
73	7.16	280	0.09	2.0
91	7.09	293	0.10	1.6
101	7.13	300	0.08	1.5
110	7.16	306	0.05	2.1
120	7.12	303	0.04	1.2
129	7.15	299	0.05	1.6

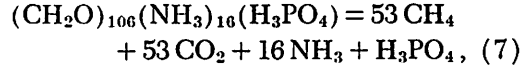
\* Limit of detection by this method was 10  $\mu\text{g-at./}$ liter of  $\text{H}_2\text{S}$ .

alkalinity to reach the high observed values. If half of the increase in  $\text{HCO}_3^-$  ions arose from the solution of  $\text{CaCO}_3$ , the calcium : chlorinity ratio should have been increased by about 5%. Because of analytical uncertainties of the base value of this ratio, it is impossible to determine if the  $\text{Ca}^{++} : \text{Cl}$  ratios in Table 3 reflect such an increase. This increase in carbonate alkalinity is, however, in good agreement with the independently estimated contribution to the  $\text{CO}_2$  content of the water by anaerobic fermentation and the oxidation of organic matter.

The slope of the correlation between ammonia and carbon dioxide (Fig. 14) would also be altered by anaerobic fermentation. The presence of methane in the water of Lake Nitinat (Table 1) is evidence that such fermentation takes place, and according to McCarty (1964), the pH of Lake Nitinat waters is in the range found to be optimum for methane formation. According to McCarty, one methane producing process observed in waste streams occurs at the expense of glucose:



Applying this process to the model organic matter,



and during the process  $\Delta\text{CO}_2 : \Delta\text{CH}_4 : \Delta\text{NH}_3 : \Delta\text{H}_3\text{PO}_4 = 53 : 53 : 16 : 1$ . The ratio of  $\text{CO}_2$  production to ammonia release is therefore one-half of the value of this ratio during sulfate reduction or one-quarter of the value to be expected if each molecule of  $\text{CO}_2$  evolved from organic matter reacts according to equation (6). This may account for the slope in Fig. 14 having a value of 141 : 16 instead of 106 : 16 as would be predicted from equation (4) or of 212 : 16 as would be predicted from equations (4) and (6) if every mole of  $\text{CO}_2$  arising from organic decomposition dissolved one mole of calcium carbonate. Conversely, the ratio in which ammonia and phosphate are released to the water should be the same during fermentation as during sulfate reduction.

#### Distribution of ferrous sulfide

During June 1965, soluble and particulate iron were determined on samples from Station 3. These results are presented in Table 4. The values for particulate iron represent single determinations, while duplicate determinations were made of soluble iron. A maximum in the soluble iron concentration occurs near the upper boundary of the sulfide zone. This agrees with the fact that ferrous sulfide,  $\text{FeS}$ , is more soluble than ferric hydroxide,  $\text{Fe}(\text{OH})_3$ , assuming that, in sulfide-bearing waters, most if not all of the ferric iron has been reduced to the ferrous state.

The apparent ion product of ferrous sulfide was determined from the data in Table 4. The ferrous iron concentration was found directly from the determination of total soluble iron. The sulfide ion,  $\text{S}^{=}$ , concentration was computed from the following expression,

$$[\text{S}^{=}] \text{ (moles/liter)} = \frac{\text{H}_2\text{S} K_1' K_2'}{[\text{H}^+]^2 + K_1' [\text{H}^+]}. \quad (8)$$

$K_1'$  and  $K_2'$  are the first and second apparent dissociation constants for hydrosul-

furic acid,  $\text{H}_2\text{S}$ , and are given as a function of salinity by Skopintsev (1957). The concentration of the hydrogen ion in Skopintsev's expression is assumed to be equivalent to the apparent hydrogen ion activity as determined by electrometric pH determinations.

$$pK_1' = 7.04 - 0.4\sqrt{\mu} \quad (9)$$

and

$$pK_2' = 14.92 - 1.2\sqrt{\mu}, \quad (10)$$

where  $\mu$  is the ionic strength and is approximately equal to 0.020 S‰. The temperature dependence of these constants is not known. Total sulfide is defined as the sum of all dissociation products of hydrosulfuric acid,

$$\Sigma \text{H}_2\text{S} = [\text{H}_2\text{S}] + [\text{HS}^-] + [\text{S}^{2-}],$$

where the square brackets indicate molar or ionic concentrations.

