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Title: PROCESSES AFFECTING THE OCEANIC DISTRIBUTION OF

CARBON DIOXIDE

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The stoichiometric model of organic decomposition in seawater

(Redfield, Ketchum, and Richards, 1963) was used to describe the

oceanic distribution of total carbon dioxide. It was assumed that the

concentration of total carbon dioxide was the sum of three terms:

(1) the initial concentration of carbon dioxide, (2) the increase in

carbon dioxide due to the oxidation of organic matter, and (3) the

increase in carbon dioxide due to the solution of calcium carbonate.

The initial concentration of carbon dioxide was calculated by assuming

that surface seawater is in equilibrium with atmospheric carbon

dioxide. This assumption allowed the temperature dependence of the

initial concentration to be estimated. The vertical and horizontal

distribution of total carbon dioxide in the Pacific, Indian, and South

Atlantic Oceans was shown to conform to this model. In particular,

values of the oxidative ratio ($\Delta C/\Delta O$) calculated from field data agreed with the theoretical value of Redfield et al. (1963).

The model for the distribution of total carbon dioxide was applied to the vertical distribution of carbon-13 at the North Pacific (1969) GEOSECS intercalibration station (Kroopnick, Deuser, and Craig, 1970). Values of δC^{13} calculated from the stoichiometric model agreed to within $\pm 0.3‰$ with the measured values at this station.

Near-bottom chemical measurements were made on three cruises: YALOC-69 to the Eastern Tropical Pacific, Y6908F off the Oregon Coast, and TT-46 to the Caribbean Sea and North Atlantic. The emphasis during these cruises was on chemical gradients in deep water, and 39 stations were occupied at depths greater than 2000 m. Salinity, oxygen, pH, alkalinity, silicate, phosphate, nitrate, and nitrite were measured at heights from 0.5 to 300 m above the bottom. No measurable salinity, oxygen, silicate, phosphate, nitrate, or nitrite gradients were observed. A statistically significant near-bottom increase in pH and alkalinity was found. However, the increase was small and could have resulted from undetected analytical and/or sampling errors.

Processes Affecting the Oceanic Distribution
of Carbon Dioxide

by

Charles Henry Culberson

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Redacted for Privacy

Professor of Oceanography in Charge of Major

Redacted for Privacy

Chairman of Department of Oceanography

Redacted for Privacy

Dean of Graduate School

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OF CARBON DIOXIDE

I. INTRODUCTION

Carbon is a biologically active element, and its distribution

in the oceans is influenced by biological uptake in surface waters,

and by the oxidation of organic matter and carbonate solution at

depth. Carbon is a nutrient and its distribution tends to follow the

distributions of other nutrients such as phosphate, nitrate, and

silicate. However, there are important differences between the

distribution of carbon and that of the other nutrients. One is that

inorganic carbon is present in excess and never limits plant growth.

A second is that the surface distribution of inorganic carbon is

influenced by exchange with atmospheric carbon dioxide. These two

differences must be considered in any study of the oceanic distribu-

tion of carbon dioxide.

The concentration of total carbon dioxide (TCO_2) in the oceans

ranges from a low of about 1.95 mmole/kg in warm tropical surface

waters to a high of about 2.35 mmole/kg at intermediate depths in

the North Pacific. Thus changes in the concentration of carbon

dioxide due to biological, chemical, and physical processes are 20%

or less of the amount initially present. The relatively constant

concentration of carbon dioxide in seawater has two implications.

(1) Analytical methods for measuring carbon dioxide must be precise.

For example, a 1% error in TCO_2 (± 0.02 mmole/kg) is a 5% error

in the maximum difference in the concentration of carbon dioxide

given above.   (2) Any model which attempts to explain the oceanic

distribution of carbon dioxide must take the background concentration

of TCO_2 into account, since changes in the background concentration

may obscure concentration changes due to in situ processes.

The purpose of this thesis was to obtain precise field

measurements of pH and alkalinity which could be used to study the

effects of organic oxidation and of carbonate solution on the vertical

and horizontal distribution of carbon dioxide.

In Chapter III, the stoichiometric model of organic

decomposition in seawater (Redfield et al., 1963) is used to develop

a model relating the distributions of total carbon dioxide and oxygen.

The model assumes that the concentration of total carbon dioxide in

any water sample is the sum of three terms: (1) the initial concen-

tration of carbon dioxide in the water sample at its surface source,

(2) the increase in carbon dioxide due to the oxidation of organic

matter, and (3) the increase in carbon dioxide due to solution of

calcium carbonate.   The model is based on earlier models developed

by Postma (1964) and by Park (1965, 1968a, b).   However, the model

differs from these earlier models in that it allows for variations in

the initial concentration of carbon dioxide.   This modification

substantially improves the agreement between the measured distributions of TCO_2 and oxygen, and the value of the oxidative ratio ($\Delta C/\Delta O$) predicted by Redfield et al., (1963).

In Chapter V, the stoichiometric model is applied to the vertical distribution of carbon-13 at the North Pacific (1969) GEOSECS inter-calibration station (Kroopnick, Deuser, and Craig, 1970). Values of δC^{13} calculated from the stoichiometric model agree to within $\pm 0.3\%$ with the measured values at this station.

Chapter VI compares the stoichiometric model with a physical model (Craig, 1969) for the vertical distribution of TCO_2 from which the rates of carbon production and of oxygen consumption can be calculated. It is shown that values of the oxidative ratio calculated from each model are in agreement with the theoretical value predicted by Redfield et al., (1963).

The effect of chemical exchange across the seawater-sediment interface on the near-bottom distributions of pH and alkalinity is studied in Chapter VIII. Alkalinity and pH measurements at 0.5 m above the sea floor showed an average increase of 0.002 meq/kg and of 0.003 pH units when compared with samples taken 15 m above the bottom. The average increases in pH and alkalinity were statistically significant. However, they were within the precision of the analytical methods and could have resulted from undetected analytical and/or sampling errors.

II. METHODS

Data Sources

The data used in this thesis was obtained on cruises YALOC-69 and Y6908F (Wyatt et al., 1970) aboard the R/V Yaquina of Oregon State University, and on cruise TT-46 aboard the R/V Thomas G. Thompson of the University of Washington.

Additional data was taken from the Southern Cross Cruise (Horibe, 1970), the Meteor Indian Ocean Expedition (Dietrich et al., 1966b), and from the TCO_2 and alkalinity data of Edmond (1970a) in the Southern Ocean (Eltanin cruise 34) and in the South Atlantic (Circe Expedition).

Water Sampling

Water samples collected during YALOC-69 and Y6908F were taken with National Institute of Oceanography polypropylene water bottles (Herdman, 1963). Samples collected during TT-46 were obtained with all plastic (PVC) and rubber samplers of a modified Emsworth design. The order of sampling during these cruises was oxygen, pH, salinity, alkalinity, and nutrients.

Water samples taken during the Meteor Indian Ocean Expedition were collected with the 3.5 liter non-metallic samplers described by Dietrich et al., (1966a, p. 45). Water samples collected during the

Southern Cross Cruise (Horibe, 1970), and by Edmond (1970a) were

taken with lined Nansen bottles.

Near-bottom Water Sampling

Near-bottom water samples were taken during YALOC-69,

Y6908F, and TT-46 with near-bottom samplers described by Culberson

and Pytkowicz (1970b). The samplers (Figure 1) consisted of a modi-

fied Van Dorn (1956) bottle with a release actuated by bottom contact.

Each water sampler (Figure 1) consisted of a plexiglass cylinder

15 cm long with an 8 cm inner diameter. The cylinder was closed

with two number 14 rubber stoppers ground to a hemispherical shape

and connected with rubber tubing. A plastic rod (Figure 1) was

inserted inside the rubber tubing where it passed through the rubber

stoppers to eliminate air pockets.

Two short cylindrical plastic segments (9.5 cm in inner

diameter) were glued to the top and bottom of the plexiglass cylinder

(Figure 1). When the sampler was closed these segments extended

above the top of the rubber stoppers and protected the stoppers from

being reopened if the samplers were dragged across the bottom.

The water samplers contained 560 ml. The stopcock consisted

of a 1 cm hole in the cylinder, through which a 5 cm length of

slightly oversized rubber tubing was inserted, so that it extended

2 mm past the inside wall of the plexiglass cylinder (Figure 1). A
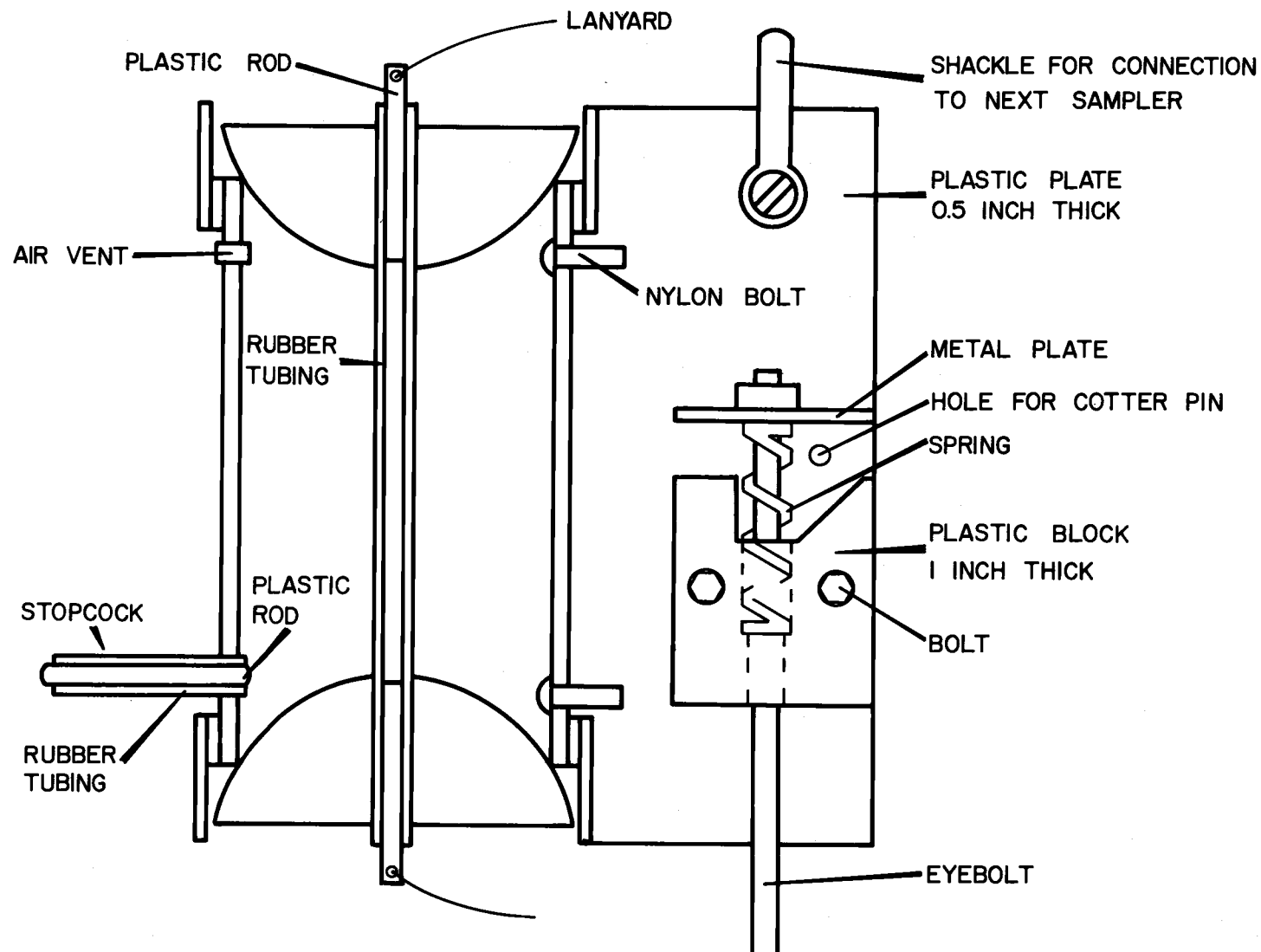
Figure 1. Design of the near-bottom water samplers. The release mechanism is shown in more detail in Culberson and Pytkowicz (1970b).

5.5 cm length of 0.5 cm diameter plastic rod was then inserted inside the rubber tubing so that the rod extended 2 mm past the inside wall of the cylinder. This stopcock design eliminated air pockets and dead volume which would have occurred with a regular stopcock. The stopcock was opened by pulling out the plastic rod, and clamping off the rubber tubing with a pinch clamp. A nylon set screw at the top of the cylinder served as the air vent.

The water bottle was attached to the release mechanism by two nylon screws (Figure 1). The rubber stoppers were held open by lanyards connected to the release mechanism which consisted of a metal plate, an eyebolt, and a stiff spring. The eyebolt was connected to the metal plate and to a 67 kg lead weight. Tension from the weight held the metal plate closed when the weight was off the bottom. When the weight hit bottom, the spring lifted the metal plate, and tension from the rubber tubing pulled the lanyards free, allowing the stoppers to close. Motion pictures, taken in air, showed that the uppermost sampler (6 m above the bottom) closed within 0.3 seconds after the weight touched bottom. Samplers nearer the bottom closed sooner.

The water bottles were cocked on deck, and a cotter pin was inserted just above the metal plate to keep the release closed. The cotter pin was removed once the bottles were attached to the wire and tension from the trip weight kept the release mechanism closed.

In the present work, four bottom bottles at heights of 0.5, 1, 3, and 6 m above the bottom were used. All connections between bottles were made by lengths of rope, the ends of which contained snap hooks.

At the beginning of a cast the rope segments between the 1 and 3 m bottles and between the 3 and 6 m bottles were snapped together and connected to the end of a long length of rope. The end of the rope containing the two short segments was then passed over a snatch block placed adjacent to the meter wheel. The first two bottles (0.5 and 1 m) were connected to the trip weight, and the top of the 1 m bottle was connected to the free end of the bottommost rope segment. The first two bottles were then lowered over the side with a capstan. The bottles were lowered until the snap hook at the top of the first rope segment was reached (the segment between the 1 and 3 m bottles). A safety line was attached to the snap hook and the bottles were lowered slightly until the safety line took up the tension. The next rope segment (that between the 3 and 6 m bottles) was disconnected, and the third bottle was connected between the ends of the two rope segments. The slack was taken up and the safety line disconnected. The bottles were lowered until the connection for the fourth bottle was reached; it was attached in the same way as the third bottle. The top of the last bottom bottle was connected to the bottom of a hydro weight at the end of the regular hydro wire.

With this method of attachment, any number of bottles could be used, and the distance between them was easily changed. The use of the bottom bottles added about 30 minutes to the time required for a hydro cast.

A series of conventional water bottles was attached above the bottom bottles. After the trip weight touched bottom, the cast was raised a few meters, and the regular water bottles were tripped by messenger. A tensiometer connected to the winch was used to determine the depth of the bottom contact. With this method the depth of bottom contact could be determined to ± 2 m at depths of 3000 m. A pinger attached to the bottom of the hydro cast is very helpful in determining the depth to the bottom. A pinger is essential in rough weather when the tensiometer cannot be used due to tension fluctuations associated with ship motion.

The near-bottom samplers have been tested extensively to depths of 6200 m. There is no evidence of pretripping or of leakage after the bottles have tripped. Table 1 compares salinity measurements in the bottom bottles with salinities from conventional bottles within 100 m of the bottom. The average salinities are not significantly different. This is evidence that the bottles neither pretrip, nor leak after closure.

The samplers have been tested in the open ocean and in two anoxic basins--the Gulf of Dulce and the Cariaco Trench. In the Gulf

Table 1. Statistical analysis of near-bottom chemical measurements. For salinity and phosphate, the mean difference is the average of the concentration differences between the four bottom bottles and the three deepest conventional water bottles (conventional minus bottom bottles). For oxygen, the mean difference is the average of the concentration differences between measurements on the same water sample by Carpenter's (1965) method and by the standard Winkler method (standard method minus Carpenter's method). The Student t-test (Freund, 1962, 1.267) was used to determine if the mean differences were significantly different from zero.

Parameter	Cruise	No. of differences	Mean difference	Standard deviation of the individual differences about the mean	t	Level of significance 90%	95%	90%
Salinity (glass bottles)	YALOC-69 Y6908F TT-46	23	-0.0015‰	0.0059‰	-1.23	no		
Phosphate	YALOC-69	26	-0.033 μmole/kg	0.058 μmole/kg	-2.85	yes	yes	yes
	Y6908F TT-46	9	+0.000 μmole/kg	0.047 μmole/kg	+0.01	no		
Oxygen	YALOC-69	58	+0.050 ml/l	0.038 ml/l	+9.99	yes	yes	yes

of Dulce and the Cariaco Trench, the 0.5 m bottle was always full of mud (6 casts). The other bottles were not visibly turbid. In the open ocean, the bottommost bottle was seldom turbid. In only 2 casts out of 35 was there visible turbidity in the bottommost bottle. None of the higher bottles were ever visibly turbid. The difference between the oxic and anoxic environments is probably due to the firmness of the sediments. In anoxic sediments the trip weight apparently sinks at least 0.5 m (but less than 1.0 m) beneath the surface before the bottles trip.

The water bottles are unsuitable for sulfide measurements. Sulfides measured in the bottom bottles on Cruise TT-46 were consistently lower (by as much as a factor of 2) than sulfides from the conventional samplers immediately above them. The decrease in sulfide occurred between the last conventional sampler and the first bottom bottle. The bottom bottles have a higher surface/volume ratio than conventional bottles, and the sulfide loss may be due to reactions with the rubber or plastic surfaces of the bottom samplers.

The rubber stoppers used to close the bottom bottles were made from number 14 rubber stoppers ground to a hemispherical shape using a drill press and a jig of metal backed sandpaper. Stoppers prepared in this way had a rough finish, and tended to pick up debris. Bottom bottles with stoppers prepared in this way were used on YALOC-69, and it was noticed that phosphate measurements in the bottom

bottles were consistently higher and more variable than phosphates

measured in the NIO bottles immediately above the bottom bottles.

At each station, water samples from conventional water bottles

were taken at three heights within 100 m of the bottom. The average

phosphate concentration in the four bottom bottles was subtracted from

the average concentration in the three deepest conventional water

samplers. The differences were averaged and the average was

tested for significance by the Student t-test (Freund, 1962, p. 267).

The average concentration difference between the bottom bottles and

the NIO bottles during YALOC-69 (Table 1) was significant at the 99%

confidence level.

It was felt that the phosphate concentration difference might be

due to contamination from material adsorbed onto the stoppers. The

stoppers used for cruises Y6908F and TT-46 were given a smoother

finish by using finer sandpaper, and by soaking the stoppers in hot

water and in acetone. This procedure gave a very smooth finish to

the rubber stoppers. Phosphate measurements in the bottom bottles

during Y6908F and TT-46 were much less variable and did not show

systematic variations as did those during YALOC-69 (Table 1).

Standard Chemical Methods

The following is a description of the chemical methods used

during cruises YALOC-69, Y6908F, and TT-46. The precision (2

standard deviations) of each method has been calculated in two ways. In the first case, the precision (2 sigma) is calculated from replicate analyses of the same sample. This is an estimate of analytical precision. In the second case, precision (2 sigma) is estimated by combining measurements from closely spaced conventional water samplers in deep-water. This estimate assumes that concentrations of the measured parameters are essentially constant over short distances in deep water. This case provides an estimate of analytical and sampling errors, and is a better test of the actual precision than is the first case. The two estimates of precision for each method are listed in Table 2.

Salinity

YALOC-69 and Y6908F: Salinity determinations were made with a Hytech inductive salinometer, model 6220 (YALOC-69), or with an Autolab inductive salinometer (Industria Manufacturing Engineers Pty. Ltd) model II (Y6908F). The salinometers were standardized with substandard seawater (salinity 35.00‰) and frequently checked against Copenhagen water.

TT-46: Salinity was measured on a University of Washington type conductivity bridge (Paquette, 1959).

Salinity samples from the conventional water samplers were stored in standard citrate of magnesia bottles. Salinity samples from

Table 2. Precision (2 sigma) estimates from replicate analyses (case 1), and from closely spaced water samples (15, 30, 100 m above the bottom) in deep water (case 2).

Parameter		YALOC-69	Y6809F	TT-46
Salinity	Case 1	- - -	- - -	- - -
	Case 2	0.002‰	0.001‰	0.007‰
Oxygen	Case 1	- - -	- - -	- - -
	Case 2	3 µg-at/kg	4 µg-at/kg	6 µg-at/kg
Oxygen (micro)	Case 1	- - -		1 µg-at/kg
	Case 2	1 µg-at/kg		- - -
Phosphate	Case 1	0.10 µmole/kg	- - -	- - -
	Case 2	0.14 µmole/kg	0.06 µmole/kg	0.09 µmole/kg
Silicate	Case 1	1 µmole/kg	4 µmole/kg	- - -
	Case 2	2 µmole/kg	5 µmole/kg	0.5 µmole/kg
Nitrate	Case 1			- - -
	Case 2			1.0 µmole/kg
pH	Case 1	0.007 pH	0.012 pH	- - -
	Case 2	0.007 pH	0.001 pH	0.004 pH
Alkalinity	Case 1	0.008 meq/kg	0.007 meq/kg	- - -
	Case 2	0.005 meq/kg	0.006 meq/kg	0.007 meq/kg

the bottom samplers could not be stored in these bottles due to the

limited volume of water available for salinity analysis. During

YALOC-69, 250 ml polyethylene bottles were initially used to store

salinity samples from the near-bottom samplers. However, it was

found that salinities from the poly bottles were always higher (average

increase 0.004‰) than salinities from the deepest NIO bottles.

Beginning with station 103 (YALOC-69) salinity samples were stored

in 125 ml glass bottles with poly-seal caps. There was no evidence

of evaporation in these bottles (Table 1).

Oxygen

YALOC-69 and Y6908F: The Winkler method described by

Strickland and Parsons (1965) was used. Duplicate titrations were

run on each sample. All oxygen samples were flushed with at least

1/2 bottle volume (120 ml) of seawater to minimize atmospheric

contamination. During YALOC-69 two checks of analytical precision

were made. At station 70, seven duplicate titrations were made with

the buret masked, so that the analyst would not unconsciously repeat

the previous measurement. This had no effect on the precision of

duplicate titrations. At station 120 a test was made to determine if

flushing the oxygen samples with 1/2 bottle volume of seawater was

sufficient to eliminate atmospheric contamination. An oxygen bottle

was flushed with 350 ml of seawater from an NIO bottle 90 m above

the bottom. Oxygen samples were drawn in the normal way (120 ml seawater flush) from NIO bottles 100 m and 50 m above the bottom. The measured oxygen concentrations in the three bottles were 3.02, 3.02, and 3.02 ml/l. Increased flushing had no effect on the measured oxygen concentration.

TT-46: Oxygen was determined with a Winkler method similar to that described by Strickland and Parsons (1965), but using the reagent concentrations recommended by Carpenter (1965). All oxygen samples were flushed with at least 1 bottle volume of seawater.

Reactive phosphate

YALOC-69 and Y6908F: Reactive phosphate was measured by the method described by Strickland and Parsons (1965). Analyses were started within 2 hours after the samples had been drawn. Samples were collected in 250 ml poly bottles, and were stored in a refrigerator prior to analysis. Standard curves at 0.0, 0.8, 1.6, 2.4, and 3.2 μM were run periodically during each cruise. The slope and intercept of the calibration curves remained constant during each cruise, and a linear least squares line through all of the standards run during a cruise was used to calculate the phosphate concentration.

TT-46: Reactive phosphate was measured with a Technicon Autoanalyzer using the method described by Richards et al., (1971).

Reactive silicate

YALOC-69 and Y6908F: Reactive silicate was measured with the method described by Strickland and Parsons (1965). Sodium silicafluoride was used as the primary standard. Samples were stored in 250 ml poly bottles prior to analysis. Standard curves at 0, 50, 100, 150, and 200 μM were run periodically during each cruise. The slope and intercept of the calibration curves remained constant during each cruise, and a linear least squares line through all of the standards run during a cruise was used to calculate the silicate concentration.

TT-46: Reactive silicate was measured with a Technicon Autoanalyzer using the method described by Richards et al. (1971).

Nitrate

YALOC-69: Nitrate was measured on frozen samples with a Technicon Autoanalyzer and the nitrate method of Hager, Gordon, and Park (1968). This method measures nitrate plus nitrite. The samples were analyzed ashore, two weeks after the cruise returned.

TT-46: Nitrate was measured with a Technicon Autoanalyzer using the method described by Richards et al. (1971).

Nitrite

TT-46: Nitrite was measured with a Technicon Autoanalyzer using the method described by Richards et al. (1971).

Non-standard Chemical Methods

Oxygen

YALOC-69, Y6908F, and TT-46: Due to the limited volume of water available, samples from the bottom tripping water bottles were analyzed by a modification of Carpenter's (1965) method. Calibrated 30 ml Erlenmeyer flasks were used instead of the 125 ml flasks recommended by Carpenter (1965). The concentrations of the oxygen reagents were changed so that addition of 0.5 ml of each reagent would result in the final concentrations recommended by Carpenter (1965). Solid sodium sulfate (220 g/l) was added to the manganous chloride reagent to decrease the solubility of oxygen in the reagent.

As a check on the accuracy of this method, samples from the two deepest conventional water bottles at each station were also analyzed. During YALOC-69 oxygens analyzed by this method averaged 0.05 ml/l lower than oxygens measured with the standard Winkler technique (Strickland and Parsons, 1965) (Table 1).

Alkalinity

YALOC-69, Y6908F, and TT-46: Total alkalinity was determined by the method of Anderson and Robinson (1946) as modified by Culberson, Pytkowicz, and Hawley (1970).

Six ml of 0.01 N HCl was added to 20 ml of seawater in a test tube (2.6 cm inner diameter, 10 cm high, 50 ml volume). The test tube was stoppered, the contents gently swirled, and then vigorously shaken.

The liberated carbon dioxide was removed by purging the mixture for 4 minutes with water saturated air. The purging apparatus consisted of a small aquarium air pump, a gas washing bottle filled with acidified seawater, and a pipet tip inserted through a rubber stopper. After the acidified seawater sample had been vigorously shaken the rubber stopper was removed, and the pipet tip inserted into the acidified seawater. After 4 minutes the pipet tip was removed, the test tube stoppered, and placed in a 25°C constant temperature water bath.

After 4 minutes a glass-calomel electrode pair (Beckman #40498 GP glass, and Beckman #39170 fiber junction calomel) was inserted into the test tube. The potential was read after 4 minutes with an Orion model 801 digital pH/mv meter.

The electrodes were standardized with pH 4.008 and pH 7.413 buffers prepared according to the recommendations of Bates (1964). The 4.008 buffer was prepared from primary standard grade potassium

hydrogen phthalate (Baker "Analyzed" #2958). The 7.413 buffer was

prepared from reagent grade KH_2PO_4 (Baker "Analyzed" #3246) and

Na_2HPO_4 (Baker "Analyzed" #3828). Both buffers were calibrated

against National Bureau of Standards 4.008 and 7.413 buffers. The

pH differences never exceeded 0.003 pH units. The pH of the acidified

seawater samples was calculated from the equation,

$$pH_{sw} = 4.008 - (E_{sw} - E_4)/(E_4 - E_{7.4})/(3.405)$$

E_{sw}, E_4, and $E_{7.4}$ are the measured potentials in acidified seawater,

4.008 buffer, and 7.413 buffer.

The electrodes were standardized with 4.008 buffer before and

after the samples from each cast (about once every 1.5 hours). The

slope of the glass electrode response is constant over long periods and

measurements in 7.413 buffer were made at the beginning and end of

each cruise.

About 10 samples an hour can be run by this method (not including

the time required for buffer calibration). After the electrodes were

calibrated with 4.008 buffer, they were rinsed with distilled water and

placed in a test tube of acidified seawater for a few minutes to condition

them to seawater. The samples from a cast were then analyzed

sequentially starting from the surface. The electrodes were not

rinsed between samples, but were placed directly into the next sample.

The 6 and 20 ml pipets were individually calibrated. Automatic pipets were used on cruise Y6908F and TT-46. The 0.01 N HCl was prepared by dilution of 0.1 N HCl prepared from Hellige (#R-1193C) 0.1 N hydrochloric acid concentrate. The manufacturer claims an accuracy of ±0.1% for these concentrates. One ampoule was standardized with primary standard grade Na_2CO_3 and found to be 0.09996 normal.

pH

YALOC-69, Y6908F, and TT-46: The pH was measured with a Beckman #46850 Micro Blood pH electrode (Kater, Leonard, and Matsuyama, 1968) (internal volume 0.5 ml) and an Orion model 801 digital pH/mv meter. All measurements were made at 25.0 ± 0.1° C.

The pH samples were drawn into 10 ml plastic syringes, fitted with stainless steel needles. Duplicate samples were taken from the shallow bottle on each cast. After being filled, the syringes were placed in the water bath for 10 to 20 minutes, and then injected into the Micro Blood pH assembly. The electrode potential was read after 2 minutes. About 25 samples an hour can be run with this method.

The electrode assembly was standardized with 4.008 and 7.413 buffers, which are described in the Alkalinity section. The pH was calculated from the equation,

$$pH_{sw} = 7.413 + (E_{sw} - E_{7.4})/(E_{7.4} - E_4)/(3.405)$$

E_{sw}, E_4, and $E_{7.4}$ are the measured potentials in seawater, 4.008 buffer, and in 7.413 buffer.

Use of the Micro Blood pH assembly had two disadvantages. (1) Approximately 12 to 24 hours were needed to obtain a stable potential (drift less than 0.1 mv/hour) when changing from buffer to seawater or from seawater to buffer. This problem was alleviated by the fact that the standard potential of the assembly remained constant during the course of a cruise. For instance, during YALOC-69 the standard potential was constant to ± 0.3 mv over a three month period. (2) The assembly is unsuitable for pH measurements in anoxic waters. During TT-46, stations were occupied in the Gulf of Dulce and the Cariaco Trench, two anoxic basins. Two casts were made at each station. The shallow cast just entered the sulfide layer, whereas the deep cast began just above the sulfide layer and continued to the bottom. It was found that pH values from overlapping bottles on the two casts were offset 1 to 2 mv, the deep cast having higher pH values.

The micro assembly contains a palladium annulus liquid junction, and the above mentioned problems were apparently due to this junction. After cruise TT-46, the palladium annulus junction was replaced by a free diffusion junction. This change eliminated both effects.

The sample syringes were kept full of seawater between stations, and it was found necessary to rinse them once or twice a week with

mercuric chloride solution. Untreated syringes drifted toward more acidic pH values at about 0.01 pH/hour, probably due to biological production of carbon dioxide. The mercuric chloride rinse eliminated this drift.

Calculations

All concentrations are reported per kilogram of seawater. Concentrations originally determined volumetrically have been divided by the density of seawater at 25°C (Knudsen, 1901).

Potential temperature was calculated from the equation given by Fofonoff (1962). The pressure in Fofonoff's (1962) equation for potential temperature was calculated from the following equation (Bialek, 1966, page 62),

$$P = 0.9807(z)(1.0267 + 2.55 \times 10^{-6}(z)) \text{ (bars)} \tag{1}$$

This equation is strictly valid only for the Northeast Pacific. However, the error introduced when it is applied to other oceans is negligible.

The apparent oxygen utilization, AOU, is defined as,

$$AOU = O_2'' - O_2 \tag{2}$$

O_2' is the solubility of oxygen, at the potential temperature and salinity of the sample, in equilibrium with a wet atmosphere at 1 atmosphere total pressure (20.94% oxygen on a dry basis). O_2 is the measured oxygen concentration. O_2' is calculated from the following equation,

$$O_2' = BUNSEN(1000)(0.2094)(760 - VPS)/760 \tag{3}$$

The vapor pressure of seawater, VPS, is calculated from the equations given by Green and Carritt (1967). The bunsen coefficient, BUNSEN, for the solubility of oxygen (ml of oxygen per ml of seawater) is taken from Weiss (1970).

Calculation of carbonate speciation was made with Lyman's (1956) values of the apparent constants. The equations given by Takahashi et al., (1970) were used. Total carbon dioxide, TCO_2 was calculated from equation (4), using the measured pH and alkalinity. A boron/chlorinity ratio of 0.237 mg-B/g-Cl (Culkin, 1965) was used to calculate the total boron, TB, concentration.

$$TCO_2 = \left[Talk - \frac{TB \cdot K'_B}{a_H + K'_B} \right] \left[\frac{a_H^2 + a_H K'_1 + K'_1 K'_2}{a_H K'_1 + 2K'_1 K'_2} \right] \qquad (4)$$

The effect of pressure on the apparent constants was calculated from the pressure coefficients given by Culberson and Pytkowicz (1968). The in situ pH was calculated from equation (4) using the measured alkalinity and total carbon dioxide, and the in situ values of the apparent constants.

The solubility of carbon dioxide in seawater was calculated from the equation given by Takahashi et al. (1970), in which Harned and Davis' (1943, eq. (8)) equation for the solubility of carbon dioxide in pure water is combined with Bohr's (1899) data for the solubility of carbon dioxide in NaCl solutions (Li, 1967). Values calculated from

this equation have an average deviation of 0.3% (maximum deviation 0.6%) from the recent CO_2 solubility data of Li and Tsui (1971).

The solubility products of calcite and aragonite at 1 atmosphere were taken from MacIntyre (1965). The effect of pressure on the solubility products was taken from the data of Hawley and Pytkowicz (1969). The final equations for the apparent solubility products were,

$$(K'_{sp})_{calcite} = (1.95 - 0.0176 \cdot T)10^{-2} \cdot S \cdot 10^{((0.693 - 0.00645 \cdot T)10^{-4} \cdot Z)} \tag{5}$$

$$(K'_{sp})_{aragonite} = (3.06 - 0.0217 \cdot T)10^{-2} \cdot S \cdot 10^{((0.650 - 0.066 \cdot T)10^{-4} \cdot Z)} \tag{6}$$

The pH values reported by the Meteor Indian Ocean Expedition and by the Southern Cross Cruise were corrected for temperature and pressure using Buch's values for the pressure and temperature effects. These corrections were removed, and the _in situ_ pH recalculated using the procedure outlined above. The equation used to remove the pressure corrections from pH values corrected according to Buch was,

$$PHT = ((1.0 + 4.389 \cdot Z \cdot 10^{-4}) - ((1.0 + 4.389 \cdot Z \cdot 10^{-4})^2 - 1.064 \cdot Z \cdot 10^{-4}$$

$$(PH + 1.8305 \cdot Z \cdot 10^{-3}))^{0.5}) / (5.32 \cdot Z \cdot 10^{-5}) \tag{7}$$

PHT is the pH at the _in situ_ temperature and 1 atmosphere pressure, PH is the pH at the _in situ_ temperature and pressure corrected according to Buch.

All calculations were made on a CDC 3300 computer. A copy of the computer program is given in Appendix 1.

III. THE RELATIONSHIP BETWEEN TOTAL CARBON DIOXIDE
AND OXYGEN IN SEAWATER

The stoichiometric model of organic decomposition in seawater (Redfield, Ketchum, and Richards, 1963) predicts that changes in the concentrations of phosphorous, nitrogen, carbon, and oxygen caused by the oxidation of organic matter occur in the ratio 1/16/106/276 by atoms.

Redfield et al. (1963) showed that variations in phosphate, nitrate, inorganic carbon, and apparent oxygen utilization (AOU) in the Western Atlantic conform approximately to this model. Pytkowicz (1964) and Park (1967) showed that the model describes the observed changes in phosphate, nitrate, and AOU for subsurface waters off Oregon.

Park (1965) found rough agreement between the model and variations in total carbon dioxide (TCO_2) and oxygen for intermediate waters in the Northeastern Pacific. For individual water masses in the Western Pacific and in the Antarctic, Sugiura (1966) and Sugiura and Yoshimura (1967) found agreement between the model and variations in TCO_2 and AOU. Culberson and Pytkowicz (1970a) showed agreement between the model and the distributions of TCO_2 and AOU for two stations in the Eastern Pacific. Ben-Yaakov (1971, 1972) obtained the oxidative ratio predicted by Redfield et al. (1963) from a

multivariable regression analysis of the vertical distribution of TCO_2 and oxygen in the Eastern Pacific.

Park (1968a, b) and Sugiura (1969) showed that pH—AOU plots in the North Pacific agree with the model.

However, Postma (1964) and Craig (1969) questioned the model. Postma (1964) plotted phosphate and TCO_2 versus oxygen and found deviations from the predicted phosphorous/carbon/oxygen ratios. In his analysis, Postma (1964) corrected TCO_2 for variations in alkalinity, but not for variations in preformed TCO_2. The neglect of preformed TCO_2 and of the difference between AOU and oxygen may explain the deviations from the model found by Postma (1964).

Craig (1969) proposed a model for the vertical distribution of TCO_2 involving vertical diffusion and vertical advection. For stations in the Central Pacific he did not find a linear correlation between TCO_2 and oxygen and he concluded that the model of organic decomposition does not apply to open systems which include eddy diffusion. Craig's (1969) analysis ignored the difference between oxygen and AOU, and ignored variations in preformed TCO_2 with depth. Pytkowicz (1968, 1971) showed that the model of organic decomposition applied to open systems if variations in the preformed quantities were allowed. It will be shown in Chapter IV that the stoichiometric model can be derived from Craig's (1969) model, thus proving that the two models are consistent.