The apparent ion product of ferrous sulfide determined by least squares regression is  $5.3 \pm 0.1 \times 10^{-18}$  moles<sup>2</sup> liter<sup>-2</sup> (Fig. 15). The thermodynamic solubility product,  $K_{\text{FeS}}$ , for ferrous sulfide at 18C is  $3.7 \times 10^{-19}$  moles<sup>2</sup> liter<sup>-2</sup> (Hodgman 1959, p. 1740).

To correct the thermodynamic solubility product for ferrous sulfide in distilled water for the ionic effects of seawater, estimates of the activity coefficients of the ferrous and sulfide ions were made. The ferrous ion activity coefficient,  $\gamma_{\text{Fe}^{2+}}$ , was estimated to be 0.27 from the activity coefficients of ferrous chloride,  $\text{FeCl}_2$ , and potassium chloride,  $\text{KCl}$  (Harned and Owen 1958). The apparent sulfide activity coefficient was estimated from the thermodynamic and apparent dissociation constants of hydrosulfuric acid:

$$\gamma_{\text{S}^{2-}} = \frac{K_1 K_2}{K_1' K_2'} \gamma_{\text{H}_2\text{S}}, \quad (11)$$

where  $K_1$  is the first thermodynamic dissociation constant of hydrosulfuric acid and  $K_2$  the second.  $\gamma_{\text{S}^{2-}}$  is the apparent activity coefficient of sulfide ion and  $\gamma_{\text{H}_2\text{S}}$  is the activity coefficient of the neutral  $\text{H}_2\text{S}$  molecule. The thermodynamic dissociation constants were taken from Hodgman (1959, p. 1744).

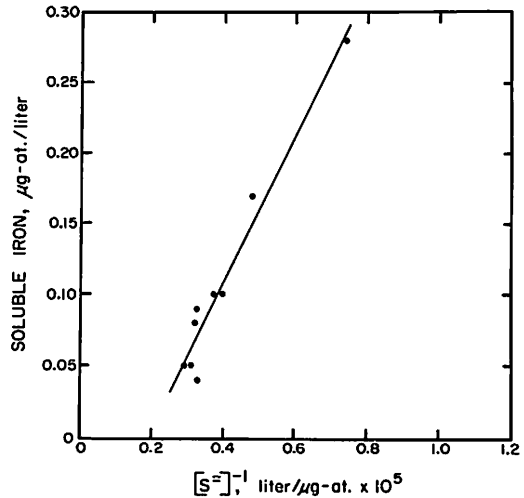


FIG. 15. Soluble iron vs.  $[\text{S}^{2-}]^{-1}$  at Station 3, June 1965. Computed slope of the line is  $[\text{Fe}^{2+}][\text{S}^{2-}] = 5.3 \times 10^{-18}$ .

$$K_1 = 9.1 \times 10^{-8}, \quad T = 18\text{C}.$$

$$K_2 = 1.2 \times 10^{-15}, \quad T = 18\text{C}.$$

Assuming  $\mu = 0.64$ ,  $K_1'$  and  $K_2'$  were calculated from equations (9) and (10).

Assuming that the activity coefficient of a neutral molecule is near 1.1 for solutions of the same ionic strength as seawater (Garrels and Thompson 1962), the apparent activity coefficient of the sulfide ion,  $\gamma_{\text{S}^{2-}}$ , was estimated to be 0.06 from equation (11). The thermodynamic solubility product of ferrous sulfide and the apparent solubility product of ferrous sulfide are related by the equation

$$\frac{K_{\text{FeS}}}{\gamma_{\text{Fe}^{2+}} \gamma_{\text{S}^{2-}}} = K_{\text{FeS}}'.$$

From the above estimates of  $\gamma_{\text{Fe}^{2+}}$  and  $\gamma_{\text{S}^{2-}}$ ,  $K_{\text{FeS}}' = 2.3 \times 10^{-17}$  moles<sup>2</sup> liter<sup>-2</sup>. The close agreement between the estimated solubility product and the observed ion product of ferrous sulfide and the linearity of Fig. 15 are strong evidence that ferrous ion concentrations are controlled in this environment by the sulfide ion concentration and the solubility of ferrous sulfide.