In the following sections, equations relating TCO_2 and AOU will be derived, and it will be shown that graphs of TCO_2 versus AOU are linear and have the slope predicted by the stoichiometric model.

Calculations

The calculation of TCO_2, pCO_2, and AOU is outlined in Chapter II, and the equations used in the calculations are listed in Appendix 1.

Carbon-oxygen Relationships

The concentration of total carbon dioxide can be written (Park, 1965),

$$TCO_2 = C_o + \Delta C_b + \Delta C_a \qquad (8)$$

C_o, the initial (preformed) value of TCO_2 at the surface source of the water sample, is a function of the temperature, salinity, initial alkalinity, and initial partial pressure of carbon dioxide. C_o is strongly temperature dependent. At constant pCO_2, C_o decreases 0.4% per degree Celsius due to the effect of temperature on the solubility of carbon dioxide.

ΔC_b is the change in TCO_2 due to biological activity. According to Redfield et al. (1963), $\Delta C_b = b(AOU)$, where $b = (106$ carbon atoms/ 276 oxygen atoms$) = 0.384$.

$\Delta C_a = 0.5(TA_m - TA_o)$ is the change in TCO_2 due to changes in the total alkalinity. The subscripts m and o designate the measured

and the initial values of the alkalinity. ΔC_a may also be written $\Delta C_a = 0.5(SA_m - SA_o)Cl$, where SA is the specific alkalinity and Cl is the chlorinity.

In terms of AOU and specific alkalinity, equation (8) may be written,

$$TCO_2 = C_o + b(AOU) + 0.5(SA_m - SA_o)Cl \qquad (9)$$

To obtain a linear correlation between AOU and ΔC_b in a vertical profile, it is necessary to remove the contributions of all non-oxidative processes from the measured TCO_2. These are (1) changes in alkalinity due to differences in chlorinity, (2) changes in SA_m due to carbonate solution or precipitation, and (3) variations in C_o and SA_o, the preformed TCO_2 and specific alkalinity.

Variations in TCO_2 due to the effect of chlorinity changes with depth, on the alkalinity term in equation (9), can be eliminated by multiplying both sides of the equation by the ratio (Cl_n/Cl), where Cl_n is some constant, arbitrary chlorinity (Postma, 1964). In this case equation (9) becomes,

$$TCO_2^* = (Cl_n/Cl)TCO_2 \qquad (10)$$

$$TCO_2^* = (Cl_n/Cl)C_o + (b)(Cl_n/Cl)(AOU) + 0.5(SA_m - SA_o)Cl_n \qquad (11)$$

In effect, multiplying equation (9) by (Cl_n/Cl) normalizes TCO_2 to a constant chlorinity.

Variations in TCO_2 due to differences in SA_m can be eliminated by normalizing TCO_2^* to a constant specific alkalinity (Postma, 1964). The normalized value of TCO_2^* is,

$$TCO_2' = TCO_2^* + 0.5(SA_n - SA_m)Cl_n \tag{12}$$

$$TCO_2' = (Cl_n/Cl)TCO_2 + 0.5(SA_n - SA_m)Cl_n \tag{13}$$

SA_n is a constant, arbitrary specific alkalinity.

Combining equations (11) and (12) yields,

$$TCO_2' = (Cl_n/Cl)C_0 + b(Cl_n/Cl)(AOU) + 0.5(SA_n - SA_0)Cl_n \tag{14}$$

The corrections used to calculate TCO_2' are identical to those applied by Postma (1964). TCO_2' will be a linear function of the quantity $(Cl_n/Cl)(AOU)$, if these corrections have eliminated the non-oxidative contributions to TCO_2.

Figures 2 and 3 illustrate the relationship between TCO_2, TCO_2', and $(Cl_n/Cl)(AOU)$ for two stations in the Eastern Pacific (Culberson and Pytkowicz, 1970a). Neither TCO_2 nor TCO_2' are linear with $(Cl_n/Cl)(AOU)$, although the corrections applied to TCO_2' decreased the deviations from linearity. If the stoichiometric model is correct, the non-linearity of TCO_2' is due to variations of C_0 and/or SA_0 with depth. These changes must be eliminated before a linear correlation can be obtained.

The specific alkalinity of Pacific surface waters varies between 0.118 and 0.123 meq/g-Cl, with values at high latitudes lying between
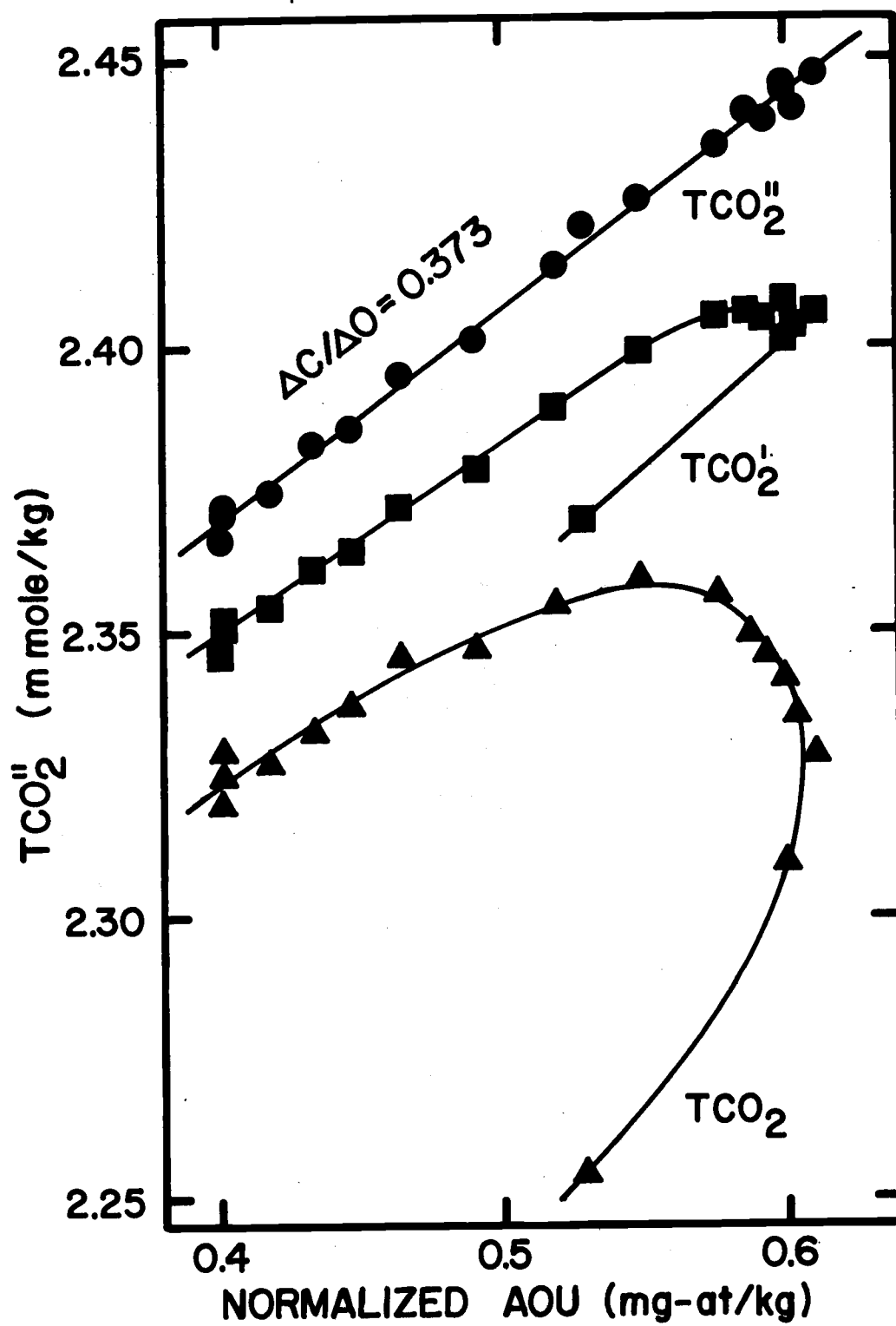
Figure 2. The relationship between total carbon dioxide and apparent oxygen utilization at station 127.
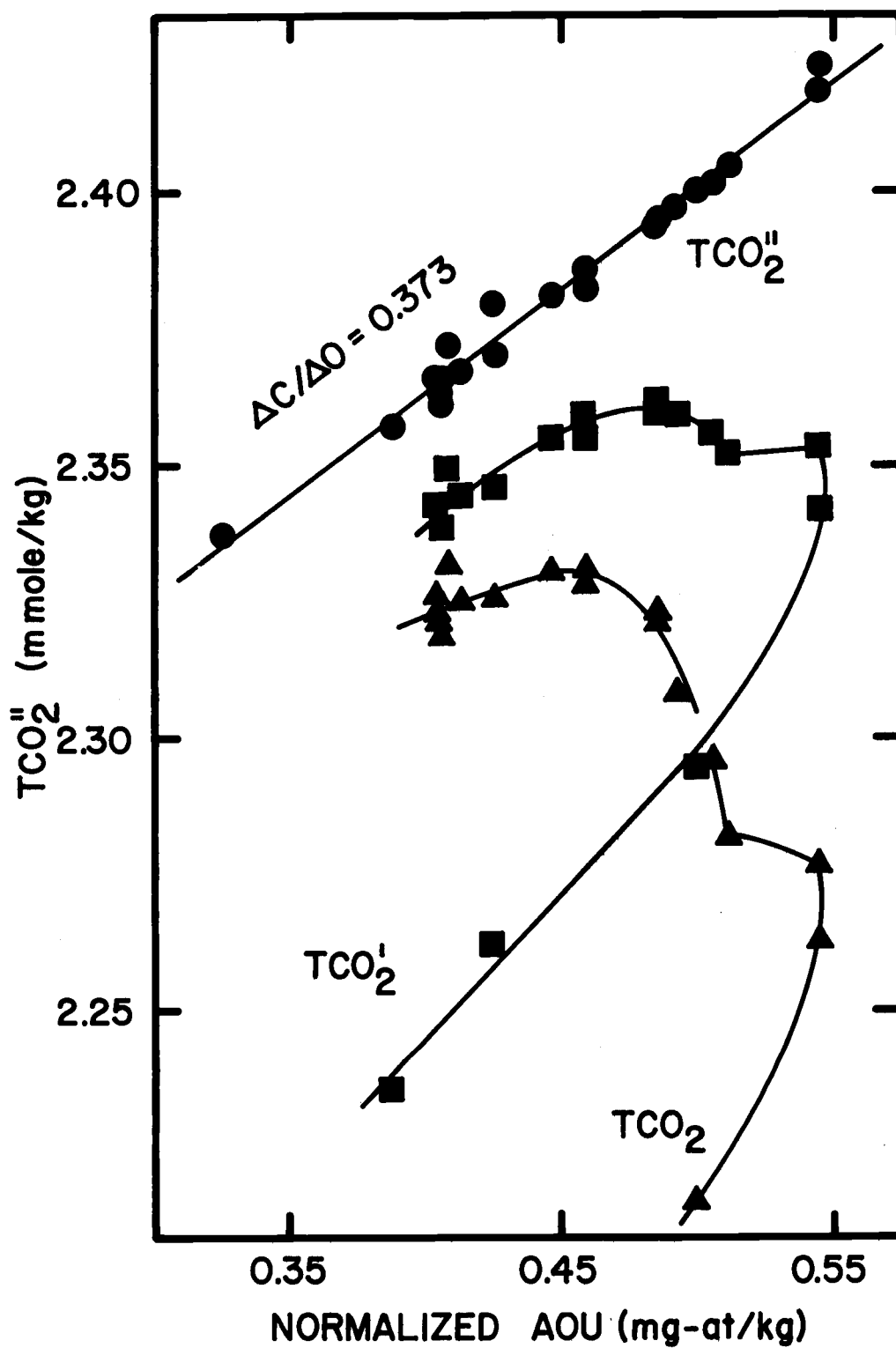
Figure 3. The relationship between total carbon dioxide and apparent oxygen utilization at station 70. Normalized AOU is the quantity $(19.20/Cl)(AOU)$. The values of TCO_2 and TCO_2' are displaced -0.04 and -0.02 mmole/kg respectively.

0.120 and 0.123 meq/g-Cl (Bruyevich, 1966; Horibe, 1970). Thus the initial specific alkalinity of water masses formed at high latitudes in the Pacific is relatively constant, and the non-linearity in TCO_2' is probably due to variations in C_0 rather than in SA_0.

The initial TCO_2, C_0, depends on the initial pCO_2, on the temperature, and to a lesser extent on SA_0 and salinity. At constant pCO_2, C_0 decreases about 0.4% per degree due to the effect of temperature on the solubility of carbon dioxide (Table 6). In the following paragraphs the measured TCO_2 will be normalized to a constant value of C_0 in order to eliminate variations in the measured TCO_2 due to the effect of temperature on C_0.

It is difficult to calculate C_0 accurately because oceanic surface waters are rarely at equilibrium with atmospheric carbon dioxide (Keeling, 1968; Gordon et al., 1971). However, as a first approximation, C_0 will be represented by C_0', the equilibrium value of TCO_2 calculated at constant pCO_2 and constant SA_0 (Table 6). TCO_2' can be normalized to a constant value of C_0' by adding the quantity $(C_0^* - (Cl_n/Cl)C_0')$ to equations (13) and (14). TCO_2'', the value of TCO_2' normalized to a constant value of C_0' is,

$$TCO_2'' = (C_0^* - (Cl_n/Cl)C_0') + (Cl_n/Cl)TCO_2 + 0.5(SA_n - SA_m)Cl_n \quad (15)$$

In terms of AOU,

$$TCO_2'' = (C_0^* + (Cl_n/Cl)(C_0 - C_0') + 0.5(SA_n - SA_0)Cl_n)$$
$$+ b(Cl_n/Cl)(AOU) \quad (16)$$

C_0^* is a constant, arbitrary value of C_0'. C_0' is the TCO_2 calculated

at some constant pCO_2, constant initial specific alkalinity, and at the

salinity and potential temperature of the water sample. If $(C_0 - C_0')$

and SA_0 are constant and if the model is correct, a plot of TCO_2''

versus $(Cl_n/Cl)(AOU)$ will yield a straight line with slope 0.384.

Figures 2 and 3 show the relationship between TCO_2'' and

$(Cl_n/Cl)(AOU)$ for two stations in the Eastern Pacific (Culberson and

Pytkowicz, 1970a). TCO_2'' was calculated from equation (15) using the

measured TCO_2, and the values,

$$Cl_n = 19.20‰$$

$$SA_n = 0.1273 \text{ meq/g-Cl}$$

$$SA_0 = 0.121 \text{ meq/g-Cl}$$

$$C_0^* = 2.16 \text{ mmole/kg}$$

$$(pCO_2)_0 = 3.2 \cdot 10^{-4}((760 - \text{vapor pressure seawater})/760) \text{ atm}$$

The values chosen for Cl_n and SA_n are the observed values in Pacific

deep water; the value for SA_0 is the average surface specific alkalinity

at high latitudes in the Pacific (Bruyevich, 1966; Horibe, 1970); the

value for C_0^* is the concentration of TCO_2 in Pacific deep water at

equilibrium with a partial pressure of carbon dioxide equal to $(pCO_2)_0$.

The values of Cl_n, SA_n, and C_0^* were chosen so that TCO_2'' would equal

TCO_2 in Pacific deep water. The initial partial pressure of carbon

dioxide is calculated for a wet atmosphere containing 0.032% carbon

dioxide on a water free basis.

The graphs of TCO_2'' versus $(Cl_n/Cl)(AOU)$, Figures 2 and 3, are linear over a wide range of depths, with an average slope of 0.371. At station 70 the graph is linear below 98 m, and the values at station 127 are linear below 398 m. The small difference between the predicted and calculated slopes indicates the essential correctness of the stoichiometric model. The figures show that the production of carbon dioxide by oxidation is easily obscured by changes in TCO_2 produced by other processes.

The linear correlation between TCO_2'' and $(Cl_n/Cl)(AOU)$ means that the term

$$(C_o^* + (Cl_n/Cl)(C_o - C_o') + 0.5(SA_n - SA_o)Cl_n)$$

in equation (16) is constant along each vertical profile. This implies that either the quantities $(C_o - C_o')$ and SA_o are constant, or that variations in these quantities cancel each other.

The alkalinity correction to TCO_2'' is reduced if SA_o increases. However, increasing SA_o also increases C_o, and the increase in the term $(C_o - C_o')$ tends to offset the decrease in the term $0.5(SA_n - SA_o)$ $\cdot Cl_n$. A 1% increase in SA_o increases TCO_2'' by 0.4%.

Changes in $(pCO_2)_o$ cause changes in C_o'. Although C_o' depends on the constant value of $(pCO_2)_o$ used in the calculations, the slopes calculated from graphs of TCO_2'' versus $(Cl_n/Cl)(AOU)$ are not sensitive to this value of $(pCO_2)_o$, because changing the assumed pCO_2 changes each calculated C_o', and thus each calculated value of TCO_2'',

by an equal amount. Setting $(pCO_2)_O$ equal to $2.9 \cdot 10^{-4}$ or to $3.5 \cdot 10^{-4}$ atm affects the calculated slope less than 1%.

C_O is a function of the initial pCO_2, and C_O increases about 0.015 mmole/kg for a $0.3 \cdot 10^{-4}$ atm increase in pCO_2. If variations of $(pCO_2)_O$ larger than $\pm 0.2 \cdot 10^{-4}$ atm occurred between the deep and intermediate waters at stations 70 and 127, the term $(C_O - C_O')$ would vary significantly with depth, and a linear correlation between TCO_2'' and $(Cl_n/Cl)(AOU)$ would not be found. The fact that a linear relation is found indicates that the initial values of pCO_2 in the intermediate and deep waters at stations 70 and 127 are approximately equal.

Carbon-oxygen Relationships in the World Ocean

As a further check, the stoichiometric model has been applied to several different oceanic areas. Data sources are listed in Table 3. Station positions are shown in Figures 4 through 7.

Alkalinity and pH values from deep casts of the Southern Cross Expedition (Horibe, 1970) show excessive scatter, possibly due to Nansen bottle corrosion (Takahashi et al., 1970). Therefore, only shallow cast data from this cruise has been used.

Alkalinity measurements at deep stations in the Somali Basin (Meteor Indian Ocean Expedition, Dietrich et al., 1966b) have a range of 6.3% at depths greater than 3000 m. The salinity range at these depths is only 0.015‰, and the pH (25°C) range is less than 0.02 pH
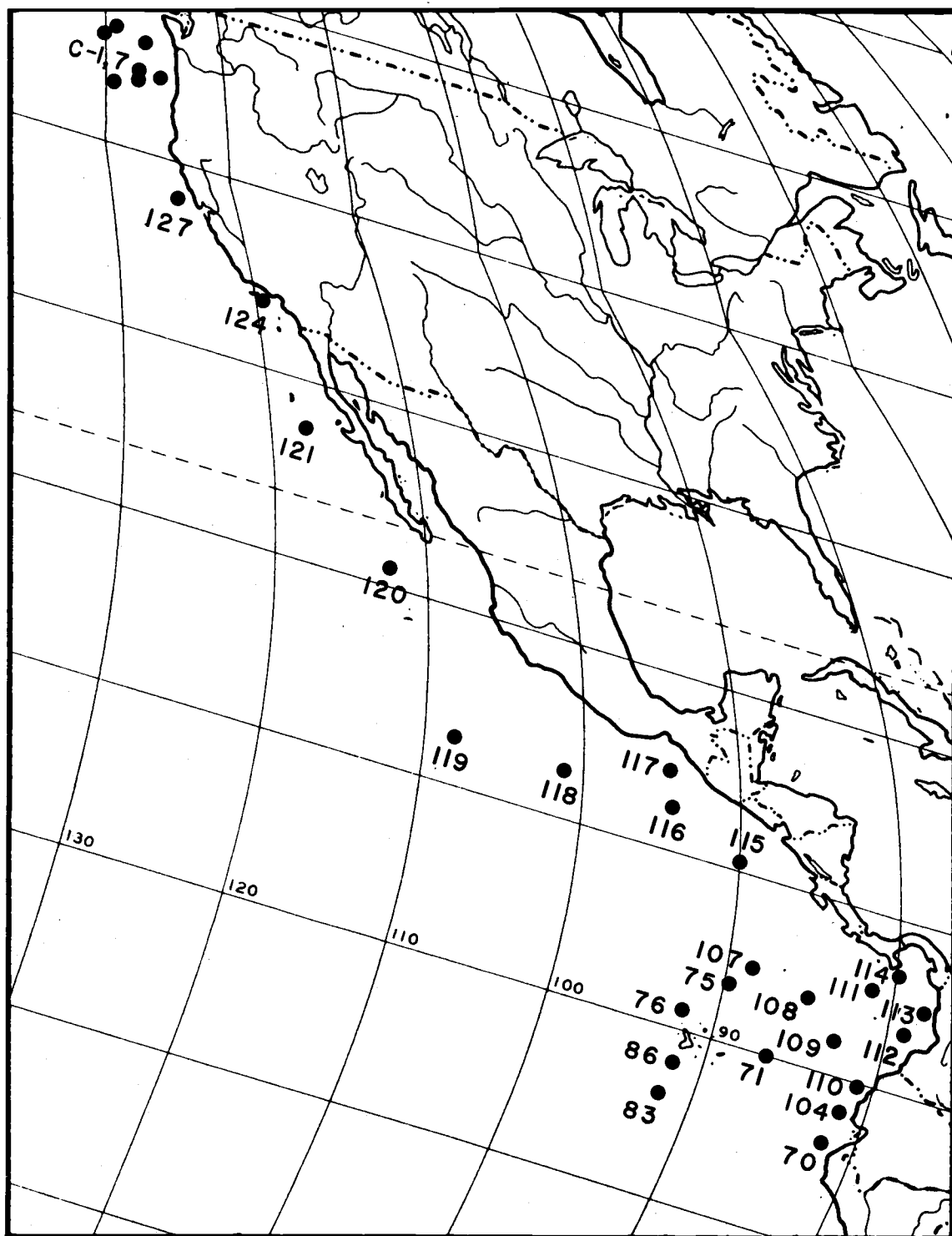
Figure 4. Stations in the Eastern Pacific occupied during cruises YALOC-69 and Y6908F.
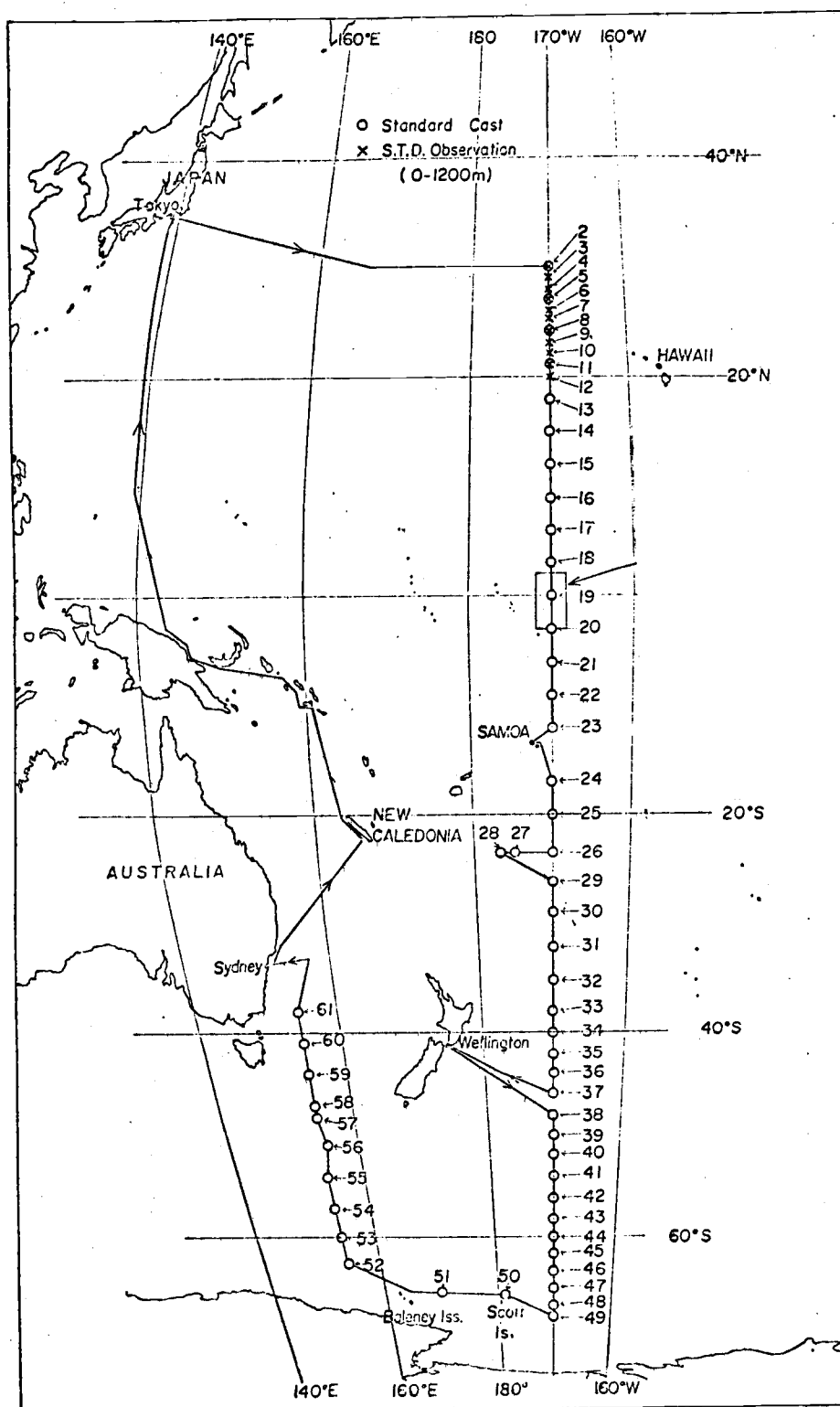
Figure 5. Stations occupied during the Southern Cross Expedition
(from Horibe, 1970).
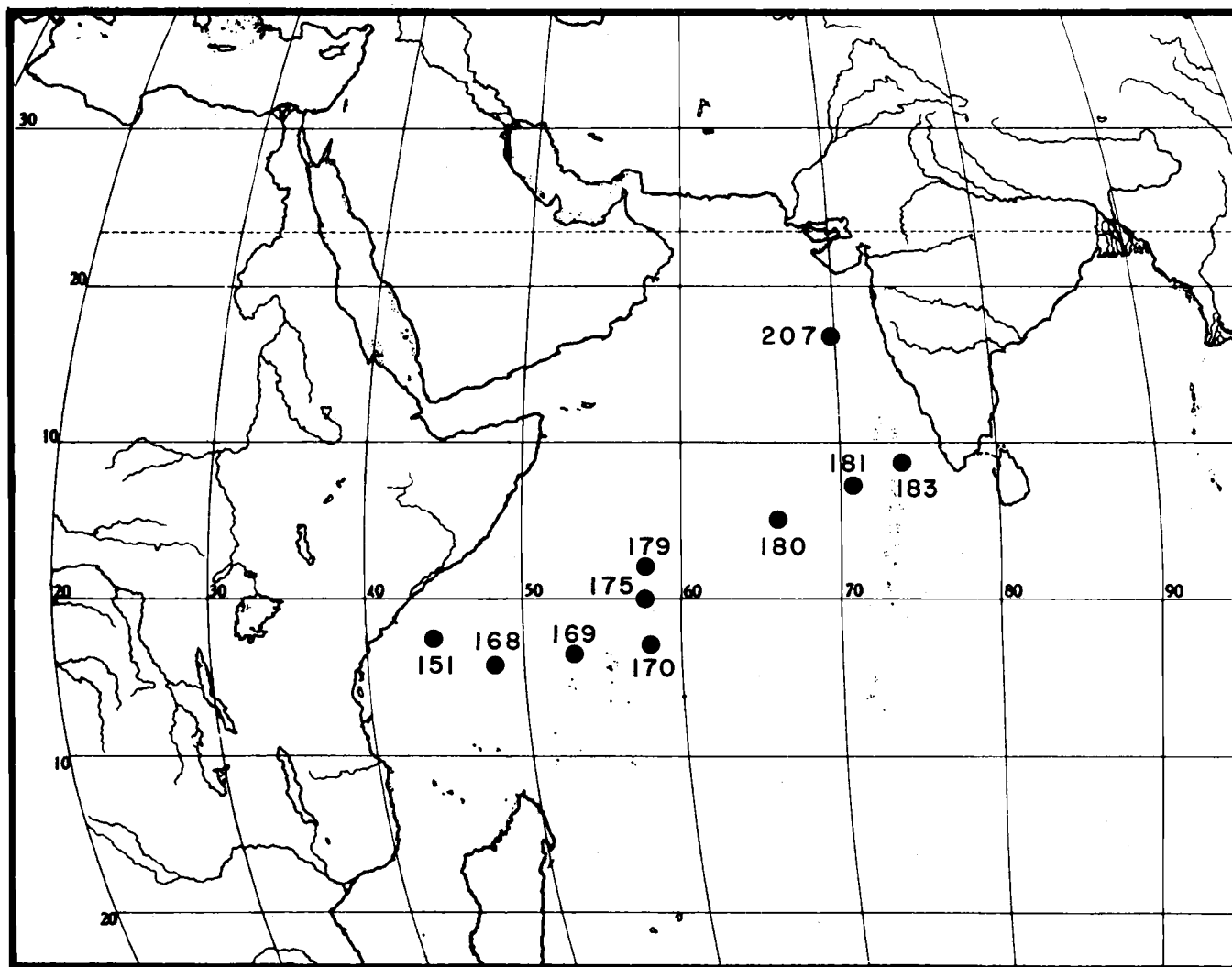
Figure 6. Stations occupied during the Meteor Indian Ocean Expedition.
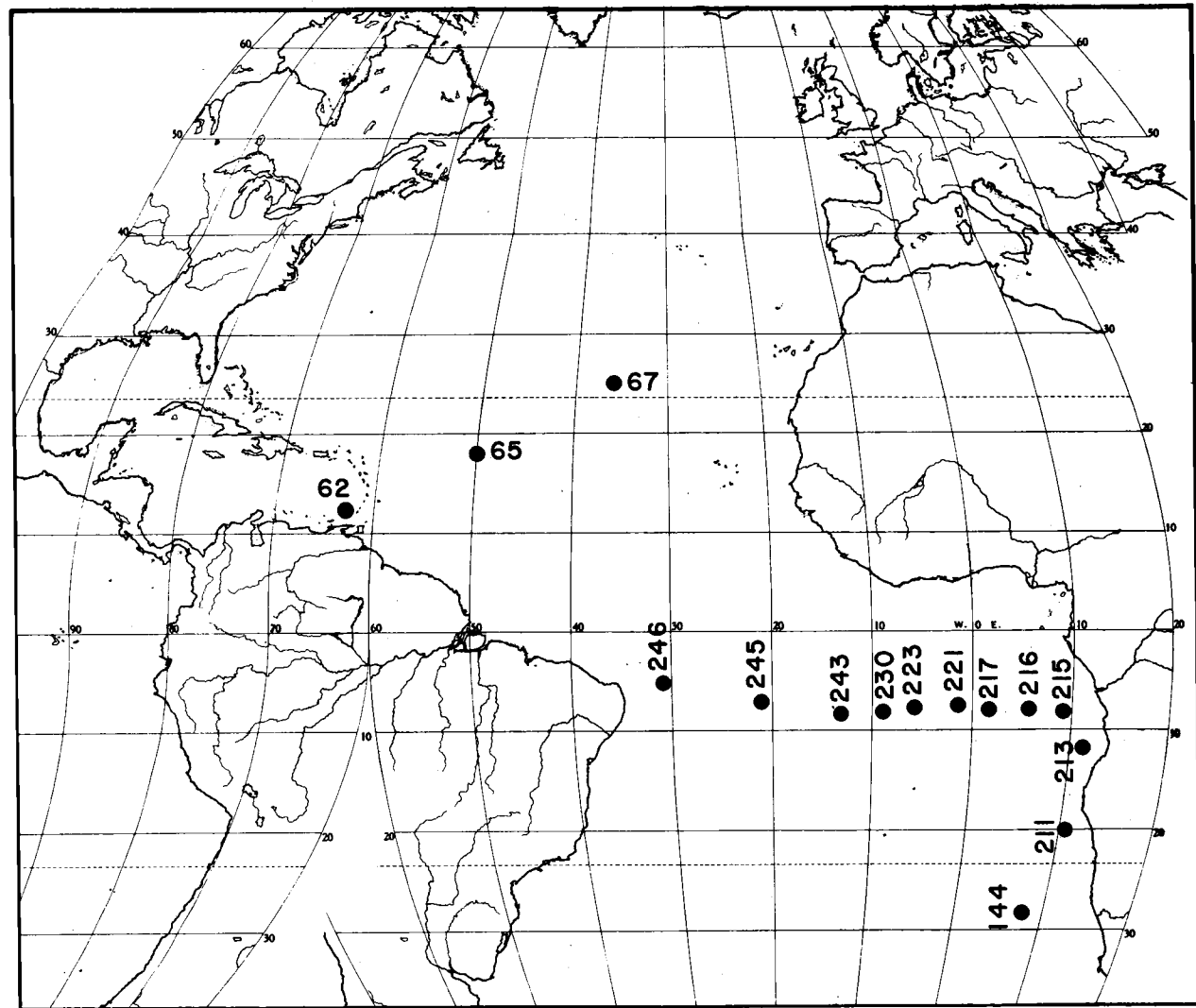
Figure 7.   Station positions in the South Atlantic (Edmond, 1970a), and in the North Atlantic (cruise TT-46, see Chapter VIII).

units. The large alkalinity range may be due to errors in the

normality of the Fixanal Acid used during the expedition. Grasshoff

(1966) standardized one ampoule of the Fixanal series used during

the cruise and found that its normality was 2.1% lower than the nomi-

nal value. Stations with alkalinities which appear systematically high

or low when compared to surrounding stations have been excluded from

Figure 10. The alkalinities of the remaining stations appear to be

internally consistent, but they may contain systematic errors due to

faulty acid normality.

Figures 8 through 11 show that the TCO_2''-$(Cl_n/Cl)(AOU)$

correlations for each area are linear and have nearly the theoretical

slope. Data from all stations within a region fall along the same line.

A statistical analysis of the least squares lines for each region is

given in Table 4. Depth ranges at each station over which a linear

correlation was found are listed in Table 5.

Eastern Pacific

The Eastern Pacific data fit the model from a depth of about

200 m to the bottom. Samples collected 0.5 m from the bottom fall on

the line. Data from the surface mixed layer lie above the line. The

scatter of points about the line is approximately equal to the precision

of the analytical methods (Tables 3 and 4). Low latitude data fit the

model closer to the surface than data from mid-latitudes (Table 5).
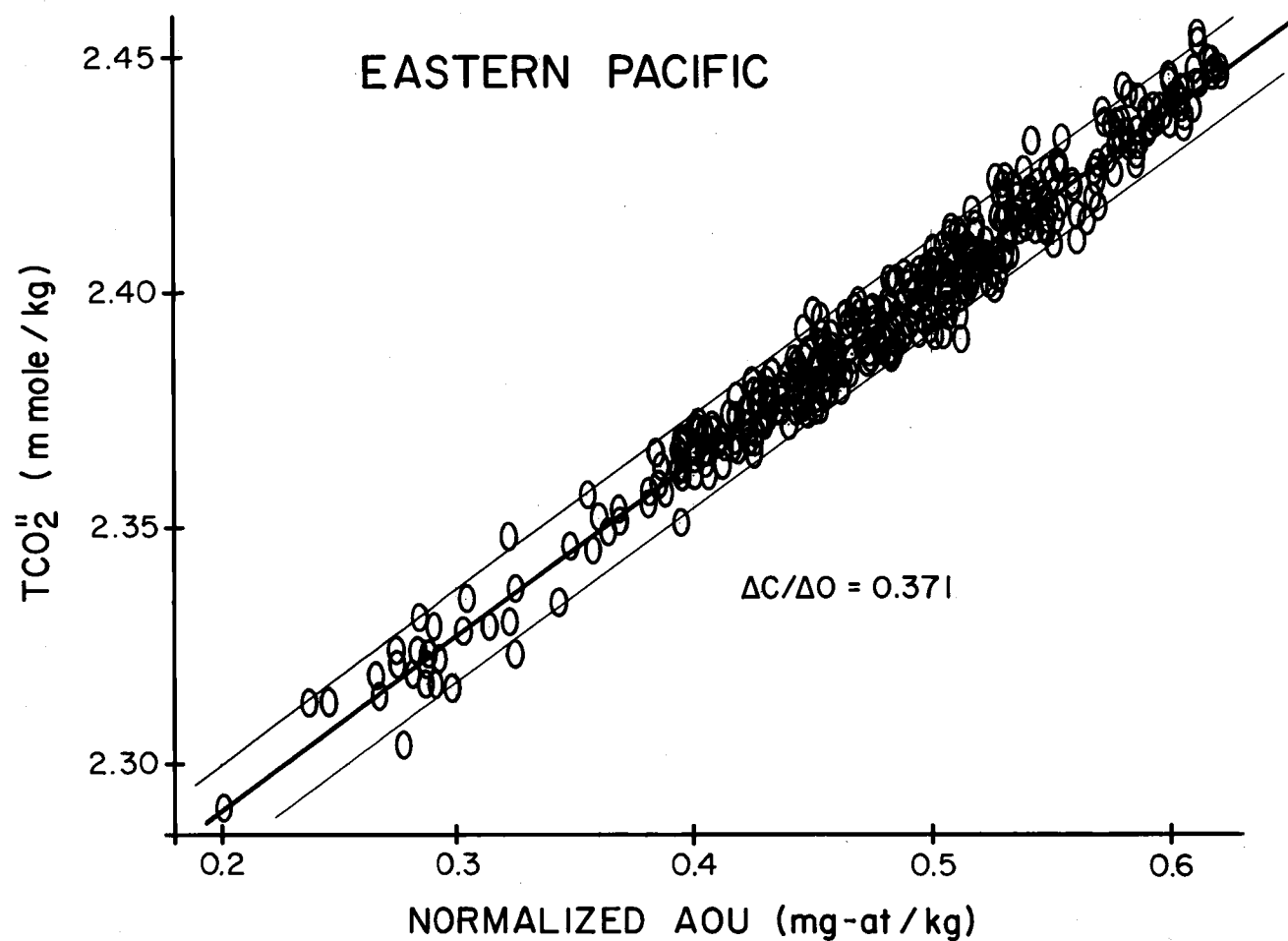
Figure 8. Total inorganic carbon-apparent oxygen utilization relationship in the Eastern Pacific. Normalized AOU is the quantity $(19.20/Cl)(AOU)$. The heavy line is the least squares line through the data. The two parallel lines are drawn $\pm\ 0.010$ mmole/kg (2 sigma in TCO_2) about the least squares line.

SOUTH PACIFIC

$\Delta C/\Delta O = 0.373$
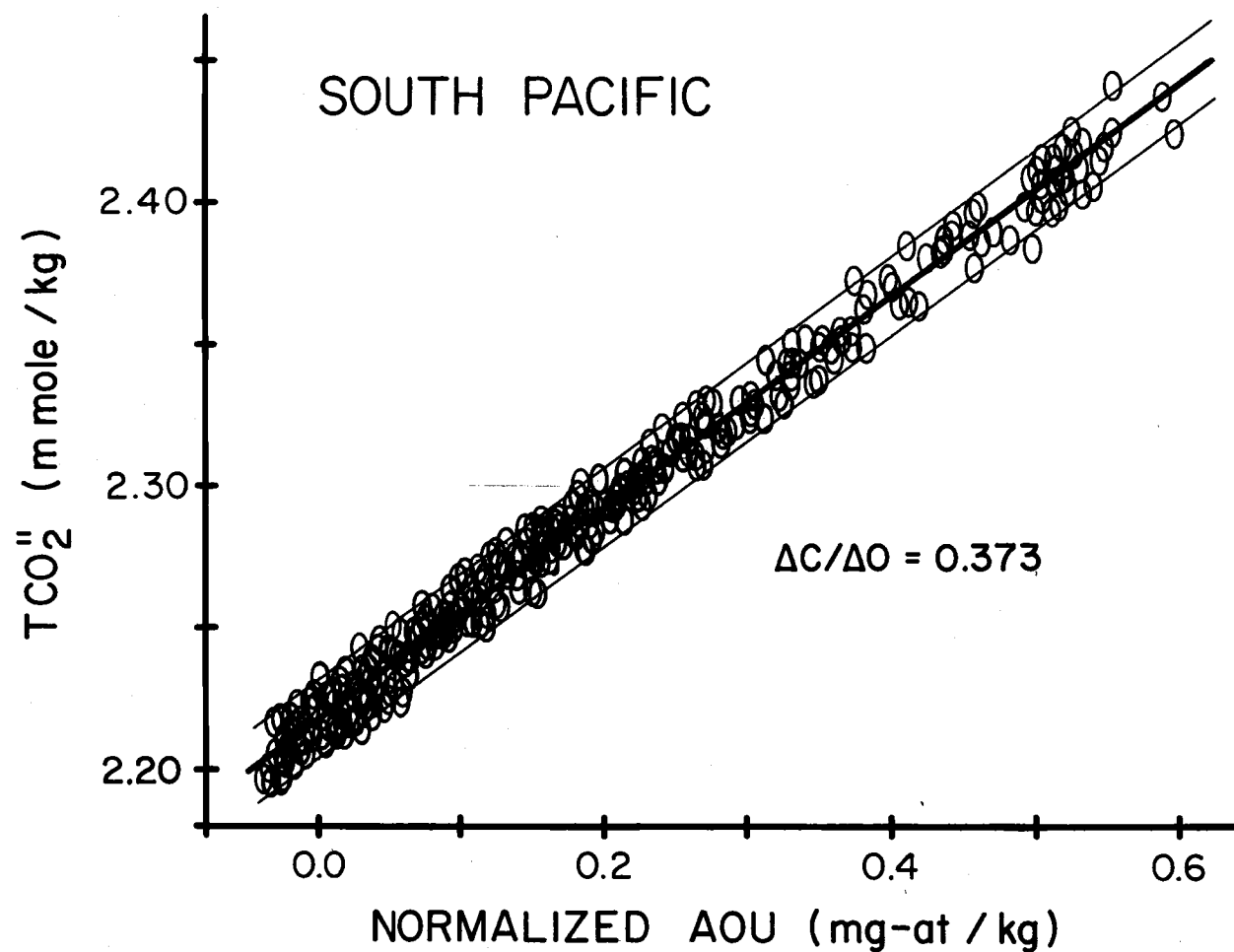
Figure 9. Total inorganic carbon-apparent oxygen utilization relationship in the South Pacific. Normalized AOU is the quantity $(19.20/Cl)(AOU)$. The heavy line is the least squares line through the data. The two parallel lines are drawn ± 0.014 mmole/kg (2 sigma in TCO_2) about the least squares line.
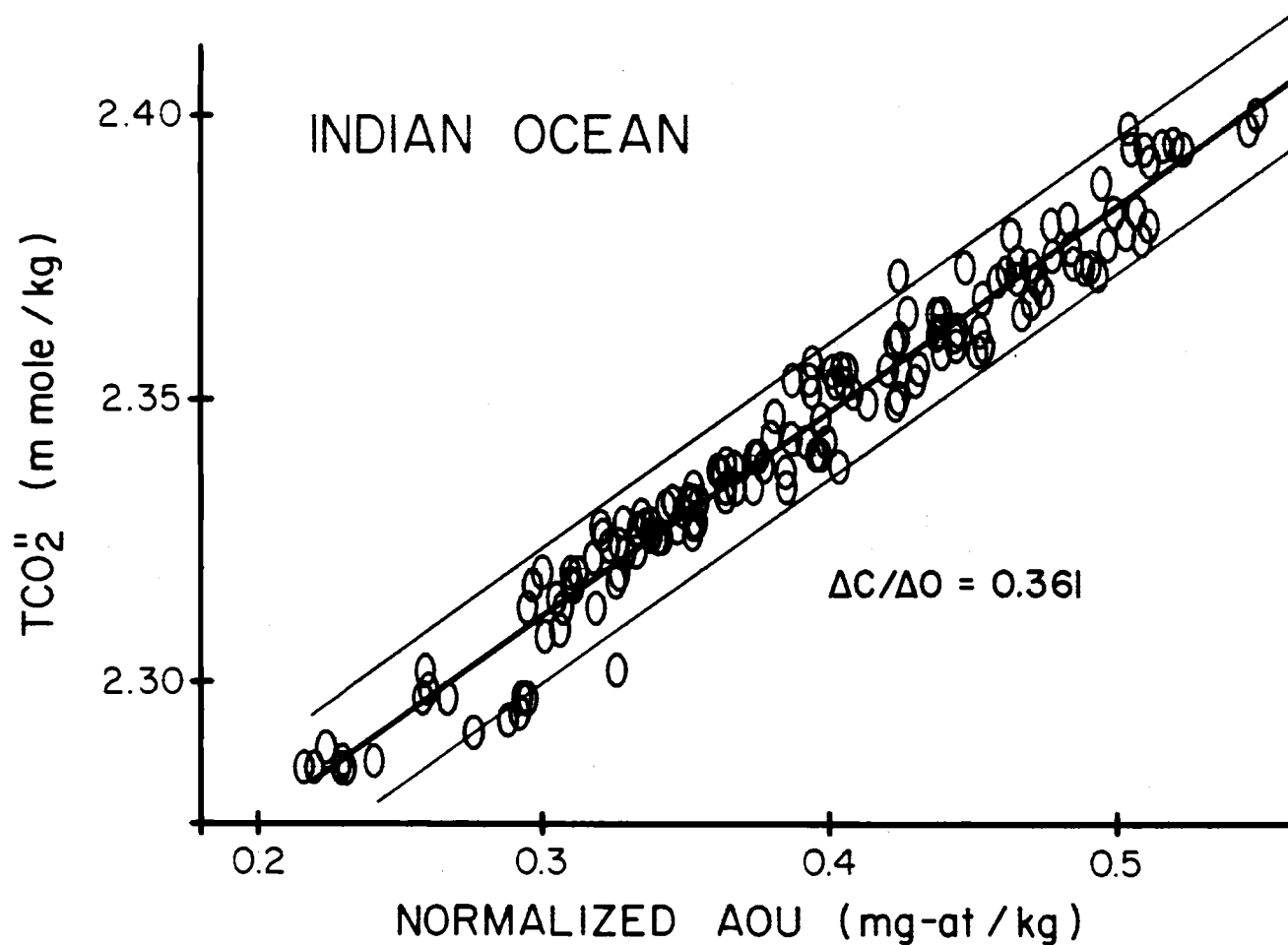
Figure 10. Total inorganic carbon-apparent oxygen utilization relationship in the Indian Ocean. Normalized AOU is the quantity $(19.20/Cl)(AOU)$. The heavy line is the least squares line through the data. The two parallel lines are drawn $\pm$ 0.012 mmole/kg (2 sigma in TCO_2) about the least squares line.
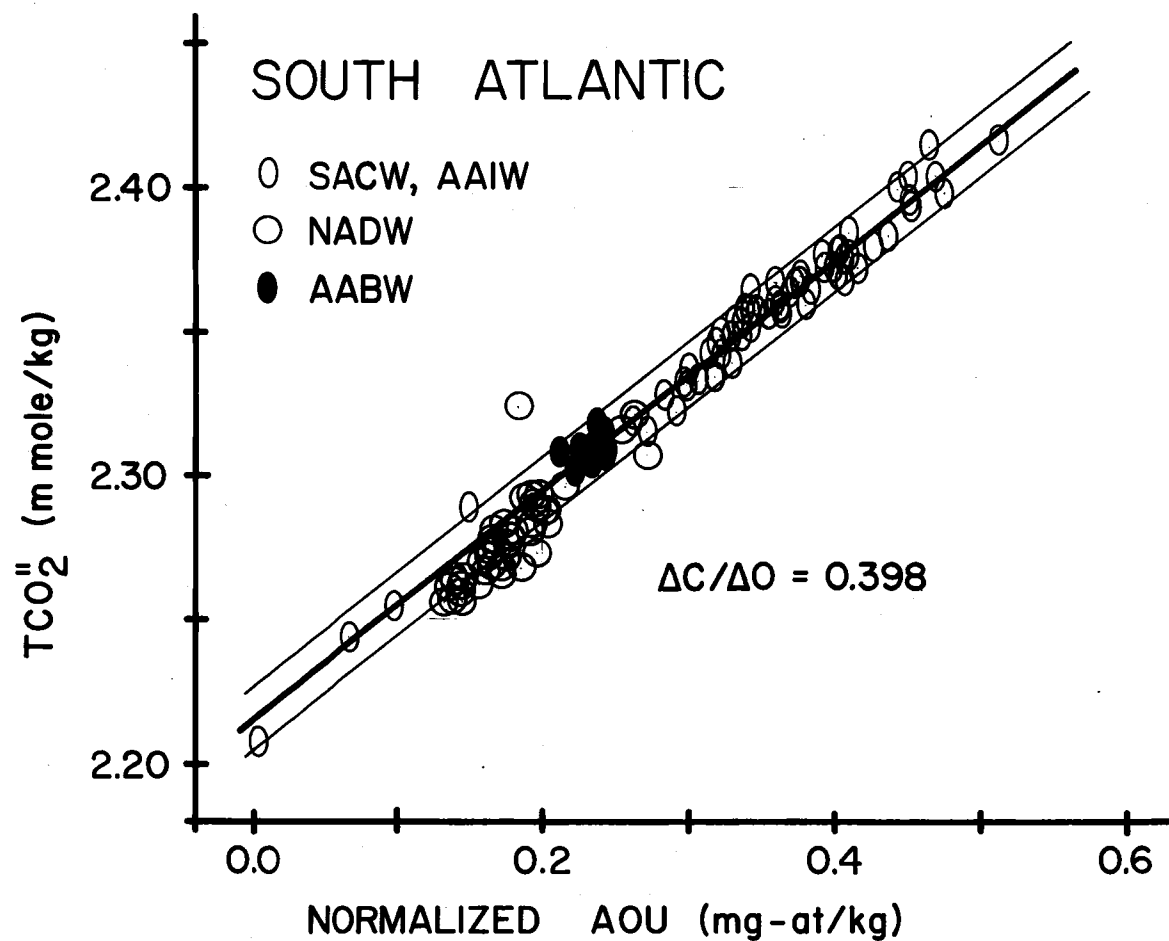
Figure 11. Total inorganic carbon-apparent oxygen utilization relationship in the South Atlantic. Normalized AOU is the quantity $(19.20/Cl)(AOU)$. The heavy line is the least squares line through the data. The two parallel lines are drawn ± 0.012 mmole/kg (2 sigma in TCO_2) about the least squares line.

Table 3. Data for carbon/oxygen correlation.

Region	Methods	Precision (2 sigma) claimed for each method
Eastern Pacific (Wyatt et al., 1970)	pH (Takahashi et al., 1970)	± 0.006 pH
	alkalinity (Culberson et al., 1970)	± 0.008 meq/kg
South Pacific (Horibe, 1970)	pH (Strickland & Parsons, 1965)	±0.01 pH
	alkalinity (modified Gran method)	± 0.01 meq/kg
Indian Ocean (Dietrich et al., 1966b)	pH (Strickland & Parsons, 1965)	± 0.01 pH
	alkalinity (Anderson & Robinson, 1946)	± 0.006 meq/kg
South Atlantic (Edmond, 1970a)	TCO_2 (Edmond, 1970b)	± 0.014 mmole/kg
	alkalinity (Edmond, 1970b)	± 0.004 meq/kg

Table 4. Statistical analysis of carbon/oxygen correlations.

Region	Number of samples	Least squares line (± 2 standard errors) intercept	slope	Standard deviation of TCO_2'' about line	Correlation coefficient
Eastern Pacific	534	2.216 ± 0.003	0.371 ± 0.006	± 0.005	0.984
South Pacific	428	2.218 ± 0.001	0.373 ± 0.004	± 0.007	0.994
Indian Ocean	153	2.203 ± 0.005	0.361 ± 0.012	± 0.006	0.981
South Atlantic	73	2.215 ± 0.005	0.398 ± 0.014	± 0.006	0.989

Table 5. The depth range over which a linear carbon/oxygen relationship is found. Station positions are shown in Figures 4 through 7.

Station	Depth Range for Linear Correlation	Station	Depth Range for Linear Correlation
	YALOC-69		SOUTHERN CROSS
70	98 - 3754 meters	2	140 - 916 meters
71	40 - 2737	5	1 - 946
75	399 - 2161	11	70 - 1140
76	98 - 2327	13	170 - 1051
83	99 - 3735	15	170 - 1080
86	99 - 3208	16	140 - 1150
104	99 - 3848	17	185 - 1140
107	98 - 2697	18	198 - 1179
108	98 - 3365	20	284 - 1148
109	75 - 3697	21	242 - 1010
110	99 - 3165	22	261 - 1077
111	49 - 3702	23	275 - 1098
112	98 - 3815	24	270 - 1100
113	74 - 1806	25	471 - 1140
114	75 - 3306	26	1 - 1126
115	98 - 3832	29	69 - 1128
116	74 - 3984	30	374 - 1129
117	75 - 6128	31	28 - 1135
118	146 - 3262	32	28 - 1136
119	147 - 2396	33	29 - 1152
120	197 - 3663	34	94 - 1140
121	398 - 3691	35	28 - 1136
124	297 - 1877	36	1 - 1158
127	398 - 3928	37	9 - 1120
		38	1 - 1100
	Y-6908F	39	1 - 1154
		40	46 - 1133
C-1	2335 - 3017	41	69 - 1088
C-2	1957 - 2735	42	91 - 1137
C-3	1617 - 2592	43	174 - 878
C-4	1765 - 2740	55	71 - 1153
C-5	1059 - 2829	56	1 - 1155
C-6	2279 - 3107	57	1 - 1019
C-7	2305 - 3380	58	29 - 982
		59	1 - 935
		60	1 - 1095
		61	28 - 1148

Table 5 (continued).

| | Depth Range for |
| Station | Linear Correlation |

METEOR-IIOE

151	147 - 3803 meters
168	144 - 4584
169	148 - 3446
170	99 - 4186
175	192 - 4606
179	296 - 4117
180	294 - 4455
181	147 - 3395
183	295 - 2676
207	394 - 3414

SOUTH ATLANTIC (EDMOND)

144	103 - 1159
211	306 - 1085
213	201 - 685
215	202 - 703
216	295 - 1058
217	198 - 693
221	198 - 695
223	203 - 981
230	201 - 703
243	242 - 982
245	226 - 698
	4363 - 5316
246	201 - 971
	4301 - 4900

South Pacific

The Southern Cross data fall along one line from 30°N to 55°S (Figure 9). Data from stations south of 55°S fall beneath the least squares line. Data taken north of 55°S fit the model from about 200 m to 1100 m (the deepest sample of the shallow casts) (Table 5). Data from the mixed layer in low and mid-latitudes lie above the line.

The least squares lines for the Eastern Pacific and for the South Pacific are identical within experimental precision (Table 4).

Indian Ocean

The Meteor data from the Equatorial Indian Ocean (Dietrich et al., 1966b) obey a linear relationship from approximately 200 m depth to the bottom (Figure 10 and Table 5). Data from the surface mixed layer lie above the least squares line. The Indian Ocean line has a slightly lower slope and intercept than the Eastern and South Pacific lines. The significance of this difference is uncertain because of possible systematic errors in the Meteor alkalinity profiles.

South Atlantic

The carbon/oxygen relationship in the South Atlantic (Edmond, 1970a) is shown in Figure 11. The points on the figure are differentiated by water mass. The open ovals are South Atlantic Central Water

and Antarctic Intermediate Water (depths 200 m to 1200 m); the circles

are North Atlantic Deep Water (depths 1200 m to 4000 m); and the

solid ovals are Antarctic Bottom Water (depths greater than 4000 m).

The least squares line has been fitted to the open and solid ovals; it

fits the data to within 200 m of the surface (Table 5). The North

Atlantic Deep Water points fall slightly below the line, indicating that

the correction scheme used to calculate TCO_2'' removes most but not

all of the initial differences between waters of North Atlantic and South

Atlantic-Antarctic origin. Data from the mixed layer fall above the

least squares line.

The difference in TCO_2'' between North Atlantic Deep Water and

water of South Atlantic-Antarctic origin may be due to differences in

the initial specific alkalinity and/or in the initial pCO_2. If the differ-

ence in TCO_2'' is due entirely to differences in initial pCO_2, the initial

pCO_2 of North Atlantic Deep Water would have to be about 30 ppm

lower than that of the South Atlantic-Antarctic waters. Keeling (1968)

shows that the pCO_2 of surface water near Greenland is from 30 to

90 ppm lower than the pCO_2 of surface water in the South Atlantic and

Antarctic. The difference in TCO_2'' might also be due to differences in

the initial specific alkalinity. The initial specific alkalinity of North

Atlantic Deep Water would have to be about 1% lower than that of the

South Atlantic-Antarctic waters, if the entire difference in TCO_2''

were due to variations in SA_0. Edmond's (1970a) alkalinity data from

the South Atlantic show that the core of the North Atlantic Deep Water

is characterized by a minimum in specific alkalinity. This discussion

shows that the observed difference in TCO_2'' may be due to variations

in either $(pCO_2)_o$ and/or in SA_o.

General Equation for TCO_2

The least squares lines for the Eastern Pacific, South Pacific,

South Atlantic, and Indian Ocean are nearly equal (Table 4). Equation

(17) which has the theoretical slope,

$$TCO_2'' = 2.210 + 0.384(Cl_n/Cl)(AOU) \tag{17}$$

describes the carbon/oxygen relationships in all of the areas studied

to $\pm 1\%$ in TCO_2''. The intercept of equation (17) has no physical signifi-

cance; it is the average of the highest and lowest values of the inter-

cepts for the individual areas (Table 4).

TCO_2 in any of the four areas can be calculated given the

temperature, salinity, oxygen, alkalinity, initial alkalinity, and initial

pCO_2. An equation for TCO_2 in terms of these parameters can be

derived from equation (15). Solving (15) for TCO_2 yields,

$$TCO_2 = (Cl_n/Cl)TCO_2'' + 0.5(SA_m - SA_n)Cl + (C_o' - C_o^*(Cl_n/Cl)) \tag{18}$$

Substituting (17) into (18) and rearranging yields,

$$TCO_2 = C_o' - 0.0611(Cl) + 0.384(AOU) + 0.5(TA_m) \tag{19}$$

Values of C_o' for various temperatures and salinities are given in

Table 6.

Table 6. Values of the preformed carbon dioxide, C_o'. These values were calculated assuming that the initial specific alkalinity was 0.121, and that the seawater was at equilibrium with a wet atmosphere in which the partial pressure of carbon dioxide was

$$320((760 - \text{vapor pressure seawater})/760) \times 10^{-6} \text{ atm.}$$

C_o' was calculated by combining equations (20) and (21) and solving them for a_H. The calculated value of a_H and the assumed value of $(pCO_2)_o$ were then used to calculate C_o' from equation (20).

$$TCO_2 = (\alpha_s)(pCO_2)((a_H^2 + a_H K_1' + K_1' K_2')/a_H^2) \qquad (20)$$

Temperature (°C)

Salinity	0	5	10	15	20	25	30	35
30‰	1.901	1.873	1.845	1.815	1.781	1.743	1.700	1.651
32	2.017	1.984	1.952	1.918	1.880	1.838	1.791	1.739
34	2.131	2.094	2.057	2.019	1.977	1.931	1.880	1.825
34.68	2.169	2.131	2.093	2.053	2.010	1.962	1.910	1.854
36	2.244	2.203	2.161	2.118	2.073	2.023	1.968	1.910
38	2.356	2.310	2.264	2.216	2.166	2.112	2.054	1.993

If the correct value of SA_o can be determined, it is possible to calculate C_o and $(pCO_2)_o$ from equation (9). This is done in Table 7 for samples from the Eastern Pacific. The calculated $(pCO_2)_o$ is sensitive to the assumed value for SA_o. Since the preformed specific alkalinity for high latitude surface waters lies between 0.120 and 0.123 meq/g-Cl (Bruyevich, 1966; Horibe, 1970), the initial pCO_2 is probably in the range 295 ± 25 ppm. Other deep water samples give similar values for $(pCO_2)_o$. For comparison, atmospheric pCO_2 before the increase due to fossil fuel combustion was approximately 290-295 ppm (Bolin and Bishof, 1970). Keeling showed that at present, Antarctic surface waters have pCO_2's 0 to 15 ppm greater than atmospheric pCO_2. If this were true before the recent increase in atmospheric pCO_2, the surface pCO_2 would have been between 290 and 310 ppm. The calculated preformed pCO_2 is consistent with this value, although the accuracy of the calculation is very poor.

Deviations from the Model

The slopes of the least squares lines (Figures 8-11, Table 4) are slightly different for each of the areas studied, and none of the calculated slopes equal the theoretical value of the oxidative ratio ($\Delta C/\Delta O$). There are several possible reasons for this discrepancy. The value of the theoretical ratio is not exact, and it may vary from region to region. The theoretical ratio used in this work, $\Delta C/\Delta O =$

Table 7. Calculation of initial pCO_2 in the Eastern Pacific (YALOC-69). The preformed total carbon dioxide, C_o was calculated from the equation,

$$C_o = TCO_2 - 0.384(AOU) - 0.5(SA_m - SA_o)Cl.$$

The value of $(pCO_2)_o$ was calculated by inserting the calculated C_o into equation (21), and solving (21) for a_H. $(pCO_2)_o$ was then calculated from (20) using the previously calculated values of a_H and C_o.

Station	Depth	SA_o(meq/gCl)	C_o(mmole/kg)	$(pCO_2)_o$
127	956	0.120	2.107	309
		0.121	2.117	295
		0.122	2.126	284
		0.123	2.136	273
127	3545	0.120	2.144	318
		0.121	2.154	304
		0.122	2.163	290
		0.123	2.173	278
70	398	0.120	2.084	316
		0.121	2.094	304
		0.122	2.104	293
		0.123	2.114	283
70	3730	0.120	2.138	312
		0.121	2.148	298
		0.122	2.158	286
		0.123	2.168	275

0.384, is the mean value of the oxidative ratios calculated from the

average composition of phytoplankton (P/N/C = 1/15.5/108.4,

$\Delta C/\Delta O$ = 0.389) and of zooplankton (P/N/C = 1/16.4/103.2, $\Delta C/\Delta O$ =

0.379) reported by Fleming (1939). Based on these analyses, the

error limits associated with the theroetical value for the oxidative

ratio are

$$\Delta C/\Delta O = 0.384 \pm 0.005.$$

This uncertainty in the theoretical ratio can account for between 22%

and 45% of the differences between the calculated and the theoretical

slopes (Table 4).

A second possible reason for the differences between the calcu-

lated and theoretical slopes, is that the correction scheme used to

calculate TCO_2'' does not entirely account for differences in the initial

pCO_2 and specific alkalinity in the water masses which make up a

vertical profile. This is obvious in the South Atlantic data (Figure

11), in which the North Atlantic Deep Water points fall below the line

connecting the South Atlantic Central Water, Antarctic Intermediate

Water, and Antarctic Bottom Water points.

A further way in which the calculated values of TCO_2'' deviate

from the model is that values of TCO_2'' in the mixed layer usually lie

above the least squares line. The most likely explanation for this is

that although these surface waters are within a few per cent of oxygen

saturation, they are usually considerably supersaturated with respect

to atmospheric carbon dioxide. Thus the measured concentration of total inorganic carbon dioxide is significantly greater than the equilibrium concentration assumed in model calculations, and the calculated TCO_2'' values are too large.

Distribution of pH

TCO_2 and pH are related by the equation,

$$TCO_2 = \left[TA - \frac{TB \cdot K_B'}{a_H + K_B'} \right] \left[\frac{a_H^2 + a_H K_1' + K_1' K_2'}{a_H K_1' + 2K_1' K_2'} \right] \qquad (21)$$

Since TCO_2'' is linearly related to $(Cl_n/Cl)(AOU)$, it is expected that a "corrected" pH calculated from the equation,

$$TCO_2'' = \left[TA_n - \frac{TB_n \cdot K_B'}{a_H + K_B'} \right] \left[\frac{a_H^2 + a_H K_1' + K_1' K_2'}{a_H K_1' + 2K_1' K_2'} \right] \qquad (22)$$

will show a non-linear dependence on AOU which can be predicted from the stoichiometric model. "Corrected" values of pH $(25°C)$ calculated from equation (22) and from the TCO_2'' data in Figure 8 (Eastern Pacific) are plotted against $(Cl_n/Cl)(AOU)$ in Figure 12. The theoretical curve predicted by the model is shown for comparison. The agreement is within ± 0.03 pH.

The theoretical curve was calculated from equation (23),

$$TCO_2'' = C_o + 0.384(AOU) = \left[TA_n - \frac{TB_n \cdot K_B'}{a_H + K_B'} \right] \left[\frac{a_H^2 + a_H K_1' + K_1' K_2'}{a_H K_1' + 2K_1' K_2'} \right]$$

$$(23)$$
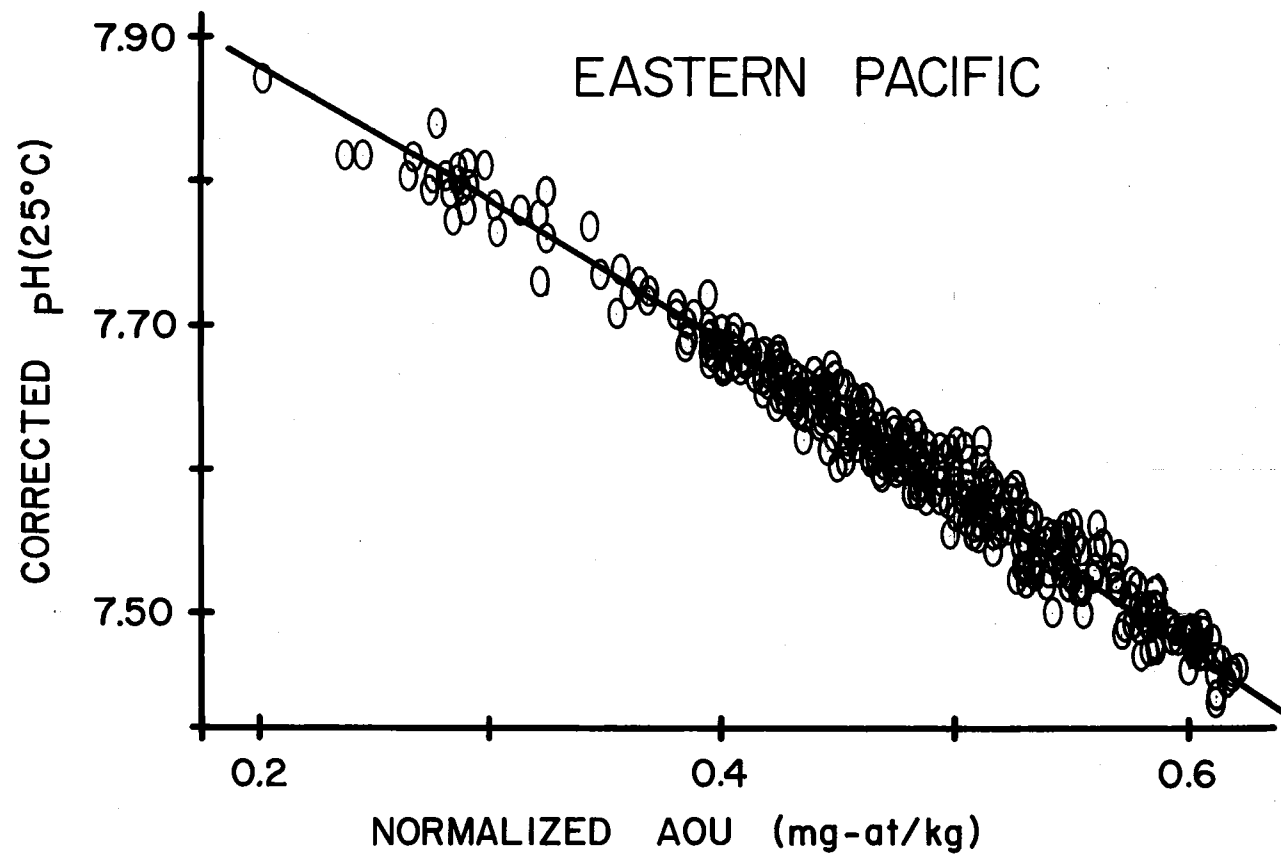
Figure 12. The pH-apparent oxygen utilization relationship in the Eastern Pacific. Normalized AOU is the quantity (19.20/Cl)(AOU). The curve through the data is that predicted by the stoichiometric model of organic decomposition.

Values of TCO_2'' were calculated from pH 7.4 to 8.5 in increments of 0.1 pH units. The lowest value of TCO_2'' (pH 8.5) was arbitrarily set equal to zero AOU, and the relative AOU corresponding to a particular value of TCO_2'' was calculated from the equation,

$$(AOU)_{relative} = \frac{(TCO_2'')_{pH_i} - (TCO_2'')_{8.5}}{0.384} \tag{24}$$

The true AOU differs from the relative AOU by an amount equal to $C_0/0.384$ (see equation (23)). A graph of pH versus relative AOU was then constructed, on which the Y-axis (pH) was fixed, but on which the X-axis was arbitrary by an amount corresponding to $C_0/0.384$. The theoretical curve was then superimposed over the experimental data and the theoretical curve shifted along the X-axis until the best fit was obtained.

Conclusions

The theoretical behavior of the TCO_2 -AOU relationship shows that three processes are needed to describe the in situ concentration of carbon dioxide beneath the surface mixed layer. These are,

a) Air-sea exchange of CO_2 and O_2 to fix the initial TCO_2 and O_2 concentrations. Temperature is a major variable affecting this exchange.

b) Oxidation of organic matter in subsurface waters according to the stoichiometric model,

c) Variations in total alkalinity due to solution or precipitation of

carbonates.

IV. CHEMICAL AND PHYSICAL MODELS FOR THE DISTRIBUTION

OF CARBON DIOXIDE

The stoichiometric model for the distribution of TCO_2 is a chemical model which ascribes changes in TCO_2 to chemical processes--oxidation and solution of carbonates--and to variations in preformed quantities. Physical processes--mixing and advection--are not explicitly considered, although they enter the model implicitly through the distributions of temperature, salinity, oxygen, and alkalinity.

Craig (1969) proposed a physical model which describes the vertical distribution of TCO_2 in terms of vertical advection, vertical diffusion, and the concentration at the upper and lower boundaries of the model. The model includes a term for the _in situ_ production of carbon dioxide, but it does not distinguish between carbon produced by oxidation or by solution.

Craig (1969) showed that graphs of TCO_2 versus oxygen are not linear, and do not have the slope predicted by the stoichiometric model. Craig (1969) concluded,

> "It is apparent that the procedures of 'normalizing' TCO_2 to constant chlorinity and carbonate alkalinity, of defining an 'apparent oxygen utilization' (AOU) as the deviation of the O_2 concentration from saturation equilibrium, and determining the 'oxidative carbon' as 0.77 (AOU), are incorrect for a 'z-diffusion water mass' as defined by the abyssal model considered here, or for any case in which diffusive effects are important. These concepts can actually be applied only when advection completely dominates the mixing process."

Since these three procedures are basic to the stoichiometric model it is necessary to examine Craig's (1969) criticisms of this model.

Pytkowicz (1968, 1971) has shown that the stoichiometric model is applicable to 1-, 2-, and 3-dimensional systems, which include both advection and diffusion, if variations in preformed quantities are allowed for. In the following section, Pytkowicz's (1968, 1971) analysis will be applied to the specific case of Craig's (1969) model.

Craig's (1969) model assumes that horizontal advection and eddy diffusion are negligible, and that the only physical processes affecting the vertical distribution of non-conservative properties are vertical advection and vertical eddy diffusion. It is further assumed that the vertical velocity and vertical eddy diffusion coefficient are constant with depth. Craig (1969) applied this model to the distribution of TCO_2 between 1000 m and 4000 m in the Central Pacific. In Craig's (1969) model the vertical distribution of O_2 and TCO_2 are related by the equation,

$$\frac{C_z - ((1 - f(z))C_o + f(z)C_m)}{O_z - ((1 - f(z))O_o + f(z)O_m)} = -\frac{J_c}{J_o} = \text{constant} \qquad (25)$$

C_m, C_o, O_m, and O_o are the concentrations of TCO_2 and O_2 at the upper and lower boundaries. J_c and J_o are the in situ rates of carbon production and of oxygen consumption, and are assumed constant. J_c includes contributions from oxidation and from solution. The term $f(z)$ is the mixing fraction,

$$f(z) = \frac{S_z - S_o}{S_m - S_o} \qquad (26)$$

Craig's (1969) model does not predict the boundary concentrations and it will be assumed that they are,

$$O_o = O_o' - AOU_o$$

$$O_m = O_m' - AOU_m$$

(27)

and,

$$C_o = C_o' + b(AOU_o) + (SA_o - SA^*)Cl_o$$

$$C_m = C_m' + b(AOU_m) + (SA_m - SA^*)Cl_m$$

(28)

In other words it is assumed that the stoichiometric model is valid at the boundaries of Craig's (1969) model. It will be shown that with this assumption, equation (25) reduces to the form,

$$(TCO_2)_z = (TCO_2')_z + b(AOU_z) + (SA_z - SA^*)Cl_z \qquad (29)$$

which is the equation used to derive the stoichiometric model in the previous chapter.