#### Distribution of hydrogen sulfide

Three processes should affect the distribution of sulfide in anoxic basins: 1) *in situ*

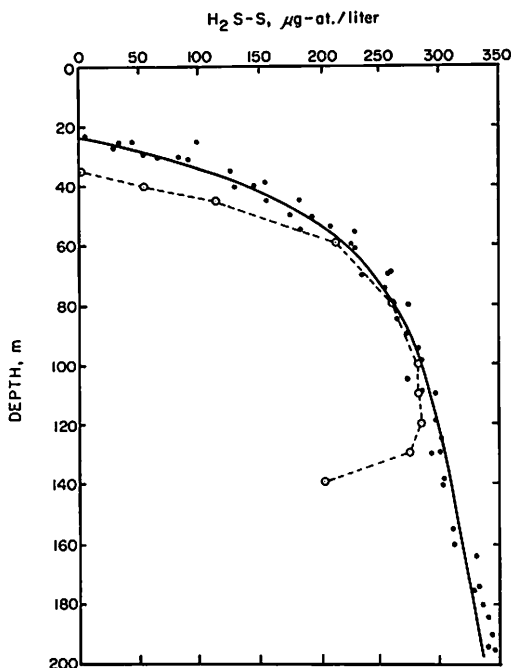


FIG. 16. Vertical distribution of hydrogen sulfide at Stations 1, 2, and 3, June 1964, (•) and at Station 4, June 1965, (○) compared with the model which is represented by the line.

production of sulfide at depths below the oxygenated surface layer, 2) removal of sulfide from the anoxic depths by diffusion and subsequent oxidation, and 3) diffusion of sulfide from or into the bottom. The distribution of sulfide is governed by the equation

$$\frac{\partial S}{\partial t} = \frac{\partial}{\partial x} K_h \frac{\partial S}{\partial x} + \frac{\partial}{\partial y} K_h \frac{\partial S}{\partial y} + \frac{\partial}{\partial z} K \frac{\partial S}{\partial z} - u \frac{\partial S}{\partial x} - v \frac{\partial S}{\partial y} - w \frac{\partial S}{\partial z} + R, \quad (12)$$

where  $\partial S/\partial t$  is the time rate of change of the sulfide concentration,  $S$ , and  $u$ ,  $v$ , and  $w$  are the components of velocity in the  $x$ ,  $y$ , and  $z$  directions ( $z$  positive downward), respectively,  $K$  and  $K_h$  are the coefficients of eddy diffusivity in the vertical and horizontal directions, and  $R$  is the rate of *in situ* production of sulfide.

Lake Nitinat has a shallow sill that restricts the inflow of water to the bottom of

the basin. Because of this restriction, horizontal and vertical velocities and horizontal gradients in the anoxic depths are small. Thus, by assuming  $w = 0$ ,  $\partial S/\partial x = 0$ , and  $\partial S/\partial y = 0$ , equation (12) can be simplified. Under these assumptions and that of a steady state, equation (12) becomes

$$\frac{\partial}{\partial z} K \frac{\partial S}{\partial z} = -R, \quad (13)$$

which can be integrated if  $K$  and  $R$  are known functions of depth. The coefficient of eddy diffusivity will be assumed to be constant. The rate of sulfide production,  $R$ , is a function of the net productivity of the water column, the rate of bacterial oxidation of organic matter using sulfate as the oxygen source, the sinking rate of organic detritus, and the downward diffusive flux of soluble organic material. The rate of sulfide production probably depends only on the concentration of oxidizable organic matter. The combined effect of these processes would be to decrease the rate of supply of sulfide exponentially with depth, thus

$$R = R_0 e^{-\alpha z}, \quad (14)$$

where  $R_0$  is the rate of supply of sulfide at the boundary between the oxygenated and anoxic layers of the basin, and  $\alpha$  is a constant describing the net effect of the depth-dependence of the supply of oxidizable organic matter and the rate constant for the bacterial sulfate reduction. Equation (14) has been derived from Barkley (1961), and the form of this equation has been tested by Wyrтки (1962).

With the above assumptions, equation (13) becomes

$$\frac{\partial^2 S}{\partial z^2} = -\frac{R_0}{K} e^{-\alpha z},$$

which can be integrated directly to give

$$S = -\frac{R_0}{K\alpha^2} e^{-\alpha z} + C_1 z + C_2, \quad (15)$$

where  $C_1$  and  $C_2$  are constants of integration. For convenience, the depth at which the sulfide concentration is zero will be taken as  $z = 0$ . The constants  $C_1$  and  $C_2$

are determined from the boundary conditions

$$S(0) = 0$$

and

$$S(H) = S_b,$$

where  $z = H$  represents the bottom. Equation (15) then becomes

$$S = \frac{R_0}{K\alpha^2}(1 - e^{-\alpha z}) - \frac{R_0}{K\alpha^2}(1 - e^{-\alpha H})z - \frac{S_b}{H}z.$$