Substituting equations (27) into the denominator of equation (25) yields,

$$O_z - ((1 - f(z))O_o + f(z)O_m) =$$

$$O_z - ((1 - f(z))O_o' + f(z)O_m') + ((1 - f(z))AOU_o + f(z)AOU_m) \quad (30)$$

The solubility of oxygen is nearly linear in temperature and salinity for small temperature and salinity changes (Redfield et al., 1963; Pytkowicz and Kester, 1966), therefore,

$$((1 - f(z))O_o' + f(z)O_m') = O_z' \qquad (31)$$

Inserting equation (31) into equation (30) yields,

$$O_z - ((1 - f(z))O_o + f(z)O_m) =$$

$$O_z - O'_z + ((1 - f(z))AOU_o + f(z)AOU_m) \qquad (32)$$

By definition,

$$O_z - O'_z = -AOU_z$$

Therefore, the denominator of equation (25) may be written,

$$O_z - ((1 - f(z))O_o + f(z)O_m) =$$

$$-AOU_z + ((1 - f(z))AOU_o + f(z)AOU_m) \qquad (33)$$

Similarly, substituting equations (28) into the numerator of equation (25) yields,

$$C_z - ((1 - f(z))C_o + f(z)C_m) = C_z - ((1 - f(z))C'_o + f(z)C'_m)$$

$$- b((1 - f(z))AOU_o + f(z)AOU_m) - ((1 - f(z))SA_oCl_o + f(z)SA_mCl_m)$$

$$+ SA^*Cl_z \qquad (34)$$

J_c, the rate of carbon production is the sum of two terms, J_{ox}, for the oxidation of organic matter, and J_{sol}, for the solution of carbonates,

$$J_c = J_{ox} + J_{sol} \qquad (35)$$

Substituting (35) into (25) yields,

$$\frac{C_z - ((1 - f(z))C_o + f(z)C_m)}{O_z - ((1 - f(z))O_o + f(z)O_m)} = -\frac{J_{ox}}{J_o} - \frac{J_{sol}}{J_o} \qquad (36)$$

Rearranging equation (36) yields,

$$C_z - ((1 - f(z))C_o + f(z)C_m) = -(J_{ox}/J_o)(O_z - ((1 - f(z))O_o + f(z)O_m))$$

$$- (J_{sol}/J_o)(O_z - ((1 - f(z))O_o + f(z)O_m)) \tag{37}$$

Substituting equations (33) and (34) into (37) and rearranging yields,

$$C_z = \underbrace{((1 - f(z))C'_o + f(z)C'_m)}_{(a)} + \underbrace{(b - (J_{ox}/J_o))((1 - f(z))AOU_o + f(z)AOU_m)}_{(b)}$$

$$+ \underbrace{(J_{ox}/J_o)AOU_z}_{(c)} + \underbrace{(((1 - f(z))SA_oCl_o + f(z)SA_mCl_m)}_{(d)}$$

$$\underbrace{- (J_{sol}/J_o)(O_z - ((1 - f(z))O_o + f(z)O_m)))}_{(e)} \underbrace{- SA^*Cl_z}_{(f)} \tag{38}$$

Term (a) in equation (38) is equivalent to the preformed TCO_2 at depth z,

$$C'_z = ((1 - f(z))C'_o + f(z)C'_m) \tag{39}$$

Term (d) is the alkalinity that would exist at depth z if alkalinity were conservative.

$$(TA_z)_{conservative} = ((1 - f(z))SA_oCl_o + f(z)SA_mCl_m) \tag{40}$$

Term (e) is the increase in alkalinity at z due to solution of carbonates,

$$\Delta TA_z = - (J_{sol}/J_o)(O_z - ((1 - f(z))O_o + f(z)O_m)) \tag{41}$$

The sum of (40) and (41) is the measured alkalinity at depth z.

$$(\text{Terms (d) + (e))} = TA_z = SA_z Cl_z \tag{42}$$

Substituting (39) and (42) into (38) yields,

$$C_z = C'_z + (b - (J_{ox}/J_o))((1 - f(z))AOU_o + f(z)AOU_m)$$
$$+ (J_{ox}/J_o)AOU_z + (SA_z - SA^*)Cl_z \tag{43}$$

If the value of the oxidative ratio outside the region of Craig's (1969) model, b, equals the value of the oxidative ratio in the region of Craig's model, (J_{ox}/J_o), then $(b - (J_{ox}/J_o)) = 0$, and equation (43) becomes,

$$C_z = C_z' + (J_{ox}/J_o)AOU_z + (SA_z - SA^*)Cl_z \qquad (44)$$

Equation (44) is identical with equation (29) which was used to derive the stoichiometric model. Therefore, the stoichiometric and physical models are consistent with each other.

V. AN AOU MODEL FOR THE VERTICAL DISTRIBUTION

OF CARBON-13

The variation of oceanic carbon-13/carbon-12 ratios has been studied by Deuser and Hunt (1969), Craig (1970), Kroopnick, Deuser, and Craig (1970), and Kroopnick (1971). Deuser and Hunt reported six vertical profiles from the North and South Atlantic. They found a significant correlation between the vertical distributions of oxygen and C^{13}/C^{12}, which they attributed to the oxidation of organic matter low in carbon-13. Craig (1970) gave one composite C^{13}/C^{12} profile for the South Pacific between 6°S and 64°S, and Kroopnick et al. (1970) reported one vertical profile at the GEOSECS intercalibration station in the Northeast Pacific. Kroopnick (1971) measured several vertical profiles in the Atlantic and Pacific Oceans. Craig (1970), Kroopnick et al. (1970), and Kroopnick (1971) treated their profiles using the vertical advection-diffusion model developed by Wyrtki (1962), Munk (1966) and Craig (1969).

In this chapter the model of organic decomposition developed in Chapter III is used to evaluate the processes responsible for the vertical distribution of carbon-13 at the GEOSECS intercalibration station.

Carbon-13/carbon-12 ratios are reported in parts per mil relative to the Chicago PDB standard,

$$\delta C^{13} = 1000 \left[\frac{(\text{carbon-13/carbon-12})_{\text{unknown}}}{(\text{carbon-13/carbon-12})_{\text{standard}}} - 1 \right] \qquad (45)$$

The carbon-13/carbon-12 ratio in the PDB standard is 0.0112372 (Craig, 1957).

Processes Affecting Oceanic Carbon-13/Carbon-12 Ratios

Vertical variations in oceanic C^{13}/C^{12} ratios are due to isotope fractionation in the physical, inorganic, and biochemical processes which affect the concentration of inorganic carbon in seawater. These processes include photosynthesis and respiration, carbonate precipitation and solution, air-sea exchange, and river runoff. δC^{13} values for various carbon reservoirs are listed in Table 8.

Sackett et al. (1965) and Degens et al. (1968a, b) found no significant differences between C^{13}/C^{12} ratios in phytoplankton and zooplankton. They found however, that the measured ratios were dependent on the temperature at which the plankton grew (Figure 13). The least squares line through the combined data of Sackett et al. (1965) and Degens et al. (1968b) is,

$$(\delta C^{13})_{plankton} = -27.3\text{‰} + 0.30(T°C).$$

Williams and Gordon (1970) determined C^{13}/C^{12} ratios in dissolved and particulate organic matter from the Northeast Pacific. They were unable to find significant variation in the C^{13}/C^{12} ratios with depth or position. They attributed this uniformity to the refractory nature of dissolved and particulate organic matter.

Table 8. δC^{13} values for various carbon reservoirs.

Surface seawater: Pacific, Atlantic, Southern Ocean	+1.92‰ (average) +1.39 to +2.50‰ (range)	Craig (1970) Kroopnick et al. (1970) Kroopnick (1971)
Phyto- and zooplankton: Pacific, Atlantic, Southern Ocean	-30.6 to -16.5‰	Sackett et al. (1965) Degens et al. (1968b)
Organic matter (NE Pacific): Dissolved Particulate	-21.2 to -24.4‰ -22.0 to -24.3	Williams & Gordon (1970)
Calcium carbonate: Forams (Eq. Atlantic) Marine limestones	+1.2, +1.9‰ -3.3 to +2.4‰ (avg. -0.2)	Craig (1954) Craig (1953)
Fresh waters: Potomac River Hudson River	-8.8 to -10.6‰ -9.0	Sackett & Moore (1966)
Atmosphere:	-6.7 ± 0.2‰	Bottinga & Craig (1969)
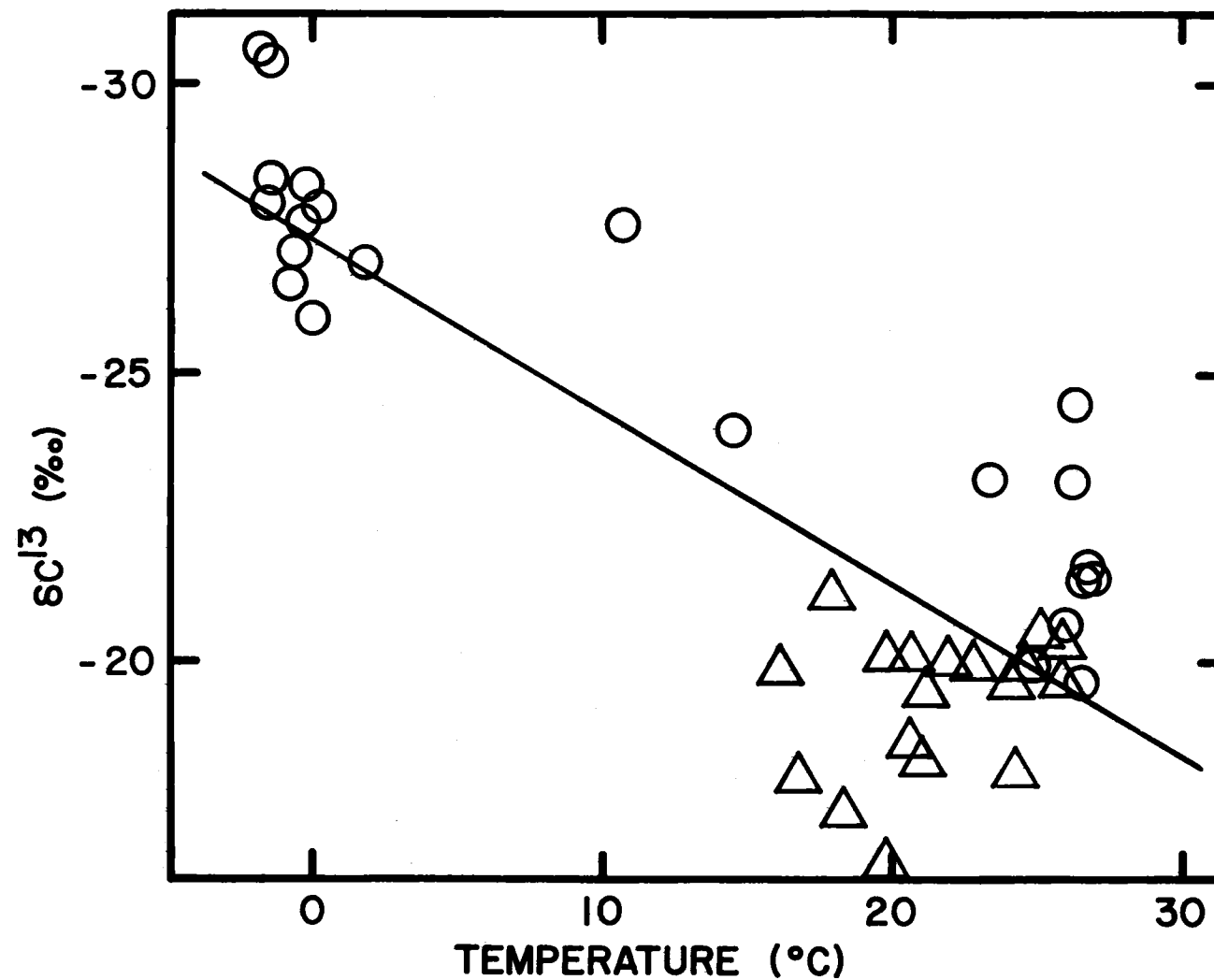
Figure 13. Temperature dependence of carbon-13/carbon-12 ratios in plankton. Circles, Sackett et al. (1965); triangles, Degens et al. (1968b). The line is the least squares line through the combined data.

Only a few analyses of C^{13}/C^{12} ratios in oceanic foraminifera appear to exist. Landergren (1954) analyzed a core from the Romanche Trench and found δC^{13} values from +3.6‰ to +2.1‰ (average +2.8‰). Foraminifera from the tops of two Equatorial Atlantic cores had values of +1.2 and +1.9‰ (Craig, 1954). Craig (1970) and Kroopnick et al. (1970) used the value +2.0‰ based on Craig (1954) and on unpublished work. Marine limestones range from -3.3 to +2.4‰, with an average -0.2‰ (Craig, 1953).

Marine atmospheric carbon dioxide has a δC^{13} value of -6.7 ± 0.2‰ (Bottinga and Craig, 1969). The fractionation between oceanic bicarbonate and atmospheric carbon dioxide is temperature dependent, and it decreases from +9.2‰ at 0° C to +6.8‰ at 30° C (Deuser and Degens, 1967), bicarbonate being enriched in carbon-13 relative to atmospheric carbon dioxide.

The AOU Model for Carbon-13/Carbon-12 Ratios

An AOU model for the distribution of total inorganic carbon was developed in Chapter III. The model assumes that the total inorganic carbon, TCO_2, is given by,

$$TCO_2 = C_o + \Delta C_b + \Delta C_a \qquad (46)$$

C_o is the initial concentration of inorganic carbon at the surface source of the water sample, ΔC_b is the increase in inorganic carbon due to oxidation of organic matter, and ΔC_a is the change of inorganic carbon

due to carbonate solution or precipitation.

In the following calculations it is assumed that $\Delta C_b = (106/276)$ · (AOU), and that $\Delta C_a = 0.5(SA - 0.121)(Cl)$, where SA and Cl are the measured specific alkalinity and chlorinity, and 0.121 is an assumed initial specific alkalinity. The validity of these assumptions was discussed in Chapter III.

Calculation of δC^{13} from the AOU Model

$$\delta C^{13} = 1000 \left[\frac{(C^{13}/C^{12})_{seawater}}{(C^{13}/C^{12})_{standard}} - 1 \right] \qquad (45)$$

$$\delta C^{13} = 1000 \left[\frac{R_{sw}}{R_{std}} - 1 \right] \qquad (47)$$

Rearranging (47) yields,

$$(1 + 10^{-3} \cdot \delta C^{13})R_{std} = R_{sw} \qquad (48)$$

By definition,

$$TCO_2 = C_T^{12} + C_T^{13} \qquad (49)$$

and,

$$R_{sw} = (C_T^{13}/C_T^{12}) = ((TCO_2/C_T^{12}) - 1) \qquad (50)$$

Adding equations (48) and (50) yields,

$$((1 + 10^{-3} \cdot \delta C^{13})R_{std} + 1) = (TCO_2/C_T^{12}) \qquad (51)$$

However,

$$TCO_2 = C_o + \Delta C_b + \Delta C_a \qquad (46)$$

Furthermore,

$$TCO_2 = (C_o^{12} + C_o^{13}) + (\Delta C_b^{12} + \Delta C_b^{13}) + (\Delta C_a^{12} + \Delta C_a^{13}) \qquad (52)$$

and,

$$R_o = (C_o^{13}/C_o^{12}) \quad R_b = (\Delta C_b^{13}/\Delta C_b^{12}) \quad R_a = (\Delta C_a^{13}/\Delta C_a^{12}) \qquad (53)$$

Introducing equations (53) into (52) and rearranging yields,

$$TCO_2 = C_o^{12}(1 + R_o) + \Delta C_b^{12}(1 + R_b) + \Delta C_a^{12}(1 + R_a) \qquad (54)$$

However,

$$C_T^{12} = C_o^{12} + \Delta C_b^{12} + \Delta C_a^{12} \qquad (55)$$

Substituting (55) into (54) yields,

$$TCO_2 = C_T^{12}(1 + R_o) + \Delta C_b^{12}(R_b - R_o) + \Delta C_a^{12}(R_a - R_o) \qquad (56)$$

The above substitution eliminates C_o, the initial concentration of TCO_2,

from equation (56). By definition,

$$\Delta C_b = \Delta C_b^{12} + \Delta C_b^{13} = \Delta C_b^{12}(1 + R_b) = 0.384(AOU) \qquad (57)$$

$$\Delta C_a = \Delta C_a^{12} + \Delta C_a^{13} = \Delta C_a^{12}(1 + R_a) = 0.5(SA = 0.121)Cl \qquad (58)$$

Introducing equations (57) and (58) into (56) yields,

$$TCO_2 = C_T^{12}(1 + R_o) + 0.384(AOU)\left[\frac{R_b - R_o}{1 + R_b}\right]$$
$$+ 0.5(SA - 0.121)(Cl)\left[\frac{R_a - R_o}{1 + R_a}\right] \qquad (59)$$

From equation (51),

$$C_T^{12} = (TCO_2)/((1 + 10^{-3} \cdot \delta C^{13})R_{std} + 1) \qquad (60)$$

Substituting (60) into (59) and rearranging yields,

$$TCO_2 \left[1 - \frac{1 + R_o}{((1 + 10^{-3} \cdot \delta C^{13})R_{std} + 1)} \right] =$$

$$0.384(AOU)\left[\frac{R_b - R_o}{1 + R_b}\right] + 0.5(SA - 0.121)(Cl)\left[\frac{R_a - R_o}{1 + R_a}\right] \quad (61)$$

Or,

$$\frac{((1 + 10^{-3} \cdot \delta C^{13})R_{std} - R_o)}{((1 + 10^{-3} \cdot \delta C^{13})R_{std} - 1)} = \frac{0.384(AOU)}{TCO_2}\left[\frac{R_b - R_o}{1 + R_b}\right]$$

$$+ \frac{0.5(SA - 0.121)(Cl)}{TCO_2}\left[\frac{R_a - R_o}{1 + R_a}\right] = Y \quad (62)$$

Finally,

$$(\delta C^{13})_{calculated} = 1000\left[\frac{R_o + Y}{R_{std}(1 - Y)} - 1\right] \quad (63)$$

It should be noted that C_o, the initial concentration of TCO_2, does

not appear in equation (63).

Results of Calculation

Vertical profiles of δC^{13} at the GEOSECS intercalibration

station were calculated from equation (63), and from the measured

temperature, salinity, oxygen, pH, and alkalinity. The calculation of

TCO_2 from pH and alkalinity measurements, and of AOU from the

measured oxygen, temperature, and salinity is outlined in Chapter II.

The assumed values of R_o, R_a, and R_b that were used in the

calculations are given in the following paragraphs. Hydrographic data

at the GEOSECS station is listed in Table 9, and the calculated results

are listed in Table 10.

In their calculations based on the vertical advection-diffusion

model, Kroopnick et al. (1970) used the values δC_b^{13} = -23‰ (from

Williams and Gordon, 1970) and δC_a^{13} = +2.0‰ (from Craig (1954)

and unpublished data). The first calculation based on the AOU model

used these values,

$$\delta C_b^{13} = -23‰$$

$$\delta C_a^{13} = +2.0‰$$

plus the value $\quad\quad\quad \delta C_o^{13} = +2.2‰$

which is the mean value for Pacific surface waters (Kroopnick et al.,

1970). The result is shown in Figure 14. Agreement between the

measured and calculated profiles was only qualitative. However, the

AOU model did reproduce the general shape of the profile.

The lack of precise agreement in the first calculation is partly

due to the fact that a constant value δC_b^{13} = -23‰ was used in the calcu-

lations. Sackett et al. (1965) and Degens et al. (1968a) have shown

that δC^{13} values for plankton are dependent upon the temperature at

which the plankton grew. The value δC_b^{13} = -23‰ used by Kroopnick

et al. (1970) represents the refractory part of dissolved and particu-

late organic matter after the more liable components have been

oxidized (Williams and Gordon, 1970).

Table 9. Hydrographic and chemical data at the GEOSECS station.

Depth (m)	T(°C)	S(‰)	Sigma-t	Oxygen (μg-at/kg)	AOU	Percent O$_2$ saturation	TCO$_2$ (mmole/kg)	Alkalinity (meq/kg)	Specific alkalinity
0002	19.47	33.700	23.93	470	-11	102	1.99	2.27	0.1217
0101	15.30	33.830	25.04	495	2	100	2.01	2.27	0.1212
0202	9.87	33.790	26.07	350	209	63	2.14	2.28	0.1219
0303	8.36	34.110	26.57	218	358	38	2.19	2.30	0.1218
0403	6.99	34.200	26.84	107	487	18	2.24	2.31	0.1220
0504	6.16	34.260	26.99	48	558	8	2.29	2.32	0.1223
0605	5.71	34.330	27.11	27	585	4	2.34	2.34	0.1231
0656	5.44	34.360	27.16	22	594	4	2.34	2.34	0.1230
0706	5.23	34.380	27.20	21	598	3	2.35	2.35	0.1235
0806	4.74	34.430	27.30	26	600	4	2.36	2.36	0.1238
0906	4.39	34.477	27.38	37	595	6	2.37	2.37	0.1242
1006	4.01	34.490	27.43	48	590	8	2.38	2.38	0.1247
1178	3.53	34.520	27.50	65	580	10	2.38	2.39	0.1251
1430	3.00	34.560	27.58	95	559	15	2.39	2.41	0.1260
1704	2.51	34.590	27.65	129	533	20	2.38	2.42	0.1264
1954	2.16	34.620	27.70	161	508	24	2.38	2.42	0.1263
2205	1.96	34.640	27.73	189	483	28	2.38	2.43	0.1267
2457	1.80	34.650	27.75	210	465	31	2.38	2.44	0.1272
2733	1.69	34.660	27.77	230	448	34	2.37	2.44	0.1272
2985	1.62	34.652	27.77	242	437	36	2.37	2.44	0.1272
3236	1.60	34.670	27.79	253	426	37	2.37	2.44	0.1271
3478	1.56	34.680	27.80	262	419	38	2.37	2.44	0.1271
3745	1.54	34.680	27.80	271	411	40	2.36	2.44	0.1271
3994	1.54	34.680	27.81	276	406	40	2.36	2.44	0.1271

Table 10. Comparison of measured and calculated δC^{13} values at the GEOSECS station. The calculated values were calculated assuming that carbon produced by the oxidation of organic matter is given by 0.384(AOU), and that carbon produced from the solution of calcium carbonate is given by 0.5(specific alkalinity - 0.121)Cl‰. The term 0.384 is Redfield's ratio (106/276), and the term 0.121 is the assumed initial specific alkalinity.

Columns 3 through 6 were calculated assuming different δC^{13} values for the initial, oxidative, and carbonate fractions of the total inorganic carbon.

δC^{13}(initial) =	+2.2‰	+2.2	+2.2	0.0
δC^{13}(carbonate) =	+2.0	+2.0	0.0	+2.0
δC^{13}(biological) =	-23.0	-27.3‰ + 0.30(T°C)		

Depth (m)	Measured δC^{13} (‰)	Calculated values of δC^{13} (‰)			
2	2.26	2.25	2.25	2.24	0.05
101	2.06	2.19	2.19	2.19	-0.01
202	0.59	1.25	1.20	1.19	-0.91
303	0.12	0.61	0.50	0.49	-1.55
403	-0.20	0.09	-0.09	-0.10	-2.10
504	-0.27	-0.16	-0.39	-0.40	-2.37
605	-0.32	-0.22	-0.47	-0.49	-2.44
656	-0.37	-0.26	-0.52	-0.54	-2.49
706	-0.34	-0.27	-0.54	-0.56	-2.50
806	-0.36	-0.27	-0.55	-0.57	-2.51
906	-0.44	-0.23	-0.52	-0.55	-2.48
1006	-0.40	-0.20	-0.50	-0.53	-2.46
1178	-0.40	-0.16	-0.47	-0.50	-2.43
1430	-0.35	-0.07	-0.38	-0.42	-2.34
1704	-0.32	0.03	-0.28	-0.33	-2.24
1954	-0.21	0.13	-0.18	-0.22	-2.15
2205	-0.25	0.23	-0.06	-0.11	-2.04
2457	-0.12	0.30	0.02	-0.03	-1.96
2733	-0.10	0.36	0.08	0.03	-1.90
2985	-0.09	0.41	0.13	0.08	-1.85
3236	-0.09	0.45	0.18	0.13	-1.81
3478	-0.06	0.48	0.22	0.17	-1.78
3745	0.04	0.51	0.24	0.19	-1.75
3994	0.02	0.53	0.27	0.22	-1.73
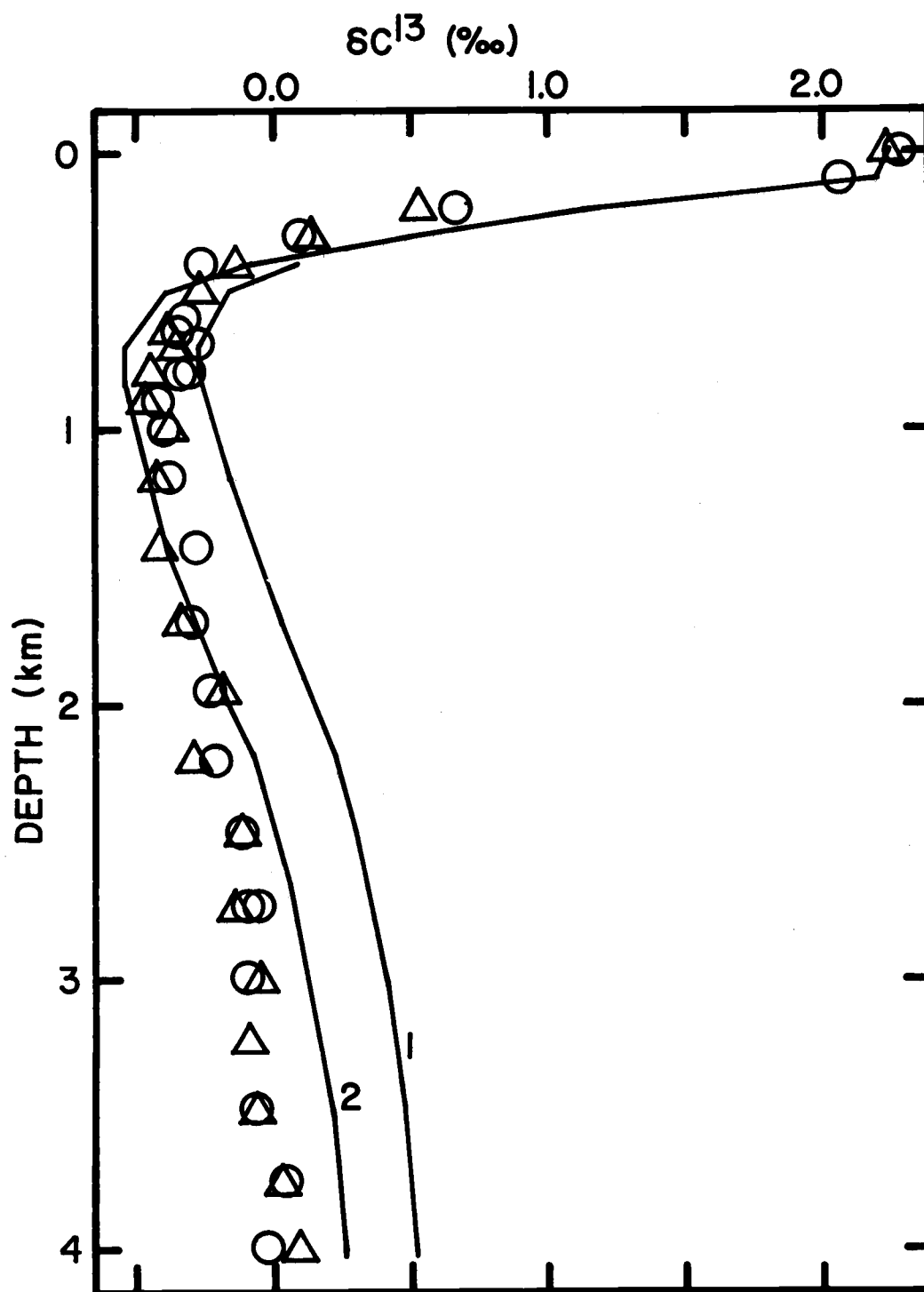
Figure 14. Measured and calculated values of δC^{13} at the GEOSECS intercalibration station. The circles (Scripps) and triangles (Woods Hole) are the measured values. Profile 1 is the result of the first calculation, profile 2 is the result of the second calculation (see text for the values of R_o, R_b, and R_a used in each calculation).

The second AOU calculation used the values,

$$\delta C_o^{13} = + 2.2\text{‰}$$

$$\delta C_a^{13} = + 2.0\text{‰}$$

and the equation $\quad \delta C_b^{13} = - 27.3\text{‰} + 0.30(T°C)$

which was derived from the combined data of Sackett et al. (1965) and

Degens et al. (1968b). The agreement between the measured and cal-

culated profiles (Figure 14) was better in this case. The differences

between the calculated and measured values were - 0.2‰ in the oxygen

minimum (700-800 m) and + 0.2‰ in the deep water.

The third AOU calculation used the values

$$\delta C_o^{13} = + 2.2\text{‰}$$

$$\delta C_b^{13} = - 27.3\text{‰} + 0.30(T° C)$$

$$\delta C_a^{13} = 0.0\text{‰}$$

This calculation determined the sensitivity of the AOU model to

changes in δC_a^{13}. Changing δC_a^{13} had little effect on the calculated

values of δC^{13} (Table 10). The reason for this is that the amount of

carbon produced by carbonate solution is only 1/3 that produced by the

oxidation of organic matter, and that the carbon input from solution

has roughly the same isotopic composition as seawater, whereas the

carbon produced by oxidation is very poor in carbon-13.

The fourth calculation checked the effect of changes in δC_o^{13} on

the calculated profile. The values used in the calculation were,

$$\delta C_o^{13} = 0.0\text{‰}$$

$$\delta C_b^{13} = -27.3\text{‰} + 0.30(T°C)$$

$$\delta C_a^{13} = +2.0\text{‰}$$

The agreement between the measured and calculated profiles was very bad in this case, which was expected since oxidation and solution add small amounts of carbon (less than 15%) relative to the initial concentration of inorganic carbon.

The second AOU calculation (Figure 14) gave the best fit to the measured data. The differences which remain are probably due to errors in the assumed values of δC_o^{13} and δC_b^{13}, and to errors in the AOU model. The measured values of δC_o^{13} in the Pacific range from +1.39 to +2.50‰. Only 20 values have been reported (Kroopnick, 1971). Small variations of δC_o^{13} with depth could easily produce the observed differences between the measured and calculated profiles. Temperature is only one of the variables affecting δC^{13} values in plankton (Degens et al., 1968a), and the equation used to represent the temperature dependence of the measured values is at best a first approximation (Figure 13). One assumption which is implicit in the second calculation is that the organic matter which has been oxidized was originally synthesized at the in situ temperature. This implies that all the organic matter which has been oxidized was entrained in

the water sample when it left its surface source. This assumption is

obviously only partially correct.

VI. APPLICATION OF THE VERTICAL ADVECTION-DIFFUSION MODEL TO A STATION IN THE NORTHEAST PACIFIC

Barkley (1961), Wyrtki (1962), Munk (1966), Craig (1969), Craig and Weiss (1968, 1970), and Kroopnick (1971) showed that the distributions of conservative and non-conservative properties in the deep Pacific are consistent with a simple model involving only vertical advection, vertical eddy diffusion, and in situ production or consumption of non-conservative parameters. The vertical advection/diffusion model assumes that the boundary conditions are kept constant by external processes, and that vertical advection and vertical eddy diffusion are the only physical processes active in the intermediate region. The vertical velocity, v_z, and eddy diffusion coefficient, K_z, are assumed constant. Horizontal processes are neglected.

In this chapter, vertical profiles of temperature, salinity, oxygen, total carbon dioxide, and alkalinity in the Northeast Pacific are fit with the vertical model. Redfield et al. (1963) predicted that the rate of carbon production by oxidation is directly proportional to the rate of oxygen consumption, or,

$$(R_{CO_2})_{oxidation}/R_{O_2} = -0.384.$$

The following calculations are an attempt to evaluate the oxidative ratio from production and consumption rates calculated by the vertical advection/diffusion model.

Equations for the Vertical Distribution of Conservative and Non-conservative Properties

The steady state distribution of a conservative parameter C (concentration per unit mass) is (Sverdrup et al., 1942),

$$\left[\frac{\partial C}{\partial t}\right] = \frac{\partial}{\partial x}\left[K_x\left[\frac{\partial C}{\partial x}\right]\right] + \ldots \ldots - \left[\frac{\partial (v_x \cdot C)}{\partial x} + \ldots \ldots\right] \quad (64)$$

Neglecting horizontal motion, and taking (K_z/v_z) constant yields,

$$\left[\frac{\partial^2 C}{\partial z^2}\right] = (v_z/K_z)\left[\frac{\partial C}{\partial z}\right] \quad (65)$$

Integrating (65) yields (Craig, 1969),

$$C = C_o + (C_m - C_o) \cdot f(z) \quad (66)$$

where,

$$f(z) = \left[\frac{e^{(z/(K_z/v_z))} - 1}{e^{(z_m/(K_z/v_z))} - 1}\right] \quad (67)$$

C_m and C_o are the concentrations of C at the upper and lower boundaries. Equation (66) is derived with z positive upwards, and with z = 0 at the lower boundary. If the vertical model is valid, the potential temperature/salinity diagram between the upper and lower boundaries must be linear. In general, the depths between which the model is applied are determined from the linear portion of the θ/S diagram.

For non-conservative properties, equation (65) must be generalized by introducing a term, R, for _in situ_ production or consumption.

$$\left[\frac{\partial^2 C}{\partial z^2}\right] = (v_z/K_z)\left[\frac{\partial C}{\partial z}\right] - R \tag{68}$$

For a constant production rate, R, equation (68) integrates to (Craig, 1969),

$$C = C_o + (C_m - C_o) \cdot f(z) + \left[\frac{R}{v_z}\right](z - z_m \cdot f(z)) \tag{69}$$

For a rate which is linear with depth,

$$R = R_o + S \cdot z \tag{70}$$

equation (68) integrates to,

$$C = C_o + (C_m - C_o) \cdot f(z) + \left[\frac{S + R_o(K_z/v_z)}{v_z}\right](z - z_m \cdot f(z))$$

$$+ \left[\frac{R_o}{2v_z}\right](z^2 - z_m^2 \cdot f(z)) \tag{71}$$

For a rate which is exponential with depth,

$$R = R_o e^{+(\alpha \cdot z)} \tag{72}$$

equation (68) integrates to (Craig and Weiss, 1970),

$$C = C_o + (C_m - C_o) \cdot f(z) + \left[\frac{(R_o/v_z)}{\alpha(1 + \alpha(K_z/v_z))}\right]((1 - e^{+(\alpha \cdot z)})$$

$$- (1 - e^{+(\alpha \cdot z_m)}) \cdot f(z)) \tag{73}$$

The vertical model is applied to field data in two steps. First, the value of (K_z/v_z) is calculated. The only unknown in equation (66) is the ratio (K_z/v_z). Once the upper and lower boundaries have been chosen, the value of (K_z/v_z) is evaluated by fitting the measured potential temperature or salinity data to equation (66). Second, this value of (K_z/v_z) and the measured vertical profile of some non-conservative parameter are used with equations (69), (71), or (73) to calculate (R/v_z), (R_o/v_z) and (S/v_z), or (R_o/v_z) and α. A non-linear least squares procedure is used in both steps to calculate the "best" values of (K_z/v_z), (R/v_z), (R_o/v_z), (S/v_z), and α.

Vertical Distribution of Properties at Station 127

Figure 15 shows the vertical distribution of potential temperature and salinity at station 127 (see Figure 4, Chapter III for station position). The θ/S diagram (Figure 16) is essentially linear below 797 m, and the potential temperature and salinity profiles were fit to equation (66) by a non-linear least squares procedure, using (K_z/v_z) as an adjustable parameter. The best fit (Figure 15) was obtained with the following values of (K_z/v_z),

Parameter	Calculated value of (K_z/v_z)	Standard deviation of fit
θ	920 meters	$\pm 0.04°$ C
S	900 meters	$\pm 0.005‰$

In the following calculations, the average value,
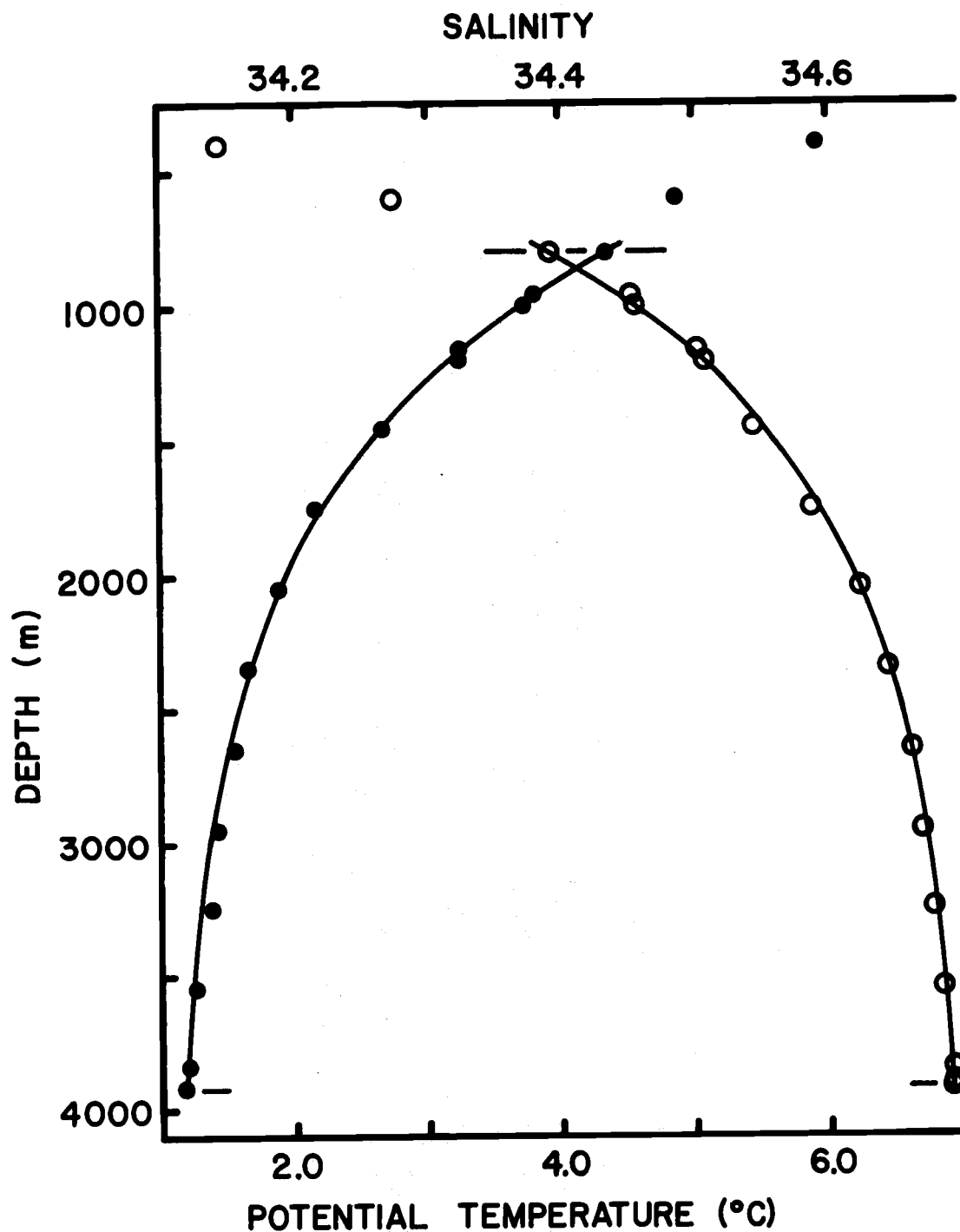
Figure 15. Potential temperature (solid circles) and salinity (open circles) profiles at station 127. The curves were calculated from equation (66), using the value $(K_z/v_z) = 910$ meters.
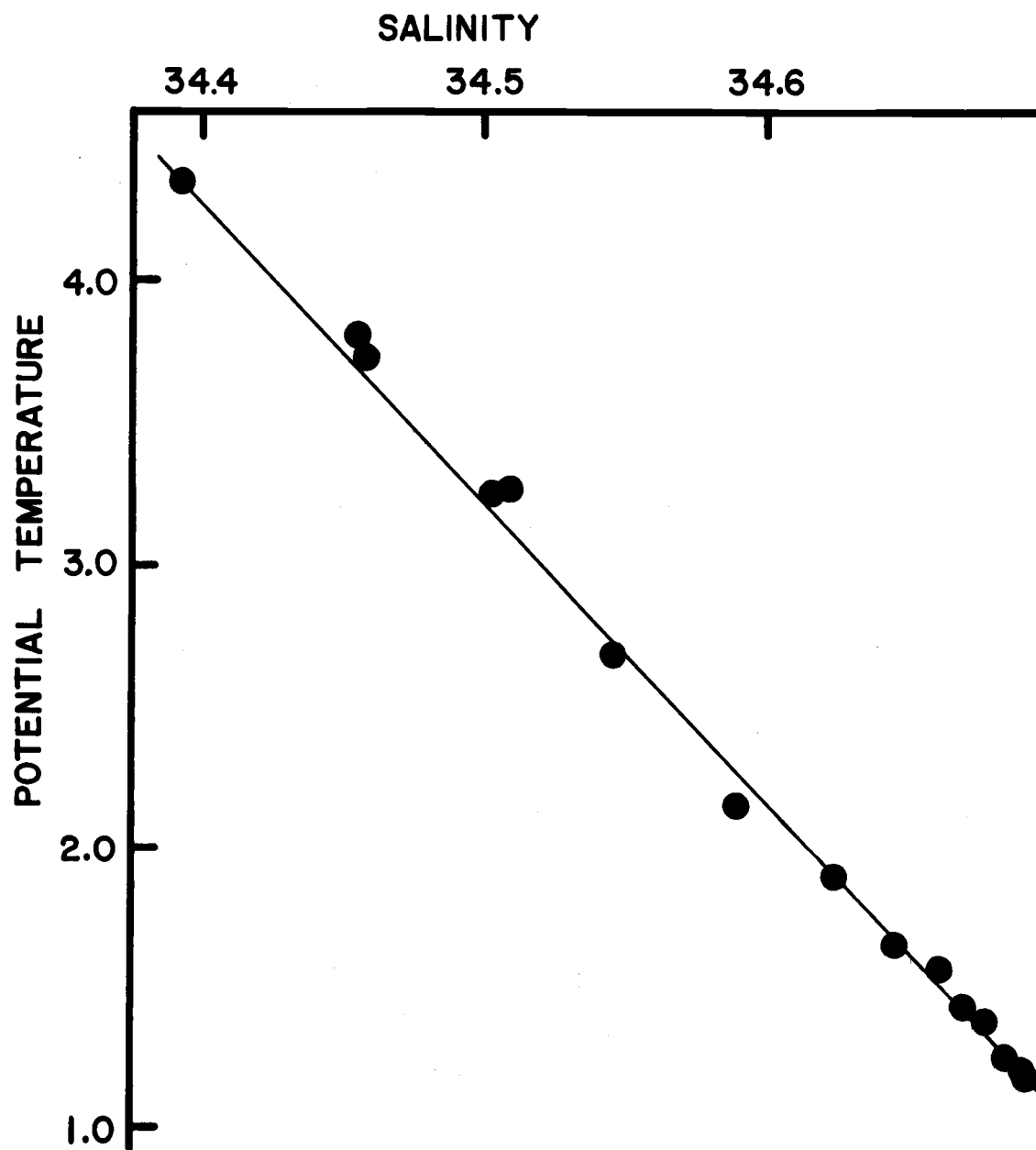
Figure 16. Temperature/salinity diagram between 797 m and 3928 m
            at station 127.

$$(K_z/v_z) = 910 \text{ meters}$$

will be used.

The vertical distributions of oxygen, total carbon dioxide, and alkalinity at station 127 are shown in Figures 17 and 18. θ/O_2, θ/TCO_2, and θ/alkalinity diagrams at station 127 are shown in Figures 19 through 21. The oxygen and TCO_2 diagrams are non-linear, indicating oxygen consumption and carbon production. The θ/alkalinity diagram is slightly non-linear suggesting solution of carbonates at depth.

In the following sections, the vertical profiles of oxygen, TCO_2, and alkalinity will be fit to equations (69), (71), and (73), and the rate laws evaluated from the least squares fit will be used to calculate the oxidative ratio R_{CO_2}/R_{O_2}.

Case 1: Constant Rates

The vertical profiles of oxygen, TCO_2, and alkalinity were fit to equation (69) by a linear least squares procedure using the value $(K_z/v_z) = 910$ meters which was calculated from the temperature and salinity profiles. The calculated values of (R/v_z) are given in Table 11, and a comparison of the calculated and measured vertical profiles is shown in Figures 17 and 18. The calculated value of the oxidative ratio is,
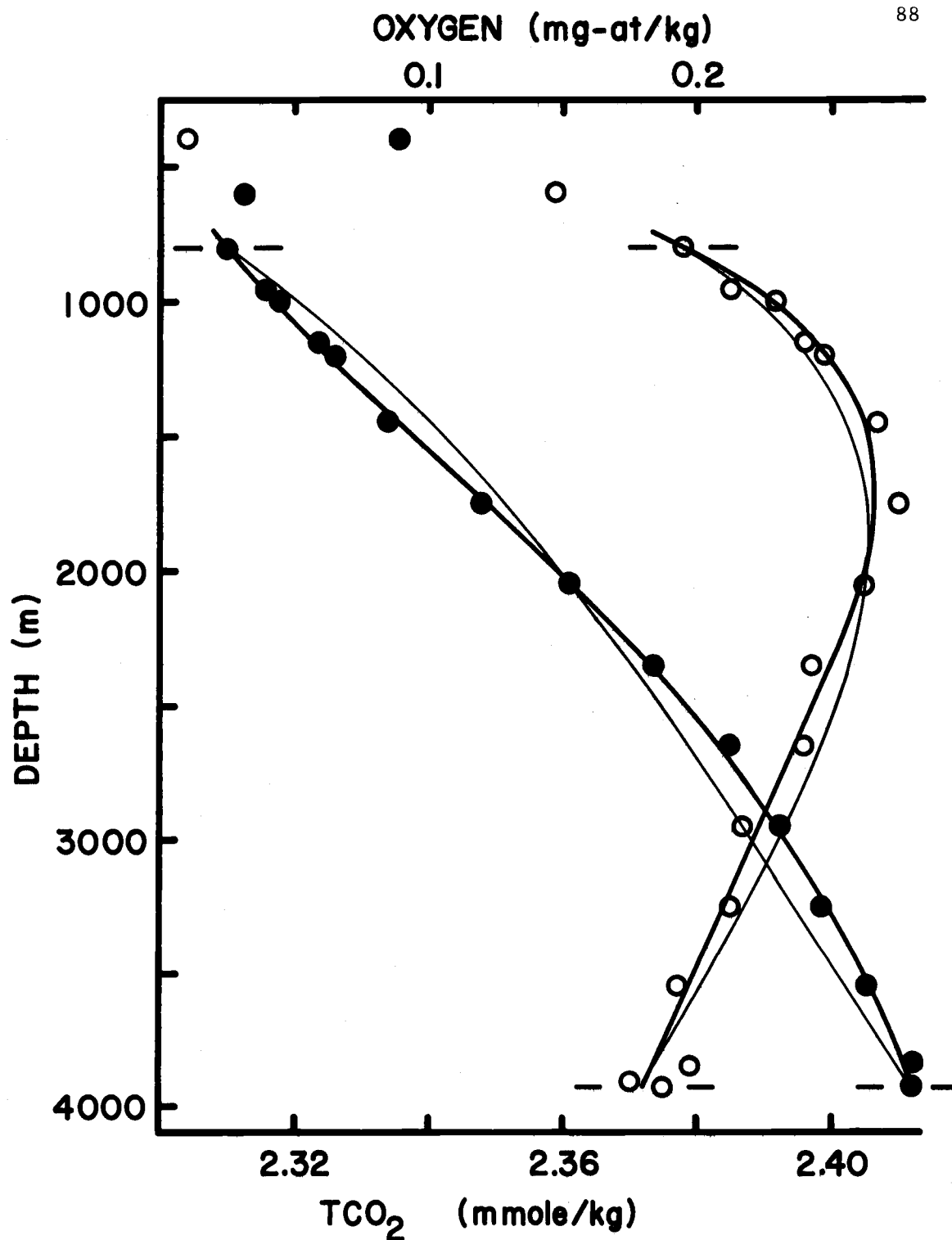
Figure 17. Oxygen (solid circles) and TCO_2 (open circles) profiles at station 127. The heavy curves are the profiles calculated for an exponential production rate (equation (73)), the light curves are calculated for a constant production rate (equation (69)).
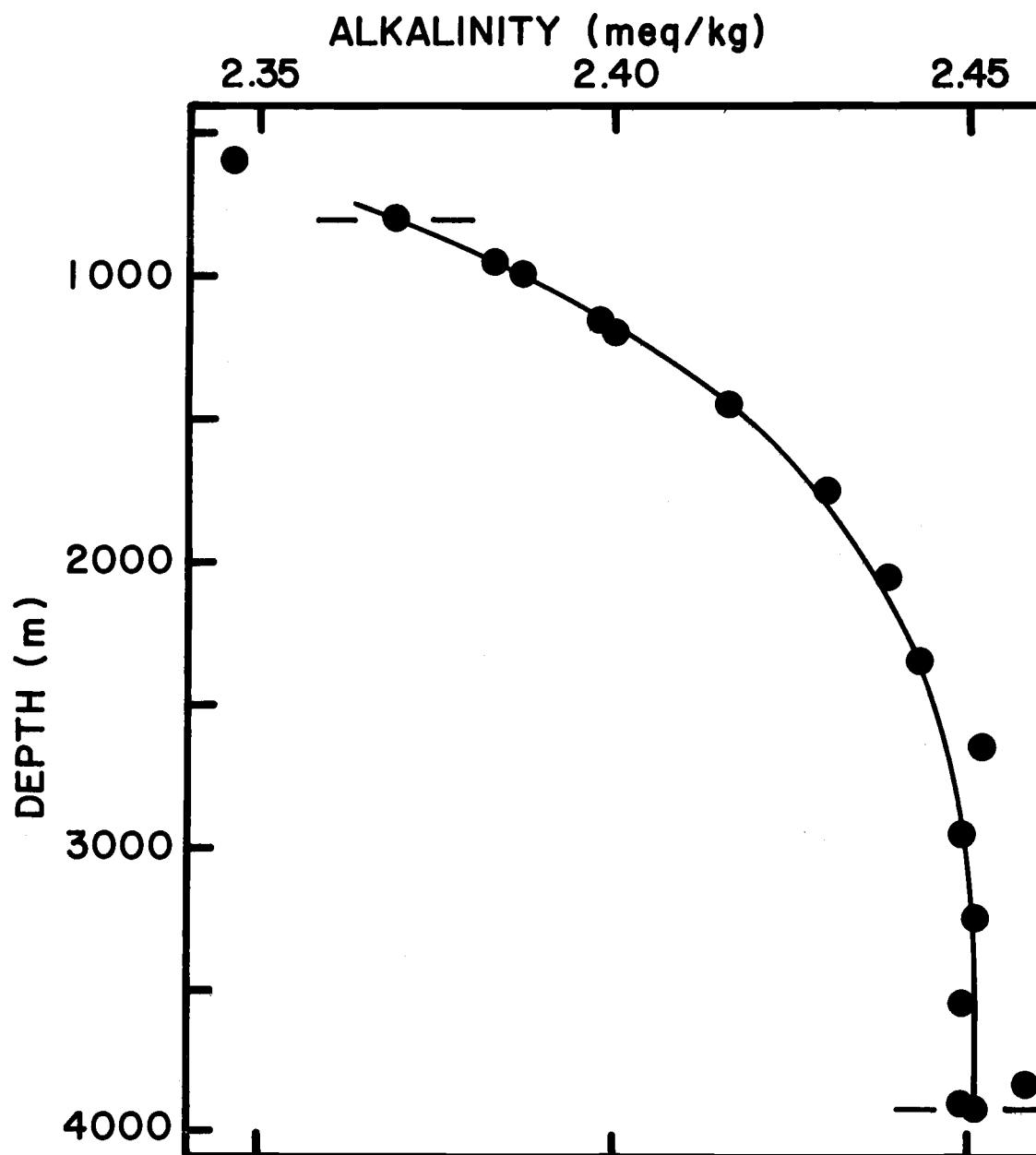
Figure 18. Alkalinity profile at station 127. The heavy curve is the profile calculated for an exponential production rate (equation (73)).
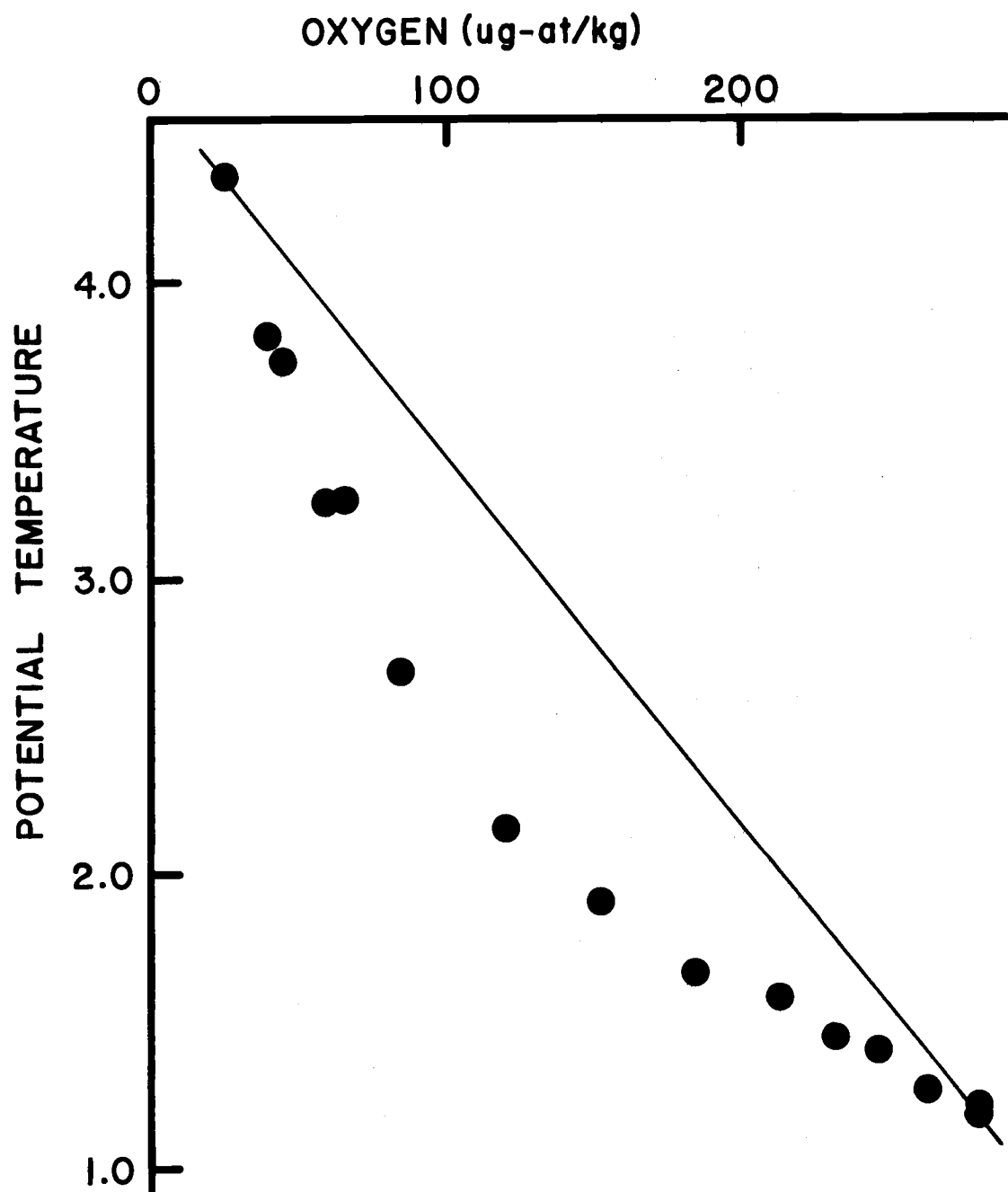
Figure 19. Temperature/oxygen diagram between 797 m and 3928 m at station 127.
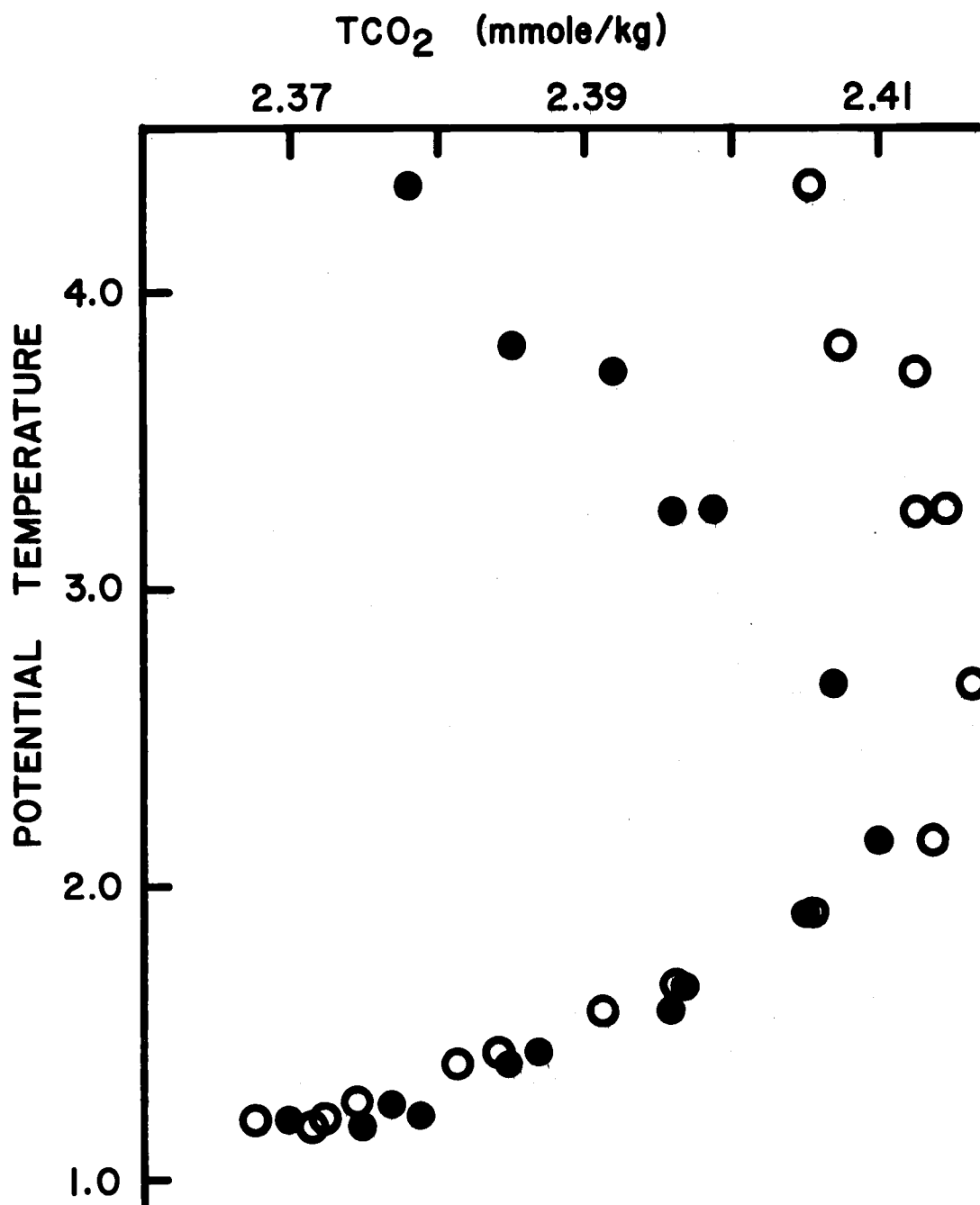
Figure 20. Temperature/TCO_2 diagram between 797 m and 3928 m at station 127. The solid circles are the measured values of TCO_2, the open circles are the values of TCO_2 corrected for variations in specific alkalinity by equation (75).
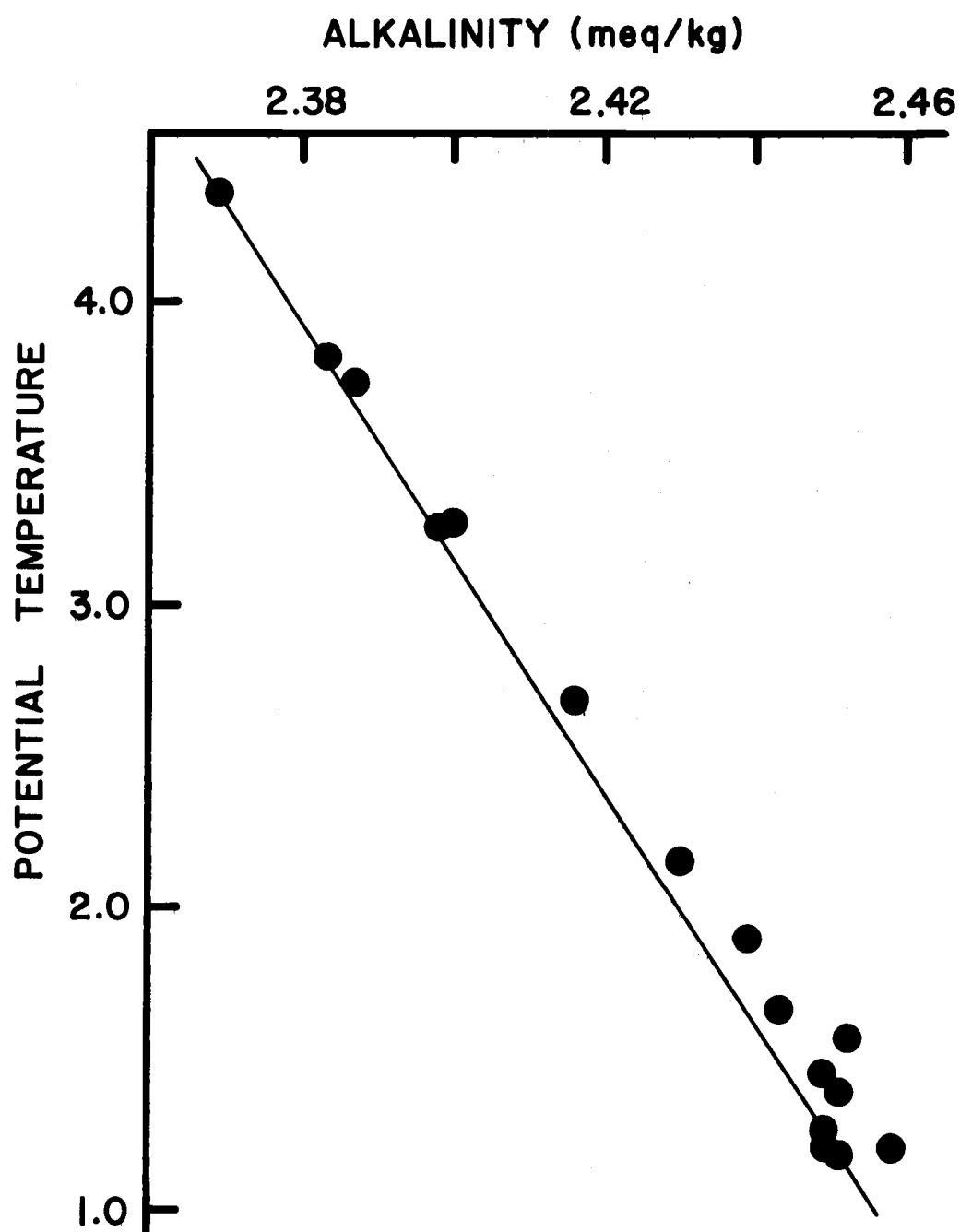
Figure 21. Temperature/alkalinity diagram between 797 m and 3928 m at station 127.

Table 11. Oxygen, total carbon, and alkalinity production rates calculated from the vertical advection-diffusion model at station 127.

Case	Calculated Rate (± 1 standard error)	Standard Deviation	Oxidative Ratio
1) Constant rate	$R_{O_2}/v_z = -(6.00\pm0.32)10^{-5}$	0.0092 mg-at/kg	
	$R_{TCO_2}/v_z = (2.69\pm0.13)10^{-5}$	0.0039 mmole/kg	
	$R_{TALK}/v_z = (0.41\pm0.05)10^{-5}$	0.0013 meq/kg	-0.415
2) Linear rate	$R_{O_2}/v_z = (1.70\pm0.65)10^{-5} - (5.25\pm0.43)10^{-8}\cdot z$	0.0028 mg-at/kg	
3) Exponential rate	$R_{O_2}/v_z = -(1.54\pm0.21)10^{-5}e^{(0.819\pm0.071)z}$	0.0029 mg-at/kg	
	$R_{TCO_2}/v_z = (1.08\pm0.28)10^{-5}e^{(0.570\pm0.147)z}$	0.0027 mmole/kg	-0.317 at 797 m -0.393 at 1752 m
	$R_{TALK}/v_z = (0.66\pm0.49)10^{-5}e^{(-0.34\pm0.57)z}$	0.0013 meq/kg	-0.485 at 2947 m -0.490 at 3928 m
4) Exponential rate, TCO_2 corrected to constant specific alkalinity	$R_{TCO_2'}/v_z = (0.60\pm0.14)10^{-5}e^{(0.825\pm0.115)z}$	0.0019 mmole/kg	-0.398 at 797 m -0.390 at 3928 m

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$$\left[\frac{\Delta C}{\Delta O}\right] = \left[\frac{R_{TCO_2} - 0.5 \cdot R_{TALK}}{R_{O_2}}\right] = -0.415.$$

The calculated value is 8% higher than the value predicted by Redfield et al. (1963), and 12% higher than the value calculated in Chapter III from the TCO_2/AOU correlation at this station. The agreement is satisfactory considering the analytical errors, and the approximations which are involved in each model.

It should be noted that the θ/alkalinity diagram is nearly linear. Carbon production by carbonate solution is only 9% of the carbon produced by oxidation.

Case 2: Linear Rates

The measured oxygen profile at station 127 was fit to equation (71) by a linear least squares procedure, using (S/v_z) and (R_o/v_z) as adjustable parameters. A linear oxygen consumption rate was tried because Packard (1969) found that his directly measured oxygen consumption rates decreased linearly with depth below 500 m in the Eastern Pacific. The rate of oxygen consumption calculated from the vertical profile was (Table 11),

$$\left[\frac{R_{O_2}}{v_z}\right] = 1.70 \cdot 10^{-5} - 5.25 \cdot 10^{-8} \cdot z \quad (mg\text{-}at/kg\text{-}m). \qquad (74)$$

This rate law predicts oxygen production below 3600 m, and is clearly unreasonable. As a check on the calculation, oxygen and phosphate

data from the station in Indian Ocean (Dm2/148/60) analyzed by Wyrtki (1962) were also fit with a linear consumption or production rate. The results were the same, oxygen production and phosphate consumption near the bottom boundary, changing to oxygen consumption and phosphate production higher up in the water column.

The calculated oxygen production near the bottom boundary is due to the sign of the constant term in equation (74). For there to be oxygen consumption everywhere between the upper and lower boundaries, the constant term must have the same sign as the term $(S \cdot z/v_z)$. A computer program was written in which the sign of the constant term could be fixed and held constant. This program was then used to fit the measured oxygen profile at station 127 to equation (71). Unfortunately, the computer would not converge when the constant term in equation (74) was constrained to be negative.

Case 3: Exponential Rates

The calculated TCO_2 and oxygen profiles for a constant rate (Figure 17) show systematic deviations from the measured profiles. Wyrtki (1962), Craig and Weiss (1970), and Kroopnick (1971) showed that an exponential rate law gave a better fit to oxygen profiles.

The oxygen, TCO_2, and alkalinity profiles were fit to equation (73) by a non-linear least squares procedure. The calculated values of (R_o/v_z) and α are shown in Table 11. The exponential rates

removed the systematic deviations between the measured and calculated oxygen and TCO_2 profiles. However, the exponential rate did not improve the fit to the alkalinity data.

Calculated values of the oxidative ratio are,

z (meters)	$(R_{TCO_2} - 0.5 \cdot R_{TALK})/R_{O_2}$
797	- 0.317
1752	- 0.393
2947	- 0.485
3928	- 0.490

The calculated values are not constant and vary systematically with depth. The reason for this is that the exponents of the calculated rates are not equal (Table 11). A constant oxidative ratio demands that the exponents be equal.

Case 4: Exponential Rates, TCO_2 Corrected for Specific Alkalinity Variations

The rate of carbon production along a vertical profile is the sum of the rates of oxidation and of carbonate solution. In the preceding cases, the oxidative ratio was calculated by subtracting the rate of carbonate solution, $0.5(R_{TALK})$, from the total rate of carbon production, R_{TCO_2}. In the following example, the contribution of carbonate solution to R_{TCO_2} is eliminated by normalizing the measured TCO_2 to a constant specific alkalinity.

$$TCO_2' = TCO_2 + 0.5(0.1273 \cdot Cl - TALK) \tag{75}$$

TCO_2, TALK, and Cl are the measured values; 0.1273 is an average deep water specific alkalinity. The calculated value, TCO_2', is the total carbon dioxide a water sample would have if alkalinity were conservative (i.e. specific alkalinity constant at 0.1273) over the depth interval 797 m to 3928 m. Calculated values of TCO_2' are plotted in Figure 20. The exponential production rate determined from the vertical profile of TCO_2' and from equation (73) is given in Table 11. The calculated value of the oxidative ratio is,

$$(R_{TCO_2'})/(R_{O_2}) = -0.390 \cdot e^{0.006 \cdot z}.$$

The oxidative ratio ranges from -0.390 at 3928 m to -0.398 at 797 m. The calculated values agree well with theory (Redfield et al., 1963). The use of an exponential production rate is a severe test of the model because the exponents for both oxygen and TCO_2' must be equal if the oxidative ratio is to be constant. This condition is closely satisfied at station 127.

The oxidative ratios calculated from the vertical distribution of TCO_2' (case 4) are more nearly constant and are closer to the theoretical value, than are oxidative ratios calculated from the vertical distributions of TCO_2 and alkalinity (case 3). There are two reasons for this. First, normalizing the measured values of TCO_2 to a constant specific alkalinity increases their precision. The original values of TCO_2 were calculated from the measured pH and alkalinity, and to a first approximation TCO_2 equals alkalinity. For example,

if the measured alkalinity were 1% too large, due to an analytical

error, the calculated TCO_2 would also be 1% too large. However, if

the measured alkalinity is 1% too large, the alkalinity correction to

TCO_2' will be reduced, and the error in TCO_2' will be less than the 1%

error in alkalinity and TCO_2 . A 1% error in TCO_2 will only cause a

0.5% error in TCO_2'. The second reason for the better agreement in

case 4 is that alkalinity is nearly conservative in the intermediate and

deep water at station 127. It is difficult to calculate an accurate alka-

linity production rate at station 127 because the deviations of the θ/

alkalinity diagram from linearity are well within the analytical error

of the alkalinity method. The large uncertainty in the exponential alka-

linity production rate (see Table 11, case 3) is removed when TCO_2 is

normalized to a constant specific alkalinity.

Discussion

The main objection to applying the vertical advection/diffusion

model to station 127 is that the depth (3944 m) is too shallow. The

vertical model involves upwelling, and hence requires a source of

water at the lower boundary. The θ/S diagram at station 127 is linear

from 797 m to the bottom, and the vertical model has been applied

from 797 m to 3928 m (16 m above the bottom). Station 127 was

chosen for analysis because it is the deepest station occupied during

YALOC-69. Munk (1966) excluded the bottom 1 km from consideration

in his calculations with the vertical model. However, Craig and Weiss

(1970) applied the model to within 200 m of the bottom.

Oxygen consumption rates calculated at station 127 can be com-

pared with those calculated by Munk (1966) and by Craig and Weiss

(1970) at other stations in the Northeast Pacific. The results for a

constant consumption rate (equation (69)) are listed in Table 12. The

vertical model allows the ratios (K_z/v_z) and (R/v_z) to be calculated,

the model does not allow the individual values of K_z, v_z, or R to be

calculated. Craig (1969) summarized various estimates of v_z, which

range from 2 m/year to 16 m/year. In the following calculations v_z

is taken as 6 m/year. Rates calculated from this value should be

accurate within a factor of three. The oxygen consumption rates cal-

culated at each of the three Northeast Pacific stations (Table 12) are

nearly equal at $3.5 \cdot 10^{-4}$ mg-at/kg/year.

Table 12. Oxygen consumption below 1 km in the Northeast Pacific.
Calculated from the vertical advection/diffusion model
(equation (69)) for a vertical velocity v_z = 6 m/year.

Station	Position	(R_{O_2}/v_z)	(R_{O_2})	Source
		(mg-at/kg/m)	(mg-at/kg/yr)	
Calcofi #60-190	33°17'N 132°43'W	$-5.4 \cdot 10^{-5}$	$-3.2 \cdot 10^{-4}$	Munk (1966)
GEOSECS	28°29'N 121°38'W	$-6.0 \cdot 10^{-5}$	$-3.6 \cdot 10^{-4}$	Craig & Weiss (1970)
YALOC-69 #127	38°00'N 124°45'W	$-6.0 \cdot 10^{-5}$	$-3.6 \cdot 10^{-4}$	This work

Packard (1969) estimated oxygen consumption rates in the Eastern Pacific (37°N to 16°S) from enzyme analysis of the respiratory electron transport system in plankton. The electron transport system is responsible for the major part of cellular respiration (Packard, 1969). The average of his values below 1000 m (29 samples, 1000 to 5800 m) is $3.8 \cdot 10^{-4}$ mg-at/kg/yr. This value agrees well with the values calculated from the vertical model (Table 12).