The parameters  $\alpha$  and  $R_0/K$  were determined empirically from the data from Stations 1, 2, and 3 in June 1964 because the depth of the oxygenated zone varied from 15 m at Station 1 to 35 m at Station 4 in June 1965 (Fig. 1C), but only from 20 m at Station 1 to 25 m at Station 4 in June 1964. The slope of the anoxic boundary observed in 1965 is probably related to the relatively weak vertical stratification resulting from low river outflow. Agreement between the model and observations is good when  $\alpha = 4.4 \times 10^{-4} \text{ cm}^{-1}$  and  $R_0/K = 5 \times 10^{-5} \text{ } \mu\text{g-at. liter}^{-1} \text{ sec}^{-1}$  (Fig. 16).

The value obtained for  $\alpha$  suggests that the fraction of oxidizable organic matter reaching the bottom is less than 1% of that present at the top of the anoxic zone. In comparison, values of  $\alpha$  obtained by Barkley (1961) and Wyrski (1962) describing the depth dependence of the oxidation of organic matter by oxygen in the open ocean were between 2 and  $9 \times 10^{-5} \text{ cm}^{-1}$ . The larger value of  $\alpha$  for Lake Nitinat suggests that the organic material in this system is more readily oxidized than that in the open sea.

Similarly, in Lake Nitinat the value of  $R_0/K$  is an order of magnitude larger than the open ocean values of this parameter obtained by Wyrski (1962) when his values for oxygen are corrected to sulfide equivalences by the relationships of equation (4). This difference implies that either the eddy diffusivity is smaller or that the rate of supply of organic matter is larger in Lake Nitinat than in the open ocean, or both. Because the productive layer in Lake Nitinat is limited to at most 30 m and because the fjord is strongly stratified, it is probable that the eddy coefficient is small.

The vertical distribution of sulfide at Station 4 in 1965 does not agree with the model near the bottom (140 m). In 1964 at Station 4, good agreement with the model was observed, and the concentration of sulfide increased continuously towards the bottom. Thus, the observed decrease in sulfide, phosphate, total carbon dioxide, and ammonia near the bottom of the 1965 Station 4 is interpreted to have resulted from the partial flushing of the fjord sometime after June 1964 and not to a diffusion of sulfides into the bottom. The effects of this intrusion of new water were barely perceptible at Station 3 and not at all at Station 2 in 1965; hence the volume of the new water must have been small.

#### CONCLUSIONS

The analysis of the data from Lake Nitinat indicates that only part of the chemical consequences of decomposition of organic matter in this environment can be accounted for on the basis of the decomposition of organic matter having the average composition  $(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4)$  at the expense of dissolved oxygen, nitrate, nitrite, and sulfate ions. Anomalous relationships involving the observed concentrations of phosphate ions suggest that phosphate may be remineralized more rapidly than ammonia or carbon dioxide, or that calcium phosphate may be precipitated onto the bottom, or both.

More carbon dioxide is present in the water than would be expected from the total oxidation that has taken place, suggesting that some, if not all, of the carbonic acid so formed reacts with up to equimolar quantities of carbonates to form bicarbonates. This view is strengthened by the high carbonate alkalinity values observed.

Anaerobic fermentation, with the concurrent production of methane and carbon dioxide, appears to take place, as evidenced by the detection of up to about  $70 \text{ } \mu\text{g-at./liter}$  of methane carbon in the water. The vertical distribution of the methane suggests that it is formed in the water column rather than diffusing into it from the bot-

tom. The low pH values in Lake Nitinat may represent a more favorable environment for bacterial methanogenesis than occurs in other marine environments.

Considerations of the vertical distributions of the undissociated and ionic forms of sulfide and of soluble iron lead to the conclusion that the sulfide-bearing waters of the fjord are in equilibrium with solid ferrous sulfide. These may represent the best available estimates of the solubility of ferrous sulfide in seawater of the salinity and temperature found in Lake Nitinat, although we have no estimate of the possible effects of complex formation on the actual activities of the ferrous and sulfide ions.

The vertical distribution of sulfides in Lake Nitinat can be described by a one-dimensional mathematical model, because horizontal components of velocity and diffusivity can be ignored. The model suggests that in Lake Nitinat the depth rate of supply of sulfide and the ratio of the initial supply of oxidizable organic matter to the eddy diffusivity are both an order of magnitude larger than values of comparable parameters obtained for the open ocean.

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