Packard's (1969) oxygen utilization profile (Figure 22) shows that oxygen consumption decreases with depth. This agrees with the fact, that for the vertical model, an exponential rate of oxygen consumption fits the measured data better than a constant rate. The exponential oxygen consumption rate calculated at station 127 is plotted on Figure 22 for comparison with Packard's (1969) rates.
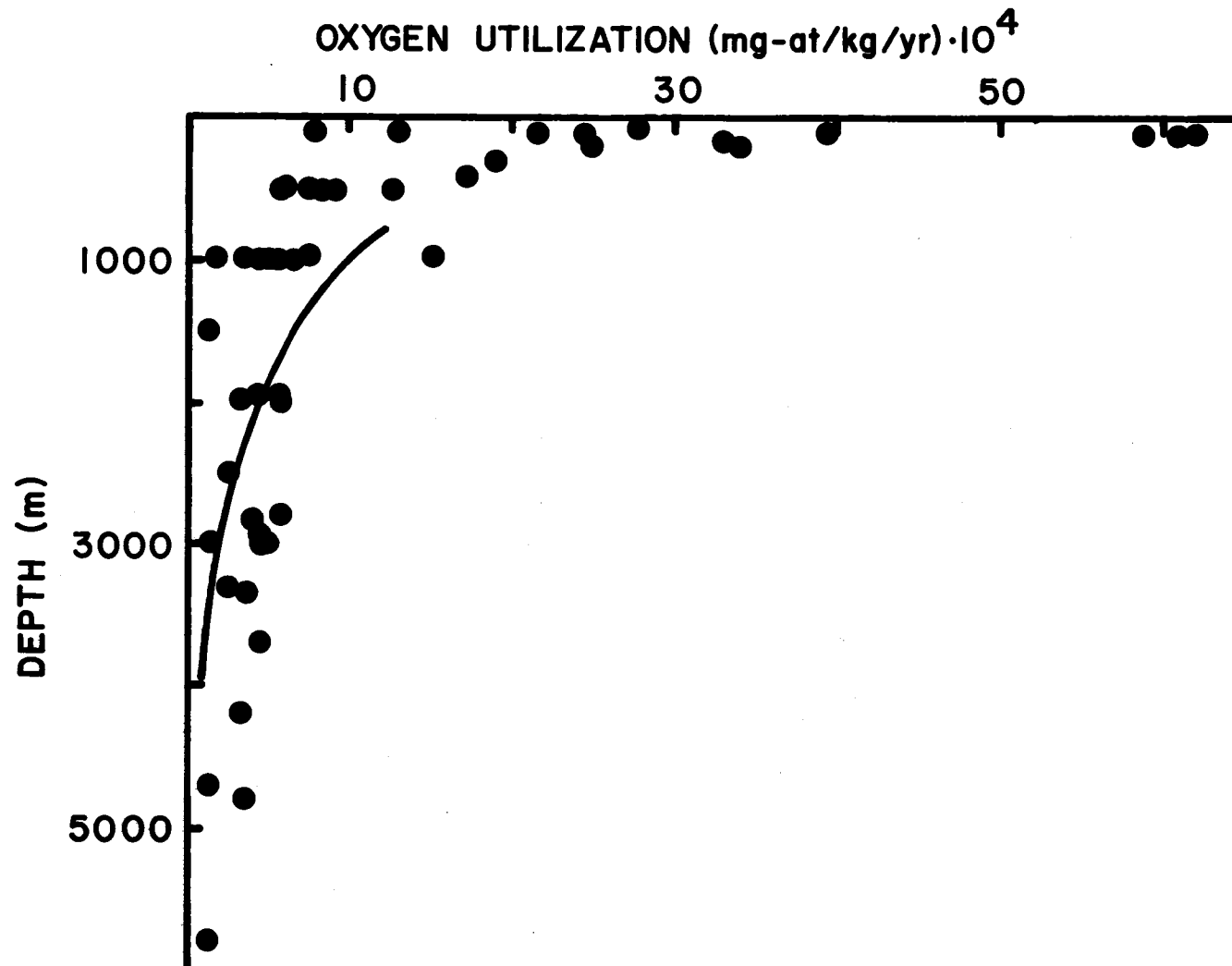
Figure 22. Comparison of oxygen consumption rates calculated from the vertical advection-diffusion model at station 127 (curve), with oxygen consumption rates determined by enzyme analysis (Packard, 1969). The calculated rate was calculated from the equation given in Table 11, case 3, using the value v_z = 6 m/year.

VII. CALCITE SATURATION IN THE WORLD OCEAN

The distribution of specific alkalinity and of carbonate sediments is influenced by the equilibria and kinetics of the carbonate system. The kinetics of calcite dissolution are poorly understood, but recent data on carbonic acid equilibria (Disteche and Disteche, 1967; Culberson and Pytkowicz, 1968) and on the solubility of calcite (MacIntyre, 1965; Pytkowicz and Fowler, 1967; Hawley and Pytkowicz, 1969) allow the in situ degree of saturation of seawater to be calculated.

Pytkowicz and Conners (1964), Pytkowicz, Disteche, and Disteche (1967), Pytkowicz and Fowler (1967), and Hawley and Pytkowicz (1969) experimentally determined the effect of pressure on the solubility of calcite and aragonite. Pytkowicz (1965, 1967, 1968a, 1968b) and Hawley and Pytkowicz (1969) used this data to calculate the degree of calcite saturation in the Pacific. Undersaturation was found everywhere below several hundred meters in the Eastern and North Pacific. Undersaturation in the Central South Pacific began below 2000 to 3000 m. Pytkowicz (1970) found that the compensation depth is at least 1000 m deeper than the transition from over- to undersaturation everywhere in the Pacific.

Berner (1965) calculated the effect of pressure on the solubility of calcite from thermodynamic data. He concluded that the Pacific and the Atlantic were undersaturated below a few hundred meters depth.

However, Li, Takahashi, and Broecker (1969) found that the change from super- to undersaturation occurred below 3000 m in the Atlantic, and between 1000 and 2000 m in the Equatorial and North Pacific. Li et al.'s (1969) conclusions have been questioned for two reasons: (1) their calculations of per cent saturation did not consider the effect of temperature on the pressure coefficients of the apparent constants (Hawley and Pytkowicz, 1969; Edmond, 1970a), and (2) many of their TCO_2 measurements appear to be systematically high due to bacterial respiration during storage of their water samples (Takahashi et al., 1970). These two effects increase Li et al.'s (1969) calculated per cent saturations. The transition from super- to undersaturation is shallower than their calculations indicate. Nevertheless, their data clearly show a marked difference between the level of 100% saturation in the Atlantic and in the Pacific.

Edmond (1970a) determined per cent saturation in the South Atlantic and in the Southern Ocean. His data place the 100% saturation level at about 2700 m in the South Atlantic, and between 1000 and 2000 m in the Southern Ocean.

Ben-Yaakov and Kaplan (1971a) determined the degree of saturation in the Northeast Pacific by in situ saturometry. Undersaturation occurred between 400 and 1800 m, the water was slightly supersaturated at 1800 m, and undersaturation occurred beneath this depth.

In the following sections the degree of calcite saturation in the Atlantic, Indian, Southern, and Pacific Oceans is reviewed. The data of Berner (1965), Li et al. (1969), and Edmond (1970a) have been recalculated using the same pressure coefficients to make the calculations internally consistent. Ben-Yaakov and Kaplan's (1971a) directly measured saturations are compared with per cent saturations calculated from pH and alkalinity measurements.

Calculation of Per Cent Saturation

Per cent saturation of calcite is defined as,

$$\% \text{ saturation} = ((IP)/(K'_{sp})) \cdot 100 \tag{76}$$

(IP) is the ion product,

$$(IP) = (Ca^{++})(CO_3^=). \tag{77}$$

The calcium/chlorinity ratio varies less than 1% with depth (Culkin and Cox, 1966) and the calcium concentration has been calculated from the calcium/chlorinity ratio determined by Culkin and Cox (1966).

The carbonate ion concentration depends on K'_1, K'_2, and K'_B and can be calculated from measurements of pH and alkalinity (Culberson and Pytkowicz, 1968), TCO_2 and pCO_2 (Li et al., 1969), or TCO_2 and alkalinity (Edmond, 1970a). In the following calculations the apparent constants at in situ temperatures and pressures are calculated from Lyman's (1956) values at 1 atmosphere, and from the pressure coefficients of Culberson and Pytkowicz (1968).

The calcite solubility product is calculated from the 1 atmosphere data of MacIntyre (1965), and from the pressure coefficients of Hawley and Pytkowicz (1969). The equation used is,

$$(K'_{sp})_{calcite} = (1.95 - 0.0176 \cdot T)10^{-2} \cdot S \cdot 10^{((0.693 - 0.00645 \cdot T)10^{-4} \cdot Z)}$$

(78)

The in situ pH is calculated from the measured parameters and from the in situ values of K'_1, K'_2, and K'_B (Culberson and Pytkowicz, 1968; Li et al., 1969; Edmond, 1970a).

All calculations were made on a CDC 3300 computer. A copy of the computer program, which includes the equations used in the computations, is listed in Appendix 1.

Results

Atlantic Ocean

In Table 13 recalculated per cent saturations based on Li et al.'s (1969) experimental data are compared with their original calculations. Recalculation displaces the 100% saturation level to shallower depths, and undersaturation begins between 3300 and 4300 m. The true depth of 100% saturation may be somewhat shallower than calculated because of possible errors in Li et al.'s (1969) TCO_2 measurements (Takahashi et al., 1970).

Recalculated per cent saturations based on Edmond's (1970a) data are given in Table 14 (Figure 7, Chapter III). In the South

Table 13. Recalculated values of per cent saturation calcite from the data of Li et al. (1969).

Z(m)	T(°C)	S(‰)	% Saturation Calcite Li et al. (1969)	Recalculated	Z(m)	T(°C)	S(‰)	% Saturation Calcite Li et al. (1969)	Recalculated
NORTHWEST ATLANTIC					**CARIBBEAN SEA**				
0	24.8	36.5	650	616	0	28.7	36.4	570	552
0	21.7	36.7	520	497	0	27.3	36.6	610	594
0	21.6	36.7	540	516	530	12.6	35.5	220	209
100	20.0	36.6	520	490	1300	5.1	35.0	160	150
200	18.5	36.6	490	460	2090	4.1	35.0	160	146
200	18.2	36.5	430	404	2920	3.4	35.0	130	118
300	18.0	36.5	460	431	3120	4.1	35.0	120	108
530	16.3	36.1	360	340	3770	4.2	35.0	120	108
700	13.0	35.6	250	240	4280	3.9	35.0	110	98
1070	6.4	35.0	160	153	4930	4.3	35.0	100	87
2250	3.4	34.9	150	139	5400	4.5	35.0	92	78
3290	2.7	34.9	130	115	6600	4.7	35.0	87	69
4170	2.1	34.9	110	95					
4820	2.2	34.9	98	83	**EASTERN EQUATORIAL PACIFIC**				
5600	2.1	34.9	84	68					
					0	27.1	35.5	350	355
NORTHEAST ATLANTIC					200	14.8	34.8	180	176
					400	13.0	34.6	120	116
300	16.9	36.2	400	383	570	7.2	34.5	97	92
710	10.6	35.4	180	174	1060	4.3	34.5	98	90
4100	2.3	35.0	96	79	1510	3.1	34.5	100	94

Table 13. Continued.

Z(m)	T(°C)	S(‰)	% Saturation Calcite Li et al. (1969)	Recalculated	Z(m)	T(°C)	S(‰)	% Saturation Calcite Li et al. (1969)	Recalculated
EASTERN EQUATORIAL PACIFIC					WESTERN EQUATORIAL PACIFIC				
2090	2.2	34.6	94	84	0	29.5	35.1	570	583
2500	2.0	34.6	95	85	0	29.0	35.1	590	602
3100	1.8	34.6	85	74	200	16.4	35.1	280	267
3330	1.4	34.6	83	72	300	11.3	34.8	160	150
3790	1.5	34.6	86	73	400	9.4	34.7	120	114
4270	1.5	34.6	87	74	400	8.3	34.6	120	117
					500	8.1	34.6	120	114
CENTRAL EQUATORIAL PACIFIC					1500	2.8	34.6	110	101
					1650	2.7	34.6	100	93
0	27.9	35.1	500	504	2000	2.1	34.6	110	95
0	29.4	35.1	540	545	2650	2.0	34.6	110	94
100	27.6	35.0	540	556	3000	1.7	34.6	100	88
300	11.4	35.0	170	170	4500	1.4	34.6	83	67
500	7.7	34.5	140	133	4500	1.9	34.6	88	72
720	5.6	34.5	120	121	5600	2.2	34.6	71	56
1000	4.6	34.5	91	85	5600	1.4	34.6	66	51
1500	3.4	34.5	100	93					
2000	2.1	34.6	87	78	NORTHWEST PACIFIC 1965				
2500	1.8	34.6	89	79					
3430	1.5	34.6	88	76	0	23.5	35.0	520	507
3830	1.5	34.6	82	70	90	20.0	34.6	450	446
4860	1.4	34.6	85	72	150	17.0	34.6	360	359

Table 13. Continued.

Z(m)	T(°C)	S(‰)	% Saturation Calcite Li et al. (1969)	Recalculated	Z(m)	T(°C)	S(‰)	% Saturation Calcite Li et al. (1969)	Recalculated
NORTHWEST PACIFIC 1965					**NORTH PACIFIC**				
300	14.0	34.4	320	315	0	16.5	33.0	230	234
450	11.0	34.2	240	236	200	6.4	34.0	210	210
600	9.0	34.3	150	147	600	4.5	34.1	110	106
800	6.1	34.2	140	135	1000	2.7	34.4	74	68
1250	3.1	34.4	100	98	3125	1.2	34.6	67	57
2000	3.0	34.6	100	116	4590	1.5	34.6	74	61
3000	2.1	34.6	96	84	6650	1.3	34.6	58	44
4000	1.8	34.6	94	80					
4550	3.1	34.6	97	82					
5000	2.0	34.6	85	71					
6000	2.7	34.6	76	62					
NORTHWEST PACIFIC 1966									
0	26.6	35.0	520	528					
300	9.0	34.4	200	194					
400	8.0	34.3	110	112					
750	7.0	34.2	110	105					
1000	4.0	34.4	73	67					
3500	2.0	34.6	86	73					
4000	1.8	34.6	80	66					
5500	2.0	34.6	80	64					

Table 14. Recalculated values of per cent saturation in the South Atlantic from the data of Edmond (1970a).

| | | | % Saturation Calcite | | | | | % Saturation Calcite | |
| | | | Edmond | | | | | Edmond | |
Z(m)	T(°C)	S(‰)	(1970a)	Recalculated	Z(m)	T(°C)	S(‰)	(1970a)	Recalculated
		Circe 223 (7°47'S, 6°09'W)					Circe 246 (5°10'S, 30°53'W)		
100	15.20	35.595	198	209	1	27.11	35.194	464	506
203	10.52	34.981	138	145	105	22.20	36.250	341	365
312	9.53	34.870	114	120	201	11.68	35.116	168	178
400	8.51	34.763	100	105	302	8.73	34.725	122	129
501	7.14	34.640	86	90	392	7.69	34.669	109	114
597	6.02	34.554	91	95	504	6.27	34.507	94	98
707	5.15	34.500	86	89	582	5.54	34.495	96	100
794	4.70	34.485	91	94	705	4.69	34.425	104	108
981	4.17	34.583	90	94	776	4.43	34.476	102	107
1238	4.10	34.767	100	104	971	4.17	34.585	99	103
1483	3.92	34.907	109	114	1477	4.32	34.941	119	124
1724	3.66	34.944	115	121	1752	3.88	34.956	122	128
1964	3.43	34.945	111	116	1914	3.64	34.919	121	127
2333	3.12	34.932	106	112	2008	3.49	34.948	117	122
2668	2.81	34.916	98	102	2483	2.96	34.921	103	108
2909	2.65	34.909	91	95	2975	2.72	34.880	96	100
3151	2.56	34.903	94	98	3203	2.63	34.920	93	97
3387	2.47	34.903	87	91	3454	2.55	34.917	90	94
3767	2.39	34.894	95	99	3704	2.37	34.882	85	90
3882	2.36	34.891	84	88	3954	1.99	34.840	80	83
4104	2.34	34.886	75	78	4179	1.43	34.774	71	74
4325	2.34	34.882	73	77	4301	1.20	34.750	59	61

Table 14. Continued.

Z(m)	T(°C)	S(‰)	% Saturation Calcite Edmond (1970a)	Recalculated	Z(m)	T(°C)	S(‰)	% Saturation Calcite Edmond (1970a)	Recalculated
Circe 223 (7°47'S, 6°09'W)					Circe 246 (5°10'S, 30°53'W)				
4347	2.31	34.885	73	76	4446	1.03	34.709	61	62
4446	2.33	34.882	71	74	4542	0.98	34.703	57	58
					4638	0.86	34.689	58	60
					4700	0.86	34.689	56	58
					4856	0.69	34.710	55	56
					4900	0.64	34.703	53	54

Atlantic, the water is supersaturated near the surface, undersaturated in the oxygen minimum layer, supersaturated beneath the minimum zone, and finally completely undersaturated beneath about 2700 m.

Berner (1965) calculated per cent saturation in the North Atlantic using pH data from the Meteor Expedition (station 264, 10° 12'N, 26° 36'W). He found undersaturation below 200 m. In his calculations, Berner (1965) used the measured pH values uncorrected for temperature or pressure (Wattenberg, 1933). These pH values correspond to the pH at 28° C and 1 atmosphere on the NBS pH scale. Table 15 gives the recalculated saturations at station 264 (Berner, 1965). The recalculated values agree well with Li et al. 's (1969) and Edmond's (1970a) data.

Indian Ocean

Table 16 gives per cent saturations in the Equatorial Indian Ocean (Figure 6, Chapter III) calculated from pH and alkalinity data collected during the Meteor Indian Ocean Expedition (Dietrich et al., 1966b). Undersaturation begins between 500 and 1000 m, and the degree of undersaturation increases continuously to the bottom.

Southern Ocean

Edmond (1970a) measured TCO_2 and alkalinity along three sections across the Southern Ocean at 135° E, 145° E, and 160° E.

Table 15. Recalculated values of per cent saturation at Meteor station 264 (10°12'N, 26°36'W) (Berner, 1965). Only two alkalinities were measured at this station. The calculations were made for a constant total alkalinity of 2.346 meq/kg.

| | | | % Saturation Calcite | | | | | % Saturation Calcite | |
| | | | Berner | | | | | Berner | |
Z(m)	T(°C)	S(‰)	(1965)	Recalculated	Z(m)	T(°C)	S(‰)	(1965)	Recalculated
0*	24.90	35.76	260	477	999	5.07	34.78		97
25	24.77	35.76		490	997*	5.07	34.79		112
49	16.99	35.61		250	1000			54	
75	14.46	35.42		183	1195	4.75	34.90		116
100	13.85	35.36		189	1595	3.88	34.964		136
150	13.02	35.28		185	1794	3.62	34.953		143
200	12.24	35.20		193	1995	3.39	34.953		144
249	11.50	35.12		186	2000			70	
251*	11.45	35.10		170	2487	3.02	34.933		115
300	11.00	35.045		150	2991*	2.72	34.913		110
400	9.89	35.025		108	3000			49	
497	8.56	34.92		107	3490	2.52	34.899		104
500			58		3990	2.42	34.892		96
595	7.73	34.87		90	4490	2.34	34.89		87
700	6.75	34.81		91	4990	2.32	34.886		70
800	5.82	34.715		97	5000			37	
900	5.37	34.74		97					

Table 16. Calcite saturation in the Indian Ocean, calculated from pH and alkalinity data taken during the Meteor Indian Ocean Expedition (Dietrich et al., 1966b).

Z(m)	T(°C)	S(‰)	% Saturation Calcite	Z(m)	T(°C)	S(‰)	% Saturation Calcite
Station 169 (3°34'S, 53°14'E)				Station 183 (8°43'N, 73°59'E)			
2	27.48	35.327	509	2	27.78	34.129	505
25	27.49	35.323	512	25	27.80	34.603	509
50	27.50	35.335	509	49	27.82	35.134	518
74	26.88	35.343	488	73	28.82	35.851	508
99	22.52	35.221	378	98	24.91	35.512	327
148	17.22	35.256	260	123	21.94	35.339	257
197	13.59	35.165	220	147	19.41	35.074	190
296	11.70	35.035	200	196	17.42	35.055	126
394	9.99	34.898	172	294	12.93	35.221	125
493	9.03	34.859	151	392	11.28	35.189	112
591	8.26	34.847	124	490	10.40	35.153	105
788	7.46	34.898	105	588	9.60	35.118	99
985	6.48	34.882	99	686	8.95	35.098	97
1231	5.08	34.835	92	1220	5.80	34.898	85
1478	4.18	34.808	90	1470	4.79	34.867	83
1724	3.07	34.780	87	1715	3.63	34.835	81
1920	2.81	34.760	86	1940	2.88	34.796	79
2160	2.41	34.752	83	2205	2.54	34.776	77
2400	2.05	34.745	80	2450	2.19	34.752	77
2640	1.85	34.737	78	2676	1.96	34.748	74
2880	1.76	34.729	75				
3120	1.72	34.733	73				
3360	1.67	34.725	69				
3446	1.63	34.725	70				

The 100% saturation level calculated from his data lies between 1600 and 2400 m along each of the transects.

The Southern Cross Expedition (Horibe, 1970) measured pH and alkalinity along two sections across the Southern Ocean at 170°W and 155°E (Figure 5, Chapter III). The crossover from super- to under-saturation occurs between 1000 and 1500 m along each transect (Figure 23).

Pacific Ocean

Per cent saturations in the Eastern Pacific calculated from pH and alkalinity measurements made during YALOC-69 (Wyatt et al., 1970) are given in Table 17 (Figure 4, Chapter III). Undersaturation begins at shallow depths in this region due to the intense oxygen minimum zone. These data are in agreement with the earlier calculations of Pytkowicz (1965).

Recalculated values of per cent saturation based on Li et al.'s (1969) data in the Equatorial and North Pacific are given in Table 13. Their data show that the 100% saturation level deepens to the west, as the oxygen minimum becomes less intense. The 100% saturation level occurs between 400 and 570 m in the Eastern Equatorial Pacific, between 720 and 1000 m in Central Equatorial Pacific, and between 1500 and 1650 m in the Western Equatorial Pacific. In the Northwest Pacific the 100% saturation level occurs between 750 and 1250 m; in
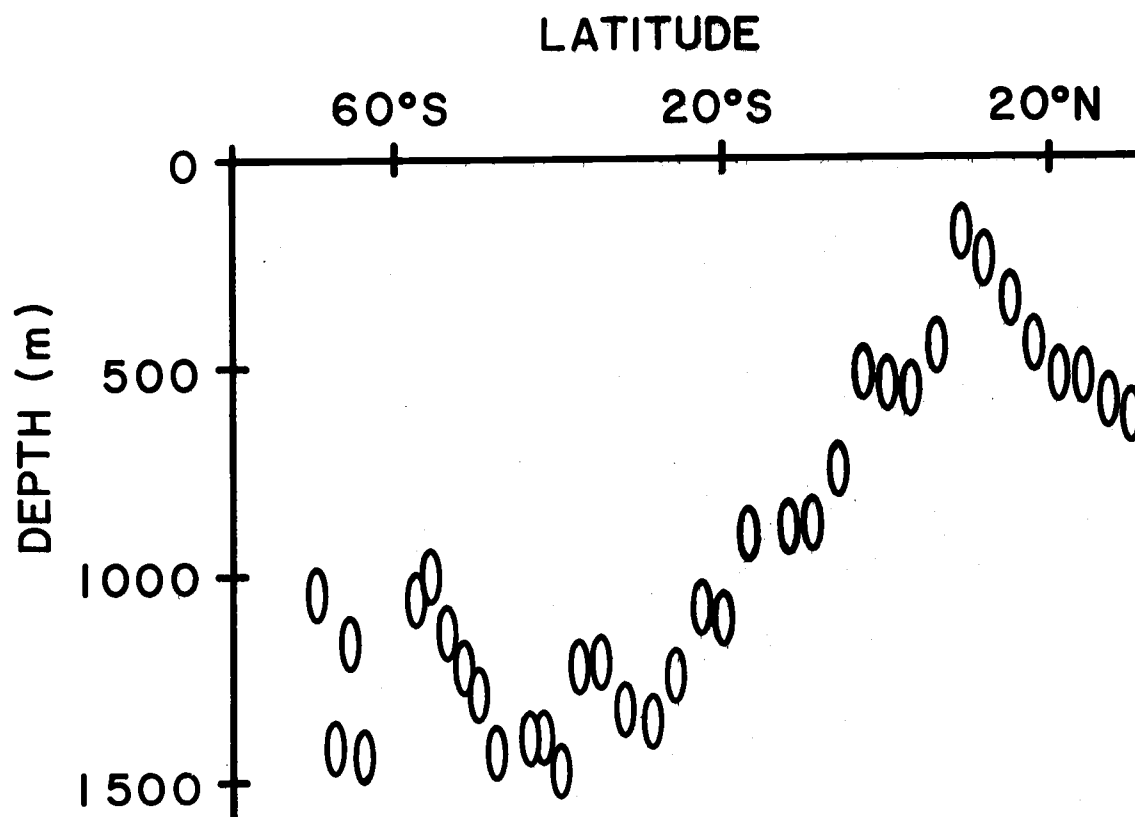
Figure 23. The depth of 100% calcite saturation along 170°W longitude (Horibe, 1970).

Table 17.   Calcite saturation in the Eastern Pacific, calculated from pH and alkalinity data taken during YALOC-69 (Wyatt et al., 1970).

Z(m)	T(°C)	S(‰)	% Saturation Calcite	Z(m)	T(°C)	S(‰)	% Saturation Calcite
Station 70 (4°00'S, 82°00'W)				Station 127 (38°00'N, 124°45'W)			
0	21.07	34.925	387	0	11.91	32.910	275
10	21.02	34.922	381	10	11.89	32.910	275
20	20.10	34.912	291	20	11.92	32.911	274
30	19.12	35.097	269	30	11.91	32.918	270
40	18.02	35.048	240	49	10.03	33.262	168
49	17.45	35.027	228	75	9.65	33.677	138
75	16.25	35.088	204	98	9.22	33.823	126
98	15.04	35.079	196	147	8.35	33.977	118
147	14.11	34.989	160	197	7.60	34.018	105
197	13.45	34.953	138	298	6.80	34.085	83
298	12.17	34.876	109	398	5.97	34.145	68
398	9.20	34.703	81	597	4.93	34.275	58
599	7.31	34.614	75	797	4.41	34.393	57
799	5.58	34.566	76	956	3.88	34.455	59
998	4.70	34.573	76	996	3.81	34.458	57
1199	3.74	34.583	76	1155	3.34	34.503	58
1446	3.23	34.616	77	1196	3.35	34.509	57
1499	3.14	34.613	75	1453	2.78	34.546	58
1943	2.35	34.649	74	1752	2.27	34.589	59
1998	2.29	34.646	76	2051	2.04	34.624	61
2190	2.16	34.660	74	2350	1.82	34.646	63
2439	1.92	34.672	77	2648	1.75	34.662	64
2687	1.83	34.681	75	2947	1.65	34.670	63
2936	1.82	34.684	72	3246	1.63	34.678	62

Table 17. Continued

Z(m)	T(°C)	S(‰)	% Saturation Calcite		Z(m)	T(°C)	S(‰)	% Saturation Calcite

Station 70 (4° 00' S, 82° 00' W)   Station 127 (38° 00' N, 124° 45' W)

Z(m)	T(°C)	S(‰)	Calcite		Z(m)	T(°C)	S(‰)	Calcite
3183	1.83	34.682	67		3545	1.53	34.685	61
3432	1.86	34.683	67		3843	1.51	34.692	60
3706	1.84	34.684	64		3913	1.51	34.693	60
3730	1.86	34.683	62		3928	1.49	34.692	58
3754	1.86	34.684	63					

the North Pacific between 600 and 1000 m.

The Southern Cross Expedition (Horibe, 1970) made pH and alkalinity measurements from 30°N to 70°S along 170°W longitude. The level of 100% saturation calculated from this data is shown in Figure 23. The 100% saturation level occurs between 1000 and 1500 m in the South Pacific, and rises toward the surface in the North Pacific as the oxygen minimum becomes more intense (Lyakhin, 1968; Hawley and Pytkowicz, 1969). Figure 23 is in qualitative agreement with a similar profile published by Hawley and Pytkowicz (1969). Their calculations place the 100% saturation level between 2500 and 3400 m in the South Pacific. This discrepancy may be due to systematic errors in the Vityaz pH and alkalinity data used by Hawley and Pytkowicz (1969). Bruyevich (1966) and Lyakhin (1968) showed that Vityaz pH and alkalinity data are systematically high due to corrosion of the metal lined Nansen bottles used aboard the Vityaz. High pH and alkalinity values would cause the calculated 100% saturation level to be too deep.

The only direct measurements of the in situ degree of saturation are those of Ben-Yaakov and Kaplan (1971a) in the Northeast Pacific. They measured the degree of saturation along two vertical profiles with an in situ saturometer (Ben-Yaakov and Kaplan, 1971b). In essence, the saturometer consists of a glass electrode surrounded by calcite crystals. In Ben-Yaakov and Kaplan's (1971a, b) design,

seawater was pumped through the crystals for 5 minutes, the pump was turned off, and the seawater surrounding the glass electrode was allowed to react with the calcite crystals for 15 minutes. After 15 minutes, the system was flushed with fresh seawater for a second 5 minutes, and the cycle was repeated. Ben-Yaakov and Kaplan (1969) described the calculation of per cent saturation from the observed pH shifts in the saturometer. Their experiments allowed only a semi-quantitative estimate of the degree of saturation, since the 15 minute equilibration interval was too short for equilibrium to be reached. Thus their calculated supersaturations are too low, and their calculated undersaturations are too high (Ben-Yaakov and Kaplan, 1971a).

In Figure 24, Ben-Yaakov and Kaplan's (1971a) measured saturations in the Santa Monica Basin are compared with saturations calculated from pH and alkalinity measurements taken in the Santa Monica Basin during YALOC-69 (Wyatt et al., 1970). Both sets of data show that the crossover from super- to undersaturation occurs at shallow depths. The crossover is between 100 and 250 m for the directly measured values, and at 200 m for the calculated values.

Ben-Yaakov and Kaplan's (1971a) results for the Northeast Pacific are compared in Figure 25 with two profiles in roughly the same area calculated from pH and alkalinity measurements made during YALOC-69 (Wyatt et al., 1970). Both profiles show an initial crossover from super- to undersaturation at shallow depths.
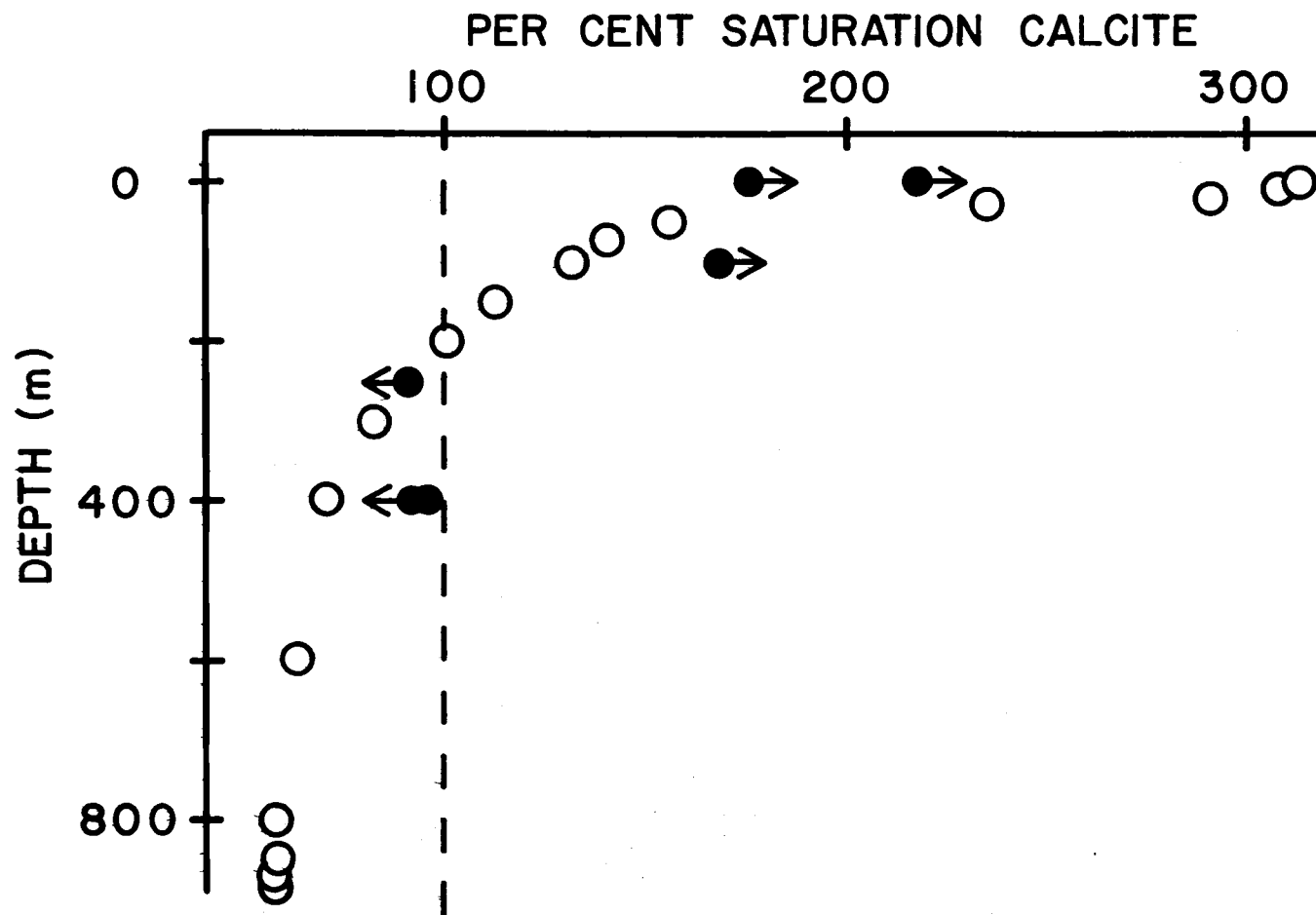
Figure 24. Comparison of measured and calculated calcite saturation profiles in the Santa Monica Basin. The open circles are calculated from pH and alkalinity measurements in the basin during YALOC-69 (station 122: 33°45.0'N, 118°46.0'W, April 22, 1969). The solid circles are Ben-Yaakov and Kaplan's (1971a) in situ saturometer measurements in the basin (33°49.8'/ 33°58'N, 118°35.5'/118°39.4'W, November 26, 1969/January 2, 1970). The in situ values are not equilibrium measurements, the arrows indicate the direction of the true value.
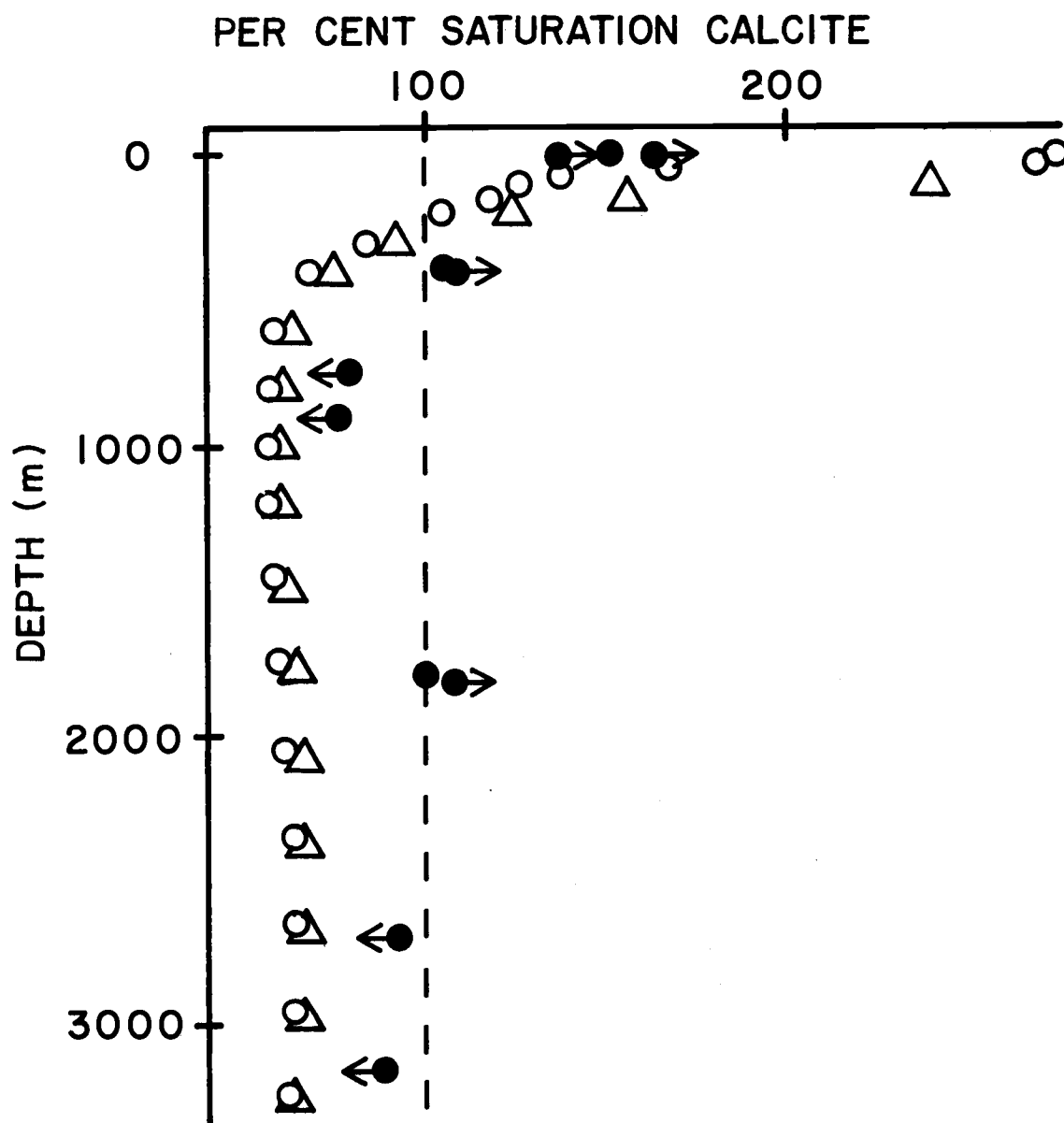
Figure 25. Comparison of measured and calculated calcite saturation profiles in the Northeast Pacific. The open circles and triangles are calculated from pH and alkalinity measurements during YALOC-69 (station 121, triangles; station 127, circles; see Figure 4, Chapter III for station positions). The solid circles are Ben-Yaakov and Kaplan's (1971a) in situ saturometer measurements in the Northeast Pacific (32°33'N, 120°26'W, January 16/17, 1970). The in situ values are not equilibrium measurements, the arrows indicate the direction of the true value.

However, the calculated profiles remain undersaturated to the bottom, whereas the measured profile shows a region of slight supersaturation at 1800 m. The reason for this discrepancy is not clear.

Ben-Yaakov and Kaplan (1971a) compared their Northeast Pacific profile with profiles calculated by Lyakhin (1968) for the Eastern Pacific, by Hawley and Pytkowicz (1969) for the Central North Pacific, and by Li et al. (1969) for the Northwest Pacific. Lyakhin's (1968) and Hawley and Pytkowicz's (1969) profiles are similar to the YALOC-69 profiles (Figure 25) in that they show the deep and intermediate waters to be undersaturated. Li et al.'s (1969) original data for the Northwest Pacific show considerable scatter, but their data suggest a deeper crossover from super- to undersaturation than do the profiles of Lyakhin (1968) and Hawley and Pytkowicz (1969). In the preceding sections (see Table 13), it was shown that part of this disagreement was due to the different pressure coefficients used by the different workers. Recalculation of Li et al.'s (1969) data using more recent values (see above) for the equilibrium constants displaces the crossover to shallower depths.

Ben-Yaakov and Kaplan (1971a) concluded that their measurements in deep and intermediate waters agreed better with Li et al. (1969) than with Lyakhin (1968) or Hawley and Pytkowicz (1969); they concluded "that the Pacific at 30°N is close to saturation between 1000 and 3000 meters." The agreement between Ben-Yaakov and Kaplan

(1971a) and Li et al. (1969) disappears if the recalculated values of

Li et al. (1969) are used instead of their original values.

Discussion

Edmond (1970a) critically reviewed the present knowledge of K_1',

K_2', K_b', and K_{sp}'. He determined "best" values for the apparent con-

stants, and concluded that per cent saturations calculated with these

"best" values were accurate to $\pm 10\%$. Lyman's (1956) values for

K_1', K_2', and K_B' are used in this work, and per cent saturations calcu-

lated in this work are 5% higher than saturations calculated with

Edmond's (1970a) "best" values (see Table 14). The calculations in

this chapter show the relative depth of 100% saturation in each of the

major oceans. The true depth of 100% saturation may differ slightly

from the calculated depth due to uncertainties in the apparent constants

used in the calculations.

Two independent methods have been used to determine the in

situ degree of calcite saturation. In the first method, the calcium

carbonate ion product is calculated from field measurements of pH

and alkalinity, TCO_2 and pCO_2, or TCO_2 and alkalinity. The ion

product is then compared with experimentally determined values of

the calcite solubility product. The previous sections have shown that

degrees of saturation calculated from field measurements of pH and

alkalinity (Wyatt et al., 1970; Horibe, 1970; Dietrich et al., 1966b;

Berner, 1965), TCO_2 and pCO_2 (Li et al., 1969), and TCO_2 and alkalinity (Edmond, 1970a) are in substantial agreement if the same equilibrium constants are used throughout the calculations. In particular, these calculations show that the Northeast Pacific is everywhere undersaturated below 500 m depth.

The second method involves the in situ measurement of calcite saturation by carbonate saturometry (Ben-Yaakov and Kaplan, 1971a). The two directly measured profiles in the Northeast Pacific show an initial shallow crossover from super- to undersaturation, in agreement with the calculated profiles (Figures 24 and 25). However, the directly measured open ocean profile (Figure 25) shows a secondary maximum in per cent saturation at 1800 m, in which the seawater becomes slightly supersaturated. The directly measured per cent saturation increases from less than 76% at 900 m to more than 108% at 1820 m. Supersaturation at 1800 m is not seen in the calculated profiles (Figure 25). The calculated profiles show a secondary maximum in per cent saturation, but it is much smaller than the directly measured secondary maximum. At station 127 (Table 17, Figure 25), the calculated per cent saturations increase from 57% at 797 m to 64% at 2648 m, and then decrease toward the bottom. Calculated per cent saturaturations at station 121 (Figure 25) increase from 59% at 1198 m to 66% at 2368 m, and then decrease toward the bottom.

Pytkowicz (1968b) showed that the secondary maximum in per cent saturation was related to the vertical distribution of oxygen. He found that per cent saturation reached a minimum at the oxygen minimum (about 500 to 1000 m) due to the low pH caused by the oxidation of organic matter, and that per cent saturation increased below the pH minimum as the amount of organic oxidation decreased. He showed that the decrease in per cent saturation beneath 2000 to 3000 m depth was due to the effect of pressure on the solubility of calcite.

Per cent saturation is calculated from the ratio,

$$(Ca^{++})(CO_3^{=})/(K'_{sp}).$$

Calcium is a major constituent of seawater and its concentration is nearly constant below 1000 m ($\pm 1\%$). It is unlikely that the difference between the measured and calculated profiles is due to the calcium concentration used in the calculation of per cent saturation.

The calculation of the carbonate ion concentration depends on the measured pH and alkalinity, and on the value of K'_2 used in the calculation. The calculated carbonate ion concentration is not very sensitive to the values of K'_1 and K'_B used in the calculation. K'_2 and K'_{sp} are smooth functions of salinity, temperature, and pressure. Temperature and salinity are nearly constant below 1000 m in the Northeast Pacific; pressure is the only variable which significantly affects the apparent constants. It is unlikely that the large secondary maximum in per cent saturation observed by Ben-Yaakov and Kaplan

(1971a) is due to interaction between K'_2 and K'_{sp}, since each of the apparent constants increases smoothly with depth.

This leaves only the field measurement of pH and alkalinity as possible sources of error. The difference between the calculated and measured saturations at 1800 m is about 45% (Figure 25). Errors of 45% in alkalinity, or of 0.2 pH units in pH are needed to account for this difference. The GEOSECS intercalibration (Takahashi et al., 1970) showed that the maximum error in field measurements of alkalinity and pH is ± 5% and ± 0.02 pH units respectively.

It does not appear possible to reconcile the calculated and measured profiles of calcite saturation in the Northeast Pacific.

VIII. NEAR-BOTTOM CHEMISTRY

Exchange across the seawater-sediment interface is one of the most important processes by which substances are introduced into or removed from the oceans. A knowledge of rates of exchange across the sea-floor is essential for accurate mass balance calculations.

Processes occurring at or beneath the seawater-sediment interface affect the composition of interstitial and near-bottom waters. For instance, the concentration of silica in interstitial water often increases with depth in the sediment (Schink, 1968). The silica produced by solution diffuses into the overlying water column (Anikouchine, 1967), and this diffusion may set up measurable gradients in the near-bottom water. A knowledge of chemical gradients in interstitial and in near-bottom waters can be used to determine the processes responsible for exchange across the interface. If the diffusion coefficient is known, the rate of exchange can be calculated from the measured concentration gradients.

The study of chemical exchange across the seawater-sediment interface can be divided into four problems: (1) measurement of near-bottom chemical gradients, (2) measurement of near-bottom diffusion, (3) measurement of interstitial water gradients, and (4) measurements of diffusion in interstitial waters. This chapter describes the results of a series of near-bottom chemical measurements in the Pacific and Atlantic Oceans.

Previous Near-bottom Studies

Some previous near-bottom studies are listed in Table 18. Koczy (1950, 1951, 1953) measured near-bottom oxygen, phosphate, silicate, pH, and alkalinity gradients which extended 10 to 20 m above the sea-floor in the Indian and Atlantic Oceans. Broecker, Li, and Cromwell (1967), Broecker, Cromwell, and Li (1968), and Broecker and Kaufman (1970) found near-bottom radon gradients which extended 20 m above the bottom. Weichart (1966, 1969) observed near-bottom oxygen, pH, phosphate, and silicate gradients which extended 3 m above the bottom in the North Atlantic. Sysoyev (1961) and Sackett (1969) measured near-bottom oxygen gradients that extended at least 1 m above the bottom. Gieskes, Meincke, and Wenck (1970) found that the concentrations of oxygen, pH, and alkalinity at 1 m above the bottom were considerably different than the concentrations 10 to 70 m above the bottom in the North Atlantic.

However, near-bottom oxygen gradients in the Mediterranean Sea observed by Brouardel and Fage (1953, 1954, 1955), Fage (1954), and Brouardel and Vernet (1958) were only present in the last half meter above the sediment. Similarly, Rittenberg, Emery, and Orr (1955) found that near-bottom oxygen, phosphate, silicate, nitrate, and nitrite gradients extended less than 1 m above the sea-floor in the basins off Southern California. Schink (1968) measured silicate at 1 m intervals above the sea-floor and did not find any near-bottom gradients.

Table 18. Studies of near-bottom chemistry.

Reference	Height of nearest sample above bottom	Measured Parameters	Region
Wattenberg (1935)	50 m	Talk	Equatorial Atlantic
Koczy (1950, 1951, 1953)	3 m	S‰, O_2, pH, Talk, Si, PO_4	Equatorial Indian, Equatorial and North Atlantic
Brouardel & Fage (1953, 54, 55) Fage (1954) Brouardel & Vernet (1958)	1 cm	O_2	Mediterranean Sea
Rittenberg, Emery, & Orr (1955)	0.5 m	S‰, O_2, pH, PO_4, Si, NO_3, NO_2	Santa Barbara, Santa Monica, and Catalina Basin
Gamutilov, Dobrovol'skii, Sabinin, & Udintsev (1960)	1 m	S‰	Western Equatorial Pacific
Sysoyev (1961)	0-3 m	O_2	North Pacific
Weichart (1966, 1969)	1 m	O_2, pH, PO_4, Si	North Atlantic
Ichiye (1966)	10 m	Light scattering	North Atlantic
Bodvarsson et al. (1967)	50 cm	Temperature	Northeast Pacific
Schink (1968)	1 m	Si	Equatorial and North Atlantic
Broecker, Li, & Cromwell (1967) Broecker, Cromwell, & Li (1968) Broecker & Kaufman (1970)	5 m	Radon-222	South Atlantic World Ocean Northeast Pacific
Sackett (1969)	2 m	S‰, O_2, dissolved and particulate organic carbon, particulate organic nitrogen	Gulf of Mexico
Gieskes, Meincke, & Wenck (1970) Gieskes (1970)	1 m	S‰, O_2, pH, Talk	North Atlantic

There appear to be inconsistencies in the above studies. Koczy (1950, 1951, 1953) observed near-bottom oxygen gradients which extended 10 to 20 m above the bottom in the Atlantic and Indian Oceans, whereas, Brouardel and Fage (1953, 1954, 1955), Fage (1954), and Brouardel and Vernet (1958) found that oxygen gradients extended less than 0.5 m above the bottom in the Mediterranean Sea. Koczy (1950, 1951, 1953) also found silica gradients which extended 20 m above the bottom, while Rittenberg, Emery, and Orr (1955) and Schink (1968) found no gradients which extended more than 0.5 m above the bottom. Schink (1968) attributed Koczy's (1950, 1951, 1953) silica gradients to sampling and/or analytical errors.

Models of the Near-bottom Layer

The magnitude of near-bottom gradients depends greatly on the degree of mixing of the near-bottom waters. Before describing the present measurements, it will be helpful to review the model which is most often used to study near-bottom processes. The general equation for the distribution of a variable in the sea is (Sverdrup et al., 1942),

$$\left[\frac{\partial C}{\partial t}\right] = \frac{\partial}{\partial x}\left[K_x\left[\frac{\partial C}{\partial x}\right]\right] + \ldots - \left[v_x\left[\frac{\partial C}{\partial x}\right] + \ldots\right] + R \qquad (79)$$

K and v are the eddy diffusion coefficient and velocity, and R is the in situ rate of production of C. To interpret near-bottom measurements, it is usually assumed that the near-bottom distribution is stationary ($\partial C/\partial t = 0$), that horizontal advection, horizontal diffusion, and

vertical advection are negligible, and that K_z is independent of the height above the bottom (Koczy, 1958). With these assumptions, equation (79) reduces to,

$$\frac{\partial}{\partial z}\left[K_z\left[\frac{\partial C}{\partial z}\right]\right] + R = 0 \qquad (80)$$

R is generally set equal to zero for non-radioactive tracers (Wattenberg, 1935), for radioactive tracers, $R = \lambda C$, where λ is the radioactive decay constant of the tracer (Koczy, 1958).

For a non-radioactive tracer (R = 0), equation (80) reduces to,

$$\frac{\partial}{\partial z}\left[K_z\left[\frac{\partial C}{\partial z}\right]\right] = 0 \qquad (81)$$

which has the solution (z = 0 at the bottom),

$$C_z = C_o + \left[\frac{B}{K_z}\right] z \qquad (82)$$

B is a constant of integration. Equation (82) is equivalent to Fick's first law. If the flux of C across the interface is balanced solely by vertical eddy diffusion, then by Fick's first law,

$$\text{Flux} = K_z\left[\frac{\Delta C}{\Delta z}\right] = K_z\left[\frac{C_z - C_o}{z}\right] \qquad (83)$$

Rearranging (83) yields,

$$C_z = C_o + \left[\frac{\text{Flux}}{K_z}\right] z \qquad (84)$$

Wattenberg (1935), Koczy (1953), and Bodvarsson, Berg, and

Mesecar (1967) used equation (83) to calculate K_z from measured near-bottom gradients, and from estimates of the flux across the interface. Schink (1968) estimated the near-bottom silica gradient from (83) and from estimates of K_z and of the silica flux across the interface. Weichart (1966, 1969) and Gieskes (1970) used (83) to calculate the flux from measured near-bottom gradients and from assumed values of K_z.

For a radioactive tracer $(R = \lambda C)$, the solution to equation (80) is (Broecker et al., 1968),

$$C_z = C_o e^{-z(\lambda/K_z)^{\frac{1}{2}}} \tag{85}$$

Broecker et al. (1967, 1968) calculated K_z from equation (85) and the near-bottom distribution of radon-222 (half life 3.85 days). It should be noted that equation (85) can be solved for K_z without knowing the flux of C across the interface. In contrast, the flux must be known to solve equation (83) for K_z. This is an important advantage of radioactive tracers over non-radioactive tracers, since fluxes of most substances across the interface are poorly known.

The various estimates of K_z in Table 19 range over 5 orders of magnitude. Calculated values of K_z in deep water away from the bottom are given for comparison. The calculated values of K_z near the bottom fall roughly into two classes (Schink, 1968): (1) values $(1 < K_z < 50)$ roughly equal to the values higher up in the water column,

Table 19. Values of the vertical eddy diffusion coefficient in deep and near-bottom waters. The height above the bottom of the bottommost sample is listed in Table 18.

NEAR-BOTTOM VALUES

Reference	K_z	Region	Method
Wattenberg (1935)	4 cm^2/sec	S. Atlantic	Eq. (83): Alkalinity flux estimated from CaCO$_3$ solution rates divided by average vertical alkalinity gradient in Antarctic Bottom Water.
Broecker et al. (1967)	1.5 to 50	S. Atlantic	Eq. (85) and measured near-bottom radon-222 distribution.
Broecker et al. (1968)	2 to 50	World Ocean	
Koczy (1953)	6×10^{-4} to 1.9×10^{-2}	Atlantic and Indian Oceans	Eq. (83): Silica flux from sedimentation rates divided by near-bottom silica gradients.
Bodvarsson et al. (1967)	0.04 to 0.19	N.E. Pacific	Eq. (83): Heat flux divided by near-bottom temperature gradients.
Ichiye (1966)	0.12	N. Atlantic	Near-bottom particle distribution.

DEEP WATER VALUES

Reference	K_z	Region	Method
Wust (1961)	10 to 50 cm^2/sec	Atlantic	Dynamic calculations
Koczy (1956)	2 to 30	World Ocean	Radium distribution
Munk (1966)	1.3	Pacific	Vertical advection/diffusion model

and (2) values (K_z < 1) considerably less than those in the overlying water column. It is significant that values of K_z calculated from equation (85) and from the near-bottom radon-222 distribution (Broecker et al., 1967, 1968) fall in the first group. These values of K_z are independent of any estimate of the radon flux across the sea-floor, and depend only on the measured radon profile.

Wimbush and Munk (1970) discussed the physical structure of the "benthic boundary layer," the seawater layer which extends a few meters above the sea-floor. They showed that the boundary layer can be divided into two regions: (1) a viscous sub-layer in which molecular diffusion is important, and (2) a logarithmic layer above the viscous sub-layer, in which the horizontal velocity increases as the logarithm of the distance above the bottom. Near-bottom current and temperature measurements in the deep-sea showed that the viscous sub-layer extended less than 3.5 cm above the sea-floor. Wimbush and Munk (1970) showed that the concentration gradient across the viscous sub-layer was a considerable fraction of the gradient across the entire boundary. Current measurements in the logarithmic layer showed that it extended between 1 and 1.5 m above the bottom. Diffusion in the logarithmic layer was turbulent, and the eddy diffusion coefficient at the top of the logarithmic layer was nearly equal to the eddy diffusion coefficient in the overlying water column.

The theoretical and experimental studies of Wimbush and Munk (1970) suggest that the value of the vertical eddy diffusion coefficient at heights greater than 1 m above the bottom is practically equal to its value in the overlying water column. Therefore, K_z is probably greater than 1 cm^2/sec at heights of more than 1 m above the bottom (Table 19).

Present Work

Near-bottom chemistry was measured on three cruises: YALOC-69 to the Eastern Tropical Pacific, Y6908F off the Oregon Coast, and TT-46 to the Caribbean Sea and North Atlantic Ocean. Station positions are shown in Figures 4 and 7, Chapter III. The emphasis during these cruises was on chemical gradients in deep-water, and 39 stations were taken at depths greater than 2000 m. Table 20 gives a brief summary of the sampling depths and parameters measured during each cruise. Near-bottom samples were taken with the special samplers described in Chapter II. The nominal sampling heights were 0.6, 1.1, 3.1, and 6.1 meters above the bottom. The exact heights varied between stations. Samples at greater distances above the bottom were taken with conventional water bottles.

A detailed description of the bottom samplers, of the technique of sample collection, and of analytical procedures is given in Chapter II. The near-bottom data from these cruises is listed in Appendix 2.

Table 20. Summary of near-bottom chemical measurements.

Cruise	Parameters measured	Stations	Bottom-bottle heights above bottom (m)	Conventional water bottle heights above bottom (m)
YALOC-69	S‰, O_2, pH, Si, Talk, PO_4, NO_3	83-127	0.6, 1.1, 3.1, 6.1	15, 30, 100, 300
		38-80	0.6, 1.2, 6.3, 15.0	30, 50, 100, 300
Y6908F	S‰, pH, Talk, PO_4, Si	C-1,7	0.5, 1.1, 3.1, 6.1	15, 30, 50, 100
TT-46	S‰, O_2, pH, Si, Talk, PO_4, NO_3, NO_2	62	0.5, 1, 2, 3	5, 25, 65, 125
		65, 67	0.5, 1, 2, 4	10, 30, 70, 170

Examination of the data in Appendix 2 shows that there are no obvious near-bottom gradients, with the possible exception of phosphate, and of station C-4 (Y6908F).

The near-bottom data were tested by the following statistical procedure to determine if near-bottom gradients occurred which were obscured by analytical or sampling errors. At each station, water samples from conventional water bottles were taken at three heights within 100 m of the bottom. There were no obvious vertical gradients in these samples, and the average concentration in the three deepest conventional water bottles was taken as the "background" concentration. The concentration in the 0.6 m sample was subtracted from the

"background" value. This procedure yielded a series of concentration differences, one for each station. The differences were averaged, and the Student-t test (Freund, 1962, page 263) was used to determine if the average was significantly different from zero.

This procedure is based on two assumptions. The first is that the same process is responsible for near-bottom gradients everywhere in the deep-sea. In other words, it is assumed that near-bottom gradients will always have the same sign. For instance, oxygen is consumed in the sediments, and the oxygen concentration should decrease near the bottom.

The second assumption concerns the statistical distribution of the concentration differences between the "background" sample and the 0.6 m sample. For large samples ($n \geq 30$), the Central Limit Theorem (Freund, 1962, p. 187) states that the distribution of the mean of the concentration differences can be approximated by the normal distribution, regardless of the distribution of the individual differences. The Student-t distribution is equivalent to the normal distribution for large samples (Freund, 1962, p. 202). Therefore, for large samples ($n \geq 30$), the Student-t distribution can be applied to the mean concentration difference, regardless of the actual distribution of the individual differences. Phosphate, silicate, and pH were measured at more than 30 bottom stations. However, less than 30 stations are available for salinity, oxygen, alkalinity, and nitrate. The Central Limit Theorem

does not apply to small samples (n < 30), and to apply the Student-t test to the salinity, oxygen, alkalinity, and nitrate data it must be assumed that the individual concentration differences have a normal distribution.

In the following analysis, a positive concentration difference means that the concentration decreases toward the bottom.

Salinity

Salinity measurements at 0.6 m were made at 21 stations. Only 3 stations were found in which the salinity at 0.6 m differed by more than 0.003‰ from the "background" salinity. The average difference of all 21 stations was -0.0004‰. This difference is not significant (t = -0.31, degrees of freedom = 20) at the 90% confidence level (see Table 21).

Oxygen

Oxygen was measured at 0.6 m at 27 stations. Only those samples analyzed by Carpenter's (1965, see Chapter II) method were used in the following statistical analysis, samples analyzed by the conventional Winkler method were not used. At five stations the difference in concentration between the conventional water samples and the 0.6 m sample exceeded 5 µg-at/kg. The average difference was +0.6 µg-at/kg. This difference is not significant (t = 0.77, df = 26) at the

Table 21. Statistical analysis of near-bottom chemical data for depths greater than 2000 m. A positive difference means that the concentration decreases near the bottom.

Parameter	No. of stations	Mean difference between "background" concentration and concentration at 0.6 m	Standard deviation of the individual differences about the mean	Range of individual differences	Level of significance 90% 95% 99%
Salinity	21	-0.0004‰	0.0057‰	-0.017 to +0.014‰	no
Oxygen	27	0.6 µg-at/kg	4.3 µg-at/kg	-9 to +8 µg-at/kg	no
Silicate	35	0.6 µmole/kg	2.3 µmole/kg	-3 to +12 µmole/kg	no
Nitrate	10	0.4 µmole/kg	0.8 µmole/kg	-1 to +1 µmole/kg	no
Phosphate	32	0.014 µmole/kg	0.089 µmole/kg	-0.21 to +0.20 µmole/kg	no
Alkalinity	24	-0.0023 meq/kg	0.0055 meq/kg	-0.017 to +0.006 meq/kg	yes yes no
pH(25°C)	34	-0.0034 pH	0.0058 pH	-0.022 to +0.004 pH	yes yes yes

90% confidence level (Table 21).

Silicate

Near-bottom (0.6 m) silicate was measured at 35 stations. The maximum difference between the "background" concentration and the 0.6 m sample was 12 μmole/kg (station C-4, Y6908F), only two stations had differences which exceeded 2 μmole/kg. The average difference, +0.6 μmole/kg (t = 1.52, df = 34), is not significant at the 90% confidence level (Table 21).

Nitrate

Nitrate at 0.6 m was measured at 10 stations. The maximum difference between the "background" concentration and the 0.6 m sample was 1 μmole/kg. The average difference, +0.4 μmole/kg (t = 1.51, df = 9) is not significant at the 90% confidence level (Table 21).

Alkalinity

Alkalinity at 0.6 m was measured at 24 stations. The maximum difference between the "background" concentration and the 0.6 m concentration was -0.017 meq/kg (station C-4, Y6908F). Only three stations had differences which exceeded 0.008 meq/kg. However, the average difference, -0.0023 meq/kg (t = -2.08, df = 23), is significant

at the 95% confidence level.

Since the near-bottom and the "background" alkalinity samples were collected in different types of water bottles, and were stored in different types of containers (see Chapter II), the observed difference may be due to systematic sampling errors. To check on this possibility two further t-tests were made.

The alkalinity in the 0.6 m sample was subtracted from the alkalinity in the uppermost bottom bottle (usually at 6 m). Comparing samples from two bottom bottles should minimize sampling errors. The average difference in this case, -0.0032 meq/kg (t = -2.39, df = 21), is significant at the 95% confidence level.

As a second check, the alkalinity from the uppermost bottom bottle was subtracted from the "background" concentration. If there are systematic sampling errors, the average difference in this case should be significantly different from zero. The average difference, +0.0013 meq/kg (t = 1.64, df = 25), is not significantly different from zero at the 90% confidence level.

pH

pH measurements at 0.6 m were made at 34 stations. The maximum difference between the "background" concentration and the 0.6 m sample was -0.022 pH. The difference was greater than 0.010 pH at three stations. The average difference, -0.0034 pH (t = -3.42, df =

33), is significant at the 99% level.

The near-bottom samples and the "background" pH samples were collected in different types of water samplers, and the observed pH difference may be due to systematic sampling errors. As a check on this possibility, two further t-tests were made.

The pH in the 0.6 m sample was subtracted from the pH in the uppermost bottom bottle. Comparing two bottom bottles should minimize sampling errors. The average difference in this case, -0.0032 pH (t = -3.25, df = 31), is significant at the 99% confidence level.

As a second check, the pH in the uppermost bottom bottle was subtracted from the "background" concentration. If there are systematic sampling errors, the average difference should be significantly different from zero. The average difference, +0.00009 pH (t = +0.14, df = 34), is not significant at the 90% confidence level.

Phosphate

Near-bottom (0.6 m) phosphate was measured at 32 stations. Analysis of the near-bottom phosphate data is complicated by the fact that phosphates from bottom-bottles during YALOC-69 appear to be systematically higher than phosphates measured in the NIO bottles. This problem is discussed in Chapter II.

Because of the apparent systematic error in the YALOC-69 bottom bottle phosphate data, the NIO data was not used in the following

statistical analysis. At each station the concentration in the 0.6 m

bottle was subtracted from the concentration of the uppermost bottom

bottle. The average difference, +0.014 μmole/kg (t = 0.84, df = 29),

is not significant at the 90% confidence level.

Discussion

The characteristic feature of the present study is the lack of

measurable near-bottom gradients in deep water at heights of more

than 0.6 m above the sea-floor. A statistically significant near-

bottom increase in pH and alkalinity was found. However, the average

increases are very small and could result from undetected analytical

or sampling errors.

The results of this study agree with the near-bottom measure-

ments of Brouradel and Fage (1953, 1954, 1955), Fage (1954),

Brouradel and Vernet (1958), Rittenberg, Emery, and Orr (1955), and

Schink (1968). None of these authors found any gradients which

extended more than 0.5 m above the sea-floor.

Schink (1968) used equation (83) to calculate the possible

magnitude of near-bottom silica gradients from estimated values of

K_z and of the silica flux across the sea-floor. This calculation could

be made for each of the measured parameters if their fluxes were

known. Unfortunately, silica and alkalinity are the only parameters

for which the flux is even approximately known. Calculated near-

bottom silica and alkalinity gradients are listed in Table 22.. The calculated gradients are small and would have to extend at least 100 m above the bottom for the concentration difference to be measurable.

Station C-4 (Y6908F) is the only station at which near-bottom gradients appear to exist. At this station alkalinity increased and silicate decreased in the 0.5 m sample. Phosphate increased in both the 1.1 and 0.5 m samples. Salinity and pH did not change. It may be significant that station C-4 was taken in an almost completely enclosed basin, approximately 20 miles wide and 600 to 1000 m deep.

Table 22. Near-bottom silica and alkalinity gradients calculated from equation (83). The silica flux is from Schink (1968), the alkalinity flux is from Pytkowicz (1968). The estimated value for K_z is from Broecker et al. (1967, 1968), the error limits on K_z were selected to include the range of values they report (see Table 19).

Parameter	K_z	Flux	(dC/dz)
Silica	$5 \text{ cm}^2/\text{sec}$ (± factor of 5)	$2 \cdot 10^{-8} \, \mu\text{mole}/\text{cm}^2/\text{sec}$ (± factor of 5)	$4 \cdot 10^{-4} \, \mu\text{mole}/l/m$ (± factor of 25)
Alkalinity	$5 \text{ cm}^2/\text{sec}$ (± factor of 5)	$2.5 \cdot 10^{-9} \, \text{meq}/\text{cm}^2/\text{sec}$ (± factor of 5)	$5 \cdot 10^{-5} \, \text{meq}/l/m$ (± factor of 25)

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APPENDICES

APPENDIX 1

Program Data. A glossary and a sample printout of hydrographic data at station 70 (YALOC-69) are listed at the end of the program.

```
      PROGRAM DATA
      DIMENSION BUF(20),B(80),ZZ(4),SS(4),ATT(4),ATSQR(4),
     1ATCU(4),ATFOR(4),DPK1C(4),DPK2C(4),DPKB(4),
     1AK1C(4),AK2C(4),AKB(4),CX(2),A(2),XN(2),XD(2),BA(2),F(2),
     1C(2),XM(2),XE(2),E(2)
      INTEGER BUF
      CHARACTER B
      EQUIVALENCE (BUF,B)
    1 IF(EOD(60)) GO TO 999
      READ(60,101)BUF
      IF(EOF(60)) GO TO 999
      IF(B(25).EQ.60B)3,2
    2 PRINT 108
      PRINT 102,BUF(1),(B(I),I=77,80),(B(I),I=5,8),B(9),
     1B(16),(B(I),I=10,14),B(15),B(17),(B(I),I=19,28)
      PRINT 103
      GO TO 1
    3 DECODE(56,104,BUF(7))Z,T,S,O2C,O2,PO4,PH,ALK,XNO3,SIO2
      CL=S/1.80655
      D25=.9972+(.753-.00045*S)*1.0E-03*S
      TALK=ALK/D25
      SA=(TALK/CL)*1.0E+04
      IF(B(67).EQ.60E)70,71
   70 XNO3=0.
   71 CONTINUE
      IF(B(50).EQ.60B)96,98
   96 O2C=0.0
   98 IF(B(73).EQ.60B)97,200
   97 SIO2=0.0
  200 IF(B(36).EQ.60B.AND.B(42).EQ.60B)201,30
  201 D25=1.023
      TALK=ALK/D25
      T=PT=AOU=AOUN=FO2=PPO4=PH25C=PHTP=CO2=HCO3=CO3=PSC=
     1PSA=AIP=PCO2=ETCO2=SIGMA=SA=TCO2=ATCO2=CTCO2=0.0
      GO TO 29
   30 IF(B(50).NE.60B.AND.B(36).NE.60B)31,32
   31 CT=T
      IF(B(36).EQ.60B)32,99
   32 IF(B(36).EQ.60B.AND.B(53).EQ.60B)33,99
   33 T=CT
      GO TO 14
   99 IF(B(36).EQ.60B)13,14
   13 T=PT=AOU=AOUN=FO2=PPO4=PH25C=PHTP=CO2=HCO3=CO3=
     1PSC=PSA=AIP=PCO2=ETCO2=SIGMA=0.0
      IF(B(42).EQ.60B)68,69
   68 SA=0.0
   69 GO TO 29
   14 AT=273.16+T
      ATSQ=AT*AT
      IF(B(42).EQ.60B)15,16
   15 S=PT=AOU=AOUN=PO2=PPO4=PH25C=PHTP=SA=TCO2=CO2=HCO3=CO3=
     1PSC=PSA=AIP=PCO2=ATCO2=CTCO2=ETCO2=SIGMA=0.0
      D25=1.023
      TALK=ALK/D25
      GO TO 29
   16 D=1.0267+2.55E-06*Z
      P=0.9807*Z*D
      PAT=AT+1.60E-05*P-1.014E-05*P*T+1.27E-07*P*T*T
     1-2.7E-09*P*T*T*T-1.322E-06*P*S+2.62E-08*P*S*T
     1-4.1E-09*P*S*S-9.14E-09*P*P+2.77E-10*P*P*T
```

```
      1-9.5E-13*P*P*T*T+1.557E-13*P*P*P
       PATSQ=PAT*PAT
       PT=PAT-273.16
       IF(B(53).EQ.60E)17,18
   17  O2=AOU=PO2=PPO4=0.0
       GO TO 21
   18  VPLOW=.32161-1.159075E-03*PAT+.9017204*S-6.69094E-03*
      1PAT*S+1.244025E-05*PATSQ*S
       W=PATSQ-293700.
       Y=647.27-PAT
       VPO=10.**(5.4266514-2005.1/PAT+1.3869E-04*(W/PAT)*(10.**
      1(1.1965E-11*W*W)-1.)-.0044*10.**(-.0057148*Y**1.25))
       VP=VPO*760.
       VPS=VP-VPLOW
       BUNSEN=EXP((-58.3877+8580.79/PAT+23.8439*ALOG(PAT/100.))
      1+S*(-.034892+1.5568E-04*PAT-1.9387E-07*PATSQ))
       O2SOL=BUNSEN*1000.*.2094*(760.-VPS)/760.
       AOU=O2SOL-O2
       PO2=(O2/O2SOL)*100.
       IF(B(56).EQ.60B)19,20
   19  PO4=PPO4=0.0
       GO TO 21
   20  OXPO4=.3236*AOU
       PPO4=PO4-OXPO4
   21  IF(B(63).EQ.60B)22,23
   22  ALK=PH25C=PHTP=TALK=SA=TCO2=CO2=HCO3=CO3=PSC=PSA=
      1AIP=PCO2=ETCO2=ATCO2=CTCO2=0.0
       GO TO 28
   23  IF(B(60).EQ.60B)24,25
   24  PH=PH25C=PHTP=TCO2=CO2=HCO3=CO3=PSC=PSA=AIP=PCO2=
      1ETCO2=ATCO2=CTCO2=0.0
       GO TO 28
   25  ZZ(1)=ZZ(3)=ZZ(4)=0.0
       ZZ(2)=Z
       SS(1)=SS(2)=SS(4)=S
       SS(3)=34.68
       ATT(1)=ATT(3)=298.16
       ATT(2)=AT
       ATT(4)=PAT
       DO 59 I=1,4
       ATSQR(I)=ATT(I)*ATT(I)
       ATCU(I)=ATSQR(I)*ATT(I)
       ATFOR(I)=ATCU(I)*ATT(I)
       DPK1C(I)=.013+1.319E-04*ZZ(I)-3.061E-07*ZZ(I)*ATT(I)-
      1.161E-06*ATSQR(I)-.02E-08*ZZ(I)*ZZ(I)
       DPK2C(I)=-.015+.839E-04*ZZ(I)-1.908E-07*ZZ(I)*ATT(I)+
      1.182E-06*ATSQR(I)
       DPKB(I)=1.809E-04*ZZ(I)-4.515E-07*ZZ(I)*ATT(I)-.169E-08*
      1ZZ(I)*ZZ(I)+1.759E-14*ATSQR(I)*ZZ(I)*ZZ(I)
       AK1C(I)=(1.864498E-05-1.66822E-07*ATT(I)-1.57054E-08*
      1SS(I)+2.61641E-10*ATSQR(I)+1.08079E-12*ATCU(I)-2.556568E-15*
      1ATFOR(I)+9.124781E-11*SS(I)*ATT(I))*10.**DPK1C(I)
       AK2C(I)=(-1.7077053E-07+1.4195923E-09*ATT(I)-1.9141124E-10*
      1SS(I)-2.0317424E-12*ATSQR(I)-8.521135E-15*ATCU(I)+
      11.947788E-17*ATFOR(I)+7.2442747E-13*SS(I)*ATT(I))*
      110.**DPK2C(I)
       AKB(I)=(2.121302E-07-1.677761E-09*ATT(I)-1.67712E-10*
      1SS(I)+2.206332E-12*ATSQR(I)+9.77043E-15*ATCU(I)-
      12.10475E-17*ATFOR(I)+6.8943376E-13*SS(I)*ATT(I))*
      110.**DPKB(I)
```

```
   59 CONTINUE
      TTA=0.121*CL
      TTB=0.0219*CL
      PP=(0.32/10.**(9.849-2385.73/(ATT(4))-0.0152642*(ATT(4)
     1-273.16)+0.002131*SS(4)-0.00002131*(ATT(4)-273.16)*SS(4)
     1))*(1.-SS(4)/1000.)*((760.-VPS)/760.)
      C(1)=1.0E-8
      C(2)=0.9E-8
      DO 60 K=1,2
      XM(K)=C(K)*C(K)*C(K)*TTA/PP-C(K)*(AK1C(4)*AKB(4)+
     12.*AK1C(4)*AK2C(4))-2.*AK1C(4)*AK2C(4)*AKB(4)
      XE(K)=C(K)*C(K)*(AKB(4)*(TTA-TTB)/PP-AK1C(4))
      E(K)=XM(K)+XE(K)
   60 CONTINUE
   61 BB=C(1)-E(1)*((C(2)-C(1))/(E(2)-E(1)))
      BM=BB*BB*BB*TTA/PP-BB*(AK1C(4)*AKB(4)+2.*AK1C(4)*AK2C(4))
     1-2.*AK1C(4)*AK2C(4)*AKB(4)
      BE=BB*BB*(AKB(4)*(TTA-TTB)/PP-AK1C(4))
      EE=BM+BE
      C(1)=C(2)
      E(1)=E(2)
      C(2)=BB
      E(2)=EE
      IF(ABS(EE).LT.1.E-27) GO TO 26
      GO TO 61
   26 CONTINUE
      PFC=PP*(1+AK1C(4)/BB+AK1C(4)*AK2C(4)/(BB*BB))
      DTC=2.160-PFC*34.68/S
      SH=-PH
      X=10.**SH
      TCO2=((X*X+X*AK1C(1)+AK1C(1)*AK2C(1))/(X*AK1C(1)+2.*
     1AK1C(1)*AK2C(1)))*(TALK-(.0219*CL*AKB(1))/(X+AKB(1)))
      BCL=SS(3)/1.80655
      BK1=AK1C(3)
      BK2=AK2C(3)
      BKB=AKB(3)
      BTA=2.443
      BTCO2=(TCO2*(34.68/S))+(.5*(2.443-(TALK*34.68/S)))+DTC
      ATCO2=34.68*TCO2/S
      CTCO2=ATCO2+(.5*(2.443-(TALK*34.68/S)))
      ETCO2=CTCO2+DTC
      DO 27 I=1,2
      A(1)=1.E-9
      A(2)=4.E-9
      DO 90 J=1,2
      XN(J)=A(J)*A(J)+A(J)*BK1+BK1*BK2
      XD(J)=A(J)*BK1+2.*BK1*BK2
      BA(J)=(0.0219*BCL*BKB)/(A(J)+BKB)
      F(J)=BTCO2/(BTA-BA(J))-XN(J)/XD(J)
   90 CONTINUE
   95 AA=A(1)-F(1)*((A(2)-A(1))/(F(2)-F(1)))
      AN=AA*AA+AA*BK1+BK1*BK2
      AD=AA*BK1+2.*BK1*BK2
      ABA=(0.0219*BCL*BKB)/(AA+BKB)
      FF=BTCO2/(BTA-ABA)-(AN/AD)
      A(1)=A(2)
      F(1)=F(2)
      A(2)=AA
      F(2)=FF
      IF(ABS(FF).LT.1.E-5) GO TO 93
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            GO TO 95
     93  CX(I)=AA
         TCL=CL
         BK1=AK1C(2)
         BK2=AK2C(2)
         BKB=AKB(2)
         BTA=TALK
         BTCO2=TCO2
     97  CONTINUE
         CA=TALK-(AKB(2)*CL*.0219)/(CX(2)+AKB(2))
         CO2=(CA*CX(2)*CX(2))/(CX(2)*AK1C(2)+2.*AK1C(2)*AK2C(2))
         HCO3=(CA*CX(2))/(CX(2)+2.*AK2C(2))
         CO3=(CA*AK2C(2))/(CX(2)+2.*AK2C(2))
         AIP=.531*CL*CO3
         AKC=(1.95-.0176*T)*1.0E-02*S*10.**((.693-.00645*T)*
        11.0E-04*Z)
         AKA=(3.06-.0217*T)*1.E-02*S*10.**((.65-.066*T)*1.E-04*Z)
         PSC=AIP*100./AKC
         PSA=AIP*100./AKA
         PH25C=-ALOG 10(CX(1))
         PHTP=-ALOG 10(CX(2))
         IF(B(29).EQ.60R)80,81
     80  PPC=9.849-2385.73/(273.15+T)-0.0152642*T+0.002131*S
        1-0.00002131*T*S
         PCO2=(1000.*CO2*10.**(PPC))/(1.-S/1000.)
         GO TO 28
     81  PCO2=0.
     28  AOU=AOU*89.31/D25
         AOUN=AOU*34.68/S
         SIGMA=8.00969062E-02+7.97018644E-01*S+1.31710842E-04*S*S
        1-6.11831499E-08*S*S*S+5.88194023E-02*PT-3.25310441E-03*
        1S*PT+2.97971530E-06*PT*S*S-8.11465413E-03*PT*PT+
        13.89187483E-05*S*PT*PT+4.76600414E-05*PT*PT*PT
     29  O2=O2*89.31/D25
         O2C=O2C*89.31/D25
         PO4=PO4/D25
         PPO4=PPO4/D25
         SIO2=SIO2/D25
         XNO3=XNO3/D25
         PFR=320.*(760.-VPS)/760.
         PRINT 107,Z,B(32),T,PT,S,SIGMA,O2,AOU,PO2,PH,PHTP,TALK,
        1SA,TCO2,PH25C,AOUN,ETCO2,ATCO2,CTCO2,PSC,PSA,AIP,PCO2
         GO TO 1
    101  FORMAT(20A4)
    102  FORMAT(2X,A4,2X,4R1,4X,2R1,X,2R1,1H.,2R1,4X,3R1,X,
        12R1,1H.,2R1,4X,2(2R1,1H/),2R1,4X,4R1/)
    103  FORMAT(4X,1HZ,5X,1HT,5X,2HPT,5X,1HS,3X,5HSIGMA,3X,2HO2,2X,
        13HAOU,X,3HPO2,2X,4HPH25,2X,4HPHTP,3X,4HTALK,3X,2HSA,
        12X,4HTCO2,3X,5HPH25C,X,4HAOUN,X,5HTCO2-,2X,5HTCO2*,X,
        15HTCO2#,2X,3HPSC,X,3HPSA,3X,3HAIP,3X,4HPCO2/)
    104  FORMAT(3X,F4.0,X,F4.2,X,F5.3,5X,3F3.2,2F4.3,F3.1,F3.0)
    107  FORMAT(X,F5.0,R1,F6.2,F6.2,X,F6.3,X,F5.2,2X,F3.0,X,F4.0,
        1X,F3.0,2X,F5.3,X,F5.3,2X,F5.3,X,F4.0,X,F5.3,2X,F5.3,X,
        1F4.0,X,F5.3,2X,F5.3,X,F5.3,2X,F3.0,X,F3.0,2X,F5.3,2X,F3.0)
    108  FORMAT(/////)
    999  END
     C                  CHEMICAL DATA--YALOC 69
     C       ALL CONCENTRATIONS ARE PER KILOGRAM OF SEAWATER
     C          PT = POTENTIAL TEMPERATURE
     C          O2 = OXYGEN BY STANDARD METHOD, UG-AT/KG-SW
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C     O2C  = OXYGEN BY CARPENTER#S METHOD, UG-AT/KG-SW
C     AOU  = APPARENT OXYGEN UTILIZATION FOR A WET ATMOSPHERE
C            CALCULATED AT THE POTENTIAL TEMPERATURE OF THE
C            SAMPLE, UG-AT/KG-SW.
C    AOUN  = AOU NORMALIZED TO S=34.68
C     PO2  = PER CENT OXYGEN SATURATION FOR A WET ATMOSPHERE
C            CALCULATED AT THE POTENTIAL TEMPERATURE OF THE
C            SAMPLE.
C     PO4  = REACTIVE PHOSPHATE, UMOLES/KG-SW
C    PPO4  = PREFORMED PHOSPHATE, UMOLES/KG-SW
C    P125  = PH MEASURED AT 25C
C    PH25C = MEASURED PH CORRECTED FOR TALK=2.443, S=34.68,
C            AND PREFORMED CO2=2.160
C    PHTP  = PH AT IN SITU TEMPERATURE AND PRESSURE
C    TALK  = TOTAL ALKALINITY, MEQ/KG-SW
C      SA  = SPECIFIC ALKALINITY, TALK/CL
C    TCO2  = TOTAL INORGANIC CARBON, MMOLES/KG-SW
C    TCO2- = TOTAL INORGANIC CARBON NORMALIZED TO SALINITY
C            34.68, TO AN ALKALINITY 2.443, AND TO A PREFORMED
C            CO2 = 2.160.
C    TCO2* = TOTAL INORGANIC CARBON NORMALIZED TO SALINITY
C            34.68.
C    TCO2# = TOTAL INORGANIC CARBON NORMALIZED TO SALINITY
C            34.68 AND TO AN ALKALINITY 2.443.
C    PCO2  = PARTIAL PRESSURE OF CARBON DIOXIDE, ATM*10E+6
C     CO2  = MOLECULAR CARBON DIOXIDE, MMOLES/KG-SW
C    HCO3  = BICARBONATE ION, MMOLES/KG-SW
C     CO3  = CARBONATE ION, MMOLES/KG-SW
C     PSC  = PER CENT SATURATION OF CALCITE
C     PSA  = PER CENT SATURATION OF ARAGONITE
C     AIP  = APPARENT ION PRODUCT OF CALCIUM CARBONATE
C      SI  = REACTIVE SILICATE, UMOLES/KG-SW
C     NO3  = INORGANIC NITRATE (PLUS NITRITE), UMOLES/KG-SW
C   SIGMA  = SIGMA-T AT THE POTENTIAL TEMPERATURE.
C   PREFORMED CARBON DIOXIDE IS CALCULATED FOR A WET
C      ATMOSPHERE.  PCO2 = 0.32(760.-VPS)/760.
C
C      TO CALCULATE CARBONATE SPECIATION, THE BOTTOM BOTTLES
C      WERE ASSIGNED THE DEEPEST MEASURED TEMPERATURE
C
C                    REFERENCES
C
C   OXYGEN SOLUBILITY(BUNSEN):  WEISS, 1970.  DSR 17:721-735.
C   VAPOR PRESSURE OF SEAWATER(VPS):  GREEN AND CARRITT, 1967.
C      JMR 25:140-147.
C   POTENTIAL TEMPERATURE(PAT):  FOFONOFF, 1962.  THE SEA, PAGE 17.
C   SIGMA-T:  COX, MCCARTNEY, AND CULKIN, 1970.  DSR 17:679-689.
C   APPARENT CONSTANTS, CARBONIC AND BORIC ACIDS(AK1C, AK2C,
C      AKB):  LYMAN, 1956.  PH.D. THESIS.
C   PRESSURE COEFFICIENTS FOR APPARENT CONSTANTS(DPK1C, DPK2C,
C      DPKB):  CULBERSON AND PYTKOWICZ, 1968.  LSO 13:403-417.
C   CALCITE AND ARAGONITE SOLUBILITY PRODUCTS(AKC, AKA):
C      MACINTYRE, 1965.  FISH. RES. BD. CANADA, MANUSCRIPT
C      REPRINT SERIES 200, 153 PAGES.
C   PRESSURE COEFFICIENTS FOR SOLUBILITY PRODUCTS(AKC, AKA):
C      HAWLEY AND PYTKOWICZ, 1969.  GEOCHIM. COSMOCHIM. ACTA
C      33:1557-1561.
C   CARBON DIOXIDE SOLUBILITY COEFFICIENT(PPC):  DERIVED FROM THE
C      PURE WATER DATA OF HARNED AND DAVIS, 1943.  JACS 33:2020,
C      AND THE SODIUM CHLORIDE DATA OF BOHR, 1899.  ANN. PHYS.,
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OS3 FORTRAN   VERSION 3.0   DATA        04/15/72  1647
    C     LPZ. 68:500.
    C   MEAN DENSITY OF SEAWATER COLUMN ABOVE SAMPLING DEPTH(D):
    C     BIALEK, 1966.  HANDBOOK OF OCEANOGRAPHIC TABLES.  SPECIAL
    C     PUBLICATION 68, U.S.N. OCEANOGRAPHIC OFFICE, PAGE 62.


 NO ERRORS FOR DATA
 LENGTH OF SUBPROGRAM        04052
 RUN
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Z	T	PT	S	SIGMA	O2	AOU	PO2	PH25	PHTP	TALK	SA	TCO2	PH25C	AOUN	TCO2⁻	TCO2*	TCO2≠	PSC	PSA	AIP	PCO2
0	21.07	21.07	34.925	24.44	465	-23	105	8.161	8.207	2.319	1199	2.026	7.972	-23	2.244	2.011	2.082	387	235	2.135	361
10	21.02	21.02	34.922	24.45	463	-20	104	8.154	8.200	2.317	1199	2.028	7.966	-20	2.247	2.014	2.085	381	232	2.105	367
20	20.10	20.10	34.912	24.69	299	152	66	8.020	8.074	2.310	1195	2.093	7.833	151	2.307	2.080	2.154	291	178	1.627	510
30	19.12	19.11	35.097	25.09	252	206	55	7.982	8.046	2.321	1195	2.121	7.808	203	2.317	2.096	2.171	269	165	1.528	545
40	18.02	18.01	35.048	25.33	232	236	50	7.936	9.011	2.317	1194	2.139	7.783	233	2.328	2.116	2.192	240	149	1.383	590
49	17.45	17.44	35.027	25.46	215	258	45	7.915	7.995	2.317	1195	2.148	7.770	256	2.333	2.127	2.202	228	142	1.322	610
75	16.25	16.24	35.088	25.79	185	299	38	7.871	7.961	2.314	1191	2.164	7.756	296	2.338	2.139	2.217	204	128	1.205	652
98	15.04	15.02	35.079	26.06	168	328	34	7.859	7.960	2.321	1196	2.177	7.760	325	2.337	2.152	2.226	196	123	1.175	644
147	14.11	14.09	34.989	26.19	114	392	23	7.777	7.882	2.307	1191	2.196	7.707	388	2.357	2.177	2.255	160	102	.972	0
197	13.45	13.42	34.953	26.31	85	428	17	7.716	7.822	2.314	1196	2.226	7.649	425	2.379	2.209	2.282	138	89	.848	0
298	12.17	12.13	34.876	26.51	24	503	5	7.629	7.736	2.310	1197	2.254	7.592	500	2.400	2.241	2.314	109	71	.688	0
398	9.20	9.15	34.703	26.90	17	546	3	7.527	7.647	2.324	1210	2.303	7.527	545	2.423	2.302	2.362	81	53	.530	0
599	7.31	7.25	34.614	27.12	45	544	8	7.523	7.651	2.336	1219	2.317	7.540	545	2.418	2.321	2.373	75	50	.518	0
799	5.58	5.51	34.566	27.31	103	510	17	7.550	7.689	2.350	1228	2.322	7.580	512	2.404	2.329	2.372	76	51	.547	0
998	4.70	4.62	34.573	27.42	122	505	20	7.569	7.711	2.370	1239	2.336	7.589	506	2.401	2.343	2.376	76	52	.573	0
1199	3.74	3.65	34.583	27.53	150	492	23	7.585	7.730	2.389	1248	2.348	7.600	493	2.397	2.355	2.379	76	52	.595	0
1446*	3.23	3.12	34.616	27.60	166	484	26	7.610	7.754	2.410	1258	2.361	7.609	485	2.393	2.365	2.379	77	53	.634	0
1493	3.14	3.03	34.613	27.61	167	485	26	7.603	7.744	2.410	1258	2.363	7.604	486	2.395	2.368	2.382	75	52	.622	0
1943*	2.35	2.21	34.649	27.71	206	459	31	7.634	7.770	2.430	1267	2.371	7.628	459	2.386	2.373	2.379	74	51	.667	0
1998	2.29	2.14	34.646	27.71	208	459	31	7.648	7.784	2.432	1268	2.368	7.641	459	2.382	2.371	2.375	76	53	.690	0
2190*	2.16	2.00	34.660	27.73	222	447	33	7.651	7.781	2.436	1269	2.371	7.643	447	2.381	2.372	2.375	74	51	.693	0
2439*	1.92	1.74	34.672	27.76	247	426	37	7.684	7.811	2.443	1273	2.366	7.672	426	2.370	2.367	2.366	77	53	.748	0
2687*	1.93	1.63	34.681	27.78	262	413	39	7.690	7.809	2.444	1273	2.365	7.680	413	2.367	2.365	2.364	75	52	.755	0
2936*	1.92	1.60	34.684	27.78	269	406	40	7.692	7.801	2.444	1273	2.364	7.683	406	2.366	2.364	2.363	72	50	.755	0
3183*	1.83	1.58	34.682	27.78	268	408	40	7.684	7.782	2.449	1276	2.372	7.669	408	2.372	2.372	2.369	67	48	.738	0
3432*	1.36	1.54	34.683	27.78	270	406	40	7.702	7.792	2.441	1272	2.358	7.697	406	2.361	2.357	2.358	67	48	.765	0
3706*	1.94	1.53	34.684	27.79	272	404	40	7.699	7.777	2.449	1276	2.366	7.685	404	2.366	2.366	2.363	64	46	.757	0
3730*	1.36	1.55	34.683	27.78	272	404	40	7.692	7.768	2.443	1273	2.363	7.685	404	2.366	2.363	2.363	62	45	.742	0
3754*	1.36	1.55	34.684	27.79	271	405	40	7.701	7.777	2.444	1273	2.361	7.693	405	2.363	2.360	2.360	63	46	.759	0

APPENDIX 2

Near-bottom Chemical Data YALOC-69

Height above bottom (m)	Salinity (‰)	Oxygen (µg-at/kg)	pH(25°)	Alkalinity (meq/kg)	Silicate (µM/kg)	Phosphate (µM/kg)	Nitrate (µM/kg)	Nitrite (µM/kg)
Station 38	02°05.0'N	089°29.3'W	30/01/69	2272 m.				
99			7.649					
50			.649					
25			.656					
15.0			.646					
6.3			.651					
1.2			.661					
0.6			.656					
Station 61	01°09.0'S	085°20.9'W	07/02/69	2289 m.				
99			7.656		144	2.71		
49			.655		145	.67		
24			.658		145	.70		
15.0			- - - -		- - -	- - - -		
6.3			.666		146	.86		
1.2			.661		146	.64		
0.6			.666		145	.66		

Height above bottom (m)	Salinity (‰)	Oxygen (μg-at/kg)	pH(25°)	Alkalinity (meq/kg)	Silicate (μM/kg)	Phosphate (μM/kg)	Nitrate (μM/kg)	Nitrite (μM/kg)
Station 68	01°07.0'S	081°21.8'W	09/02/69	2989 m.				
98			7.694		146	2.61		
50		265	.695		148	.66		
26		263	.699		149	.99		
15.0		264	.702		148	.77		
6.3		264	.697		148	.80		
1.2		265	.699		147	.85		
0.6		267	.695		148	.65		
Station 69	01°56.8'S	081°32.1'W	10/02/69	2982 m.				
100			7.690		146	2.69		
50		268	.699		146	.62		
25		267	.702		146	.68		
15.0		272	.695		146	.63		
6.3		272	.690		146	.50		
1.2		272	.685		146	.61		
0.6		269	.701		146	.59		
Station 70	04°00.0'S	082°00.0'W	14/02/69	3784 m.				
78			7.699		147	2.72		
54			.692		146	.61		
30		268	.701		147	.62		
15.0		269	.694		147	.64		
6.3		268	.707		147	.57		
1.2		268	.702		146	.59		
0.6		267	.706		146	.61		

Height above bottom (m)	Salinity (‰)	Oxygen (µg-at/kg)	pH(25°)	Alkalinity (meq/kg)	Silicate (µM/kg)	Phosphate (µM/kg)	Nitrate (µM/kg)	Nitrite (µM/kg)
Station 71	00° 04.2'N	086° 29.0'W		16/02/69	2763 m.			
100			7.661		151			
50		220	.668		151			
26		221	.668		150			
15.0		223	.663		151			
6.3		221	.670		151			
1.2		222	.661		151			
0.6		218	.672		149			
Station 75	03° 28.0'N	089° 43.0'W		18/02/69	2186 m.			
100				2.429	145			
50				.435	147			
25				.440	148			
15.0				.444	146			
6.3				.442	147			
1.2				.444	146			
0.6				.438	146			
Station 76	01° 00.1'N	092° 00.0'W		19/02/69	2353 m.			
100			7.663	2.429	146	2.84		
51		238	.655	.430	146	2.71		
26		238	.653	.430	146	2.81		
15.0		242	.666	.436	145	2.65		
6.3		239	.665	.428	146	2.72		
1.2		239	.656	.436	146	3.00		
0.6		239	.661	.436	146	2.86		

Height above bottom (m)	Salinity (‰)	Oxygen (μg-at/kg)	pH(25°)	Alkalinity (meq/kg)	Silicate (μM/kg)	Phosphate (μM/kg)	Nitrate (μM/kg)	Nitrite (μM/kg)
Station 80	01°00.0'S	092°00.5'W	20/02/69	3492 m.				
99			7.689		149	2.63		
48		267	.692		150	.60		
24		267	.694		148	.73		
15.0		262	.687		149	.67		
6.3		264	.687		149	.67		
1.2		261	.692		148	.66		
0.6		262	.697		149	.55		
Station 83	04°00.0'S	092°00.6'W	21/02/69	3765 m.				
51			7.695		143	2.85		
30		276	.701		144	.64		
15		276	.695		143	.71		
6.1		273	.694		143	.68		
3.1		272	.694		142	.72		
1.2		272	.699		143	.65		
0.6		273	.695		143	.69		
Station 84	04°00.0'S	091°40.0'W	22/02/69	3730 m.				
51			7.695		142	2.61		
31		275	.690		143	.53		
16		273	.699		142	.56		
6.1		278	.695		142	.56		
3.1		276	.702		143	.55		
1.2		277	.704		142	.57		
0.6		283	.706		145	----		

Height above bottom (m)	Salinity (‰)	Oxygen (μg-at/kg)	pH(25°)	Alkalinity (meq/kg)	Silicate (μM/kg)	Phosphate (μM/kg)	Nitrate (μM/kg)	Nitrite (μM/kg)
Station 86	02°00.5'S	091°40.0'W		23/02/69	3242 m.			
103			7.687		149	2.65		
34			.689		149	.61		
19		268	.690		148	.65		
6.1		270	.685		147	.73		
3.1		271	.687		146	.66		
1.2		271	.690		148	.65		
0.6		271	.685		147	.68		
Station 97	00°30.0'N	091°39..8'W		25/02/69	2762 m.			
105			7.666		148	2.69		
36		258	.672		147	.62		
21		---	.666		148	.68		
6.1		256	.677		149	.73		
3.1		255	.673		148	.66		
1.2		255	.673		149	.61		
0.6		255	.672		149	.76		
Station 104	02°11.0'S	081°29.0'W		04/03/69	3861 m.			
99	34.686		7.695	2.441	145	2.70		
28	.685	279	.692	.437	145	.54		
13	.686	279	.687	.441	145	.70		
6.1	.689	280	.701	.441	143	.70		
3.1	.688	279	.699	.438	144	.64		
1.2	.687	280	.702	.437	145	.71		
0.6	.686	279	.713	.436	143	.60		

Height above bottom (m)	Salinity (‰)	Oxygen (μg-at/kg)	pH(25°)	Alkalinity (meq/kg)	Silicate (μM/kg)	Phosphate (μM/kg)	Nitrate (μM/kg)	Nitrite (μM/kg)
Station 105	00°06.0'N	084°03.7'W		09/03/69	3408 m.			
98	34.671			2.445	153	2.68		
28	.671	224		.446	152	.64		
13	.672	224		.446	152	.65		
6.1	.673	216		.444	152	.80		
3.1	.671	216		.444	152	.83		
1.2	.671	218		.448	152	.69		
0.6	.672	217		.444	152	.69		
Station 107	04°47.1'N	088°26.5'W		11/03/69	2711 m.			
97	34.671		7.665	2.440	155	2.71		
29	.672	230	.666	.444	155	.68		
14	.671	230	.668	.442	154	.73		
6.1	.670	230	.668	.437	155	.79		
3.1	.669	228	.663	.438	154	.89		
1.2	---	---	---	---	---	---		
0.6	.669	227	.663	.450	154	.80		
Station 108	04°06.3'N	085°00.1'W		13/03/69	3381 m.			
49	34.669		7.651	2.448	150	2.84		
29	.668	214	.653	.448	150	.81		
16	.669	214	.651	.450	151	.86		
6.1	.668	223	.656	.446	150	.85		
3.1	.668	221	.656	.448	150	.77		
1.2	.667	219	.656	.453	150	.79		
0.6	---	219	.661	---	149	.83		

Height above bottom (m)	Salinity (‰)	Oxygen (μg-at/kg)	pH(25°)	Alkalinity (meq/kg)	Silicate (μM/kg)	Phosphate (μM/kg)	Nitrate (μM/kg)	Nitrite (μM/kg)
Station 109	02°05.7'N	082°57.8'W		14/03/69	3710 m.			
97	34.676		7.668	2.450	147	2.65		
28	.674		.668	.444	147	.66		
13	.675	232	.666	.444	146	.67		
6.1	---	237	.670	.444	144	.73		
3.1	.674	234	.673	.440	145	.65		
1.2	.673	234	.670	.439	145	.60		
0.6	.674	231	.677	.440	146	.66		
Station 110	00°12.0'S	081°05.2'W		16/03/69	3181 m.			
101	34.683		7.690	2.442	142	2.60		
30	.684	265	.690	.442	142	.53		
16	.684	266	.692	.442	142	.64		
6.1	.684	265	.690	.442	142	.71		
3.1	.685	266	.694	.442	142	.67		
1.2	.686	263	.690	.440	142	.63		
0.6	.686	263	.690	.446	142	.63		
Station 111	05°29.7'N	081°13.3'W		22/03/69	3732 m.			
80	34.674		7.670	2.445	147	2.90	38	
30	.671	222	.670	.447	147	.81	38	
15	.671	---	.668	.445	147	.92	38	
6.1	---	219	.666	---	149	.92	38	
3.1	.671	218	.668	.447	148	.86	38	
1.2	.670	219	.668	.452	147	.87	37	
0.6	.671	218	.675	.451	147	.89	37	

Height above bottom (m)	Salinity (‰)	Oxygen (μg-at/kg)	pH(25°)	Alkalinity (meq/kg)	Silicate (μM/kg)	Phosphate (μM/kg)	Nitrate (μM/kg)	Nitrite (μM/kg)
Station 112	03°24.0'N	079°00.0'W	23/03/69	3827 m.				
68	34.676		7.684	2.440	146	2.59	39	
28	.675	243	.685	.437	145	.64	37	
13	.675	244	.680	.440	144	.68	38	
6.1	.675	240	.684	.435	145	.71	38	
3.1	.677	243	.682	.437	146	.71	38	
1.2	.675	239	.682	.442	144	.66	37	
0.6	---	---	---	---	---	---	--	
Station 114	06°43.0'N	079°45.5'W	25/03/69	3321 m.				
124	34.674		7.672	2.446		2.67		
30	.675	227	.668	.456	149	.66		
15	.674	225	.663	.452	148	.83		
6.1	.675	228	.661	.456	149	.71		
3.1	.673	227	.661	.458	149	.67		
1.2	.679	227	.661	.458	150	.73		
0.6	.675	229	.665	.460	150	.88		
Station 115	10°27.5'N	089°56.5'W	03/04/69	3847 m				
99	34.675		7.675	2.451	148	2.74	38	
29	.675	238	.675	.446	149	.72	30	
15	.676	238	.677	.451	150	.68	38	
6.1	.674	244	.672	.445	151	.79	37	
3.1	.674	245	.673	.445	148	.80	38	
1.2	.675	247	.672	.445	150	.80	38	
0.6	.675	244	.672	.451	150	.81	37	

Height above bottom (m)	Salinity (‰)	Oxygen (μg-at/kg)	pH(25°)	Alkalinity (meq/kg)	Silicate (μM/kg)	Phosphate (μM/kg)	Nitrate (μM/kg)	Nitrite (μM/kg)
Station 116	12°32.2'N		094°17.7'W	05/04/69	3998 m.			
129	34.669		7.682	2.444	149	2.66	37	
29	.671	245	.684	.455	146	.58	38	
14	.670 ·	245	.684	.444	147	.82	38	
6.1	.670	247	.682	.440	147	.74	38	
3.1	.668	251	.684	.438	148	.66	38	
1.2	.669	247	.682	.440	147	.74	38	
0.6	.670	249	.682	.448	147	.63	37	
Station 117	14°26.1'N		094°25.0'W	05/04/69	6144 m.			
100	34.676		7.666	2.446	156	2.69	38	
31	.676	232	.665	.452	155	.73	31	
16	.676	233	.661	.451	155	.74	38	
6.1	.676	230	.663	.449	154	.85	38	
3.1	.676	231	.663	.443	155	.85	36	
1.2	.676	228	.665	.451	154	.87	37	
0.6	.674	224	.660	.445	153	.81	37	
Station 119	12°50.4'N		107°55.8'W	11/04/69	3811 m.			
106			7.689	2.438	155	2.64	36	
36		272	.690	.438	156	.60	38	
19		272	.689	.441	152	.71	31	
6.3		269	.687	.434	150	.80	38	
3.3		272	.690	.432	151	.72	37	
1.1		---	---	---	---	---	--	
0.6		275	.690	.436	153	.60	37	

Height above bottom (m)	Salinity (‰)	Oxygen (μg-at/kg)	pH(25°)	Alkalinity (meq/kg)	Silicate (μM/kg)	Phosphate (μM/kg)	Nitrate (μM/kg)	Nitrite (μM/kg)
Station 120	21°08.8'N	112°27.6'W	15/04/69	3680 m.				
102	34.680		7.677	2.438	165	2.68	38	
92		258						
32	.681	258	.677	.438	165	.74	37	
17	.681	258	.675	.438	167	.68	38	
6.3	.682	256	.675	.437	165	.81	38	
3.3	.681	251	.677	.438	165	.73	38	
1.1	.682	256	.678	.438	165	.74	37	
0.6	.681	252	.680	.448	165	.74	37	
Station 121	27°14.9'N	117°29.8'W	18/04/69	3708 m.				
102	34.684		7.680	2.445	163	2.56	36	
32	.683	269	.677	.445	165	.52	38	
17	.683	268	.682	.445	165	.69	27	
6.3	.684	266	.680	.440	163	.70	37	
3.3	.684	264	.680	.444	164	.69	38	
1.1	.684	264	.680	.442	165	.80	37	
0.6	.685	268	.684	.444	165	.71	38	
Station 127	38°00.2'N	124°45.0'W	24/04/69	3944 m.				
101	34.692		7.687	2.458	172	2.57	35	
31	.693	279	.690	.449	170	.59	36	
16	.692	279	.680	.451	169	.60	37	
6.3	.692	279	.687	.446	169	.70	37	
3.3	.692	277	.690	.446	169	.66	37	
1.1	.692	---	.687	.457	169	.60	37	
0.6	.692	279	.699	.449	169	.74	37	

Height above bottom (m)	Salinity (‰)	Oxygen (μg-at/kg)	pH(25°)	Alkalinity (meq/kg)	Silicate (μM/kg)	Phosphate (μM/kg)	Nitrate (μM/kg)	Nitrite (μM/kg)
			Near-bottom Chemical Data Y6908F					
Station C-1	43°54.0'N	127°10.0'W	19/08/69	3032 m.				
50	34.653		7.631	2.453	174	2.85		
30	.654		.631	.449	172	.83		
15	.653		.631	.449	173	.75		
6.1	.652		.631	.453	177	.76		
3.1	.650		.632	.451	179	.73		
1.1	.649		.631	.453	174	.61		
0.5	.649		.631	.449	175	.83		
Station C-2	46°06.4'N	126°32.3'W	23/08/69	2797 m.				
92	34.646		7.603	2.450	187	2.88		
77	.646		.603	.444	193	.83		
62	.646		.603	.453	189	.85		
6.1	.640		.605	.447	190	.89		
3.1	.642		.605	.449	192	.92		
1.1	.645		.607	.445	184	.92		
0.5	.645		.605	.449	188	.92		
Station C-3	46°38.2'N	129°09.2'W	24/08/69	2607 m.				
49	34.635		7.588	2.426	176	2.90		
30	.636		.588	.433	183	.88		
15	.637		.588	.433	186	.88		
6.1	.634		.590	.433	183	.89		
3.1	.633		.591	.438	181	.91		
1.1	.633		.591	.435	181	.90		
0.5	.636		.590	.433	181	.90		

Height above bottom (m)	Salinity (‰)	Oxygen (μg-at/kg)	pH(25°)	Alkalinity (meq/kg)	Silicate (μM/kg)	Phosphate (μM/kg)	Nitrate (μM/kg)	Nitrite (μM/kg)
Station C-4	46°11.0'N	130°04.9'W	25/08/69	2759 m.				
54	34.620		7.581	2.435	174	2.92		
34	.618		.581	.437	172	2.94		
19	.620		.583	.438	173	2.92		
6.1	.619		.582	.435	170	2.91		
3.1	.617		.583	.437	170	2.91		
1.1	.615		.582	.436	170	2.97		
0.5	.616		.582	.454	161	3.07		
Station C-5	44°35.0'N	125°27.6'W	28/08/69	2844 m.				
50	34.642		7.607	2.450	190	2.85		
30	.643		.606	.449	191	.90		
15	.642		.607	.449	190	.93		
6.1	.642		.607	.448	189	.95		
3.1	.641		.608	.450	189	.98		
1.1	.639		.607	.449	186	.94		
0.5	---		---	---	---	---		
Station C-6	44°26.4'N	127°13.0'W	29/08/69	3122 m				
49	34.654		7.622	2.442	175	2.76		
29	.655		.623	.442	173	.76		
15	.654		.623	.437	176	.74		
6.1	.655		.619	.435	176	.76		
3.1	.655		.620	.440	171	.75		
1.1	.654		.621	.436	175	.66		
0.5	.651		.619	.446	173	.74		

Height above bottom (m)	Salinity (‰)	Oxygen (μg-at/kg)	pH(25°)	Alkalinity (meq/kg)	Silicate (μM/kg)	Phosphate (μM/kg)	Nitrate (μM/kg)	Nitrite (μM/kg)
Station C-7	43°33.1'N	129°15.9'W	30/08/69	3392 m.				
47	34.670		7.658	2.444	174	2.68		
27	.670		.658	.443	171	.68		
12	.670		.658	.443	175	.68		
6.1	---		---	---	---	---		
3.1	.671		.658	.443	175	.62		
1.1	.667		.658	.442	174	.71		
0.5	.669		.658	.453	175	.66		

Near-bottom Chemical Data TT-46

Height above bottom (m)	Salinity (‰)	Oxygen (μg-at/kg)	pH(25°)	Alkalinity (meq/kg)	Silicate (μM/kg)	Phosphate (μM/kg)	Nitrate (μM/kg)	Nitrite (μM/kg)
Station 62	12°21.3'N	062°58.9'W	19/01/70	3055 m.				
65	34.982		7.838	2.373	33.4	1.70	21.1	0.00
26	.971		.835	.368	33.9	1.73	21.1	0.00
5	.974	422	.833	.377	35.1	1.71	20.8	0.00
3.2	.982	423	.838	.368	34.8	1.69	20.6	0.00
2.1	.979	423	.842	.372	35.0	1.69	20.8	0.00
1.0	.976	421	.840	.372	35.0	1.70	20.6	0.00
0.5	.988	419	.842	.373	34.7	1.68	20.5	0.10

Height above bottom (m)	Salinity (‰)	Oxygen (μg-at/kg)	pH(25°)	Alkalinity (meq/kg)	Silicate (μM/kg)	Phosphate (μM/kg)	Nitrate (μM/kg)	Nitrite (μM/kg)
Station 65	18°08.0'N	050°02.0'W	28/01/70	5188 m.				
75	34.861		7.843	2.356	42.5	1.97	19.3	0.20
26	.863		.843	.356	42.3	1.96	19.3	0.00
8	.860	510	.843	.355	42.3	1.95	17.4	0.50
4.2	.874	507	.846	.358	42.2	1.89	18.3	0.03
2.1	.882	507	.846	.362	42.3	1.95	18.5	0.06
1.0	.875	505	.846	.358	42.0	1.92	18.4	0.04
0.5	.878	504	.846	.360	42.0	1.93	18.1	0.10
Station 67	25°12.0'N	035°46.0'W	02/02/70	5216 m.				
60	34.883		7.857	2.370				
30	.880		.857	.367				
10	.886	503	.857	.365				
4.2	.898	507	.859	.372				
2.1	.911	510	.858	.374				
1.0	.905	508	.859	.369				
0.5	---	---	---	---				